

Rishikesh Singh · Pardeep Singh ·
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Rahul Bhadouria *Editors*

Xenobiotics in Urban Ecosystems

Sources, Distribution and Health Impacts

 Springer

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Rishikesh Singh
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Foreword

In the last century when the chemical industries were a hot cake for the industry, it was thought that synthesising and producing novel compounds in laboratories for the use in health, agriculture and provisional sectors shall provide enormous options for the commercially viable synthetic products on comparatively lower cost and in a shorter duration. When one successful compound is commercialised, hundreds of its by-products and other chemicals involved in the production process are put to the waste pipeline and finally enter into the rivers, lakes and other water bodies or get emitted through the chimanies in the air. These new synthetic substances, which are considered as xenobiotic compounds are generally non-biodegradable and due to its non-natural origin are highly persistent in the ecosystems.

The urban ecosystems are specific in nature with cluster of houses and commercial centres with a high population in small areas. The industrial clusters in the urban or peri-urban regions with its regular discharges are major source points for the release of several toxic xenobiotic compound in huge quantity. It contaminates water, soil, air and food stuff, which subsequently get transferred to human bodies through the food systems, liquid intakes and breathing etc. and cause several serious health concerns.

The present book entitles “*Xenobiotics in Urban Ecosystems; Source, Distribution and Health Impacts*” edited by the subject experts Drs Rishikesh Singh, Pradeep Singh, Sachidanand Tripathi, K.K. Chandra and Rahul Bhadauria and authored by about twenty subject experts across the world is a very significant contribution in this field in which the analyses and discussions are focused on the xenobiotic contaminations of the complex urban ecosystems and its health concerns which may impact a large number of the human population of different ethnic and socio-economic backgrounds.

I appreciate the concept, contents and presentations in this book which will fulfil the long awaited need to understand the contemporary xenobiotic contaminations in the urban ecosystems and their emerging health impacts. I believe that the book will enrich our knowledge in this field.

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Preface

The release of domestic, industrial and agricultural toxins into the ecosystem has polluted the environment at a wider scale. Chemicals and pharmaceutical interactions are ubiquitous in our daily lives. They help to ensure our high standard of living, safety and mobility, communication technology, food, health, textiles, and drinking water purification. Anthropogenic activities such as chemical manufacturing, storage, transportation, and use discharge the organic and inorganic compounds into the environment every day. It has been observed in recent years that the goods from chemical and pharmaceutical industries are producing novel environmental contaminants, which may be hazardous to people's health. In so-called open applications, such as personal care, hygiene, plant protection, health, and textiles, most chemicals are used at excessive levels. Many chemicals, such as scents, detergents, textile chemicals, surface disinfectants, insecticides, and others, are inevitably emitted into the environment due to their intended usage. Among these chemicals, some are existing naturally, and due to anthropogenic activities released into the environment in large amount, however, a majority of them are not found in biological systems and classified as 'xenobiotics'. Xenobiotic substances have been reported to negatively influence ecosystem components (air, water, and soil) and the ecosystem services they provide. These xenobiotic pollutants may influence on the ecosystems from both point and non-point sources. This has raised worldwide concerns, prompting the international scientific community to invent and develop methods for combating this threat. Urban ecosystems act as a hotspot of these chemicals. Moreover, among different components of an urban ecosystem, urban soils act as a suitable resort for the long-term persistence of these chemicals. Thus, the need for sustainable management of urban soils has been emerged in the past few years.

In recent years, various remedial measures have been adopted against xenobiotic pollutants. Among these, in bio-remedial measures, microbial applications were proved significant, owing to the presence of a number of metabolic catalysts in microbes that may help in detoxifying xenobiotics. Moreover, an extensive metabolic capability and genetic flexibility allow microbes to break down virtually all organic molecules from natural or anthropogenic xenobiotics, and transform or acquire heavy metals existing as environmental contaminants. Hence,

microorganisms may play an important role in ‘bioremediation’ of these environmental pollutants. Ex situ treatment of soil or water that has been removed from a polluted site or in situ clean-ups of a contaminated site through in-place treatment are examples of such processes. Microbes have also been applied in bio-remedial measures such as bio-stimulation, bioaugmentation, rhizo-stimulation, bioleaching, and bio-immobilization. Degradation or decomposition of xenobiotics using plants is ‘phytoremediation’. In recent years, many plants including the transgenic plants have been adopted for phytoremediation of xenobiotics from soil and water from the urban ecosystems. It is noteworthy that bioremediation and phytoremediation processes are an innovative, ecologically beneficial, and cost-effective techniques for the removal or degradation of xenobiotic pollutants. Further, advancement in microbiological and plant biotechnology techniques have made the use of these remedial processes more efficient. New techniques such as next-generation sequencing can be applied to identify and utilize microbial communities having potential to degrade xenobiotic substances.

This book encompasses the wide range of issues from xenobiotic chemical characterization to their environmental fate, advancement in assessment techniques along with remediation methods of xenobiotics in urban systems. The book contains 20 chapters which have been further categorised in six different parts, viz., (I) Xenobiotics in the Urban Ecosystems: An Introduction, (II) Fate and Transport of Xenobiotics in the Urban Ecosystems, (III) Impact of Xenobiotics on Biotic Components of the Urban Ecosystems, (IV) Remediation Strategies for the Xenobiotics in Urban Systems, (V) Analytical Tools and Techniques for Assessment of Xenobiotics, and (VI) Socio-economic Aspects, Livelihood Status and Policy Regulations. A brief insight on the key outcomes of different chapters has been given as following:

Part I of the book consists of three chapters (chapters “[Impact of Xenobiotics Under Changing Climate Scenario](#)”, “[Xenobiotics in the Urban Water Cycle](#)”, and “[Assessment of the Consequences of Xenobiotics in Soil Ecosystem](#)”) providing an introduction on the topic. Abhay Punia et al. explore the wide range of xenobiotics, their interaction with the soil environment, and techniques used for soil decontamination and bioremediation in chapter “[Impact of Xenobiotics Under Changing Climate Scenario](#)”. In chapter “[Xenobiotics in the Urban Water Cycle](#)”, Greeshma Odukkathil et al. discuss the source and translocation along with the toxicological effect of different categories of xenobiotics in the urban water cycle. Alok Bharadwaj et al. explore various xenobiotic components, their types along with their mechanism of action, and remediation techniques in soil ecosystem in chapter “[Assessment of the Consequences of Xenobiotics in Soil Ecosystem](#)”.

Chapters “[Transport and Metabolism of Xenobiotics in the Urban Ecosystem](#)” and “[Xenobiotics: Sources, Pathways, Degradation and Risk Associated with Major Emphasis on Pharmaceutical Compounds](#)” have been categorized in Part II presenting fate and transport of xenobiotics in urban systems. Soumita Paul et al. discuss different transporters and metabolic genes that are associated with xenobiotics metabolism as well as removal in chapter “[Transport and Metabolism of Xenobiotics in the Urban Ecosystem](#)”. In chapter “[Xenobiotics: Sources, Pathways, Degradation](#)”.

and Risk Associated with Major Emphasis on Pharmaceutical Compounds”, Manbir Singh et al. focus on the types and sources of various xenobiotics, their introduction in the atmosphere and soil, pathways and migration in the soil and aquatic systems, and the decomposition of pharmaceutical chemicals in the environment.

The next five chapters (chapters “Food Chain Contamination and Impact of Xenobiotics on Human Health”, “Pesticides and Chemical Fertilizers: Role in Soil Degradation, Groundwater Contamination, and Human Health”, “Ingression of Heavy Metals in Urban Agroecosystems: Sources, Phytotoxicity and Consequences on Human Health”, “Polyaromatic Hydrocarbons (PAHs): Sources, Distribution and Health Impacts in Aquatic Vertebrates”, and “The Effects of Xenobiotics on Soil and Human Health”) placed in Part III of the book present a thorough insight on the impact of xenobiotics on different biotic components of the urban ecosystems. Hadia Hemmami et al. explore the potential of selected plants for the phytoremediation of xenobiotics in chapter “Phytoremediation and Xenobiotics: Exploring the Potential of Selected Plants”. Anamika Nath et al. analyse the effects of chemical pesticides and fertilizers on soil health, groundwater quality, and human health along with the regulatory measures to safeguard the ecosystem from their hazardous effects in chapter “Pesticides and Chemical Fertilizers: Role in Soil Degradation, Groundwater Contamination, and Human Health”. In chapter “Ingression of Heavy Metals in Urban Agroecosystems: Sources, Phytotoxicity and Consequences on Human Health”, Siril Singh et al. discuss about heavy metal pollution of urban agroecosystems and food chains along with their adverse consequences on human beings. The authors conclude that the transfer of heavy metals via the food chain in urban ecosystems declines the health and nutritional status of soil and crops and poses detrimental impacts on human health. Chapter “Polyaromatic Hydrocarbons (PAHs): Sources, Distribution and Health Impacts in Aquatic Vertebrates” by Sukhendu Dey et al. emphasize on diverse pathways of polycyclic aromatic hydrocarbons distribution in different environmental segments along with human health risks and harmful effects. Ruchi Urana et al. explore the impacts of xenobiotics on soil and human health in chapter “The Effects of Xenobiotics on Soil and Human Health”.

Part IV of the book comprises six chapters (chapters “Remediation Strategies of Xenobiotics in Urban Soil and Water”, “Explosive Contamination in Soil: Sources, Environmental Concerns, and Phytoremediation”, “Phytoremediation and Xenobiotics: Exploring the Potential of Selected Plants”, “Bioremediation: An Alternative Tool for Restoration of Urban Agro-Ecosystem Contaminated with Harmful Xenobiotics”, “Potential Application of Bacteria in Degrading Xenobiotics for Sustainable Environmental Management”, and “Bioremediation Strategies for Microplastic Removal in Impacted Aquatic Environments”) dealing with various bioremediation techniques adopted for managing different types of xenobiotic compounds present in the urban ecosystems. In chapter “Remediation Strategies of Xenobiotics in Urban Soil and Water”, Ritika Sharma et al. emphasize on various xenobiotic sources, toxicity, and risks to human health and the environment along with their remediation techniques. In chapter “Explosive Contamination in Soil: Sources, Environmental Concerns, and Phytoremediation”, Dickson Heisnam et al.

assess the sources of explosives in urban soils, environmental concerns, transport, and various explosive removal techniques in general and phytoremediation in particular. Bachir Ben Seghir et al., in chapter “[Food Chain Contamination and Impact of Xenobiotics on Human Health](#)”, elaborate on the different categories and sources of xenobiotics and recent advancement in technologies for characterizing microorganisms to degrade it. In chapter “[Bioremediation: An Alternative Tool for Restoration of Urban Agro-Ecosystem Contaminated with Harmful Xenobiotics](#)”, Shamshad Ahmad and Swati Sachdev discuss the sources and health impact of xenobiotic contaminants on soil, microorganisms, plants, and humans – problems related to the use of conventional methods for the decontamination of soil – and explore the potential of the sustainable biological approach to reduce harmful effects of xenobiotic on urban agriculture. Shreya Banerjee et al., in chapter “[Potential Application of Bacteria in Degrading Xenobiotics for Sustainable Environmental Management](#)”, review the importance of bacteria in controlling xenobiotics for human well-being in the urban settlements. Milena Roberta Freire da Silva et al. focus on the bioremediation strategies for microplastic removal in the impacted aquatic environments in chapter “[Bioremediation Strategies for Microplastic Removal in Impacted Aquatic Environments](#)”.

Part V, the penultimate part of the book consisting of chapters “[Recent Advancements in Bioremediation of Xenobiotics Using Microbes](#)” and “[Advancements in the Analytical Techniques for Precise Xenobiotics Assessment: A Special Emphasis on Pesticides Detection](#)”, provides a brief insight on different tools and techniques utilized for assessing the presence of xenobiotics in different urban systems. Anwasha Gohain et al. provide insights into different types of xenobiotics and the capability of microbes to degrade xenobiotics and their compounds in chapter “[Recent Advancements in Bioremediation of Xenobiotics Using Microbes](#)”. The chapter also discussed advanced techniques such as omics approaches to understand their metabolic machinery in the degradation process. Jatinder Singh, in chapter “[Advancements in the Analytical Techniques for Precise Xenobiotics Assessment: A Special Emphasis on Pesticides Detection](#)”, provided an insight on the understanding of advanced methods to assess the various xenobiotics in the environment. The chapter mainly focus on the assessment of pesticides.

The ultimate part, i.e. Part VI of the book consisting of two chapters (chapters “[Impacts of the Pesticides on Urban Aquatic Ecosystems and Their Regulation Measures](#)” and “[Xenobiotics in Urban Soils and Water: Remediation Strategies, Socio-Economic Impacts and Regulatory Provisions](#)”), deals with the socio-economic aspects and policies for the regulation of xenobiotics in the urban systems. In chapter “[Impacts of the Pesticides on Urban Aquatic Ecosystems and Their Regulation Measures](#)”, Karolayne Silva Souza et al. review the impact of pesticides on urban aquatic ecosystems along with their regulation measures. In chapter “[Xenobiotics in Urban Soils and Water: Remediation Strategies, Socio-Economic Impacts and Regulatory Provisions](#)”, Sharda Bharti and Awanish Kumar discuss the remediation strategies, socio-economic impacts, and regulatory provisions of xenobiotics in urban soils and water systems.

Overall, the content of the book provides a state-of-the-art information on xenobiotics present in the urban ecosystems, in addition to providing up-to-date information on xenobiotic types and chemical composition, environmental fate, remedial approaches, socio-economic impacts, and regulatory policies. The book incorporates theoretical and practical aspects pertaining to the xenobiotics to assess their threat level in urban ecosystems, while determining appropriate response and remediation measures to curb harmful impacts and prevent future contaminations. The content of the book will be of interest to the students and researchers working in the field of urban agriculture and environmental sciences, mainly agriculturists, ecological engineers, soil scientists, and urban policymakers.

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Part I
Xenobiotics in the Urban Ecosystems:
Introduction

Impact of Xenobiotics Under Changing Climate Scenario



Abhay Punia, Ravindra Pratap Singh, and Nalini Singh Chauhan

1 Introduction

Xenobiotic pollutants are present everywhere and are introduced into the ecosystem as a result of human activities brought on by rapid urbanization. The most significant and crucial characteristics of xenobiotics are their increased production, environmental persistence, and biological impacts. Concerns have been raised around the world due to studies showing an increase in the number of xenobiotic chemicals discovered in aquatic systems (Embrandiri et al. 2016). In recent decades, there has been a lot of focus on their existence and destiny in urban hydrological cycle (Ternes and Joss 2007).

Animals that are a component of the food chain are the most affected by xenobiotics (Rosi-Marshall and Royer 2012). Xenobiotics are man-made substances behaving as foreign substances in both humans and animals. These have been created in a lab, such as insecticides, antibiotics, synthetic steroids, and substances found in biomedical waste (Bhatt et al. 2019). It is also possible to classify xenobiotics as the anomalous high quantities of any material present, such as the detection of antibiotic medications of humans that are neither normally consumed nor synthesized by the body itself. Occasionally, a natural chemical might be labeled as a xenobiotic when it enters into animals or people. To characterize the biochemical and physiological impacts of extraneous substances, whether they are organic or synthetic on the cellular or organs of animals, Bonjoko (2014) originally created the

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word “xenobiotic.” Due to the fact that they are not recognized by any metabolic processes in microbes and plants, numerous xenobiotic substances are harmful to humans and the ecosystem.

The xenobiotic sources that are caused by humans include industrial, domestic, pharmaceutical, agricultural, and transportation sources (Essumang 2013). Xenobiotic substances include pesticides like acephate, diazinon, N,N-diethyl-meta-toluamide (DEET), and hydrocarbons as well as food products, environmental contaminants, and carcinogens. Xenobiotics can have a range of impacts, such as immunological reactions, medicine toxicity, and climate change. Many industries in the chemical and drug fields use these materials to create drugs, polymers, detergents, creams, chemicals for research labs, biological kits, fragrances, pesticides, etc. (Rieger et al. 2002). Xenobiotics are either resistant to biodegradation or merely partially biodegradable and may remain in the ecosystem for a longer period. Xenobiotics, both natural and synthetic, are a major reason of global pollution and are emitted as air pollutants, sewerage, and industrial dumping into waterbodies. Their concentration may increase as these persistent organic pollutants move up the trophic levels of the food chain (Dubey et al. 2014). Xylene, naphthalene, pyrene, and acenaphthene are only a few examples of the many xenobiotic chemicals that are reaching traditional wastewater treatment units. However, because these plants cannot process these substances, they are transmitted untreated into intricate matrices (Thakur 2008).

Xenobiotics could build up in live organisms since they are hard to break down due to their complex structures. Further bigger problems may occur as a result of their partial degeneration (Pande et al. 2020). Knowing the origin of these substances is essential for reducing the amount of xenobiotics in the ecosystem. Environmental pollutants may be emitted directly or indirectly, such as through discharge from the hospital, or these may be emitted as the by-products or as part of production. They may affect environment intentionally or unintentionally and come from moving (such as an automobile) or still sources (industry) (Saravanan et al. 2021). There are numerous regulations and directives for releasing xenobiotics into the environment and also regulating the sources that can lead to the production of xenobiotics (Stefanac et al. 2021). It is important to educate people about the immediate and long-term consequences of xenobiotics on the environment since xenobiotics that come from homes are challenging to control. This chapter will give an overview of impact of xenobiotics on environment under changing environment scenario.

1.1 Xenobiotics in the Environment

Exogenous xenobiotics are xenobiotics that an organism does not naturally make but that still enter the organism through food, medication, or environmental inhalation. Pesticides, herbicides, contaminants, pharmaceuticals, and food additives are a few examples. Wastewater and solid waste emissions from industries such as

Table 1 Different sources of xenobiotic compounds

S. no.	Sources	Example
1.	Agriculture	Pesticides, herbicides
2.	Medicine	Drugs
3.	Food industry	Additives, food
4.	Energy industry	CO ₂ , SO ₂
5.	Transport	NOx, lead, CO ₂
6.	Consumer industry	Coating, dyes
7.	Plastic industry	Number of complex organic compound antioxidant plasticizer, cross-linking agents
8.	Petrochemical industry	Oil/gas industries and refineries produced some chemicals, for example, benzene, vinyl chloride
9.	Paper industry	Paper and pulp effluent, chlorinated organic compound
10.	Pesticide industry	These are benzene and benzene derivatives and chlorinated and heterocyclic
11.	Insecticides	Dichlorodiphenyltrichloroethane (DDT)

chemical and pharmaceutical, plastics, paper and pulp mills, textile mills, and agricultural are the main direct sources of xenobiotics. The various sources of xenobiotic compounds are listed in Table 1 (Source: Mishra et al. 2019). Phenolics, hydrocarbons, various colors, painting industry effluent, herbicides, insecticides, etc. are a few of the usual residues discovered in wastewater and other industrial effluents.

Due to molecular interactions and connections, plastics are strong and durable and degrade slowly (Chamas et al. 2020). Polystyrene, polyvinyl chloride, polyethylene, and its derivatives are required for production of plastics. Modern industries use polymers made from crude oil as fuel (Tschan et al. 2012) which can be easily broken down into liquid hydrocarbons. In recent years, microbial decomposition of plastics has attracted attention; however, the fragmented substances can cause further ecological issues. Because of its toxic nature even at low concentrations and its ability to form substitute materials through oxidation and disinfecting reactions, phenolics are one of the most common chemical compounds and pharmaceutical pollutants (Postigo and Richardson 2014). Only a few of its direct environmental effects include the destruction of the ozone layer, modifications of the earth's thermal equilibrium, diminished visibility, and the addition of acidic pollutants to the air (Basha et al. 2010). Prior to wastewater disposal, phenol treatment from industrial wastewaters is crucial in reducing all of these consequences. Since phenol is a carcinogenic substance, it must be biodegraded using a process that produces few secondary compounds as well as safer products (Prpich et al. 2006).

Petroleum by-products primarily consist of saturated hydrocarbons, polycyclic (polynuclear) aromatic hydrocarbons, and a large number of organic compounds containing sulfur, nitrogen, and oxygen (Gojgic-Cvijovic et al. 2012). The significance of bio-treatments, which had an effect on reducing the toxicity of these

molecules, was emphasized because remediating such petroleum compounds with physicochemical approaches is not economical and can result in higher environmental instability. In particular, petroleum-contaminated environments are a rich supply of microorganisms that may biodegrade these by-products (Prakash et al. 2014). In comparison with branched alkanes, straight-chain saturated hydrocarbons (n-alkanes) are more susceptible to microbial breakdown. As a chemical's aromaticity grows, biodegradation becomes less sensitive since it takes greater effort to break degrade aromatic components (Milic et al. 2009).

Dye adhesion on microbial surfaces is how this is accomplished. Subsidiary or indirect sources of xenobiotics include things like pharmaceuticals, artificial fertilizers, pesticide residues, and nonsteroidal anti-inflammatory drugs. Synthetic dyes are widely employed in a number of industrial operations, such as the textile industry, printing, and photography (Al-Tohamy et al. 2022). These dyes typically feature intricate aromatic molecular structures. These businesses frequently utilize colors such as azo, anthraquinone, and phthalocyanine (Vigneeswaran et al. 2012; Shahid et al. 2013). These break down into aromatic compounds that can be linked to cancer and mutation. Due to the presence of negatively charged ligands in cell wall components, microorganisms have the ability to not just remove dyes but also detox them (Hemapriya and Vijayanand 2014). This is accomplished by dyes adhering to the surface of microorganisms. Nonsteroidal anti-inflammatory medication, pharmaceutical items, synthetic fertilizers, pesticide residues, etc. are examples of secondary sources of xenobiotics. Pharmaceutically active substances serve as a secondary source of xenobiotic released directly by pharmaceutical companies or as hospital effluents after they have had their desired clinical implications into the environment in either their whole or fragmented form. According to Iovdijova and Bencko (2010), they mostly consist of hormones, anesthetics, and antibiotics that bioaccumulate in an organism and are transferred to other organisms via different trophic levels. Although biomaterials made from synthetic polymeric materials are biocompatible, they can degrade in the body into hazardous chemicals (Baun et al. 2008). Despite being indirect sources, they have a negative impact on the ecological cycle.

Soil and aquatic pollution can harm local flora and wildlife as well as cause hazardous substances to be absorbed and accumulated in food chains. Planning for the long-term disposal of industrial waste in ecosystems requires research on the bioaccumulation characteristics of different ecosystems (Iyovo et al. 2010). Pesticide bioaccumulation and biomagnifications can cause harmful behavioral effects in both animals and humans. Although these pesticides are now prohibited worldwide, dichlorodiphenyltrichloroethane (DDT) and benzene hexachloride (BHC), which have a half-life of one decade, accumulate in plants or in its parts. Nonsteroidal anti-inflammatory medications (NSAIDs) are a class of pharmaceuticals used to treat fever, bodily pain, and inflammation in both humans and animals (analgesic aspects) (Parolini 2020). According to sources, the number of vultures in Pakistan has drastically decreased as a result of the usage of diclofenac sodium in livestock, with a 95% loss in 2003 and a 99.9% fall in 2008 (Oaks et al. 2004). Xenobiotics come from different sources and enter organisms as well as into the aquatic ecosystem.

These can also travel through the food chain and enter the whole ecosystem. Thus, the negative impacts of these compounds are to be kept in mind before taking into consideration their economic benefits.

1.2 Environmental Impact of Xenobiotics

Xenobiotic pollutants are present everywhere and are introduced into the ecosystem as an outcome of human activities brought on by rapid urbanization. The common contributors of xenobiotics include agriculture and pharmaceuticals (Fig. 1). While the consumption for pharmaceuticals is currently rising as a result of population expansion, this also leads to xenobiotics increment in the environmental components (Embrandiri et al. 2016). The various medications ingested have caused toxins to be discharged into aquatic areas, which have multiple immediate and long-term repercussions on natural ecosystems. Ecosystems are directly impacted by xenobiotics in terms of change in characteristics of the community, structure of the community, diversification, productivity and transfer of energy, and succession and density of population (Grechi et al. 2016). Changes in productivity, reproduction, genetics, and composition will have an impact on population dynamics, an impact on all of the trophic levels and also on the ecosystem as a whole (Gianfreda and Rao 2008; Bhat 2013). Globally, herbal drugs and various botanical plant species are becoming more popular, and these substances may also have some xenobiotic characteristics. Some plants pollute the environment and have the potential to affect the biology of species living in waterbodies (Guengerich 1997a, b). Some plants pollute the environment and may have an impact on aquatic creature's biological processes.

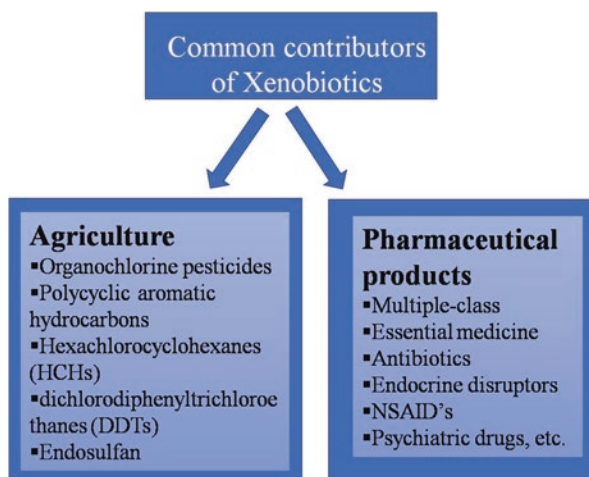


Fig. 1 The common contributors of xenobiotics

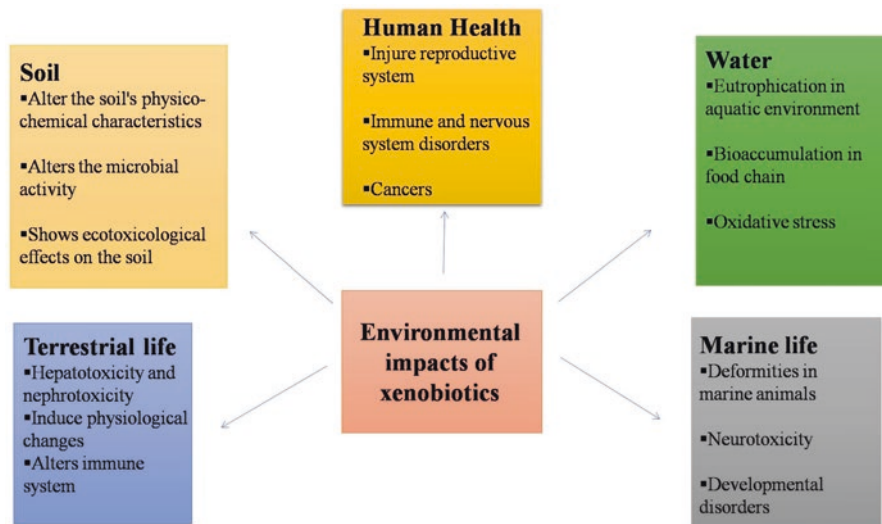


Fig. 2 Impacts of xenobiotics on environment

The environment, plants, animals, and people are all adversely affected by significant xenobiotic substances (Fig. 2). In the below sections, the impact of these xenobiotic compounds on water, air, and soil is discussed.

1.2.1 Impact of Xenobiotics in Water

Until the early 1960s, the primary sources of xenobiotics in surface water and groundwaters throughout most of Western Europe were industrial operations like the manufacturing of coal and steel, as well as the chemical industry. These days, there are a wider variety of sources available. As a result of the introduction of ever-stricter regulations that specifically target industrial pollution, for instance, the Integrated Pollution Prevention and Control Directive, the manufacturing facilities are typically no longer the main sources of xenobiotic emissions to urban waters. For instance, using cleaning supplies and personal care items like dishwashing liquid and laundry detergent results in the immediate release of a variety of xenobiotics into sewerage.

In addition, it is now believed that chemicals that leak or evaporate from products and building materials contribute more to xenobiotics in wastewater than was previously thought (Gupta et al. 2022). Plasticizers, flame retardants, and perfluorinated compounds from various materials, such as flooring, carpeting, and wall coating, evaporate or leak into the indoor atmosphere. Chemicals released into the air by items like furniture, textiles, TVs, and refrigerators can collect in dust, get inhaled, and ultimately end up explicitly or implicitly in the sewage system. During washing, textile agents are liberated.

Building materials, including paint, concrete, metals, and plastics, also cause pollution. Vehicular exhaust, catalysts, and tires release metals, polycyclic aromatic hydrocarbons (PAHs), and other pollutants into the environment (Revitt et al. 2004). Common xenobiotic receptors can exist in traditional sewage treatment plants, and prior to being released into aquatic environment, it must undergo treatment with municipal wastewater. Water bodies may include trace amounts of metals, xenobiotics, compounds such as PAHs, phthalates, and insecticides (Essumang 2013). The main pharmaceutical breakdown by-products and these xenobiotic substances have an impact on traditional sewage remediation facilities and may check processes like nitrogen fixation. The oxidation of ammonium to nitrite, the initial stage in the nitrification process, is sensitive to the presence of xenobiotic chemicals. Under uncontrolled conditions, xenobiotics can completely stop the biological nitrogen process by inhibiting the first stages of nitrification (Essumang et al. 2009). Xenobiotic substances such as pharmaceuticals, PAHs, phthalates, biocides, and corrosion inhibitors released into surface water can reach the groundwater via leaching, and thus, it should be strongly prohibited as the discharge of these compounds and may impair the biology of marine ecology (Al Shibli et al. 2021). Important biological markers of xenobiotic contamination include some aquatic organisms (Fent et al. 2006). Xenobiotic chemicals can infiltrate the ecosystem as metabolites or in their natural forms. Xenobiotic agents in humans can track the process of intake and excretion with wastewater disposal pathways (Singh et al. 2016a, b).

Overuse of personal grooming products along with pharmaceutical remnants is one of the top challenges faced by the scientific community. Xenobiotics such as surfactants, oil and wax, perfumes, biocides, UV filters, and pigments are all ingredients found in personal care and cosmetic goods (Eriksson et al. 2003). Most customers favor products with synthetic flavors and smell over those without knowing their chemical composition. Most softeners, washing powders, cleaning detergents, etc. also include significant amounts of fragrances like nitro and polycyclic musks. Since cosmetics typically contain significant amounts of water, preservatives, or biocides like triclosan, it has been demonstrated that fragrances, biocides, and UV blockers are released into receiving urban water channels (Poiger et al. 2004). There has been a widespread change in the use of musk fragrances in various items, according to data from some countries beginning in 1980. For instance, the consumption of polycyclic musks reduced in contrast to earlier levels when the bulk of consumer goods in Northern Europe stopped using nitro musk perfumes. The maximum concentrations are currently determined for more odorous chemicals like tetramethyl acetyloctahydronaphthalenes (Bester et al. 2010). These modifications in how different substances are used partly emerge from ecological concerns, but they also respond to changes in the fashion industry. Consumer magazine articles highlighting concerns about nitroaromatics and polycyclic musks attributing to a decline in their usage have helped boost public understanding of environmental problems in nations like Germany and Scandinavia (Tobler et al. 2007). The discovery of individual service products in the aquatic ecosystems continues to be a concern despite changes in consumption trends (Tilman et al. 2001). The most recent class of emerging toxic compounds discovered in the urban environment is illicit drugs. These

substances, as previously indicated medicines, unchanged or slightly altered, enter the environment through urban wastewater effluents (Castellano-Hinojosa et al. 2023).

Pharmaceutical leftovers along with their transformed products and their metabolites are released into the ecosystem at trace levels by irrigation techniques or discharges of treated wastewater. They become “pseudo-persistent” when they are continuously introduced into the ecosystem by regular irrigation or other sorts of discharge activities. Their prolonged release may have hazardous or other negative consequences on aquatic or terrestrial ecosystems. Additionally, their potential uptake by plants must also be taken into account (Rosi-Marshall and Royer 2012). The pharmaceutical groups most usually encountered in treated effluents around the world include antibiotics, lipid regulators, anti-inflammatory medications, beta-blockers, cancer medications, birth control pills, and other hormones (Hernando et al. 2003; Nikolaou et al. 2007). The natural excretions of humans result in the presence of steroid hormones in the urban wastewater. With androgenic compounds receiving comparatively little research, estrogenic hormones have received the majority of focus. While men and nonpregnant women also emit estrogenic steroids, their levels are often lower than in pregnant women. Male fish may produce egg yolk proteins in their testicles in response to estrogenic substances, per reports by Jobling et al. (1998). Synthetic steroid hormones like mestranol and ethinylestradiol are used for birth control and hormone therapy. Because it is more potent and less biodegradable than natural hormones, ethinylestradiol’s destiny and mass flow have received special attention. There are facts in the published studies that cannot be simply explained by normal excretions exclusively, but it is extremely challenging to evaluate at large volumes in ambient samples. Even if every woman in the specific research region received ethinylestradiol treatment and was excreting this substance entirely unmetabolized, another source, such as manufacturing effluents, would still be necessary (Bester et al. 2010).

For several reasons, xenobiotics such as biocides are presently found in many daily products. These include biocides used for extending the expiry date of products like cosmetics and paints, preventing fruit rot (e.g., carbendazim), preserving wood, stabilizing construction materials (mold and algae growth inhibition), and preventing the growth of vegetation on flat roofs. More significant to urban aquatic systems are construction-related biocides than agricultural pesticide-related ones, and greater levels of biocides like triclosan have been found in wastewater (Wilson et al. 2003). The mass movements of many of these chemicals, however, are still poorly understood. In addition to being widely used anticorrosives and deicing and anti-icing agents in the aviation industry, the complexing agent’s benzotriazole and tolyl triazole are also used in dishwashing detergents in urban households (Bucheli et al. 1998; Kupper et al. 2006). Extremely high median benzotriazole concentrations (1 g/L) were found in surface water as a result of inadequate elimination within wastewater treatment facilities (Giger et al. 2006; Weiss et al. 2006). These substances are included among the xenobiotics that are present mostly in higher

concentrations in urban groundwater due to surface water leaching, along with other xenobiotics like carbamazepine, sulfamethoxazole, and amidotrizoic acid (Hollender et al. 2007).

1.2.2 Impact of Xenobiotics on Soil

Some xenobiotic substances, like pesticides, have an impact on both the yield and the functions of the soil. The toxicity of xenobiotics may have an impact on specific soil variables. Different issues could be brought on by certain xenobiotics that persist in the environment, and their presence in the soil for longer period could result in the following:

1. These substances can be taken up by the fauna and may build up in their edible parts.
2. Soil bacteria break down xenobiotic substances, and their metabolites may build up in the soil environment.
3. Xenobiotic substances could build up in the food web and alter the balance in the ecological environment (Alexander 1965).
4. Mineralization that is not complete can produce dangerous intermediate chemicals.

Secondary metabolites of natural resources led to the discovery of new medicines, which frequently act as precedents for the creation of synthetic antibiotics (Kumar et al. 2014).

1.2.3 Impact of Xenobiotics on Air

Humans release large amounts of xenobiotic contaminants into the environment without even being aware of their toxicological impacts. Certain xenobiotic substances, like PAHs, are just environmental contaminants. These organic substances are all around us and are released into the ecosystem as a result of incomplete combustion of resources. Different processes, such as heating and burning fuel, coal, and agricultural waste and occasionally even grilling food, are some of the sources of xenobiotic chemicals, such as PAHs. Trucks, ships, airplanes, and cars are examples of mobile sources that might emit these chemicals into the environment. Major sources of PAHs in the environment are industrial processes such as electricity generation, aluminum manufacture, cement kilns, and oil refineries (Essumang 2013). The distribution and recurrent patterns of food chains and webs are disrupted by these xenobiotic chemicals, which also have an impact on the different trophic levels. These substances may have an impact on the climate and ecosystem and are also carcinogenic resulting in a wide range of problems in humans (Essumang 2013).

2 Pesticides as Xenobiotics in Urban Soil

Pesticides are a general term for the primary groups of chemicals used to interfere with living organism's development and metabolism (Al-Saleh 1994). Insecticides include organochlorines, organophosphates, carbamate esters, pyrethroids, acetamides, triazoles, triazines, and neonicotinoids (Pandya 2018). Environmental scientists are concerned about organochlorines when discussing pollution driven by pesticides since they have a higher probability to do so (Tripathi et al. 2020; Dhuldhaj et al. 2023). Common pesticide classes include chlordane, DDE (dichlorodiphenyldichloroethylene), DDT (dichlorodiphenyltrichloroethane), HCHs (hexacyclochlorohexanes), and DDD (dichlorodiphenyldichloroethane) (Da Silva Augusto et al. 1997). Pesticides and other harmful substance's activity depend on certain environmental reactions that occur naturally. A complex set of chemical, biological, and physical interactions occurs when a pesticide component combines with soil, water, or a living thing (Mahmood et al. 2016).

Due to manufacture, transportation, improper storage, usage, and other factors, pesticides may be discharged into the urban ecosystem and result in significant environmental issues (Relyea et al. 2005). For instance, significant doses of the herbicide glyphosate are released into the environment during the formation of this chemical (Ren et al. 2018). The possible emission routes of pesticides in polluting soil, water, air, plant tissues, and ultimately the ecosystem are inadequate storage, poor mixing, packing into tanks, and washing and rinsing the tanks after application of pesticides (Ramakrishnan et al. 2019). Inadvertent spillage also contaminates soil with pesticide, negatively affecting both human health and the environment. A large amount of soil, water, and air pollution can be caused by pesticides used carelessly or even by spray drift or wash-off from treated plants or seeds (Luo and Zhang 2010; Ramakrishnan et al. 2019). Long-range air transmission occurs after the use of organic pesticides that are volatile and persistent, such as fumigants, polychlorinated biphenyls, and organochlorine pesticides (OCPs) (Meftaul et al. 2020). The soil also serves as a sink for all of these pesticides that are discharged into the environment by direct application, unintentional leakage from storage, spreading sewage sludge on fields, and atmospheric deposition (Pokhrel et al. 2018). According to Ma et al. (2011), persistent organic pollutants (POPs) have accumulated in the soil as a result of global warming and are linked to high amounts of organic matter. According to Yu et al. (2020), urban soil in China was a source of low chlorinated PCB emissions. Numerous studies have already proven the damaging consequences of such illicit substances (opiates, cannabinoids, amphetamines, cocaine, etc.) (Boleda et al. 2009; Wick et al. 2009). Additionally, sewage sludge biosolids applied to soil and wastewater treatment plants (WWTPs) are major sources of pesticide emissions in cities. According to Köck-Schulmeyer et al. (2013), most of the pesticides found in WWTPs are of urban and agricultural origin. In reality, biosolids included around 143,000 compounds registered for industrial use in the European Union (Clarke and Smith 2011). As a result, organic pollutants can readily contaminate the environment, whether biosolids are employed in agricultural or urban areas.

3 Antibiotics as Xenobiotics in Soil

Effective natural antibacterial biosynthesis is present in soil microbial communities and plant roots (Thomashow et al. 2019); these communities frequently contain fungal, pseudomonad, and actinomycete species (Raaijmakers et al. 2002; Butler and Buss 2006). According to the reports, producing antibiotics in naturally occurring microbial communities may enhance microbial competitiveness, fitness, defense, signaling, and gene regulation (Mavrodi et al. 2012). Antibiotics are therefore viewed as a component of soil disease management. Fast breakdown, significant substantial sorption to the surrounding soil, and quantities that are close to the detection limit make it difficult to detect and quantify natural antimicrobials in nutrient-poor soil (Raaijmakers et al. 1997; Mavrodi et al. 2012). Antibiotic resistance is thought to have emerged in naturally occurring microbial communities as a result of exposure to antimicrobial substances that present in the ecosystem (Singh et al. 2021). The reaction to man-made synthetic antibiotics can likewise be altered by such exposure (Aminov and Mackie 2007). More and less strains that are resistant to antibiotics are likely found in soil microbial communities, indicating coadaptations to some anthropogenic antimicrobials. A major issue is the pollution of terrestrial soil and aquatic ecosystems with anthropogenically produced antibiotics, which starts with animal excretion and hospital waste (Kumar et al. 2019).

The majority of antibiotics have relatively short half-lives and are intended to be easily eliminated after administration (Pico and Andreu 2007). Antibiotics are susceptible to microbial change when introduced to the solid phase of soil. Sulfonamides are one class of chemicals that have been widely employed in pig production and animal husbandry (Zhou et al. 2012). The use of photodegradation in soils as a secondary pathway for the degradation of pharmaceuticals is constrained by insufficient illumination (Ozaki et al. 2021). Because of surface runoff and particle-facilitated environmental transfer, all antibiotics might disperse (Burch et al. 2014). This explains why the majority of antibiotics added to manure-containing soils typically end up in the uppermost layer of soil (Ostermann et al. 2013; Pan and Chu 2017). One of the greatest threats to public health in the twentieth century is the enrichment of antibiotic-resistant bacteria in soil environments (Singh et al. 2021). By adding animal dung from animals treated with antibiotics to soils, which is thought to be a reservoir for resistance genes, these genes are introduced into the food supply (Rauseo et al. 2019). The spreading of sulfonamide resistance genes to soil bacteria is caused by the use of pig dung (Hruska and Fránek 2012). Furthermore, even though the cows that produced the manure were not given antibiotics, adding cow manure to soil accelerated the proliferation of genes that code for lactamases and naturally present antibiotic-resistant microbes (Allen 2014). Human infections could increase as a result of the proliferation of resistance genes to antibiotics. The possibility of creating new resistance increases when the human microbiota carrying the residues is introduced into the ecosystem where the bacteria-enriched resistant components are present (Scarpellini et al. 2015). Thus, it is emphasized that residuals from hospitals should be kept to a minimum at all times in order to prevent

the exchange of genetic material (Sire's and Brillas 2012). Due to its possibility for spreading pathogens into the environment and high pathogenic potential, hospital discharge poses a threat to human health due to its high pathogenic potential and propensity for transferring infections into the environment (De Souza et al. 2006). In addition to medicines, antibiotics, antiseptics, pain killers, trace metals, and non-metabolized drugs, these discharges also transmit resistance-causing genes via horizontal gene transfer into the urban ecosystem. Opportunistic infections, frequently present in free-living organisms, can attain resistance characteristics through extensive genetic exchange during effluent treatment (Szczepanowski et al. 2008).

The ability of wastewater treatment systems (WTS) to reduce the chemical and physical properties of the pollutants to permissible level is used to measure how effective they are, frequently omitting crucial biological parameters (such as microbial abundance). The transmission of antibiotic-resistant microbes into urban areas, however, may be facilitated by hospital sewage treatment systems, according to a growing body of data (Chitnis et al. 2004; Sayah et al. 2005; Kim and Aga 2007; Prado et al. 2008; Fasih et al. 2010; Robledo et al. 2011). Hospital waste is regularly thrown into water bodies and municipal wastewater systems in developing countries, frequently without any kind of treatment meant to reduce the risks to the public's health (Meirelles-Pereira et al. 2002). Therefore, one of the biggest problems facing healthcare facilities is handling hospital sewage and healthcare waste to reduce possible concerns for nearby populations. Action must be taken right now to stop the spread of the numerous hospital and aquatic ecosystem reports of resistant and multiresistant bacteria. Since numerous isolates of the genus *Pseudomonas* have been found in hospital effluents and frequently exhibit antibiotic resistance, this genus is of particular importance (Fuentefria et al. 2011). The diverse range of ecological niches that *Pseudomonas* species may invade includes water, sewage, soil, plants, and animals (Goldberg 2000). This genus contains a number of potentially harmful species that are known for their significance to both health and the economy (Widmer et al. 1989).

4 Xenobiotics and Changing Climate Scenario

Xenobiotics are a significant environmental stressor, along with eutrophication and global warming (Niinemets et al. 2017). The interaction between xenobiotic compounds and climate change, however, has only been the subject of a small number of researches; it would be intriguing to examine how xenobiotics respond to changing climatic conditions. There's a good chance that xenobiotic usage will rise soon (Navarro et al. 2000; Bloomfield et al. 2006), potentially causing significant environmental pollution. Solubility in water and evaporation rate, and other ecological parameters such as moisture and temperature differences, the origin of the molecules, and density of fine particulates, all influence the presence of xenobiotics in the ecosystem and also affect it. Climate change and the environment are impacted

by the release of xenobiotic chemicals from vegetation and soil, wind-driven soil erosion, and airborne pollution emissions (Mosleh et al. 2005; Coscolla et al. 2011).

4.1 Xenobiotics with Changing Temperature

Temperature variations cause numerous alterations in xenobiotic substances and also have an impact on the dynamic process of marine ecosystems (Gagne et al. 2007). A significant rise in temperature can boost organism's metabolic activity and reduce the pace at which xenobiotics, especially toxicants, are absorbed by the environment. As surroundings change, xenobiotic characteristics and behavior patterns will change which could have an impact on the global climate (Brubaker and Hites 1998; Wania 1999; Sinkkonen and Paasivirta 2000; MacDonald et al. 2002; Meyer and Wania 2008). Temperature variation could cause changes in biotransformation in water, soil, as well as some biota. It has the potential to raise the xenobiotic pollutant's levels and make it easier for them to enter the water bodies (MacDonald et al. 2002). Rising soil and water temperature can accelerate the breakdown of xenobiotics, potentially increasing the level of xenobiotic contaminants from eluent depletion procedures (Sinkkonen and Paasivirta 2000; Moyo et al. 2020). As temperatures rises, there may be a steadily rising volatilization of xenobiotic compounds in the ecosystem. They will be susceptible to transportation damage and photodeterioration in these situations (Feitkenhauer et al. 2001; Scheyer et al. 2005). Certain biological parameters can influence xenobiotic behavior and alter species migration patterns, which can have an impact on the changing climatic conditions. Some climate change distributional mechanisms such as climatic variations will modify the recurrence and quantity of xenobiotics used in farming (Choudhary and Kumar 2019).

4.2 Xenobiotics with Increased Pesticide Use

Pesticide use is an inevitable step in present farming practices, and changing climatic conditions affect pesticide use as well as pesticide losses to the environment (Noyes et al. 2009). In the event of a changing climate, the occurrence of dry months, wetter humid months, and excessive temperature and rainfall events will likely increase (Salinger 2005; Wang et al. 2013). Pesticide losses to the environment will increase as the climate changes. The reasons could be increased rainfall frequency and intensity, which has led to an increased likelihood of leaching through soil macropores, as well as higher precipitation events, which significantly raise pesticide losses through the surface runoff (Meite 2018). Leaching of pesticides brought on by rainfall may occasionally be countered by a stronger thermal deterioration brought on by a high temperature. However, higher temperatures can cause extreme drought, which slows the degradation of pesticide (Castillo and Torstensson

2007; Dhakal et al. 2019). It is generally known that soil organic matter and pesticides can bind together to reduce pesticide leakage (Zhang et al. 2020). However, as a result of the decay of organic material brought on by greater temperatures, its capacity to bind pollutants may be diminished. As a result of the interaction of these different variable parameters, pesticide fate forecasting is highly challenging. The balance between sorbed and non-sorbed pesticides will be altered by periodic freezing and thawing, which will modify the amount of pesticides that are available for decomposition, leaching, and runoff (Boe 2017). In addition to these immediate effects, climate change might lengthen the growing season for crops, which would give pesticides more time to breakdown. However, an extension of the crop growth season during wet months may make the leaching event worse as the frequency of rainfall occurrences is predicted to rise.

Crop agronomic practices are being affected by climate change as well, which affects the type and quantity of pesticides required and, ultimately, the fate of those pesticides (Dadhich and Meena 2014; Delcour et al. 2015). It is anticipated that increased pesticide use will result from elevated precipitation and temperature events that can enhance the incidence of pests and diseases and alter weed flora. Therefore, increased usage of insecticides and fungicides may eventually replace occasional usage of pesticides in temperate areas. The growth of bacteria is influenced by climate change, and the functional makeup of the soil has a big impact on the network of bacteria that break down pesticides (Chakraborty et al. 2012; Ukhurebor et al. 2021). Pesticides and other xenobiotics have thus raised serious concerns since how they are handled will determine how healthy our ecosystem is (Bernardes et al. 2015). It is clear that the significant climate change will have an impact on agronomic practices. Temperature, precipitation, and wind action are examples of weather variables that have an impact on the environmental retention and mobility of pesticides (Chen and McCarl 2001; Tiryaki and Temur 2010; Gentil et al. 2020).

Pesticide degradation, reemission behavior, mobility, source-sink connections, availability, transport, and lethality throughout food chains are all directly impacted by climate change (Delcour et al. 2020). Climate change may also result in an increase in the application of pesticides because crops will be under more stress due to a potential rise in pest and disease incidence (Shrestha 2019). However, the effectiveness of insecticides will decline because of their high rate of degradation in a changing climate scenario (Delcour et al. 2015). The formation of more toxic metabolites could result from altered pesticide degradation pathways caused by climate change, which could have detrimental consequences on both human and aquatic health (Tripathi et al. 2020; Singh et al. 2022). Because of the changing climate and the high leaching of pesticides, there is a possibility of more frequent pesticide detection in groundwater and other waterbodies (Bloomfield et al. 2006). Although there is a lot of data regarding what will happen to persistent organic pollutants (POPs) in the event of climate change, cumulative information on pesticides is alarming. Organochlorine pesticides such as DDT and toxaphene are included in persistent organic pollutants (POPs), according to the UN Stockholm Convention, and their fate under a scenario of climatic change has been extensively discussed

(Hardy and Maguire 2010). However, due to the widespread use of pesticides like atrazine, chlorpyrifos, and aldicarb, less information is accessible, making it difficult to predict what will happen to them over time as a result of shifting climatic circumstances (Noyes et al. 2009).

4.3 Effect of Xenobiotics on Humans Under Changing Climatic Scenario

Changing climatic scenario can result in bioaccumulation and biomagnification of xenobiotics, such as organic pollutants in the environment; thus, concerns exist regarding their impact on animals at various trophic levels (Borga et al. 2010; Derby et al. 2021). The importance of such pollutants has recently grown as various xenobiotics have been identified as culprits of hormonal disruption, compromising the functionality of both reproductive and endocrine systems in animals as well as humans (Maurya and Malik 2016). Such pollutants can persist in lipid molecules for longer times resulting in chronic disorders such as birth deformities, decreased immunity, interruption of patterns of development, neurological problems, genetic abnormalities, intellectual disabilities, respiratory problems like asthma, and behavioral abnormalities in both people and animals (Harrison et al. 1997). Environmental pollutants are a reason for concern in the domain of reproductive and immunological dysfunction, hormone difficulties, cancer, and neurobehavioral disorders, according to the findings of ecological studies undertaken (Kelce et al. 1995; Kavlock et al. 1996). A decrease in resistance, diseases, neurobiological dysfunction, developmental anomalies, and tumor induction can all be consequences of exposure to these toxins in children and unborn children. Children are more sensitive as they progress through their developmental phases because cells during developmental stages are more vulnerable to environmental xenobiotics and hence more prone to being exposed to and influenced by these toxic molecules (Crinnion 2009).

4.4 Effect of Xenobiotics on Species Diversity and Ecosystem

Some microbes in an environment rely on species relationships, but xenobiotics may cause these connections to break, potentially resulting in the loss of a keystone species (McClanahan et al. 2002). A keystone species is one that has a strong connection to other species further down the food chain. There are numerous other links to keystone species since they govern the organization and structure of an entire group (Jordan 2009). The disappearance of a keystone species could result to the loss of other species in the ecosystem, which could have an effect on the trophic level, food chain, and numerous chain linkages (Mills et al. 1993; Hale and Koprowski 2018). A large proportion of xenobiotic chemicals are utilized in the ecosystem that ultimately reaches the soil, where they are transferred into plants

through the nutrient cycling. Microorganisms present in the soil combine with some xenobiotics, which have an impact on nutrient cycle processes in an ecosystem, either directly or indirectly. Xenobiotics present in soil inhibit the process of nitrogen fixation, which is essential for the growth of flora (Lu et al. 2020). Natural pollinators like honeybees and lepidopterans are especially vulnerable to xenobiotic chemicals. Natural pollination is suffering as a result of the extinction of pollinator species and the decline in pollinator species induced by xenobiotics, which might result in lower seed and fruit yield (Ara and Haque 2021). As a result, xenobiotics may have an impact on ecological behavior, economy, and climate change (Landis et al. 2003).

5 Conclusions and Future Recommendations

With increased population and urbanization, there is a considerable risk of xenobiotic exposure in our food and drinking water systems. The presence of hazardous xenobiotics has been identified in items ranging from personal care to agricultural purposes. Despite the fact that there are a variety of water treatments and monitoring technologies, xenobiotics are quickly turning into a hazard to our ecosystem, since long-term consequences are unavoidable. Since xenobiotics have the potential to disrupt the ecosystem, especially air and aquatic bodies, additionally to healthcare, the vast majority of scientists are currently focusing on the influence of climate change on xenobiotic metabolism. Increases in temperature will speed the breakdown of xenobiotics; these xenobiotics may penetrate both surface water and groundwater and damage aquatic life. The food cycle and all tropic levels are impacted by xenobiotic contaminants that infiltrate food chain and the ecosystem. The addition of xenobiotics to humus is controlled by a number of environmental variables that change with the season, weather conditions, soil type, and agricultural methods. To lessen the future effects of xenobiotics on the environment, it may be more economically advantageous to innovate novel synthetic compounds that integrate with the naturally existing metabolic abilities of the bacteria. Soil is the initial chain in the food production process in terms of ecological health, and after that it significantly affects both humans and animals. As a result, investigations on xenobiotics in the food system must be linked between ecological and microbial perspectives.

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Xenobiotics in the Urban Water Cycle



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1 Introduction

Increase in world population along with industrial revolution and economic development has led to the release of many toxic contaminants to the environment. Many of these contaminants like antibiotics, personal care products, perfluorinated compounds, etc. are not previously listed for routine monitoring in the water source by USEPA (2021). Such groups of contaminants are now in focus and are called emerging contaminants (Singh et al. 2021a). These emerging contaminants are toxic to both human and environment. It has been reported worldwide that urban water contains both previously listed xenobiotics and emerging contaminants (Singh et al. 2021a). Previously listed chemicals include pesticides, petroleum hydrocarbons, heavy metals, and polychlorinated biphenyls, and emerging contaminants are personal care products (PCPs), perfluorinated compounds (PFCs), brominated flame retardants (BFRs), pharmaceuticals and microplastics, toxins released due to algal blooms, etc. (Alves et al. 2017).

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The sources of xenobiotics in urban water systems are numerous and can come from many different pathways. These pathways include wastewater discharges from households, industrial facilities, hospitals, and pharmaceutical plants. Other sources of xenobiotics include agricultural runoff, stormwater runoff, and atmospheric deposition (Kumar and Chopra 2020). These sources contribute to the accumulation of xenobiotics in the environment and the urban water cycle, leading to contamination of water resources and posing a significant risk to human health and the environment. As many of the xenobiotic are being released via multiple sources, controlling the xenobiotic at their sources needs a better understanding regarding their source of origin. Once in the urban water system, emerging contaminants can undergo various processes that affect their fate, transport, and persistence. These processes include adsorption, desorption, degradation, transformation, and bioaccumulation. The fate of emerging contaminants in urban water systems is influenced by several factors, including the physicochemical properties of the compounds, the characteristics of the urban water systems, and the environmental conditions. Some emerging contaminants may degrade or transform into less harmful compounds, while others may persist and accumulate in the environment, leading to bioaccumulation in aquatic organisms (Štefanac et al. 2021).

Many of these compounds are lipophilic; hence, their presence in water may lead to bioaccumulation in the biotic system leading to the outbreak of many waterborne diseases and chronic and acute health complications (Álvarez-Ruiz et al. 2021). Sometimes these are lethal also. The presence of these xenobiotics in the urban water cycle will ultimately result in surface water, groundwater, and soil contamination (La Farre et al. 2008). Hence, understanding the sources and fate of these compounds in the urban water is of major concern for improving the quality of both human and environment health. This chapter explores the various sources of xenobiotics in urban water, as well as their different types and fate. This chapter categorizes xenobiotics into pharmaceutical products, personal care products, pesticides, petroleum hydrocarbons, polychlorinated biphenyls, other xenobiotic-perfluorinated compounds, brominated flame retardants (BFRs), phthalates, perfluorinated compounds (PFCs), benzophenones, and some phenols (such as bisphenol A and parabens). For each category, this chapter highlights some of the commonly reported compounds found in the water cycle and their concentration in global samples. The section also describes the sources of each type of xenobiotic and their cyclic translocation in urban water systems. Additionally, this chapter describes the fate of xenobiotics in the environment and the potential ecotoxicological effects they can have on human, animal, and aquatic life. Some of the effects include endocrine disruption, reproductive and developmental toxicity, neurotoxicity, genotoxicity, and carcinogenicity.

2 Types of Xenobiotics

2.1 *Pharmaceutical and Personal Care Products (PPCPs)*

Pharmaceutical products include veterinary/human drugs like antibiotics, blood lipid regulators, analgesics, natural/synthetic hormones, antidiabetics, β -blockers, antihypertensive, and other products which are used in healthcare (Ternes et al. 2004). Recently the pharmaceutical product production and consumption had increased because of the demographic changes and increase in human disorders and infectious diseases. Personal care products include musks (nitro cyclic, polycyclic or macrocyclic), sunscreen agents (benzophenone), camphor (methylbenzylidene), N,N-diethyltoluamide, antiseptic lotion (triclosan), chlorophene, etc. (Lozano et al. 2022). These contaminants are being reported in surface water and groundwater as many of these compounds reach rivers and oceans via contaminated wastewater from urban environment. Thus, these xenobiotics will get into water cycle and reach drinking water because of its hydrophilic nature (Okoye et al. 2022). Some of the commonly reported pharmaceutical compounds are sotalol diclofenac, venlafaxine, tramadol, gemfibrozil, carbamazepine, tetracycline, sulfonamides, macrolides, fluoroquinolones, β -lactams, diatrizoic acid, metaprolol, metformin, guanlyurea tramadol, paracetamol, acetaminophen sulfate, ibuprofen, etc. Some of these xenobiotics are reported in higher concentration even after wastewater treatment, and some are converted to their metabolites. Hoffman et al. (2010) reported a total pharmaceutical xenobiotic and its metabolites ranging from 14 to 28 $\mu\text{g/L}$ in an effluent from wastewater treatment plant.

The major source of pharmaceuticals in urban water cycle is human excreta and urine which reach the urban water cycle via household and hospital wastewater. Disposal of medicines without proper treatment is the second source where it leaches to urban water cycle by runoff (Okoye et al. 2022). Pharmaceutical wastewater which is not properly treated also contributes to some quantum of pharmaceuticals in urban water cycle. Prime sources of personal care products are discharged from household wastewater and disposed used personal care products. The cyclic translocation of pharmaceutical xenobiotics and their metabolites in urban water cycle is depicted in Fig. 1. Wastewater from the abovementioned sources is treated in wastewater treatment plants, and effluent from treatment plant is discharged in surface water. Even after effective treatment, some of these still exist in the wastewater as parent compound itself or as its metabolites (Archer et al. 2017). There is an immediate need for finding an effective treatment option for stopping the release of these compounds to the surface water. The discharged xenobiotics further end up in drinking water source and bioaccumulate in different trophic level, and their cyclic transportation continues in urban water cycle. Studies even report that these pharmaceutical xenobiotics bioaccumulate in shellfishes (Bridges 2002) and other aquatic organisms.

Zhang et al. (2019b) reported the presence of diazepam around 1.22 ng/L in treated water of China. Residues of ibuprofen, ketoprofen, and diclofenac were

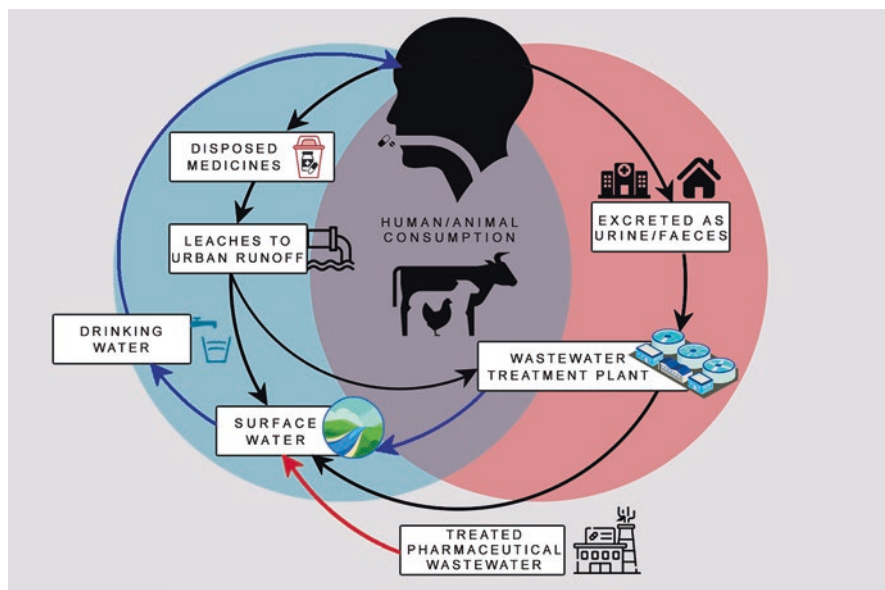


Fig. 1 The cyclic translocation of pharmaceutical products and their metabolites in urban water cycle

detected in surface water, and ibuprofen and ketoprofen were detected in treated water of Spain (Jurado et al. 2021). Around 8 ng/L of diazepam was detected in treated water of the United Kingdom (Baker and Kasprzyk-Hordern 2013). Italy marked higher concentration of pharmaceutical xenobiotics in surface water (Tewari et al. 2013). In France, residues of ibuprofen, naproxen, and diazepam (~250 ng/L) were reported in water which was treated (Togola and Budzinski 2008). Subedi et al. (2017) reported that residues of diazepam (25 ng/L and 9 ng/L) were present in the inlet and outlet samples of wastewater treatment plants. Ibuprofen, naproxen, diazepam, ketoprofen, and diclofenac were detected in a concentration within the World Health Organization prescribed limit 0–10⁴ ng/L in Canada, South Africa, Sweden, and Spain, respectively (Guerra et al. 2014; Larsson et al. 2014; Madikizela and Chimuka 2017). Above studies revealed and confirmed the cyclic movement of pharmaceutical products in the urban water cycle.

Personal care products (PCPs) are products used by human beings for self-care like cleaning and washing, and these include lotions, soaps, fragrances, cosmetics, toothpaste, and sunscreens (Brausch and Rand 2011). The widespread use of these products and their improper disposal and improper treatment of urban wastewater are the root causes of detection of personal care products in urban water cycle (Roberts et al. 2016). According to Blair et al. (2013) and Liu and Wong (2013), effluents from the sewage treatment plants are the main and the largest contributing sources of PCPs to aquatic environment because many of them could not be degraded completely by wastewater treatment. Many of the reported PCPs are

persistent, bioactive, bioaccumulative, and endocrine disrupting compounds. They are toxic to aquatic organism and human beings. The fate and concentration of xenobiotics depends on their usage pattern, region, and the environmental conditions. According to the literature study done by Montes-Grajales et al. (2017), 43 PCPs were identified as emerging pollutants in surface water around the world in places like Antarctica, Australia, Czech Republic, China, Denmark, Germany, France, Japan, India, Singapore, Romania, Spain, South Korea, Switzerland, the United Kingdom, Taiwan, and the United States. Among these, the largest number of personal care products was detected in Spain and the United States which is followed by the United Kingdom and Germany. Among the PCPs, tonalide (AHTN), galaxolide (HHCB), celestolide (ADBI), and phantolide (AHMI) belonging to fragrances; triclocarban (TCC) and triclosan (TCS) belonging to disinfectants and antiseptics; N,N-diethyl-m-toluamide (DEET) belonging to insect repellents; and benzophenone-3 (BP-3) belonging to UV filters were most frequently reported in surface water (Montes-Grajales et al. 2017). The study also reported that around 23 PCPs in groundwater and 64 PCPs in wastewater were detected from 8 and 26 countries, respectively (Fig. 2). China and Spain recorded the highest number in groundwater. The largest number of PCPs in wastewater was detected in Spain. Different xenobiotics in different category of personal care products were detected around the world (Fig. 3). Detected xenobiotics from cosmetics are 2-phenylphenol, 4-chloro-3-methylphenol, butylated hydroxytoluene, butylparaben, chlorophene, ethylparaben, methylparaben, and propylparaben. Reported xenobiotics from deodorant includes 2-(p-nonylphenoxy) ethanol, 3,4,5,6-tetrabromo-o-cresol, 2-nonylphenol, 4-nonylphenol, 4-tert-octylphenol, chloroxylenol, methyltriclosan, nonylphenol, p-benzylphenol, triclocarban, and triclosan (Oluwole et al. 2020). Fragrance chemicals detected were 1-(1,2,3,4,5,6,7,8-octa-hydro-2,3,8,8-tetramethyl-2-naphthalenyl) ethenone, 2-amino musk ketonne, 2-amino musk xylene, 4-amino

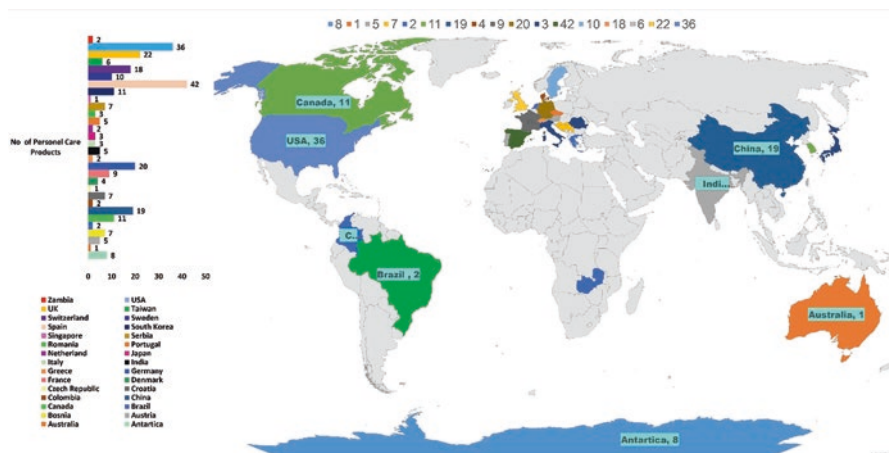


Fig. 2 Personal care products reported from different countries worldwide. (Source: Montes-Grajales et al. (2017))

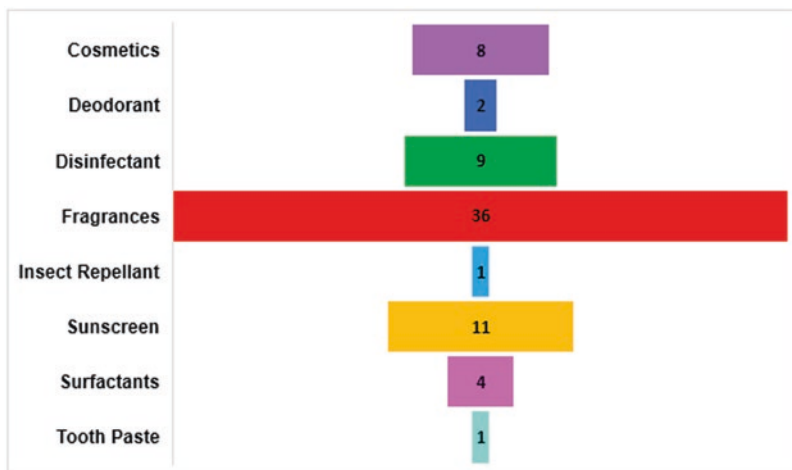


Fig. 3 Xenobiotics detected under different class of personal products

musk xylene, acetophenone, ambrettolide, amino musk moskene, amino musk xylene, benzyl salicylate, cashmeran, celestolide, ethylenedodecanedioate, ethylenetridecanedioate, 6 eugenol, exaltolide, exaltone, galaxolide, lactone, galaxolidone, TBCr, helvetolide, lilial, Limonene, linalool, muscone, musk ambrette, musk moskene, musk ketonne, musk tibetene, phantolide, romandolide, tonalide, traseolide, and versalide (Oluwole et al. 2020). Among the class of insect repellent, N,N-diethyl-m-toluamide was detected. Among the class of sunscreen, 2-2-ethylhexyl-p-methoxycinnamate, 4-methylbenzylidenecamphor, benzophenone-1, benzophenone-2, benzophenone-3, benzophenone, benzophenone-4, octocrylene, octyl methoxycinnamate, ethyl hexyl methoxycinnamate, and octyl triazone were detected (Montes-Grajales et al. 2017).

2.2 *Pesticides, Petroleum Hydrocarbons, and Polychlorinated Biphenyls*

Xenobiotics like pesticides, petroleum hydrocarbons, and heavy metals are age old xenobiotic in water, soil, and air. The main source of pesticides is agriculture practice and other sources including pesticides used for gardening, insect repellents, and disinfection purposes (Tripathi et al. 2020; Dhuldhaj et al. 2023). Pesticides used for agriculture get adsorbed to food crops; these adsorbed pesticides being washed off may reach urban water cycle via gray water. The pesticides in soil and water reach urban water via agriculture runoff. Some of the frequently reported pesticides in the recent studies include endosulfan, dichlorodiphenyldichloroethene (DDE), dichlorodiphenyldichloroethane (DDD), heptachlor epoxide, dieldrin, β -hexachlorocyclohexane (β -HCH), heptachlor, bromobutide, isoprothiolane,

carbofuran, malathion, carbaryl iprobenfos, monochrotofos, mevinphos, acephate, butamifos, diazinon, cadusafos, chlorpyrifos, dichlorvos, carbendazim, imidacloprid, imidacloprid, tebuconazole, propiconazole, difenconazole, buprofezin, butachlor, pendimethalin, and endrin (Abessa et al. 2019). Most of these pesticides being hydrophobic in nature persist in the water. These pesticides get bioaccumulated and get circulated in the water cycle. Growing population and corresponding increase in crop production have increased the application of pesticides. Only 0.1% of the pesticide applied on the food crops reach the target insects, and the remaining will leach out from the plants and the soil via agriculture runoff. These leached out pesticide will persist in soil and water depending on its chemical nature. Some amount of the pesticide will be adsorbed by the plants, and some get adsorbed to the soil. The soil adsorbed pesticide will get degraded, and other pesticide leaches into groundwater and surface water. The surface water which reaches the drinking water supply chain ultimately turns up in the urban water cycle (Pal et al. 2014).

Compared to other xenobiotics, the concentration of pesticides in surface water was high ranging from parts per billion to microgram. There are many studies around the globe on residues of pesticide in soil and drinking water sources. India and China are one of the worst affected countries. Kaushik et al. (2012) reported 23 organochlorine pesticides in water in concentration ranging from 0.01 to 0.34 $\mu\text{g/L}$. In China, around 42 organochlorine pesticides were detected in water sample, and their concentration varied from 0.001 to 2.65 $\mu\text{g/L}$. Manjarres-López et al. (2021) reported the presence of 30 pesticides in water samples of Spain, and average total concentration of pesticide from 3 $\mu\text{g/L}$ was detected. Some of the pesticides reported globally and their maximum mean concentration are given in Table 1. The mean concentration of dimethoate was 14,438 ng/L which was highest among the other pesticides. The highest amount of pesticide was 61,200 ng/L which was detected in surface water sample of Costa Rica (Carazo-Rojas et al. 2018). This high concentration in surface water indicates that the pesticide is widely used and is frequently identified in the environment. This pesticide belongs to organophosphate pesticides, and its solubility is 2.5 g/100 mL. Besides the chemical nature of pesticides, their occurrence either as single or mixture and environmental factors like rain intensity, climatic condition, soil property, and water pH aid in the mobility and translocation of pesticide in water (Zhang et al. 2012). Sometimes rainfall leads to dilution of pesticide in water, and in some cases, intense rain will wash off pesticide from soil and plant and increase the concentration in water. The above described is one way in which pesticides enter urban water cycle. The other sources include direct washing of fruits and vegetables, gardening activities, mosquito/rodent control, veterinary use as pest control, and vegetation control. According to Jiang et al. (2016), pesticide containing dust may also contribute to the pesticide contamination in urban water cycle.

Petroleum hydrocarbons find their way to urban water by means of runoff (Liu et al. 2019). Polyaromatic hydrocarbon (PAH) contamination of urban water can be due to natural or anthropogenic sources (Karyab et al. 2013). Natural source includes diagenesis of sedimentary organic material to form fossil fuel at moderate temperature; phyto- and microbial synthesis; forest fire which disperses the suspended PAH

Table 1 Pesticide detected in global water samples

Pesticide	Mean concentration ($\mu\text{g/L}$)
2,4-D	3000
Acephate	310
Acetamiprid	8.01
Acetochlor	80.6
Alachlor	2.52
Aldrin	90
Atrazine	1020
Bentazone	551
Carbendazim	574.91
Chlorfenvinphos	1.7
Chlorpyrifos	340
Clothianidin	25.3
Dimethoate	14,438
Diuron	4811
Fenitrothion	35
Heptachlor	730
Imidacloprid	118.5
Isoproturon	186.91
Malathion	130
Metolachlor	53.75
Molinate	39.81
Omethoate	46
Simazine	10
Tebuconazole	67
Terbuthylazine	34.78
Terbuthylazine	254.38
Thiamethoxam	50.2

Source: Abessa et al. (2019)

even in remote areas; accidental spillage and/or leakage of waste oils, gasoline, etc.; urban runoff; leachates from landfills and creosoted pilings; industrial and domestic wastewaters; coal- and gas-fired boilers; gasification of coals and liquefaction of coals; production of carbon black; coal tar pitch and asphalt; coke ovens; catalytic cracking towers; petroleum refineries and related activities; industrial incinerators; electrical generating plants; municipal incinerators; agricultural and refuse burning; and emission from petroleum products using automobiles and other vehicles. Direct sources of PAH in urban water are petroleum spillage, atmospheric fallout, wastewater runoff, and residential, industrial, and commercial sources. Most commonly detected PAH in environment and priority PAH listed in the environment are naphthalene, acenaphthene, acenaphthylene, phenanthrene, fluorene, pyrene, anthracene, chrysene, benzo[b]fluoranthene, benzo[a] pyrene, benzo[k]fluoranthene, indeno [1,2,3]pyrene, benzo[g,h,i] perylene, benzo[a]pyrene, and dibenzo [a,h] anthracene (Janneh et al. 2023). Polyaromatic hydrocarbons were detected in

the groundwater samples near oil field located in Brahmaputra Valley of India. The concentration of PAH in the water was in the range of 5–48 ng/mL with naphthalene concentration of 20.5 ng/mL and 17.884 ng/mL (Deka et al. 2023). Zhao et al. (2017) reported that priority listed PAH concentration in the surface water of Nanjing was in the range of 4067–29,455 ng/L. The study revealed coke oven, combustion of coal, oil, and emission from vehicles as the four major sources for PAH contamination. Zhao et al. (2023) reported the contamination of Yangtze River delta by runoff contaminated with street dust. Sixteen priority PAHs were detected in Qinhuai River due to the runoff water containing petrogenic fuel combustion products. The concentration of PAH in the groundwater sample of North Local Government Area of Osun State was higher than the WHO maximum permissible limit of 10 µg/L (Adekunle et al. 2017). Another study in China revealed the presence of priority PAH with mean concentration of 56.25 ng/L (Zhang et al. 2019a, b).

Polychlorinated biphenyls (PCBs) are polychlorinated organic compound which is less soluble in water. They are abundant pollutants in the environment, which are persistent, get transported to a long distance, and bioaccumulate in food chain. It is highly lipid soluble which makes them to bioaccumulate in biota. There are about 209 congeners of PCB. The main source of PCBs in urban water is by their diffusion from old sites where electrical products are manufactured or old electric product contaminated sites (Othman et al. 2022). PCB was used in capacitors along with electrical insulating fluid and transformers, before its ban. It has widely been used in closed systems such as fire-resistant transformers, capacitors used as insulators, open systems in consumables such as ink, plasticizers for painters, paper, and paints. Residues of PCB are reported even now due its improper disposal and unauthorized use in many places. Even after its ban years ago, still residues of PCB in environment are being reported. Wang et al. (2023a, b) reported residues of PCB in water of Beiluo River in Shaanxi Province, China, and the study concludes that the reason for PCB residues may be due to technical PCB mixtures, industrial emissions, and coal and wood combustion. The total PCB concentration in that river was from 0.065 to 1.92 ng/L. Residues of PCBs were even detected in urban air of Germany at a concentration of 50 pg/m³ which confirms the chance of PCB in urban water due to precipitation (Dreyer and Minkos 2023). Balasubramani et al. (2014) reported the residues of PCB in wastewater in the range of 1.01–8.12 ng/L. Waste incineration, accidental fires, old transformers and capacitors, and atmospheric deposition seem to be the sources of PCB in Volturno River, Italy, even after its ban (Montuori et al. 2020). The concentration of PCBs in Volturno River water was 33.2 ng/L.

2.3 Other Xenobiotics

There is a tremendous increase in the load of xenobiotics in the urban water cycle (UWC) by which emerging organic compounds (EOCs) also increase. These include brominated flame retardants (BFRs), phthalates, perfluorinated compounds (PFCs), benzophenones, and some phenols (bisphenol A (BPA) and parabens). BFRs are released from textiles, and organophosphates are released from construction

materials. The most common BFRs are polybrominated diphenyl ethers (PBDEs), hexabromocyclododecane (HBCD or HBCDD), and tetrabromobisphenol A (TBBPA). PBDEs have three technical mixtures, penta BDE, octa polybrominated diphenyl ethers, and the fully brominated deca polybrominated diphenyl ethers (de Wit Cynthia 2002). Organophosphate flame retardants include chloroethyl (TCEP), the dichloropropyl (TDCP), and the dibromopropyl (TBPP). These compounds are released mainly from commercial activities like construction, renovation, and demolition of buildings. Phthalates are used as plasticizers for PVC materials and also added in some paints. Perfluorooctanesulfonate (PFOS) and perfluorooctanoic acid (PFOA) are two most promptly studied PFASs which are reported in environmental samples and are widely used in many applications in industries and consumer products such as surface treatments in fabrics, carpets, and paper packaging (Axmon et al. 2014). The main sources of emerging organic contaminants (EOCs) are household waste/wastewater, hospital waste, construction works, landscaping, industrial scale animal feeding operations, dairy farms, transportation, commerce, and manufacturing. EOCs also enter urban water via sewer pipe leakage, landfill runoff, and improper disposal of wastes. Some of EOCs reported are perfluorinated compounds (PFCs) (Nguyen et al. 2016), polycyclic aromatic hydrocarbons, polychlorinated biphenyls, methyl tert-butyl-ether (Sablayrolles et al. 2011), nonylphenols, etc.

Hu et al. (2014) reported residues of organophosphate flame retardants tris-(2-chloroethyl) phosphate (TCEP) (741.9 ng/L), tris-(1,3-dichloro-2-propyl) phosphate (TDCPP) (84.12 ng/L), tris-(2,3-dibromopropyl) phosphate (TDBPP) (109.28 ng/L), and tris-(2-chloropropyl) phosphate (TCPP) (134.4 ng/L), respectively, in water samples of China. Li et al. (2012) reported around 205 ng/L organophosphorus flame retardants (OPFRs) in tap water. Residues of OPFR (71 ng/L) were present in the drinking water of Pakistan (Khan et al. 2016). Organophosphorus flame retardants (OPFRs) were detected in surface water samples of Changjiang River in China (47.04 ng/L) and river water sample of Sweden 56 ng/L (Jacob et al. 2018; Zhao et al. 2018). Concentration of OPFRs in three Spanish rivers was in the range of 0.0076 to 7.2 µg/L (Cristale et al. 2013). Residues of OPFRs were also detected in Elbe River in Germany (Jacob et al. 2018), and tris-(2-butoxyethyl) phosphate (TBEP), tris-(2-chloroethyl) phosphate (TCEP), and tributyl phosphate (TBP) in the range of 100 and 11,000 ng/L, 1500 and 24,000 ng/L, and 360 and 6100 ng/L, respectively, were detected in the effluent of sewage treatment plant in Sweden (Marklund et al. 2005). Thirty-six polar pollutants including flame retardants were detected in wastewater treatment plant of Europe (Reemtsma et al. 2006).

Perfluorinated compounds are fluorinated organic compounds which are a newly emerged xenobiotics grouped among the class of persistent organic pollutants. Under this category, perfluorooctane sulfonates (PFOS) and perfluorooctanoic acid (PFOA) are much reported class of fluorinated compounds and have got research attention. These compounds have chemical stability and thermal stability and high capability to reduce surface tension and form stable foam. These chemical properties led to their widespread application in plastic, electronic, textile, and upholstery industries (Sunantha and Vasudevan 2016). They are widely been used in many

industrial and consumer products like waterproof/stain resistant fabrics and food packaging (Glüge et al. 2020). They are highly persistent in nature because of the strong carbon fluorine bond. The presence of perfluorinated compounds in water has been reported from the United States, India, China, etc. and is predicted to be widespread in other countries (Barbo et al. 2023). In the USA, potential sources of perfluorinated compounds (PFCs) in water include manufacturing facilities, wastewater treatment plants, airports, municipal landfills, and sites where PFAS-containing fire-fighting foams are used (Andrews et al. 2021). The extended perfluorinated compound pollution is so high in the United States that its residues have been reported in both environmental and human serum. Several toxicological impact was also reported (Bartell and Vieira 2021), including high cholesterol level (Nelson et al. 2010), thyroid related disease (Melzer et al. 2010), and issues with reproductive and developmental stages (Fenton et al. 2021). Reported perfluorinated compounds in urban waterways are homologs of perfluoroalkyl carboxylates, perfluorooctane, perfluorohexane, 6:2-fluorotelomer sulfonate (FOSA), perfluorooctane sulfonamide, N-ethyl FOSA (sulfuramid), N-ethyl sulfonamidoethanol (N-EtFOSE), and N-methyl and N-ethyl sulfonamidoacetic acid (N-Et FOSAA and N-MeFOSAA). The reported concentration of perfluorinated compounds varied from 1 to 300 ng/L. Residues of perfluorinated compounds are also detected in groundwater, and it ranged from 22 to 718 ng/L in Brazil (Stefano et al. 2023).

Another xenobiotic which belongs to the category of emerging contaminants is phthalates and bisphenol. Phthalates and bisphenol are widely used in plastic producing industry, healthcare products, medical devices, emulsifying agents, epoxy resins, lubricants, auto parts, dispersants, food packaging and services, cosmetics, insecticides, paints, gelling agents, and many other households and consumer products (Duenas-Moreno et al. 2022). Chemically phthalates are a diester structure having a benzene ring, two carbonyl groups, and two alcohol groups, and bisphenols are 2,2-bis(4-hydroxyphenyl) propane. Phthalate is a colorless liquid and bisphenol is a crystalline powder (Duenas-Moreno et al. 2022). Most commonly used phthalates and USEPA listed priority phthalates are diethyl phthalate (DEP), dimethyl phthalate (DMP), di-n-butyl phthalate (DnBP), benzyl butyl phthalate (BBP), di-2-ethylhexyl phthalate (DEHP), and di-n-octyl phthalate (DnOP) as priority pollutants (USEPA 2009). Wastewater treatment plant is one of the major sources of phthalates and bisphenol in urban water. Residues of phthalates and bisphenol were detected in many wastewater treatment plants. The mean concentration of phthalates and bisphenol varied from 0.06 to 1146.37 µg/L and 0.02 to 416 µg/L, respectively. Qian et al. (2021) reported that phthalate and bisphenol removal efficiency of the wastewater treatment plant varied from 14% to 66% and the rest will get adsorbed to the sludge. The adsorbed phthalates and bisphenol undergo less mineralization because of its hydrophobic nature. Gao et al. (2014) reported that low molecular weight phthalates are removed in treatment process because of its polar nature. In general, phthalates and bisphenols are not fully eliminated from wastewater treatment plants, and their subsequent release into the surface water leads to the contamination of groundwater. Another source by which phthalates enter urban water cycle is by leaching from landfills. Phthalates and

bisphenol residues in the leachate were reported globally. Phthalates and bisphenol were detected in high concentration of 8200 $\mu\text{g/L}$ and 4500 $\mu\text{g/L}$, respectively. This is mainly due to the leaching of xenobiotic from the solid waste. According to Tran et al. (2022), soil contaminated with fertilizer, additives, plastic film, plastic waste, wastewater, and sludge also contributes to the release of phthalates and bisphenol to urban water. The above discussed sources will ultimately bring these compounds to surface water and groundwater. As they are insoluble ones, they enter the water media, and their attenuation rate decreases and starts persisting and bioaccumulating. Phthalates were also detected in mineral water (Net et al. 2014), and this can be attributed to the leaching of phthalates from the plastic cans or bottles. The distribution of phthalates and bisphenol in water may vary in different regions, and they mainly depend on hydrological/hydraulic factors, adsorption, and their biodegradation (Duenas-Moreno et al. 2022).

Antibiotic is another xenobiotic which has recently caught global attention. There are different sources by which antibiotics are released into environment (Singh et al. 2021b). These are antibiotic manufacturing industries, hospitals and municipalities, waste from large-scale animal farms, and aquaculture. Humans are one of the major contributors of antibiotics which reach environment via urine, excreta, and direct source by disposal of the used and unused antibiotics. Chemical oxygen demand, biological oxygen demand, nitrogen, phosphorus, microelements, pathogens, heavy metals, and priority organic compounds such as pesticides and industrial chemicals are some of the traditional water quality assessment parameters, but recent studies have confirmed the presence of several emerging contaminants which could cause serious toxicological impact in urban water cycle. These diverse compounds belong to different categories of organic compounds, and their concentration usually detected were in 1 ng/L to 1 $\mu\text{g/L}$. Figure 4 depicts some of the commonly detected xenobiotics in urban water during the recent years.

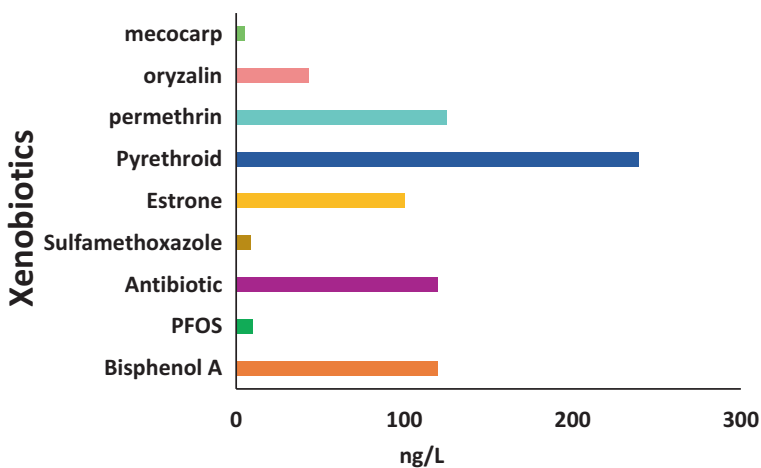


Fig. 4 Concentration of some frequently detected xenobiotics in urban water

3 Xenobiotics in the Environment

One of the important ways by which xenobiotics enter in the environment is by the use of reclaimed water. Many studies reveal that xenobiotics from the urban water get bioaccumulated in the plants. For example, pharmaceutical products like sulfonamide concentration in the hydroponic culture was 180–2000 mg/g in a greenhouse study (Schneider 2008). One of the pharmaceutical products being reported is the presence of different antibiotics. The antibiotics enter surface water bodies via urban runoff and untreated wastewater. Their presence in water may affect microbiome in water and lead to antibiotic resistance among pathogens which is one of the alarming issues, globally. Other xenobiotics frequently being reported are PFOA and PFOS, BPA, plasticizers, terbuthylazine, chlorpyrifos, atrazine, alkylphenolethoxylates, N,N-diethyl-m-toluamide, etc. These chemicals in the urban water reach various water bodies and enter food chain via different trophic level. These chemicals will progressively accumulate in biota finally leading to biomagnification. The biomagnification will depend on the chemical property of the specific xenobiotic. This biomagnification may induce changes in the biochemical homeostasis followed by physiological/physiopathological disorders. Gradually occurs the so-called chemical stress, caused by the increase in the xenobiotics that could lead to physiopathological perturbations originating in biochemical dyshomeostasis (Schneider 2008; Egodawatta et al. 2013).

Urban water cycle includes different sources of water by which contaminants get circulated in urban environment. This includes direct and indirect reuse of water, recharge, and artificial recharge. Direct reuses include by advanced wastewater treatment, indirect water reuse via surface water, and artificial recharge of aquifers with effluent. These all sources receive contaminants via runoff; direct discharge from houses, hospitals, industries, etc.; and deposition from atmosphere (Donner et al. 2010). Figure 5 represents the cyclic movement of xenobiotics and their fate in the environment.

The translocation of xenobiotic in urban water cycle depends on many factors like solubility of the xenobiotics, adsorption, rain intensity, biodegradability, adsorption by bioforms, stability toward environmental conditions, and wastewater treatment efficiency (Donner et al. 2010). A xenobiotic released into the environment undergoes different modifications, and some remain unaltered. The main conversion process is the abiotic and biotic conversion of xenobiotics. Abiotic conversion includes photochemical transformation in aquatic environment or in atmosphere and chemical reaction in soil and water. Biotic conversion includes microbial conversion and biochemical conversion within plants, human, and animals. During this conversion, some xenobiotics get completely degraded and mineralized to carbon dioxide and water, but some undergo partial mineralization and co-metabolic transformation (Greeshma and Vasudevan 2013). Unaltered xenobiotics get adsorbed to soil or sludge and may further undergo desorption and end up in soil, surface water via runoff, volatilization, and groundwater. The xenobiotics

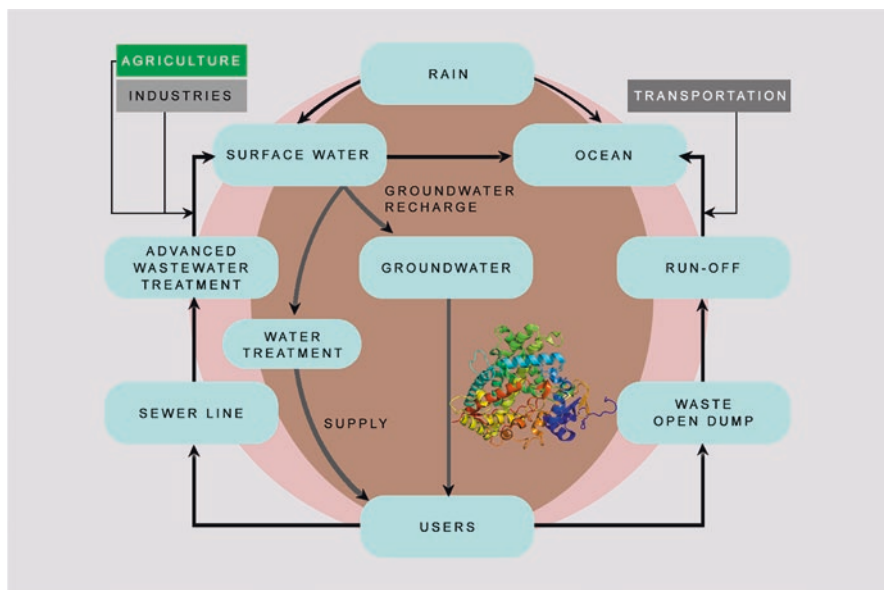


Fig. 5 Xenobiotic translocation in urban water cycle

which are more lipid soluble will bioaccumulate in various bioforms and result in biomagnification. Altered xenobiotics by abiotic and biotic conversion may undergo humification or become bound residues and be further desorbed. The desorbed xenobiotics are introduced into the soil and surface water through runoff, volatilization, and groundwater transport. Additionally, the transformed xenobiotics can undergo biomagnification. In certain instances, these altered xenobiotics exhibit heightened toxicity and increased persistence compared to their original compounds. A few such xenobiotics are the metabolites of DDT, endosulfan, chlorpyrifos, etc. (Vasudevan and Greeshma 2017).

The destiny of xenobiotics in urban water cycle depends on wastewater treatment plant. Studies over different regions around the world reveal that conventional wastewater treatment plant could not completely remove the xenobiotics especially those belonging to the category of emerging contaminants (Castiglioni et al. 2018). The fate and removal rate of xenobiotics depend on their physical-chemical properties and treatment processes. Sorption to solids and sludge, biological degradation, and stripping are some of the proposed mechanism by which these xenobiotics can be removed from the wastewater. Hence the conventional treatment plants should be upgraded in terms of their efficiency based on the xenobiotic profile to minimize the release of xenobiotics into the surface (Castiglioni et al. 2018).

4 Ecotoxicological Effect of Xenobiotics in the Environment

The potential toxicological impacts of xenobiotics in humans include carcinogenic effect, thyroid issues, low sperm count, endocrine disruption, inhibition of the growth of hepato cells in embryo, errors in chromosomal segregation, mutagenic and reproductive toxicity, etc. (Abdelsalam et al. 2020). In animals, they cause meiotic aneuploidy, synaptic defects, endocrine disruption, reduction in body weight and cholesterol level, increased weight of liver, and neonatal mortality; arcinogen excites thyroid-stimulating hormones in plasma and, thereby, causes thyroid tumors in rats (Pal et al. 2014), cardiotoxicity in dogs; endocrine disruption, chronic hepatotoxicity in mice at high concentration, cytotoxic, genotoxic effects to mammalian cells, increase the weight of gonads and increase steroid hormone production in male rats, disrupts hepatocyte cytoskeleton, DNA disruption (Gicevic et al. 2020). Its impact in aquatic animals include estrogenic and reproductive effect, mussel mortality, adverse effect on endocrine and neuromuscular systems of larval fish, effects on embryonic development of zebrafish, abnormal growth of the testis in male at low concentration (ng/l), feminization, anemia, and kidney failure in carps. The following subsections highlight the details of the toxicological impact of some xenobiotics.

4.1 *Phthalates and Bisphenol A*

Phthalates and BPA cause toxicity to genes, neuron, cells, and reproductive organ and cause endocrine disrupting effects (Wang et al. 2022). It also causes cancer of the breast, skin, liver, and testicles. It may also lead to autism, diabetes, obesity, and thyroid dysfunction.

4.2 *Perfluorinated Compounds*

Perfluorinated compounds induce breast cancer in the human body. PFOA adsorbed in the human body gets transferred to the breast, serum, liver, kidney, and where they start accumulating. This is because the human body cannot metabolize perfluorinated compounds. The half-life of such compounds in the human body is high. In animals, these xenobiotics cause toxicity to the nephron, immune system, nerves, during embryonic development, kidney cells, genes, pancreas, cardiac system, and thyroid (Abudayyak et al. 2021). Wang et al. (2018) and Steenland and Winquist (2021) observed that perfluorinated compounds cause pregnancy diabetes and cancer of the kidney, testis, liver, breast, etc. Reports are also there in Taiwan, where it has been reported to cause asthma in children (Fairley et al. 2007; Dong et al. 2013). Perfluorinated compounds would enhance immunoglobulin E (IgE) response to

allergens by increasing the production of serum IgE. High concentration of perfluorinated compounds in serum leads to attention deficit hyperactivity disorder (ADHD). Toxicological studies have shown that perfluorinated compounds will affect glomerular filtration and elevated uric acid production (Costa et al. 2009). According to Lu et al. (2019), this is because of upregulation in human cells, which upon oxidation get converted to uric acid. Perfluorinated compound exposure also leads to chronic kidney disorder resulting from a higher glomerular filtration (Levey et al. 2005). PFOA exposure can result in alteration of metabolic pathway in the kidney, like peroxisome proliferator activated receptor pathway, oxidative stress pathway, autophagy pathway, inflammatory pathway, and DNA methylation.

4.3 Personal Care and Pharmaceutical Products

Residues of pharmaceutical products and personal care products in water result in bioaccumulation in various aquatic forms in different trophic level. Some reported toxicological impacts are growth inhibition and photosynthetic toxicity in aquatic plants, lethal, liver damage, and abnormal development of embryo in zebra fish, reduction of carbohydrates and fatty acid methyl esters, inhibits the antioxidant system, reducing cell growth, chlorophyll pigment and rate of photosynthesis in algae, growth inhibition and reduced food intake in hydra, increase hydrogen peroxide activity and glutathione peroxidase activity in rainbow trout, induce stress due to oxidation and cause damage to DNA in daphnia, cytopathology damage to liver, degeneration of hyaline droplet, dilation, vesicle formation in kidney, necrosis in gill cells of rainbow trout, deviations in embryonic development, alters motor behaviour of zebra fish, cause male feminization in frogs (Wang et al. 2021). Even though the residues of pharmaceutical products occur in minor concentration level and the potential hazard is less, they can induce some risks as they belong to the category of pseudo persistent pollutants (Hawash et al. 2023). Their impact is more in other life forms like aquatic plants and animals and terrestrial animals. Reports are there on reduction in the population of vulture in India, Pakistan, and some other countries due to intake of diclofenac indirectly by eating cattle. Polycyclic musk fragrances are reported in breast milk (Kannan et al. 2005). Pharmaceutical products are biologically active, and they modulate endocrine and immune system and signal transduction; hence, ingestion of these products will affect the biochemical and physiological functions of biological systems and ecosystems. In some cases, like antibiotics, the residues will cause indirect effect like the microbes will get adapted to antibiotic residues in the environment and will become resistant to antibiotics. There is resistance to antibiotics which will ultimately lead to human susceptibility to pathogens.

4.4 Other Persistent Organic Pollutants

Pesticides, petroleum hydrocarbons, and polychlorinated biphenyls are age old pollutants which have been posing serious threat to various life forms. The toxicological effects caused by persistent organic pollutants are endocrine disruption, carcinogenic, impairs immune and nervous system, diabetes, thyroid problem, causes diseases like Parkinson's disease, Alzheimer's, problems in kidney, liver, respiratory disease, birth defects, etc. by entering the human cells and interfering with the cellular function (Fig. 6). The impacts on other biota include changes in metamorphosis of frog, reproduction in rat, fecundity in snail, postnatal growth and neurobehavioral development in rats, impact on spermatogenesis in mice, and changes in intercellular calcium level in phagocytes of the kidney and blood leucocytes of rainbow trout, and it reduces the availability of plants and other prey for fish, affects the habitat of aquatic organisms, and results in biomagnification, diseases in wildlife species, and abnormalities in behavior and birth defects in fish, birds, and mammals (Greeshma and Vasudevan 2013). Global studies and reports reveal that there is considerable increase in the type and concentration of xenobiotics being distributed in environment. The impact of which is also being frequently reported. The release of these chemicals by direct source should be restricted, and there is an immediate need for implementing a proper wastewater treatment and other waste management options for preventing the transport of xenobiotics in urban water cycle.

5 Conclusion and Future Prospective

Global studies and reports reveal that there is considerable increase in the type and concentration of xenobiotics being released to the environment. The impact of which is also being frequently reported. Since the majority of these xenobiotics enter urban water systems through various pathways, comprehending the origin and volume of xenobiotics released from different sources is crucial for managing their discharge at specific points. The release of these chemicals by direct source should be restricted. The pattern of xenobiotic usage varies globally, within country and within different regions also. Hence, understanding of various xenobiotics and their quantification and fate in water cycle is of concern to suggest proper mitigation options for their removal. Studies over different countries reveal that the removal of many of the emerging contaminants is not possible by conventional wastewater treatment system; hence, research should concentrate more on designing and installation of most suitable wastewater treatment system. There is an immediate need for implementing a proper wastewater treatment and other waste management options for preventing the movement and release of xenobiotics in urban water cycle.

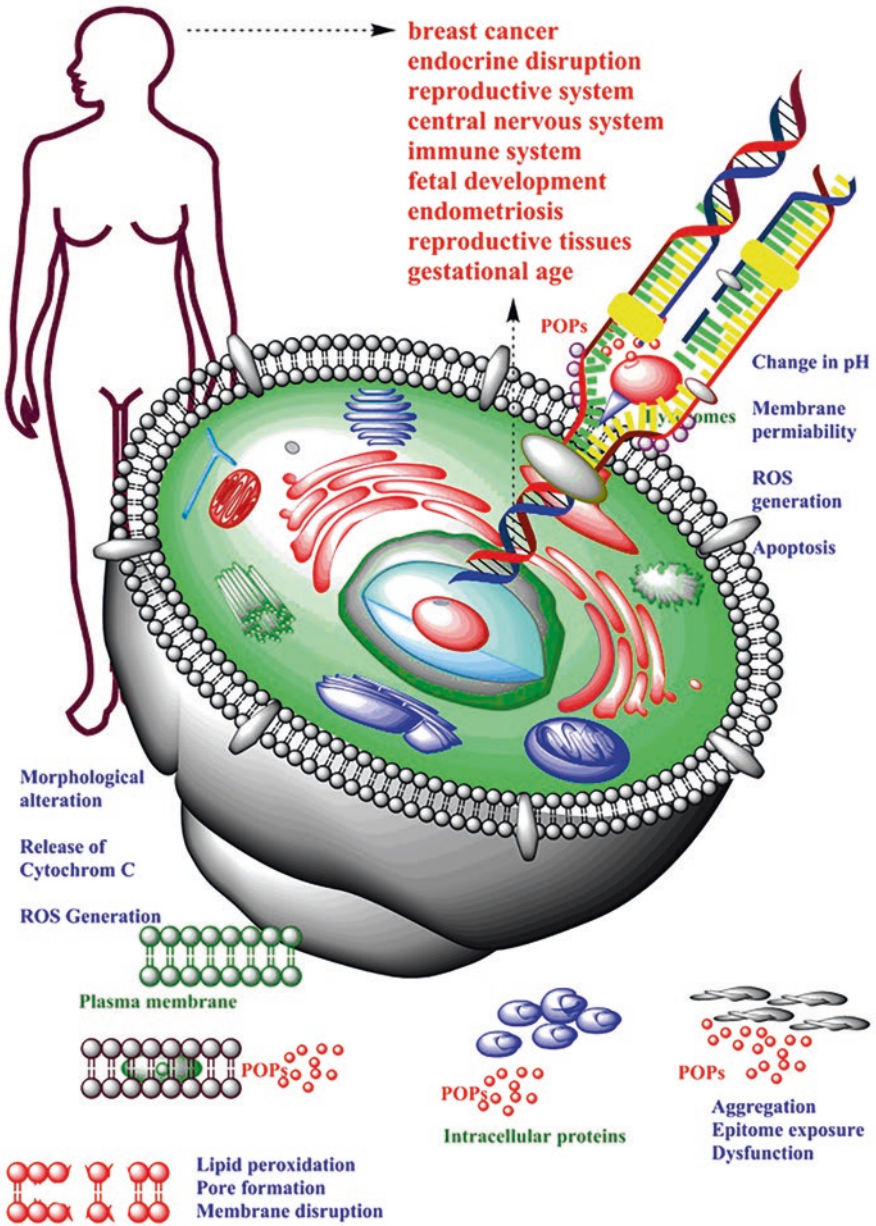


Fig. 6 Mode of action of persistent organic pollutants (POPs) at cellular level

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Assessment of the Consequences of Xenobiotics in Soil Ecosystem



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1 Introduction

India is a predominantly agriculture-based country with a diverse climate, and the main economic sector is agriculture and its supporting industries. Various chemicals (xenobiotics) like dichlorodiphenyltrichloroethane (DDT), hexachlorocyclohexane (HCH), etc. have been widely utilized for enhancing the agricultural yield in the country for more than 50 years (Jayaraj et al. 2016; Tripathi et al. 2020). Globally, decades ago, environmental pollution by xenobiotics, therefore, increased rapidly (Kobzev et al. 2020). The introduction of these substances into the ecosystem can lead to an increase in allergies, biological death, genetic mutations, a decrease in immunity, and metabolic disorders and create interference with natural ecosystem processes up to ecosphere level (Kovaleva et al. 2019). Xenobiotic cell injury and genetic anomaly lead to damage or disease. Accordingly, these substances are proven to be serious threat to the well-being and medical health of the living beings (Omelchenko et al. 2017). Juveniles become “target” of exposure to xenobiotics. It is characterized by increased physical inactiveness, fatigue, dysfunction (i.e., metallic and laboratory pathways), various disorders of digestive organs, central nervous system (CNS), bile-duct related disorders, and genitourinary system and decreased interest in outer world things, severe acute respiratory syndrome (SARS) recurrent, respiratory congestion, pneumonitis, and multiple allergic reactions (Stapleton et al. 2012). Contamination of foods with pesticides, trans-fatty acids, and hormones is very dangerous. According to a study in the USA, there were 100% DDE (1,1-dichloro-2,2-bis (p-chlorophenyl) ethylene) residues in dried leafy spinach and beef; 93% in cheese, chicken, turkey, sausages, and ice cream; 87% in oil and

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salamis; and 81% in cheddar and half sliced pepperoni sausages (Bharadwaj 2018). More than two million tons of pesticides are used yearly globally, and only 0.1% reached pests; the remaining 99.9% are submerged (Alavanja 2009). The pesticide, which is composed of chemical chlorine and lasts in soil for 10 years, is composed of DDE and DDT (Kip et al. 2011).

Xenobiotics are present in foods such as flavorings, food preservatives, colorants, emulsifiers, thickeners, stabilizers, etc. and turn into more harmful every year. Smoke from air conditioners, printers, copy paper production, office dust, etc. is hazard imported in people's lives during office work. Building-related illness (BRI) or sick building syndrome is characterized by nasal congestion, chest tightness, low breathing level, flu-like conditions, etc. In addition influence of harmful and noxious gases emanating from cars and electromagnetic radiations, which are constantly surrounding factors, so need to protect the human body, against these negative effects of the environment is evident. Pesticides, commonly used in agricultural lands, crops, and various industries as a plant safeguarding factor, have been found in many products. Studies determine the potential health risks of substances that differentiate their pathways to human exposure: water use, food chain, or direct contact (Bespalov and Kotlyarova 2018). In the present chapter, we have discussed about the various xenobiotic components and their types along with their mechanism of action and treatment techniques with respect to soil ecosystem.

2 Classification of Xenobiotics

On the basis of nature and structure of chemical, following defiant categories can be used to categorize xenobiotic substances as described by Bharadwaj (2018) with modifications based on the literature (Fig. 1).

2.1 Halocarbons

Halocarbon compounds are mostly employed in the manufacturing of insecticides and pesticides, etc. Such mutations when released in surrounding atmosphere lead to ozone depletion and, when accumulated into soil, will lead to increased biomagnification.

2.2 Polychlorinated Biphenyls (PCBs)

PCBs are naturally inert (generally not reactive) compounds and are used in cooling insulators in transformers, manufacture of plasticizers, etc.

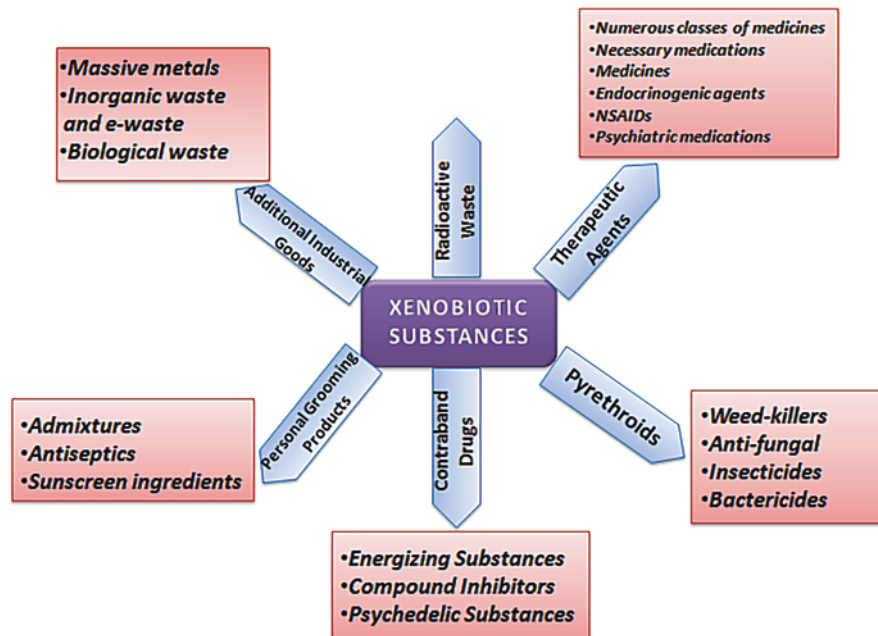


Fig. 1 Classification of xenobiotics on the basis of nature and structure of chemicals

2.3 Synthetic Polymers

These are humic-like substances i.e., high-molecular mass compounds, not soluble in water mainly used in manufacture of plasticizers such as polymers, PVC (polyvinylchloride), etc.

2.4 Alkylbenzene Sulfonates

Linear alkylbenzenes (LABs) or alkylbenzene sulfonates will not be damaged by the effect of microflora due to the presence of sulfonate group. It is mainly used in the manufacture of cleaning products.

2.5 Oil Mixtures

Due to the accidental spillage of oil in the oceans, oil spills over the surface of the water and decomposed by bacteria causing malfunction. Fat does not dissolve in water. Therefore, it becomes a defiant.

From this discussion, it has become clear that the opposing factor of the xenobiotic compound is directly related to its complexity, and it has been noted that the antagonistic material is enhanced as its complexity increases.

3 Interaction of Xenobiotics with Soils

After xenobiotics are liberated into the environment, an irrecoverable series of mutations is set to move, and different interactions of xenobiotics with soil have been observed (Jayaramaiah et al. 2022). When xenobiotic is released into the soil, it can be transported or chemically modified by biotic or abiotic processes. Xenobiotic behavior will depend on its chemical and physical and biological properties of the soil. The processes that affect the transport of the original compound within the soil are surface assimilation, percolating, concentration, and dehumidification, whereas its conversion is affected by redox reactions, chemical weathering, and microbial conversion (Ukalska-Jarug et al. 2020). But these processes do not occur independently, so their level and extent to which one process occurs will control the quality and magnitude of other processes. For example, the adsorption of 2,4-D in clay minerals and organic matter has been shown to reduce its decay (Ogram et al. 1985). The most versatile and effective mechanisms involved in the conversion of xenobiotics to soil are biotic (Tinsley 1979). Many xenobiotic compounds have little structural similarity to natural compounds, and the degradation of these xenobiotic compounds will depend on their ability to induce the synthesis of needed destructive enzymes (Stefanac et al. 2021).

Biodegradation is less likely to be a molecule with structural features that are rarely or have never been seen in natural products. In addition to the properties of the xenobiotic structure, environmental conditions (e.g., presence or absence of oxygen, usable water content, temperature, and pH) must correspond to the function of those microorganisms that contain the suitable enzymes. Some common types of chemical reactions caused by microorganisms are oxidation of methyl group reactions, dehalogenation (removal of halogens), para-compound oxidation, deamination, decarboxylation, hydroxylation, reduction of three and double bonds, sulfur oxidation, double bond hydration, polymerization, and nitrogen metabolism (Alexander 1981; Jayaramaiah et al. 2022). The effects of xenobiotics on the abiotic properties of the soil, both physical and chemical, have not received much attention. Xenobiotic incorporation into mineral and biological environments can alter soil chemical properties by increasing or decreasing most importantly pH, cation and anion exchange capacities, and base fullness, as well as altering the hydrophobic and hydrophilic properties of adsorbent (i.e., mineral or natural substances). The effects of xenobiotics on the visible areas of the soil include the following:

1. Changes in porosity by staying in the pore area, thereby reducing the Earth's energy due to the movement of water
2. A reduction in water holding capacity due to non-installation of water

3. A reduction in the stability of soil particles, due to the disruption of mineral-organic matter interaction

In addition to the direct effects xenobiotics can have on abiotic soils, it may also indirectly affect these structures. For example, bacteria that use xenobiotics as a source of nutrients can cause a decrease in soil hydraulic activity by releasing metabolic products that close soil pores (Frankenberger et al. 1979). Soil environmental pollutants may be neutralized through the naturally occurring bioremediation mechanism. It is widely accepted that inorganic minerals play a critical role in xenobiotic transformation due to their strong interaction with xenobiotics.

4 Xenobiotics' Effects on Soil Microbial Communities

Soil microorganisms are most important living beings for many soil functions such as biological decay, biogeochemical cycles, soil conservation, and prolificacy (Wainwright 1978). Xenobiotics react with soil along with the native soil microflora, alter biological and social structures, and with this affect enzymatic activity and biochemical reactions (Hussain et al. 2009; Munoz-Leoz et al. 2011). Therefore, it is crucial to specify effect of xenobiotics on soil microflora in order to maintain important soil functioning. The cellular respiration of TCE (trichloroethylene), organochlorine in laboratory-based experiment, was reflected a change in the microflora colony structure when heterotrophs rise up to 500 times during incubation with TCE and toluene, but only 3 times during incubation with TCE only (Hubert et al. 2005). In a field experiment, phenol and TCE had also depicted to change the feature of the microflora community by expanding population of *Burkholderia cepacia* and *Variovorax* (Gram-negative bacteria) in groundwater contaminated by TCE (Humphries et al. 2005).

On the other hand, various studies have examined the impact of pesticides on soil communities (population), finding mixed or no effects (Jjemba 2002; Pandey and Singh 2004; Singh and Singh 2005a). According to one study, using external endosulfan increased bacterial biomass by 76% and reduced fungal biomass by 47% (Xie et al. 2011). However, the potential microbial nitrification of the soil was very sensitive to the addition of fenamiphos (10 mg/kg), which clearly shows the risk to soil health. Recent studies have not shown an influence of fenamiphos on the activity of urease and dehydrogenase (Australian soil) (Cáceres et al. 2008). Moreover, continuous application of pesticides, e.g., methyl parathion, has reflected in the reduction of soil microbial heterogeneity (Zhang et al. 2006). Opposite results were obtained during the impact of microbial communities in the soil when studies were conducted employing continuous application of one or more pesticides with distinct chemical characteristics (Gundi et al. 2005; Wang et al. 2007; Chu et al. 2008).

Excessive use of CP (cyclophosphamide) in the agroecosystem has led to effects on soil microbial communities. The lifespan of a CP is usually between 10 and 120 days in the soil but can be up to 1 year depending on soil types and weather

conditions (Singh and Walker 2006). Perseverance of CP residues in the soil may impair the function and stability of the microbial community (Kulkarni et al. 2000). It has been found that microbial biomass, i.e., an excellent marker of microbial activity, showed negative impact (Schultz and Urban 2008) to CP management in amalgamation of 10 mg/kg, the minimum dose employed in agricultural practices (Vischetti et al. 2008). In an experiment, it has been noticed that application of CP in doses of 10–300 $\mu\text{g/g}$ in fields considerably lowers the population of *Azotobacter* sp. (an aerobic dinitrogen-fixing bacteria), though statistically the mentioned concentration has not shown such effects over fungal and bacterial population (Martinez-Toledo et al. 1992). It has also reported that microbial population in soil considerably reduced by applying CP up to 18.2%, 30.5%, and 27.7% when used in concentration of 4, 8, and 12 mg/kg, respectively (Fang et al. 2009). Moreover, the bacterial population considerably decreased when 20 mg/kg of CP has been applied to the soil (Chen et al. 2014a, b).

As these studies exhibited unfavorable impact of CP on the soil's microbial population, another experiment had possessed almost no impact of CP individually or in combination with some other compound (pesticides) on microbial activity of soil and other characteristics including total biomass of microbial population (Singh et al. 2002a, b). Also, with this, CP utilization has been exhibited to change microbial population (Wang et al. 2010) which in return decreased the accessibility to phosphorous and nitrogen ratios in the soil (Sardar and Kole 2005) and also decreased the plant prolificacy. One study by Menon et al. (2005) has mentioned key results of CP on nitrogen mineralization in sandy loam soils.

A number of studies have exhibited that CP affects the microbial activity of the soil. We barely know about the characteristics of imidacloprid (IC) and its effect on soil microbial population structure and function. In soil the duration of this pesticide seems to range from 40 days in non-amended soil to 124 days in soil which is a short time ago treated with some organic fertilizers, and duration turned up from 28 to 1250 days in soil with traditional seed treatment (Rouchaud et al. 1994; Goulson 2013). The results of certain experiments are sufficient to assess the impact of IC on soil microbial population and other parameters (Cycon et al. 2013; Cycon and Piotrowska-Seget 2015a, b). When put in an application at field rate (1 mg/kg), the studies claimed that IC did not affect soil microbial population. But, at the doses IC in 10 mg/kg persuaded relevant variation among population. It is anticipated that high and continuous use of IC would result into its buildup in soils in near future (Goulson 2013), which will lead to change in microbial soil function. IC may show negative impact over the microbial population in soil and their functions at high concentration (10 mg/kg soil). Moreover, it has been claimed that excessive use of IC poses negative impact over soil nitrification rates by altering the population of ammonia oxidizing microorganisms. Thus, it has affected the nitrogen cycle and degraded the soil quality (Cycon and Piotrowska-Seget 2015b).

In another study, it has noticed that IC has temporary or almost no effect on soil enzymatic activities such as ureases and dehydrogenases in a field like ground nut and turfgrass (Ingram et al. 2005; Singh and Singh 2005b); also, at field rates of 2.8 gm active ingredient/kg seed (Singh and Singh 2005), it has been said that use of IC

has negative impact on fungi and actinomycete population structure. Similarly, Tu (1995) also observed the repressive effect of IC upon the fungal community at about 10 µg active ingredient/gm of soil. Also, the adverse effects of the xenobiotics can be reduced or moderated by some of the environmental factors such as properties of soil, its perseverance, toxicity, amount of xenobiotics present, and its availability to the microorganisms in the soil (Hussain et al. 2009).

5 Degrading Xenobiotics by Capable Microbes

There is application of microorganisms in eradicating xenobiotics from soil or water by their alteration into harmless products such as water (H₂O) or carbon dioxide (CO₂) which is one of the most basic concepts in terms of bioremediation (Ortiz et al. 2013; Singh et al. 2016). Certain bacterial strains like *Bacillus*, *Rhodococcus*, *Pseudomonas*, and *Methanospirillum* with some yeasts such as *Rhodotorula*, *Candida*, and *Exophiala* have been claimed to have effective role in bioremediation and biodegradation of xenobiotics compounds from any of the polluted soil or water (Sathishkumar et al. 2008; Nzila 2013; Sunita et al. 2013; Zhao et al. 2017; Bharadwaj 2018; Yang et al. 2018a, b; Yu et al. 2019; Bhatt et al. 2020).

Some ecological factors which may comprise of soil salt content, temperature, carbon sources, pH, humidity, some nitrogen sources, etc. may influence the biodegradation potential of the microorganisms (Megharaj and Naidu 2010; Wu et al. 2014; Bhatt et al. 2019). Some catabolism potentials such as enzymes, certain degradation pathways along with the genes, utilized in the reaction called as bioremediation may be carried by the microorganisms, which may become the reason for the development of novel characters (Widada et al. 2002; Scholer et al. 2017; Yang et al. 2018a, b; Zhu et al. 2020). Furthermore, microbial plasmids are the key factor that can be employed for the regular growth, development, and dispersal of biodegradable genes and enzymes (Zhang et al. 2016; Jeffries et al. 2019). The obtained genes and enzymes have provided microorganisms' biodegradation ability to abolish or detox several kinds of environmental pollutants because of their ability of lateral gene transfer (Singh et al. 2018; Jaiswal et al. 2019; Li et al. 2019; Phale et al. 2019; French et al. 2020). The mechanism of bioremediation can be refined by modifying existing strains using genome editing and other biochemical techniques. This will eventually lead to the evolution of GMOs (genetically modified organisms), which can quickly degrade a variety of xenobiotics (Shanker et al. 2011; Zhang et al. 2016; Hussain et al. 2018; Janssen and Stucki 2020).

With the help of improved genetic manipulation techniques, it becomes possible to get more details and inspects future perspectives of bioremediation of xenobiotic compounds by the use of highly skilled microbes (Sayler and Ripp 2000; Shapiro et al. 2018; Wong 2018; Liu et al. 2019). One of the most important examples of xenobiotics includes synthetic pesticides specially the organochlorine pesticides which are used enormously across the world for an extended time period in the field of agriculture (Dhuldhaj et al. 2023). It has been noticed during ICP (insect control

program) that many organochlorine pesticides (OCPs) like most famous DDT, aldrin, and hexachlorocyclohexane possess very toxic nature because of their stable and biomagnification nature (Aktar et al. 2009; Jayaraj et al. 2016; Awasthi and Awasthi 2019). Previous study has found that lindane, a poisonous xenobiotic compound, which is organochlorine in nature; several studies are going on (physical and chemical) for its microbial biodegradation (Kaur and Kaur 2016; Bashir et al. 2018; Zhang et al. 2021). Lindane concentration is increasing on the daily basis in the environment which is causing health problems such as carcinogenicity, mutagenicity, and immunocompromised diseases in humans (Cuozzo et al. 2017; Zhang et al. 2020). In recent research, it has become evident that *Pseudomonas*, *Chromohalobacter*, and *Bacillus* are able to degrade lindane through the process of dehydrogenation, dehydrochlorination, and sometimes hydroxylation (Giri et al. 2014; Cuozzo et al. 2017; Wang et al. 2018; Nagata et al. 2019; Zhang et al. 2020).

One large range pesticide specifically used as agricultural and household pesticide is pyrethroids. Cypermethrin, cyfluthrin, deltamethrin, and bifenthrin are some of the common examples of pyrethroids (Chen et al. 2012; Chen et al. 2014a, b; Bhatt et al. 2019; Zhan et al. 2020). The abovementioned chemicals (pesticides) are very poisonous and may result into impairment on molecular, neural, and even reproductive level (Sharma et al. 2018; Bhatt et al. 2019; Gammon et al. 2019). Among them, there is one compound named cypermethrin which causes neurotoxicity after crossing the blood-brain barrier (Singh et al. 2012). Such chemicals (pesticides) retain for an extended duration of time in the surrounding that causes severe risk to human health and other organisms including both terrestrial and aquatic systems (Burns and Pastoor 2018; Ullah et al. 2018; Lu et al. 2019).

Some of the microorganism strains such as *Raoultella*, *Pseudomonas*, *Trichoderma*, *Bacillus*, and *Acinetobacter* have been outlined for their ability to perform systematic degradation of large range pesticides like some of the pyrethroid pesticides (Cycon and Piotrowska-Seget 2016; Zhan et al. 2018; Bhatt et al. 2019; Chen and Zhan 2019). Because of the partial ignition of the organic components, polycyclic aromatic hydrocarbons (PAHs) have become strong environmental pollutants that cause environmental contamination and xenobiotics that are today extensively spread in the environment. Polyaromatic hydrocarbons (PAHs) show a specific range of toxicity, i.e., moderate to high to life range from aquatic to bird's life (Abdel-Shafy and Mansour 2016; Pandey et al. 2017). Some known polycyclic aromatic hydrocarbons like benzopyrene, naphthalene, and anthracene are known to be the one that leads to the production of injurious biological impacts like mutagenicity, carcinogenicity, and genotoxicity and, thus, present as major ultimatum to human wealth (Kim et al. 2013; Lin et al. 2020). Some microbes have been claimed as good degraders of PAHs, and these are *Sphingomonas*, *Sphingobium*, and *Novosphingobium* (Lee et al. 2016; Fida et al. 2017; Auti et al. 2019). Some microorganisms are found to possess an ability to degrade naphthalene and phenanthrene; these are *Rhodococcus*, *Pleurotus ostreatus*, *Agmenellum*, *Nocardioides*, and *Oscillatoria* (Ghosal et al. 2016; Siles and Margesin 2018). The result of a study revealed that *Amycolatopsis* sp. Poz14 has the ability to degrade 100% of naphthalene and 37.87% of anthracene in about 45 days (Ortega-Gonzalez et al. 2015).

Cycloclasticus sp., a marine bacterium that can break down xenobiotics, pyrenes, naphthalene, and numerous other hydrocarbons, has been identified as a PAH degrading marine bacterium (Wang et al. 2018).

As far as bioremediation is concerned, the microbial consortium culture poses a positive impact over it. Likewise, they possess enhanced capability in the form of elimination of pollutants. Moreover, they also undergo mutualistic association with many other microbial strains (Patowary et al. 2016). Henceforth, now it has become clear that microbial consortia have the ability to decline the metabolic limitations of any culture and magnify the process of biodegradation via enhancing microbial population (Zafra et al. 2016; Li et al. 2020).

6 Conclusion and Future Perspectives

Xenobiotics are becoming a complicated area of research as these are present in different variety and forms. Several factors affect the xenobiotic metabolism. Features of metabolism of an individual may be affected by the genetic variations in enzyme activity. The most important bodily component is age. The metabolism in little ones and in adult appears to be different from each other. A large number of newborns have the enzymes that have the ability to perform oxidative metabolism and conjugation underdeveloped or in inadequate quantities. Factors affecting metabolism of drugs include dose, parity, exposure route, distribution in tissues, and ability of the compounds to bind with the protein.

To rectify these soils, bioremediation techniques are efficiently working. But then also in large areas of the world, physiochemical techniques are also in use very frequently. In the ecosystems, soils and plants possess relation with microbes that have the ability to break down the toxic elements present in the soil into the non-toxic substances.

- Advances in plant biotechnology and microbiology is required to make these bioremediation techniques more efficient such as next generation sequencing which can more efficiently utilize the total microbial population for the degradation of the pollutants.
- Novel genetically modified strains with powerful catabolizing genes are needed to achieve outstanding advances in bioremediation and create xenobiotic-free habitats.
- In addition, microbe-mediated bioremediation, which is a part of green nanotechnology, deserves special consideration as a means of combating xenobiotic contamination.
- The government, legislators, and stakeholders all need to be on board with the idea that sustainable policies should be established often utilizing cutting-edge technologies.

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Part II
Fate and Transport of Xenobiotics
in the Urban Ecosystems

Transport and Metabolism of Xenobiotics in the Urban Ecosystem



Soumita Paul, Ujjal Ghosh, and Mousumi Saha 

1 Introduction

Urban ecosystem is an exceptional strange ecosystem, and being anthropologically made, this ecosystem is so much different from any natural ecosystem (Hassan et al. 2005; Schaefer 2011). Although sometimes it consists of river, lakes, parks, forests, and agricultural fields, human activities have firm impact on this ecosystem. In the last few decades, urbanization has increased globally (Embrandiri et al. 2016). Population increases in urban region are a major threat to the ecosystem (Mollashahi and Szymura, 2022). Urbanization and industrialization lead to the drastic changes in the environment as well as in species diversity (Kowarik 2011; Roccaro et al. 2013).

The word xenobiotic was first derived from the Greek word *xenos*, which means odd or foreign, and *bios*, which means life (Fetzner 2002). It can be defined as a foreign artificial chemical compound that is not naturally found within an organism, but everyday living organisms encountered these compounds, and their metabolism is also foreign for that living entity (Croom 2012). These compounds are generally originated in bulk amount from industry, agricultural farms, domestic uses, etc. and can survive in the environment for a long time (even years) (Embrandiri et al. 2016; Atashgahi et al. 2018). Different types of xenobiotic compounds available are

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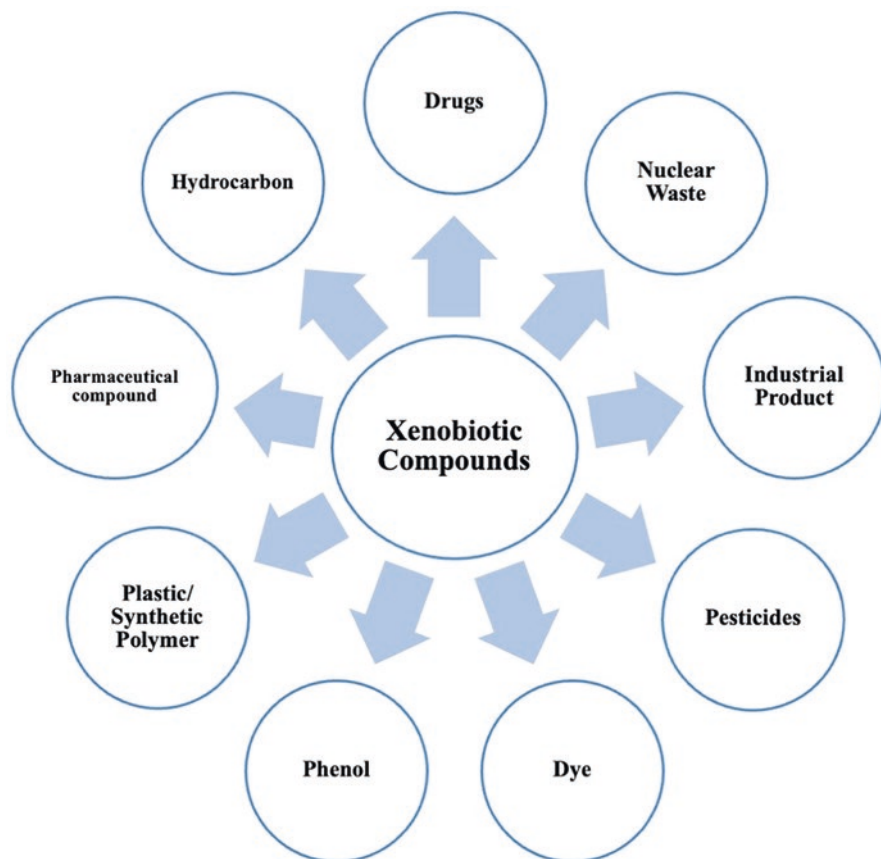


Fig. 1 Diagrammatic representation of different types/classes of xenobiotic compounds that are present in various industrial and other wastes

depicted in Fig. 1. Naturally hydrophilic xenobiotics are removed from the surroundings faster than the hydrophobic compounds (Streit 1992). The bioaccumulation of xenobiotics determines the toxicity in the organism, and this toxicity can be increased to dangerous levels if metabolism is not occurred in organism (Croom 2012).

Organisms in lower trophic level encounter the xenobiotic pollutants and are affected by it. But more harmful toxic impacts have been found in higher trophic level due to biomagnifications of the xenobiotic compounds (Newman 2019). A very good and appropriate example is that antibiotics are sometimes considered as xenobiotics as they are not naturally formed in our body or they are consumed as a part of regular diet (Embrandiri et al. 2016). With the increase of technological advancement in the last century, several products were available for mankind, those made the life easier, but it is not necessary that all of the products can be found in nature or their anthropogenic activity-induced concentrations differ greatly from

those of their naturally occurring concentrations (Štefanac et al. 2021). Their physicochemical structures including low molecular weight, ionization, solubility in water and organic solvent, lipophilicity, hydrophilicity, polarity of the molecules, and volatility of the organic chemical make them challenging to determine, quantify, and eliminate from the nature (de Oliveira et al. 2020). Basically, our daily life products such as drugs, toothpaste, shoes, mobile phones, laundry reagents, cosmetics, food colors, preservatives, fragrances, toys for child, etc. consist of xenobiotics. In the urban society, these can also be found in pesticides, car washes, railway sleepers, industrial chemicals, wastewater treatment, environmental pollution, etc. (Donner et al. 2010). These toxic substances are accumulated in the body through food web and biomagnifications. The only way to get rid of these toxic effects is the metabolism of xenobiotic compounds.

Phase I monooxygenase enzymes, phase II conjugating enzymes, and phase III transporter enzymes are the three categories of xenobiotic-metabolizing enzymes that are involved in xenobiotics metabolism. Phase I xenobiotic-metabolizing enzymes frequently break down lipophilic xenobiotics first, increasing their polarity and supplying conjugation reaction sites. Phase II metabolizing enzymes function as conjugating enzymes that have the ability of direct interaction with xenobiotics; however, they do so more frequently with the metabolites that phase I enzymes produce. These more polar metabolites are then excreted by both passive and active transport; thus, the body became toxin-free (Croom 2012).

This chapter provides an insight into the transport of toxic xenobiotics and metabolism of those compounds for detoxification. In this chapter, we mainly focused on the transport and metabolism of those xenobiotic compounds that are generally found in the urban ecosystem. The broad ranges of xenobiotic transport systems inside the human body are also thoroughly discussed. At the same time, we extensively explored various types of xenobiotic-metabolizing enzymes and their functions. Finally, a detailed overview of the transport of xenobiotic compounds and their metabolism is presented here.

2 Transport of Xenobiotics

Nowadays, urban ecosystem is the home for xenobiotic pollutants and these are profusely increased day-by-day. These compounds have feasible roles to damage environment. They can be classified into several groups according to their sources and uses. In urban areas, industrial contaminants are much more prominent than the agricultural pollutants such as different types of pesticides, herbicide, bactericides, etc. Except all these, daily used products and personal care products also contain the xenobiotic substances (Ebele et al. 2017). Xenobiotic compounds are concentrated inside the living entity as they are hard to break down due to their complex forms. Even much more hazards may arise because of their partial breakdown. To know the origin of these substances is essential for reducing the amounts of xenobiotics from

the environment (Štefanac et al. 2021). The main origin of pharmaceutical compounds in urban territory is municipal wastewater, coupled with industrial and hospital effluent (Roccaro et al. 2013). According to literature, most risky compounds found in the sewage treatment plants (STPs) and wastewater treatment plants (WWTPs) are bleach and motor oil, while washing powder and vegetable oil provide additional concern (Knops et al. 2008). Nearly 200 types of xenobiotic substances were identified from the water of urban washrooms. According to the study of water-using activities, handwashing produced the maximum waste, followed by showering and brushing teeth (Eriksson et al. 2003).

Personal care items and chemicals formed from household works are the dangerous source of xenobiotic compounds. In urban areas, the most significant sources are laundry detergents and cleaning agents. These products are regularly discharged into the sewage and further transported to STPs and WWTPs (Knops et al. 2008). Although these xenobiotic compounds are introduced into the environment as a result of human activity, they sustain and transport into the ecosystem in consequence of inappropriate disposal of STPs, WWTPs, manufacturing industries, livestock plants, etc. In agriculture, insecticides and herbicides are applied directly on agricultural land, and these pollutants either consequently end up in the soil, or the rain helps to transfer these substances into ground streams, aquifers, rivers, ponds, lakes, ocean, sea, etc. Pharmaceutical and personal care products (PPCPs) are the mostly used dangerous pollutants which are found in generous amount in urban and industrial area. These substances are not directly transported into the organism; they take two different pathways that go through our food chain (Chopra and Kumar 2018). Firstly, the enzymes, which are found in humans and animals, are unable to do the total breakdown of PPCPs but converted it to several more toxic metabolites (Kumar and Chopra 2020). Both the parent compound and their metabolites are present in the excretory products of the organism. Secondly, these compounds penetrate in the STPs and WWTPs through animal excretion, and ultimately, they contaminate the soil, lakes, water streams, seas, groundwater, ocean, etc. followed by the consumption of these products by plants and aquatic species. Thus, this system provides a route for them to enter the food chain.

After oral intake of medications, food components coupled with water and food additives and environmental toxins, the intestine is the first part of the digestive tract where xenobiotic compounds are frequently exposed and can cause harm by direct exposure (Niu et al. 2013). There are various ways that xenobiotics might harm the intestinal tract in the role of a toxicological target (Lin et al. 1999). Henceforth in toxicology, the intestine plays vital roles as a target organ as well as a point of entry for xenobiotics into the body (Sambruy et al. 2001). In addition to this, drug-metabolizing enzymes (DMEs) that can produce reactive metabolites are expressed at relatively high levels in intestinal cells. The huge amount of the drug and its metabolites in biliary excretion along with their rhythmic exposure can interrupt the homeostasis of the lumen of the intestine (Treinen-Moslen and Kanz 2006). Lastly, the gut microflora may potentially play a role in the production of harmful

metabolic compounds that may damage the intestine (Kent et al. 1969). Drug induced intestinal injuries are usually undetected at the time of screening due to the rapid repairing mechanism of intestinal lumen. Therefore, drug induced intestinal injuries can be induced if the damage must be surpassing the potentiality of the surrounding cells in damage repairing or the ability of the stem cells in lining replacement (Treinen-Moslen and Kanz 2006).

In optimum biological circumstances, multiple efflux pumps are functional in the liver and the kidney (both are helpful to remove xenobiotics from the body) and in the epithelium of the organs like the blood-brain barrier (BBB), small intestine, etc. These pumps are involved in the export of probable toxic substances (Schinkel 1997). The study of Schinkel (1994) revealed two facts about Mdr1a (one of the multidrug resistant proteins in rodents); one of the facts is that endothelial cells of the blood-brain barrier (BBB) express the Mdr1a, and another one is the physiological significance of Mdr1a in the protection of the brain from different xenobiotic compounds (Schinkel et al. 1994). Another group led by Mayer et al. (1997) also established the same fact that Mdr1 protects the brain by inhibiting numerous substances that penetrate the blood-brain barrier (BBB) (Mayer et al. 1997). Apart from MDRs, multidrug resistance-associated protein (MRP) transporters also play crucial role as drug efflux pumps. The MRP family consists of seven transporter proteins (MRP1 to MRP7) in which only MRP1 and MRP2 are extensively studied. Both MRP1 and MRP2 export the xenobiotics from tissues (Borst et al. 1999). While MRP1 aids in defending the organism against harmful elements (Rappa et al. 1999), MRP2 acts as a detoxification component of the liver, brain, kidney, and small intestine to save them from fatal substances (Kartenbeck et al. 1996; Miller et al. 2000). Other membrane transporters, organic anion-transporting polypeptides (OATPs), efflux the xenobiotic compounds along with transport of hormones and drug neuroactive peptides in various tissues. These types of transporters transport the molecules in both directions (Meier et al. 1997; Tamai et al. 2000).

Renal transporters are another type of transporter that is found in the kidney and responsible for enhancement of kidney toxicity through the aggregation of xenobiotic components and their metabolites. Maximum renal transporters are involved in the elimination of toxic compounds, wherein some of them are associated with reabsorption phenomenon (Burckhardt and Burckhardt 2003). Sometimes as a consequence of these transporters' function, the absorption of drug by proximal tubule cells (PTC) is more rapid than its efflux; the result may be the aggregation of toxic compounds in the kidney. Numerous toxic xenobiotic compounds and prescribed medications are found in the kidney and eliminated through it as it is the primary excretory organ of human being. In this elimination procedure, the proximal tubule cells (PTC) present in the kidney perform a significant function as they consist of multiple bidirectional transporter and enzymes involved in metabolism. The PTC is the main location for toxicity and have immense role in the removal of xenobiotic compounds (Lock and Reed 1998; Knights et al. 2013; Nigam et al. 2015; Miners et al. 2017; Bajaj et al. 2018).

3 Metabolism of Xenobiotics

The term metabolism, in general, describes all chemical reactions that are required for continuing the living state of the cells, thereby organisms. Except some spontaneous metabolic reaction, energy is necessary for the majority of metabolic activity occurring inside the cell. Energy is required to accomplish these reactions. The catabolic part of metabolism detoxifies a compound, thus helping in the reduction of toxic properties of xenobiotics. In a few cases, metabolism enhances the toxicity for the reason that metabolites are more harmful than the original compounds (Croom 2012). William in 1959 first proposed the process of xenobiotic metabolism that often undergoes two phases of metabolism (Williams 1959). Caldwell et al. (1995) studied the fate of xenobiotic substances in parallel with drugs, and according to their study, these substances take one or more of four possible paths: (1) elimination unchanged, (2) retention unchanged, (3) spontaneous chemical transformation, and (4) enzymatic metabolism (Caldwell et al. 1995).

Both hydrophilic and lipophilic compounds are quite possibly removed by the urine and feces sequentially through elimination unchanged procedure. A couple of xenobiotics remain in the body so long as a consequence of retention unchanged fate of the compounds. While the enzymatic metabolism pathway is preeminent in the removal of xenobiotics, spontaneous chemical transformation is extremely rare mechanism for them (Croom 2012). Enzymatic metabolism is the key process for biotransformation of xenobiotic compounds. A couple of chemical reactions as an example of hydrolytic reactions, enzymatic activity of lyase enzymes, reduction transformation, transfer of functional groups, radical enzyme activity, etc. occur to achieve the xenobiotic metabolism (Koppel et al. 2017). Drug-metabolizing enzymes (DMEs), also coined as xenobiotic-metabolizing enzymes, are essential for the metabolism of xenobiotic compounds and their detoxification and further removal from the body. In most cases, these enzymes have immense role to protect the organisms from toxic xenobiotics by preventing accumulation of these elements inside the body (Kaur et al. 2020). A number of DMEs are present in several organs and take part into the biotransformation to reduce the toxic effect of xenobiotics. These metabolizing enzymes are highly expressed at the basal level, and their levels are amplified in the presence of xenobiotics. Phase I and phase II xenobiotic-metabolizing enzymes and drug transporters (Fig. 2) are the three categories that are involved in this biotransformation (Wang and LeCluvse 2003; Croom 2012).

3.1 Phase I Enzymes

Xenobiotic-metabolizing enzymes, phase I and phase II, are profusely expressed and show polymorphism in multiple tissues or organs of the organism. Though these enzymes are abundantly present in almost all tissues, for example, the liver, kidney, digestive tract, lungs, and brain in humans, they are mostly concentrated in

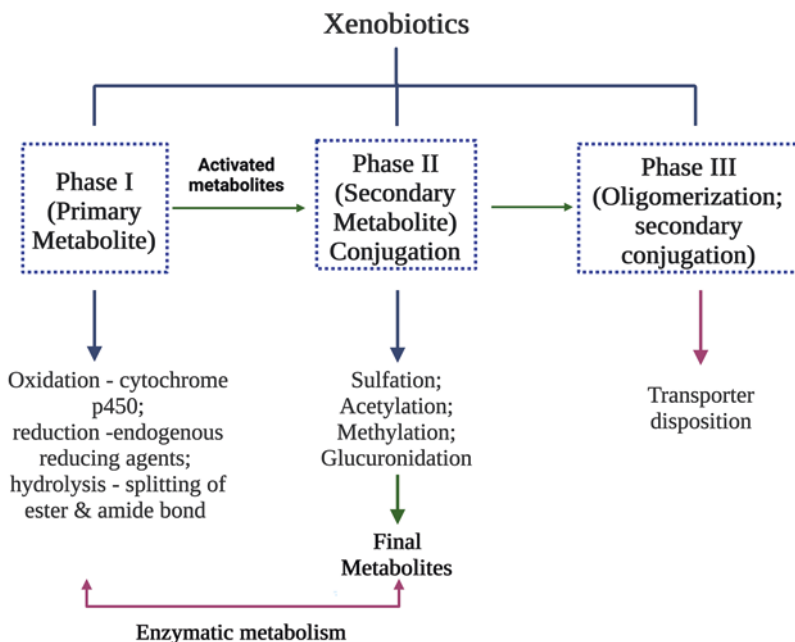


Fig. 2 Schematic illustration of different phases with their mechanisms involved in the degradation of various xenobiotics

the liver. Despite the possibility that the liver's detoxifying processes are crucial, some metabolic pathways that mostly bypass the liver may also be associated with higher levels of toxicity (Rose and Hodgson 2004). When metabolic activity is linked to the toxicity, the toxicity occurs at the locations with the highest concentrations of the activating enzymes.

There are many enzymes associated chemical reactions collaborated with the phase I part of the xenobiotics catabolism or transformation, but the monooxygenation reaction performed by the cytochrome P450 (CYPs; P450s) is likely the most remarkable route in this system (Guengerich 2003). Apart from CYPs, carboxylesterase and flavin monooxygenase (FMOs), hydroxylases, epoxidases, dehydrogenases, and amidases are other most common phase I enzymes, while prostaglandin synthetase and some other enzymes are less common, but all of them are equivalently significant in xenobiotic metabolism (Wang et al. 2008). These enzymes serve to establish conjugation sites and are involved in a significant part of the toxic compound metabolism.

3.1.1 Cytochrome P450 Monooxygenase

The majority of phase I xenobiotic-metabolizing enzymes are made up of the cytochrome P450 (CYP) superfamily. This CYP enzyme superfamily is the terminal oxidase element of the microsomal electron transfer enzyme system, which is made

up of several families and their descendant subfamilies, and these are categorized based upon the similarities of their primary structure that indicates the amino acid sequence (Gonzalez and Nebert 1990; Nelson et al. 1996; Guengerich 2003). All mammalian enzymes fall into 1 of 12 families, each of which contains 22 subfamilies. In the case of humans, CYP1, CYP2, CYP3, CYP4, and CYP7 consist of five CYP gene families and are thought to be essential for both hepatic and extra hepatic metabolism of xenobiotic compounds and drugs, thus helping in the removal of those substances. All of these isoforms of cytochrome P450 (CYPs; P450s) enzymes consist of protoporphyrin IX ring attached to iron (Fe) that acts as a prosthetic group for them (Gonzalez and Nebert 1990; Nelson et al. 1996; Simpson 1997).

The enzymes are named as CYP P450 as they absorb the light at 450 nm and became active. This activation results in heme group reduction followed by binding with carbon monoxide (CO). This binding changes the heme group orientation thus inactivating the CYPs and absorbs the light spectrum at 420 nm (Zeldin 2007). The CYPs perform multiple reactions for proper function in particular N- and O dealkylation, N- and S oxidation, hydroxylation of aromatic and aliphatic compounds, and deamination in addition to purification and/or bioactivation of a large variety of xenobiotic substances. This system can metabolize a large number of procarcinogenic chemicals like benzene and polyaromatic hydrocarbons in tandem with toxicants like nicotine and acetaminophen (Lewis 2003; Omiecinski et al. 2011). CYPs can regulate the effect of drug responses through drug metabolism by controlling the drug action in the tissues, bioavailability, safety level, and drug resistance in several drug affecting organs as well as different metabolizing organs (Zhao et al. 2021).

All monooxygenation reactions of CYPs entail two simultaneous chemical reactions; at first water is reduced by releasing one oxygen atom, and then that oxygen atom binds with the substrate. The NADPH-cytochrome P450 oxidoreductase transfers the electrons needed to reduce CYP from NADPH, with the second electron occasionally coming from NADH through cytochrome b5 (Annemarie 1997). CYP3A4 relies on cytochrome b5 as it participates in numerous biotransformation processes.

3.1.2 Flavin-Containing Monooxygenases (FMOs)

For a while, the microsomal flavin-containing monooxygenase (FMO) was thought to be an amine oxidase, but it was later discovered that they are characteristically a sulfur and phosphorus oxidase. Similar to cytochrome P450 monooxygenases (CYPs), FMOs are also microsomal monooxygenases that require both NADPH and oxygen as an electron donor and also exist in a number of isoforms in different tissues. It was observed that the FMO is crucial for drug and xenobiotic metabolism reason being purified FMO1 oxidized a variety of amine-containing medications and was also coupled with FMO1 activity (Ziegler 1980). Subsequent studies have shown that other FMO enzymes are as always participated in different drug substrate metabolism; in some instances, they may be the main processing enzyme in

drug metabolism (Krueger and Williams 2005). In the year 2008, Hodgson et al. discussed about the attributes of xenobiotic metabolism through the action of different FMOs (Hodgson et al. 2008). Drug used in chemotherapy and other medications and xenobiotics all depend on FMO3 enzyme for proper metabolism (Wang et al. 2008). Among various types of FMOs, FMO1, FMO2, and FMO3, these three types have shown wide range of substrate specificity, while FMO5 has a constrained extent of substrate specificity. FMO5 is well known for its activity to oxidize the primary amines. Few studies have been done on FMO4 but that is not detailed. At the time of birth, the foremost fetal FMO1 converts to the adult FMO3. When transitioning from fetal to adult FMO, there might occasionally be a noticeable delay. This delay may cause a brief buildup of extra trimethylamine inside the body and the temporary onset of trimethylaminuria (Koukouritaki et al. 2002).

3.1.3 Epoxide Hydrolases

Epoxide hydrolases enzymatically transform specific alkene and arene compounds to trans-dihydrodiols through the hydration of the epoxide rings of those compounds. This enzyme family is found in both cytosol and endoplasmic reticulum of the cell. Arand (2005) and Hodgson (2008) described the general characteristics of these enzymes in detail (Arand et al. 2005; Hodgson et al. 2008). Epoxide hydrolases react with several xenobiotic compounds such as pesticides, insecticides, pharmaceuticals, combustion by-products, etc. (Dorough and Casida 1964).

3.1.4 Alcohol Dehydrogenase

Alcohol dehydrogenases are another type of phase I enzyme which catalyzes alcoholic compounds to either aldehydes or ketones at various rates. Alcohol dehydrogenases easily break down the primary alcohols, but metabolism of secondary alcohol is much slower than the primary alcohol metabolism. Alcohol dehydrogenase enzymes do not have significant role in metabolism of tertiary alcohol. The transformation of methanol to formaldehyde by alcohol dehydrogenase is the most common and important chemical reaction (Croom 2012).

3.1.5 Aldehyde Dehydrogenase

Humans have five distinct isoforms of aldehyde dehydrogenases, each with a unique expression pattern and different site of action. Apart from their alcohol metabolism, they are also engaged in the subsequent metabolism of alcohol secondary metabolites, including phenoxybenzyl alcohol, metabolite of permethrin, as well as the metabolism of those alcohols that are generated endogenously and xenobiotics that have alcohol groups. These enzymes are found in various tissues, for example, kidneys, liver, and lungs. The early synthesis of aldehydes generates toxicity inside the

body, and their further metabolism helps to reduce the toxic effect. Aldehydes are metabolized by aldehyde dehydrogenases and produce acids. Acids can be eliminated more easily than their corresponding aldehydes because of their polarity. Phase II conjugation now has a new target due to the creation of the acid (Croom 2012).

3.1.6 Amine Oxidases

There are two types of amine oxidases found in humans that are monoamine oxidases and diamine oxidases. All three types of amines are deaminated by monoamine oxidases. Their main locations are the liver, kidneys, and brain. They have significant functions in the metabolism of biogenic amines, but they have the property to oxidize xenobiotics. Diamines are deaminated by diamine oxidases when oxygen is present. They are located in the placenta, kidneys, and gut. Distance between the two amines affects the diamine oxidase reaction rate; fastest rate can be observed for shorter diamines, whereas diamine oxidases cannot metabolize the longer diamines that have distance for more than eight carbons so that they might be deaminated by monoamine oxidases (Benedetti 2001; Gong and Boor 2006).

3.1.7 Prostaglandin Synthetase

Mammals produce prostaglandins through a series of reactions that begin with arachidonic acid as a substrate. Co-oxidation of xenobiotics produces compounds that are comparable to those generated by different isoforms of CYP during the various steps of prostaglandin synthetase action (Marnett and Eling 1983). Numerous insecticides, including parathion, as well as aromatic amines, like benzidine, act as substrates. These substrate-enzyme reactions might be significant in extrahepatic tissues like seminal vesicle in male and in the inner renal medulla, which have low CYP and high prostaglandin synthetase levels (Eling et al. 1983).

3.1.8 Proteases

The body normally uses a number of proteases to convert the proteins present in foods into the relevant amino acids, and this process includes proteolytic cleavage. These proteases are crucial for both eliminating damaged proteins and keeping hormone levels in check. Synthetic protein-based medicines are being used more frequently in recent days. Protein-based poisons that are consumed or administered as venoms must also be eliminated from the body. For example, hirudin, a proteinaceous compound found in leeches, has significant properties to anticoagulate the blood that further produces the synthetic protein biliverdin.

3.2 Phase II Enzymes

R. T. Williams (1959) first discussed about the chemical understanding of phase II associated xenobiotic metabolism (Williams 1959). Various studies revealed the fact that metabolic conjugates of xenobiotics formed from xenobiotic metabolism were cooperatively less hazardous than the parent compounds or the by-products of phase I enzyme reactions. The “transferase” enzymes that carry out conjugating reactions frequently catalyze the phase II biotransformation. Conjugation procedures can be lucid, but sometimes they involve more difficult procedures where the end product is produced through a number of steps (Caldwell 1986). Glucuronidation, acetylation, sulfation, methyl group addition, and glutathione and amino acid conjugation are all part of the phase II chemical reaction pathways. The hydrophilic properties are more observed in the metabolites of phase II conjugations than the initial parent molecules; hence they are excreted frequently through the bile followed by urine and finally exhibit the detoxified effect. Although they are detoxification reaction, sometimes they produce activating molecules, thus increasing the toxicity (Chen et al. 2000).

The phase II xenobiotic-metabolizing enzymes or conjugating enzymes are classified into multiple superfamilies as an example of UDP glucuronosyltransferases (UGTs), sulfotransferases (STs), N-acetyltransferases (arylamine N-acetyltransferase; NATs), glutathione S-transferases (GSTs), and various methyltransferases (Xu et al. 2005). The superfamily of phase II drug-metabolizing enzymes is made up of several families and their descendant subfamilies that consist of several isoforms, and these are categorized based upon the substrate selectivity, expression in different tissues, producibility, and inhibitory effect of xenobiotics (Schilter et al. 1993; Hinson and Forkert 1995).

3.2.1 Glutathione S-Transferases (GSTs)

Due to its role in the halogenated substance metabolism, glutathione conjugation serves as a crucial detoxification process for several pollutants found in drinking water, including arsenic and purification by-products. This process involves the metabolization of a number of pesticides (Motoyama 1980; Fukami 1984). These enzymes are only found in mammalian liver cells. The glutathione S-transferases (GSTs) are the member of dimeric protein family. They have the potentiality to couple with glutathione (GSH) and a wide range of substances that have electrophilic sites and produce many reactive intermediates, especially when reduced GSH levels are found in the cell, thus resulting in toxicological implications (Bolton et al. 2000; Bolton and Chang 2001).

3.2.2 Sulfotransferases (STs)

Many xenobiotics are metabolized and eliminated by the processes of sulfation and sulfate conjugate hydrolysis, which are catalyzed by different members of the STs and sulfatase enzyme superfamilies. Sulfotransferase enzyme interactions with

different xenobiotics typically produce water-soluble sulfate esters, which are then excreted. Sulfatases catalyze the hydrolysis of the sulfate esters produced by the action of STs, which in general catalyze the sulfation reaction (Banoglu 2000).

3.2.3 UDP Glucuronosyltransferases (UGTs)

Glucuronidation is a crucial method for eliminating xenobiotic compounds through the biotransformation of the xenobiotic molecules (Steventon 2020). UDP glucuronosyltransferases (UGTs) have a significant role in glucuronidation reaction. More than ten UGTs are found in humans. Many medicines and multiple xenobiotics with the functional hydroxyl (OH) groups—either in the original form or after the biotransformation with the help of phase I metabolizing enzymes like CYPs—are conjugated and ultimately excreted and eliminated via glucuronidation (Tukey and Strassburg 2000; Sugatani et al. 2001).

3.3 Phase III Transporters

This is a relatively recent term coined for phase III biotransformation that indicates the active membrane transporters involved in the transfer of several medicines and different xenobiotic compounds through the plasma membrane. Three types of phase III drug transporters are found in mammals including P-glycoprotein (P-gp), multidrug resistance-associated protein (MRP), and organic anion-transporting polypeptide 2 (OATP2). These transporters are found in the kidneys, liver, brain, and intestinal tract. They construct a gateway for drug entry and are simultaneously involved in different activity like absorption of drug, metabolism inside the cells, and elimination of drug (Mizuno et al. 2003). P-gp (permeability glycoprotein) and MRP are the type of ATP-binding cassette (ABC) transporters and use the energy generated by the ATP hydrolysis to carry the substrate through the plasma membrane (Mizuno et al. 2003). ABC transporters import or export a wide variety of substrates, such as amino acids, ions, carbohydrates, lipids, xenobiotics, and many medicinal compounds (Brinkmann and Eichelbaum 2001; Kerb et al. 2001; Thomas and Tampe 2020). Leaving aside ABC transporter superfamily, there are other superfamilies named solute carrier family 22A (SLC22A) and SLCO which play vital roles in xenobiotic trafficking. SLC22A superfamily consists of both the organic anion and cation transporters, while SLCO superfamily only contains the organic anion-transporting polypeptides such as OATP2 (Tirona and Kim 2002; Hagenbuch 2010; Jetter and Kullak-Ublick 2020). The monocarboxylate transporter (MCT) is the member of another solute carrier family, SLC16, that regulates the intracellular concentration of xenobiotics (Felmlee et al. 2020).

4 Conclusions and Future Recommendations

This chapter provides a brief introduction of xenobiotics, different types of xenobiotics compounds in urban area, transport of those compounds, and their fate through the metabolism. It also gives an overview of multiple sources of toxic xenobiotic substances, and their level of toxicity is also part of this discussion. In this chapter, we addressed the different transporters involved in xenobiotic metabolism and their function at different tissues. As we all know that the liver is the chief organ engaged in detoxification of endo- and foreign xenobiotics in the human, we deliver a perception about the transport and metabolism of these xenobiotic compounds in other organs like the kidneys, intestine, brain, etc. Due to the complex structures and bioaccumulation in living organisms, xenobiotics are challenging to break down. Partial breakdown can produce chemicals that are more dangerous than the parent molecules. So, in this study, their complete metabolism in the body is highlighted. Different types of metabolizing enzymes are elaborated in this chapter. This chapter might be helpful to study the xenobiotic transport and metabolism found in urban ecosystem. This chapter collated all the knowledge about the production to detoxification of the xenobiotic compounds, and it would definitely provide new insights into the finding of new pathway for detoxification of the compounds. With the time and advancements of the technology, human being frequently encountered several xenobiotics. As in this chapter, source of xenobiotics is also elaborately discussed, and it certainly contributes some aspects to the researcher so that in near future release of anthropogenic xenobiotics from urban areas can be controlled.

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Xenobiotics: Sources, Pathways, Degradation, and Risk Associated with Major Emphasis on Pharmaceutical Compounds



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1 Introduction

Despite the fact that xenobiotics have both beneficial and negative effects on our lives, urbanization, population expansion, industry, and globalization are undoubtedly bringing about progress in human lifestyle (Gu 2019). Global issues include the integration of diverse economies, and circulation of goods and services has been made easy by international connections, technical advancement, and market development (and by the world becoming a global village). Nonetheless, apart from the advantages and from a socioeconomic standpoint, globalization has a negative influence on environment. A healthy environment is a prerequisite for a stable and healthy life (Stobierski 2022). With increased access medical facilities for humans and animals, with regular use of personal care products, medications, pesticides and chemicals, we all contribute to the introduction of novel compounds (mentioned as ‘xenobiotics’ here) in various environmental matrices, viz., soil, air and water (Nikolaou et al. 2007; Ebele et al. 2017). Xenobiotics, separately or in combination, have the potential to cause problems and should be thoroughly researched, taking in consideration their immediate and lasting effects on people, other biota, and physical components of ecosystems (air, water, and soil). Environmental issues have been caused by inadequate drug education to common populace and irresponsible behavior of the industry toward environment, despite the fact that public knowledge of the issue is growing every year (Embrandiri et al. 2016). Anthropogenic toxins cannot

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get degraded physicochemically and biologically in environmental matrices (or do so very slowly) and there are no effective or practical methods for artificially induced degradation that can reduce the environmental pollution from xenobiotics (Singh 2017). Natural substances can turn into xenobiotics if consumed by other organisms, as in case of human hormones' uptake by fish in downstream of sewage treatment plant or chemical defenses used by some organisms against predators (Mansuy 2013). The word "xenobiotics" refers to foreign substances in the living systems. It is derived from two Greek words: *xenos* (foreign) and *bios* (life). Wastewater treatment facilities and runoff during rainy season can be held responsible in major part for the presence of xenobiotics in freshwater (Pedersen et al. 2003; Benotti et al. 2009; Roccaro et al. 2013).

The removal of xenobiotics from wastewater by treatment plants is inadequate, allowing introduction of xenobiotics in public sewers leading them in food chains, causing risk to humans (De Oliveira et al. 2020; Karthigadevi et al. 2021), and contributing to contamination of water bodies (Clara et al. 2005; Vieno et al. 2007; Gabet-Giraud et al. 2010). Activated sludge is frequently insufficient for the removal of contaminants; still populations of bacteria and other microorganisms have been found to be efficient in bioremediation of xenobiotics. A lot of work is being done to develop and refine biotic or physicochemical mechanisms which are more efficient in the elimination of xenobiotics from water. Secondary treatment methods were observed to be inconsistent (also ineffective) at eliminating pharmaceutical pollutants (Lin et al. 2009). Numerous European and international organizations, including the European Environment Agency (EEA), European Medicine Agency (EMA), and US Environmental Protection Agency (USEPA), have carried out research work on effects of xenobiotics on physical environment and biota. A lot of work has been done to avoid or minimize the adverse effects of xenobiotics, and methodologies have been invented to detect detrimental compounds. As per the US Environmental Protection Agency (USEPA), xenobiotics are novel and have an adverse effect on both environment and health, and their potential for harm is not fully recognized yet. Through routine monitoring a list of dangerous substances, many guidelines and regulations seek to make environmental quality better. The following sections discuss about sources, classification, soil and food chain contamination, and risk associated with xenobiotics, particularly pharmaceuticals.

2 Classification and Sources

Various compounds used to enhance quality of daily life (including allopathic medicines, pesticides, colors, pharmaceutical and personal care products (PPCPs), food additives, and so on) are not found naturally in the environment. The fundamental issue is physicochemical nature and behavior of these compounds, which make them challenging to detect, measure, and eliminate (Windsor et al. 2019; De Oliveira et al. 2020). These characteristics include small size, ability to ionize, solubility in water, lipophilic nature, molecular polarity, and volatility. When these compounds

exist in the environment at high concentrations, several naturally occurring compounds (endobiotics) turn into xenobiotics (Soucek 2011; Stefanac et al. 2021). They are categorized in different categories depending on use and chemical nature (Kumar and Chopra 2020) as shown in Fig. 1. Anthropogenic activities like consumption and excretion, treatment facilities for sewage and effluent, livestock rearing and animal waste, manufacturing facilities, and agricultural practices are some examples of the many anthropogenic activities that can release xenobiotics into the environment (Patel et al. 2020). Pesticides are administered through crop to soil, where they are then washed into nearby rivers and groundwater. Humans use PPCPs, which then indirectly infiltrate the environment because some of their metabolites are more harmful than the original compound as they cannot be entirely digested. They eventually get up in rivers, lakes, seas, soils, groundwater, and sewage/wastewater treatment facilities after excretion. Both PPCPs and pesticides can be uptaken by plants and water-based life and make their way in the food chain. It is possible to categorize xenobiotic sources and substances on the basis of nature, use, physical state, and pathophysiological effects (Table 1).

Xenobiotics have complex architectures, which make them challenging to break down and allow them to accumulate in living things (Noman et al. 2019). Even bigger hazards may arise as a result of their partial degeneration (Fig. 2). Knowing the origin of these substances is essential for reducing the amount of xenobiotics in

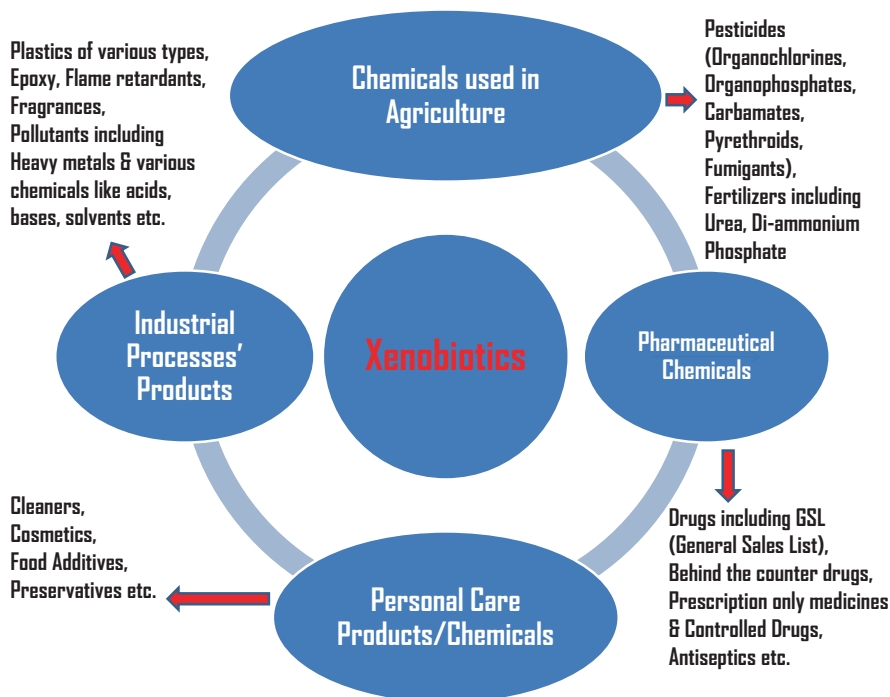


Fig. 1 A glance on various xenobiotics

Table 1 Xenobiotics and their sources

Classification			
Types (based on)	Category	Example	Xenobiotic sources
Sources	Natural	Chemicals or toxins from bacterial and plant origins, zootoxins	<i>Direct sources:</i> pharmaceutical industries (phenols), petroleum products and combustion emissions (hydrocarbons), plastics, solvents, acids, alkalis, dyes, pesticides, toxic metals, tannery effluents, biomedical waste, etc.
	Anthropogenic	Industrially produced substances/materials	
Uses	Directly use	Pesticides of various chemical groups, colors and dyes, paints	<i>Indirect sources:</i> agricultural runoff and leachate, industrial disposal and leachate, pesticides or herbicide application leading to residual accumulation
	Used in substance processing	Preservatives and additives, carrier molecules and ions	
Physical state	Gaseous form	Benzene, aerosol; oxides of C, S, and N	<i>Product and processes:</i> industrial processes, waste burning, fuel combustion, unethical disposal
	As particulates	Asbestos, fugitive dust containing Pb	<i>Process generated and accidental causes:</i> chemicals applied in paper and pulp industries during bleaching and processing, dismantling of ships, traffic pollution deposition
	Liquid form	Effluent disposal	<i>Industrial and domestic:</i> wastewater disposal on land and in water bodies
Physiological impacts	Tissue/organs	Nephrotoxins, neurotoxins, and hepatotoxins (Pb, Hg, Cr, Cd)	<i>Regulated and unregulated:</i> traffic, groundwater contamination from leachates, solid waste disposal leading to leaching of metals, nitrate leaching from agricultural soils
	Physiological and biochemical mechanisms	Methemoglobinemia (MetHb), secondary toxins	

environmental matrices. Pollutants may be released into the environment either directly, as mentioned in Table 1 (Mathew et al. 2017), or indirectly, such as through hospital dispose. Additionally, xenobiotics may be disposed as a by-product or during a procedure. They may do it intentionally or unintentionally and come from moving (such as an automobile) or still sources (industry).

For instance, the European Parliament and Council's Directive 2013/39/EU, Directives number 2000/60/EC (the Water Framework Directive) and 2008/105/EC have been released in relation to various materials in the field of water management being major directives regarding surface water pollution (Eur-Lex 2022). This demonstrates the need to recognize the reasons behind pollution and address emissions from their source in efficient, affordable, and eco-friendly way possible.

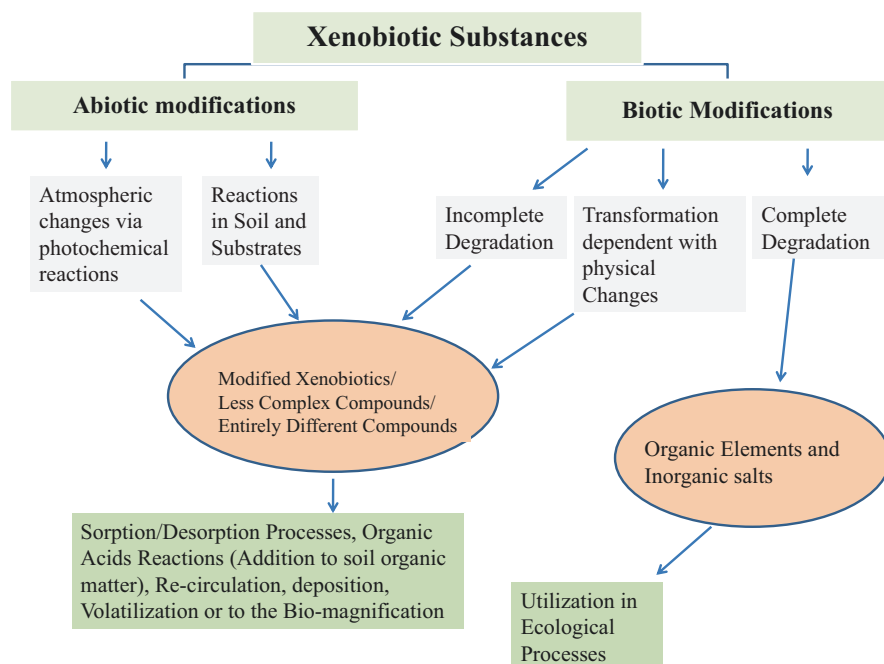


Fig. 2 Possible environmental fate of a xenobiotic compound

The initial list of 33 major substances or cluster of substances in area of water quality policy was established by Directive 2000/60/EC, and environmental quality standards (EQS) for these major substances are established by Directive 2008/105/EC. Continual updates to the list of concerned substances are made in light of reliable monitoring data as well as information on ecotoxicological and toxicological effects. A list of 45 compounds is included in Directive 2013/60/EC as a concern in the area of water quality policy.

The most recent information in scientific and technical fields is included in the EQS for those chemicals. The study “Modes of Action of the Current Priority Chemical List Under the Water Framework Directive (WFD) and Other Substances of Interest” is a major publication on modes of action (MoA) and the impacts of concerned substances and major substances in Watch List (WL) under WFD. Information regarding assessing these compounds using effect-based techniques (biomarkers and bioassays) is included in that study, with a focus on combinations of substances and potential interactions of these substances in aquatic surroundings. Second, they divide chemicals on the priority list in 17 groups and those on the watch list in 8 groups. The European Medicine Agency provides scientific guidance on the best approach to comply with legislative requirements that apply to pharmaceutical chemicals in the European Union (European Medicines Agency 2022). At the European Union level, monitoring of a total of 156 emergent polar organic pollutants in 90 effluent treatment plants was carried out (Loos et al. 2013).

Additionally, 125 molecules representing 80% of the target compounds were discovered at various doses (from nanograms to milligrams per liter). However, xenobiotics released from domestic sources are challenging to control, so it is difficult to inform people about the short- and long-term effects of xenobiotics on the components of environment. There are several potential environmental fates of xenobiotics including deposition, volatilization, biomagnification, and mineralization.

3 Xenobiotics in Atmospheric and Aquatic Environments

Most of the world's population is inhaling unhealthy air that exceeds air quality standards prescribed by various regulatory bodies. Over 6000 places in most countries are now measuring air quality, a record amount, yet people living at those places are still breathing unhealthy levels of nitrogen dioxides (NO_x) and particulate matter (both PM-10 and PM-2.5), with the most exposure in the poor and less developed nations (WHO 2022). The World Health Organization (WHO) has emphasized the significance of reducing the use of fossil fuels and taking other practical measures to lower air pollution. A recently updated database by the WHO on air quality has drawn significant attention toward nitrogen dioxides (NO₂), a common urban air pollutant, and precursor secondary pollutants like ozone and peroxyacyl nitrates (PAN). All these pollutants are mostly the result of anthropogenic activities connected to the burning of fossil fuels and industrial activities. The new air quality database covers air pollution exposure on the ground to the greatest extent yet.

Since the database's 2011 inception, reporting has increased by almost six times. In the meantime, the amount of research supporting the harm that air pollution causes to humans is expanding quickly and indicates that numerous air pollutants, even at low concentrations, can cause significant harm to humans. Particulate matter, especially PM_{2.5}, has the ability to penetrate deeply into the lungs and into the circulation, impacting the heart, brain, and lungs. There have been rising evidences that PM-2.5 affects pulmonary and other organs and contributes to the development of further disorders. NO₂ is linked to respiratory conditions, especially asthma, which can cause hospital admissions, emergency clinical visits, and respiratory symptoms including coughing, wheezing, or breathing difficulties. In an effort to aid nations in improved assessment of the local air quality, the WHO amended its Air Quality Guidelines last year, tightening them up.

“Current energy concerns highlight the importance of speeding up the transition to cleaner, healthier energy systems,” as quoted by Dr. Tedros Adhanom Ghebreyesus, Director-General, WHO. “High fossil fuel prices, energy security, and the urgency of addressing the twin health challenges of air pollution and climate change, underscore the pressing need to move faster towards a world that is much less dependent on fossil fuels.”

On April 7, World Health Day draw attention to the critical measures required to maintain the health of people and the environment to build societies that prioritize

well-being. According to WHO estimates, preventable environmental factors are to blame for more than 13 million casualties globally, every year (WHO 2022). They also contribute to a number of issues with the aquatic ecosystem. The main source of medicines is municipal wastewater, coupled with hospital and manufacturing effluent (Narvaez and Jimenez 2012). Some medications disturb the biofilm community, which has an impact on the entire ecosystem. Animals' reproductive and immunological systems are tending to be affected by xenobiotics (Zhu et al. 2017; Massanyi et al. 2020). Plants with pharmacological qualities should be treated carefully to prevent contamination of crops, vegetables, and surface water given the increasing global influence of herbal medicines. Many pesticides, including insecticides, herbicides, and rodenticides, are dangerous to humans and animals, creating neurological problems, lung irritation, and cancer (Pluth et al. 2019). To properly dispose of pesticides is the greatest method to preserve the environment while continuing to utilize them for their advantageous effects on agriculture. Although they are continuously being explored, the processes through which surrounding factors alter fundamental biochemical processes to cause autoimmune disorders remain mostly unclear (Pollard et al. 2018; Zabrodskii 2020).

These chemicals, which include pesticides, dyes, medications, personal care items, and endocrine-active substances, have a detrimental effect on biodiversity. Waste from homes, businesses, and agriculture are the main sources of their transmission to aquatic habitats, together with industrial and municipal wastewater discharges. Determining xenobiotics in the environment, outlining transformation mechanisms, evaluating the effects of these compounds on specific trophic levels, and characterizing their potential toxicity are all extremely important (Piwowska and Kiedrzyńska 2021). Urban water systems are frequently contaminated by anthropogenic activities, both diffuse and direct (Ternes 1998; Ricking et al. 2003). The aquatic environment in urban areas is too contaminated by probable ecotoxic substances like pharmaceuticals, daily use products, and industrial disposal (Heemcken et al. 2001; Heberer 2002; Stachel et al. 2003) as well as trace elements, which are brought in by diffusion and leaching processes. Urban catchments of both surface water and groundwater are currently under scrutiny because of the rise in human activity, including disposal from industry, transportation, and housing (Möller et al. 2003).

Because of their polarity, several xenobiotics, such as medicines and solid disposal, are not considerably preserved in solid waste disposal and sediments and may contaminate groundwater (Clara et al. 2005; Peck and Hornbuckle 2004; Peck et al. 2006). Active pharmaceutical substances get into the wastewater and then interact with natural receptors. Traces of such 46 chemicals have been found at ppb levels in the outflows of German and US wastewater treatment plants (WWTPs) during 1998–2000 (Ternes 1998). Ternes et al. (2004) reported new compounds into the environment with growth of synthetic chemistry and pharmaceutical stuff through a variety of manufacturing and utilization activities. It is commonly acknowledged that domestic wastewater becomes the primary exposure pathway. The UK Water Industries' Chemical Investigation Program 3 (CIP3) evaluated pharmaceuticals at various levels of effluent and sewage treatment and issued a warning that about

113% of the United Kingdom's WWTPs would surpass the anticipated no effect downstream streams' concentrations (Comber et al. 2018).

More lipophilic chemicals, such as endocrine-active pollutants, can build up in organic (biofilms) and silt material. Given that the state of the sewage system has a significant impact on both surface water and groundwater, it is obvious that urban disposed wastewater constitutes significant channel for anthropogenic xenobiotics (Ahel et al. 2000). Additionally, carbamazepine (CBZ), a drug used to treat epilepsy and can contaminate urban water, can have unprecedented effects on the health of people (Andreozzi et al. 2002). The Umweltbundesamt (German Environmental Agency, UBA) has proposed setting a current maximum limit of 0.1 g L^{-1} for a range of pharmaceuticals until the database has been upgraded in order to safeguard drinking water supplies (Geiler 2006). This necessitates expanding our understanding of these compounds' origins, distribution, migration, sorption, and reaction mechanisms as well as their ecotoxicological characteristics and evaluating how they can affect health of people through water distribution. In order to research the outcome of water-bound xenobiotics, it is required to find and employ appropriate indicators (Schirmer et al. 2007).

4 Major Paths of Xenobiotics Entering the Soil Environment

From studies on stable and acutely harmful pollutants including insecticides, toxic metals, herbicides, and nondegradable organic pollutants, water research has expanded to cover home applications of medicinal drugs and domestic individual care products (Ternes et al. 2004). Typically, pharmaceuticals are released back in components of environment, in one of two ways: through release of effluent, post-treatment, or by the disposal of disposed sewage sludge deposits (Kinne et al. 2006). The bulk of wastewater sludge ultimately ends up on farms where it is sprayed as biosolids to increase local soil nutrients and increase agricultural yields (Ofwat 2016).

Notably, wastewater products are not subjected to normal tests before being deposited on agricultural land. Because there is no legislative framework governing the pollutants in biosolids' pretreatment, hence it may have an impact on food chains and terrestrial health. For instance, organic chemicals are substantially eliminated by biodegradation during the secondary sewage treatment stage in WWTPs. Pharmaceutical elimination rates, however, vary depending on the individual drug qualities. Since hydrophilic chemicals only weakly bond to organic matter, activated sewage bacteria in WWTPs are effective in removing them. Physicochemical and biological properties of pharmaceutical chemicals with the design of wastewater treatment plants affect degradation pathway and efficiency (e.g., incidence of diverse biodegradation mechanisms may advance or hinder removal process). Adsorption to microbes or physical elements is another method of elimination. This process is primarily driven through hydrophobic exchanges between various functional groups and polar interactions between positively and negatively charged functional groups. Organic substances that have been adsorbed can be extracted via

sedimentation as major pathway. Once, pH of the surrounding environment is greater than the bacterial isoelectric level, and the majority of microbes have negatively charged surfaces (typically pH 3–4). The presence of deprotonated carboxylic mutuality (moieties that are negatively charged) in the gel-like matrix of extracellular polymeric substances (EPSs) further supports the idea that acidic medications are eliminated less effectively in comparison with their balanced and positively charged counterparts (Sato et al. 2013; Olivieri et al. 2014).

Most parts of the world use recycled water for irrigation. Thebo et al. (2017) found that catchment areas with elevated degrees of reliance on treated (sometimes even untreated) urban wastewater produce were part of nearly 65% irrigated croplands. Many nations, especially in Asia, use urban raw wastewater for irrigation especially India and Pakistan. Domestic wastewater is major source of active pharmaceutical compounds beside effluent from pharmaceutical industries. Other sources comprise solid waste- and water-dependent sources (such as surface runoff, industrial effluents, hospital discharges, leachate from solid waste landfills). Bacteria in activated sludge process, during the secondary treatment of wastewater, associated with organic matter decomposition, may be inhibited by specific molecules and/or a composite blend of latent drugs, even though existence of major part of pharmaceutical chemicals in WWTPs has been found low (Yang et al. 2017). As a result, there would be a greater chance that medicines would not be completely eliminated from effluents and other by-products. PPCPs that have expired or are redundant are disposed in landfills as another source of exposure. Insect repugnant, anti-inflammatory drugs, sensory stimulants, and drugs used as anticonvulsants with antibiotics are the most prevalent in landfill leachates and the surrounding environment. The maximum observed quantity of diethyltoluamide crossed the concentration of 52,800 g/L in leachate from landfill sites but was found only in range of 0.06–1000 g/L in adjacent groundwater sources, indicating that some of the compound may be adsorbed, fixed, or attenuated in soil systems. The underlying causes of the discrepancies that have been noticed but not fully comprehensible and efforts to remove medicines from current domestic solid waste disposal are yet in the planning stages. The numerous historical landfills shut down during the 1990s present a further leaching danger because they are rarely monitored and frequently do not have enough impermeable barriers (Yu et al. 2020).

5 The Transport of Pharmaceutical Xenobiotics in Soil

Medications exhibit the capacity to be bioactive or effective at very low dosages; hence, their discovery in soils and biosolids has raised concerns. Antibiotics are one example of a substance that can lead to microbial resistance, while diclofenac and 17-estradiol are examples of a substance that can induce acute toxicity. The main pharmaceutical chemicals in the soil matrix include nonsteroidal and anti-inflammatory drugs (abbreviated usually as NSAIDs), antibacterial drugs, cardiovascular drugs (calcium channel blockers), psychostimulants, hormonal supplements,

etc. (Gao et al. 2012; Thelusmond et al. 2016; Thebo et al. 2017). Some of these are given in Table 2, as reported in various matrices.

Paltiel et al. (2016) observed that after consuming fresh food that had been watered with treated wastewater, carbamazepine and its secondary products were found in urine samples of humans. The physicochemical features, beginning concentrations, and soil characteristics all have an impact on how pharmaceuticals travel through soil matrix, including migration, alteration, decomposition and metabolizing, and accumulation via plants and soil biota.

Mobility within the soil matrix is influenced by physicochemical characteristics of pharmaceuticals, viz., polarity of molecules, log K_d (solid-water distribution coefficient), and K_{ow} (octanol-water partition coefficient). Additionally, many pollutant behaviors in soil environments were thought to be caused by ionization, cation-bridging, cation-exchange, and preservation in dormant pore water (Carter et al. 2014). The same authors showed that soil having an elevated organic content, particularly soil modified using biosolids, showed significant drug retardation in soil columns. The specific interface among sorbate molecules and type of soil organic matter (chemicals and functional groups) that prevail at lower sorbate concentrations can explain this behavior (Delle Site 2001).

Ibuprofen and naproxen, on the other hand, appeared to exhibit important differences between single and mixed drug formulations, causing multilayer bonding properties and complex formation with cations present in soil. This was suggested by sorption and desorption research on a small number of NSAIDs (Zhang et al. 2017). However, Koba et al. (2016), who conducted an experiment of matrix effect evaluation using 13 different types of soil, claimed that the type of matrix did not

Table 2 Reported pharmaceutical and personal care product (PPCP) levels in some matrices

PPCP	Matrix	Concentration	References
Amoxicillin trimethoprim	Lettuce and carrot	6 mg/kg (lettuce)	Goldstein et al. (2014)
Sulfamethoxazole (S) and trimethoprim (T)	Cabbage	20.10 ng/g (leaf) (S) 138.26 ng/g (root) (S) 91.33 ng/g (root) (T) 11.42 ng/g (leaf) (T)	Levy (1998)
Sulfamethoxazole	Radish, rape	Radish leaf (0.9–2.7 mg/kg) Rape leaf (0.2 mg/kg)	Malchi et al. (2014)
Caffeine and ibuprofen	Tomato and cucumber (both fruits)	Detected in both samples	Li (2014)
Bisphenol A (BPA), diclofenac sodium (DCL), naproxen (NPX), and 4-nonylphenol	Lettuce and collards	Concentrations ranged from 0.22 ± 0.03 to 927 ± 213 ng/g in decreasing order of BPA, NP, DCL, NPX	Herklotz et al. (2010)
Sulfamethazine	Maize, potato, lettuce	Reported in all samples in the range of 0.1–1.2 mg/kg	Miller et al. (2016)

significantly affect the adsorption of their examined chemicals, namely, atenolol, metoprolol, and carbamazepine. Barron et al. (2009) proposed that hydrophobic mechanisms may not fully account for the drug molecules' migration in composite of soils and biosolids. Haham et al. (2012) reported similar enhanced mobilities and suggested that the amalgamation of compounds with solubilized organic matter present in wastewater could be an important part. The authors recommended using artificial programmed neural networks to measure and identify correlations among various physicochemical and biochemical alteration pathways and mimic the behavior of medicines in soil matrices. Higher mobilities raise the risk that drugs will seep into the groundwater, which could have further negative effects on the ecosystem.

6 The Potential Transfer of Pharmaceutical Xenobiotics Through Food Chains

Drug use and trophic transmission in aquatic food webs have been established, as the idea of ecological contamination has been expanded to comprise pharmaceutical chemicals such as carbamazepine and roxithromycin (Li et al. 2013). Regarding the buildup of pollution in food webs in terrestrial ecosystems, plant communities have received the majority of attention. The bio-concentration factor (BCF), which is used to assess the bioaccumulation capacity of pharmaceuticals and forecast plant absorption pathways, is used in conventional uptake tests, which are normally carried out under hydroponic settings. The discrepancies in BCFs between soil and hydroponic trials suggest that soil minerals reduce the bioavailability of several medications. The drug carbamazepine is frequently found in soil systems and exhibits high potential for soil to plant transfer. It was discovered that triclosan and triclocarban were absorbed by roots before moving to photosynthetic sites and reproductive parts of plants (Wu et al. 2012). Ion trapping and polar repulsion/attraction are primary forces causing uptake of ions and slow rate of selective passage through membranes, which may account for ionic medical medications' reduced absorption ability in comparison with neutral drugs. The processes for transfer or migration of acidic/basic medications are not yet clear, but majority of the findings concentrate on ion trapping and ionic repulsion/attraction (Armitage and Gobas 2007; Sauvêtre et al. 2018).

Triclosan, carbamazepine, and lamotrigine metabolites are exceptions since they have the potential to exceed the verge of concern in toxicological terms (Malchi et al. 2014). There is a scarcity of information on bioaccumulation and risks associated with absorbing contaminants in petite mammals, apes, and people. Although the majority of medications undergo fast transformation and elimination, the ongoing addition of pharmaceutical chemicals to soil systems by human actions may possibly surpass the efficiency of removal and offer unprecedented risks to soil health.

The possibility of trophic transfer was discovered by Ding et al. (2015) through a lab study, in which an antibiotic named roxithromycin was transferred through an aquatic food succession, and changes in tissue accretion were assessed in subsequent consumers. It's possible that this secondary/subsequent poisoning in the food succession also affects predators who consume similar terrestrial creatures in their meals in the terrestrial food web. Recent years have seen regulatory bodies in Europe rely heavily on aquatic designs/models to evaluate the bioaccumulation of various chemicals. It might have given inaccurate information regarding the migration of xenobiotic pollutants due to variations in biomagnification of some medications in both water and soil systems (Fremlin et al. 2020). The methods use bioaccumulation factors or biomagnification factors to assess possible dangers, but these factors only apply to creatures that breathe in water.

In order to research the accretion tendencies of xenobiotic contaminants of rising concerns in invertebrates in/on soil and further in food chains, clear and precise estimation models are needed. Most models take food/dietary inputs into consideration and can be adjusted for both aeroponics and aquaponics. The biomagnification factors (BMF) partially tackle this shortcoming (Borgå et al. 2012). However, because of their position in the food chain and the availability of minute concentrations of some medications, determining transfer factors when concentrating on lower levels of any food chain is problematic (Conder et al. 2012). In addition, earlier research mainly used straightforward models to calculate trophic amplification factors (Armitage and Gobas 2007). Therefore, pertinent field research and data gathering are essential since they will aid in the creation of biomagnification models and offer pragmatic information on transfer of chemicals for future research.

Earthworms, categorized as principal consumers, are connected to higher trophic levels through their participation in a number of food chains. Previous studies revealed that several animal predators, including moles, shrews, badgers, and foxes, feed on earthworms which may be a major source of bioaccumulation of xenobiotics (Dodgen et al. 2013; Malchi et al. 2014). Earthworms make up a significant portion of the diet of some small carnivorous mammals. For instance, they make up 29% of diet of a shrew (*Sorex araneus*) and range from 38% to 95% in the diet of moles (Nesterkova et al. 2014). Research found that shrews are more susceptible to undergo serious health effects while consuming contaminant laden earthworms, stressing the possible adverse impacts by bioaccumulation via food sequences even though earthworm consumption was somewhat less than 33% of the everyday consumption (Hamers et al. 2006).

Since European moles being choosy mammals consume mostly earthworms, they are likely to be directly harmed by the transfer of contaminants up the food chain. The mole, however, barely makes up 0.05–4.5% of diet of owls, buzzards, hawks, and kestrels because of its overpowering musky odor indicating that it is at the bottom of the terrestrial food sequence (Nesterkova et al. 2014). Earthworms are mobile macroinvertebrates that play an important role as consumers in terrestrial food networks. They make up to at least a couple of major food networks, with small mammals or birds serving as the top predators in each. Related species have different but comparable nutritional components, which makes it more difficult to

find and transport trace medicines up the food chain. The main difficulty for further research will be precise measurement of drug levels in the blood and association of introduction through food to environmental exposure.

7 Metabolism of Xenobiotics

Microbiologically assisted contaminant degradation (bioremediation) of xenobiotic contaminants has emerged during the last few decades as the most efficient, beneficial, and environmentally benign method. Microorganisms are essential to the bioremediation process because they have a distinct metabolism, the ability to modify their genetic makeup, a variety of enzymes, and different degradation pathways. Although microbial xenobiotic degradation is efficient, the process is slow, which restricts its use in bioremediation.

Recent advances in technology have made it possible to characterize the metabolic apparatus, novel proteins, and metabolic genes from microbes engaged in the degrading progression. The aforementioned techniques include metagenomics, proteomics, transcriptomics, and metabolomics. The type of pollutants and the efficiently degrading enzymes, viz., cytochrome P450, dehydrogenases, laccases, hydrolases, proteases, lipases, etc., that can turn these pollutants into harmless products may be helpful to get rid of xenobiotics (Rathore et al. 2022).

A pharmaceutical drug may turn into less detrimental compound to soil systems through deterioration, notably photodissociation and biodegradation, or it may become more hazardous to the environment by producing new, more toxic metabolites. The rate of photodegradation increases with target area latitude. Turbidity may decrease photodegradation of xenobiotics. There is scarce knowledge about the degradation of medicines through sunlight, and prior studies have only concentrated on a few often identified medications (such as carbamazepine, naproxen, and triclosan) and antibacterial drugs (Delle Site 2001; Borgman and Chefetz 2013). Target pollutants' photodegradation levels in soil samples were found to be much lesser in comparison with aquatic samples that could be attributed to the lower light infiltration through solid soil matrix (as photolysis happens only in 0.5 mm top layer).

Additionally, even within the photic zone of soil, the elevated amount of carbonates present in soil (build up through wastewater irrigation with soil chemistry) may result in a decrease in the rate of pollution photolysis (Mountacer et al. 2014). The degree of photolysis of solubilized organic content, which may add to production of free radicals (may be oxygen-based radicals or charged solubilized molecules of organic matter), may be influenced by soil texture/structure, moisture content, and organic matter in soil. These radicals, which are created in the soil's top layer, may subsequently combine with other contaminants to cause further degradation (Frank et al. 2002). The majority of studies reported have concentrated on degradation of pharmaceutical chemicals in water-based environments and with particular microbes or catalytic factors. In biofilms seeded with activated sludge, recent investigations

have correlated bacteria to pharmaceutical drug decomposition processes (Bessa et al. 2017).

In aqueous media, *Brevibacterium* sp. D4 and *Enterobacter hormaechei* D15 extracted from the activated sludge and *Enterobacter cloacae* extracted from domestically formed compost have been found related to degradation of diclofenac. Bacteria *Pseudomonas fluorescens* MC46 along with bacteria *Ochrobactrum* sp. MC22 have been found to degrade triclosan (it is still unknown if these microorganisms can break down carbamazepine (CBZ) and triclosan (TCC) in agricultural field soils laden with these pharmaceutical chemicals) (Mountacer et al. 2014). Carbamazepine has been under extensive degradation study in terrestrial ecosystems as it is widely approved as an effective analgesic, nonnarcotic, and anticonvulsant drug (Koba et al. 2016). Carbamazepine may be a fine marker for existence of pharmaceuticals in soil (Mompelat et al. 2009) and is regarded as a suitable anthropogenic representative for wastewater distribution.

The hydroxyl derivatives (10,11-epoxy carbamazepine and 10,11-dihydro-10-hydroxy carbamazepine, also known as EPC and DHC) are formed by hydroxylation of the active site in CBZ. The metabolites resulting from epoxidation support the idea that the activities of these enzymes are what cause the terrestrial biodegradation process. Similar epoxides to those produced by CYP450 oxidation have been seen during the metabolism of polycyclic aromatic hydrocarbons (PAHs). Due to the epoxides' unstable nature, the three different intermediates are consequence of additional ring contraction and its conversion. It should be emphasized that the presence of free 10,11-epoxy carbamazepine in serum of patients is directly related with severe adverse effects, indicating that this pathway's end product acridine, which hinders DNA repair and cell growth, has hazardous biological effects on living things (Kim et al. 2017). EPC is highly likely to migrate to deeper zones in soil and create a high risk in soil and water matrices due to its low hydrophobicity (as compared to CBZ) and more mobility in the terrestrial environment. Additional intermediates were seen in additional studies (Li 2014; Franklin et al. 2018).

Bacterial experiments including *Phragmites australis*, *Diaphorobacter nitroreducens*, *Aspergillus niger*, *Rhizobium radiobacter*, and *Diaphorobacter nitroreducens* converted CBZ into DHC and EPC with acridine, separately (Sauvêtre et al. 2018). Unknown further metabolites through the *Phragmites australis*-mediated mechanism and *Aspergillus niger*-derived decomposition processes exist. These results underline how crucial it is to clarify the potential pharmaceutical drug degradation mechanisms in soil matrix because their metabolic products may have greater mobility and higher toxicity than the original xenobiotic materials.

Around 52 million chemicals have been created by humans; 75% of them are marketed and could expose people to them. There is a negligible portion of these chemicals whose physiological chemistry has been determined in animals and humans. At present, researchers are showing more interest in utilizing chemometrics to discover metabolites that are associated with xenobiotics. Sun et al. (2009) discovered the novel xenobiotics, metabolites of tolcapone (an inhibitor of catechol-O-methyl transferase), in rats. Liu et al. (2009) identified novel metabolites of the

drug fenofibrate (used to treat cholesterol and obesity issues) in *Cynomolgus* monkeys. Tolcapone and fenofibrate both had their metabolic maps extended.

The most prevalent heterocyclic amine was studied by Felton et al. (2007) which is produced in cooking of meat and fish in 2-amino-1-methyl-6-phenylimidazo (4,5-b) pyridine (PhIP), a dietary mutagen. 2-Amino-1-methyl-6-phenylimidazo (4,5-b) pyridine and associated heterocyclic amines are primarily absent from food cooked or boiled below a temperature of 200 °C. The majority of N-hydroxylation with CYP1A2 sequenced by combined action of the hydroxylamine by sulfotransferase and N-acetyltransferase occurs during the metabolic activation of PhIP to N2-acetoxy-PhIP and N2-sulfonyloxy-PhIP. There have been reports of interspecies variations in PhIP metabolism patterns, posing it as challenging to apply laboratory results to risk calculations for PhIP introduction in humans. Human P450 enzymes create the N-hydroxy metabolic products which results in esterification and the generation of the dynamic electrophilic metabolite, whereas P450 enzymes in rodents primarily lead a detoxification process (4'-hydroxylation).

It should be emphasized that the group of heterocyclic amines is amid most significant mutagenic compounds that have been studied, and there is a serious concern that human exposure to them through diet could increase the chance of developing cancer. Through nutrition, the epithelium in the colon is exposed to a variety of substances, some of which are pro-carcinogens and others of which have a protective impact. The entire balance of all the relevant parameters determines how these substances will ultimately affect human health. Strong scientific evidence has shown a link between cancer and the main genotoxins produced during food preparation and cooking including nitrosamines (NA), polycyclic aromatic hydrocarbons (PAHs), and heterocyclic amines (HCAs). Although mechanisms relating dietary toxic chemical xenobiotics to cancer risk are still not fully understood, it has been proposed that variations in food have an impact on the colonic environment by altering the constitution and action of the gut microbiota as well as directly affecting the introduction and effect of mutagens. The advance of neoplastic abrasions and the concentration of enterotoxigenic microbial types and strains in feces have both been linked to various changes in the quantity of particular microbiota. Additionally, dietary modifications alter the opus and action of microbiota in the gut altering the fecal genotoxicity/cytotoxicity, which may be linked to higher or lower risk of developing cancer. As a result, future research should pay more attention to the connection between dietary elements and gut microflora, which may be an amendable factor in the emergence of colorectal carcinomas in humans (Sinha 2002; Patterson et al. 2010).

8 Conclusions and Future Prospects

Different regions can have significant aquifer heterogeneity, widespread subsurface infrastructure, and a diverse spectrum of contaminants, necessitating the development of novel and effective investigation, monitoring, and evaluation

methodologies. Most of the time, methods and technology that created over the last half century industrially polluted areas serve as a suitable starting point. Still, they must be improved for the unique needs of different environments. It is evident from the early quantification that lab experiments and phenomenological assessments at the watershed scale cannot provide deep process knowledge necessary for predicting pollutant behavior in ecological and metropolitan settings. In situ pollutant movement and outcome can be measured by installing monitoring equipment at the boundary between the separate zones with high and low concentrations. The expansion of sustainable environmental remediation solutions for contamination of both surface and groundwater may be suitable for megacities too and should be a part of new studies. These strategies should also aim to minimize pollutant input. Aquifers are frequently used sources for the extraction of drinking water, both in urban and rural areas. On one hand, urban ecosystems are frequently a possible source of contaminants for plants and animal communities with ecosystems below them. As a result, we must make a significant effort to safeguard urban aquifer supplies with greater emphasis. Close cooperation between researchers and practitioners is crucial as we shift more toward a preventative approach to water protection.

This chapter includes recent research on prospective pharmaceutical xenobiotics' sources, transportation routes, and systemic transformations. Regarding the first issue, it should be emphasized that the majority of studies solely consider the original chemical and ignore any potential by-products. We still have a limited understanding of how pharmacology and soil microbiology are related, making it difficult to correlate the processes of degradation and the development of pharmacological metabolites. To find out how much soil characteristics affect the movement of pharmaceuticals and their rate of photodegradation, more investigation is required. Due to their absorption by plants and animals as well as their migration through food webs, medicines can have an impact on the health of ecosystems. It has been proposed that crops and other fresh foods can expose people to metabolites and pharmaceutically active substances. When taken as a whole, this analysis emphasizes the urgent need to concentrate on the threats to public health caused by the inadvertent and indirect introduction of medications to soil. Future studies to evaluate the ecological and human danger presented by xenobiotics and their metabolites will be guided by a more complete understanding of how medicines migrate and alter in the terrestrial systems (Zhang et al. 2021). There are some major factors for future research which have to be considered, including the following:

1. Controlled studies should be done with pharmaceuticals in soil matrix for the study of natural attenuation of chemicals.
2. Studies of migration of pharmaceutical chemicals from soil to plants should be done considering soil quality parameters like pH, electrical conductivity, cation exchange capacity, organic carbon, and cation content as Na^+ , K^+ , and Ca^{++} .
3. Application studies with different microbes are required in context of soil matrix.
4. Extensive research is required for removal of nonionic species from wastewater.

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Part III
Impact of Xenobiotics on Biotic
Components of the Urban Ecosystems

Food Chain Contamination and Impact of Xenobiotics on Human Health



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1 Introduction

The effects of urbanization, population growth, industry, and globalization on our daily lives are mixed but undeniable (Štefanac et al. 2021). However, despite the economic gains, globalization severely influences the environment because a healthy ecosystem is essential to human flourishing (Gu 2019). New compounds enter the environment due to technological development, increased longevity, increased access to treatment (for both people and animals), as well as the extensive use of insecticides and personal care goods (Ebele et al. 2017). The short- and long-term effects of these substances can be seen on people, animals, and the environment (water and air including the soil) (Nikolaou et al. 2007).

The pollution of the environment with xenobiotics, and consequently their uptake by active organisms, has grown considerably over the past few decades

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(Kobzev et al. 2020; Kucherenko et al. 2021). Adding these substances to ecosystems could result in a rise in the prevalence of numerous diseases. Consequently, these compounds pose severe threats to the well-being and health of living beings (Omelchenko et al. 2017; Kovtunova et al. 2020). Recently, the rise in certain diseases has been observed worldwide. The root cause behind this drastic shoot-up in diseases has been attributed to some endocrine disrupting chemical compounds, also known as xenobiotics, as they are known to derange metabolic control of the body (Goel 2021).

The xenobiotic-induced cell damage and mutations are a significant risk to the health of the living organism as they lead to malignancy and cause various heart diseases. Their presence is everywhere, including food items. They can manifest various health conditions like nasal congestion, allergies, chest heaviness, shallow breathing, etc., which can lead to other severe health conditions (Kucherenko et al. 2021). The globe develops up to one million new products annually, including around one hundred thousand chemical substances. The possible xenobiotics comprise around 15,000 molecules. Pesticide, hormone, and trans-fatty acid contamination of food is particularly harmful. Xenobiotics can be found in food as flavorings, preservatives, thickeners, emulsifiers, stabilizers, colorants, etc. Their methods of exposure to people's direct contact, water intake, or food chain are getting more dangerous with each year (Kucherenko et al. 2021). This chapter provided uniquely a complete overview of xenobiotic substances and their different characteristics, their effects on human health, and the factors affecting the metabolism of chemicals.

2 What Are Xenobiotics?

Xenobiotics are either naturally occurring or artificially introduced chemical compounds (Livingstone et al. 1992). These natural and anthropogenic substances enter the environment via numerous mechanisms, including direct and indirect discharge and transfer through the food chain (Joss et al. 2006; Ternes 2007). Natural

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compounds may act as xenobiotics in specific conditions, e.g., if they are ingested by another organism or in the form of chemical defense materials, e.g., mycotoxins, herbal or bacterial toxins, etc., produced by the prey for protection from predators (Brodie Jr et al. 2002).

Xenobiotics are gaining public interest, which is evolved by various human activities. Xenobiotics are considered very harmful when these are involved in the food chain. Exposure of humans to xenobiotics cannot be escaped as these are present everywhere. Some substances of xenobiotics are ingested voluntarily in medicines, like dietary supplements, antibiotics, etc. (Goel 2021).

Xenobiotics are often referred to as pollutants, e.g., dioxins and polychlorinated biphenyls, and they impact the living organisms as they are entirely foreign substances to a biological system (Patel and Sen 2013; Gupta et al. 2022).

3 The Ways of Xenobiotics' Genesis

Xenobiotics are often categorized according to their origin; however, this chapter examines the other possible methods of their genesis (Fig. 1): first, fermentation of food ingredients and products that have passed expiration dates and storage requirements. Second, fruit and vegetable seeds also develop xenobiotics due to genetic mutations. Because of this genetic change, the body's enzyme systems usually cannot process these foods (Visioli 2015). Because the human body is an inertial system, it does not have fast ways to adapt to changes in absorption systems or the growth of new ones. Low oxidation or repair of food molecules in the body, accompanied by incomplete digestion of organic compounds, is resulted in another kind of xenobiotic expression. In this instance, there is energy parity (Zemlyanova et al. 2012) (Table 1).

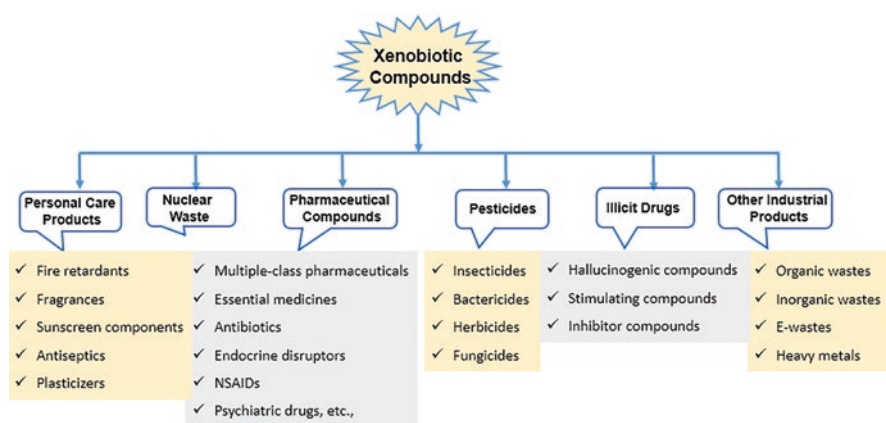


Fig. 1 A detailed overview on types of different xenobiotic compounds. (Based on Štefanac et al. (2021))

Table 1 Revised classification by origin of xenobiotics

Feature	Natural origin	Technogenic origin	Biotransformed xenobiotics
Formation mechanism	Volcanoes and natural emissions Non-biological organic compounds Biological compounds	Industrial Agricultural Construction materials Household chemicals Pharmaceuticals Transportation	Fermentation products Genetically modified seeds and field crops Expired food products Food industry Toxic substances formed in food as the endogenous impurities
Typical representatives	Carbon and sulfur mono- and dioxides Fluorine, hydrogen sulfide, and chlorine compounds Aliphatic and aromatic hydrocarbons Animals and plant poisons (aconite, hemlock)	Chrome, nickel, manganese, formaldehyde Organochlorine pesticides, organophosphate insecticides, bactericides, herbicides, zoocides, fungicides Aniline, Freon, methyl alcohol, styrene, plasticizers, polymers (polyvinyl chloride), formaldehyde, phenol, epoxy resin Alcohols, heavy metals, organophosphate insecticides, dimethyl phthalate, methylene chloride Antibiotics, sulfonamides, mercury preparations, iodides, arsenic preparations, barbiturates, dietary supplements Methane, butane, propane, heavy metals, chloramine, mono- and carbon dioxide, polycyclic aromatic hydrocarbons (benzo(a) pyrene)	Alkaloids, cyclopeptides Products with genetically engineered ingredients, products of processing of transgenic raw materials, transgenic vegetables, and fruits Microscopic fungal metabolites and bacterial toxins Antioxidants, preservatives, vitamins, minerals, flavors, food colorants, emulsifiers, stabilizers, thickeners Toxins of nonpathogenic and pathogenic fungi

Based on Kucherenko et al. (2021)

4 Different Categories and Sources of Xenobiotics

Products such as pesticides, industrial chemicals, synthetic pharmaceuticals, antibiotics, and heavy metals are xenobiotics, often known as foreign compounds (Table 2). These substances are created synthetically and are therefore considered to be foreign. Toxins and poisons found in animals, antibiotics, medications, and poisonous byproducts derived from plants and food are all examples of natural xenobiotics.

Table 2 Substances and sources of xenobiotics

Classification	Xenobiotic substances	Characteristics	Classification	Example
		Nature	Natural	Bacteriotoxins, zootoxins, phytotoxins, serotonin
		Synthetic	Artificial substances, pesticides	
	Uses	Active	Pesticides, dyes, paints	
		Passive	Additives, carrier molecules	
	Physical state	Gaseous	Benzene, aerosol form	
		Dust-form	Asbestos powder	
		Liquid	Chemicals liquified in water	
	Pathophysiological effects	Tissue/organs	Kidney toxins	
		Biochemical mechanism	Methemoglobin-producing toxins	
	Xenobiotic sources	Direct sources		Pharma industries (phenols), petroleum effluent (hydrocarbons), plastics, paints, dyes, pesticides, insecticides, paper, and pulp effluent
		Indirect sources		Hospital discharge, pesticides, or herbicide residues
		Product and processes		Product of reaction of any processes – domestic or industrial scale
		Deliberate and unintentional causes		Chemicals that are utilized in the paper and pulp industries, accidentally released into the environment
		Movable and stationary		Automotive and industries
		Organized and unorganized		Big industries and home auto business

Based on Štefanac et al. (2021)

4.1 Natural Xenobiotics

There are three categories of natural xenobiotics: biological molecules created by microbes, fungi, vegetations, and animals, inorganic substances, and organic compounds with non-biological origins. Ordinary compounds of xenobiotics are found in fruits, vegetables, and mushrooms.

Kucherenko et al. (2021) and Omelchenko et al. (2017) reported that xenobiotics of natural origin account for 2 g of the daily diet, while pesticides account for 0.09 mg (Omelchenko et al. 2017; Kucherenko et al. 2021). Many naturally occurring xenobiotics are carcinogenic. Nonetheless, several food components

(ascorbic acid, vitamins A and E, and the plant monoterpene limonene) possess anticarcinogenic qualities that counteract the impact of carcinogens (Panter and Stegelmeier 2011; Kucherenko et al. 2021).

4.2 *Industrial Xenobiotics*

Numerous studies have stated that industrial sectors including those involved in the processing of oil and gas, thermal and nuclear energy, air and land transportation, etc. are the main sources of technical xenobiotics (Omelchenko et al. 2017; Fountoucidou et al. 2019; Kobzev et al. 2020). In addition, there are many synthetic xenobiotics with high toxicity that circulate in the biosphere. However, the term “technology xenobiotics” is not widely accepted. Its application is somewhat arbitrary. Among many contaminants, it is nonetheless possible to classify those that pose the highest threat to human health (Kobzev et al. 2020). This comprehensive collection of dangerous substances comprises agents (dioxins, polychlorinated biphenyls, and several organophosphorus compounds) that can cause acute poisoning and death at relatively large local concentrations linked with accidents or armed actions (Goel 2021).

4.3 *Food Xenobiotics*

Various products, including pesticides and insecticides, pose a high risk to humans from food, water, and the environment. The primary concern is the health risk imposed by foodborne toxins, preservatives, and artificial sweeteners. Artificial sweeteners, ingested by consuming “diet” recipes, may also affect hormonal control of energy metabolism and, thus, can be termed endocrine disruptors (Michael 2015). Smith-Spangler et al. (2012) reported a significant amount of polyphenols, phosphates, and n-3 fatty acids in organic food products. As per Joselow (1983), xenobiotics can be incorporated into food in many ways. Some are added food, color additives, or food packaging material. During crop growth and maturation or harvesting, environmental pollutants may become part of the food. The effect of food-derived xenobiotics was studied by Nogacka et al. (2019). Meat and fish foods derived from xenobiotic compounds like nitrosamine, heterocyclic amines, and polycyclic aromatic hydrocarbons produced due to some cooking procedures at high temperatures are known to induce carcinogenesis (Goel 2021).

5 **Xenobiotic Pollution Types**

Several industrial processes produce xenobiotic pollutants. Pharmaceuticals, personal care goods, dyes, pesticides, petroleum products, polyaromatic hydrocarbons, and heavy metals are the main businesses (Gupta et al. 2022).

5.1 Pharmaceuticals

The well-being of society is positively impacted by pharmaceutical drugs. However, excessive use of pharmaceutical products following abuse leads to the release of these drugs in a variety of ways to urban runoff (Ternes 2007; Kümmerer 2008; Mutiyar et al. 2018). During metabolism, these compounds go through partial or whole changes to become secondary or tertiary metabolites. They are removed through feces or urine in their natural state. The great majority of pharmaceutically active substances (PACs) is mostly removed by urine, with some also being passed through feces and other forms (Lienert et al. 2007). The misuse of these medical wastes and poor disposal of expired pharmaceuticals are major contributors to the exponential buildup of pharmaceutical residue in nearby ecosystems (Comoretto and Chiron 2005; Bound et al. 2006; Gil 2007). Figure 2 summarizes the majority of PACs reported in the environment.

5.2 Personal Care Products

Personal care product (PCP) residues are pervasive in the environment as a result of their broad use, where the cosmetics, lotions, fragrances, toothpaste, and other PCPs are extensively used and have become a part of daily life (Comerton et al. 2009; Brausch and Rand 2011). Thus, they are continuously released into the ecosystem. The highly bioactive compounds in PCPs and their metabolites accumulate in the environment after being released into the environment as PCPs and their metabolites (Boxall et al. 2012) which poisoned terrestrial and aquatic

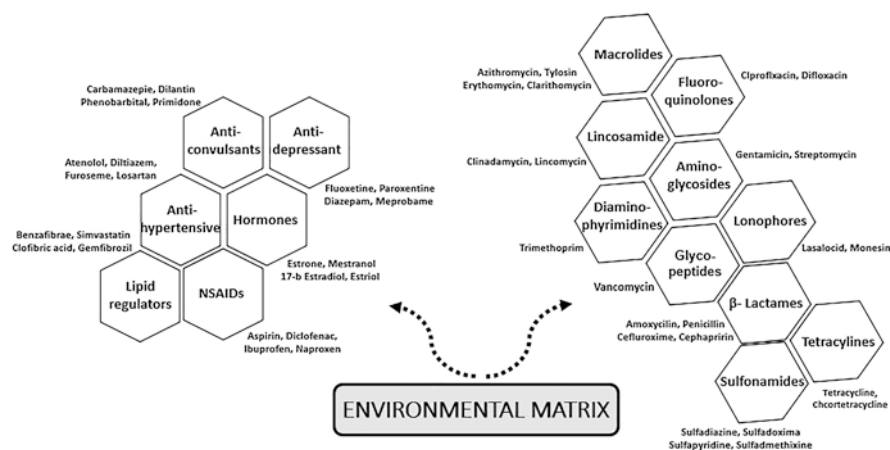


Fig. 2 Common pharmaceuticals found in the environment (Based on Gupta et al. 2022)

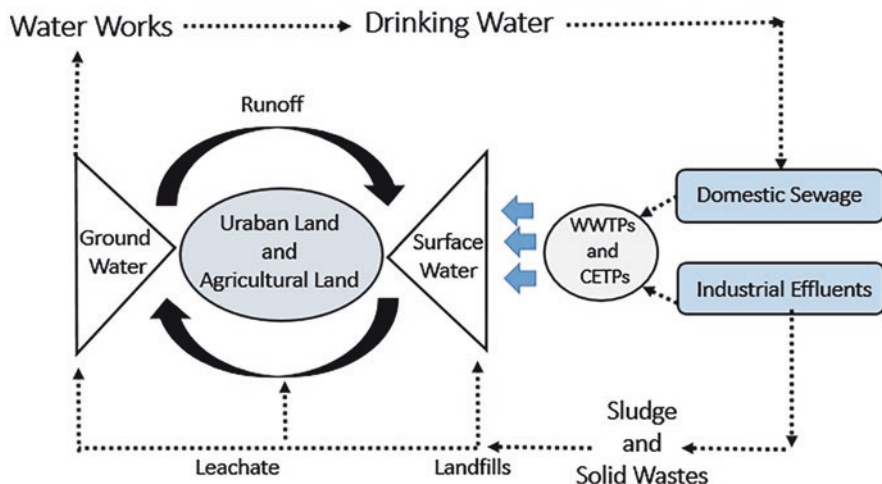


Fig. 3 Pathways in the environment for drugs and personal care items (Gupta et al. 2022)

creatures. The main source of pharmaceutical and personal care products (PPCPs) in surface water is discharged by wastewater treatment plants (WWTPs) (Carballa et al. 2004; Liu and Wong 2013; Meador et al. 2016). Nevertheless, because of ongoing human involvement, eradicating these chemicals is still futile. In recent years, these contaminants have unintentionally been present in aquatic ecosystems like water, sediments, and biota at levels that could be detrimental to aquatic life (Nikolaou et al. 2007) which has been observed. Figure 3 depicts the eventual destiny of PACs and PCPs.

5.3 Pesticides

Pesticides are classified as a type of chemicals coming under the xenobiotics category. Organochlorine compounds were the most frequently used synthetic organic pesticides in the 1940s (Abhilash and Singh 2009; Al-Wabel et al. 2011). It is an efficient pesticide with high solubility in organic matter and low biodegradability (Hoai et al. 2010; Kumarasamy et al. 2012). However, it is also deadly to humans and animals. These pesticides' physicochemical features facilitate their entry into the food chain. Many pesticides have a long half-life and can still be found in aquatic environments (Velasques et al. 2017). Pesticides' physicochemical properties, such as instability, molecular size, water solubility, lipophilicity, polarizability, and volatility, have a major impact on the contamination and toxicity of water and soil (Koester and Moulik 2005; Navarro et al. 2007; Masci et al. 2014).

5.4 *Dyes*

A chemical compound that is artificially colored and has an affinity for the substrate to which it will be applied is referred to as a dye (Pereira and Alves 2012). However, the majority of synthetic colors is long-lasting and immune to biological deterioration. As a result, once released, it has harmful effects and persists in the ecosystem for decades. The degradation of aesthetic attractiveness caused by dye contamination of terrestrial environments or natural aquatic bodies is a serious issue. Additionally, there is a negative impact on light penetration into receiving water bodies. Instead, the majority of colors is converted into more dangerous metabolites as a result of the treatment process. The manufacturing of textiles, cosmetics, food, color photography, the leather industry, pharmaceuticals, and paper printing all make substantial use of synthetic dyes (Rafii et al. 1990; Kuhad et al. 2004; Couto 2009).

5.5 *Petroleum Products and Polyaromatic Hydrocarbons*

For many years, petroleum products have been common environmental pollutants. A sizable amount of petroleum sludge is produced as waste during the storage, refining, and processing stages of oil production and refining. About 85% of the petroleum sludge is made mostly of water, followed by 5–20% solids and 10–30% hydrocarbons (Tanacredi 1977). Chemicals and petroleum wastes are harmful because of saturated hydrocarbons and polyaromatic hydrocarbons (PAHs). The organic chemical complexes known as PAHs are made up of two or more fused benzene rings organized in different structural configurations. In addition to geochemical and biogenic natural sources, human activities are the leading source of PAHs. As extremely hydrophilic, organic micro-pollutant molecules (Berset et al. 1999) with a long half-life (Helaleh et al. 2005), PAH pollution is one of the dangerous environmental safety difficulties. Most PAHs are exceedingly hazardous, carcinogenic, and mutagenic (Krishnamurthi et al. 2003). PAHs' toxicity and degradability rely on their chemical composition and physicochemical properties (Berset et al. 1999).

5.6 *Supplementary Xenobiotics*

Endogenous xenobiotics are compounds that are produced physiologically and are found in the human body, including bile acid, bilirubin, eicosanoids, steroids, and certain fatty acids. These endogenous xenobiotics closely mimic exogenous

xenobiotics. Few organisms produce endogenous xenobiotics as part of their defense systems (Mishra et al. 2019). These comprise cytotoxins, herbal toxins, and bacterial toxins.

Other harmful synthetic polymers like nylon and plastic polymers like polystyrene, polyvinyl chloride, etc. are examples of xenobiotics. These materials are frequently used in apparel, food packaging, and wrappings. Some chlorinated solvents are pervasive contaminants that enter the environment through plasticizers, paint additives, adhesives, and other chlorine-based products. Examples include trichloroethylene, perchloroethylene, and chloroform (Rosner and Markowitz 2013). The fate of xenobiotic metabolism in human body is depicted in Fig. 4.

5.7 Heavy Metals

Heavy metals are often defined as elements with a density greater than 5 g/cm^3 (Barakat 2011). Heavy metals in natural water, soil, and sediments are naturally derived from the earth's crust. Over 50 elements are classified as heavy metals, and approximately 17 are considered highly hazardous (Singh et al. 2011). Commonly toxic metals include As, Hg, Ni, Pb, Cd, etc. (Glanze 1996). The concentration of the majority of these poisonous compounds has sharply increased to a hazardous level in water, soil, and all food products as a result of significant anthropogenic

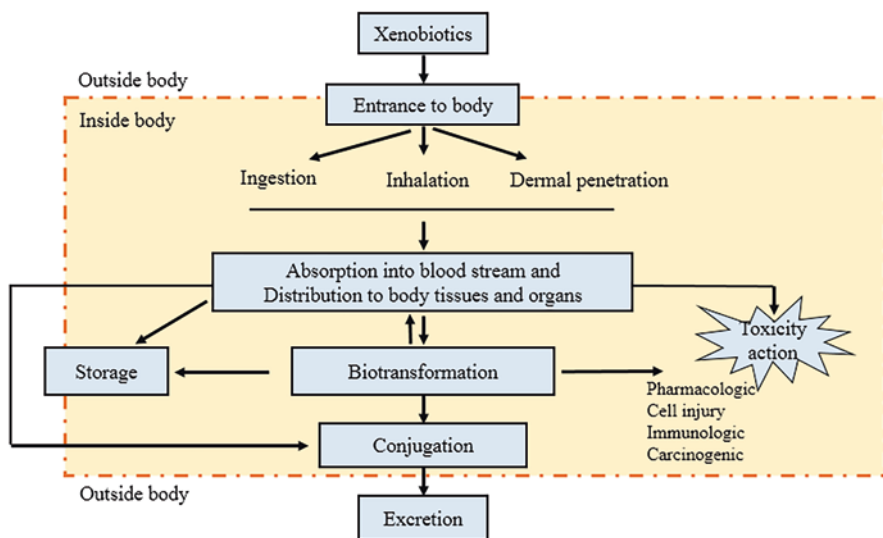


Fig. 4 The fate of xenobiotics in the human system entering via food chain

activity (Hamelers et al. 2010; Gupta et al. 2014, 2015, 2016, 2018). Therefore, metal contamination in diverse environmental components has become a major global issue.

6 Quantitative Study, Negative Effects, and the Use of Xenobiotics in the Food Chain

Complex substances can now be identified and detected in environmental samples with low concentration levels thanks to modern analytical techniques. However, these methods are being updated in order to enhance current ones and possibly create new ones that can produce better data regarding the pollution of natural resources (Petrovic et al. 2013; Santos et al. 2013; de Oliveira et al. 2020). The advancement of waste evaluation in environmental samples is only achievable with the creation and use of diverse processes that allow researchers to identify features or analytes in progressively more complicated samples. The most important step here is sample preparation, where methodological advancements play a big part in problem-solving by teaching us about pharmaceutical concentration levels and sub-products at different locations in the environment, the dispersion of these products into water resources, and especially the removal efficacy of wastewater treatment plant (WWTP) contaminants (Dębska et al. 2004; de Paiva Pessoa et al. 2012). The literature has described a variety of analytical methods for drug detection in aqueous solutions; these methods are particularly applicable to biological matrices like blood, tissue, and urine. The examination of residual pharmaceuticals in WWTP effluents in rivers, the subsurface, and drinking water, however, also requires the development of increasingly sensitive techniques in order to detect concentrations in the microgram per liter and nanogram per liter ranges (Hedenmo and Eriksson 1995; Ternes 2001; Rosal et al. 2010; Santos et al. 2013).

Identification of xenobiotic substances in the environment necessitates the employment of extremely sensitive and focused analysis techniques. Gas chromatography (GC) and high-performance liquid chromatography are the two most often used chromatographic techniques (RP-HPLC). A suitable detector is a critical part of an analytical equipment because it can identify pharmaceutically active ingredient components even at extremely low concentrations. The most popular systems are RP-HPLC and GC, both by themselves and in combination with mass spectrometry (MS) (Lin et al. 2009). Sample preparation is a necessary step because of the high environmental matrix complexity and often low analyte concentration. According to the literature, the following are the most widely used techniques for isolation and enrichment: solid-phase extraction and liquid-liquid extraction (Kolpin et al. 2002; Sliwka-Kaszyńska 2007). To obtain a result that accurately reflects the concentration of the material being analyzed in the environment, each analytical technique entails a number of procedures that must be carefully prepared. The

amount of pollutants in an environmental sample often changes over time. This serves as an example of the ideal sample plan to implement, while setting up a task to track environmental contamination. Most of the time, “flow proportional composite” sampling is the best type of sampling to use since it ensures that sampling is done at regular intervals and that the volume of the samples obtained is proportional to the flow rate of each sampling (Verlicchi and Ghirardini 2019).

7 Xenobiotics Produced in the Food Processing Industry

According to certain studies, humans have experienced significant changes in their nutrition and way of life at the beginning of agriculture and animal husbandry in prehistoric times (Larsen 1995; Wells and Stock 2020), where these researches concluded that the current increase in the spread of the so-called diseases of civilization may be the result of the conflict between the digestive system of the Paleolithic era and modern diets. On the other hand, there is scientific evidence that proves that the diet or the most commonly consumed or generalized foods around the world are limited salt, sauces, meat and animal products, fatty and sugary foods, and processed foods (Kuipers et al. 2012). Xenobiotics are substances that are found in living beings but were not produced by them. Certain naturally occurring compounds (endobiotics) transform into xenobiotics, when present in the environment in excessive amounts. The Greek term “xenos” which means visitor, friend, or stranger is where the “xeno” in “xenobiotics” derives from (Schwab 2008).

Chemicals that are alien to animal life are referred to as xenobiotics, and this category includes, among other things, pharmaceuticals, insecticides, cosmetics, flavorings, scents, food additives, industrial chemicals, and environmental contaminants. In their lifetimes, humans are thought to be exposed to between one and three million xenobiotics, with the majority of these substances entering the body through food, air, water, and drugs (Štefanac et al. 2021). The majority of xenobiotics is created by human activities, and because of their propensity to interact with the living world, they have garnered public attention. As a part of their defense mechanism, some species may also produce them; examples include mycotoxins, bacterial and herbal toxins, etc. Xenobiotics become hazardous when they infiltrate the food chain. Xenobiotics are so commonplace in modern society that human exposure to them cannot be avoided. Moreover, because of their predicted positive benefits on human health, some xenobiotics (such as medications, antibiotics, dietary supplements like antioxidants, etc.) are subject to voluntary exposure (Croom 2012). Mahmood et al. (2017) reported that recently interest in this subject has increased, because environmental contaminants persist in nature, have negative effects, and bioaccumulate higher up the food chain. Some studies hypothesize that the accumulation of these xenobiotics may also raise the risk of human breast cancer because it can also cause immune system decline, endometriosis, diabetes, neurobehavioral damage, learning difficulties, and intellectual disability over time (Ross et al. 1995).

Among the reasons for using xenobiotics in food chain and produced in the food industry, it finds the use of pesticides in agricultural crops, where pesticides were widely used by farmers to protect crops since 1860 like wheat and rice. But after World War II, more basic chemicals against insects appeared, like dieldrin, aldrin, benzene hexachloride, etc. The majority of these substances has been prohibited since the 70s of the last century, yet the Third World continues to utilize them (Thurman et al. 2000); around 900 chemical pesticides have been used for agricultural purposes globally in recent years, either officially or illegally (Thurman et al. 2000). On the other hand, due to its strong affinity with organic compounds, once xenobiotics are released into the environment, they can bioaccumulate in the food chain and have serious adverse effects on the protection of humans, animals, and natural ecosystems; they may then have harmful long-term effects, including those that are carcinogenic and mutagenic, immune system damage, pulmonary bronchitis, neurological system dysfunction, behavioral and developmental issues, and impacts that cause respiratory tract infections (Paul et al. 2005).

8 The Complementary Chemistry of Microbial Xenobiotic Metabolism

As a result of technological development in the twentieth century, numerous compounds that are used to improve daily life (such as antibiotics, dyes, pesticides, etc.) either do not necessarily occur naturally in the environment or whose naturally occurring concentrations are very different from those caused by anthropogenic activity; it is also challenging to detect, quantify, and eliminate them because of their complex physicochemical properties, which include their small molecular dimensions, solubility in water, polarity, and instability (de Oliveira et al. 2020).

Patterson et al. (2010) reported that there are over 52 million organic and/or inorganic compounds which have been produced and more than 39 million of which are readily available on the market and could be exposed to humans. There is a negligible portion of these xenobiotics whose metabolism has been determined in humans and lab animals. It is well-known that xenobiotics can cause hazardous responses via processes involving the biotransformation of those substances into reactive chemical species. Due to their toxicity, there are hitherto unseen concerns to environmental security and safety as well as health. Additionally, the administration or inoculation of pharmacologic medications or other chemicals as part of a standard conditioning or experimental operation may have the same impact as xenobiotic exposure (Miglani et al. 2022).

Humans are exposed to a variety of xenobiotics throughout their lives through ingestion, inhalation, skin contact, or another intravenous exposure route that involves nonessential exogenous substances, such as medications, that may be harmful to their health. Also, the introduction of xenobiotics into ecosystems, however, has the potential to exacerbate allergic reactions, organism deaths, genetic changes, immune system deterioration, metabolic abnormalities, and disruptions of

typical ecosystem functions. As a result, both directly and indirectly, these substances have detrimental and unpleasant effects on a variety of human organs and systems (Kobzev et al. 2020; Kucherenko et al. 2021).

9 Recent Advanced Technologies for Characterizing Microorganisms That Degrade Xenobiotics

According to scientific studies, a person may be exposed to millions of xenobiotics throughout the course of their lifetime. Most of these chemicals are ingested by humans or animals through food, air, water, or drugs. Knackmuss (1996) stated that almost one or more microbial species will destroy any natural product, regardless of its chemical, molecular, or structural complexity, in a particular habitat. However, when it comes to molecules with more complex molecular and complex structures, the situation becomes more complicated and challenging to understand.

Štefanac et al. (2021) reported that because of their complicated structures, xenobiotics are difficult to break down; thus it is important to understand their origins in order to reduce the amount of these substances in the environment. Environmental contaminants may be released from moving or static sources, either directly or indirectly, such as through hospital discharge, automobile, and industry. On the other hand, there are many modern methods and techniques for the analysis and characterization of microorganisms that degrade xenobiotics. For the destruction and detoxification of such xenobiotic substances, a variety of physical, chemical, and treatment procedures, including coagulation, electrolysis, filtration, precipitation, etc., have been utilized, but because of their high price, waste removal issues, and tendency to produce poisonous byproducts that can often be much more dangerous than the parent molecule, not all of these technologies are very practical. Despite these more advanced techniques, biological remediation, or “bioremediation,” is a frequently used cleanup approach for the nonhazardous breakdown of xenobiotics from polluted settings (Singh et al. 2020). Bioremediation is now the most suited and promising approach since it uses microorganisms’ metabolic ability to remove contaminants (Mathon et al. 2017; Bharadwaj 2018). Moreover, among these methods, we mention them as follows.

9.1 *Physicochemical Processes*

Increasing a xenobiotic’s complexity causes physicochemical processes to degrade it. Moreover, the complete catabolic pathways cannot realistically be expected to exist in a single organism. When co-metabolic processes within a microbial community complement one another, in addition to incomplete oxidation and accumulation of dead-end metabolites, a higher amount of biodegradation and even

mineralization might be anticipated. These syntrophic interactions do occur naturally, and in some circumstances, the coordinated activity of a two-species culture is better understood (Jin et al. 2007).

Štefanac et al. (2021) showed that the compounds can be physically adsorbed onto the activated carbon bed during treatment with activated carbon, which eventually has to be replaced or regenerated, and it is a widely utilized technology that can get rid of up to 90% of xenobiotics. Additionally, the ozonation or photolysis processes are quite effective in treating organic molecules. Their primary oxidants are strong hydroxyl or sulfate radicals, which may quickly degrade and eliminate contaminants. It is sometimes required to assess the toxicity of the byproducts since the target material does not always completely disintegrate and byproducts might sometimes be more dangerous than the original component (Mathon et al. 2017). Additionally, using filtering techniques like steric exclusion and electrostatic interactions, xenobiotic substances can be eliminated (Jin et al. 2007).

9.2 *Membrane Process*

Many chemical compounds may be effectively removed from drinking water and wastewater, using membranes, although the rate of removal depends on both the molecular characteristics of the contaminants and the characteristics of the membranes (Roccaro et al. 2013). Membranes with pores smaller than the impurities to be removed emerged as a promising solution because it is well-known that they act as a physical barrier to the passage of contaminants. Near the Méry-sur-Oise water purification facility in Paris, reverse osmosis and nanofiltration were both found to be quite effective at removing xenobiotics from the water used to produce potable water. So, even these extremely thin pore membrane processes, nevertheless, could lead to insufficient elimination. Because the main mechanism of retention for xenobiotics is adsorption on the membrane, removal of xenobiotics by microfiltration and ultrafiltration is very low. Combining those with other procedures (such using activated carbon) can significantly enhance the elimination of xenobiotics (Semião and Schäfer 2010).

9.3 *Biological Process*

Using the biological processes of living things like bacteria, fungi, and enzymes, bioremediation is one of the most effective ways to remove chemical pollution because many xenobiotic chemicals have a significant negative impact on the ecosystem due to their high toxicity, long persistence, and poor biodegradability (Mishra et al. 2021). Mishra et al. (2021) reported that the microorganisms are amazingly capable of catabolizing a wide range of genes, enzymes, and

biodegradation pathways. However, one of the limitations of this process is that the predominant microorganisms involved in bioremediation cannot be cultured under *in vitro* environments and instead live in viable but non-culturable environments. This method has a great deal of potential to facilitate the biodegradation of habitats with xenobiotic contamination in soil and water.

Croom (2012) reported that there are a large number of xenobiotic-metabolizing enzymes that exist in human tissue and their organ, with polymorphic forms, while certain indigenous substrate-metabolizing enzymes are quite selective in the substrates they can metabolize, but there are many different types of xenobiotics, and xenobiotic-metabolizing enzymes are frequently able to metabolize an extensive variety of substrates (e.g., CYP3A4). So, often when metabolic activation is linked to toxicity, the areas with the highest concentrations of the activating enzymes are frequently the sites of toxicity. In this context, bioremediation refers to a procedure where environmental contaminants are either detoxified or degraded using metabolites as enzymes; however, generally, the conversion of a pollutant into an inert substance requires a chain of reactions, i.e., an enzyme complex which frequently necessitates the use of other organisms for a successful outcome (Pereira and de Freitas 2012). Consequently, it may be more beneficial to apply enzymatic extracts of organisms than the organisms themselves, because of better process control (knowing enzymatic concentration); quicker and more uniform action may be provided (Rao et al. 2014).

9.4 Bioelectrochemical System

Many studies have shown that many xenobiotic substances penetrated the environment and may be hazardous to living things and the ecosystem. However, using different personal care products, such as hair shampoos and conditioners and moisturizing oils, as well as various forms of food and additives, led to the identification of the majority of biological foreign pollutants in wastewater and natural water (Hlavinek et al. 2007). Various techniques have been used to get rid of microorganisms from the environment, and among them is a technology called bioelectrochemical system. It is a multifunctional technique based on electrochemistry and fermentation consisting of two electrically linked electrodes that are normally separated by an ion-selective screen. The substrate is subjected to an oxidation or reduction process by electroactive microorganisms at the electrode in the bioelectrochemical system. These microorganisms can effectively catalyze the substrates because of their extracellular electron transfer capacities, which let them act as electron donors and acceptors. While xenobiotics are broken down by bacteria using organic materials that are oxidized at the anode, energy is created by reducing a substrate at the cathode. Hydrogen is created during the process by reduction (Zhang et al. 2020).

10 Conclusion

Chemical substances known as xenobiotics can be introduced accidentally or on purpose. There are many ways that these compounds can reach the environment, including direct and indirect discharge and transfer through the food chain. This chapter summarizes some definition of the xenobiotics and some variety of it in the ecosystem and their susceptibility to biodegradability. Moreover, fate and transport of xenobiotics through food system and related human health issues have also been discussed. Advance techniques utilized for identification and measurement of xenobiotics in the food contaminants have been briefly explained.

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Pesticides and Chemical Fertilizers: Role in Soil Degradation, Groundwater Contamination, and Human Health



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Abbreviations

AOA	Ammonia-oxidizing archaea
AOB	Ammonia-oxidizing bacteria
CKD	Chronic kidney diseases
DDE	Dichlorodiphenyldichloroethylene
DDT	Dichloro-diphenyl-trichloroethane
EDC	Endocrine-disrupting chemicals
EM	Effective microorganism
ETL	Economic threshold level
F	Fungicides
FAO	Food and Agriculture Organization
FFS	Farmer field school
GHG	Greenhouse gas
H	Herbicides
HCH	Hexachlorocyclohexane
HYV	High-yielding varieties
I	Insecticides
ILO	International Labour Organization
IPM	Integrated pest management
IRM	Insecticide resistance management
N	Nitrogen
NGO	Nongovernmental organization
NPK	Nitrogen phosphorous potassium
OCPs	Organochlorine pesticides

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POPs	Persistent organic pesticides
SOC	Soil organic carbon
UNDP	United Nations Development Programme
UNEP	United Nations Environment Programme
UNFCC	United Nations Framework Convention on Climate Change
USDA	US Department of Agriculture
USEPA	US Environmental Protection Agency
USGS	US Geological Survey
WHO	World Health Organization

1 Introduction

To ensure the food and nutritional security of the growing population with limited land resources, the use of fertilizers and pesticides in crop production is increasing at an alarming rate. A pesticide is a chemical or biological agent that kills, eliminates, or controls pests either alone or in a mixed form. Globally, a wide range of pesticides including insecticides, herbicides, weedicides, fungicides, and rodenticides have been developed to target specific pests in agriculture, horticulture, and residential settings (Van de Merwe et al. 2018; Jaffar et al. 2022). China (1,404,166 tons) had been reported as the largest consumer of pesticides in the world, followed by the United States (406,684 tons) and Brazil (221,582 tons), whereas pesticide exports from European nations were the highest in the world, followed by the United States, China, and Japan (FAO 2021; Singh et al. 2021). In 2019, India was the fifth largest exporter of agrochemicals, with pesticides valued at USD 3.4 billion. In 2020, India's exports amounted to USD 313.4 billion, representing around 10.9% of the country's GDP (Singh et al. 2021). Additionally, with the introduction of high-yielding varieties (HYV) during the mid-1960s, the country saw steep growth in the manufacturing and consumption of N fertilizers. As a result, India became the world's second largest producer and consumer of N fertilizers (Tewatia and Chanda 2017).

The world is experiencing rapid urbanization with the increase in population. By 2050, the global population will reach 9.7 billion, with the majority of this growth occurring in urban areas (World Population Prospects 2019; Salomon et al. 2020). An urban area comprises various agricultural/nonagricultural settings (Meftaul et al. 2020). Pesticides are often used in farming practices specific to cropping systems, but their uses in an urban context are broader and more diverse. This includes their application in gardens, lawns, golf courses, sealed areas, roads, wastewater treatment plants, etc. (Shamim et al. 2014; Stehle et al. 2019). Additionally, both homeowners and pest control experts use various pesticides to safeguard their furniture against insect damage, maintain sanitation, preserve esthetics, and reduce insect and disease threats (Meftaul et al. 2020; Srivastav 2020). Researchers had reported a comparatively higher concentration of persistent organic pesticides (POPs) in urban centers in developing countries such as Pakistan, India, and Nepal in Southern Asia (Nasir et al. 2014; Pokhrel et al. 2018). In 2016, US homeowners spent over USD 47.8 billion on lawn and garden products, with insecticides accounting for

roughly 80% of the total (Tran et al. 2020). Thus, in urban contexts, the reckless use of these chemicals is more prevalent, resulting in numerous accidents and exposures (Meftaul et al. 2020). Pesticides are frequently detected in residential runoff and surface waters and are likely to enter waterways following rainy events, mainly when applied to impervious surfaces such as driveways and pavements (Jiang et al. 2016; Van de Merwe et al. 2018). Extensive use of pesticides in household gardening is the primary cause of urban drinking water contamination, as polluted water percolates into the ground and contaminates groundwater, affecting human health when consumed (Khan et al. 2018; Syafrudin et al. 2021). Additionally, due to the constant release of pesticides into urban waters by wastewater treatment plants, aquatic creatures in urban waterways may be continuously exposed throughout the year (Shamim et al. 2014). One of the chief nonpoint sources of heavy metals in the upper Ganges is the extensive use of fertilizers (Prasad et al. 2020). Excess transportation of these nutrients into stagnant water has resulted in accelerated eutrophication (Khan et al. 2018). The overconsumption of dissolved oxygen by algae in aquatic environments kills the fish and other organisms, and the water becomes unusable for other purposes. The major health issues with exposure to pesticides are neuronal disorders, congenital abnormalities, fetal growth, and even cancers in humans (Asghar et al. 2016).

This book chapter discusses the adverse impacts of agrochemicals on the major components of the environment with a special reference to urban ecosystems. We also discuss the preventive and regulatory measures that can be taken by different stakeholders to safeguard the ecosystem from its hazardous effects.

2 Effects of Pesticides and Fertilizers on the Environment

2.1 Effects on Soil

Soil is the pivotal component of the earth's ecosystem. It provides water and nutrients to the plants and harbors the microorganisms that maintain the environmental quality. The following sections discuss the negative impacts of agrochemicals on soil health and soil microbial activities and biochemical reactions with reference to urban settings.

2.1.1 Soil Health

The term "soil health" refers to the soil's overall physical, chemical, and biological characteristics as they relate to crop production (Knight et al. 2013). Soil health is a subset of ecosystem health. Consistency in nutrient cycling, energy flow, stability, and resilience to stress are all representations of a well-fit ecosystem. Physical, chemical, and biological changes indicate soil health. Physical indicators include

texture, bulk density, porosity, field infiltrability, soil aggregate dynamics, water-holding capacity, and compaction. Chemical indicators include pH, salinity, sodicity, nutrient availability, and heavy metals. Biological indicators constitute organic matter content, active carbon, enzyme activity, C:N ratio, microflora and fauna, and soil respiration (Hubanks et al. 2018; Tripathi et al. 2020).

Urban soil is severely influenced by anthropogenic activities than natural soil (Meftaul et al. 2020). Urban soil exhibits high unpredictability, poor structure, and soil disturbances which affect the structural and functional characteristics such as porosity, bulk density, nutrient cycling systems, etc. (Attanayake et al. 2014; Igalavithana et al. 2017). Further addition of pesticides will inhibit soil microorganisms involved in the nutrient cycling of soils and have adverse effects on the soil health (Mandal et al. 2020).

2.1.1.1 Effects of Pesticides on Soil Health

Urban agriculture can enhance the sustainability and resilience of urban areas and contribute to a lower carbon economy by reducing the amount of fuel required to transport food at the city level; however, pesticide residues in soil, water, and air pose a risk to urban agriculture, particularly food safety (Ferreira et al. 2018; Meftaul et al. 2020). The long-term impact of pesticides on soil health depends on both soil and pesticide properties that influence the processes like sorption, biodegradation, chemical transformation, microbial transformation, volatilization, leaching, uptake by the organisms, etc. (Chiaia-Hernandez et al. 2017; Tudi et al. 2021). Properties that define the residency period of the pesticides, their fate, and the

Properties of pesticide that decide the residence time in the soil (Tripathi et al. 2020)	Factors affecting the fate of pesticides (Tripathi et al. 2020)	Factors influencing pesticides degradation (Singh 2012; Su et al. 2017; Tudi et al. 2021)
Chemical structure	Types of soil	Temperature
Volatility	Content of soil organic matter	pH
Water solubility	Hydrogen ion concentration	Soil moisture
Formulation	Half life period of pesticides	Intensity and exposure length of sunlight
Application	Diversity of soil microflora	Properties of pesticides

Fig. 1 Soil and pesticide properties that define the residency period, fate, and degradation of pesticide

degradation of pesticides are given in Fig. 1. On application, pesticides undergo various processes like degradation, transportation, sorption, and desorption (Okada et al. 2019; Liu et al. 2021). The longer these pesticides are found in their original form, the higher the chances of leaching into the soil (USEPA 2012). Pesticide concentrations showed an increasing trend as we move from suburbs to urban centers, and their concentrations increase with the increase in the age of the urban soil (Yang et al. 2012). Organochlorine pesticides such as aldrin, dieldrin, chlordane, p,p-dichlorodiphenyltrichloroethane, mirex, and toxaphene are categorized as persistent bioaccumulative and toxic chemicals by the US Environmental Protection Agency (USEPA). These chemicals are detrimental and affect the living systems due to their bioaccumulation within the food chain (Tripathi et al. 2020).

It was found that the residual effect of toxic pesticides changes with the initial application dosage (Tripathi et al. 2020). The application dose of pesticides determines the toxicity with more detrimental effects from higher doses than the lower. Thus, pesticides that persist in the soil for a long time are more harmful (Mandal et al. 2020). Application of lindane at a concentration of 156 and 125 g/ha inhibits microbial activities and crop growth. However, there were no changes in the crop yield when applied at a lower concentration (Glover-Amengor and Tetteh 2008).

2.1.1.2 Effects of Fertilizers on Soil Health

Overuse of agrochemicals is the main cause of the deterioration of soil health. The extent of the impact due to fertilizer on soil health and ecosystem function is controlled by their effects on primary productivity (Singh 2018; Tripathi et al. 2020). There are barely any direct toxic or lethal effects of excessive fertilizer use. The effects are slowly recognized in different soil processes and thus the productivity. Moreover, an optimum level of plant-accessible soil N and P is important for the proper functioning of the soil ecosystem. Variations in different soil properties like soil organic carbon (SOC), N, pH, availability of nutrients, and moisture content have been observed due to prolonged use of fertilizers (Wu et al. 2011). Before N fertilizers were introduced (in the mid-twentieth century), leguminous plants and organic matter were the main sources of N for crops (Singh 2018). The application of fertilizers increases the activity of soil microbes, which were otherwise limited by low concentrations of nutrients. However, continuous use of fertilizers causes soil acidification leading to the release of base cations (Ca, Mg, Al) from soil minerals, and the persistence of this situation for a prolonged time elicits nutrient disorder in plants (Tripathi et al. 2020). Moreover, soil acidification also interferes with the decomposition and mineralization of soil organic matter.

Rousk et al. (2009) had observed a fivefold decline in the growth of bacteria and fungi due to the lowering of pH from 8.3 to 4.0. In addition, soil acidification leads to nitrogen losses by NO_3^- , nitrogen leaching, and NO , N_2O , or N_2 emissions caused by nitrifiers and denitrifiers (Tang et al. 2016). Leaching of nitrate due to excessive use of fertilizers in the subsoil might result in pyrite oxidation, releasing sulfate and other trace elements. The application of fertilizers also adds heavy metals to the soil

and can be associated with their transportation to adjacent water bodies (Khan et al. 2018). Some radioactive matters like ^{238}U , ^{232}Th , ^{210}Po , and ^{40}K are found in phosphate fertilizers and heavy metals (Kara et al. 2004; Hassan et al. 2016).

2.1.2 Soil Microbial Activities and Biochemical Reactions

Soil is a divergent and suitable habitat for different microorganisms. Soil microorganisms are a vital component of agricultural and urban ecosystems as they actively enhance the fertility and productivity of the soil. Soil properties such as porosity, structure, aeration, and water infiltration are regulated by soil microflora by forming and stabilizing soil aggregates (Srivastava et al. 2016). Functions of soil microflora include nutrient cycling, biocontrol of soilborne phytopathogens, organic matter decomposition, nutrient supply, detoxification of contaminated soil, and other plant growth functions such as phytohormone production (Prashar and Shah 2016; Tripathi et al. 2020).

Pesticides are frequently sprayed on urban soils in order to maintain idyllic urban green zones and lessen damage from insects and weeds (Nugent and Allison 2022). Due to the long persistent nature of agrochemicals, they affect the soil microorganisms and, thereby, the soil health (Prashar and Shah 2016). Incorporating agrochemicals affects the beneficial soil microorganisms involved in vital enzymatic components and synchronizing important chemical processes in soil (Malik et al. 2017). Thus, on the removal of beneficial nontarget soil microbes, they have a detrimental effect on nutrient cycling and retention, soil's nutrient pool, and soil fertility (Hashimi et al. 2020).

2.1.2.1 Effects of Pesticides on Soil Microbial Activity and Biochemical Reactions

Soil microorganisms' response to a range of chemical pesticides varies and depends on the nature of pesticides, microorganisms in the soil, and soil properties. In addition, toxicity potential and pesticide application change the structural and functional diversity of soil microbes (Prashar and Shah 2016). Table 1 shows the effects of pesticides on soil microbes. The utilization of agrochemicals continues to alter the diversity and structure of beneficial plant rhizobacteria in agricultural systems (Malik et al. 2017). Leguminous crops fix 100–200 kg N per hectare per year. Herbicides' application has the highest detrimental impact on symbiotic nitrogen fixation compared to all other potential unfavorable effects (Burul et al. 2022). With the elevated use of pesticides, changes in microbial biomass, genetic diversity, and catabolic activities were observed (Wang et al. 2008; Sumalan et al. 2010). Many researchers had reported the pesticide impacts on soil enzyme activities (Table 2). These include hydrolases, nitrate reductase, urease, oxidoreductases, nitrogenase, and dehydrogenase activities. Furthermore, the impacts of pesticides are seen in the biological nitrogen fixation along with their biotransformation processes

Table 1 Effects of pesticides on soil microbes

Pesticide name (type)	Effects on soil microbes	References
Chlorpyrifos (I)	Colony-forming units of bacteria and fungi number decrease	Supreeth et al. (2016)
Cypermethrin (I)	Microbial diversity decreases with an increased dose of insecticide	Tejada et al. (2015)
Imidacloprid (I)	With increased dose of insecticide, number of bacteria decreased	Cycoń and Piotrowska-Seget (2015)
Triazole (F)	Capability to inhibit the proliferation and metabolism of beneficial bacteria and their associated transformation of soil nutrients through cell wall lysis	Satapute et al. (2019)
	Strongly affects the structure of the microbial communities in soil and usually decreases the soil microbial population	Roman et al. (2021)
Glyphosate (H)	The presence of glyphosate reduced the population of bacteria, microbial biomass, and acidobacteria	AL-Ani et al. (2019)
Malathion (I)	Malathion-treated soil samples had the lowest microbiological activity and counts of bacteria, fungi, and actinomycetes	AL-Ani et al. (2019)
Fluoxastrobin (F)	As per the average well color development (AWCD) tests, the soil microbial diversity was found to be influenced, i.e., it inhibited microbial strains	Zhang et al. (2019)
Boscalid (F)	Multiple boscalid treatments decreased soil microbial diversity and network complexity, disrupted soil microbial community, and inhibited soil microbial function	Han et al. (2022)
Mesotrione (H)	Soil microbial community structure and microbial diversity declined after mesotrione exposure Bacteria, fungi, and actinomycetes were all present in lower quantity in the soil treated with mesotrione at 1.0 and 5.0 mg/kg.	Du et al. (2018)
Bromoxynil (H)	Bacterial population decreased by 30%, actinomycetes population decreased by 23.4%, and fungus population decreased by 34%	Abbas et al. (2015)

H herbicides, *F* fungicides, *I* insecticides

(ammonification, nitrification, denitrification, phosphorus solubilization, and S-oxidation) (Monkiedje and Spiteller 2005).

2.1.2.2 Effects of Fertilizers on Soil Microbes

Long-term fertilization has a substantial effect on the soil microorganisms and their extracellular enzyme activity in urban agricultural soils (Igalavithana et al. 2017). Inorganic fertilizers can increase nutrient availability in the soil. However, inappropriate and excessive use of fertilizers does not always result in increased crop yield

Table 2 Effects of pesticides on soil enzymes

Pesticide (types)	Effects on soil enzymes	References
Mesotrione (H)	Decrease the soil dehydrogenase activity with increased herbicide doses	Pose-Juan et al. (2015)
Triazole (F)	Facilitate changes in the activity of soil enzymes and negatively affect the biochemical activity and can impair soil fertility and productivity	Satapute et al. (2019)
	Strongly affects the activity of enzymes present in the soil	Roman et al. (2021)
2,4-Dichlorophenoxyacetic acid (H)	Application of 2,4-D caused the greatest decline in soil dehydrogenase activity	Arora et al. (2019)
Fluoxastrobin (F)	Enzymatic activities such as β -glucosidase, dehydrogenase, and urease were significantly lower on the application of pesticide dose in the samples than those of the controls	Zhang et al. (2019)
Mesotrione (H)	Mesotrione (5.0 mg/kg) treatment resulted in a decrease in β -glucosidase activity	Du et al. (2018)
Bromoxynil (H)	With the application of bromoxynil herbicide at 2250 ml/ha, urease activity decreased by 30%, dehydrogenase activity was inhibited by 36%, and alkaline phosphatase activity decreased by 34%	Abbas et al. (2015)
Azoxystrobin (F)	Dehydrogenase activity is the most sensitive to azoxystrobin Urease activity was initially inhibited by azoxystrobin; however, the inhibitory effect faded off and recovered to the level of control in the end	Wang et al. (2018)
Chlorpyrifos (in presence of earthworms) (I)	Inhibits cholinesterase and carboxylesterase activities of earthworm strongly	Sanchez-Hernandez et al. (2018)
Cypermethrin (I)	With increased dose, arylsulfatase soil dehydrogenase, urease, phosphatase, and β -glucosidase activities decrease	Tejada et al. (2015)
Linuron (H)	Linuron in 100-fold dose decreases dehydrogenase activity of the soil	Medo et al. (2021)
Dimethachlor (H)	Dimethachlor in 100-fold dose decreases soil enzymatic activities	Medo et al. (2021)
Triticonazole (F)	Barley and wheat seeds treated with various dosages of triticonazole were sown in chernozem soil, and the activities of dehydrogenase and phosphatase decreased, whereas urease activity increased	Roman et al. (2022)

H herbicides, *F* fungicides, *I* insecticides

and can cause environmental problems in agroecosystems (Wimalawansa and Wimalawansa 2014a; Yousaf et al. 2017). Proton release to the soil by N cycling and the acidic reaction of soluble P fertilizers resulted in soil acidification (Guo et al. 2010; Van der Bom et al. 2018). Again, soil pH, along with SOC and N, is an

important driver of microbial community change, whereas P plays a minor role (Hartmann et al. 2015; Francioli et al. 2016). Long-term input of ammonium-N-containing fertilizers decreases soil pH and influences the biomass, structure, microbial diversity, and activity of soil microbial communities (Geisseler and Scow 2014; Francioli et al. 2016). Zhou et al. (2015) had also reported similar observations on the application of inorganic fertilizers for 44 years. In contrast, NPK combined with organic manure increases microbial biodiversity and bacterial population (Sun et al. 2015).

A change in fertilization pattern (inorganic/organic fertilizer) did not change the composition and richness of ammonia-oxidizing archaea (AOA) but altered the ammonia-oxidizing bacteria (AOB) in calcareous and neutral soils exposed to N fertilizer (Shen et al. 2008, 2011). However, different responses to organic and inorganic fertilizers had been reported by Zhou et al. (2015). Adding inorganic fertilizers increases AOB, whereas AOA increases under the influence of organic N fertilizers. Additionally, after 23 years of fertilization, using chemical fertilizers with or without organic manure can alter the richness and composition of AOA and AOB in neutral soil (Xue et al. 2016). Thus, excessive and unjustifiable use of synthetic fertilizers and pesticides has led to massive soil contamination, which has negatively impacted the soil biodiversity. Similarly, pesticide poisoning in the water system especially groundwater is another well-known and widespread global problem. The following sections discuss the effects on the urban water system.

2.2 *Effects on the Urban Water System*

Pesticides used in urban areas pose a risk to surface water systems since impervious pavement increases runoff, which can result in severe contamination and aquatic toxicity (Cryder et al. 2019). Jiang et al. (2016) had reported that hydrophobic pesticides such as pyrethroids and fipronil can bind to loosen particles of impervious substances. These particles prove to be an important source of pesticide contamination in the runoff in urban settings. Global urban land area is projected to increase tremendously during the year 2000–2030 due to urbanization, which will aggravate urban pesticide runoff and surface contamination (Cryder et al. 2019). In addition, pesticides related to turf grass management were detected in storm runoff and surface water of urban watersheds (Rice et al. 2017). The extent to which pesticides contaminate surface waters is influenced by physicochemical characteristics such as retention by soil components, degradation rate, water solubility, and properties of the medium in which the compounds are applied and degraded (Barra Caracciolo et al. 2009; Khatri and Tyagi 2015).

Groundwater has been considered as a pure and reliable form of drinking water for a long time. Pesticide contamination of groundwater is a huge concern since the majority of water requirement is fulfilled by groundwater in most part of the world (Khatri and Tyagi 2015; Malyan et al. 2019). Thus, a detailed understanding of the various urban sources of pesticide pollution, their entry points, and their dynamic

contributions to the urban environment is required for the implementation of appropriate strategies to mitigate these dangers (Meftaul et al. 2020). The poisoning of groundwater by agrochemicals and its ecological consequences are addressed in the following sections.

2.2.1 Contamination of Groundwater by Agrochemicals

The primary way by which pesticides reach the groundwater is due to their ability to penetrate the soil and make their way through the unsaturated region to the water table. They also reach the groundwater by leaching or percolating processes (Malyan et al. 2019). The transportation of pesticides in groundwater is different from that of streams (surface water). Water-soluble pesticides can travel large distances in groundwater. Numerous variables affect the transportation method (Table 3).

Groundwater contamination is a significant concern in areas where groundwater aquifers are the primary source of drinking water. Contaminated groundwater, when resurfaced, affects nontargeted organisms, including endangered species (Agarwal et al. 2010). Figure 2 shows the movement of pesticides through the environment. As reported by the US Geological Survey (USGS), groundwater contained no less than 143 pesticides and 21 transformation products. These include pesticides from every significant chemical class (USGS 2014). In the last few years, several cases of groundwater pollution due to pesticide residues had been reported all across the world. For example, Somashekar et al. (2015) had reported methyl isocyanate in water samples obtained from the city of Mysore in the Indian state of Karnataka. Herbicides such as diuron, dibromochloropropane, bromacil, simazine, and others were found in groundwater of the San Joaquin Valley, California, at concentrations that are harmful to the ecology and human health (Troiano et al. 2013). Given the above evidence, it is crucial to develop effective ways to make proper strategies that would prevent the flow of excessive agrochemicals to groundwater.

2.2.2 Ecological Implications of Agrochemical Contamination in Groundwater

Numerous detrimental alterations caused by pesticide pollution are prevalent in urban aquatic ecosystems (Meftaul et al. 2020). Due to its persistency and stability in the environment, it results in biomagnification and bioaccumulation in living organisms once it enters the food chain. The disproportionate use of nitrogenous fertilizers is the main reason for the high nitrate content in groundwater. A variety of health diseases are caused by drinking nitrate-contaminated water. Pesticides also affect the groundwater microbial system. The relevance of groundwater microorganisms is acknowledged because they provide ecosystem services such as drinkable water, nutrient cycling, and toxin degradation (Jacobsen and Hjelmsø 2014). Other implications due to the application of agrochemicals (pesticides and

Table 3 Factors affecting the possibility of pesticides reaching groundwater

Factors	Properties	Reasons	References
Pesticide properties	Solubility	The higher the solubility of pesticides, the greater potential to leach down to the groundwater	Trautmann et al. (1989); Damalas and Eleftherohorinos (2011)
	Adsorption	Pesticide with strong adsorbing capacity is unlikely to reach the groundwater irrespective of its solubility	
	Degradation	Pesticide degradation includes processes like photolysis, hydrolysis, and oxidation	
	Volatility	Higher vapor pressure is subjected to faster vaporization of pesticide to the atmosphere, making it less available to leach down	
Soil properties	Organic matter	Soil organic matter affects the adsorption of pesticides to the soil	Trautmann et al. (1989); Damalas and Eleftherohorinos (2011)
	Soil texture	Movement of the water along with the dissolved chemical pesticides through the soil is affected by "soil texture." The coarser the soil texture, the greater the chance of pesticide leaching down	
	Soil permeability	Proper timing and well-designed application methods minimize leaching to groundwater in highly permeable soil	
	Soil structure	Aggregation of soil particles affects the movement of water. Loosely packed soil is more likely to allow dissolved pesticides to easily percolate down	
Site conditions	Depth to groundwater	Shallow depths of groundwater; degradation and adsorption opportunities are low along with filtering action provided by soil	Trautmann et al. (1989)
	Topography	Rate of infiltration is higher than runoff in flat or depressed areas, which enhances the vulnerability to leaching	
	Climate	Climatic conditions like rainfall affect the transport process. Areas with high rainfall are susceptible to leaching of pesticides	
	Geologic conditions	Areas with quick permeability of geologic layers are vulnerable to groundwater quality	
Management practices	Pesticide application method, application rate, time of application	The way of pesticide application affects the leaching potential. High amount of pesticides used in proximity to a heavy rainfall or irrigation makes it more likely to leach down to groundwater	Trautmann et al. (1989); Ramsay et al. (1991); Arias-Estévez et al. (2008)

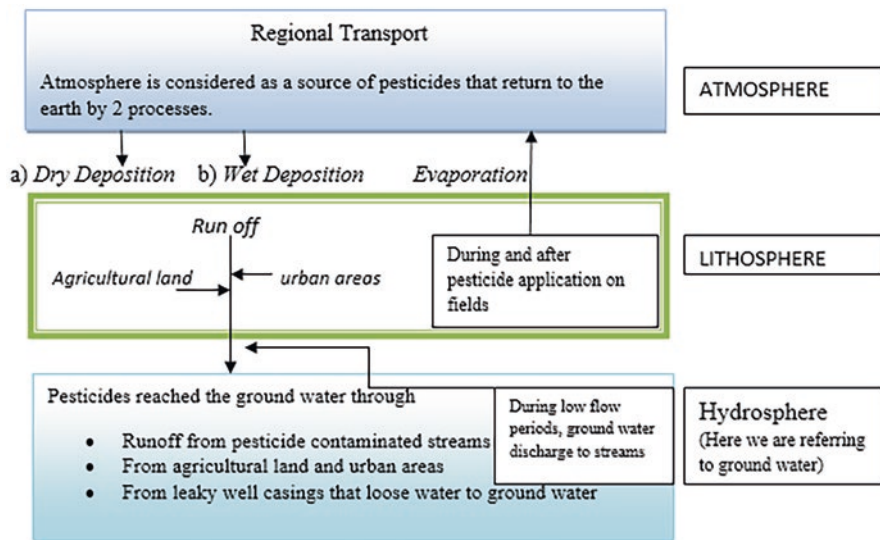


Fig. 2 Pesticide movement in the environment (air, land, and groundwater) (based on/adapted from Majewski and Capel 1995; Gilliom et al. 2006)

fertilizers) include its impacts on crop health and human health (Srivastav 2020; Dhuldhaj et al. 2022).

The above sections have discussed the contamination of groundwater by agrochemicals. Urban population is more affected due to high population density, different land use pattern, and presence of impervious structures. The effect of pesticides on human health has been discussed in the following sections.

2.3 Effects on Human Health

The widespread use of organochlorine pesticides (OCPs) to increase agricultural production and to prevent vector-borne diseases such as malaria, dengue, and leishmaniasis, particularly in urban areas, had created a significant threat to human health (Guida et al. 2021; Ashesh et al. 2022). Lack of knowledge on pesticide handling, improper storage and disposal, use of cheaper but toxic pesticides, and lack of enforcement and regulatory systems are some of the factors identified that worsen the health hazards (Nath and Deka 2022). In developing countries, urban areas were found to be at greater risk than semi-urban or rural agricultural areas (Anand et al. 2021). For example, Sharma et al. (2014) had reported a higher concentration of OCPs in urban areas of Punjab. Muller et al. (2017) had reported a higher amount of PCB congeners in human milk of urban areas compared to rural

areas of northern Tanzania. The enhanced toxicity in the urban environment is caused by the additives or carrier elements of pesticides (Castro et al. 2014). Richards et al. (2016) had found the prevalence of pyrethroids in the dust particles on the paved surfaces of individual houses in urban environments and found them to be uniformly distributed in the areas adjacent to each residence, indicating significant redistribution. The route of exposure includes oral, dermal, respiratory tract, and ocular exposure (Meftaul et al. 2020). There are limited research works on the effects of pesticides in typical urban environments, even though ten times larger dosages of different pesticides are applied simultaneously to control a variety of pests and to maintain urban lawns and golf courses (Ali et al. 2014; Bekken et al. 2021). This poses a risk for children and individuals who spend a significant time of the day in playing and recreational activities in those areas.

2.3.1 Acute Health Effects of Pesticides

Acute health effects are adverse effects that occur immediately or within a short span of time after the exposure to pesticides. Human exposure to these pesticides might lead to acute health effects such as fatigue, dizziness, nausea, headache, body aches, skin rashes, skin discomfort, excessive sweating, vomiting, impaired vision, tremors, panic attacks, and cramps (Kumari and Reddy 2013; Suryawanshi and Patil 2016; Nath and Deka 2022; Dhuldhaj et al. 2022). Organophosphate is the most common toxic agent for acute poisoning (Chowdhury et al. 2011). Delayed polyneuropathy, cholinergic syndrome, intermediate syndrome, and chronic organophosphate-induced neuropsychiatric illness are the four main neurotoxic effects of organophosphate pesticides in people (Jokanović 2018). Malathion, parathion, and carbamates are common organophosphates that cause interruption of impulse transmission at the synaptic level and act as acetylcholine esterase (AChE) inhibitors. ACh accumulation results in the over-activation of neurons affecting muscles (Dixit et al. 2021). Similarly, OCPs are typically characterized as chemicals that are bioaccumulative and persistent and are suitable for long-distance transportation (Taiwo 2019). Organochlorines such as DDT (dichloro diphenyl trichloroethane) and endosulfan are potent pesticides. Endosulfan is a debatable agrochemical due to its acute toxicity, bioaccumulation potential, and endocrine disruptor activity (Lozowicka et al. 2015). Herbicides also affect the nervous and excretory systems (Casida 2009; Singh et al. 2016).

2.3.2 Chronic Health Effects of Pesticides

Pesticides used for an extended time, even a relatively small amount, can induce chronic sickness in humans. Some of the major chronic illnesses caused by chronic exposure to pesticides are discussed below.

2.3.2.1 Neurotoxicity

Pesticides that target the neurological system include organochlorines, organophosphates, and carbamates (Dixit et al. 2021). Neurological effects such as memory loss, impaired visual ability, coordination loss, altered or uncontrollable mood and general behavior, decreased motor abilities, and neurodevelopmental impacts were reported from pesticide poisoning (London et al. 2012; Biswas et al. 2014; de Joode et al. 2016). Prolonged exposure to low or high levels of pesticides during adulthood, childhood, or pregnancy (utero-exposure) causes nervous disorders like Parkinson's disease and Alzheimer's disease. Organophosphate and organochlorine pesticides affect synaptic junctions in the nervous system by regulating acetylcholinesterase, which may lead to Alzheimer's disease when exposed later in life (Hayden et al. 2010). The substantia nigra, a basal neuron in the brain, cannot produce dopamine causing Parkinson's disease. Qi et al. (2014) suggested that herbicides like rotenone and paraquat disrupt this neuron and inhibit dopamine production, leading to Parkinson's disease.

2.3.2.2 Reproductive Health

Exposure of pesticides to women of reproductive age has several consequences, such as infertility disorders due to their effects on the hormones or follicle count (Rani et al. 2021). Exposure to pesticides during pregnancy might lead to premature or spontaneous abortions, incessant stillbirth, neurodevelopment alterations in the child, etc. (Neghab et al. 2014; Chilipweli et al. 2021; Rani et al. 2021). Anand et al. (2021) and Sharma et al. (2020) had reported the presence of organochlorine, pyrethroids, and DDT and DDE (dichlorodiphenyldichloroethylene) in the breast milk of mothers in semi-urban and urban areas of Kolkata and northwestern parts of the Himalayas in India, respectively. Sharma et al. (2014) had also reported higher intake of DDT and HCH (hexachlorocyclohexane) by infants than the recommended values in some of the samples. Exposure to pesticides affects male fertility in terms of semen quality, DNA fragmentation, and chromosome aneuploidy (Giulioni et al. 2022). Researchers had reported that mothers with higher pesticide metabolites in their breast milk have children (boys) having cryptorchidism (Damgaard et al. 2006; Desalegn 2022).

2.3.2.3 Cancer

Several studies have shown strong evidence between pesticide exposure and cancer occurrences. Pesticide application on a significant commercial level or at home highly increases the risk of leukemia, thyroid (Alavanja et al. 2013), kidney (Xie et al. 2016), lung, and pancreatic cancer (Shankar et al. 2019; Porta et al. 2022). Kumar et al. (2022) and Wan et al. (2022) had reported that exposure to

xeno-estrogenic pesticides results in elevated breast cancer risk. Similarly, Kabir et al. (2018) had reported a positive correlation between pesticide exposure and prostate cancer death. Child leukemia was positively correlated with exposures to unidentified household pesticides, insecticides, and herbicides during pregnancy (Kim et al. 2017). Studies had also reported that exposure to pesticides during pregnancy may contribute to acute leukemia in children under 2 years of age (Ferreira et al. 2013).

2.3.2.4 Other Health Effects of Pesticides

Pesticide exposure could lead to hypothyroidism in women at childbearing age and menstrual irregularities (Suhartono et al. 2018; Abdel-Rasoul et al. 2019). Additionally, pesticides might harm the respiratory system and cause dry cough, wheezing, bloody sputum, and respiratory system irritation (Fareed et al. 2013). Buralli et al. (2018) had reported the danger of lung disorders, increased mortality, and morbidity rates in those exposed to pesticides. Furthermore, endocrine-disrupting chemicals (EDC) like DDE, a major metabolite of insecticide DDT (Cano-Sancho et al. 2017), could be involved in causing diabetes (Ruiz et al. 2018). Moreover, the size of B-islet cells decreased, and blood glucose and calcium level stimulation increased during the preparation of imazamox-based herbicides (Sevim et al. 2019). Guzzardi et al. (2016) conducted a study to explore the relationship between organochlorine pesticides and aging. They had reported that telomere length was affected by oxychlordan and TNC Biological Fungicide pesticides, which may lead to accelerated aging.

2.3.3 Effects of Fertilizers on Human Health

Higher than the suggested level of fertilizers like phosphate pollutes the water bodies and makes them unsafe for human use. This causes chronic kidney diseases (CKD) (Wimalawansa and Wimalawansa 2014a). Excessive nutrients in a water body (eutrophication) alter the water's natural vegetation, change the color, and render it unfit for human consumption. Likewise, excessive use of fertilizers results in contamination of groundwater with nitrate. Human exposure to nitrate results in the immobilization of hemoglobin in the blood due to nitrate-concentrated water, causing methemoglobinemia (Sharma and Singhvi 2017). High nitrates in drinking water had been reported to cause disorders like hypertension (Kumari and Rai 2020), non-Hodgkin's lymphoma (Poh et al. 2022), thyroid cancer (Bivolarska and Gatseva 2015), and enhanced infant mortality (Ashraf et al. 2019). Carcinogenic compounds form a nitrosation reaction in the stomach when other organic compounds react with nitrate compounds. These carcinogenic nitroso compounds are thought to be the origin of some forms of cancers in humans (Ashraf et al. 2019).

It is clear from the above discussion that society needs proper implementation of strict reforms and laws to reduce the effects of pesticides on human health and the

environment. More innovative agricultural practices and sustainable approaches of pest control could be a significant step in safeguarding the environment. Preventive measures for agrochemicals are discussed below.

3 Preventive Measures of Agrochemical Pollutants

Agrochemical pollution is one of the severe threats to the environment in the present-day scenario. Excessive use of these agrochemicals adversely affects water bodies, soil, and health. Therefore, farmer communities directly exposed to these chemicals face profound health implications (Tripathi et al. 2020; Dhuldhaj et al. 2022). The leading causes of pesticide contamination include ignorance of the adverse effects, irresponsible behavior on the part of farmers and agrochemical sellers, and substantial government fertilizer subsidies (Wimalawansa and Wimalawansa 2014a). Due to the persistent nature of these agrochemicals in the environment, more stringent laws and policies must govern their preventive measures.

3.1 Organic Farming and Integrated Pest Management System

The Food and Agriculture Organization (FAO) and World Health Organization (WHO) have defined organic agriculture as “Organic agriculture is a holistic production management system which promotes and enhances agro-ecosystem health, including biodiversity, biological cycles, and soil biological activity. Furthermore, it emphasizes the use of management practices in preference to using off-farm inputs, considering that regional conditions require locally adapted systems. This is accomplished by using, where possible, agronomic, biological, and mechanical methods, as opposed to using synthetic materials, to fulfill any specific function within the system.” Nowadays, farmers who have adopted organic practices are familiar with modern equipment, knowledge of resistant crop varieties, soil and water conservation practices, and modern techniques related to livestock (Reganold and Wachter 2016).

The organic farming practice is known for its sustainable production with minimum environmental impacts and high-quality food without residues of agrochemicals. In addition, research indicates that under extreme drought conditions, organically managed farms are more productive than their conventional equivalents. This could be attributed to greater water-holding ability of organically farmed soil (Siegrist et al. 1998; Lotter et al. 2003). This property will help to cope with the severe drought conditions in recent years. In addition, crop rotations, the growth of leguminous plants to provide nitrogen to the farmed soil, fewer external nutrient inputs, and a rejection of mineral fertilizers and synthetic chemicals are other vital components of organic farming compared to conventional agriculture. Organic

practices control the soil organic carbon (SOC) content through soil carbon sequestration (Leifeld and Fuhrer 2010).

According to the United Nations Framework Convention on Climate Change (UNFCCC 2008), the process of soil carbon sequestration can counterbalance large proportions of methane and nitrous oxide released from agricultural fields. Many international reports have recognized organic agriculture as a highly demanding and innovative farming system, which helps balance multiple sustainability goals and eventually plays a vital role in global food and ecosystem security (Food and Agriculture Organization of the United Nations; The National Academies 2012). In addition, studies have revealed that organic farming is more energy efficient than conventional agrochemical practices (Tuomisto et al. 2012; Lee et al. 2015).

In India, Sikkim officially adopted a resolution to switch to organic farming in India in 2003. Now, Sikkim is the first state in the world that is 100% organic (Sikkim State Policy on Organic Farming, India 2004). In recent years, Sikkim has evolved as a major exporter of organic fruits, flowers, spices, and vegetables. After the adoption of organic practices, the state has turned its economic conditions more uplifted. Similarly, Sri Lanka, a developing nation, has enhanced productivity and decreased environmental contamination by implementing ancient agricultural practices, such as using animal manure and compost in the fields, relying on cascade tanks, and using modern methods (Wimalawansa and Wimalawansa 2014b).

3.1.1 Integrated Pest Management (IPM)

Integrated pest management (IPM) is another tool to minimize the harmful impacts of synthetic chemicals on the environment without compromising crop production. According to FAO (2020) and the US Department of Agriculture (USDA) (2018), IPM is an inclusive program that incorporates various other techniques such as cultural, biological, physical, and chemical controls and minimizes environmental and human health risks. Adopting IPM in urban, agricultural, and wildland or natural areas can manage all kinds of pests and prevent long-term damage by managing the ecosystem. Usually, in IPM, the use of chemical pesticides is the last resort to manage the pest population below the economic threshold level (ETL). Therefore, pesticide use should be judicious so that no associated problems would exist.

For the last three to four decades, both developed and developing countries have adopted the IPM techniques in agricultural fields, which tremendously reduced the use of agrochemicals (Peshin and Zhang 2014). For instance, the USEPA (2011) estimated that during 2006–2007, the use of organophosphate insecticides declined by approximately 63%, i.e., from 40 million kilograms in 2000 to 15 million kilograms in 2007. Furthermore, studies have shown that Italy reduced pesticide use in agriculture and horticulture by 56%, followed by the United Kingdom and France (44%) (Peshin and Zhang 2014). By following IPM practices, India has reduced dependency on pesticides in cash crops like cotton, rice, and vegetables. The Directorate of Plant Protection Quarantine and Storage, Ministry of Agriculture and Cooperation, Government of India, shows the impact of IPM programs

implemented since 1985. The following indicates that IPM has reduced the need for pesticides: Rice and cotton production increased in IPM fields from 6.74% to 40.14% and 22.70% to 26.63%, respectively. The spraying of chemical pesticides decreased from 50% to 100% in rice and from 29.96% to 50.50% in cotton. Biopesticide usage increased from 123 MT in 1994–1995 to 7804 MT (Tech Grade) in 2019–2020, and total chemical pesticide consumption decreased from 61,357 MT (Tech Grade) in 1994–995 to 60,599 MT (Tech Grade) during 2019–2020.

Within the IPM, insecticides are considered as an essential part. In urban ecosystems (e.g., agricultural systems and situations), pesticides are often a convenient, economical, and fast-acting method of crisis management. As part of IPM, insecticide resistance management (IRM) strategies are undertaken in urban ecosystems (Zhu et al. 2016). IRM strategies include the state and mechanisms of insecticide resistance, overcoming or delaying resistance to current chemicals, and preventing the development of resistance to new pesticides by reducing insecticide selection pressure (Denholm and Rowan 1992; Georghiou 1994). Recent development in green practices in agricultural industries is bringing positive changes to the economy. In India, the agrochemical industry is gradually adopting more environment friendly practices. Companies have adopted implementing zero discharge solutions, which has yielded considerable benefits. Many companies have developed several green biopesticides, biofertilizers, and biostimulants. Various new technologies have been developed and adopted in urban and rural agricultural practices to prevent pollution from the agrochemical. Among these, formulations with nanoparticles, the use of drones for spray, improved nozzles, electrically charged liquids, and high-performance adhesives that enhance retention, lowering the use of agrochemicals, are some of the prominent technologies. These technologies improve productivity, reduce costs, and keep the environment safe (Alawadhi 2022).

3.2 Training Programs and Workshops for Raising Awareness

Studies have revealed that little knowledge on proper utilization and management of agrochemicals, careless handling, and lack of information and training are among the factors leading to pollution of the environment and adverse health risk to farmers (Recena et al. 2006; Polidoro et al. 2008). Therefore, it is crucial to engage every grower in some training program or awareness program. Community participation is the key to the success of IPM and organic farming practices. The USEPA (2022) has recognized that for implementing IPM, awareness, education, and outreach programs are the key facilitators. Adequate training and technical support are essential for IPM to be successful in implementation (Parsa et al. 2014).

International bodies like the International Labour Organization (ILO), Food and Agricultural Organization (FAO), and World Health Organization (WHO) have provided various guiding rules and regulations for the use of agrochemicals in different developed and developing countries. On the other hand, the FAO Asian Regional IPM/Pesticide Risk Reduction Programme has conducted many farmers' education

programs and participatory research activities. They promote and support IPM in vegetables by Asian smallholder farmers in collaboration with government and non-governmental organizations. This kind of training approach by the FAO Regional IPM Programme is primarily known as the farmer field school (FFS).

Three types of human resource development programs have been implemented in India under the National Policy on Integrated Pest Management. They are as follows:

- Farmer field school program
- Season-long training program
- Short-duration training programs on IPM

Farmers' participation in various workshops and training programs depends on how they get motivated by the same objectives. For example, through various non-governmental organization (NGO) campaigns, farmers can be motivated and requested by consumers' positive aspects, such as demand for pesticide-free products. However, studies have revealed that the primary source of information for the farmers is their fellow men and extension advisors (Farooq et al. 2007). Furthermore, the seller or dealer is the source of popularity for a particular agrochemical in a rural community. Therefore, it is essential to introduce various information programs frequently through mass media like TV and radio talks and training programs about precautionary measures and hazardous effects of pesticide overuse directly to the farmers.

3.3 Role of Government in Strengthening the Laws and Policies

Governments are the key controller of the unregulated and indiscriminate use of agrochemicals by strengthening the prevailing laws and policies. Various international partnership programs have been adopted in recent years to support IPM programs. For example, the "Global IPM Facility" program, cosponsored by the Food and Agriculture Organization of the United Nations (FAO), the World Bank, the United Nations Development Program (UNDP), and the United Nations Environment Program (UNEP), has been in operation since 1995 (Kelly 2005). To abate agrochemical pollution, the government must take appropriate initiatives regarding strict laws and policies. Furthermore, depending on the toxicity and hazardous nature of the agrochemicals, policies and regulations have to be framed for modern technologies such as nanotechnologies and earthworm assisted technologies for the remediation of agrochemical pollution.

In India, the Govt. of Sikkim has turned their agriculture organic by reducing the subsidy on fertilizers and pesticides by 10% every year. Thus, the increasing rate of fertilizers and pesticides leads to lesser use. The state has also banned the import of chemicals and fertilizers from outside states, intending to discourage farmers from

using the chemicals. Again, to reduce the use of chemicals, the government has implemented several alternative strategies, including the use of vermicompost made in vermin hatcheries, biofertilizer, seed processing units, government farms, rural compost pits, organic manure, effective microorganism (EM) technology, integrated pest management, and the establishment of organic farming schools (Kumar et al. 2018).

4 Conclusion and Future Recommendations

Extensive and unjustifiable application of agrochemicals in agricultural/nonagricultural settings to control a diverse range of pests hinders virtually every aspect of the ecosystem, including groundwater, soil, and human health. Homeowners ignore pesticide doses while spraying pesticides. In addition, the indiscriminate use of pesticides in urban environments (parks, lawns, pest control, drainage systems, pathways, etc.) causes runoff during storms or rainfall into urban waterways contaminating both surface water and groundwater. These residues enter the human body through dermal contact, inhalation, ingestion, or eye exposure and may result in various life-threatening diseases in humans as well as animals. Therefore, sustainable agricultural practices such as integrated management of nutrients and diseases are important to achieve a contamination-free environment, healthy food products, and potable drinking water. Emphasis should be given on the following:

- Formulation of less persistent, biodegradable pesticides
- Organic agricultural practices
- Implementation of laws to regulate the production, marketing, and use of pesticides and chemical fertilizers
- Awareness among the farmers and common people on agrochemical uses and its consequences

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Ingression of Heavy Metals in Urban Agroecosystems: Sources, Phytotoxicity and Consequences on Human Health



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1 Introduction

Globalisation and industrialisation have gradually altered and posed challenges to the agricultural growth and crop production system in peri-urban areas (Liu and Li 2017). Recent years have seen a lot of pressure placed on crop production systems due to shrinking peri-urban agroecosystems, climate change, unsustainable land use, human-driven ecological degradation and growing population to name a few (Kremen and Merenlender 2018; Fantini 2023). Due to these food security threat phenomena, global action plan and policy reforms are much needed to transform our food systems (Liebig et al. 2022; Woodhill et al. 2022). Structuring food systems efficient of provisioning urban clusters that guarantee food security as well as a healthy environment is crucial since the development of the agricultural-industrial paradigm has permitted the fast rise in urban population on a universal scale (Fantini 2023). As the world gradually urbanises, many regions are losing biodiversity and local food sources. Moreover, there is more emphasis on economic gains and crop production maximisation rather than environmental and human health values (Usman et al. 2021). Urban agroecosystems have been thought of as a strategy to encourage and maintain urban residents' access to food (Peroni et al. 2022). Urban farming is the practice of growing crops in or near a village, town, city or metropolis with at least some of their output intended for urban consumption (Mulier et al. 2022).

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Despite these advantages, urban agroecosystems may nonetheless confer a risk to human health because of the many anthropogenic activities that frequently result in high concentrations of risk components in urban soil (Malone 2022). Therefore, multiple potential drawbacks are associated with urban agriculture including human health risks and implications for the environment as well (Stewart et al. 2013). The skeleton and body of urban ecosystems depend upon energy use, import, transformation and export of materials (Bai 2016). Such energy and material transformations have beneficial implications on urban growth; however, in this process, certain xenobiotic compounds may pose potential negative impacts on ecosystem and human health (Stewart et al. 2013). The usage of wastewater, for instance, may contaminate the crops with organic and inorganic xenobiotics, alter the soil properties and pollute the groundwater owing to leaching (Lyu et al. 2022). Extensive application of pesticide and fertilisers may potentially endanger the environment and pose health hazards to urban residents.

Xenobiotics are the compounds, mainly the contaminants, that are not found in the natural environment and are generated or introduced as a consequence of human interventions (Stefanac et al. 2021). These xenobiotics usually impart negative influences on human population and their environment by meddling with metabolic and ecological processes (Ortiz et al. 2022). Xenobiotics can have lethal, mutagenic or teratogenic impacts on people even in minute quantities, when exposed over an extended time period (Dhuldhaj et al. 2023). In recent past, researchers become interested in the contamination of agroecosystems with xenobiotics since it has the propensity to contaminate the food chain, cause biomagnification in trophic levels and pose serious health risks to both humans and animals.

Xenobiotics may include inorganic contaminants, organic contaminants and biological contaminants (Atashgahi et al. 2018). Inorganic contaminants include heavy metals that are transferred to urban agroecosystems owing to anthropogenic activities required to fulfil energy and economy demands of human population in urban ecosystem (Singh et al. 2022). Organic wastes chiefly contain fertilisers, pesticides, pharmaceuticals, personal care products (PPCPs) and other emerging contaminants (ECs). These may be composed of polyaromatic hydrocarbons, chlorofluorocarbons and other highly toxic and hazardous contaminants (Gupta et al. 2022). In general, biological waste is discharged from labs, care establishments, nursing homes, mortuaries, autopsy centres and blood banks (Pepin et al. 2014). If not managed properly, this medical waste may further be a source of deadly microorganisms such as virus, bacteria or fungi and may pose severe health threats for human population (Ramteke and Sahu 2019).

It is vitally important to handle these wastes containing potentially harmful xenobiotics that could harm both human and ecological health (de Oliveira et al. 2020). However, in third-world countries, xenobiotics may end up concentrating in the urban components such as agroecosystems, water bodies and air owing to lack of high-end waste management facilities and eventually distressing the human health (Kumar and Chopra 2020; Karthigadevi et al. 2021). Agroecosystems are the ecosystems that have been altered by human intervention for the crop cultivation (Khumairoh et al. 2012). Due to the human interventions, agroecosystems have

recurrent presence of heavy metals and agrochemicals, including pesticides, fertilisers and other anthropogenic contaminants (Alengebaway et al. 2021; Okereafor et al. 2020). Soil is an integral part of the agroecosystem and a living media for plants, microbes and animals. The soil has always been important to human and their health, providing a resource that can be used for food crop production (Steffan et al. 2018). It is also the foundation for various ecological processes; therefore, proper management is necessary to safeguard food safety and human health (Alengebaway et al. 2021).

With an atomic density greater than 5 g cm^{-3} , a class of metals and metalloids are referred to as “heavy metals” (Hawkes 1997). Heavy metal contamination affects food crops, water resources and agroecosystems and can endanger the health and welfare of both man and animal (Briffa et al. 2020). An excessive build-up of heavy metals may contaminate the soil, lower crop quality and compromise food safety (Liu et al. 2013). Several variables, including soil pH, organic matter, cation exchange capacity, crop growth phases, crop type, fertilisers, soil type, metal speciation, soil microorganisms present and other characteristics, affect the uptake, distribution and transport of heavy metals in the soil and crops (Liu et al. 2006). It is crucial to safeguard this resource and preserve its sustainability because heavy metal contamination in agroecosystems may cause soil dysfunction, interfere with crop growth and potentially harm human health through a polluted food chain (Singh et al. 2021).

Henceforth, this chapter provides a comprehensive and critical explanation of the distribution and sources of heavy metals in urban agroecosystems, as well as the factors that impact their ingression, accretion and migration within these systems and the consequences they have on crop plants and human health.

2 Sources of Heavy Metals in the Urban Agroecosystems

2.1 Wastewater Irrigation

Utilisation of wastewater for irrigation is a common practice in developing countries, particularly in arid and semi-arid regions (Minhas et al. 2022). Prolonged use of untreated municipal and industrial wastewater for irrigation leads to the heavy metal accretion in the soil, transferring it in the food crops, and causes numerous health disorders on contaminated crop consumption (Kumar and Chopra 2014; Pal et al. 2023). Long-term wastewater irrigation has potential to change the soil's physical and chemical properties and lead to heavy metal uptake by plants, mostly vegetables (Mahmood and Malik 2014). The high occurrence of Cd, Cr, Ni and Pb were reported in sewage water used to irrigate the urban agroecosystems of Faisalabad, Pakistan, by Jabeen et al. (2022). Wastewater irrigated vegetables had heavy metal concentrations higher than those allowed by the European Union and the World Health Organization (WHO). The hazard ratio for these heavy metals was larger

than 1, indicating a severe health risk upon consumption of these vegetables by the region's urban residents. Wastewater irrigation practice over an extended period of time has been demonstrated to affect the crop growth by altering the physiology and biochemistry of crop plants and pose human health risks in India (Kumar et al. 2020). Thus, prolonged wastewater irrigation has been reported as a primary route to food chain contamination, leading to severe human health risks globally. Multiple sources of heavy metal contamination in agroecosystems have been shown in (Fig. 1).

2.2 Fertilisers and Pesticides

Application of inorganic fertilisers, herbicides, insecticides, composts and manure, among other agricultural techniques, is thought to increase the concentration of heavy metals including As, Cr, Cu, Zn and Cd in agricultural soils (Zhang et al. 2010). Because phosphorous is regarded as a vital mineral for agricultural plants' growth and development, phosphate-based fertilisers are the most popular among the many fertiliser types (Gupta et al. 2014). An Indian study reported that prolonged application of inorganic fertiliser acted as significant contributor to the Cd augmentation in top soil, further causing the Cd build-up in paddy (Rao et al. 2018). It was revealed that heavy metal concentrations were associated to fungicides and copper-based fertilisers (Schneider et al. 2019). Arsenic-based fungicides accounted

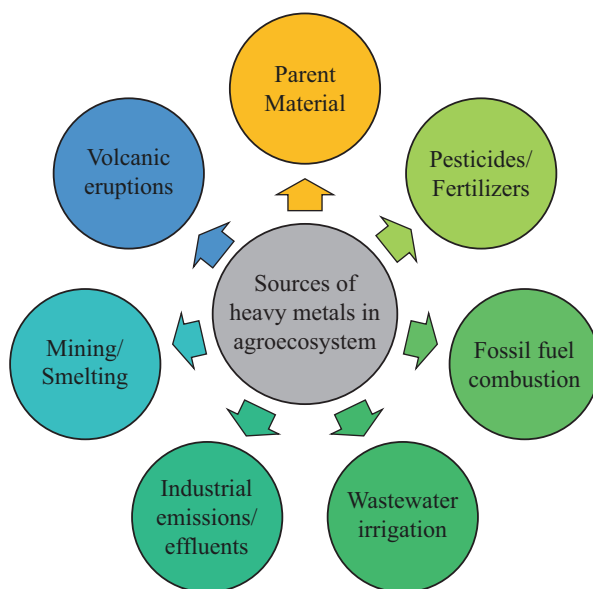


Fig. 1 Representation of natural and anthropogenic sources of heavy metal contamination in agroecosystems

for 0.28 to 3.84 mg ha⁻¹ of the yearly arsenic influx into paddy fields (Wang et al. 2018). Since these agrochemicals have high shelf life and mostly are non-biodegradable in nature, their uncontrolled and prolonged application has resulted in the contamination of agroecosystems around the world.

2.3 Atmospheric Deposition

Heavy metals can be released into the atmosphere through both natural and human-driven processes in the form of particles, vapours or primary oxides. The principal contributors to the atmospheric deposition of heavy metals include the burning of fossil fuels, vehicular emissions, mining activities, metal smelting and other industrial processes. Particles containing heavy metals enter biological cycles and food chains by dry and moist deposition, depositing in topsoil and surface water layers (Guo et al. 2016). The atmospheric deposition of metal elements that fall as dust and are settled on the above-ground tissues of plants during mining activities may directly or indirectly absorb metal elements from the air. Prior research has shown that various heavy metals, viz. As, Cd, Cu, Hg and Pb, are released into the atmosphere from coal combustion, Zn, emanates from vehicular emissions and mining and Cr, from smelting (Huang et al. 2014).

2.4 Industrial Activities

Different industrial processes, which contribute to heavy metals contamination, discharge industrial effluent, solid waste and dry and wet deposition into the environmental components. Fly ash discharge, smoke, the dumping of untreated or inadequately treated effluent and the disposal of solid waste in that area all make the agroecosystems close to industrial areas susceptible to trace metal pollution. The soil contamination with Hg comes primarily from coal-fired power stations. According to a study, foods including lettuce, amaranth, water spinach, cowpea and cereals cultivated in soils with high levels of Hg are detrimental for human health if consumed over an extended period of time (Li et al. 2018). Industries, for instance, tannery, chrome plating, ammunition factories, steel and alloys, are the major sources of chromium into the environment (Nagarajappa et al. 2017), whereas the majority of the Pb is released from various smelting, mining and acid battery manufacturing (Cwieląg-Drabek et al. 2020). However, Zn is used for agrochemical manufacturing such as herbicides (Zinc sulphate), while Ni is associated with petrochemical emissions. Mombo et al. (2016) reported foliar transfer and Pb accumulation in lettuce (9.8 mg kg⁻¹) in kitchen gardens situated near a lead recycling factory.

2.5 Solid Waste Disposal

The massive production of municipal solid waste (MSW) worldwide as a result of expanding urbanisation and population growth is posing significant challenges for its management (Gui et al. 2019). Incineration, landfills and open dumps situated in urban areas are significant metal-release pathways into the soil. Incineration is the easiest way of disposing of the solid waste; however, large volume of fly ash, containing organic and inorganic pollutants (heavy metals), is generated during incineration (Singh et al. 2023). Hence, fly ash from the MSW incineration process has a potential to pose threats to human and environmental health and yet is frequently disposed of in landfills (Lo and Liao 2007). The frequently found heavy metals in fly ash include Pb, Hg, Ni, Cr, Cu, Cd and Zn (Tang et al. 2015). The leaching of heavy metals from landfills to the agroecosystems present in the vicinity may act as a potential route of heavy metal transfer to soil and the crops and subsequently into the food chain. Ma et al. (2018) found that the agroecosystems in an MSW incinerator's vicinity in North China were found severely contaminated by potentially toxic heavy metals (As, Hg, Pb, Cd) representing the incineration process as the chief cause of heavy metal contamination.

2.6 Mining

Across the globe, there is a lot of concern about heavy metal contamination in mining areas where farming is also practised (Wu et al. 2023). Heavy metals are released into the environment as a result of mining operations, viz. ore concentration, and transportation processes, which can endanger human health, ecological integrity, habitat and food security. Significant soil pollution in villages close to artisanal gold mining operations was documented by Xiao et al. (2017). Hg and Cd were discovered to have polluted surface soils significantly. In addition, it was discovered that the region's vegetables and cereal grains had increased levels of Pb and Hg. Consumption of heavy metal-contaminated food crops grown in close proximity to an acidic mining drainage area was reported to be linked to serious health concerns for humans (Xiao et al. 2017).

3 Factors Affecting Heavy Metal Transfer and Mobility in Urban Agroecosystems

3.1 Soil Parameters

Soil pH and redox potential (Eh) play key role in heavy metal mobility in soil-plant system. Heavy metal solubility decreases at high pH levels and increases at low pH levels (Sheoran et al. 2016). This is a result of soil components with varied surface

charges and solute adsorption, such as silicate clays, organic compounds and Fe and Al oxides. The change in surface charge is what determines how pH affects adsorption (Bhargava et al. 2012). Low pH soils are more likely to have heavy metals migrate from the solid soil components into the soil solution. In alkaline soils, there is less of a risk of heavy metal leaching (Mn, Cu and Zn) and their bioavailability to agricultural plants, according to research conducted by Huang et al. (2014). The soil solution's propensity to receive or donate electrons is determined by the Eh of the soil (Sheoran et al. 2016). Dynamics of Eh conditions can directly or indirectly alter the dynamics of heavy metals, due to modifications in pH, dissolved organic carbon and the chemistry of Fe and Mn oxides (Husson 2013). Under anaerobic conditions, heavy metals associated with Fe/Mn oxides release because of the oxides' reduction-induced dissolution (Antoniadis et al. 2017). Change of Eh towards reducing conditions is usually accompanied with pH increase due to the consumption of protons required to reduce Mn and Fe (Rinklebe and Shaheen 2014).

A crucial component of the soil that has a significant role in maintaining the soil fertility is soil organic matter (SOM). SOM has the ability to retain heavy metals by complexation and adsorption; however an inner sphere and ion exchange reaction may also be occasionally involved (Evans 1989). Soil temperature mostly impacts the rate of organic matter transformation, which in turn affects how bioavailable heavy metals are in the soil. Temperature was found to have a significant impact on the bioavailability of metals in a study by Antoniadis and Alloway (2001); soil extracts and plant samples treated at 25 °C had higher amounts of Cd, Ni and Zn than those treated at 15 °C. The quick decomposition of organic matter at a greater temperature was the root of this. The soil texture reflects the particle size distribution of the soil and the content of fine particles such as oxides and clay. The heavy metal retention is higher in fine-textured soils than coarse-textured soils due to the presence of more pore spaces (Sheoran et al. 2010). Heavy metals in soil are dynamically mobilised and bioavailable due to cation exchange capacity (CEC). Compared to clay, which has stronger binding force, sand has a lower affinity for heavy metals and other cations, because clay has a large cation exchange capacity (Antoniadis et al. 2017). According to reports, clayey soils tend to have greater CEC values, which slow down the movement of cationic metals and reduce their availability in soils (Antoniadis and Golia 2015). While CEC only apprehends cations by description, anionic species are maintained at higher amounts in high-CEC soils than in low-CEC soils (Becquer et al. 2001). Additionally, it was observed that a rise in soil CEC could promote the precipitation and complexation of heavy metals in agricultural soils (Vega et al. 2010).

3.2 Interactions with Soil Microbiota

The release of organic acids, siderophores, enzymes, surfactants and other oxidation-reduction activities as well as biosorption makes microbial communities a powerful influencer in the soil that considerably alters the heavy metal mobility in the

agroecosystems (Luo et al. 2011). Bacterial species such as *Stenotrophomonas* spp., *Bacillus subtilis* and *Escherichia coli* are fast growing and possess functional groups on their surface that can adsorb or precipitate heavy metals in the soil (Wang et al. 2014). *Bacillus* spp. and *Paenibacillus* spp. are known to adsorb and precipitate the heavy metals in the rhizospheric zone owing to their surface functional groups (Radhakrishnan et al. 2017). The polysaccharide-rich surface in *Paenibacillus* helps in the immobilisation of heavy metals such as Pb, Cu, Co and Zn (Prado et al. 2005). The majority of bacteria and fungi found in plants makes siderophores, which are stable complexes of iron with metals such as Al, Cd, Cu, Ga, In, Pb and Zn (Schalk et al. 2011). Some researchers have reported that organic acids released by plant-allied microbes aid in the uptake of heavy metals like Cu, Zn and Cd as well as Pb by plant roots (Sheng et al. 2008). Mycorrhizal fungi have a large surface area, their cell wall components and intracellular compounds that confer them a solid capacity to immobilise the metals in the interior of plant roots heavy metals from soil (Meharg 2003).

3.3 Plant Parameters

Numerous plant characteristics affect the uptake of heavy metals, including crop type, leaf area, leaf inclination angle, branching pattern, smoothness of exposed sections, canopy type, stomata size, exposed surface area and rate of transpiration, to mention a few (Shahid et al. 2017). Due to their rapid development, increased translocation and increased transpiration rates, leafy greens acquire more heavy metals than other vegetables (Gupta et al. 2021). A plant with many thin roots has a higher capacity to accumulate heavy metals than one with thick roots because of the increased surface area that allows for improved precipitation and ion exchange processes at the root surface (Page and Feller 2015). The rhizosphere's ability to move heavy metals is also impacted by root exudates.

4 Heavy Metal Toxicity on Crop Plants

Due to their universal occurrence and severe and long-lasting detrimental effects on crop plants, their growth and developmental processes, toxic heavy metal contamination of urban agroecosystems has become a solemn environmental-ecological health concern. At the molecular level, heavy metals can result in membrane disintegration, mutations of genetic material, breakage in DNA strands, molecular cross-linkage, oxidative stress, damage from reactive oxygen species (ROS) and ultimately stunt the development of crops (Hossain et al. 2010).

The production of ROS enhances a series of effects of heavy metal toxicity in crop plants resulting in oxidative stress, leading to membrane disintegration, biomolecule deterioration, ion leakage, lipid peroxidation and, most important, DNA

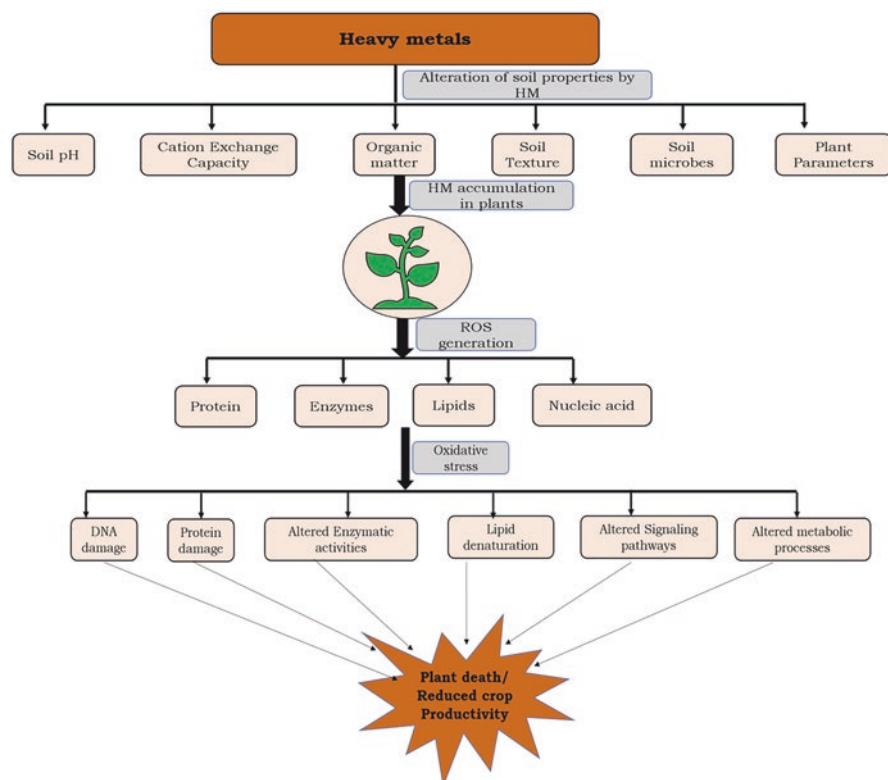


Fig. 2 Heavy metal-induced toxicity in crop plants

strand cleavage (Shahid et al. 2014) (Fig. 2). Heavy metals pose detrimental physiological impacts on several growth phases in crop plants, especially onset of germination and its frequency, seedling development and reproduction (Table 1). Ni in higher concentration is linked with seed germination inhibition and retardation in many crops owing to its toxic effects on biochemical activities affecting enzyme action. Additionally, it is reported that it interferes with the assimilation, uptake and mobilisation of food reserves (proteins, lipids and carbohydrates) in germinating seeds (Ashraf et al. 2011).

One of the key factors affecting photosynthesis that has a significant impact on CO₂ fixation, electron transport, photophosphorylation and enzyme action is Cr stress. On the other hand, when there is a high concentration of Pb in the soil, a number of plant species display abnormal morphology. High Ni concentrations in plant tissues indicate nutritional imbalance impairment and lead to dysfunctional cell membrane functioning. Delayed germination, leaf necrosis and wilting are signs of As phytotoxicity. These are followed by root discolouration and slowed shoot growth (Joardar et al. 2019). The mechanism of action leading to As toxicity includes, alteration in signaling pathways involved in membrane degradation, electrolyte leakage, and ROS generation (Smith et al. 2010).

Table 1 Heavy metal-induced phytotoxicity on morphological, physiological and reproductive traits of food crops

Heavy metals	Crops	Phytotoxic effects	References
Arsenic	<i>Vigna radiata</i>	Reduced shoot and root development; reduced biomass, total chlorophyll and carotenoid content; aberrant stomata caused by altered and delayed mitosis; cytoplasmic and microtubule assembly disintegration	Gupta and Bhatnagar (2015), Das and Sarkar (2018)
	<i>Oryza sativa</i>	Reduced growth and production, shorter roots and shoots, less dry biomass and elevated oxidative stress	Nath et al. (2014), Awasthi et al. (2017), Kalita et al. (2018)
	<i>Glycine max</i>	Reduced root absorption, metal uptake, stomatal conductance and osmotic potential in leaf, reduced chlorophyll content, cell death of root tips, structural damage to xylem and phloem tissues, lipid peroxidation, overall hampered growth, rise in ROS generation and DNA oxidation	Armendariz et al. (2017), Chandrakar et al. (2017), Veza et al. (2018)
	<i>Allium sativum</i>	Reduction in root, shoot and plant biomass	Torres et al. (2017)
	<i>Brassica juncea</i>	Inhibition of root length, decrease in number of lateral roots, decreased root length ratio and root mass ratio, overproduction of ROS species	Pandey et al. (2016)
	<i>Pisum sativum</i>	Reduced seed germination	Yoon et al. (2015)
	<i>Brassica juncea</i>	Reduced growth and generation of ROS species	Kanwar and Poonam (2015)
	<i>Vicia faba</i>	Reduced photosynthetic rate due to stomatal limitations	Austruy et al. (2013)
	<i>Helianthus annuus</i>	Reduced plumule length, radicle length and seedling vigour index	Imran et al. (2013)
Cadmium	<i>Zea mays</i>	Reduced fresh weight percentage and root length	Mallick et al. (2011)
	<i>Zea mays</i>	Reduced plant growth, antioxidants and enzymatic activities, altered photosynthetic pigments	Akinyemi et al. (2017), Anjum et al. (2015)
	<i>Cucumis sativus</i>	Decreased nutrient uptake and photosynthetic performance	Sun et al. (2017)
	<i>Solanum tuberosum</i>	Reduced shoot and root length and dry weight of potato	Hassan et al. (2016)
	<i>Brassica oleracea</i>	Reduced leaf area and dry weight of leaf stem and root	Jinadasa et al. (2016)
	<i>Capsicum annum</i>	Reduced root length, shoot area and root tips	Huang et al. (2015)

(continued)

Table 1 (continued)

Heavy metals	Crops	Phytotoxic effects	References
	<i>Glycine max</i>	Decreased net photosynthetic rate, stomatal conductance and total chlorophyll content	Xue et al. (2014)
	<i>Beta vulgaris</i>	Reduced number of PSII super complexes, increase in monomeric form of the light-harvesting complex II (LHCII) antennae	Basa et al. (2014)
	<i>Brassica napus</i>	Cracked cell walls, undeveloped mitochondria, plasmolysis and the absence of endoplasmic reticulum in cells of root tips	Ali et al. (2013)
	<i>Tomato</i>	Decrease in Zn, Mn and K concentration in aerial parts of plant	Bertoli et al. (2012)
	<i>Solanum tuberosum</i>	DNA damage in root cells of seedlings	Gichner et al. (2008)
Chromium	<i>Eruca sativa</i>	Decrease in root growth	Kamran et al. (2015)
	<i>Triticum aestivum</i>	Reduction in plant biomass	Ali et al. (2015)
	<i>Allium cepa</i>	Genotoxicity	Kumari et al. (2016)
	<i>Pisum sativum</i>	Reduction in chloroplast volume and auto fluorescence	Rodriguez et al. (2012)
	<i>Oryza sativa</i>	Reduction in uptake of N, P, K, Cu, Zn, Fe	Sundaramoorthy et al. (2010)
Copper	<i>Glycine max</i>	Alteration in chloroplast structure	Sanchez-Pardo et al. (2014)
	<i>Zea mays</i>	Decrease in seedling biomass, reduction in plant height and leaf area	Barbosa et al. (2013), Dresler et al. (2014)
	<i>Triticum aestivum</i>	Reduction in seed germination, alteration in DNA and RNA structure and content, decrease in shoot, root and leaf weight	Gang et al. (2013) Kumar et al. (2012)
	<i>Brassica juncea</i>	Decrease in photosynthetic pigments and leaf chlorosis	Feigl et al. (2015)
	<i>Cucumis sativus</i>	DNA damage/alteration, reduction in leaf number and area	Zheng et al. (2010), Işeri et al. (2011)
	<i>Vigna radiata</i>	Reduction in growth, dry matter and yield	Manivasagaperumal et al. (2011)
Lead	<i>Medicago sativa</i>	Lipid peroxidation leading to oxidative stress	Hattab et al. (2016)
	<i>Pisum sativum</i>	Damage to oxygen-evolving centre (OEC), inhibition of photosystem I and II	Rodriguez et al. (2015)
	<i>Zea mays</i>	Chlorophyll reduction in leaves, reduction in root and shoot macro- and micro-nutrient concentrations	Singh et al. (2015)

(continued)

Table 1 (continued)

Heavy metals	Crops	Phytotoxic effects	References
	<i>Sesbania grandiflora</i>	Disruption of several metabolic processes, which leads to the decrease in biomass production	Malar et al. (2014)
	<i>Oryza sativa</i>	Morphological alteration in guard cells, stomatal dysfunction	Srivastava et al. (2014)
	<i>Allium cepa</i>	DNA damage in root cells	Jiang et al. (2014)
	<i>Triticum aestivum</i>	Biomass reduction	Ramesar et al. (2014)
	<i>Luffa cylindrica</i>	Decrease in fresh weights of cotyledons, hypocotyls and radicals	Jiang et al. (2010)
Mercury	<i>Helianthus tuberosus</i>	Delayed seedling emergence; decrease in plant height, internode length and leaf area; enhanced lipid peroxidation; reduced chlorophyll content and plant biomass	Lv et al. (2018)
	<i>Jatropha curcas</i>	Decreased growth	Negrete et al. (2016)
	<i>Allium sativum</i>	Inhibition of seedling growth, rotting of roots	Zhao et al. (2013)
	<i>Arachis hypogaea</i>	Decrease in seed germination, chlorophyll content, protein content	Abraham and Damodharan (2012)
	<i>Oryza sativa</i>	Inhibition in germination percentage, shoot and root length, lower fresh and dry weight	Gautam et al. (2010)
	<i>Brassica oleracea</i>	Inhibition of seed germination, reduced coleoptile growth and root elongation	Ling et al. (2010)
Nickel	<i>Hordeum vulgare</i> L.	Reduced grain and straw yield; reduced plant height, number of ears and grain weight; altered micronutrient levels	Kumar et al. (2018)
	<i>Glycine max</i> L.	Reduced dry and fresh weight of roots and shoots	Reis et al. (2017)
	<i>Triticum aestivum</i> L.	Reduced plant height, shoot and root growth	Parlak (2016)
	<i>Coriandrum sativum</i>	Reduced seed germination frequency and seedling growth	Poozesh and Tagharobian (2014)
	<i>Arachis hypogaea</i>	Reduced root and shoot length, number of nodules, leaf area, dry weight of root and shoot and biochemical constituent pigments, sugars, starch, amino acids, protein and proline contents of leaves	Kaveriammal and Subramani (2015)
	<i>Brassica juncea</i>	Reduced growth and yield	Gopal and Nautiyal (2012)

Heavy metals are translocated from roots of the plants to edible portions (Wijeyaratne and Kumari 2021). Therefore, the high concentration of heavy metals in the soil causes several adverse effects on the growth and productivity of crop plants (Table 1).

5 Consequences on Human Health

Owing to consumption of contaminated crops and food items, heavy metals are transferred into the food chain (Fig. 3). Even at very low exposure levels, heavy metals have the potential to interfere with physiological processes after entering the human body and bonding with biomolecules like proteins and lipids. For instance, inorganic arsenic (iAs) has the potential to cause cancer (IARC 2012), and chronic exposure has been linked to diabetes, cardiovascular disease and skin lesions. Overexposure to Pb could have harmful consequences on the immunological, circulatory and nervous systems (Liu et al. 2018).

Complex relationships exist between methyl mercury and developmental and cognitive disorders (Liu et al. 2017). It has been recognised that Cd is a powerful endocrine disruptor that can cause cancers of the prostate and lung, as well as anaemia, renal tubular failure, pulmonary oedema and osteoporosis (Kabir et al. 2015). Acute and chronic toxic effects of heavy metals on human health have been summarised in Table 2.

Human health risk in the soil-dust fall-plant system was evaluated by Wang et al. in 2018. It was discovered that the target hazard quotient (THQ) of the Cr in corn kernels and the Cr, Pb and Cd in rice grains and vegetables was more than 1, indicating that Cr via consumption of corn kernels and the Cr, Pb and Cd via consumption

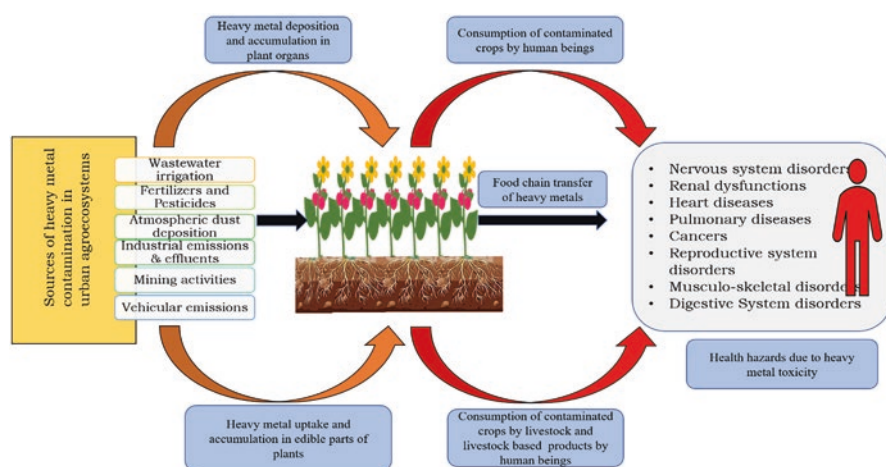


Fig. 3 Transfer of heavy metals in food chain and associated human health disorders

Table 2 Acute and chronic toxicity of heavy metals on human health

Heavy metal	Target organ/organ system	Clinical effects	References
Arsenic	Gastrointestinal, cardiovascular, pulmonary, renal, nervous, reproductive and integumentary system	Nausea, vomiting, headache, delirium, encephalopathy, seizures, respiratory failure, pulmonary oedema, encephalopathy, spontaneous abortion, low birth weight, blackfoot disease, ischaemic heart disease, cerebrovascular diseases, hypertension, dermatitis, diabetes mellitus, chronic bronchitis, liver damage, Bowen's disease	Chakraborti et al. (2016)
Cadmium	Skeletal system, reproductive system, renal organs	Spontaneous abortion, stillbirth; kidney damage; pregnancy-induced hypertension syndrome; proteinuria; bladder cancer, pancreatic cancer and lung cancer; osteoporosis; male infertility; prostate cancer; itai-itai disease	Hagino and Yoshioka (1961), Jaishankar et al. (2014)
Chromium	Respiratory system, integumentary system, renal organs, reproductive system	Dermatitis and skin ulcers, bronchial carcinomas, bronchitis, dyslipidaemia, increased skin sensitivity and dermatitis, decrease in sperm count, cardiovascular collapse, facial erythema, renal dysfunction	Neghab et al. (2015), Buters and Biedermann (2017), Tsai et al. (2017)
Lead	Nervous system, reproductive system, digestive system, respiratory system	Dementia, anaemia, premature birth, low birth weight, arthritis, allergies, autism, birth deformities, brain damage, dyslexia, paralysis, weight loss, Parkinson's disease, loss of neurons, muscular tremors, reduced spermatogenesis, suppressed testosterone formation, abnormal sperm size	Eibensteiner et al. (2005), Pfadenhauer et al. (2014), Rodrigues et al. (2016)
Mercury	Nervous system, digestive system, immune system, pulmonary and renal organs	Eye and skin corrosion; impaired memory; impairment of the kidneys, lungs, digestive, immune and nervous systems; asthma; dermatitis; autoimmunity diseases, central nervous system damage; Alzheimer's disease	de Vos et al. (2007), WHO (2017), Aaseth et al. (2018), Kaur et al. (2018)

of rice grains and vegetables would pose a serious health risk to local residents in the Tongling mining area. Roy and McDonald (2015) used six species of houseplants to analyse soil contaminated with a range of heavy metals, such as Pb, Zn, Cd and Cu. They then assessed the health risk for inhabitants of Spelter, USA, based on the concentration of heavy metals in the plant's edible tissues. It was found that carrots accumulated Cd (40 mg kg^{-1}) at concentrations that were 5, 8 and 12 times, respectively, higher than the maximum allowable limits for males, females and children. They came to the conclusion that carrot and lettuce may increase the risk of Zn and Cd poisoning in adults, children and women.

As per an estimate, the global health risks, such as heavy metals, result in 420–960 million cases of food-borne disease and 420,000 fatalities each year (WHO 2021). To limit the presence of heavy metal residues in foods, governments and organisations have set severe norms and restrictions (OJEU 2006; SAMR 2017).

6 Conclusion and Recommendations

Research information reported in this chapter allowed us to understand, expand our knowledge and establish the source distribution of heavy metals in the urban agroecosystems, mechanisms and factors affecting their distribution and mobility in the agroecosystems and their phytotoxic effects on the crop plants along with the possible human health risks allied with consumption of heavy metal-contaminated crops over an extended period of time. Source distribution studies have revealed that prolonged application of fertilisers, pesticides, wastewater irrigation, vehicular emissions and industrial/urban activities in the vicinity of urban agroecosystems has resulted in the accretion of heavy metals in soils and food crops. The mobility and ingression of heavy metals in agroecosystems was shown to be influenced by factors, including pH, organic matter, temperature, texture, cation exchange capacity, type of microorganisms and other coexisting metals. Additionally, it was shown that the phytotoxic effects of heavy metals not only lower crop output but also contaminate the food chain, posing serious health risks when such contaminated products are consumed over an extended period of time.

Due to the transfer of heavy metals through the food chain, contamination of agroecosystems has resulted in a decline in the health and nutritional condition of soil and crops as well as posed threats to human health. The hazards to human health linked with heavy metal transfer to agroecosystems could be lessened through research and regulatory actions.

The following recommendations should be made in regard to the future control of the potential increase in heavy metal pollution of soil and food crops and their potential abatement:

- Avoiding cultivation of food/forage crops in urban and peri-urban areas with a high concentration of industries, traffic or mining activities that could seriously contaminate crops with heavy metals
- Monitoring of the urban/industrial effluents for the presence of heavy metals on a regular basis and provision of effluent treatment within the urban/industrial premises to prevent the release of untreated wastewater into the environment
- Providing kits for fast and easy detection and monitoring of soil/water/effluents at low cost
- Collaborations between governments; stakeholders, such as experts, professionals and politicians; and industry can catalyse innovation and create incentives for cleaner production and remediation technologies

- Creating global governance standards with the goal of enhancing agroecosystem management and protection for long-term soil-food productivity
- Focus on exploration of emerging underlying links between heavy metal pollution and associated adverse health outcomes

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Polyaromatic Hydrocarbons (PAHs): Sources, Distribution, and Health Impacts in Aquatic Vertebrates



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1 Introduction

Polycyclic aromatic hydrocarbons (PAHs) are just one of the xenobiotics discharged into the nature as a consequence of the countless anthropogenic activities brought on by rapid urbanization and industrialization (Mojiri et al. 2019). Sixteen PAHs have been listed by the United States as priority pollutants for the twenty-first century (USEPA 2012). According to the International Agency for Research on Cancer, seven of them, including benz[a]anthracene, chrysene, benzo[a]pyrene (B(a)P), benzo[b]fluoranthene (B(b)F), benzo[k]fluoranthene (B(k)F), dibenz[a,h]anthracene (DbA), and indo[1,2,3-cd]pyrene, are extremely carcinogenic to humans (Li et al. 2018). A very recent study identified four PAHs (benzo[a]pyrene, benz[a]anthracene, benzo[b]fluoranthene, and chrysene) as primary markers of the existence of mutagenic/genotoxic PAHs, particularly in food (Montuori et al. 2022). Since PAHs are tenacious contaminants with a variety of biological hazards owing to their inherent characteristics, remediation has become a worldwide concern. PAHs are widespread, found in both terrestrial and aquatic habitats, as well as the atmosphere (Adeniji et al. 2019). Owing to their greater hydrophobic nature and low water solubility, it was discovered that PAH deposition rates accelerated in the aquatic

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ecosystem. The aquatic ecosystem turns as an utmost sink for PAHs because they are ultimately entering into aquatic body (Kuppusamy et al. 2017). PAH's introduction into watercourses increased significantly in the twentieth century due to rapid population growth and economic expansion. In aquatic ecosystem, generally three kinds of water PAH contamination are identified: uncontaminated (PAHs < 200 ng/g), mildly contaminated (PAHs, 200–600 ng/g), and substantially contaminated (PAHs > 1000 ng/g) (Wu et al. 2019).

About 80,000 tons of PAHs are thought to be released annually into aquatic environments on a global scale (Wright and Welbourn 2002). PAHs upon entry into waterways either might bind to dissolving organic material or persist in the water's free dissolved phase, or they might adsorb to dispersed particulate matter or silt (Qin et al. 2014). Their ecological fate and possible impacts on the aquatic biota are greatly influenced by interchangeable PAHs between sediment and water. This distribution is basically determined by partition coefficient of water-sediment (Yang et al. 2019) and is very dynamical. Resuspension is generally used to move sediment-bound PAHs into the water column; this process is also applicable with smaller molecular weight (Dong et al. 2016).

Human health and welfare, together with the well-being and health of other organisms worldwide (collectively called ecosystem health), are being negatively impacted by PAH contamination, either indirectly or directly (Patel et al. 2020). Numerous studies were carried out in different watercourses to appraise and measure the PAH concentrations in water/suspended matter and soil particles. Toxic consequences also were evaluated to confirm the negative impact on the ecosystem and the potential biotic threats for living creatures in the water bodies. Still there is dearth of data available. Accordingly, the present book chapter addressed the frequency of polycyclic compounds considering the effects of aromatic hydrocarbons on aquatic ecosystems to the dangers brought on by its contact with aquatic life. This book chapter's objective is to highlight the state of the art and most recent advancements in PAH status in aquatic ecosystem. This chapter also thoroughly discusses the attributes, sources, dosages, toxicology, and health impacts of PAHs and challenges encountered during PAH toxicity assessment.

2 Sources of PAHs in Aquatic Ecosystem

Polycyclic aromatic hydrocarbon (PAH) contamination in aquatic ecosystem is generally originated from two prime sources, namely, human-made sources and environmental sources (Mojiri et al. 2019). Natural forest fires, moorland fires, biological deterioration, and volcanic eruptions are examples of environmental and/or natural sources of PAH contamination in aquatic ecosystems, although the causes of lightning bolts are negligible or less relevant (Abdel-Shafy and Mansour 2016). The primary determinants of anthropogenic PAH contamination in aquatic ecosystem are generally of four different types, i.e., emissions from transportation, industry, households, and agriculture sources (Patel et al. 2020). Incomplete combustion is prime industrial origin of PAHs which includes garbage burning, the manufacturing

of iron/steel, manufacture of aluminum, cement, coal-tar pitch production, rubber tire making, bitumen industry manufacture, manufacturing of fungicides and insecticides, and exhaust from power plants and refineries (Gupte et al. 2016; Mojiri et al. 2019; Patel et al. 2020). Coal gasification, blast/oxygen furnaces, diesel engines, and gasoline-powered engines of big machinery are further industrial emission sources (Patel et al. 2020). Aircraft, trains, ships, and off-road heavy- and light-weight vehicles are only a few examples of the various vehicles whose vent is a producer of mobile emissions (Patel et al. 2020). The sources of domestic emissions are things like rubbish burning, coal burning, wood burning, and cooking. Other domestic heating methods include oil/gas burners, kerosene/wood stoves etc. (Gupte et al. 2016). Open feedstock burning and incineration of agricultural waste when done so in less-than-ideal combustion conditions are contributors of agricultural emissions (Patel et al. 2020). Rural areas with high PAH contamination are mostly affected by agricultural and residential sources; however, in an urban setting, PAH contamination originated from household, transport, and industrial sources. Figure 1 presents various sources of PAH contamination in aquatic ecosystem.

In addition, depending upon origin of their formation, the sources of PAH contamination in aquatic ecosystem is categorized into three groups, namely, pyrogenic (smaller than two to three rings), petrogenic (molecules with 4–6 rings and a greater size), and biogenic origin (Mojiri et al. 2019). Pyrogenetic PAHs are created when organic matter accidentally burns imperfectly at very extreme temperatures (350–1200 °C) with minimal or without oxygen present. Pyrogenic PAHs are also generated by some intentional pyrolysis processes, such as thermal conversion of coal into coal tar and coke and thermal disintegration of complicated hydrocarbons in petroleum. In addition to this, the phenomenon of pyrolysis, which takes place whenever organic compounds are exposed to extreme temperatures while being oxygenated or not, results in the formation of pyrogenic PAHs. The prime origin of pyrogenic PAHs is industrialized operations, the burning of wood/fossil fuels, wild-fire, and volcanic activity (Abdel-Shafy and Mansour 2016).

The most prevalent and widespread ambient PAHs, especially in freshwater environments, are pyrogenic PAHs (Li et al. 2019; Jesus et al. 2022). According to Mojiri et al. (2019) and Patel et al. (2020), metropolitan areas typically have greater quantities of pyrogenic PAHs. Owing to the storage, transportation, utilization, and leaking of crude oil or its derivatives, petrogenic PAHs are found in large quantities in petroleum and its byproducts (Patel et al. 2020). High molecular weight (HMW) PAHs are the predominant PAHs in pyrogenic sources, while low molecular weight (LMW) PAHs are the predominant PAHs in petrogenic sources (Marris et al. 2020). In particular, when petroleum hydrocarbons are extracted offshore, the PAHs of petrogenic origin are discharged into the ecosystem as petroleum-based products/crude oil. They are also discharged during the transportation, storing, and usage of petroleum and related byproducts (Jesus et al. 2022). Petrogenic PAHs molecules with 4–6 rings and a greater size has acute toxicity, significant mutagenic and carcinogenic potential.

Biogenic/diagenetic PAHs are produced by living things, namely, microbes, planktons, microalgae, and plants as well as when organic compounds undergo a slow biological conversion (Mojiri et al. 2019). In addition, the diagenetic PAHs



Fig. 1 Drivers of polycyclic aromatic hydrocarbon (PAH) contamination in aquatic ecosystem

autonomously develop from bioactive substrates like plant terpenes during the breakdown of organic substances, a phenomenon that frequently takes place in sedimentary conditions (Jesus et al. 2022).

3 Salient Features of PAHs

Organic contaminants, falling under PAH category, are made up of two or more aromatic carbon fusion rings and predominantly colorless, white, and pale yellow which are solid chemicals. The configurations of aromatic molecule space have

angular (e.g., dibenz[a,h]anthracene), clustered (e.g., pyrene), as well as linear (e.g., anthracene) rings (Abdel-Shafy and Mansour 2016). Except for naphthalene, which was historically utilized as “moth balls,” PAHs are hydrophobic and do not easily solubilize in water or vaporize into air. The strong adsorption efficiency, lower water solubility, and chemical resistance of all PAHs significantly increase their environmental persistence (Jesus et al. 2022). These compounds are hydrophobic in nature, chemically and thermodynamically very stable, highly resistant to biodegradation, have very low solubility in aqueous medium, have low vapor pressure, are soluble in an organic solvent, and have very high solubility in lipid vesicle. As PAHs have a very high affinity toward lipid vesicles, these compounds are absorbed by the mammalian gastrointestinal tract. Absorbed PAHs are immediately distributed among the various tissues and localized within the lipid body. Since most of the PAHs have carcinogenic or mutagenic properties, they may cause apoptosis and endocrine disruption, which overall suppresses the immune system (Wootton et al. 2003). The physicochemical attributes of 16 PAHs are shown in Fig. 2.

4 Classification and Types of PAHs

Polycyclic aromatic hydrocarbons (PAHs) are classified based on their molecular weight, structure, source, and process of formation. In terms of quantity of rings in compounds, more specifically molecular weight, PAHs are divided into two groups: high molecular weight (HMW) PAHs (e.g., pyrene, dibenz[a,h]anthracene, benzo[a]pyrene, chrysene), which have four or more aromatic rings, and low molecular weight (LMW) PAHs (e.g., naphthalene, acenaphthene, fluorene, phenanthrene (Phe)), which have two or three aromatic rings. HMW PAHs tend to be less water soluble, have lower Henry's constants and vapor pressures, and partition more readily into organic materials than LMW. As the molecular weight increases from low to high, these compounds are emitted into the environment as a gaseous form to a particulate form. Furthermore, PAHs are categorized into two classes based on their ring structures: alternant PAHs, which only have 6-carbon aromatic ring, and non-alternant PAHs, namely, fluorene, which fuse 6-carbon aromatic ring plus a second ring with less than six carbons (Gupte et al. 2016). The overall PAH structure has an aromatic character and very high π -electron density, which is behind the reason for its very high thermodynamic stability and reluctance to nucleophilic attack (Patel et al. 2020).

Depending upon sources, PAHs are divided into two categories, naturally emitted PAHs and anthropogenically originated PAHs (Mojiri et al. 2019). Based on formation, these compounds are also categorized into pyrogenic PAHs, petrogenic PAHs, digenetic PAHs, and biogenic PAHs. The formation process of the pyrogenic PAHs is called pyrolysis, generally occurring in 350–1200 °C temperature range, some of which may occur even higher than this temperature range. Petrogenic PAHs are formed at the time of crude oil maturation (Marris et al. 2020). Diagenetic PAHs

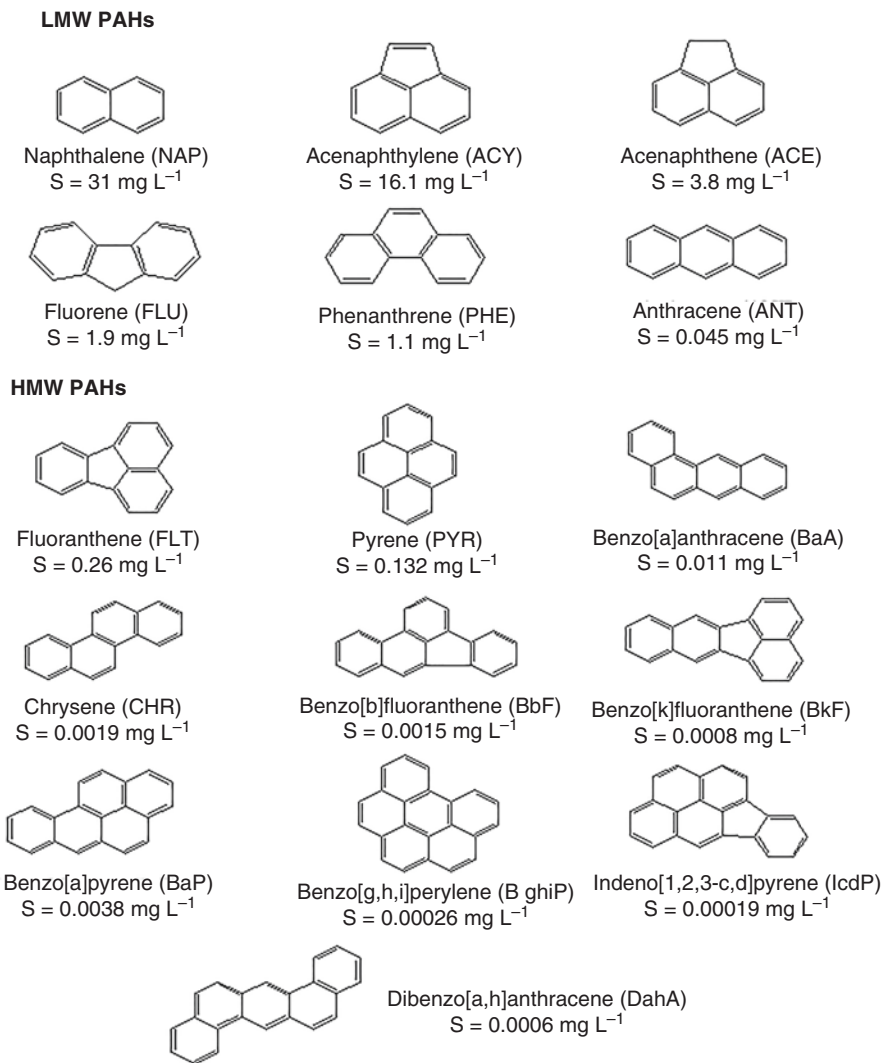


Fig. 2 Structural representation and water solubility at 25 °C of 16 priority PAHs according to the US Environmental Protection Agency. LMW low molecular weight, HMW high molecular weight

are generated spontaneously from biogenic precursors of terrestrial plants (e.g., terpenes) in an anoxic sedimentary environment, and the process is known as the diagenetic process (Bouloubassi and Salot 1993). There is a contradiction whether higher plants, unicellular algae, or bacteria can synthesize such PAHs or organisms just accumulate these PAHs instead of synthesis (Wilcke 2000). Climate conditions (e.g., temperature, wind, humidity, etc.) and types of fuel clouds play a dominant factor in the production of these natural PAHs.

5 Distribution of PAHs in Environmental Segments

Polycyclic aromatic hydrocarbons (PAHs) generated from diverse origins are dispersed all over the environment (soil, terrestrial, and aquatic environment) through air and water motion. The urban area or near-urban region has more PAH pollutant concentration than the rural sector due to industrialization. Emitted PAHs from different sources break up in the atmosphere either into vapor phase or solid phase and the solid phase sorbeting into particulate matter (PM) (Lin et al. 2018). It was noted that PAH compounds having high molecular weight or low vapor pressure favored sorbet into particulate (e.g., benzo[a]pyrene) while preferring vapor phase compounds having low molecular weight or high vapor pressure (e.g., naphthalene) (Kameda 2011). Dust particles in the air influence the stability of the particulate phase; thus in the summer season and tropical region, PAH distribution in the vapor phase is more dominant over the particulate phase; opposite trends are observed in the arctic region and winter season (Lai et al. 2011). PAHs are absorbed into PM depending on the humidity and suspended particles (e.g., dust particles, fly ash, soot, etc.). Emitted meteorological PAHs are distributed in diverse environmental compartments (earth soil surface, terrestrial and aquatic ecosystem) through dry deposition and wet deposition. In the aquatic ecosystem, in addition to the above process, these pollutants move by water, river stream, sewage system, ocean wave, and particularly industrial and urban effluents (Huang et al. 2019; Li et al. 2019).

5.1 Deposition of PAHs in Soil Surface

Polycyclic aromatic hydrocarbons (PAHs) are deposited on the earth's crust through the processes of dry deposition and wet deposition, as was previously indicated. Part of these soil surface aromatic pollutants are coming from neighboring sources (e.g., transport vehicles, industry, etc.), and the remaining portion came from far away through wind flow. The deposited PAHs over the earth's surface can be static or mobile depending upon the nature of adsorbate and sorbent. A bulk portion of the adsorbed PAHs are bound to the soil particles; thus, this pollutant mobility depends upon the size of the sorbent soil and its pore size (Cachada et al. 2012). Mobility became restricted if PAH could not pass through the sorbet soil pore size. To determine PAH concentration with significant accuracy in soil, combined solvent extraction and mass spectrometry (pseudo-multiple reaction mode gas chromatography (GC)/MS/MS) techniques were mostly used (Shang et al. 2014).

5.2 Sediments in Water

In addition to wet and dry deposition, the aquatic systems can be contaminated by different paths (river streams, sewage systems, ocean waves, and particularly industrial and urban effluents) as mentioned earlier. PAHs tend to be adsorbed by the

adsorbent and ultimately sediments at the bottom of the aquatic environment owing to their hydrophobic property and limited solubility in an aqueous medium. The concentration of a PAH pollutant in bulk water is determined by partition coefficient of sediment-water (K_{sw} , $\mu\text{g Kg}^{-1}/\mu\text{g L}^{-1}$) (Yang et al. 2019), also known as octanol-water partition coefficient (K_{ow}):

$$K_{sw} = \frac{C_s}{C_w} \quad (1)$$

where C_s indicates the PAH concentration in sediments ($\mu\text{g kg}^{-1}$) and C_w ($\mu\text{g L}^{-1}$) indicates the PAH concentration in bulk water above the sediment. Some physical parameters like total organic carbon (TOC) in sediment, particle size, and sediment surface are also modified by the equilibrium distribution. The partition coefficient of sediment-water (Table 1) indicates that much higher soluble in water as that of HMW. By contrast, HMW PAHs have more affinity to be adsorbed by the sediment particle or organic matter owing to their lower solubility and higher hydrophobicity (Lee et al. 2021). Many authors represent the sediment-water partition coefficient by the function of carbon content known as normalized partition coefficient of organic carbon (K_{oc}) (Gou et al. 2019; He et al. 2020) and in situ organic carbon

Table 1 Partition coefficient of PAHs in between sediment and water

PAH	Log $K_{sw} \pm \text{SD}^a$	Log K_{oc}^b	Log K_{oc}^c	ff ^c
NAP	2.601 ± 1.127	3.11	3.25	0.05
ACY	1.985 ± 1.949	3.51	3.78	0.10
ACE	2.638 ± 1.080	3.43	4.15	0.06
FLU	2.655 ± 1.160	3.70	3.58	0.04
PHE	2.860 ± 1.037	3.87	4.22	0.06
ANT	2.745 ± 1.337	3.40	4.00	0.06
FLT	3.585 ± 1.018	3.70	4.79	0.09
PYR	3.322 ± 1.076	4.66	3.88	0.08
BaA	3.132 ± 1.780	5.30	4.29	0.12
CHR	3.854 ± 1.300	5.43	4.05	0.18
B(b)F	3.883 ± 1.300	5.36	1.21	0.27
B(k)F	3.635 ± 1.572	5.57	1.18	0.23
B(a)P	4.131 ± 1.415	5.61	2.22	0.12
Bghip	4.097 ± 1.146	6.64	0.41	0.28
IcdP	4.284 ± 1.336	6.62	2.10	0.10
DahA	4.415 ± 1.338	6.90	0.83	0.05

For details of abbreviated names of different polyaromatic hydrocarbons, refer to Fig. 2

^aJesus et al. (2022)

^bGuo et al. (2009)

^cMontuori et al. (2022)

coefficient (K_{oc}) (Fakhradini et al. 2019; Zhao et al. 2020). In situ carbon coefficient is defined by the following equation:

$$K_{oc'} = \frac{K_d}{f_{oc}} \quad (2)$$

where f_{oc} indicates proportion of organic carbon (OC) resuspended in sediment particles. In an aquatic condition, the values of $\log K_{oc}$ and $\log K_{oc'}$ are the indicators of the PAHs equilibrium state (Zhao et al. 2020). PAHs are in a more adsorbed state than the water exchange state when the value of $\log K_{oc}$ is lower than $\log K_{oc'}$. The fugacity parameter determines the motion of PAHs from one region to another region, defined as (ff):

$$ff = \frac{K_{oc'}}{K_{oc'} + K_{oc}} \quad (3)$$

A lower value of fugacity ($ff < 0.3$) for a PAH suggested that sediment behaves as a sink for it and has a very high affinity toward sediment particles, and a high value of fugacity ($ff > 0.7$) describes the wavering toward water from sediment. A value between 0.3 and 0.7 denotes that PAH remains in equilibria between water and sediment. Montuori et al. (2022) reported that in Sele River, Italy, most of the PAHs tend to be adsorbed by the sediment particle from water except B(b)F, B(k)F, and IcdP (Table 1).

The aromatic pollutants in the aqueous phase especially at the top of the aqueous layer are degraded by photooxidation in the presence of intense radiation, higher oxygen concentration, and temperature (Xiao and Shao 2017). In the aqueous phase, LMW PAHs are further degraded by specific algae, fungi, and bacteria (e.g., NAP, ACY, etc.), but HMW PAHs that are in sediment mainly remain unaffected (e.g., B(a)P, DahA, etc.) by these organisms. Although water PAH value depends upon the sediment-water partition coefficient (K_{sw}), many dynamic processes (water flow, bioturbation) and the timescale of these processes (Dong et al. 2016) alter the equilibrium distribution. Frequent PAH resuspension phenomenon elevated the risk to aquatic species by direct contamination with these pollutants mainly those living species at the water-sediment boundary (Dong et al. 2016).

Very low solubility in aqueous media, negligible photobleaching phenomenon, and an anoxic environment within sediments increase the PAH potential flux. Adsorbed PAHs are observed within the pore water of sediment particles; thus, concentrations of these pollutants are significantly more in pore water in comparison to bulk water in the aquatic environments. The adsorbed PAHs are not entirely insoluble and immobilized, especially the low molecular weight pollutants. Reduced polarity in pore water elevated the dissolved PAH concentration and diffused across the sediments. Consequently, the bioavailability and mobility of PAHs increase within sediments (Dong et al. 2012) and lead to a high threat to the benthic community (Ha et al. 2019).

Table 2 Total PAH concentration in the river experimentally obtained from different locations of the world (N represents PAH quantity, i.e., sampling size)

	Location	N	WDP (ng/L)	SPM (ng/L)	Sediment (ng/g)
River water ^{a, b, c}	Daliao River Estuary, China	16	139–1718	227–1405	–
	Yellow River Delta, China	16	65–335	66–675	–
	Yellow River Beach, China	16	144–2366	507–10,510	–
	Susquehanna River, USA	36	17–150	–	–
	Gaoping River, Taiwan, China	16	10–9400		
	Weihe River, China	16	351–2321	3557–147,907	362–15,667
	Sarno River Estimate, Italy	16	124–2321	6–779	
	Sele River, Italy	16	10.1–567.2	121.2–654.4	331.8–872.0
	Tianjin River, China	16		938–64,200	787–1,943,000
	Athabasca River, Canada	16	–	–	10–34,700
Soltan Abad River, Iran	16	–	–	246–442	

WDP water dissolved phase, SPM suspended particulate matter

^aChen et al. (2015)

^bKafilzadeh (2015)

^cMontuori et al. (2022)

Industry and cities around the world are primarily developed near the riverside. Thus, rivers are considered as a prime object for discharge of sewage sludge, industrial/domestic wastes, degraded waste materials containing ample loads of PAHs, heavy metals, petroleum hydrocarbon, etc. River water containing a high level of PAHs and heavy metals significantly damages the river ecosystem as well as public health via food chain. So, monitoring and maintaining levels of PAHs and heavy metal concentration in river ecosystems are essential all over the world. Table 2 reported the total PAH values in water-dissolved phase (WDP), suspended particulate matter (SPM), and sediment experimentally from different rivers around the globe. The reported value of total PAH level in SPM in Weihe River, China, and sediment in Tianjin River, China, was highest than the world's major rivers even Sarno River, Italy, which is widely recognized as “the most polluted river in Europe” (Montuori and Triassi 2012). Susquehanna River in the United States had the lowest overall PAH concentration in WDP out of all the rivers listed in Table 2. Rivers have very high concentrations of total PAHs in SPM and WDP, but relatively lower sediment concentrations suggested that pollution might be due to the fresh addition of pollutants.

Scientific community has imposed their attention to evaluate the levels of PAH concentration in marine environments as these compounds have very high detrimental effects on marine organisms (Nasher et al. 2013). Table 3 reported the total PAH concentration at different coastal regions around the world. Pollutant contamination in the coastal region partly arises from far away by ocean waves, river water, and other part affected by nearby land site activities. Gerlache Inlet Sea, Antarctica,

Table 3 Total PAH levels (ng/L) in subsurface marine water around the various locations of the earth (*N* represents the number of PAHs included during the study)

	Location	<i>N</i>	Subsurface concentration (ng/L)	Sediment concentration (ng/gm)
Subsurface water from various marine sites around the world ^a	Chesapeake Bay, USA	17	20–66	
	Baltic Sea	14	300–594	3.96–22,100
	Alexandria coast, Egypt	–	13–120	–
	Daya Bay, China	16	4228–29,320	115–1134
	Northern Spanish	25	190–28,800	–
	Saronikos Gulf (Greece)	17	425–459	–
	Gerlache Inlet Sea (Antarctica)	–	5–9	–
	Deep Bay, South China	15	24.7–69	353.8–128.1
	Mumbai Harbour Line, India	15	866–46,740	17–134,134
	Kitimat harbor, Canada	15	–	310–52,800
	Northern Adriatic Sea	22	–	30–600
	Cienfuegos Bay, Cuba	–	–	180–5500

^aDhananjayan et al. (2012)

subsurface water has the lowest level of PAH concentration (~ 5–9 ng/L) as there is no nearby human civilization. On the other hand, the Mumbai Harbour Line, India, marine subsurface water has the highest level of contamination (~ 860–46,740 ng/L), which is significantly higher than the water quality recommended by various statutory agencies (Zhu et al. 2015). Chesapeake Bay, USA, and Alexandria coast, Egypt, coastal area subsurface seawater has the least contamination with PAHs close to the human civilization (Table 3).

6 Impact of PAHs on Aquatic Invertebrates

6.1 Impact on Fishes

Despite the rarity of large-scale fish deaths caused by the contamination of freshwater or saline watercourses with PAH pollutants, there is ample data to conclude that such substances have detrimental effects on fish's survival. PAH metabolism in fish has resulted in the generation of reactive chemical species with the potentiality to

attach covalently with proteins and deoxyribonucleic acid (DNA), similar toward the majority of research examining the PAH metabolism in vertebrate. Fish might suffer major health implications from toxins like PAH because of the extremely porous structure of their gills and skin. Bussolaro et al. (2019) observed no cytotoxic effect in the gill and intestine of rainbow trout (*Oncorhynchus mykiss*) exposed to 3-nitrobenzanthrone (3-NBA) and B(a)P and no DNA alteration in gill epithelial cells for both the exposures, but in intestinal cells, there was increasing DNA damage under 3-NBA exposure. Ezenwaji et al. (2013) recorded the liver enzyme activity in *Clarias gariepinus* to diesel exposure; the mean liver alanine aminotransferase (ALT) activity was reduced in control in comparison to treatment, but a totally opposite phenomenon was observed for liver aspartate aminotransferase (AST) activity. Kim et al. (2008) noticed the reduction of RBC count, Hb concentration, and hematocrit value and increasing value of AST activities and no significant changes in ALT activities, total protein, and calcium in B(a)P-exposed rockfish, *Sebastes schlegelii*. Santana et al. (2018) observed significantly increased activities of glutathione S-transferase (GST), ethoxyresorufin-o-deethylase (EROD), superoxide dismutase (SOD), glutathione peroxidase (GPx), lipid peroxide (LPO), and oxidized glutathione (GSSG) under PAH-exposed fish, but catalase (CAT), glutathione reductase (GR) activity, and reduced glutathione (GSH) levels remain unaltered. Nunoo et al. (2019) recorded the nutritional profile and PAH level in three marine fish species such as the yellow fin tuna, *Thunnus albacares*; barracuda, *Sphyraena sphyraena*; and the common white grouper, *Epinephelus aeneus*, which were smoked with a fuel wood smoker (Chorkor smoker) and a gas smoker (Abuesi Gas Fish Smoker). They observed that nutritional profiles such as total carbohydrate, protein, fat, moisture and the ash contents and PAH concentration were different and also observed that good-quality smoked fish was produced by the Abuesi Gas Fish Smoker than the Chorkor smoker.

Sunmonu et al. (2009) recorded the increasing gamma-glutamyl transferase (GGT), ALT, and AST levels in the stomach and liver of *Heterobranchus bidorsalis*, exposed to anthracene, and also postulated that GGT, AST, and ALT activities could be considered as biomarkers for anthracene exposure in *H. bidorsalis*. Tiwo et al. (2019) reported the effects in *Cyprinus carpio* and *Clarias gariepinus* on the nutritional value and PAHs after that showed the decreased amount of protein content and lipid content. Ekere et al. (2019) observed the PAH concentration, such as naphthalene, phenanthrene, anthracene, B(b)F, B(k)F, and B(a)P, in catfish and tilapias. Biuki et al. (2012) recorded the hepatocytic necrosis, blood sinusoid dilation, vacuolations, lipidosis, and bile stagnation in the liver of *Chanos chanos* exposed to PAHs. Vasanth et al. (2012) noticed the increasing lactate dehydrogenase (LDH), ALT, and AST levels in the liver compared with the kidney, gill, and muscle of *Labeo rohita* under anthracene exposure. Phalen et al. (2014) demonstrated that no significant changes occurred in erythrocyte/thrombocyte level of every tissue and showed decreased T cells, B cells, and myeloid cells in the blood, head kidney, or spleen of *Oncorhynchus mykiss* due to B(a)P exposure. Karami et al. (2016) strongly established that the increasing mRNA level, plasma ALT activity, LDH levels, lactate and glucose content, glycogen content, and no change occurred in triploid in

Clarias gariepinus exposed to waterborne phenanthrene. Nyarko et al. (2011) measured PAH concentration in two fishes, *Sardinella maderensis* and *Galeoides decadactylus*, by using gas chromatography (GC) and recorded that the ratio of high molecular weight PAHs/low molecular weight PAHs was <1 which indicated the pyrogenic and anthropogenic origin of PAHs in Ghanaian coastal environment. Vehniäinen et al. (2019) recorded that retina has more adverse effects as action potentials (APs) than phenanthrene in *O. mykiss*; and both exposures affected the cardiac function of rainbow trout, and Na⁺ and Ca⁺ also increased. Jafarabadi et al. (2018) observed higher PAH concentration in the liver than muscle based on lipid content of *Scomberomorus guttatus*, *Lutjanus argentimaculatus*, and *L. microdon* from the Persian Gulf. Abdel-Shafy and Mansour (2016) reported PAH accumulation, and phase I and II biotransformation enzymes are highly effective in the livers and gills than muscle.

Manju et al. (2008) noticed the higher damage in the brain than the liver tissue in *Anabas testudineus* in the presence of thiobarbituric acid reactive substance (TBARS) content exposed to salicylcucumin. It also revealed the decreasing level of CAT, GSH, and GPx and increasing level of the superoxide dismutase (SOD) activity but no change in glutathione reductase (GR). Patnaik et al. (2016) observed the decreasing value of protein, glycogen, acetylcholine esterase activity, adenosine triphosphate, and brain acetyl cholinesterase (AChE) activity in *Anabas testudineus* exposed through naphthalene. They also revealed that the blood cells of *Anabas testudineus* showed aggregation and chain formation for naphthalene toxicity. Ahmad et al. (2003) reported the increasing total cell count (TCC) value in phagocytes apart from the head kidney, gill, and peritoneum during short-term exposure to naphthalene in *Anguilla anguilla*, but the long-term exposure period showed decreased value of TCC and respiratory burst activity (RBA), increasing peroxidative damage, and persisted concentration in the gill and kidney and lipid peroxidation (LPO) activity. Hossain et al. (2014) measured the naphthalene concentration in some fish species like bata, puti, baim, chapilla, prawn, taki, and kakila and showed the permissible limit is under recommended value according to the US Environmental Protection Agency (EPA) and European Union. Among these fishes, bata fish consumed highest amount of naphthalene.

According to Dey et al. (2019), anthracene exposure on *Anabas testudineus* caused increasing count of white blood cells (WBC), lymphocyte count, mean corpuscular hemoglobin (MCH), mean corpuscular hemoglobin concentration (MCHC), and mean corpuscular volume (MCV) and decreasing content of hemoglobin, packed cell volume (PCV), red blood cell (RBC), and platelet (PLT). They also reported the increment of PRO, CHOLEST, triglyceride (Trig), and ALB and reduction of GLU, low-density lipoprotein (LDL), high-density lipoprotein (HDL), glutamic pyruvic transmission (GPT), and Ca level. In another study, Dey and Ghosh (2019) reported the enhancing activity of ALP and GPT but decreasing value of PRO and ALB due to anthracene exposure on *Anabas testudineus*. Kim and Kim (2016) recorded increasing DNA damage along with EROD and vitellogenin (VTG) levels in *Cyprinus carpio* which was exposed by dibenz[a,h]anthracene (DbA) and acetyl cholinesterase (AChE). Kim et al. (2008) observed the decreasing of red

blood cell (RBC) count, hemoglobin, and hematocrit but increasing of AST activities and LDH concentration, and no effect was found in total PRO, ALT activities, and magnesium or calcium in rockfish, *Sebastes schlegelii*, due to B(a)P.

Haque et al. (2018) observed decreasing value of WBC, lysozyme, and total protein concentration and increasing cortisol and activities of AST, ALT, ALP, CAT, SOD, and GSH content and also showed insignificant difference in RBC count, albumin, Hb, and glucose content compared with control in juvenile *Paralichthys olivaceus* due to waterborne phenanthrene (Phe). Advaiti et al. (2013) observed the higher anthracene accumulation in the gill, kidney, and liver tissue in *Rasbora daniconius*, in comparison to naphthalene and the higher accumulation of naphthalene in intestinal tissue. It also revealed the maximum toxicity level in intestine tissue due to bioconcentration factors (BCF) for naphthalene exposure, but, on the other hand, for anthracene exposure, *Rasbora daniconius* showed maximum toxicity in the liver tissue. Pampanin and Sydnes (2013) and Wickliffe et al. (2014) revealed that the PAHs are omnipresent pollutants in marine ecosystem coming from different origins like oil-based activities through waste production and leakage, natural oil seeps, fossil fuel burning, smelter industries, marine transportation, and even open environment runoff. Collier et al. (2013), Diamante et al. (2017), and Pampanin (2017) revealed that PAHs have carcinogenic potential to induce contrary effects, namely, cancer, abnormalities in development and respiratory shortcomings, neoplastic disease, and blood.

According to Fanali et al. (2018), B(a)P has potentiality to affect the life cycle of amphibians which has genotoxic effect. It noted the increasing micronucleus frequency and mast cell density, decreased melanin area, and no significant change in leukocyte percentage and little changes in lymphocytes, neutrophils, and eosinophil in *Physalaemus cuvieri* and *Leptodactylus fuscus*. Rahmanpour et al. (2014) assessed the PAH concentration in fish liver of *Alepes djedaba*, carnivore; *Aurigequula fasciata*, omnivore; and *Liza abu* and *Sardinella albella*, phytoplanktivores, obtained from Persian Gulf area and showed that the accumulation of pyrene, acenaphthylene, and naphthalene were high in all fish species than the other constituents of PAHs. It was also recorded that the accumulation of PAH concentration was high in males than the females. In another study Al-Saleh and Al-Doush (2002) reported that B(a)P, naphthalene, and pyrene were accumulated significantly in fish species at the Persian Gulf. Disner et al. (2017) observed no mortality in *Astyanax lacustris* and *Geophagus brasiliensis* when exposed with naphthalene and also showed no significant difference in the liver of *A. lacustris* but increasing GST enzyme activity, and in *G. brasiliensis*, there was no deference in liver tissue and gill cells, but showed increasing DNA damage and GST activity.

Disner et al. (2017) also noticed that naphthalene can be accumulated and absorbed in the gall bladder and highest PAH accumulation was found in *A. lacustris*, whereas in *G. brasiliensis* it was not significant, and it was also revealed that the concentration of naphthalene was not genotoxic for fish sample, whereas, it can potentially be accumulated into the fish body. Van Anholt et al. (2003) postulated that GST activity endorses detoxification and excretion of xenobiotics and attributes to defensive adaptation mechanism against the organic compound and their

metabolites. Shirdel et al. (2016) demonstrated the increasing ALP, AST level, glucose level, and triglyceride and decreasing ALT level, cholesterol level, and albumin in *Cyprinus carpio* due to pyrene exposure. Shirdel et al. (2016) also showed the decreasing thyroid hormones but not affected plasma potassium, calcium, and sodium level. Datta et al. (2007) and Kuzminova et al. (2014) also recorded the decreasing ALT level and hepatocyte death in fish due to higher concentration of pyrene.

Akpoghelie (2018) analyzed the individual PAH concentration on smoked fish and Nigerian suya meat and showed higher PAH value in smoked catfish and suya meat than the smoked fish soaked in boiled water. Akpoghelie (2018) also observed that the mean highest levels of individual PAH consumption by smoked catfish are phenanthrene, naphthalene, fluorene, fluoranthene, and pyrene. Ayoola and Alajabo (2012) reported severe congestion and cytoplasmic vacuolations because of glycolysis phenomenon which ultimately caused mitochondrial and microsomal dysfunction and inflammation in the kidney; the gill showed the highest damages including mild and severe congestion and calcification, and no significant effect was shown in muscle tissues of blackchin tilapia (*Sarotherodon melanotheron*) exposed with engine oil.

Shi et al. (2005) strongly established that craniofacial skeletal deformities and spinal curvature were found in *Sebastiscus marmoratus*, exposed by pyrene. Jifa et al. (2005) noticed the increasing GPx, SOD, and CAT in Japanese seabass (*Lateolabrax japonicus*) exposed to B(a)P. Ahmad et al. (2004) reported the increasing GST level found in the liver during short-term exposure but decreasing GST level in long-term exposure in *A. anguilla* fish in the presence of naphthalene exposure. Pathiratne and Hemachandra (2010) also reported induced GST level in *O. niloticus* due to fluoranthene and chrysene. Wahidulla and Rajamanickam (2009) examined co-exposure (phenanthrene and nitrite) in *Oreochromis mossambicus* by using electrospray ionization tandem mass spectrometric (ESI-MS/MS) which reported the formation of PAH-DNA adducts in fish, and several adducts were available in the untreated bile samples of that fish. Wahidulla and Rajamanickam (2009) also noticed that mass spectrometry (MS/MS) is very useful for identification and classification of different types of phenanthrene or derivatives of DNA adducts in complex fish bile mixture as well as modified and normal guanosine also available in bile samples which were co-exposed with phenanthrene and nitrite. Oliva et al. (2010) recorded the substantial difference present between CAT, LPO, and glutathione reductase (GR) biomarkers and control fish, and all biomarkers are sensitive toward chronic pollution. Further, GST, CAT, and GPx represent the correlations with liver PAHs and sediments in *Solea senegalensis*. Sturve et al. (2006) noticed increased CAT level in Atlantic North Sea oil-exposed *Gadus morhua*. According to Vieira et al. (2008), although the toxicity and subsequent remedial mechanism of PAHs were not understood clearly, PAH impacts on antioxidant enzymes were significant on a time- and dose-dependent manner. Vieira et al. (2008) also found a statistical variation between control and anthracene-exposed fish (*Pomatoschistus microps*), and anthracene helped to generate O_2 , which may transform into H_2O_2 through catalytic activity.

Kerambrun et al. (2012) demonstrated necrosis, lipofuscin, leukocyte abnormalities, blood accumulation, and increasing macrophage numbers due to PAHs metabolized in the liver. Zhou et al. (2011) also demonstrated inflammation and hepatic damage in the liver due to PAH exposure. Horng et al. (2010) reported the disruption in the endocrine system and effects in reproductive function and growth of fish due to PAH exposure. Dessouki et al. (2013) strongly established lamellae mild congestion, moderate atrophy, and epithelial lining shortening in *Tilapia zillii* exposed with crude oil. Incardona et al. (2004) reported the carcinogenicity and immunotoxicity of PAH toxicity in teleost fish as hallmarks, and each PAH compound has specific and distinct developmental effects on early stage of fish after exposure. Dupuy et al. (2014) reported DNA damage, expression of detoxification, and deregulation of the immune system under short-term exposure to PAHs in European flounder juveniles. Xing et al. (2010) recorded the decreasing acetylcholine esterase (AChE) activity and carboxylesterase level in the muscle and brain of *Cyprinus carpio* exposed to chlorpyrifos. Jee et al. (2006) observed increasing ALP activity for cell necrosis in the liver due to 7,12-dimethylbenz(a)anthracene exposure on *Sebastes schlegelii*. Pampanin et al. (2016) demonstrate that higher value of CAT activity, GST activity, and EROD activities were shown in Atlantic cod (*Gadus morhua*) exposed to PAHs.

6.2 Impact on Birds

Both aquatic and land-based bird species are expected to have different lifelong sensitivity levels and types to hydrocarbons. Land-based birds might come into contact with PAH by ambient deposit or dietary food, while aquatic birds, particularly those that live in the water, may do so through major petrochemical spillage episodes, ambient exposure, and feeding. In contrast to several aquatic bird species that are either wingless, discovered in specialized separated surroundings, or in sizable nesting clusters that rely primarily on conventional resettlement and feeding lifestyles, being a terrestrial-dwelling bird species has the advantage of exposing individuals to PAH xenobiotic compounds in a minimally harmful way by allowing them to resettle apart from polluted sites with convenience.

6.3 Impact on Amphibians

Amphibians, particularly toads, are frequently employed as indicator species to assess the state of conservation for wide environmental niche. The majority of frogs start out in stagnate watercourses as embryos and undergo metamorphosis as they grow. The transformation of frog embryos into toads, which ultimately become frogs, serves as a simplification of this process. Environmental pollutants, including

certain PAH xenobiotic compounds, have indeed been utilized as markers for changes in normal metamorphosis timeframes and performance outcomes (such as morphological mutation).

6.4 Impact on Human

Limited research on xenobiotics in urban ecosystems affecting the human health have been conducted because of the potentiality of these xenobiotic compounds to induce harmful health effects (Dhuldhaj et al. 2022). These xenobiotic compounds are exposed to humans by bioaccumulation of hydrophobic organic xenobiotics that results in its effectiveness can become lipid-rich structures like cell membranes compromise. If the xenobiotic concentration is high, then narcosis happens by impaired function of membrane protein or loss of membrane polarization. Generally, normal method of xenobiotic uptake within the human body is primarily through food chain. Xenobiotic health as well as ecological risks could be evaluated by utilizing different mitigation techniques, thus easing decision-making and risk mitigation activities. This might, in turn, improve the performance of regulators or public health managers to stop the xenobiotic practice globally.

7 Mitigation Strategies

There are many different approaches used for mitigation; some concentrate too extensively on raising consumer and normal citizen knowledge; on the other hand, some involve more loosely organized industry, public environmental administration, nongovernmental organizations (NGOs), and other politicians. Achievements like withdrawal and nitro-masks polycyclic masks are focused on more “expert level” with lower consumer engagement whenever the Sweden country campaign is about eco-labels, medications, washing powder, and others are real examples of regular consumer impact. So, efficacy of mitigating technique can be extremely high involvement in local dependent like national or even regional. For example, high involvement in local dependent likes national or even regional based initiatives like “The Yellow Fish” project, launched by Scottish Environmental Protection Agency and Scottish Water was aimed at cooperating with school children and local normal communities for awareness regarding safe discharge of oil residue and wastes. Finally, this abovementioned approach has been carried out successfully all over Scotland. Go Green is increasingly recognized as one of the most powerful tools and produces more impact on the market and eco-friendly products. Local organization frequently purchases high volume of different products like polybrominated diphenyl ethers (PBDEs) for office purpose, PAHs or nonylphenol in fabrics, that can be a powerful catalyst for changing the perception.

8 Conclusions and Future Perspectives

The present book chapter demonstrated that PAHs are significant pollutants in surface aquatic habitats, and the majority of them exists at comparable to or even above greater than those of the analogous PAHs. PAHs have a propensity to concentrate in aquatic animals; they pose a substantial environmental risk to surface aquatic habitats. Considering this, substantial research on toxicity of specific PAHs to various aquatic invertebrates, especially fish species, have been well-documented. Apart from this the PAH distribution in water and soils of aquatic system documented in this book chapter cannot be overlooked. Anthropogenic activities are directly correlated with PAH distribution in aquatic environment. Accordingly, for achieving the sustainability, it is recommended that PAH levels in aquatic system be continuously monitored and controlled.

Primary obstacles will need to be encountered during study of PAH distribution and toxicity assessment to aquatic invertebrates. The foremost, and perhaps most pressing, is related to the revision of PAH list of priority concern. The said list is utilized extensively in toxicity assessment, but latest evidence has demonstrated that non-included PAHs are potentially more toxic than USEPA PAH priority list at present, which, coupled with their widespread occurrence and higher chemical stability, puts a lot of concern regarding their adverse impacts on the environment. Secondly, more research on benthic toxicity in relation to PAHs is urgently required to close the research gap of aquatic invertebrate toxicity. Thirdly, the PAH toxicity to aquatic invertebrates should not be assessed individually as it is adversely impacted by stressors like climate impact, presence of other compounds, etc. Finally, for an ecologically meaningful evaluation of ecological dangers presented by these chemicals, the PAH toxicity evaluation should consider long-term impacts or chronic toxicity, instead of just merely immediate or short-term impacts. Accordingly, people's understanding of the ecosystem and the use of xenobiotic substances needs to be raised in order to protect the environment from PAH pollution in aquatic ecosystem. Further, shift toward cleaner options like reduced use of fossil fuels and use of alternate energy options should be adopted in order to slow down the entry of petrogenic or pyrogenic PAHs for achieving the Sustainable Developmental Goals (SDGs).

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The Effects of Xenobiotics on Soil and Human Health



Ruchi Urana, Jyoti Jaglan, and Bhagwan Narayan Rekadwad

1 Introduction

Globalization, urbanization, and industrialization have both positive and negative perspectives on the living world (Gu 2019). They act as a connective between the countries and the technical process, which leads to the centralization of the market. Despite that, they positively affect the economy and market but also harm the environment (Soucek 2011; Strobierski 2021). In this techno era, many compounds are used to make life easy like pentachlorophenol (PCP), dyes, pesticides, antibiotics, etc. The xenobiotics term has been taken from the Greek word “xenos” which means strange or foreign, whereas “bio” means life. The chemical compounds have unusual characteristics or are present in the environment at a high concentration, so these compounds are known as xenobiotics (Fetzner 2002). Some characteristics that are shown by xenobiotics are inherently very stable (Kanaya et al. 2019). They are not recognized as substrates by degenerating organisms, poorly soluble or insoluble in water (Liu et al. 2015). They are very poisonous. This means that the compounds produced are highly toxic. The molecular weight of xenobiotic compounds is very high, making them less likely to enter microbial cells (Zheng et al. 2012). These compounds are resistant to biodegradation processes and have branched linear chains containing halogens instead of hydrogen (Chan and Chan 2012).

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Other compounds exist, including nitrates, amines, etc.; chemicals cannot promote the formation of degradative enzymes (Darnerud 2003). They do not cooperate with other chemicals. Simply these are the compounds exhibiting normal chemical structure and characteristics (Chen et al. 2022). In other words, we can also consider unusual or high concentrations of any substance, i.e., xenobiotics. The presence of antibiotics or “magic bullets” inside the human body is also an example of xenobiotics (Gullberg et al. 2011; Salcedo et al. 2015). The main reason behind this is antibiotics themselves are not produced by the human body nor are part of the normal diet. “For example, antibiotics like polymixin, amphotericin, and pyrazinamide, when these were taken by humans to cure ailments then affect the body cells, tissues or any organ of the organism like the liver and kidney damage” (Bouki et al. 2013). Xenobiotics are a potent threat to organisms if they remain exposed to such environmental conditions. On the contrary, the bioavailability of these potent threat substances depends upon chemical and environmental characteristics as well. According to Maenpaa’s (2007) report related to xenobiotics, bioaccumulation in organisms in chemical residue can remain preserved in the environment for a long time period up to months or years. For example, in a natural environment, lignin, a polymer structure, does not degrade rapidly (Fetzner 2002). Hydrophobic pollutants are quite similar examples that are present in the aquatic environment, which become hazardous to benthic organisms upon exposure. Because of the pollutant’s residual storage in sediments, these contaminated sediments directly affect the lower trophic level upon exposure and show biomagnification as well which results in toxic effects at the top consumer or at higher trophic levels (Kojima et al. 2009; Karpeta et al. 2014, 2016). Some antibiotics in the environment become xenobiotics by increasing their concentration (Kumar and Chopra 2020). It classified xenobiotics present in the environment as industrial products, drugs, pesticides, personal care products or pharmaceutical products, etc. (Mathew et al. 2017). The WFD (Water Framework Directive) categorizes the xenobiotics into different groups, i.e., priority substances which are having 17 groups and the watch list comprising 8 groups (Table 1).

These xenobiotics enter into the environment through various anthropogenic activities like excretion, pesticide treatment to crops, wastewater treatment plants, industrial and agriculture practices, etc. (Tripathi et al. 2020; Dhuldhaj et al. 2023).

2 Sources of Xenobiotics

The xenobiotics persistent in the environment can be through two methods, i.e., direct method or by indirect method.

Table 1 Priority group and watch list of xenobiotic compounds

Priority group	Watch list
Alkylphenols	Antibiotics
Antifouling biocide	Antioxidants
Aromatic chlorine	Carbamate insecticides
Benzene	Hormones
2,2',4,4'-Tetrabromodiphenyl ether (BDEs)	Herbicides
Chlorinated solvents	Insecticides
Chloroalkanes	Neonicotinoid
Dioxins	Pharmaceuticals
Herbicides	Sunscreen agents
Hexabromocyclododecane	
Insecticides	
Metals	
Organochlorine	
Organophosphorus	
Polybrominated biphenyl	
Perfluorinated surfactant	
Phthalate	
Polyaromatic hydrocarbons	
Pyrethroid	
Quinoline fungicide	

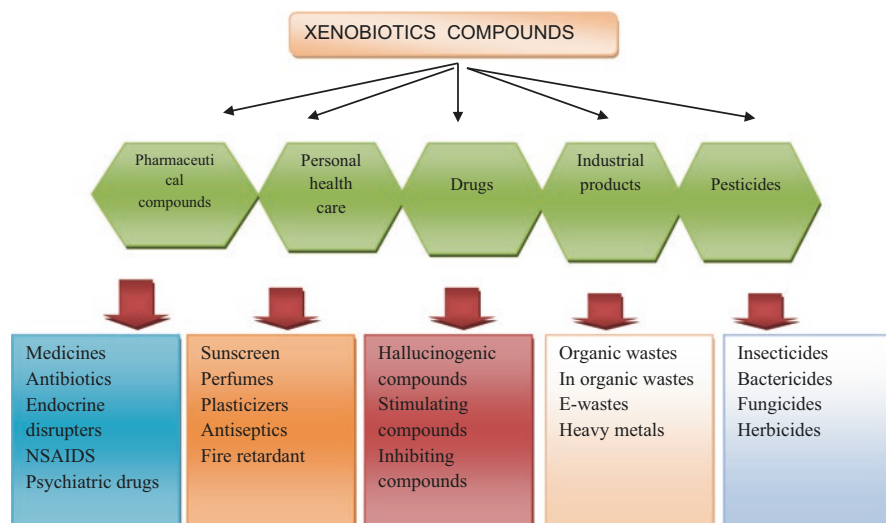


Fig. 1 Classification of xenobiotic compounds and their potential examples

2.1 Direct Sources

The direct sources of xenobiotics in the environment are due to the release of wastes from the industries in wastewater and solid form (phenols, pesticides, dyes, paints and insecticides, etc.) which is shown in Fig. 1.

- (a) **Plastics material:** It consists of the molecules which are held by the strong molecular forces of attraction which cannot break easily (Kathiresan 2003). It is a tough, hard, and good insulator of electricity. It is made up of polyvinyl chloride and polyethylene or other derivatives. Plastics are prominently used in industries as fuel to break liquid hydrocarbons (Raaman et al. 2012).
- (b) **Paint material:** Paint consists of different types of volatile substances like emulsifier which is harmful to microbial sources and creates hygroscopic stresses (Dixit et al. 2015).
- (c) **Phenolic compounds:** These compounds are extensively used as chemicals in pharmaceutical industries. During the process of oxidation, this will lead to the form of other substituted compounds which are directly harmful to the environment like ozone depletion, smog formation, reduced visibility, etc. (Yeom et al. 2010).
- (d) **Petrochemical products:** The petroleum products consist of polyaromatic hydrocarbons, saturated hydrocarbons, nitrogen-sulfur-containing compounds, etc. (Gojgic-Cvijovic et al. 2012). This will lead to a direct impact on the environment because of toxicity.
- (e) **Coloring/staining dyes:** Dye is the major cause of the persistence of xenobiotics in the water bodies which is released by the industries. These dyes will inhibit the photosynthetic activities in the water bodies due to a reduction in the penetration of light (Kumari et al. 2014). There are many industries that are using synthetic dye for papermaking, photography, etc. (azomethines, hemicyanine, etc.) (Vigneewaran et al. 2012; Shahid et al. 2013).

2.2 Indirect Sources

The indirect sources include anti-inflammatory drugs, chemical fertilizers, pharmaceutical products, etc. These compounds are directly released by pharmacy companies or by the hospital which have biological effects on living beings and then passed into the environment. This includes the hormones, antibiotics, and anesthetics which passed through the food chain and accumulated in living organisms and show biomagnification (Iovdijová and Bencko 2010). Pesticides which are directly applied to the land seep down into the water bodies which ultimately transfer into the living organism. These living organisms excrete their wastes which go into sewage, water bodies, etc. Hence, the release of biological waste matter also affects the environment indirectly (Mathew et al. 2017).

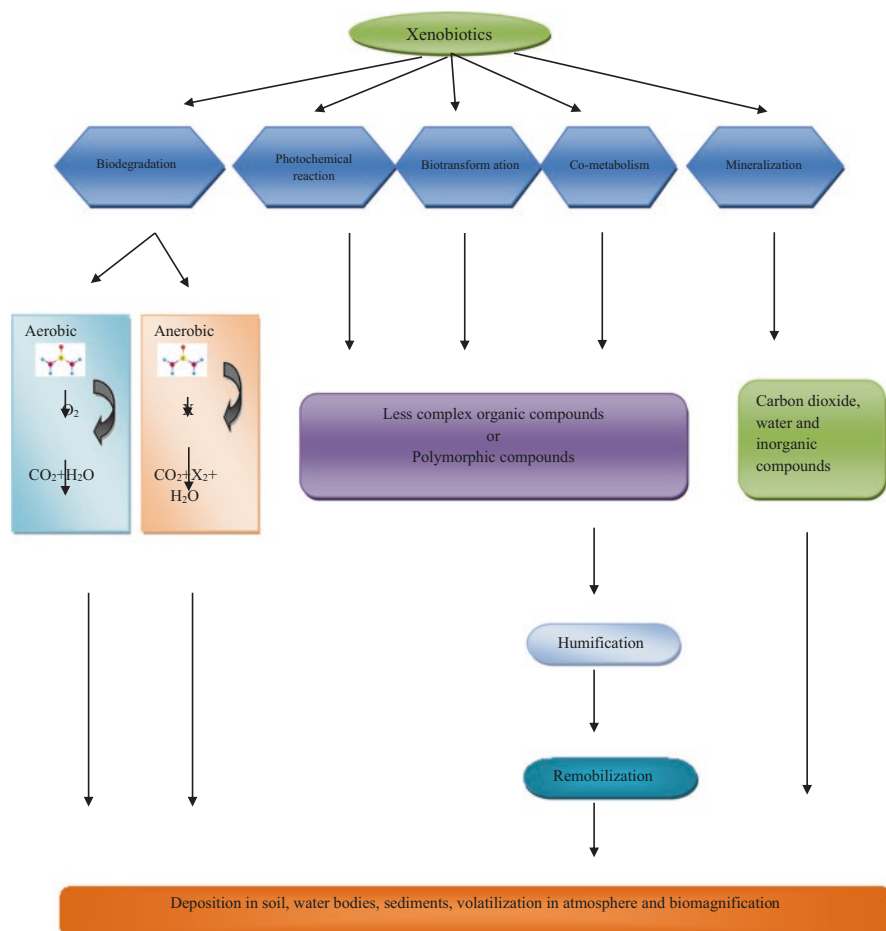


Fig. 2 Degradation process of xenobiotic compounds in the environment

3 Degradation of Xenobiotics

The hazardous nature of xenobiotic compounds leads to a harmful impact on the micro- and macroflora of the world. The recalcitrant nature of xenobiotics allows the persistence in the environment, which leads to biomagnification and bioaccumulation in the food chain. To tackle this problem, the microflora in the environment is an efficient tool which performs the biodegradation, biotransformation, and co-metabolism activities (Kelly et al. 2008; Bute et al. 2020) which are shown in Fig. 2.

3.1 Biodegradation

Biodegradation is the process by the help of which complex organic compounds are converted into less complex or simple compounds by using living organisms. These living organisms can be unicellular microorganisms or multicellular. This process will lead to the complete breakdown of compounds which is known as mineralization, whereas incomplete breakdown leading to form the subsidiary compounds is known as partial degradation.

3.2 Biotransformation

Biotransformation is the modification of the structure of compounds because of the change and loss of the characteristic properties of compounds. This process will affect the solubility, compound mobility in the corresponding environment, and toxicity level.

3.3 Co-metabolism

Co-metabolism is the process in which microorganisms transform the chemical nature of the compound, which cannot be further used as an energy and food supplement source, and this process is also known as the “co-oxidation process.”

The degradation of xenobiotic compounds through the microbial process proved to be efficient, environment-friendly, and cost-effective (Finley et al. 2010). Most of the previous research was focused on the biodegradation process because microorganisms can be cultivated easily in the lab and are susceptible to genetic modifications (Ortiz-Hernández et al. 2011). Many bacterial species assist in the biodegradation process of xenobiotics, which are given in Table 2.

4 Effects of Xenobiotics on Soil and Human Health

Xenobiotics have been present in the soil for up to 100 years, thus, acting like a potential threat to human health and also adversely affecting environmental microbiota. Phytoremediation activities and the dependence of plants on the soil for micronutrients take this problem to the next level. Air pollutants, fertilizers, pesticides, dust, fossil fuel combustion, and precipitation in crops contribute to this problem. And it is becoming an additional source of amplification of xenobiotic pollution (Dghaim et al. 2015). Field studies in *Brassica juncea*, *Helianthus annuus*, *Brachythecium populeum*, *Populus* sp., *Salix viminalis*, and *Pteris vittata*

Table 2 Degradation of xenobiotic compounds by microbial communities

Xenobiotic compounds	Microorganisms	References
Aromatic compounds	<i>Sphingomonas</i> and <i>Sphingobium</i>	Zhao et al. (2017)
Naphthalene	<i>Gordonia</i> spp. 1D	Delegan et al. (2019)
Xenobiotics	<i>Bacillus megaterium</i> STB1	Nascimento et al. (2020)
Polyaromatic hydrocarbons (PAHs)	<i>Cycloclasticus</i> spp., P1	Wang et al. (2018)
Petroleum compounds	<i>Gammaproteobacteria</i> and bacteroid classes within bacterial communities	Siles and Margesin (2018)
Organophosphate compounds	Microbial communities	Jeffries et al. (2019)
Di(2-ethylhexyl)phthalate		Zhu et al. (2020)
PAHs	<i>Actinomycetales</i>	Zafra et al. (2016)
Lindane	<i>Actinobacteria</i> , <i>Acidobacteria</i> , <i>Planctomycetes</i> , and <i>Proteobacteria</i>	Negi and Lal (2017)
Toluene and benzene	<i>Geobacteraceae</i> and <i>Peptococcaceae</i>	Hidalgo et al. (2020)
Organochlorines	Microbial communities	Sun et al. (2019)
Biphenyls	<i>Pseudomonas</i> , <i>Rhodococcus</i> , <i>Bordetella</i> , <i>Achromobacter</i> , and <i>Varivorex</i>	Garrido-Sanz et al. (2018)
Trichloro ethane	<i>Dehalococcoides mccartyi</i>	Mao et al. (2019)
Phenol	<i>Rhodococcus</i> sp. CS-1	Gu et al. (2018)
Chlorimuron-ethyl	<i>Rhodococcus erythropolis</i> D310–1	Cheng et al. (2018)
Methyl parathion	<i>Burkholderia zhejiangensis</i> CEIB S4–3	Castrejon-Godinez et al. (2019)
Polyphenol	<i>Sphingomonas haloaromaticamans</i> P3	Perruchon et al. (2017)
Phenanthrene	<i>Novosphingobium</i> sp. LH128	Fida et al. (2017)
Sulfonic acid	<i>Novosphingobium resinovorum</i> strain SA1	Hegedus et al. (2018)
2,4,6-Trinitrotoluene	<i>Pseudomonas putida</i> KT2440	Fernandez et al. (2009)
Heavy oil	Activated sludge microbiome	Sato et al. (2019)
PAHs	<i>Cycloclasticus</i> sp. P1	Wang et al. (2018)
Aromatic hydrocarbons	Microbial communities	Sharma et al. (2019)
Aromatic xenobiotics		Singh et al. (2018)

represented a significantly higher concentration of cadmium (Cd) and lead (Pb) in leaves (Jordan-Ward et al. 2022). Greenhouse and pot studies, also in laboratory experiments, conducted with plants such as *Portulaca grandiflora*, *Raphanus sativus*, *Alternanthera philoxeroides*, *Brassica napus*, *Sanvitalia procumbens*, *Brassica juncea*, *Agrostis capillaris*, *Brassica rapa*, and *Rishia* sp. represent the similar results (Van Ginneken et al. 2007; Chandra et al. 2009; Dghaim et al. 2015; Gupta et al. 2009; Zheng et al. 2020). At a higher level, Cd shows carcinogenic activity and

can be very toxic. Continued intake of Cd leads to accumulation, which can lead to lung damage, bone fragility, and dysfunction of vital organs, such as the kidneys and the renal tract (Baslar et al. 2005; Pehlivan et al. 2009). Constant contact or prolonged exposure of our bodies to lead can damage our sight and hearing. In more adverse cases, it also showed harmful effects on the brain and kidneys, defects in reproductive organs, gastrointestinal issues, and weak coordination between muscles and bones. Low levels of bioaccumulation in living tissues and long-term bioaccumulation at low levels can have adverse effects on humans and other organisms (Sastre et al. 2002; Jordan-Ward et al. 2022).

In addition to heavy metal contamination, increasing bacterial antibiotic resistance is becoming a major threat to the public good. According to the World Health Organization (WHO), about 30% of the population in developed countries is affected by diet-related illnesses each year (Bouki et al. 2013). Similarly, by 2050, multidrug resistance (MDR) will be the leading cause of death worldwide. This situation has been exacerbated by the misuse and abuse of antibiotics. This situation leads to bacteria acquiring resistance through various mechanisms, such as horizontal and vertical gene transfer. These activities support bacteria in becoming resistant to multiple drugs (Gullberg et al. 2011; Salcedo et al. 2015). The environment behaves as a reservoir for antibiotic resistance genes and resistomes. Commensal bacteria such as *Proteobacteria*, *Bacteroidetes*, *Acidobacteria*, *Firmicutes*, *Chloroflexi*, and *Actinobacteria* are the main dominating phyla in wastewater treatment plants carrying multiple drug resistance genes with them (López-Esparza et al. 2016).

Pesticide exposure showed hazardous effects like throat, nose, and eye irritation and severe effect on the kidney and the central nervous system and can cause cancer as well. Humans affected by pesticide toxicity showed symptoms like muscular weakness, dizziness, headache, and nausea (Agrawal and Sharma 2010; Garcia et al. 2012; Abdulhamid et al. 2015; Dhuldhaj et al. 2023). However, chronic exposure to certain pesticide in humans could cause kidney, nervous system, liver, and endocrine system damage (Dhuldhaj et al. 2023). An elevated level of pesticides like cyclodiene exposure or its inappropriate handling caused symptoms like muscular twitching, tingling sensation, headaches, nausea, and dizziness (Cataudella et al. 2012). It is hypothesized that cyclodienes might heighten the risk of cancer, as well as long-term damage to the central nervous system and liver (Alexander et al. 2008; Singh et al. 2017).

Endocrine disruptors showed their effects on steroid receptors for androgen and estrogen functions related to the cardiovascular system, brain, urinogenital system, and skeletal system. These are regulated with the help of steroid hormones, and therefore, these can be easily affected by the presence of endocrine disruptors (Banerjee et al. 2008; Bulucea et al. 2012; Eugene and Vincent 2016). These can result in low sperm count, reduced semen quality, high spermatozoa mortality, and low ejaculate volume in the case of males. Other effects may include malfunctioning of reproductive tissue, small penis size, undescended testes, prostrate disease, and many other unrecognized abnormalities of the male reproductive system along with testicular cancer also (Bonde and Giwercman 2014; Ozaydin 2017). Bisphenol

A is also another example of xenobiotics that adds to the situation. It is a particular component used for plastic products which shows the potential to bind with local anesthetic receptors, resulting in blockage of human heart sodium channels. In females, these may result in polycystic ovarian syndrome, uterine fibroid, reproductive tissue cancer, endometriosis, fibrocystic disease of the breast, and pelvic inflammatory disease (Julvez and Grandjean 2009; Soderland et al. 2010; Descamps and Descamps 2012). In cosmetic products like nail polish, phthalates are often used, which is linked to a serious issue. This is supposed to cause infertility in women due to its direct effect on the endocrine system. Endocrine disruptors also caused severe health effects in children as well. The reason behind this is children are most prone to environmental contaminants (Embrandiri et al. 2016; Dinka 2018).

To analyze xenobiotics in nature, first of all, it is necessary to understand that bioconcentration of xenobiotics refers to the accumulation of xenobiotics in amounts greater than those found in the immediate environment of a particular tissue of an organism. A bioconcentration factor (BCF) is defined as the concentration of a chemical in an organism divided by the concentration of the same chemical in the environment or environmental components, such as water. Initially, BCF was used for the prediction of organic pollutant accumulation in water by fish.

$$\text{BCF} = \frac{\text{Concentration of chemical in tissue of organisms}}{\text{Concentration of chemical in water}}$$

For terrestrial animals, food is typically the major source of many xenobiotic compounds, which eventually form a steady state if the uptake rate is constant.

4.1 *Xenobiotic Bioaccumulation*

Bioaccumulation of persistent hydrophobic foreign substances in aquatic species can occur in a variety of ways, including biomagnification and bioaccumulation. Bioaccumulation itself should be considered a hazard criterion, as certain adverse effects may not be noticed until later in life, even if sub-chronic, chronic, or acute consequences are not apparent. Bioaccumulation of foreign substances in biota can be a prerequisite for adverse ecological effects to estimate the xenobiotic concentration in animals; the formula is given below:

$$\text{Concentration of a xenobiotic}(Q) = (f \cdot c) / K_{01}$$

f = the weight of food consumed per day

c = the concentration of xenobiotics in food

K_{01} = the rate of constant excretion of unchanged compound plus metabolism per day.

It is closely related to the metabolic capacity of the predator.

The availability of foreign substances in dissolved form in the surrounding water plays a major role in their uptake by organisms. Suspended particles, sediments, and adsorption to humic acids and other macromolecules, along with the formation of colloidal suspensions, chelation, complexation, and ionization, are all important processes that reduce the bioavailability of contaminants in water (Karpeta et al. 2016). Lipophilic xenobiotics with high bioaccumulation potential are also found in the organic fraction of silt or suspended solids (Kanaya et al. 2019). By reducing the concentration of lipophilic xenobiotics in water, suspended particles and adsorbents such as humic acid limit their uptake (Byrne et al. 2022).

5 Conclusions and Future Prospects

This chapter provides the information related to the classification, sources, and degradation process of xenobiotics and the effects of xenobiotics on the human health. Xenobiotics are recalcitrant, so it is difficult to degrade. Xenobiotics shows biomagnification in the food chain, which indirectly affects human. Therefore, there is a need to control the spread of these compounds in the food chain and prevent their further increase. To tackle with this bioremediation, techniques are used nowadays which are economic, sustainable, and eco-friendly. Bioremediation is the part of biotechnology which involves the microflora to degrade the contaminants in the environment. This chapter has described advanced processes and techniques that can be used to reduce the harmful effects of xenobiotics on the environment. Bioremediation, specifically microbial bioremediation technology, has recently emerged as the best alternative for removing and detoxifying toxins from the environment. Synthetic biology deals with decontamination and remediation solutions for contaminants and related compounds in the environment. Understanding the existing metabolic pathways has been found to be a prerequisite for the removal of xenobiotic compounds.

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Part IV
Remediation Strategies for the Xenobiotics
in Urban Systems

Remediation Strategies of Xenobiotics in Urban Soil and Water



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1 Introduction

Anthropogenic activities, such as industrial operations, urbanisation, waste disposal, agriculture, breeding, etc., directly introduce different chemicals into the ecosystem. These either are not generated naturally or are produced considerably less frequently than what is produced by humans. These substances are referred to as recalcitrant because of their resistance to biodegradation and long-time existence in the environment. Chemicals created by humans and found in greater quantities in the environment are known as xenobiotic substances. The release of toxic and carcinogenic compounds (including dyes, hydrocarbons, pesticides, heavy metals, polychlorinated biphenyls (PCBs), fertilisers, pharmaceutical wastes, etc.) in bulk quantity results in the deterioration of biotic communities (Bharagava et al. 2018; Sabouni and Gomaa 2019). Miglani et al. (2022) reported that xenobiotic compounds may be resistant because of the following:

- Degradative microbes do not recognise them as a substrate.
- Having a totally strong nature.
- Water insoluble.
- Extremely hazardous.
- Unable to enter microbial cells due to their enormous molecular weight.

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The molecule contains halogens instead of hydrogen and takes more energy to cleave due to the presence of other groups like nitro, sulphonate, methoxy, amino, etc. Presence of branched linear chains in cycloalkanes, heterocyclic compounds and aromatic compounds is responsible for the increased biodegradation resistivity.

Since the industrial revolution, scientific and technological progressions have allowed people to use resources excessively, disrupting the natural ecosystem. Numerous synthetic substances (e.g. pesticides, fertilisers, dyes, solvents, hydraulic fluids, pigments) created by industrial processes are also utilised in agriculture. Pharmaceutical wastes have received widespread recognition as sources of enduring environmental contamination as a result of their frequent use in human and veterinary pharmaceuticals. These substances are thought to function in the body in a certain way. Comparatively to other chemical compounds, the chemical make-up of pharmaceuticals makes them more likely to have an impact on aquatic flora and wildlife (Donner et al. 2010).

The environment contains a variety of artificial compounds that may interact differently with exposed humans and ecosystems. They are a particular class of pharmacological substance (Jones et al. 2005; Bonjoko 2014). Water bodies all over the world contain substances known as environmental persistent pharmaceutical pollutants (EPPPs). Bonjoko (2014) stated that exposure to the EPPPs may cause environmental imbalance and extinction of certain species due to the adverse effects on reproductive systems of aquatic animals. The sewage systems of pharmaceutical industries contain considerable levels of pharmaceutical chemicals including antibiotics and analgesics (Fent et al. 2006). The possible points of entry of pharmaceuticals in environment include:

- Using waste from patients
- Direct discharge into the wastewater system from businesses, hospitals or garbage dumped in sinks and commodes
- Terrestrial depositions, such as leaching from landfills for solid waste and irrigation with wastewater that has been both treated and untreated
- Non-pharmaceutical industrial sources, such as plastic products
- Waste from agriculture, including pesticides, herbicides and fertilisers
- As a result of deteriorating infrastructure, specifically from exposure to artificial compounds like analgesics and antihistamines in streams and rivers
- Drugs used to treat plant diseases

In this chapter, we have presented brief outline on types of xenobiotics, their presence and impact on urban soil and water systems, followed by detailed insight on various physical, chemical and biological methods used for remediation of the xenobiotics from urban systems.

2 Types of Xenobiotic Compounds

2.1 Halocarbons

These compounds substitute hydrogen (-H) atoms with varying quantities of halogens including chlorine (Cl), bromine (Br), fluorine (F) or iodine (I) atoms. They are employed as propellants in spray cans of cosmetics, paints and other liquids as solvents (chloroform, CHCl_3). Additionally, they are utilised in the agriculture field as herbicides (dalapon, 2,4D, 2,4,5T, etc.), insecticides (DDT, BHC, lindane, etc.) and condenser units of cooling systems (Freons, CCl_3F , CCl_2F_2 , CClF_3 , CF_4). Freons and chloroform, which are flammable, escape into the atmosphere and deplete the ozone (O_3) layer, which resulted into increased UV radiation (Chaudhry and Chapalamadugu 1991).

2.2 Polychlorinated Biphenyls (PCBs)

Instead of -H, halogens are attached with two benzene rings by covalent bonds. These are mostly utilised as heat exchange fluids, plasticisers and insulator coolants in transformers.

2.3 Synthetic Polymers

Synthetic polymers, such as nylons and polyethylene, used for manufacturing of clothing, wrapping paper and other items, are resistant due to their large molecular size and insolubility in water (Siracusa 2019).

2.4 Alkyl Benzyl Sulphonates

These surface-active cleaners are discovered to be superior to soaps. One end sulphonate (SO_3) group is resistant to microbial deterioration, but if it is branched, the other end becomes recalcitrant. In this case, resistance level rises as branching length does. At the moment, non-branched alkyl ends on alkyl benzyl sulphonates are employed; these are biodegraded by β -oxidation from their alkyl ends (Sakai et al. 2017).

2.5 Oil Mixtures

Oil is resistant mostly because some of its constituents are poisonous and its insolubility in water. It is a natural product that is biodegradable and has a variety of components. The biodegradation procedure is mostly employed to deal with minor oil leaks. But when significant spills happen, the environmental issue gets much worse. The majority of these substances have a recalcitrant character.

2.6 Other Xenobiotic Compounds

Most pesticides have aliphatic, cyclic ring structures with replacements for the halogen group in the form of nitro (NO_2), sulphonate ($\text{R-S(=O)}_2\text{-O}^-$), methoxy (CH_3O), amino ($-\text{NH}_2$) and carbonyl (C=O) groups. They become recalcitrant due to these alterations. Figure 1 represents the structure of various xenobiotic compounds.

3 Role of Xenobiotics in Urban Soil and Water

Most foreign materials that pollute soil are called xenobiotics. Dioxins, halocarbons (halogens in pesticides), PCBs, synthetic polymers and alkyl benzyl sulphonates found in detergents and mineral oil combinations are a few among them. They are introduced to soils through agrochemicals, anthropogenic pollution, airborne ash

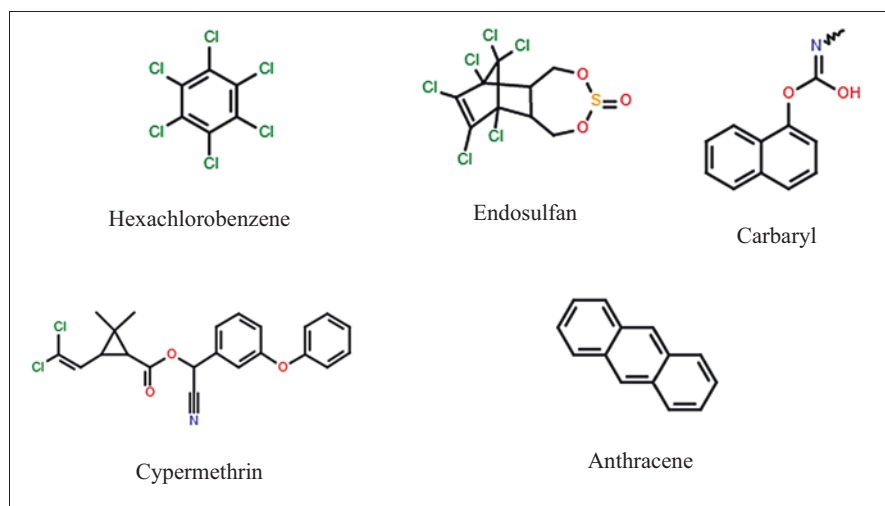


Fig. 1 Chemical structure of various xenobiotics

and volatilisation. Many xenobiotics in the soil can be broken down by some microbes, but the microenvironment parameters, such as pH and temperature, must be favourable for the biodegradation. Utilisation of various chemicals (e.g. solvents, oxidisers, acids, chelators, immobilisers) for elimination or reduction of xenobiotics in soil is known as chemo-remediation. A detailed insight on different remediation approaches for xenobiotics from urban systems has been given in the following section.

4 Remediation Methods for Xenobiotics

4.1 Chemical and Physical Methods

Chemical and physical methods of xenobiotic remediation compounds have been used for decades. Although these methods have proven results, they also show the disadvantages of releasing toxic and harmful by-products to the environment. Various physical and chemical methods (vitrification, precipitation, ion exchange, chemical leaching, etc.) are applied for the remediation process but due to their high cost and non-eco-friendly nature lead towards the development of other remediation techniques (Hashim et al. 2011; Somu et al. 2022).

4.2 Bioremediation

The drawbacks of physico-chemical methods lead towards the development of alternate strategy that should be cost-effective and eco-friendly, i.e. bioremediation (Kumar et al. 2020). The practice of employing plants and microorganisms to eliminate environmental contaminants is known as bioremediation. The core of bioremediation is the biological elimination of pollutants for environmental clean-up.

4.2.1 Types of Bioremediation

The efficient control of dangerous and toxic pollutants (xenobiotics) via bioremediation is the most crucial component of environmental biotechnology. On the basis of application site, there are two ways to use bioremediation: in situ and ex situ methods.

4.2.1.1 In Situ Bioremediation

A direct method used for the biological breakdown of xenobiotics at the pollution site is called in situ bioremediation. Microbial development is encouraged by the addition of sufficient amount of nutrients at the sites. These microorganisms acquire the metabolic capacity to breakdown xenobiotics (pollutants) when they are exposed to them. The bioavailability of vital nutrients is necessary for the growth of microorganisms as well as for their capacity to cause biodegradation (nitrogen, phosphorus, etc.) (Bala et al. 2022).

4.2.1.2 Ex Situ Bioremediation

The waste or hazardous materials can be removed from polluted sites, and the remediation process can then be performed at designated locations using the necessary microorganisms (often a group of organisms). This method has been applied effectively in several locations and is unquestionably an improvement over in situ bioremediation.

4.2.2 Microbial Methods

Microbial degradation of xenobiotics primarily involves aerobic, anaerobic and enzymatic reactions and sequential degradation.

- Aerobic Bioremediation
- For the oxidation of organic molecules during aerobic biodegradation, O₂ is used. These substances could act as sources of carbon and energy for the microbes. Monooxygenase and dioxygenase are two types of enzymes that participate in aerobic biodegradation. Whilst dioxygenase oxidises aliphatic molecules, monooxygenase can function on both aliphatic and aromatic substances.
- Anaerobic Bioremediation
- O₂ supply is not necessary for anaerobic biodegradation. Anaerobic bacteria grow slowly, which slows down the degradation process. They are primarily found in solids and sediments (Zhang and Benett 2005). The following is a list of some significant anaerobic reactions and instances of organic molecules being broken down:
 - (i) Benzoate, phenol and catechol undergo hydrogenation and dehydrogenation.
 - (ii) Dehalogenation of chlorinated ethylene and polychlorinated biphenyls (PCBs).

Schmidt et al. (2014) reported that under aerobic conditions, trichloroethylene (TCE) composites can be degraded. Aerobic biodegradation is generally briskly and

more effective than anaerobic degradation. Brzeszcz and Kaszycki (2018) identified several aerobic bacterial strains (e.g. *Bacillus*, *Acinetobacter*, *Burkholderia*, *Pseudomonas*, *Streptomyces*, *Corynebacterium*, *Sphingomonas*) responsible for xenobiotic degradation. Several other authors reported that hydrocarbon-oxidising bacteria (*Pseudomonas*, *Xanthobacter*, *Nitrosomonas*, *Rhodococcus*) are capable of co-metabolising chlorinated solvents and dioxane by producing oxygenase enzyme (Jaiswal and Shukla 2020). As the individual microorganisms might not have the capability to degrade or complete mineralisation of the single or mixed xenobiotic compounds, the application of microbial consortia with broad enzymatic spectrum might be more beneficial due to the synergistic relations with microbial communities (Khalid et al. 2009; Jiao et al. 2016). Biodegradation mainly depends upon the microbial diversity of contaminated sites, so the recent knowledge on xenobiotic degrading microbial consortia is of great interest (Pannekens et al. 2019).

4.2.2.1 Microbial Degradation of Xenobiotics

Pesticides, the most common xenobiotics, are present in various forms, including nitrophenols, tri-azines, phenyl carbamates, organochlorines, organophosphates and chlorophenoxy alkyl carboxylic acid. Among various agricultural systems, organophosphates, such as diazinon, methyl parathion and parathion, are probably the most widely employed insecticides. As the most important processes in the detoxification of organophosphorus chemicals, *Pseudomonas diminuta* and *Flavobacterium* hydrolyse p-o-aryl bonds by biodegradation. Since the invention of fungicides, organomercurials (such as Semesan, Panodrench and Panogen) have been used in agriculture. Ziram, ferbam, thiram, etc., the water-soluble derivatives, are the main fungicides employed in agriculture, which are broken down by the microorganisms. A broad-spectrum biocide known as pentachlorophenol (PCP) has been employed as an antimicrobial agent majorly in agriculture. Topp et al. (1992) reported the elimination of PCP from contaminated water using bioreactors containing PCP-degrading *Flavobacterium* (ATCC39723) cells immobilised in polyurethane foam and immobilised in alginate. Kumari et al. (2021) also reported that ligninase enzyme obtained from *P. chrysosporium* was responsible for degradation of halogenated PCP.

4.3 Plant-Associated Remediation Techniques

There are various methods for the removal of xenobiotics present in the urban soil and water. Various mechanisms present in plants are responsible for alleviation of xenobiotic toxicity: (a) transformation, (b) accumulation and stabilisation within plant tissues and (c) combination of two different agents (e.g. plants and microorganisms) (Hashmi et al. 2017).

4.3.1 Phytoremediation

Phytoremediation refers to the degradation or disintegration of pollutants by plants within the plant tissues. This mechanism has a strong connection to the breakdown activities of pollutants in the rhizospheric region or in the plant body. Phytoremediation is a cutting-edge, environmentally responsible and economically advantageous method for the degradation of residues (Hansda et al. 2022). Similar to bioremediation, phytoremediation uses a number of processes, including as phytovolatilisation, phytotransformation, phytodegradation and rhizoremediation, to break down any remaining contaminants.

The fundamental prerequisite for phytotransformation, phytodegradation and phytovolatilisation is accumulation or adsorption of xenobiotics in efficient plants (accumulator/hyperaccumulator). According to current knowledge, many plants have a propensity to efficiently store pesticides. A variety of environmental factors, such as soil moisture, pH, temperature, the amount of organic matter present and pesticide residues in the soil, all affect pesticide uptake, whilst time-dependent reductions in availability may be brought on by the residues' ageing or weathering (Lunney et al. 2004). The type of pesticide and the features of the plant have a significant impact on the variation in pesticide absorption and translocation efficiency. Soil-to-plant interaction also acts as a key factor for bioavailability of pollutants in plants (Hansda et al. 2022).

In the case of soil-to-plant absorption, numerous plant properties, such as root depth or structure and water uptake potential, might have an impact on pesticide accumulation potential (Lee et al. 2003). Pesticides are first retained by plant root tissues before being either stabilised there or transferred to the plants' aerial portions, where they can subsequently be stored, processed or volatilised. *Eichhornia crassipes* (water hyacinth) has a greater ability to accumulate the pesticide ethion in its root system compared to its shoot system, according to Xia and Ma (2006). With the aid of the transpiration stream, pesticide molecules that had collected in plant roots are mostly transferred through xylem cells. The processes of plant development, such as cultivability, may have a significant role in the dispersion of pesticides inside crops and in their species (Vila et al. 2007). After the absorption phase, when phytoremediation utilising just phytoaccumulation is used, plant shoots must be harvested. When plant shoot tissues are burned, composted or otherwise disposed of after the phytoremediation process is finished, xenobiotics may be released and volatilised into the atmosphere. It results in the mere relocation of contaminants and considered as the unwanted side effects of bioremediation process (Pascal-Lorber and Laurent 2011).

Some chemicals can completely biodegrade through plant metabolic processes; however, the majority of pesticides comprises many aromatic cycles that are hard for nature to break. Fungi- or bacterial-enhanced phytoremediation play important roles in this setting. Endophytic bacteria found in *Potamogeton crispus*, *Najas marina*, *Nymphaea tetragona* and *Phragmites communis*, according to Chen et al. (2012), were effective in cleaning up contaminated water that included a combination of fenpropathrin, chlorpyrifos, bifenthrin and naphthalene. Utilisation of

endophytes in the phytoremediation process is advantageous for pesticide degradation. Apart from this, they also exhibit some plant growth-promoting properties (e.g. phosphate solubilisation, auxin production, mineralisation) (Verma et al. 2001; Ryan et al. 2008).

Rhizoremediation is a naturally occurring process, although it has been improved by the growth of specific plant species and the correct bacteria. When compared to bulk soil, pesticide breakdown is higher in plant-associated soil, or rhizosphere soil, and this phenomenon is referred to as the “rhizosphere effect” (Hussain et al. 2009). Rhizosphere soil is closely related to plant roots, root movement and compounds released by plants that have an impact on rhizosphere soil. Rhizosphere soil has microbial communities that can be 10–100 times more diverse than bulk soil or uncultivated land (Pascal-Lorber and Laurent 2011). It may be inferred that the presence of this rhizospheric community can have a significant impact on bulk soil adjacent to the rhizospheric region, as well as improve the local microbial population and pesticide degradation (Leigh et al. 2006). The plant will benefit from improved growth, development, phytoremediation capacity and a decrease in plant toxicity as a result. Numerous researchers have injected rhizospheric bacteria with the ability to break down pollutants in earlier investigations (Kidd et al. 2008; Wang et al. 2011). Temperature, organic matter level and pH at the location all have a significant impact on how quickly things degrade.

4.4 Enzymatic Method

Although phytoremediation is an environmentally friendly and economically advantageous method for the removal and degradation of xenobiotics, its main drawbacks include the difficulties in disposing of used plants, the lengthy process, the relocation of toxic compounds and the build-up of contaminants in edible parts (Ghosh and Singh 2005; Chintakovid et al. 2008). The maintenance of the microbial population and variety at the polluted site and their requirement for the right nutrients and ambient conditions for their optimum development and survival are all problems that are particularly challenging to manage in the field (Chatterjee et al. 2022).

As compared to the other bioremediation strategies, enzymatic bioremediation has been proven to be advantageous due to its potential of degrading pollutants over a various environmental condition as well as its persistence even in the adverse change in conditions (Somu et al. 2022). Enzymatic reactions are more economical as they are responsible for lowering the activation energy which results in the higher reaction rate as compared to non-enzymatic reactions resulting in the efficient use of energy and low waste generation (Sheldon and van Pelt 2013). As the enzymes are biodegradable proteins, removal of biomass is not required as in the case of other bioremediation methods. It has been reported that various enzymes such as laccases, oxidoreductases, hydrolases and peroxidases actively participate in the bioremediation process (Mishra and Maiti 2019).

Enzymatic bioremediation is highly promising, but it also has significant drawbacks. The enzymes must be renewed often in order to maintain their concentration because they cannot multiply themselves like bacteria can; otherwise, after interacting with contaminants, they may lose their reactivity or become entirely inert (Gianfreda and Rao 2004). Other drawbacks include high cost, poor stability and little likelihood of reuse due to enzyme recovery difficulties when remediation work is finished. Enzymes can be immobilised on solid support carrier materials to get over this restriction, which will increase their stability and reusability (DiCosimo et al. 2013). Enzymes are immobilised on carriers which have the ability to increase or decrease their activity (Netto et al. 2013). Immobilisation of enzyme also results in better degradation of pollutants as compared to free enzymes (Duan and Esposito 2000; Kandelbauer et al. 2004). Immobilisation of enzymes on a proper carrier provides longer existence as well as easy recovery and reusable ability.

4.5 *Biotransformation*

It is the general word for the physiologically mediated change or conversion of one form of xenobiotic substance into another one (Parkinson and Ogilvie 2008). Multiple modifications to the parent chemical are frequently made during the biotransformation of one xenobiotic substance into another. These modifications could happen as a result of several subsequent reactions that produce one or more products. Due to the new compound's unique physical and chemical characteristics, it also exhibits unique toxicological characteristics (Kleinow et al. 1987). The toxicological characteristics of the xenobiotics may change as a result of:

- (i) Biotransformation of an active chemical into another active/inactive chemical
- (ii) Biotransformation of an inactive chemical into another active/inactive chemical

Sometimes, biotransformation can also result in the synthesis of more toxic, difficult-to-expel chemicals from more active molecules that were previously inert or less active. Typically, hydrophilic substances are quickly and easily removed from an organism's body. However, lipophilic chemicals are difficult for organisms to expel from their bodies. As a result, biotransformation frequently results in the biological conversion of lipophilic compounds into their hydrophilic counterparts, which facilitates their excretion.

4.5.1 **Biotransformation of Xenobiotics in Higher Organisms**

Biotransformation of xenobiotics can be viewed as a defence mechanism that may speed up the process of xenobiotic termination from the body because xenobiotics are poisonous to organisms. As a result, if the process of biotransformation is seen as a sort of defence, it is better to administer it as soon as the skin, lungs or digestive system have been exposed to xenobiotics. The tissues of the aforementioned organs

have enzymes that catalyse this biotransformation process; however, the liver of vertebrates is the optimum place for this to occur. The primary site of xenobiotic biotransformation occurs in the liver's hepatocytes. The kidney also absorbs a substantial number of xenobiotics despite not being one of the gateways. It also has a high concentration of xenobiotic-metabolising enzymes and acquires toxicants during excretion. Additionally, the placenta, testicles, ovaries, foetal and embryonic liver, corpus luteum, aorta and blood platelets contain various enzymes (oxidases, reductase, hydrolases, esterases, amidases, transferases) responsible for transformation of xenobiotics (Patterson et al. 2010).

Various chemical and environmental factors are responsible for affecting biotransformation of xenobiotics. Some xenobiotics with quick effects may significantly harm tissue, which may impede biotransformation enzymes due to their binding to active sites. Therefore, it is thought that these compounds prevent the biotransformation of xenobiotics. On the other hand, some chemicals may increase the activity of these enzymes, which would, therefore, increase their capacity for biotransformation. These activators may speed up the biotransformation of xenobiotics within living things (Magan et al. 2010).

Similar to other enzymes, xenobiotic biotransformation enzymes exhibit *in vitro* effects of light, temperature and radiation. Variations in temperature may act as a form of stress, causing changes that are mediated by hormone changes. As opposed to light intensity, several xenobiotic biotransformation enzymes exhibit a diurnal rhythm. High hydroxyindole-O-methyltransferase concentrations are maintained by non-stop darkness. Its activity varies throughout the day, peaking at night. These enzymes' activity and the biotransformation of xenobiotics may be connected. The rate of xenobiotic biotransformation is slowed down in rodents (mice and rats) exposed to ionising radiation. The fact that ionising radiation exposure decreases steroid hydroxylation, desulphuration activity and glucuronide formation has been used to support this theory. It has also been noted that there is less inhibition of pseudocholinesterase activity after exposure to ionising radiation.

5 Conclusions and Future Prospects

Microbial communities have been found to have a role to play in a successful bioremediation process in xenobiotic-contaminated environments. The fundamental understanding of the microbial community and variety aids in the creation of clean-up plans for polluted areas. The usage of bioremediation techniques varies depending on the geographic location, geochemical parameters, type and concentration of pollutants, degree of pollution and influence on environmental system. Instead of using single microbial species, utilisation of mixed enriched consortia for xenobiotic removal should be considered for better degradation efficiency. Omics approach can be considered as an effective way for in-depth understanding of environmental toxicology and its role in remediation by applying hybrid or integrated methods. Understanding the numerous genes and enzymes involved in the degradative

pathways of xenobiotic clean-up is one of the benefits. Recent developments in the use of nanomaterials for remediation processes have produced encouraging results in terms of faster removal of pollutants, lower costs and shorter remediation times. More research is required for accomplishment of remarkable advancements in bioremediation of xenobiotics by developing genetically modified organisms (GMOs). Apart from these, the sustainable policies should be developed frequently for using contemporary technologies.

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Explosive Contamination in Soil: Sources, Environmental Concerns, and Phytoremediation



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1 Introduction

Globally, explosive chemicals are widely used in different civil and military operations. During the production, transport, weapon testing, and mining activities, explosives reach to the environment and contaminate it (Lapointe et al. 2020). The problem of explosive contamination has been reported in Asia, Sweden, the United States, Germany, and Australia (Eisentraeger et al. 2007; Vanek et al. 2007; Celin et al. 2020; Aamir Khan et al. 2022). They readily bind with different components of humus and persist for long periods in soil due to their recalcitrant nature (Rylott et al. 2011). Eventually, groundwater and surface water are polluted when leaching of explosives occurs from the soil. Rainfall aggravates the contamination of surface water as explosive compounds reach to the aqueous environment through surface runoff (Srivastava 2015; Şener et al. 2017; Tauqeer et al. 2021).

Explosives compounds release substantial energy and hot gases rapidly when they are ignited and detonated. Expansion of gases creates high pressure on the environment leading to an explosion. A high amount of oxygen and nitrogen are

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present in explosives which leads to the formation of nitrogen, carbon dioxide, oxygen, carbon monoxide, and water vapors during the explosion (Srivastava 2015). Generally, explosives are used as a powerful tool to avert war situations and maintain a balance of power between two parties (Gledhill et al. 2019). They have several other important applications in diverse sectors such as construction, military operations, mining activities, engineering, currency production, propelling of rockets, etc. (Chatterjee et al. 2017). The employment of explosives in various sectors has contaminated the environment significantly (Kalderis et al. 2011; Lotufo 2013).

Chemically, explosives consist of heterocyclic nitramines in general and derivatives of toluene, phenol, and benzene, in particular. They can be divided into two different categories, main or primary and secondary, based on their propensity to begin when exposed to heat, friction, or shock. Primary explosives are used to fire up secondary explosives, such as RDX (1,3,5-trinitro-1,3,5-triazinane), TNT (2,4,6-trinitrotoluene), tetryl (*N*-methyl-*N*,2,4,6-tetranitroaniline), and HMX (1,3,5,7-tetranitro-1,3,5,7-tetrazocane) as they get initiated very rapidly (Smith et al. 2015). Explosives belonging to class nitroaromatic (TNT (2,4,6-trinitrotoluene)), heterocyclic nitramines (RDX (hexahydro-1,3,5-trinitro-1,3,5-triazine, hexogen) and HMX (octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine), and octogen) are some common explosives known to contaminate the environment. The concentration of different explosives varies in soil (Chatterjee et al. 2017). TNT (2,4,6-trinitrotoluene) has been documented as a dominant soil contaminant among different explosives. The concentration of TNT (2,4,6-trinitrotoluene) in soil has been recorded in the range of 4000–87,000 mg/kg. The US Environmental Protection Agency (US EPA) has identified 2,4,6-trinitrotoluene as a prominent (class C) human carcinogen (Clark and Boopathy 2007). The concentration of RDX in soil has been recorded to be 800–1900 mg/kg, while the concentration of HMX has been found in the range of 5700–74,000 mg/kg (Clark and Boopathy 2007; Panz and Miksch 2012). Explosives are recalcitrant as they are not easily biodegraded by microorganisms in soil and water. Keeping in view their toxicity concerns to living organisms, it is exigent to remove these pollutants from the contaminated environment. The existing physical and chemical methods of removal of explosives from the contaminated environment are costly and not eco-incentive. Also, these methods can be only used under *ex situ* conditions (Jugnia et al. 2019; Kafle et al. 2022).

Recently, biological methods involving microorganisms (bacteria, fungi, and blue-green algae) and plants have drawn significant attention from the researchers as an environmentally safe and cheaper alternative to conventional methods (Tripathi et al. 2020). Bacteria effectively remove explosives from the contaminated environment as they utilize explosives as nitrogen sources. Fungi degrade explosives by the action of ligninolytic as well as non-ligninolytic enzyme systems. Explosives that are toxic and inert persist for longer periods and inhibit the growth of the microorganisms thereby affecting the removal of explosives from the contaminated environment (Kao et al. 2016). Under such circumstances, plant-based removal of explosives from the contaminated environment is more appropriate as plants are less susceptible to the toxicity of explosives. A very efficient method of cleaning up the environment that has been damaged by harmful substances, such as explosives, is

phytoremediation (Kiiskila et al. 2015; Celin et al. 2020). Phytoremediation drew attention as a prominent technique of removal of environmental pollutants when it was found that plants can metabolize toxic pesticides (Sandermann 1999; Kao et al. 2016). At present, phytoremediation is a well-proven bioremediation technique for the removal of several pollutants like heavy metals, inorganic nutrients like nitrates and phosphates, persistent organic pollutants, etc. Plants effectively remove soil pollutants when they develop a symbiotic relationship with rhizospheric bacteria (Doty 2008). Phytoremediation is a time-consuming technology of removal of environmental pollutants. However, it is best suited for the cleanup of explosive-contaminated sites as these sites are abandoned/unused. In the backdrop of the aforesaid context, the present chapter is an attempt to highlight the various aspect of environmental contamination by explosives, environment concerns, mitigation strategies, etc.

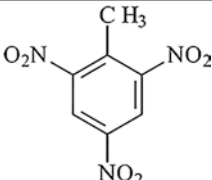
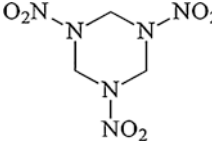
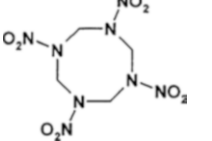
2 Explosives: General Chemistry and Classification

Functionally, explosives have been categorized into two broad groups, i.e., low and high explosives. Low explosives are employed as gunpowder and propellant. Low explosives ignite and combust quickly. High explosives are also called as detonating explosives which are employed for generating waves of shock which spread at faster speed across explosive material. Without any external source of oxygen, high explosives set off spontaneously (Zapata and García-Ruiz 2020). Primary explosives and secondary explosives are the two further classifications for high explosives. Primary explosives, also known as initiators, explode when touched by heat, mechanical shock, and friction. The primary explosives do not catch fire. They produce shock waves on detonation called brisance. Secondary explosives are friction, heat, and shock resistant. However, they may undergo deflagration to some extent (Chatterjee et al. 2017).

Chemically, explosives have been categorized into three groups, viz., nitroaromatics, nitramines, and nitrate esters (Zapata and García-Ruiz 2020). Depending on chemical formula, explosives can be demarcated as compounds containing nitro ($-\text{NO}_2$) functional group (Douglas et al. 2012). Explosives are not susceptible for electrophilic attack due to electronegativity. A result of this is that explosives are not hygroscopic, are not soluble in water, and do not react with metals (Lal and Srivastava 2010). Explosives belonging to the nitroaromatics contain aromatic ring with several nitro group. These groups are also called as aryl nitro groups. TNT is widely used explosive of this group which comprised of toluene connected with three nitro groups which are involved in deactivation of aromatic ring by withdrawing electrons (Table 1).

Due to this conformation, the aromatic ring is not subjected to electrophilic attack, thereby making TNT as highly recalcitrant compounds for hydrolysis and oxidation (Douglas et al. 2012). TNT tends to bind with functional groups of the compounds of humus and different other compounds. Due to this property, TNT is

Table 1 Chemical properties of different explosives

Compound name	Chemical formula	Chemical structure	Molecular weight (g mol ⁻¹)	Water solubility (% at 100 °C)
TNT (2,4,6-trinitrotoluene)	C ₇ H ₅ N ₃ O ₆		227.13	0.15
RDX (hexahydro-1,3,5-trinitro-1, 3,5-triazine, hexogen)	C ₃ H ₆ N ₆ O ₆		222.12	0.015
HMX (octahydro-1,3,5,7-tetranitro-1, 3,5,7-tetrazocine, octogen)	C ₄ H ₈ N ₈ O ₈		296.155	0.02

not biologically degraded in soil by microorganisms (Douglas et al. 2012). Nitroaromatics, 2,4- and 2,6-dinitrotoluene, are similar nitroaromatic isomers, called as DNTs. Due to the absence of one of the three nitro groups, these isomers differ from TNT. Nitramine explosives differ from nitroaromatics as they do not contain N-nitro groups. RDX is the prominent example of nitramine which is a widely used explosive compound throughout the globe (Hannink et al. 2002). It is frequently used in combination with TNT for ordinance and land mine blast applications. RDX is known by different names such as hexagon, cyclotrimethylene-trinitramine, and hexolite. It is a widely used explosive in military operations (Singh and Mishra 2014). RDX is more readily available and highly mobile as it does not bind with soil and its components. Because of this reason, contamination of groundwater due to leaching of RDX frequently occurs. O-nitro groups are frequently present in nitrate ester explosives, which are nitric acid esters. Pentaerythritol tetranitrate (PETN) and glyceryl trinitrate (nitroglycerine, GTN) are the main examples of nitrate esters.

3 Sources of Explosives in the Environment

Explosive contamination in soil and water is a growing concern all over the world. The environmental contamination mainly occurs during manufacturing, transport, assembling, and application in defense and industrial sector (Rodgers and Bunce

2001; Adamia et al. 2006; Vila et al. 2007a). In defense and military operations, explosives, like octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX), 2,4,6-trinitrotoluene (TNT), and hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX), are widely used. Explosives like 2,4-dinitrotoluene (DNT), nitrocellulose (NC), nitroglycerin (NG), nitroguanidine (NQ), and other perchlorate combinations are employed in missile and rocket applications (Marshall and Oxley 2009).

There are a variety of ways that explosive substances can get into the urban soils (Yu et al. 2017), such as (i) facilities used in the production of ammunition, such as wastewater lagoons and filtration pits; (ii) packing or storage facilities; (iii) facilities for disposing of waste and destroying it, such as fire pits, open landfills, and incinerators; (iv) weapons shooting ranges; and (v) weapon impact zones (Pichtel 2012). The ongoing confrontation between Russia and Ukraine, which has ramifications for infrastructure, infrastructure development, and health, is the most significant conflict in Europe since the Second World War. The effects of the war are extremely harmful to both people and the environment (Charles et al. 2014; Pereira et al. 2022).

Both physical and chemical harm are caused by the explosions. Explosives like RDX, TNT, and HMX are discharged into the urban soil and air after every explosion. These explosives enter the food chain and may pose adverse health impacts to human beings (Pereira et al. 2022). Globally, more than 1000 tons of TNT is produced annually. Nearly 2 million liters of TNT and other nitroaromatic compound containing wastewater pollute the natural environment (Serrano-González et al. 2018). In the United States of America, military operations at 2000 designated sites are responsible for TNT contamination in more than 15 million acres of the land. Out of 2000 TNT-contaminated sites, more than 87% sites are the source of major contamination. In Canada, 103 defense training sites are polluted with TNT (Hawari et al. 2000). Wars and serious armed conflicts all over the world lead to massive explosive contamination in soil and water. Africa, Eastern Europe, Australia, and the Middle East region are facing serious environmental problems due to explosive contamination. During the Second World War, the explosive nitramine, a member of the class of nitrated organic compounds, was used as an explosive (Serrano-González et al. 2018). Worldwide, the United States and Germany are the largest manufacturers of TNT and other explosives (Van Aken et al. 1997; George et al. 2008).

4 Environmental Concerns, Fate, and Transport of Explosives

Explosives are stable compounds, but they react with chemical components of the humus in the soil (Yu et al. 2017). The toxicity concerns of TNT start from its manufacturing, wherein the step of purification generates red-colored effluent which is highly toxic to the soil and water biota. Compounds like 1,3,5-trinitrobenzene, 2-methyl-1,3-dinitrobenzene-3,5-dinitro-p-toluidine, 1-methyl-2,4-dinitrobenzene,

and 2-methyl-3,5-dinitrobenzoamine, among other nitroaromatic chemicals, are common in the red-colored effluent. To reduce the risk of environmental contamination, the effluent is subjected to the process of evaporation (Ludwichk et al. 2015). The hazardous residue left after evaporation is finally incinerated. studied the toxicity of effluent contaminated with TNT on a different bacterial strain, viz., *Pseudomonas putida*, *Escherichia coli*, *Danio rerio*, and *Daphnia similis*. *Pseudomonas putida* is least affected by the toxicity of the TNT (Ribeiro et al. 2012). Leffler et al. (2014) reported that TNT and its breakdown products have a negative impact on aquatic life. The chemical analysis revealed that the degradation products of TNT 4-amino-2,6-dinitrotoluene (4-ADNT) and 2-amino-4,6-dinitrotoluene (2-ADNT) inhibit the growth of Atlantic salmon alevins. The accumulation of degradation products of TNT was seen higher in salmon fish as compared to parent compound TNT. In salmon tissue, the bioconcentration factor for TNT, 2-ADNT, and 4-ADNT was found 0.34, 52, and 134 ml/g, respectively, indicating significant uptake of TNT and its degradation products.

Trinitrotoluene (TNT) also negatively affects the growth of the plants in terms of reduced root length, germination, and biomass (Vila et al. 2008; Nehrenheim et al. 2013). The results of the study demonstrated that various species react differently to the phytotoxic effects of the water-soluble phases of the sludge that included trinitrotoluene (SLP). RDX generally does not affect the germination of the seed but cause teratogenicity, stunted shoot and root growth, and impairment in the development of leaf (Vila et al. 2007b). Lachance et al. (2004) studied the effect of acute toxicity on earthworm *Eisenia andrei* and found that TNT resulted in a decrease in fertility rate and biomass production. The physicochemical characteristics of the soil determine how toxic TNT and RDX are to the phylum Annelida (Kuperman et al. 2013).

RDX causes more toxic effect on plants growing in coarse-finished sandy soil of top most layer of soil profile. The toxic effect of RDX is less in case of soil with fine texture. TNT and its breakdown products affect rat gene expression for NRF2-mediated oxidative stress response, aryl hydrocarbon receptor signaling, and cytochrome P450 metabolism of xenobiotics (Kiiskila et al. 2015). In Europe and the United States, occupational exposure of explosives causes vomiting, unconsciousness, convulsions, and vertigo in factory workers (ATSDR 1996). Among different explosives, TNT is the most toxic nitro explosive followed by RDX and HMX. The chemical characteristics of the soil determine how explosives react with various soil elements. The interaction of TNT and its degradation products like nitrobenzene and aniline reacts with organic fraction of the soil under controlled kinetic equilibrium (Kuperman et al. 2013; Wu et al. 2017).

TNT is degraded biotically and abiotically in soil, producing a number of derivatives that, through persistent leaching with soil's organic components, contaminate soil and water ecosystems more and more (Kiiskila et al. 2015). Under oxidative conditions, humic components of the soil's organic matter react with TNT and its breakdown product, 4-amino-2,6-dinitrotoluene (4-ADNT). Polyphenol oxidases belonging to the enzyme class oxidoreductases catalyze this reaction in two steps. Firstly, explosive substances are converted to semiquinone free radical via

oxidation. Oxidative coupling of free radical with monomeric humic substances leads to the formation of anilinoquinone via nucleophilic addition through condensation (Wang et al. 2003). In Fig. 1, the fate and transport of explosive substances have been represented.

5 Removal of Explosives from the Environment: Existing Technologies

5.1 Abiotic Removal of Explosives

Abiotic removal of explosive compounds from a contaminated environment is undertaken via chemical methods. Commonly used chemical methods for removal of explosives include (a) advanced oxidation processes, (b) electrolytic transformation, and (c) Fe-dependent removal methods (Kuperman et al. 2013).

5.1.1 Advanced Oxidation Processes

Advanced oxidation processes (AOPs) are promising chemical techniques of the removal of explosives from soil and water. This technology employs ultraviolet rays, Fenton reagent, photo-Fenton reagent, hydrogen peroxide (H_2O_2), photocatalysis, and ozone for the removal of explosives from the contaminated environment. By the addition of the TiO_2 layer on the borosilicate glass substrate, the

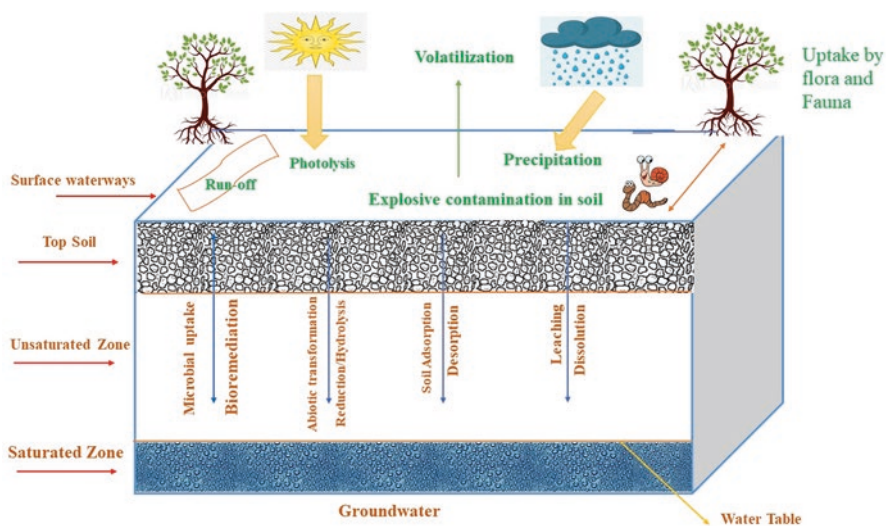


Fig. 1 Distribution, fate, and transport of explosives in soil (Based on Celin et al. (2020))

photocatalytic degradation of explosive-contaminated wastewater and sludge can be improved (Ludwichk et al. 2015).

5.1.2 Degradation Through Electrolytic Transformation

Explosives from contaminated soil and water can also be removed by electrolytic transformation and its subsequent degradation. Removal of RDX and TNT from deep aquifers is carried out by direct electrochemical transformation under alkaline conditions. Existing physical and chemical methods of removal of explosives are not cost-effective and efficient. In addition, the generation of toxic intermediates/products has made it exigent to explore new approaches for the remediation of explosive-contaminated environment. One such advantageous approach is the bioremediation which offers cheap and eco-friendly alternative for the removal of explosives (Cabrera et al. 2020).

5.1.3 Iron (Fe)-Dependent Depletion

Explosives like TNT and RDX can be effectively removed using zerovalent iron (Fe⁰) from soil and water. Soil contaminated with 6400 mg/kg RDX and 5200 mg/kg TNT can be treated with 10% Fe⁰ (w/w soil). During this treatment, the concentration of RDX and TNT reduces up to 5.8 and 17.2 mg/kg, respectively. Nanoscale zerovalent iron has more explosive removal efficiency as compared to bulk Fe⁰ (Jiamjitrpanich et al. 2010).

6 Phytoremediation of Explosives

Bioremediation technologies have emerged as promising, sustainable, cost-incentive, and green technologies for the removal of explosives from soil and water. These techniques employ living organisms, i.e., plants, bacteria, fungi, and blue-green algae, to remove explosives from a contaminated environment (Cabrera et al. 2020; Celin et al. 2020). Plant-based removal of explosives from the contaminated environment is called phytoremediation. During phytoremediation, plants detoxify explosives by secreting different enzymes and other metabolites which enhance microbial growth in root zone which helps in biodegradation and mineralization of explosive substances in soil (Chatterjee et al. 2013; Gupta et al. 2016).

In the rhizosphere, both aerobic and anaerobic bacteria perform the degradation of explosives and mineralize them into inorganic constituents (Gupta et al. 2014; Zhu et al. 2015). Plants remove explosives via different techniques (Singh and Mishra 2014; Rane et al. 2022). Explosives are accumulated in the plant's harvestable areas during phytoextraction. Contaminants can be made bioavailable by binding to plant tissues through phytostabilization. Hazardous compounds are detoxified

through phytodegradation by plant enzyme systems and related microorganisms, whereas pollutants are discharged into the atmosphere through phytovolatilization. For the remediation of explosive or other heavy metal-contaminated soil ecosystems, phytoremediation techniques are appropriate (Smith et al. 2015; Via 2020). Explosives like TNT promptly transform in plant tissues and bind with leaves, wood, and stem. Approximately 80% of absorbed TNT is non-extractable. TNT is converted into 2,4-diaminotoluene (2,4-DAT) by aquatic plant *Myriophyllum aquaticum* via 4-amino-2,6-dinitrotoluene (4-A-DNT) and 2-amino-4,6-dinitrotoluene (2-ADNT) (Hoehamer et al. 2006).

Transgenic plants that express nitroreductase demonstrate a considerable improvement in TNT tolerance, uptake, and detoxification (Hannink et al. 2001). The nitroreductase enzyme in these plants catalyzes the transformation of TNT into HADNT, which is then transformed into derivatives of aminodinitrotoluene (ADNTs). Before ring cleavage, it is advised that RDX go through di-denitration-di-hydration under aerobic conditions. This procedure paved the way for the formation of NDAB (Fig. 2). Plants in association with rhizospheric bacteria efficiently

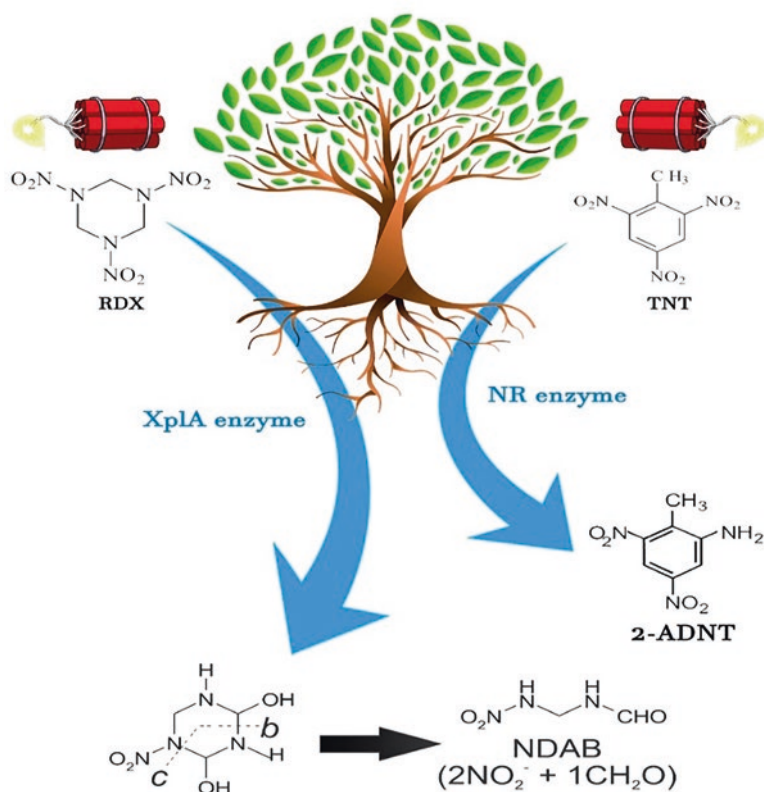


Fig. 2 Phytodegradation of explosives

transform explosives into less toxic compounds. TNT, HMX, and RDX are transformed into less toxic forms by different plants like maize, wheat, and rice (Vila et al. 2007a). TNT is assimilated by *Glycine max* (soybean plant) with the help of enzyme nitroreductase which, in the presence of NADH and NADPH, attacks nitro groups of TNT (Adamia et al. 2006). Different plant species like Indian joint vetch (*Aeschynomene indica*), Indian mallow (*Abutilon avicennae*), barnyard grass (*Echinochloa crus-galli*), vetiver grass (*Vetiveria zizanioides*), and sunflower (*Helianthus annuus*) have been reported to rapidly transform TNT and its degradation products (Makris et al. 2007; Panja et al. 2018). The presence of nitrogenous fertilizers like urea facilitates the plant-based removal of explosives (Makris et al. 2010; Das et al. 2013). When the rhizosphere of the maize plant is bio-augmented with the bacteria *Pseudomonas putida* JLR11, the remediation of TNT, RDX, and HMX is enhanced in the explosively polluted environment (Van Dillewijn et al. 2007).

Reed canary grasses and rice plants have also been reported to assimilate and transform cyclic nitramines (RDX and HMX) efficiently (based on Just and Schnoor 2004; Vila et al. 2007a). According to Thompson (2010), mycorrhizal fungi work in conjunction with plants like hybrid poplar trees (*Populus deltoides x nigra*, DN34) and switchgrass (*Panicum virgatum*) to efficiently bioaccumulate RDX from soil. Some plants, like *Baccharis halimifolia*, have shown incredible physiological endurance to TNT and RDX (Ali et al. 2014). Coniferous trees like dwarf Alberta spruce and Scots pine deposit RDX in cell walls as non-extractable wastes, according to (Via and Manley 2023). Groom et al. (2002) reported that plants like a bromegrass (*Bromus sitchensis*), alfalfa (*Medicago sativa*), canola (*Brassica rapa*), bush bean (*Phaseolus vulgaris*), blueberry (*Vaccinium* sp.), wheat (*Triticum aestivum*), perennial ryegrass (*Lolium perenne*), waxberry (*Symphoricarpos albus*), western wheatgrass (*Agropyron smithii*), wild bergamot (*Monarda fistulosa*), anemone (*Anemone* sp.), western sage (*Artemisia gnaphalodes*), koeleria (*Koeleria gracilis*), goldenrod (*Solidago* sp.), and common thistle (*Cirsium vulgare*) accumulate HMX. The accumulation and degradation of explosives do not take efficiently; therefore, the explosive removal capacity of the plants can be improved with the help of the genetic engineering approaches. Different researchers have genetically modified plant species for optimum removal of explosive compounds from soil (Hannink et al. 2002, 2007; Rylott et al. 2006; Eapen et al. 2007; Van Dillewijn et al. 2008; Van Aken 2009).

7 Mechanism of Phytoremediation

The uptake and degradation of explosive substances is governed by the process of diffusion and degradative enzymes (Singh and Mishra 2014). Plants undergo a three-step detoxification process as a result of the transfer of metabolites to plant biomass through a process known as sequestration. The “Green Liver” model is another name for this kind of variety. With the help of this approach, plants may

uptake explosives from other cellular components and lessen their hazardous effects (Jackson et al. 2007). Plants transform explosive compounds via the Green Liver model once they are absorbed from contaminated soil (Singh and Mishra 2014). In phase I, explosive substances are transformed by chemical reactions like oxidation, reduction, and hydrolysis (Fig. 3). These chemical reactions make explosive compounds very reactive by removing nonreactive functional groups with reactive polar functional groups like hydroxyl (-OH), sulfhydryl (-SH), and amino (-NH₂) (Kiiskila et al. 2015).

In plants, cytochrome P450 monooxygenase catalyze oxidative reactions leading to the conversion of explosives into polar electrophilic compounds (Kiiskila et al. 2015). In phase II, transferase enzymes catalyze the process of conjugation in the cytosol (Rodrigues et al. 2020). In conjugation, the reactive functional groups of explosives combine with hydrophilic molecules like protein and carbohydrates resulting in the formation of more reactive soluble products (Hannink et al. 2002). For instance, D-glucose combines with carboxyl (-COOH), hydroxyl, amino, and sulfhydryl groups. Conjugation leads to the conversion of more toxic compounds to fewer toxic compounds (Rodrigues et al. 2020). With the aid of ATP-binding cassette, ABC, and multidrug resistance proteins, conjugates are sequestered in

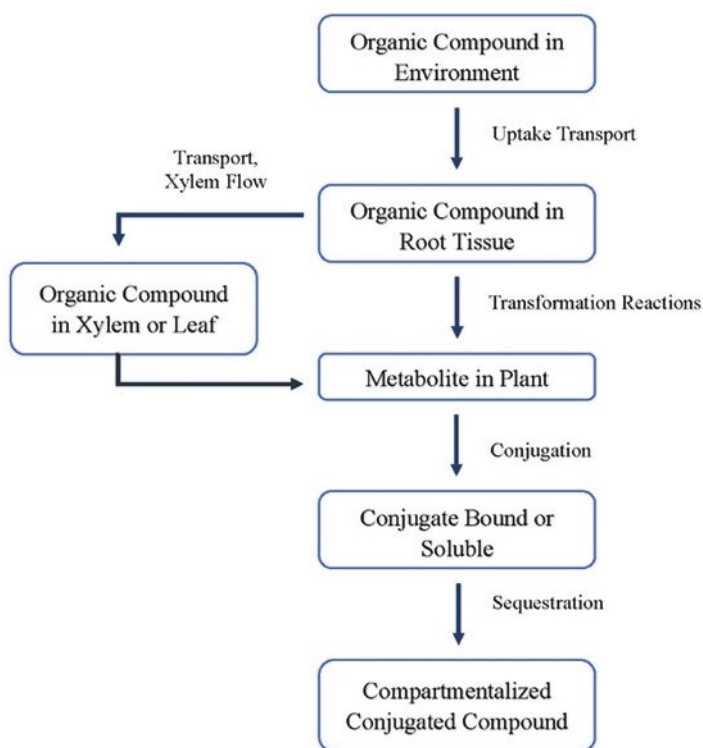


Fig. 3 Metabolism of explosives in plants (Green Liver model) (Based on Burken et al. (2000))

particular cellular compartments during phase III. Soluble conjugates sequester into vacuole and cell wall, and finally, they are incorporated into lignin, hemicellulose, or other components represented in Fig. 3 (Singh and Mishra 2014).

8 Commonly Used Plants in Phytoremediation of Explosives

Plants are effective phytoremediators of TNT and RDX. However, aspects like susceptibility for toxicants (phytotoxicity), proficiency of uptake of targeted pollutants, and pollutant removal efficiency under different environmental conditions should be checked, while selecting plants for phytoremediation of explosives. The prevailing environmental conditions have a profound impact on plant growth (Via and Zinnert 2016). In addition, types and physicochemical properties of soils affect plant growth, contaminant kinetics, root penetration depth, and bioavailability of pollutants (Kiiskila et al. 2015). The proportion of clay fraction and organic matter in soil has been reported to control the uptake of TNT. In plants, organic carbon and proportion of clay display reverse correlation with the uptake of TNT from the soil. Soil containing abundant clay favors optimum removal of TNT (Singh et al. 2010) (Table 2).

Plants have natural tendency to accumulate explosives and biologically convert them into less toxic forms (Abhilash et al. 2009). Degradation of explosive compounds can be performed easily by the development of transgenic plants (Van Aken 2009; Chatterjee et al. 2017). The plant of tobacco (*Nicotiana tabacum*) is the first genetically modified plant that was developed for the removal of organic pollutants from soil. To change the tobacco plant, pentaerythritol tetranitrate reductase, a bacterial enzyme, was inserted. The enzyme was derived from an *Enterobacter cloacae* strain that was previously isolated from explosive-contaminated soil. PETN reductase is responsible for the breakdown of nitrate esters and nitroaromatic explosives (Panz and Miksch 2012). Genetically modified tobacco plant secretes nitroreductase which demonstrates optimum assimilation and detoxification of TNT to hydroxyaminodinitrotoluene (HADNT) (Hannink et al. 2007; Zhang et al. 2017). Earlier studies have reported that the grasses like alfalfa, wheatgrass, switchgrass, and bromegrass have been reported as potent plants to transform TNT (Rodgers and Bunce 2001). Vetiver grass, *Chrysopogon zizanioides*, and Eurasian watermilfoil, *Myriophyllum spicatum*, are two most prominent kinds of grass which transform TNT (Hughes et al. 1997; Makris et al. 2007). Plant species like *Phalaris arundinacea*, *Carex vulpinoidea*, and *Oryza sativa* effectively remediate RDX-contaminated soil (Hannink et al. 2002; Vila et al. 2007a).

9 Limitations of Phytoremediation

Plant-based removal of explosive substances from a polluted environment is a cheap, eco-friendly, easily applicable technology with less environmental disturbances (Panz and Miksch 2012). However, the requirement of a longer period

Table 2 Uptake of different explosives by terrestrial plants in soil

Plant species	Explosive	Initial concentration (mg/kg) * [(mg/L) **for solutions]	Incubation period (days)	Uptake by plant (mg/g dry biomass)	References
<i>Lolium perenne</i>	HMX	30*	77	8.1	Groom et al. (2002)
<i>Populus deltoides</i>	HMX	1.77**	21	45	Yoon et al. (2002)
<i>Brassica rapa</i>	HMX	30*	77	5.2	Groom et al. (2002)
<i>Abutilon avicenna</i>	TNT	120*	50	n.a.	Chang et al. (2004)
<i>Oryza sativa</i>	TNT	500*	40	0.8	Vila et al. (2007a)
<i>Triticum aestivum</i>	RDX	138*	42	64.54	Vila et al. (2007b)
<i>Oryza sativa</i>	RDX	138*	42	3.71	Vila et al. (2007a)
<i>Vetiveria zizanioides</i>	TNT	80*	12	n.a.	Das et al. (2010)
<i>Zea mays</i>	RDX	100*	28	1.21	Chen et al. (2011)
<i>Arabidopsis thaliana</i> (Arabidopsis)	RDX	250*	49	1.34	Rylott and Bruce (2009)
<i>Pascopyrum smithii</i>	RDX	40**	12	3	Zhang et al. (2019)
<i>Pascopyrum smithii</i>	TNT	35**	12	5	Zhang et al. (2019)

* Represents initial concentration of explosive in soil

** Star represents the initial concentration of explosive in liquid medium

HMX = 1,3,5,7-tetranitro-1,3,5,7-tetrazocane, RDX = 1,3,5-trinitro-1,3,5-triazinane, TNT = 2,4,6-trinitrotoluene

toward remediation of pollutants and plant susceptibility for biotic and abiotic stress are some principal drawbacks of phytoremediation technology. Environmental factors like pH, temperature, moisture contents, and nutrients directly control the growth and survival of the plants (Vanek et al. 2007). In situ applicability of the phytoremediation technique makes it more relevant and acceptable for the abatement of soil pollution of explosives (Alkorta and Garbisu 2001). Over the past few years, researchers have very well updated the information on the role of plants in phytoremediation of explosives, the mechanism of uptake, transport, and detoxification of explosives. However, there is a need to research the correlation between fundamental plant processes and role of different microbial interactions in phytoremediation (Thijs et al. 2014). Sometimes, the toxicity of explosive compounds hampers the growth of the plants. The removal of explosives from the soil using phytoremediation is a well-established technology. However, the remediation of

explosives using some autotrophic plants is slow as these plants lack enzymatic mechanisms to transform explosives (Panz and Miksch 2012). The application of transgenic plants for the removal of explosives is not fully accepted as transgenic plants may suppress the growth of wild and indigenous plant species (Panz and Miksch 2012). Risk evaluation is more difficult because of their long life cycle, so more focused research is required (Lal and Srivastava 2010).

10 Conclusion and Future Perspectives

Explosive chemicals are widely used in different civil and military operations. During the production, transport, weapon testing, and mining activities, explosives reach to the environment and contaminate it. Chemically, explosives consist of heterocyclic nitramines in general and derivatives of toluene, phenol, and benzene, in particular. Explosive contamination in soil is a growing concern all over the world. Explosives are recalcitrant as they are not easily biodegraded by microorganisms in soil and water. The existing physical and chemical methods of removal of explosives from the contaminated environment are costly and not eco-incentive. Phytoremediation has emerged as a highly effective, well-proven bioremediation technique for the cleanup of the contaminated soils by explosives. Plants have natural tendency to accumulate explosives and biologically convert them into less toxic forms. Plants transform explosive compounds via the Green Liver model once they are absorbed from contaminated soil. Degradation of explosive compounds can also be performed easily by the development of transgenic plants. In situ applicability of the phytoremediation technique makes it more relevant and acceptable for the abatement of soil pollution of explosives. However, the requirement of a longer period toward remediation of pollutants and plant susceptibility for biotic and abiotic stress are some principal drawbacks of phytoremediation technology. Recent studies have established phytoremediation as a promising, low-cost, ecologically acceptable technology for the cleanup of explosives by using transgenic and non-transgenic plants from urban soils.

Although there has been significant progress in the study of phytoremediation of explosives, there is still much work to be done in order to create practical models that can be used in the field. It is predicted that additional research on the following points will result in the development of affordable, robust, and eco-friendly methods for the remediation of explosive-contaminated soils:

- The role of different environmental factors, viz., topography, soil, moisture, temperature, and pathogens, in the remediation of RDX, TNT, and HMX in phytoremediation should be addressed.
- The developments in genetic engineering technology have enabled scientists to effectively decontaminate an explosive-polluted environment. The impacts of transgenic plants on local plant communities should be addressed as the use of transgenic plants may have the risk of gene pool contamination and suppression of indigenous plant species.

- Optimized protocols for genetically transforming native grass species should be developed, and strategies for gene containment require to be evaluated.
- The development in the area of genomics may contribute toward the identification of genes that are responsible for explosives tolerance and their regulatory systems.
- Public acceptance of genetically transformed plants must also be considered, while engineering transgenic plant lines.
- Down the line, there is a need to develop effective phytoremediation models for large-scale field applications.

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Phytoremediation of Xenobiotics: Principles and Applications in Environmental Pollution Removal



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1 Introduction

Global human life and sustainability are being negatively impacted by environmental contamination (Manisalidis et al. 2020). Agricultural intensification (Móznér et al. 2012), rapid urbanization, and industrialization (Wu et al. 2016) are just a few of the anthropogenic activities that are seriously contaminating the environment by metalloids, heavy metals (He et al. 2015), radionuclides (He et al. 2019), organic substances (Afzal et al. 2014), agrochemicals (Malik et al. 2017), and spills of oil (Ron and Rosenberg 2014). Soil contamination has been caused by mining operations, the discharge of effluents from businesses and homes, the extensive usage of fertilizers, irrigation, and pesticides, with water that is polluted (Tang et al. 2015). Numerous soil characteristics are impacted by mining, such as cation exchange capacity, electrical conductivity, and pH (Saleem et al. 2020a, b).

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High levels of pollution cause biomagnification across the food chain, which has an impact on the entire planet's biota. Reverse osmosis (Al-Alawy and Al-Ameri 2017), chemical precipitation (Huang et al. 2017), ion exchange (Levchuk et al. 2018), adsorption, and solvent extraction (Burakov et al. 2018) are only a few of the methods used to eliminate contaminants from the environment. These methods are typically not sustainable and involve extensive maintenance costs and functions. As a quick and inexpensive alternative to decontaminating heavy metal-contaminated locations, one of the most ecologically friendly techniques is phytoremediation strategies to combat pollution in urban systems (Fig. 1) (Liu et al. 2020). Since there is no need to alter the soil's structure, this approach has little effect on the environment (He et al. 2012). After phytoremediation is finished, the area can be used again for farming (Pusz et al. 2021). This innovative approach eliminates the toxicity of pollutants from contaminated places using hyperaccumulators (Nedjimi 2020).

In order to further improve the phytoremediation of pollutants in urban systems, this chapter aims to consolidate information on the mechanisms that plants employ and how choosing the right species might optimize each mechanism's advantages. The findings are summarized on the issue of phytoremediation and how it has been used to remove various toxins from the environment after searching published literature using several online search engines.

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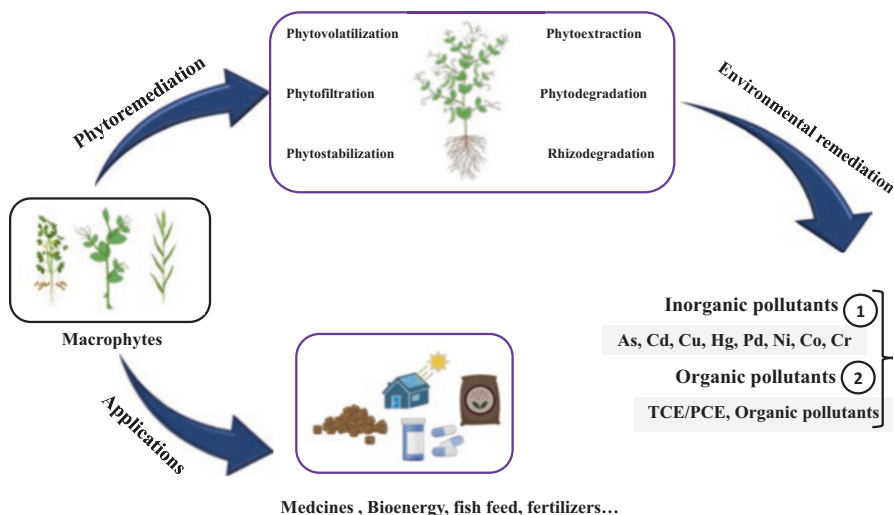


Fig. 1 Perspectives on employing macrophytes in phytoremediation to remove heavy metals and other contaminants

2 Phytoremediation of Xenobiotic Pollutants (Detoxification of Xenobiotics by Plants)

Phytoremediation is a term that combines the Latin suffix *remedium*, which is to mean “restore,” with the Greek word *phyto*, which means “plant.” Natural and transgenic plants are both used in the phytoremediation method to clean up contaminated habitats (Tripathi et al. 2020). The use of hyperaccumulators for the extraction, absorption, and degradation of hazardous contaminants and toxic metals was originally described in 1983 (Sarwar et al. 2017). As illustrated in Table 1, the process employs a variety of phytotechnologies based on naturally occurring and genetically engineered plant species to eliminate xenobiotics in urban systems (Kushwaha et al. 2018).

The process of phytoremediation can be carried out utilizing both in situ and ex situ techniques. Since the in situ application methods reduce the growth of pollutants in water, soil, and volatilized waste, the risk to the surrounding environment is automatically reduced (Raskin and Ensley 2000). The key parameters for ex situ bioremediation include the contaminated site’s geographic location, treatment costs, pollutant types, and degree of pollution. Compared to other remediation methods used posttreatment, phytoremediation is more cost-effective (Cristaldi et al. 2017) since it is a straightforward, labor-free technique requiring no installation of specialized equipment. Where other regularly used approaches are ineffective and too expensive, the process can be used to a great extent (Leguizamo et al. 2017).

Avoidance and tolerance are two defense strategies that can be used for the application of the phytoremediation approach for the cleanup of heavy metals (Thakur et al. 2016). These two techniques are employed by plants to maintain heavy metal

Table 1 Plants that are used in mechanisms for phytoremediation

Phytoremediation mechanisms	Scientific name	Common name	Contaminants	Results	Reference
Phytoextraction	<i>Sesbania drummondii</i>	Rattlebush	Pb	EDTA increased Pb absorption and buildup	Barlow et al. (2000)
	<i>Lactuca sativa</i> Higher	Lettuce	Ni, Co, and Fe	Decreased intrinsic velocity and increased absorption capacity	Hernández et al. (2019)
	<i>Pelargonium hortorum</i>	Geranium	Pb	Used bacteria that are Pb-tolerant	Manzoor et al. (2019)
	<i>Nicotiana tabacum</i>	Tobacco	Cd	Higher in leaves and stems	Y. Yang et al. (2019a)
	<i>Zea mays</i>	Corn	Ti, Pb	Chelators supported Pb and Ti phytoextraction	Huang et al. (2019)
	<i>Eupatorium cannabinum</i>	Holy rope/hemp-agrimony	As	Phytostabilization was favored by the addition of 20 mg/L of citric acid (CA)	González et al. (2019)
	<i>Kosteletzkya pentacarpos</i>	Seashore mallow/coastal mallow	Zn, Cd	Salinity protects plants from the toxicity of metals. Zn resistance is promoted by cytokinin	Zhou et al. (2019)
Phytostabilization or phytoimmobilization	<i>Salix</i> sps.	Willow	Cd	Salix does not flood; hence, it has a greater BCF than species that do	W. Yang et al. (2019b)
	<i>Solanum nigrum</i>	Black nightshade	Cu, Zn, Cd	Recommend addition of 10% biochar/attapulgitte	X. Li et al. (2019)
	<i>Helianthus annuus</i>	Sunflower	As, Cu, Hg, Pb, Zn, Ni, Cd	Vermicompost is used as a supplement, typically for metal contamination with low levels	Jadia and Fulekar (2008)

Rhizofiltration	<i>Azolla caroliniana</i>	Carolina mosquito fern/water velvet	As		BCF:0.000397	Favas et al. (2012)
	<i>Callitriche lustrantica</i>	Water starwort	As		BCF:0.002346	Favas et al. (2012)
	<i>Callitriche stagnalis</i>	Pond-water starwort	U		BCF:0.00194841	Pratas et al. (2012)
	<i>Fontinalis antipyretica</i>	Water moss	U		BCF:0.00023479	Pratas et al. (2012)
	<i>Lemna minor</i>	Duckweed	U		BCF:0.000529	Pratas et al. (2012)
	<i>Callitriche brutia</i>	Water starwort	As		BCF:0.000523	Favas et al. (2012)
	<i>Ranunculus trichophyllus</i>	Threadleaf corwfoot	As		BCD:0.00054	Favas et al. (2012)
	<i>Juncus effuse</i>	Common rush	Ammonium		Released methane	Wiessner et al. (2013)
	<i>Brassica juncea</i>	Mustard	Se		<i>Brassica</i> spp. able to phytovolatilize selenium	Banuelos et al. (1997a, b)
	<i>Scirpus robustus</i>	Saltmarsh bulrush			Wetland plants	Arthur et al. (2005)
Phytovolatilization	<i>Myriophyllum brasiliense</i>	Parrot's feather			Wetland plants	Pilon-Smits et al. (1999)
	<i>Juncus xiphioides</i>	Iris-leaved rush			Wetland plants	
	<i>Typha latifolia</i>	Broad leaf cattail			Wetland plants	

(continued)

Table 1 (continued)

Phytoremediation mechanisms	Scientific name	Common name	Contaminants	Results	Reference	
Phytodegradation	<i>Blumea malcolmii</i>	Blumea	Malachite green (after 24 h, a 93.41% decolorization)	Industrial waste phytodegradation	Kagalkar et al. (2011)	
	<i>Pueraria thunbergiana</i>	Kudzu	DDT	DDT dehalogenation via reduction	Garrison et al. (2000)	
	<i>Chlorella pyrenoidosa</i>	Unicellular green algae	Pentachlorophenol	The cycling of light exposure may have decreased algae activity	Headley et al. (2008)	
	<i>Erythrina cristia-galli</i>	Cockspur coral tree	Petroleum	Variations in the anatomical makeup of roots	de Farias et al. (2009)	
	<i>Phragmites australis</i>	Perennial reed grass	Ibuprofen	<i>P. australis</i> can be a useful plant for wetland building	Y. He et al. (2017)	
	<i>Spirodela polyrhiza</i>	Duck weed	Ofloxacin (OFX)	Reduced OFX by 93.73–98.36%	V. Singh et al. (2019)	
	Rhizodegradation	<i>Tripsacum dactyloides</i>	Eastern gamagrass	Herbicides (atrazine)	Degradation of atrazine (ATR) was accelerated by 84–60%	C. H. Lin et al. (2011)
		<i>Cynodon dactylon</i>	Bermuda grass	Total petroleum hydrocarbons	81% of the total petroleum hydrocarbons (TPHs) have been degraded	Matsodoum Nguemtié et al. (2018)
		<i>Kandelia candel</i> (L.) Druce	Mangrove	Phenanthrene (Ph) and pyrene (Py)	Ph (47.7%) and Py (37.6%) dissipated in the rhizosphere	Lu et al. (2011)
		<i>Melia azedarach</i>	Chinaberry tree	Benzo(a)pyrene	To degrade benzo(a)pyrene, a Cd-resistant plant is necessary	Kotoky and Pandey (2020)
	<i>Rubus fruticosus</i>	European blackberry	Polycyclic aromatic hydrocarbons (PAHs)	Natural-grown blueberries degrade high molecular weight PAHs	Alagüé et al. (2016)	
	<i>Salix nigra</i>	Black willow	Perchlorate	Rhizodegradation is accelerated using organic carbon	Yifru and Nzengung (2008)	

Phytodesalination						
<i>Typha latifolia</i>	Cattail	Na ⁺ , Cl ⁻		Irrigation may accelerate the bioaccumulation of contaminants	Xu et al. (2019)	
<i>Sesuvium portulacastrum</i>	Sea purslane	Na ⁺		<i>S. portulacastrum</i> in dry areas; Na ⁺ buildup is more suited	Rabhi et al. (2010)	
<i>Alternanthera philoxeroides</i>	Alligator weed	Na ⁺		The phytodesalination capacity of alligator weed is 105 kg Na ⁺ ha ⁻¹	Islam et al. (2019)	
<i>Ludwigia adscendens</i>	Water primrose	Na ⁺		<i>L. adscendens</i> produce 80 kg Na ⁺ ha ⁻¹ of plant-based desalination	Islam et al. (2019)	
<i>Lonicera japonica</i> Thumb	Honeysuckle	Na ⁺		Honeysuckle is favorable to Na ⁺ leaching	K. Yan et al. (2016)	

concentrations below the limits that are fatal (Hall 2002). Plants can restrict and limit the uptake and transfer of heavy metals into their tissues through a method called avoidance (Dalvi and Bhalerao 2013). Different defense mechanisms (metal precipitation, exclusion, and root sorption) are used in this process (Dalvi and Bhalerao 2013). The mechanism of root sorption contributes to the immobilization of plants when they come into contact with heavy metal.

3 Approaches to Phytoremediation

The interaction and buildup of heavy metal in the plant are caused by a number of processes, including phytoextraction, phytodegradation, phytostabilization, phyto-volatilization, and rhizodegradation (Sarwar et al. 2017). The underlying mechanisms are briefly described and explained in Fig. 2.

3.1 Phytoextraction

The intake of heavy metals and their migration to higher portions of the plants, for example, the stems, leaves, and other parts, are included in phytoextraction (Saleem et al. 2020a, b). Research reviews reveal that a variety of hyperaccumulator metallophytes have a lot of potential for the treatment of heavy metal-contaminated soils (Jakovljević et al. 2016).

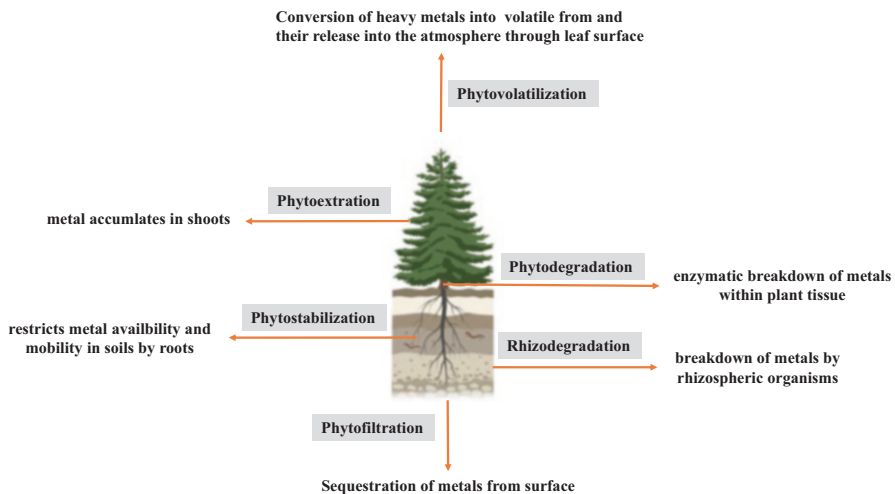


Fig. 2 Methods for phytoremediation and the destinations of contaminants

The kind and quantity of chelators control how quickly hyperaccumulators sequester heavy metals in vacuoles (Saleem et al. 2020a, b). Currently, synthetic chelators are being added to increase mobility and absorption, increasing the effectiveness of phytoextraction. Two important traits that characterize plant species from a phytoextraction perspective are their ability to accumulate heavy metals and surface-based biomass; as a result, plants that have high aboveground biomass production and hyperaccumulate heavy metals are used in phytoextraction (Ali et al. 2013). Additionally, it has been discovered that some of these species have the capacity to accumulate multiple elements, such as *Sedum alfredii* (Bing 2002). Scientific studies are currently being conducted all over the world to increase the efficiency of phytoextraction, where new hyperaccumulators are being targeted to better understand their biological channels. Brassicaceae, Asteraceae, Violaceae, Euphorbiaceae, Fabaceae, and Flacourtiaceae are the plant groups that have been shown to collect higher quantities of heavy metals. Brassicaceae species have demonstrated exceptional potential to remove and scavenge heavy metals, including nickel, cadmium, lead, and zinc (Robinson et al. 1998).

3.2 Rhizofiltration

Rhizofiltration makes use of the roots to collect, hold onto, and settle metal pollutants within the roots, limiting their passage into various environments (Midhat et al. 2019). The settling of metal pollutants on the root surface is greatly influenced by environmental parameters in the root microbiome, including the rhizosphere's pH, root turnover, and root exudates (Zhu et al. 1999). *Mycobacterium* spp., *Pseudomonas aeruginosa*, and *Rhodococcus* spp. are the most often utilized bacteria in rhizoremediation (Verma and Rawat 2021). Rhizoremediation success is greatly influenced by environmental elements such soil type, pH, temperature, and plant species (Sharma et al. 2018).

Plants from both terrestrial and aquatic can be employed for rhizofiltration. Hyacinth, duckweed, azolla, poplar, and cattail are some examples of aquatic organisms that are frequently used to treat wetland water because of their high capacity for accumulation, high carrying capacity, and higher biomass output (Hooda 2007). Similar to this, terrestrial plants (*H. annuus* and *B. juncea*) exhibit a significant capacity to accumulate heavy metals during rhizofiltration due to their larger hairy root systems (Dhanwal et al. 2017); studies have shown that sunflower has a remarkable capacity to detoxify Pb-contaminated locations (Raskin and Ensley 2000).

3.3 Rhizodegradation

Organic contaminants degrade through a process called rhizodegradation in the soil and are biodegraded in conjunction with rhizospheric microorganisms that release certain enzymes that either break down or change very polluted organic pollutants

into safer forms (Li et al. 2016). One of the essential components of rhizodegradation, which emphasizes the complete mineralization of the organic pollutants following compound transport to the plant or atmosphere, is the dissolving of the pollutant at the source (Fiorentino et al. 2018). Rhizodegradation has a number of drawbacks, including the fact that it is a slow, drawn-out process that only functions up to a certain depth, typically between 20 and 25 cm. Rhizodegradation is impacted using the type of soil and specific plant species (Kaimi et al. 2006).

3.4 *Phytostabilization*

Inhibiting contaminant movement into underground water and preventing biomagnifications are achieved through the processes of phytostabilization and phytorestoration (Van Oosten and Maggio 2015). For the stability of toxins in polluted environments, the procedure mostly relies on the use of particular plants (D. Singh et al. 2012). These remediation techniques have been successful in reducing the mobility of pollutants in soil environments (Mench et al. 2010). Insoluble chemicals are created in the rhizosphere as a result of the process (Burgess et al. 2018). The metallophytes are used to successfully recover polluted sites, and they are suitable for removing metals like Cu, Zn, As, Pb, Cr, and Cd (Yang et al. 2016). Phytostabilization serves to immobilize and inactivate potentially harmful pollutants. As long as contaminants are present in the soil, it is merely a temporary management strategy that restricts the flow of metal ions (Gong et al. 2019). The plant must be able to adapt to various soil conditions and develop quickly with a long life span for phytostabilization to be effective (Cunningham and Berti 2020). Numerous investigations have demonstrated that Pb, Zn, and Cd can be eliminated using medicinal and aromatic plants (Saha and Basak 2020).

3.5 *Phytodegradation*

Organic pollutants isolated by the plant across the variety of metabolic processes or that have been broken down by the enzymes that are a part of the plant's metabolism are called phytopollutants (P. Sharma and Pandey 2014). Various plants can be employed in this process; the most popular ones are *Leucocephala* for ethylene dibromide (Doty et al. 2003) and sunflower (*Helianthus annuus*) for methyl benzo-triazole (Castro et al. 2003). This method is restricted in that the soil must be 3 feet deep and the groundwater must be no more than 10 feet below the surface. Chelating agents are required to increase plant absorption using attaching pollutants to soil particles (Miller 1996).

3.6 *Phytovolatilization*

By using the stomata to help with transpiration, phytovolatilization is the process by which pollutants are converted into various volatile chemicals and released into the atmosphere (Leguizamo et al. 2017). Commonly utilized plants for phytovolatilization include *Nicotiana tabacum*, *Arabidopsis thaliana*, *Trifolium repens*, *Crinum americanum*, *Bacopa monnieri*, and *Triticum aestivum* (R. Singh et al. 2018). Either a direct or indirect approach can be taken. Volatile organic compounds are directly vaporized by leaves, and the stem, whereas plant root interactions with the soil cause indirect volatilization (Limmer and Burken 2016). Organic pollutants like acetone, phenol, and chlorinated benzene (BTEX) are all degraded by phytovolatilization (Herath and Vithanage 2015). The phytovolatilization technique yields the most positive results for mercury (Hg) and selenium (Se) (Ahmadpour et al. 2012).

Phytovolatilization is the most contentious technique of phytoremediation (McCutcheon and Schnoor 2003). As a remediation strategy, phytovolatilization just speeds up the transfer of pollutants, which can occasionally contaminate the surrounding atmosphere as they rise from the soil. Additionally, precipitation has the ability to redeposit these into the soil (Vangronsveld et al. 2009).

3.7 *Phytodesalination*

The most popular biological option for decontamination is phytodesalination, a recently developed and emerging technology that uses halophytic plants to repair saline soils (Ali et al. 2013). There is not much information available about this procedure in the researches when compared to the other phytoremediation methods. As compared to glycophytic plants, halophytes are thought to be naturally well-adapted to heavy metals (Manousaki and Kalogerakis 2011; Singh et al. 2023). The plant's ability to phytodesalinate depends on the species as well as on the salinity, sodicity, and porosity of the soil as well as other environmental variables, mainly rainfall (Hussain et al. 2018). According to a review of the literature, two halophytic plants, *Suaeda maritima* and *Sesuvium portulacastrum*, can each take almost 504 and 474 kg of NaCl from a hectare of saline soil over 4 months (Ravindran et al. 2007). The remediation of soil impacted using chloride, and sodium ions have been reported to exhibit encouraging outcomes in desalination tests of halophytic plants (Singh et al. 2023). The decontamination of soils contaminated with heavy metal and polycyclic aromatic hydrocarbons is not appropriate for this bioremediation technology; nonetheless, it is promising for soils impacted by salinity (Zorrig et al. 2012).

4 The Progression of Genetic Engineering

Genetic engineering has been an important strategy for enhancing plants' ability to clean up heavy metal contamination through phytoremediation. With the use of genetic modification, a foreign gene from another organism is moved and installed into the target plant's genome, followed by DNA recombination, which grants the plant specific features in a shorter amount of time (Marques et al. 2009).

Exertion has demonstrated a lot of potential for phytoremediation. However, knowledge about plants' heavy metal tolerance and accretion mechanisms should be taken into consideration when choosing genes. The exaggeration of genes entangled in the antioxidant mechanism (Kozłowska et al. 2018). Similar to this, heavy metal chelators can be produced through genetic engineering to improve heavy metal uptake and translocation (G. Wu et al. 2010). Although the use of genetic engineering has shown promising results in phytoremediation, there are still several issues that need to be resolved. Since their use raises questions about the safety of food and ecosystems, genetically modified plants sometimes struggle to obtain clearance and approval in some parts of the world. This calls for alternate strategies that, if genetic engineering proves to be impractical, could augment and increase species of plants' performance utilized in phytoremediation. The many studies about genetically modified plants utilized in phytoremediation are summarized in Table 2.

Table 2 Use of genetically modified plants in phytoremediation

Scientific name	Common name	Contaminants	Nature of contaminants	Reference
Grass <i>Polypogon monspeliensis</i>	Rabbitfoot	As	Releases dimethylchloroarsine ($\text{AsCl}(\text{CH}_3)_2$) and pentamethylarsine ($\text{As}(\text{CH}_3)_5$)	Ruppert et al. (2013)
<i>Juncus efuses</i>	Common rush	Artificial sewage	Methane and ammonium are emitted	Wiessner et al. (2013)
<i>Phragmites australis</i>	Perennial need grass	Organochlorines	1,2,4-Trichlorobenzene (TCB), γ -hexachlorocyclohexane (γ HCH), and 1,4-dichlorobenzene (DCB) are volatilized	San Miguel et al. (2013)
<i>Brassica juncea</i>	Mustard	Se	Additionally, <i>Brassica</i> spp. may cause Se to be phytovolatilized	Banuelos et al. (1997a, b)
<i>Scirpus robustus</i>	Saltmarsh bulrush	Se	Plants in wetlands	Arthur et al. (2005)
<i>Arabidopsis thaliana</i>	Thale cress	Cd, Pb	Cd and Pb tolerance	Song et al. (2003)

5 Phytoremediation of Inorganic and Organic Compounds

The word “phytoremediation” is a broad term and includes a wide range of methods used by plants to reduce, eliminate, or stabilize pollutants in water, soil, or the environment (Song et al. 2003). This technology incorporates natural mechanisms that plants and the related microbes breakdown and/or sequester inorganic and organic pollutants shown in Table 3, making it a less expensive and more ecologically friendly alternative to existing techniques of removing toxins from soil (Nwoko 2010). The results of studies on the potential of phytoremediation demonstrate that it can be used to remove a variety of pollutants, such as metals (Jadia and Fulekar 2009), organic compounds, radionuclides such as chlorinated solvents, toluene, xylene, ethylbenzene, polychlorinated biphenyl and BTEX-benzene (Chen et al. 2010), polyaromatic hydrocarbons (PAHs) (Denys et al. 2006), and pesticides (Chang et al. 2005). The ability of plants to ingest and/or collect organic and inorganic pollutants in their cellular structures, as well as to carry out profound oxidative degradation of organic xenobiotics (Kvesitadze et al. 2009), is necessary for phytoremediation to be successful. Although it may be feasible to overcome this by employing species with a quick growth cycle and high biomass (Olson et al. 2007), the primary disadvantage of phytoremediation is the amount of time it takes to reach the target concentrations.

5.1 *Phytoremediation of Organic Compounds*

Organic pollutants can be released into the urban systems by a variety of industrial processes, including the treatment of wood (Robinson and Anderson 2007), oil prospecting (Rogge et al. 1997), benzene, trichloroethylene (TCE), polyaromatic hydrocarbons (PAHs), xylene (BTEX), and others. Due to their extensive occurrence as a result of human activities and by-products of significant industrial processes, like the pyrolysis reaction, PAHs are the most prevalent organic pollutant in contaminated soils (dos Santos Barbosa et al. 2006). The fact that organic molecules come in a variety of structural and chemical configurations makes them difficult to remediate. The chemicals must be converted into nontoxic molecules, such as NH_4^+ , NO_3^- , CO_2 , and Cl^- (Meagher 2000), in order for phytoremediation to occur. With increasing molecular weight, they become less soluble (Werner 2003) because they become more hydrophobic and may get swollen to the soil (Neuhauser et al. 2006).

Pollutants move through the plant with transpiration fluid during the passive process, while transporters like carrier proteins are engaged in active transport (Nardi et al. 2002). This mechanism, which results in sluggish desorption of organic pollutants and little microbial decomposition, is crucial to the fate and transit of PAHs in soil (Hwang and Cutright 2002). Organic chemicals may become less labile and bioavailable as they deteriorate in soil; however, this would have less of an impact on their overall concentration. For instance, Cofield et al. (2008) found that the

Table 3 Selected examples of phytoremediation trials for different types of contaminants

Type of contaminants	Pollutants	Soil concentration (mg kg ⁻¹)	Scientific name of plant	Growth circumstances	Modification	Measure of success	Reference
Organic	PAH	1251.7	<i>Triticum aestivum</i> , <i>Zea mays</i> , <i>Vicia faba</i>	Field	None	PAH dissipated	Diab (2008)
	TPH	6400	<i>Lolium perenne</i>	Glasshouse	None	Loss of TPH	Hou et al. (2001)
	TNT	80	<i>Vetiveria zizanioides</i>	Spiked/ glasshouse	Urea	Urea aided in the removal of TNT	Das et al. (2010)
	Chrysene	500	<i>Trifolium repens</i> L, <i>Lolium perenne</i>	Spiked soil/ glasshouse	None	Degradation of chrysene	Johnson et al. (2004)
Inorganic	Zn, Cd	Zn-600, Cd-8	<i>Pennisetum atratum</i> , <i>Pennisetum americanum</i>	Spiked soil/ glasshouse	Basic fertilizer	Removal of metal	X. Zhang et al. (2010)
	Cd	1.6 ev	<i>Averrhoa carambola</i>	Field	N		J. Li et al. (2009)
	Zn, Cd, Pb	Zn -500, Cd-20, Pb-1000	<i>Vetiveria zizanioides</i> , <i>Dianthus chinensis</i>	Greenhouse	EDTA	Increased metal removal with EDTA	Lai and Chen (2004)
	Cu	1200	<i>Elsholtzia splendens</i>	Field, greenhouse	KH ₂ PO ₄ , urea	Removal of Cu	Jiang et al. (2004)
	Pb	20	<i>Vetiveria zizanioides</i>	Greenhouse	EDTA	Removal of metal	Gupta et al. (2008)

Mixed	Cu, PCD	Cu-300, PCP-100	<i>Lolium perenne</i> L., <i>Raphanus sativus</i>	Spiked/ glasshouse	Fertilized	PCP dissipates more quickly below 50 mg/kg as the concentration of copper rises	Q. Lin et al. (2006)
	Cu, PCP	Cu-300, PCP-100	<i>Lolium perenne</i> L., <i>Raphanus sativus</i>	Spiked/ glasshouse	Fertilized	PCP dissipates more quickly below 50 mg/kg as the concentration of copper rises	Q. Lin et al. (2006)
	Pyrene, Cd	CD-4.5, Pyrene-100	<i>Zea mays</i>	Spiked/ glasshouse	Fertilized: NPK	Pyrene uptake is increased when Cd is present	H. Zhang et al. (2009a, b)
	Cd, pyrene, phenanthrene	Cd-50, Phenanthrene-250, Pyrene-250	<i>Juncus subsecundus</i>	Spiked/ glasshouse	Fertilized	Cd has an impact on how PAH dissipates	Z. Zhang et al. (2011)

TPH total petroleum hydrocarbons, *EDTA* ethylenediaminetetraacetic, *PAH* polycyclic aromatic hydrocarbons, *PCP* pentachlorophenol, *TNT* 2,4,6 trinitrotoluene.

non-labile PAHs were unaffected whereas the total PAHs in the soil dropped when *Festuca arundinacea* and *Panicum virgatum* were present.

5.2 *Phytoremediation of Inorganic Contaminants*

In contrast to organic pollutants, which can be mineralized or decomposed, inorganic contaminants are made of minerals (Cunningham et al. 1996). Some plants are capable of transmitting, stabilizing, or collecting inorganic substances. For the latter, the plant species just has to tolerate the inorganic compounds and refrain from absorbing them, whereas hyperaccumulator plants have shown the capacity to accumulate large amounts of inorganic compounds and afterward eliminate the pollutants from the soil for the former (Ghosh and Singh 2005). Nickel is accumulated by the majority of hyperaccumulators, but others accumulate manganese, cadmium, zinc, and cobalt. One of the most researched hyperaccumulators is the zinc and cadmium hyperaccumulator, viz., *Thlaspi caerulescens* (A. S. Wang et al. 2006). Metal speciation within the soil is essential for preventing metal absorption. With the exception of mercury, plants may take up metals from the aqueous phase. Even when some critical metals are not present, there are signs of increased metal uptake in non-accumulating plants. One way that this happens is when plants alter the rhizosphere, releasing phytosiderophores or increasing acidity to make some metals more mobile (Marschner 2011). During the phytoremediation of inorganics, microbial communities in the rhizosphere may also be crucial (Whiting et al. 2001). Numerous glasshouse and laboratory investigations on the phytoremediation of inorganics have been successfully completed, as indicated in Table 3.

5.3 *Phytoremediation of Organic-Inorganic Mixed Contaminated Soils*

Since most sites are exposed to both organic and inorganic pollutants, phytoremediation of mixed polluted soils is essential (Chigbo et al. 2013). Phytoremediation may be impacted by the interaction of pollutants with one another, with plants, and with the rhizosphere when they are mixed or combined (Chigbo and Batty 2013). Additionally, it has been shown that dangerous metals like Cd, which promote microbial activity, significantly restrict the biodegradation of organic pollutants (Maslin and Maier 2000). The presence of appropriate, active microorganisms and favorable environmental conditions are crucial for the phytoremediation process because they facilitate the degradation of organic contaminants. Heavy metals were found to reduce the diversity and number of particular populations of microorganisms, according to (Dobler et al. 2000). Additionally, it has been demonstrated that mixtures of organic and inorganic pollutants have detrimental consequences,

including toxicity and an impact on plant growth. Chigbo and Batty (2013) revealed in a field investigation that the presence of metals like Pb, Cu, and Zn improved the elimination of hydrocarbon by *Populus deltoides* x *wettsteinii* and *Pinus sylvestris*. However, toxicity caused around 80% of the trees to perish. *Zea mays* L.'s root and shoot pyrene accumulation was demonstrated to be improved by cadmium, while plant-promoted rhizosphere biodegradation was found to be more crucial for pyrene dissipation (H. Zhang et al. 2009a, b), and utilizing a variety of plant communities could help solve the co-contamination problem. According to research, the microbial community in a plant's connected rhizosphere is influenced using the diversity of the plant (Kowalchuk et al. 2002).

6 Factors Affecting the Metal Uptake

Numerous variables such as plant species, temperature (Liao and Chang 2004), pH, the root zone (Sarma 2011), the addition of chelators, and cation exchange capacity (CEC) influence the accumulation of heavy metals using plants. These environmental factors' effects are described in Fig. 3:

Plant Species It is decided to use plant species with varying potentials for different cleanup techniques. Faster development in terms of plant mass, root depth per unit volume, lateral extension, and surface area is emphasized by processes such as rhizodegradation, rhizofiltration, and phytostabilization (Hasan et al. 2019), because it can extract and remove sizable amounts of heavy metals from sterile material. *Robinia pseudoacacia*, for instance, can be utilized successfully and ecologically to

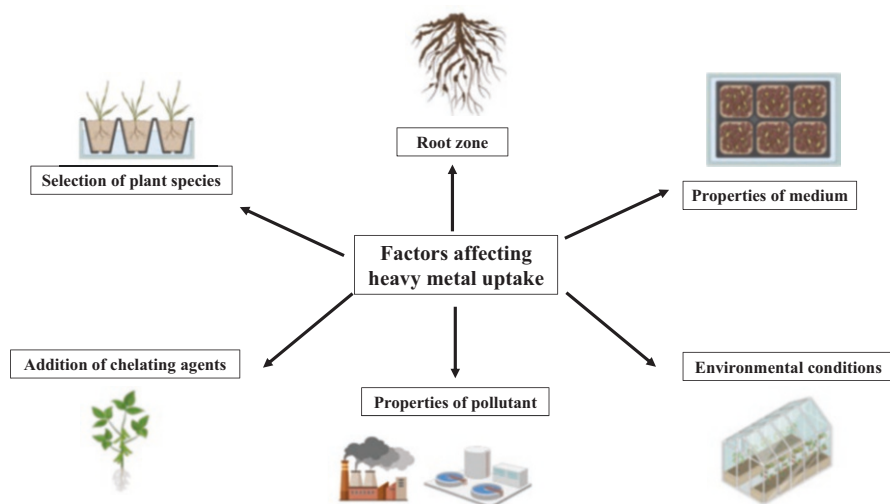


Fig. 3 Elements affecting the absorption of heavy metals

remediate sterile wastes (Babau et al. 2020). By producing enzymes and root exudates, the rhizobium should promote microbial development. Additionally, plants should have strong remediation potential, adequate biomass yield and storage, rapid growth, high waterlogging tolerance, and resilience to high salinity and pH (Gerhardt et al. 2017).

pH It is considered to be among the most significant impacting variables in retention and the solubility of heavy metals in soil. Higher pH results in more retention and less solubility (Basta and Gradwohl 1998), while lower pH makes hydrogen ions more accessible. For instance, pH has a significant impact on how well plants absorb Pb. With the use of lime, soil pH is raised to values between 6.5 and 7.0 in order to decrease the uptake of Pb by plants (Anton and Mathe-Gaspar 2005). Plants can raise the bioavailability of heavy metals by using root exudates to alter the pH of the rhizosphere and increase the solubility of the metals (A. Yan et al. 2020). The metal is subsequently absorbed at the metal surface and diffuses into the root cells via symplastic (active diffusion) and apoplastic (passive diffusion) channels through the cell membrane (Plant and Raiswell 1983). The solubility of metals is significantly influenced by soil pH and soil properties. Most heavy metals are easily transportable in acidic and oxidizing settings, but they are substantially maintained in alkaline and reducing environments (Brümmer and Herms 1983). Zn, Pb, Cu, Cd, Hg, and Co are all more soluble at pH 4–5 than they are in the range of pH 5–7 (Gerritse and Van Driel 1984).

Root Zone The root zone is crucial to phytoremediation because it metabolizes and absorbs down contaminants inside plant tissue or by releasing enzymes to break them down (Babau et al. 2020). The rate of cleanup must be based on the root zone. For instance, the fibrous root system contains a large number of little roots that cover impacts the entire soil, and offer a larger surface area, enhancing the plant's ability to make the greatest possible contact with the soil (Kvesitadze et al. 2006). Another phytoremediation method is the detoxification of soil pollutants using plant enzymes released from the roots (Benjamin and Leckie 1981).

Cation Exchange Capacity (CEC) CEC gauges the quantity of cations that can be maintained on soil particle surfaces or the rate of metal adsorption at the soil interface. Calcium absorption is decreased when Pb and Cu are added, according to research conducted by the scientific community (Salt et al. 1998).

Addition of Chelators Chelating agents are known to increase or speed up the uptake of heavy metals and are, therefore, known to be the cause of induced phytoremediation (Van Ginneken et al. 2007). Chelators have been employed to make metals more soluble, which might significantly increase the amount of metal that accumulates in plants.

Temperature A notable aspect that influences how much metal plants take up is soil temperature (Q. Wang and Cui 2011). For instance, a significant increase in the Cd and Zn content of sorrel and maize shoots has been documented during high temperatures and low soil pH (Sinha et al. 2013).

7 Plant Assortment Benchmarks for Phytoremediation “Candidate Plants”

Numerous plants have been employed to examine phytoremediation of xenobiotic contaminants in urban ecosystems, including poplar, *Leucaena*, rye grass, fescue, rice, and Indian mustard. Poplar trees provide excellent candidate for phytoremediation plants, according to a number of lines of evidence, as they produce a lot of biomass, have deep roots, and can withstand both organic and inorganic contaminants (Burken and Schnoor 1997). In phytoremediation, elements like root complexity, soil contaminants, soil, and local climate are crucial. Numerous studies have revealed that plants with shorter growing seasons than perennial plants are a better choice to be used in phytoremediation (Tordoff et al. 2000). It has also been advised to utilize species of plants that are appropriate to the regional or local soil characteristics of the location where decontamination is to be carried out (Compton et al. 2003). Because they are naturally equipped to withstand the stress conditions of the area and have low preservation costs, noninvasive species of plants should be chosen. In addition, native plants are more hospitable to humans and the environment than alien species (Haq et al. 2020). Additionally, according to numerous scientific studies, grasses grow more quickly than trees and shrubs, produce a large amount of biomass, are more resilient, and are better able to clean up different types of soil (Verbruggen et al. 2009).

8 Plants Known to Utilize in Phytoremediation

Organic and inorganic pollutants from soil can be eliminated by plants (Dary et al. 2010). The contaminant, the soil, and species of plants all affect the effectiveness of remediation. The efficiency of remediation is significantly influenced by plant biomass and metabolism, which in turn is influenced using electric conductivity, soil pH, organic matter content, microbial activities, and various soil enhancements (Anton and Mathe-Gaspar 2005; Guidi Nissim et al. 2018). The translocation factor, which is the ratio of elemental accumulation in the plant’s shoot compared to plant’s root, and the bioconcentration factor, which is the ratio of pollutant concentration in the plant parts to that in the medium, are typically used to assess the phytoremediation potential of the plants (Q. Wu et al. 2011).

9 Advantages of Phytoremediation

Because they make use of solar energy and the physiological processes of the plant, plants provide an environmentally benign alternative to the decontamination technologies and traditional ways for cleaning up the environment (Susarla et al. 2002).

Plants have the ability to reduce contaminants in a variety of media, including soil, air, and water. The use of phytoremediation may indirectly improve carbon sequestration since planting more plants to remove harmful contaminants from the environment will reduce atmospheric carbon dioxide levels. When phytoremediation and sustainable site management are integrated, the result is a larger range of advantages for the economy, the environment, and society as a whole (Burges et al. 2018). Some researchers proposed for the idea of tying phytoremediation to ecosystem services like carbon sequestration, fertility, water flow, and water purification. These services also include nutrient recycling (Tully and Ryals 2017). Monitoring metrics such as texture, pH, exchange capacity for cations, and the quantity and variety of the microbial community will reveal the indicators that represent the functionality and quality of the restored soil. Ecological risk assessment is used to evaluate the condition of the soil in a phytoremediated region, and Gutiérrez-Ginés et al. (2014) suggested the idea of long-term monitoring programs for the prediction of phytomanagement success. Table 4 shows many of the pros and cons of phytoremediation technology.

10 Limitations of Phytoremediation

Although phytoremediation offers a powerful alternative technique for removing contaminants from the urban ecosystems, it has a number of restrictions and disadvantages. For starter, the majority of research is done quickly and in a controlled atmosphere. This might not produce results that are true representative, even if it were done for a long time in the field. In order to determine the full potential of phytoremediation, more field studies based on longer time frame are required. Another drawback is that the success of phytoremediation is dependent on the plant species' ability to develop quickly and successfully. The exact phytoremediation method used for one type of plants at one site could not be effective at another due to differences in the soil and temperature at each location. It is therefore site-specific. In addition to soil and climate, other living things and microbes (pests, pathogens, and insects) on the site may have an impact on a plant's physiology. Combining viruses, insects, and pests with contaminants like heavy metals, organic pollutants, antibiotics, or radionuclides may render plants more susceptible to disease and imperil phytoremediation efforts. Additionally, plants can only grow at specific levels of pollutant concentration. The phytoremediation capacity of plants may be impacted by their slower growth due to their sensitivity to greater levels of pollutants (Greenberg 2001).

11 Field Testing and Risk Assessment

When creating transgenic plants, it's crucial to weigh factors like field testing and risk evaluation. Transgenic plant phytoremediation may have some benefits, although research on the potential biosafety risks is lacking (Davison 2005). Except for those created for herbicide degradation, no transgenic plant created for

Table 4 Pros and cons of phytoremediation technology

Phytoremediation techniques	Advantages	Limitations	Reference
Phytoextraction	Plants that produce hyperaccumulators can serve as resources	These plants grow more slowly, produce less biomass, and have shallow root systems There is a chance that certain metals will be phytotoxic	Newman (1997); Adams et al. (2000); Ghori et al. (2016)
Phytostabilization	It is an inexpensive and less disruptive technique Replanting helps the ecosystem recover	To prevent pollutant release, metal absorption, and transport to aboveground components, soil, vegetation, root zones, and root exudates must be continuously monitored Soil removal as well as hazardous materials and biomass are not necessary. Phytostabilization is seen as a stopgap action	
Rhizofiltration	Plants from both the land and the water can be utilized The methods employed are either ex situ (a designed tank system) or in situ (floating rafts on ponds)	For optimum metal absorption, a well-engineered design is necessary to regulate influent concentration, pH, flow velocity, chemical speciation, and interaction with other species	
Phytovolatilization	When contaminants are discharged into the atmosphere, they can be more efficiently analyzed, such as via photodegradation	A harmful metabolite or pollutant may build up in plants and then be transferred to subsequent goods like fruit or lumber. Low metabolite concentrations Been discovered in plant tissue	
Phytodegradation	A plant's enzymes may break down pollutants in an environment devoid of microorganisms	Toxic degradation or intermediate products are produced	
Rhizodegradation	Degradation of contaminants happens in situ and at the source Mineralization of the contaminant can happen	Although the end extent or degree of degradation may be identical in rhizosphere and non-rhizosphere soil, the rhizosphere might affect an increase in the beginning degradation rate when compared to a non-rhizosphere soil For a wide root zone to form, considerable time is needed	

phytoremediation of refractory xenobiotic contaminants has yet been commercially used. The risks connected to xenobiotic pollutant degradation by plants need to be thoroughly investigated (Davison 2005), and the degraded materials need to be less dangerous than the original contaminant. Prior to commercialization, it is also necessary to consider the risk of xenobiotic pollutant volatilization. Additionally, using chloroplast transformation to create transplastomic plants helps minimize the issue of genes escaping from transgenic plants to distant relatives or crop plants. Use of unpalatable species and appropriate fencing off of the area can help prevent some of the risk of wild animals ingesting transgenic plants.

12 Conclusions and Future Perspectives of Phytoremediation

One of the major worldwide issues affecting ecosystems, biodiversity, and human health is the organic and inorganic xenobiotics. Phytoremediation technology breaks down xenobiotics from urban ecosystems to become a less disruptive, more cost-effective, and environmentally friendly cleaning technology. Additionally, phytoremediation only requires a limited amount of specialized involvement and can be used for a long time. Transgenic techniques can be used to improve the molecular capacity of several plant species for cleanup. Genetically engineered species that have exhibited noticeably high tolerance and metal absorption capacity have been successfully created using gene editing, alteration, and deletion approaches. It will offer fresh and cutting-edge research techniques for improved outcomes through the following:

- Research into whether plants are highly resistant is necessary to determine whether they are appropriate for particular environmental circumstances. For the first identification of such species, *in situ* toxicity testing may be helpful.
- Comparing the phytoremediation technique to physicochemical methods, the phytoremediation technology symbolizes a practical and viable option to get benefits in both monetary and environmental terms.
- In the near future, the application of this method for soil remediation can be improved by more thorough investigations into the potentials and limitations of phytoremediation.
- Finally, the usage of genetically engineered plants can further take advantage of this plant-microbe relationship and provide quick solutions for cleanup.

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Bioremediation: An Alternative Tool for Restoration of Urban Agroecosystem Contaminated with Harmful Xenobiotics



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1 Introduction

Food is a source of energy and its continuous availability is crucial to sustain life on the earth. The production of food at a rate which could endure the gradually increasing human population is crucial. To increase food production, the concept of urban agriculture came into existence, which involves activity of food production and animal rearing done within the boundaries of a city (Saloman and Cavagnaro 2022). Urban agriculture, in addition to fortifying food production, facilitate development of sustainable cities, provide economic benefits to cultivar, and foster mitigation of climate change (Buscaroli et al. 2021; Saloman and Cavagnaro 2022). Urban agriculture includes community gardens, rooftop gardens, greenhouse, and vertical farming methods for crop cultivation (Lal 2020; Buscaroli et al. 2021). It has been approximated that almost 200 million people living in urban areas, particularly in developing nations, produce food through urban agriculture and fulfill 15–20% of world's food requirements (Ferreira et al. 2018). Like rural agricultural lands, urban agroecosystem is also affected with environmental pollution and unsustainable agricultural practices (Ferreira et al. 2018; Buscaroli et al. 2021). The agricultural activities, such as use of agrochemicals and untreated wastewater, contaminate plant-growing media and affect quality of the agricultural produce (Sachdev and Singh 2018a; Bibi and Ilyas 2020). For instance, substantial amounts of pesticides are used to reduce biotic stress, but only a small fraction actually works against target organisms, and the rest accumulates in the environment, affecting nontarget organisms (Sachdev and Singh 2016a, b; Sachdev and Singh 2018b). Moreover,

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activities allied to industrialization and urbanization have dramatically amplified the amount of xenobiotic compounds such as heavy metals, polycyclic aromatic hydrocarbons (PAHs), dyes, antibiotics, microplastics, phenols, and dioxins in urban agroecosystems (Buscaroli et al. 2021; Mishra et al. 2021; Anerao et al. 2022; Jayaramaiah et al. 2022).

Assimilation of toxic xenobiotics can degrade soil quality by negatively stimulating biotic diversity and their functioning (Qian et al. 2018; Shen et al. 2019; Sachdev et al. 2022a). Abridged soil quality, in turn, diminishes food quality and production rate. Even plants growing in contaminated matrix bioaccumulate these xenobiotics, which increases the risk of health hazards to consumers (Bibi and Ilyas 2020). Urban agricultural practices also involve use of wastewater, which often results in contamination of food produce with toxic xenobiotic compounds present therein. The deteriorating situation urges sustainable remedies to revive the functioning of the urban agroecosystem for production of nutritious food. Bioremediation of degraded or contaminated growth media is the best possible approach to accomplish the target of global food security. The present chapter aims to discuss the sources of xenobiotics in urban agroecosystem; their toxic implications on soil, plants, microorganisms, as well on humans; the challenges faced by conventional remediation methods; and benefits of using biological approaches for remediation.

2 Sources of Xenobiotic Contamination in Urban Agroecosystem

Industrial activities, agricultural practices, vehicular exhaust, and waste incineration are major anthropogenic sources that generate xenobiotics in urban agro-environment (Ferreira et al. 2018; Aboubakar et al. 2021; Orellana et al. 2022) (Fig. 1). For instance, dyes used in textiles and printing industries find their way to the environment through effluent discharge and land disposal, eventually contaminating surface water and soil used for urban agriculture (Dubey et al. 2010). Antibiotics which have been used in animal husbandry, agriculture, aquaculture, and beekeeping to protect animals from microbial diseases (Wang et al. 2019) are emerging as environmental contaminants (Carvalho and Santos 2016; Singh et al. 2021). Antibiotics enter agricultural soil through use of animal excreta as a manure and unsafe waste disposal (Xu et al. 2018; Lüneberg et al. 2018). Moreover, atmospheric deposition and industrial and traffic emission are indirect sources of urban soil pollution that introduce toxic xenobiotics in urban agro-environment (Ferreira et al. 2018; Buscaroli et al. 2021). In particular, xenobiotic like POPs (persistent organic pollutants) (by-product of waste combustion) (Buscaroli et al. 2021) that has the ability to travel long distance due to semi-volatile nature and high stability; remain present in water, soil, and air; and find their course to urban agro-environment, resulting in bioaccumulation in plant tissues (McLeod et al. 2014; Arslan et al. 2017).

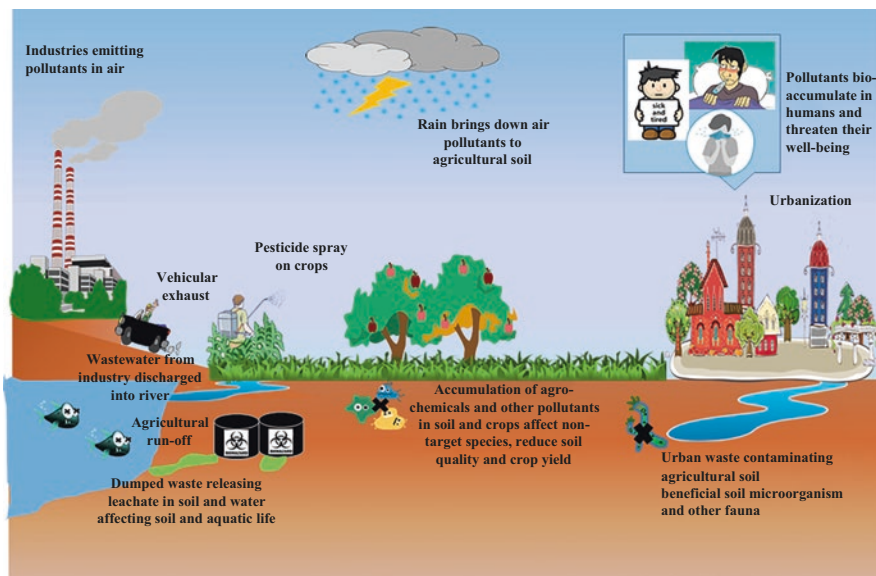


Fig. 1 Various sources releasing xenobiotics to agricultural soil which affect soil, flora and fauna, animals, humans, and other ecosystems

POPs have excellent affinity for organic matter and, therefore, remain in organic matter-rich soil for several years (Fabiotti et al. 2010).

Use of plastic films as mulch and/or in greenhouse introduces phthalate esters (PEs), another harmful xenobiotic compound, into urban agriculture (He et al. 2015a). Plastic films contain 20–60% phthalate esters (PEs) that are readily released in soil in the presence of solvent and heat (He et al. 2015a). Apart from plastic films, biosolids, wastewater, fertilizers, and pesticides are the source of PEs in urban agricultural soil (Park et al. 2011; He et al. 2015a). Heavy metals and metalloids such as cadmium (Cd), chromium (Cr), nickel (Ni), lead (Pb), zinc (Zn), copper (Cu), and arsenic (As) are significant xenobiotics (Safarik et al. 2011; Singh et al. 2016). Application of fertilizers, pesticides, industrial and municipal wastewater for irrigation, and fly ash and atmospheric deposition of vehicular exhaust introduce them to the urban agro-environment (He et al. 2015b; Liu et al. 2018; Aboubakar et al. 2021). With increase in human population and decrease in agricultural land, food production practices have been shifted from rural land to urban ecosystems. However, unsustainable human activities like injudicious use of resources and improper disposal of waste as a consequence have released xenobiotic into the urban environment, contaminating urban agroecosystem. Thus, there is a need to understand the health impacts of xenobiotic pollution on urban environment, particularly on agroecosystem and humans.

3 Associated Health and Ecological Risk of Soil Contamination

Soil contamination is a ubiquitous and a critical problem in both rural and urban agroecosystem as it affects soil potentiality to produce food and fodder. Urban soil is also known as anthropic soil due to anthropogenic regulation of its pedogenic processes, which disturb and drastically perturb soil characteristics (Lal 2020). Urban soil pollution takes place due to industries and vehicular traffic, which input loads of trace metals (Lal 2020). Contamination of soil with xenobiotics not only abridges soil productivity but also alters soil physicochemical properties and microbial community dynamics. For instance, prolonged application of fertilizers contributes to nutrient and heavy metal pollution that causes soil acidification due to nitrification of ammonium ions (NH_4^+), reduces soil organic carbon (SOC) content, and ultimately deteriorates soil quality, structure, fertility, and productivity (Chakraborty et al. 2011; Xin et al. 2016). The impacts of various xenobiotic compounds on soil and various living organisms including humans have been shown in Table 1.

3.1 *Effect on Soil Quality and Microbial Dwellers*

The quality of soil to a large scale is influenced by the residential microbial structure and composition (Qian et al. 2018). Microorganisms facilitate regulation of soil structure as well as fertility by participating in nutrient recycling, energy flow, organic matter composition, degradation of pollutants, and improvement of plant growth (Rebello et al. 2021). Contaminants present in soil affects structural as well as functional diversity of microbial population by disrupting cell membrane integrity, denaturing proteins, and altering metabolism, which in turn reduces nutrition absorption by plants (Xie et al. 2016). The development and activity of several soil-inhabiting microbes inhibit the xenobiotic contamination; however, different microorganisms have differential sensitivity toward toxicity. Labud et al. (2007) reported hindrance in microbial growth and hydrolase activity that facilitate cycling of nutrients in sandy soil and clayey soil due to the presence of gasoline (petroleum hydrocarbons), whereas diesel oil increased the activity of the enzyme in clayey soil alone at higher concentration. The study showed that different petroleum hydrocarbons had dissimilar effects on distinct microbes and was dependent on soil type. The presence of PEs, a refractory organic plasticizer, in agricultural soil as well as pesticides and antibiotics has been reported to inhibit the population size and enzymatic activity of microorganisms (Wang et al. 2016; Ge et al. 2020; Sazykin et al. 2021) by reducing soil basal respiration and activity of catalase enzyme due to impairment of their metabolic activities (Ahemad and Khan 2011; He et al. 2015b). The effect of six antibiotic residues on microbial and soil activities was studied by Liu et al. (2009), who observed significant reduction in soil respiration within

Table 1 Effect of xenobiotic compounds on soil, microbes, plants, and humans

Contaminants	Effect(s)	References
Cr	Negatively affected microbial carbon, mineralization, and soil enzymatic activity. 70%, 61%, and 43% reduction in dehydrogenase, alkaline phosphatase, and fluorescein diacetate were recorded, respectively	Dotaniya et al. (2017)
Cu, Pb, Zn	High metal concentration altered microbial community structure; negatively affected soil respiration and Chao1 diversity index	Chodak et al. (2013)
Pb	Inhibit growth and biomass of tea plants. Quality of tea depreciated due to increase in catechin content and slight decrease in caffeine and amino acid content	Yongsheng et al. (2011)
60% bromoxynil + 3% prosulfuron	Reduced microbial population and dehydrogenase activity	Pampulha and Oliveira (2006)
Herbicides (glyphosate), insecticides (imidacloprid), and fungicides (hexaconazole)	Continuous reduction in plant growth-promoting (PGP) activities of <i>Bradyrhizobium</i> MRM6 except exopolysaccharide production was reported with increase in pesticide concentration, and the maximum toxicity was reported at concentration threefold higher than recommended doses	Ahemad and Khan (2011)
Fenitrothion-organophosphate insecticide	Abridge seed germination as well as seedling vigor, nonenzymatic antioxidants content in soybean	Dhungana et al. (2016)
Pendimethalin herbicide	Seed germination of <i>Zea mays</i> L. cv NAAC 6002 was reduced by 69% at concentration 10 ppm probably due to degradation and mobilization of seed reserves	Rajashekar and Murthy (2012)
Oxytetracycline, doxycycline hydrochloride, ofloxacin, enrofloxacin lactate	Significant inhibition of root and bud elongation of cucumber, Chinese cabbage, and rape	Wang et al. (2019)
Ciprofloxacin, enrofloxacin, levofloxacin	Antibiotics individually and in combination significantly reduced wheat plant growth by inducing oxidative stress and damaged physiological structure of the plant at young stage	Riaz et al. (2017)
Chloramphenicol, spiramycin, spectinomycin, vancomycin	Presence of antibiotic at different concentrations does not affect tomato seed germination but impaired root elongation at concentration 10 mg/L and above	Bellino et al. (2018)
Petroleum hydrocarbons	Increase in concentration of total petroleum hydrocarbon (TPHs) reduces microbial count and urease activity	Guo et al. (2012)
Herbicide Lumax 537.5 SE	Interfered with soil microbial equilibrium by changing colony developing index of various microorganisms and ecophysiological diversity index of fungi. Strongly inhibited dehydrogenase activity and growth of <i>Zea mays</i> . The effect of three active compounds was low to negligible on β -glucosidase, arylsulfatase, catalase, and phosphatase enzymes	Borowik et al. (2017)

(continued)

Table 1 (continued)

Contaminants	Effect(s)	References
Organochlorine pesticides (OCPs), polychlorinated naphthalene (PCN)	Presence of such contaminants in wheat and rice was found to be related with the marginal risk of cancer in humans	Mehmood et al. (2017)
OCPs, polychlorinated biphenyl, octachloro-p-dibenzodioxin	Adverse effect on liver due to dysfunction of marker bilirubin, alkaline phosphatase, and alanine aminotransferase	Kumar et al. (2014)
Polychlorinated biphenyls (PCBs)	Prenatal exposure to PCBs has negative effect on early psychomotor development due to potential neurotoxicity at low dose	Forns et al. (2012)
OCPs	Exposure of humans to OCP residues was associated with the risk of gallstone disease	Su et al. (2012)

4 days of exposure and inhibition of phosphatase activity. Reduced microbial activity in turn decreases soil organic matter, inorganic carbon and nitrogen, soil porosity, and fertility (Wang et al. 2016; Qian et al. 2018).

Presence of heavy metal(loid)s above threshold level in soil has also shown toxicity toward microorganisms by inhibiting cellular functions and enzymatic reactions (Gao et al. 2010), thereby reducing soil microbial diversity. Heavy metal(loid) reduces dehydrogenase, phosphatase, and urease enzyme activities in soil, which mediate transformation of different nutrients into the form which is easily accessible by the plants (Gao et al. 2010). Pollution of soil with toxic metals even at modest concentration affects microbial activity (McGrath et al. 1995). Nitrogen fixation activity of free-living heterotrophic bacteria, symbiotic N_2 -fixing bacterium *Rhizobium leguminosarum* bv. *trifolii*, and free-living phototrophic cyanobacteria were reported to be inhibited completely, reduced by several folds, and reduced to half, respectively, in the presence of different concentration of heavy metals (McGrath et al. 1995; Singh et al. 2020). Further, the presence of multiple pollutants in soil could enhance their toxic implications on microbial population (Lu et al. 2013). Contamination of urban soil used for agricultural activity with xenobiotics not only alter the physicochemical activities of soil but also hamper the biological characteristics, which diminishes the soil fertility.

3.2 Influencing Plant Growth and Development

Plants thriving in the urban agro-environment are encountered with multiple stresses. To promote their growth and reduce impact of environmental cues, agrochemicals, animal manure, municipal solid waste, and wastewater are used in urban agriculture (Ferreira et al. 2018). Although use of agrochemicals and other materials reduces intervention of stress and increases plant productivity, it induces several deteriorating effects on plant physiology (Gupta et al. 2019). Moreover,

unintentional inputs of xenobiotic compounds such as PAHs and dioxins through atmospheric deposition, traffic exhaust, and landfill dumping to water and soil, which are used for urban agriculture, affect plant growth and development (Langenbach 2013; Ferreira et al. 2018). Pesticides, heavy metals, antibiotics, and PAHs, such as pyrene and phenanthrene, affect biochemical, physiological, and morphological functions of plants, damage cell organelles, and decelerate plant growth and development that ultimately abridge crop produce (Parween et al. 2016; Shahzad et al. 2018; Nikolaeva et al. 2021; Carballo et al. 2022). Certain heavy metals display tendency to be easily absorbed by the plants and bind with a sulfhydryl group of protein that disrupts structure of enzymes and inhibit their functioning (Shahzad et al. 2018). Heavy metals also mediate generation of reactive oxygen species (ROS), particularly, superoxide radicals ($O_2^{\cdot-}$), hydrogen peroxide (H_2O_2), and others in plants, which disrupt cell membranes and other macromolecules by peroxidation (Shahzad et al. 2018; Sachdev et al. 2021; Sachdev et al. 2022b). Antibiotics and dyes released into the urban agricultural environment have demonstrated negative influence on plants. Liu et al. (2009) studied the effect of six antibiotics (sulfamethoxazole, sulfamethazine, trimethoprim, tetracycline, tylosin, and chlortetracycline) on rice, cucumber, and sweet oat. The result revealed inhibition of seed germination by all the antibiotics, and three of them (sulfamethoxazole, sulfamethazine, and trimethoprim) displayed toxic effects on plant growth. Toxic effect was more pronounced on rice and sweet oats than on cucumbers. Analogously, the toxicity of textile dyes (azo dyes and anthraquinone dyes) on plant physiology was studied by Copaciu et al. (2013) who observed reduction in stomatal conductance, net assimilation rate, photosynthesis, and photosynthesis pigments of wheat in the presence of azo dyes especially with those which contain Cr ions. Presence of xenobiotics in urban agroecosystem eventually interferes with the physiological and biochemical activities of plants, influencing their productivity. Moreover, it elevates the chances of bioaccumulation of toxic compounds in food chain, threatening health and life of consumers.

3.3 *Effect on Humans*

Contaminants present in urban agricultural soil are absorbed by the plants and move into the food chain (Arslan et al. 2017). Humans, being the top consumers, are at the maximum risk of exposure due to bioaccumulation of contaminants (Peralta-Videa et al. 2009). Presence of xenobiotics like phthalates and POPs in the food chain can cause toxicity in humans (Varjani et al. 2017; Wang et al. 2018a). Due to recalcitrant and lipophilic nature of POPs, they are easily absorbed by the adipocyte tissue and gastrointestinal tract and get bioaccumulated (Varjani et al. 2017), resulting in metabolic disorders. POPs can cross the placenta and expose the fetus to toxicants before birth and even after birth through breastfeeding, causing severe damages (Carré et al. 2017). Several pesticides are reported to be an endocrine disrupter, neurotoxic, cytotoxic, genotoxic, and carcinogenic compounds that can cause oxidative stress in

humans. Pesticides like organophosphate and carbamate have potential to irreversibly inhibit the activity of acetylcholinesterase (AChE) enzyme, which affect the nervous system and impairs functioning of peripheral organs like the lungs (Chakraborty et al. 2009; Jayaraj et al. 2016). Similarly, metals present in agricultural produce on ingestion induce toxic effects in humans by interfering with normal body functions (Duruibe et al. 2007). Metals on ingestion get converted into stable form in the stomach due to acidic conditions and bind with protein and enzymes forming strong and stable bonds (Duruibe et al. 2007). This results in inhibition of enzymatic activity, which eventually causes toxicity in humans (Jaishankar et al. 2014). For example, lead (Pb) can enter in a body via ingestion of contaminated food and affect the nervous systems, renal function, cardiovascular and reproductive system, synthesis of hemoglobin, and gastrointestinal tract causing psychosis, oxidative stress, paralysis, birth defect, kidney dysfunction and damage, hypertension, arthritis, autism, and mental retardation (Duruibe et al. 2007; Khanam et al. 2020).

As the contamination of soil has become a ubiquitous problem in the urban environment, there is a need to restore its attributes to promote local farming practices. Soil remediation is a process of soil cleanup, which focuses on reduction or elimination of contaminants for the restoration of structure and function of the ecosystem. Soil remediation is achieved through adopting various physical and chemical means (conventional methods) and biological approaches either individually or in combination. The type of method that can be adopted for soil remediation depends on factors such as nature, toxicity potential, and origin of contaminant, their concentration, physicochemical properties of soil, land uses, time required for restoration process, and social and economic benefits attained (Lombi and Hamom 2005).

4 Conventional Methods for Remediation of Contaminated Soil and Their Limitation

Physical and chemical procedures that are either used on-site (in situ) or off-site (ex situ) are common approaches used to treat contaminated urban soil. Chemical procedures involve treating contaminated soil with various acids, liquids, chelating, or leaching agents, while physical approaches include soil immobilization, replacement, and/or thermal desorption. Commonly used conventional techniques for soil remediation involve capping of contaminated soil on site known as cap and contain method, landfill dumping, soil replacement, chemical leaching (soil washing), electrokinetics, vitrification, oxidation/reduction, immobilization, and many more (Lombi and Hamon 2005; Koul and Taak 2018; Sharma et al. 2018). The common conventional physicochemical approaches for soil remediation with their advantages and disadvantages are presented in Table 2.

Heat treatment can be used to eliminate xenobiotic substances from soil. Thermal desorption is a physical method wherein high temperature (300–400 °C) causes evaporation of volatile contaminants from soil which are collected by desorption

Table 2 Advantages and limitations of conventional physicochemical approaches used for soil remediation

Treatment method	In situ/ ex situ	Contaminants treated	Advantages	Disadvantages	References
Physical methods					
Landfill dumping	Ex situ	Inorganic and organic materials	Prevent potential leakage and groundwater contamination	Risk of excavation, handling, and transport of hazardous materials; high disposal cost; space requirement for dumping; continuous monitoring required; and can only be opted if content of free liquid is low	Lombi and Hamon (2005); Liu et al. (2018) and Fenyvesi et al. (2019)
Surface capping and encapsulation	In situ	Heavy metals, radionuclides, heavy petroleum hydrocarbons, PAH	Prevent exposure of contaminated soil with environment and water infiltration	Require continuous monitoring and maintenance to prevent leaching and volatilization of contaminants; soil no longer support plant growth; costly technique	Liu et al. (2018)
High-temperature incineration/thermal desorption	In situ/ ex situ	Heavy metals and organic pollutants	Simple and efficient process, large volume of soil can be treated, decontaminated soil can be reused	High cost; production of gaseous pollutants; reduces soil organic matter; time-consuming method; affect microbial population of soil	Yao et al. (2012) and Dhaliwal et al. (2020)
Vitrification	In situ/ ex situ	Heavy metals, radioactive and organic pollutants	Highly efficient method suitable for treating heavy metals and radioactive materials	Intensive energy is required; complicated; expensive; decontaminated soil cannot be used for agriculture; this technique cannot be used to treat soil containing high organic matter; high moisture, volatile, or inflammable organics	Liu et al. (2018) and Dhaliwal et al. (2020)

(continued)

Table 2 (continued)

Treatment method/ dilution	In situ/ ex situ	Contaminants treated	Advantages	Disadvantages	References
Soil replacement/ dilution	In situ	Heavy metals and organics	Reduce contaminant concentration	Increase volume of contaminated soil; costly technique; suitable only for small areas with heavy pollution load	Lombi and Hamon (2005) and Yao et al. (2012)
Electrokinetic extraction	In situ	Heavy metals, pesticides, certain organic and inorganic pollutants	Suitable for soil with low permeability and hydraulic conductivity; less time-consuming; cost-effective technology with ease in installation and operation	Require high-energy inputs; efficiency is low; create thermal hotspot around electrodes and alter soil pH hence affect soil environment	Liu et al. (2018); Fenyvesi et al. (2019) and Dhaliwal et al. (2020)
Chemical methods					
Chemical oxidation	In situ/ ex situ	Heavy metals and organic pollutants such as pesticides, PAH, VOCs, etc.	Simple method and reproduce quick results; enhance solubility and availability of contaminants at subsurface enhancing biodegradability; convert toxic and hazardous contaminants into less toxic or nonhazardous compounds	Use of excessive oxidants may adversely affect environment (microbes); costlier technique; not effective for soil with low permeability and heterogeneity	Pavel and Gavrilescu (2008); Liu et al. (2019) and Fenyvesi et al. (2019)
Chemical dehalogenation	Ex situ	Halogenated compounds like pesticides, polychlorinated dibenzofurans (PCFs), dioxins	Convert toxic and hazardous pollutants into nontoxic or nonhazardous compounds	Efficiency is low in soil with high water, clay, and organic content; not cost-effective for large volume contaminants	Pavel and Gavrilescu (2008) and Fenyvesi et al. (2019)

<p>Chemical immobilization or chemical fixation (solidification/stabilization)</p>	<p>In situ/ex situ</p>	<p>Inorganic (heavy metals, leachable metals) and some organic compounds</p>	<p>Reduce availability of contaminants to plants, microbes, and water; less time-consuming method; remediate soil even with low pollution load; cost-effective</p>	<p>Reduces land utility for agricultural purpose; immobilized contaminants may mobilize due to action of environmental factors</p>	<p>Liu et al. (2018) and Ossai et al. (2020)</p>
<p>Chemical leaching (soil washing/soil flushing)</p>	<p>In situ/ex situ</p>	<p>Heavy metals and organics</p>	<p>Cost-effective; short-duration process; recovered fluid can be reused</p>	<p>Require sequential washing with different solutions; not effective for soil with low permeability, heterogeneity and pollutants that partition strongly to soil surface; require efficient collection system to prevent migration of pollutants and toxic extraction fluid to uncontaminated zone</p>	<p>Liu et al. (2018) and Fenyvesi et al. (2019)</p>

(Yao et al. 2012; Sharma et al. 2018; Ossai et al. 2020). At 60 °C, ex situ thermal desorption of PCB-contaminated soil in the presence of 1% calcium hydroxide showed 94% PCB elimination (Liu et al. 2019). Incineration and pyrolysis of contaminated soil are other heat-based remediation methods which operate at very high temperature, either in the presence of low oxygen level or no oxygen, respectively. Incineration at temperature 870–1200 °C causes complete disfigurement of organic compounds, for instance, chlorinated hydrocarbons, petroleum compounds, dioxins, and others due to burning or combustion (Ossai et al. 2020). Heat treatment is an effective method, but high operating temperature, production of gaseous pollutants, and reduction of soil quality are some major associated drawbacks (Zhao et al. 2019). Vitrification method applied to remediate soil also requires high-temperature (1700–2000 °C) inputs. It involves melting of contaminants like heavy metal(loid)s and radioactive wastes into molten lava on subjection of very high temperature followed by rapid cooling resulting in the formation of glass-like solids or vitrified products (Sharma et al. 2018). Vitrification results in destruction of organic materials and encapsulation of heavy metals in product form (Liu et al. 2018).

Electrokinetics is a physical technique for elimination of contaminants, particularly, heavy metal(loid)s, and PAHs from soil. Contaminants under influence of electric gradient moves toward cathode or anode via electromigration, electroosmosis, and electrophoresis and then easily recovered from the electrodes (Yao et al. 2012; Sharma et al. 2018). The limitation of electrokinetic remediation is the poor separation of pollutants from soil; however, pre-acidification of soil or use of enhancing agents such as nonionic surfactant can enhance the competence of the technique (Sharma et al. 2018). Soil replacement for reduction of pollutants load from soil includes three different methods, viz., (1) removal of contaminated soil, (2) augmentation of non-polluted soil to dilute pollutant concentration, and/or (3) deep burrowing/soil spading leading to degradation of contaminants. Soil replacement method can only be used for reclamation of heavily contaminated small areas and is an expensive technique (Yao et al. 2012). Further, the contaminated soil that has been removed requires adequate treatment; otherwise it can lead to secondary pollution, which could detrimentally influence the urban environment (Sharma et al. 2018). Apart from these techniques, landfill dumping, surface capping and encapsulation, steam-induced volatilization, and vacuum pumping are some other physical methods, which can be applied for restoration of contaminated soil (Ossai et al. 2020).

Traditional chemical procedures for removing pollutants from soil include leaching (soil washing or soil flushing), oxidation/reduction, fixing, and dehalogenation through application of different chemicals (Song et al. 2017; Dhaliwal et al. 2020). Immobilization or fixing by chemical agents or organic amendments (silica, lime, metallic oxides) immobilizes or reduces mobility and solubility of contaminants due to solidification, precipitation, or enhanced surface sorption property (Khalid et al. 2017; Koul and Taak 2018; Liu et al. 2018; Sharma et al. 2018). Chemical immobilization involves multiple mechanisms of precipitation, ion exchange, complexation, and adsorption (Khalid et al. 2017). Precipitation is a cost-effective, simple, nontoxic, but time-consuming method, which generates secondary waste,

results in aggregation of different metal precipitates, has poor settling rates, and has gradual sludge degradation (Sharma et al. 2018). The ion exchange method reduces contamination load by replacing toxic ions with nontoxic ions in soil. For instance, use of zeolite can exchange cations like Cu, cobalt (Co), Zn, and manganese (Mn) from soil (Sharma et al. 2018; Belviso 2020). However, ion exchange techniques possess some drawbacks such as pH sensitivity, membrane fouling, and nonselectivity of membrane (Sharma et al. 2018). Chemical leaching (soil washing) is a process of dissolving pollutants in fluids, solvents, or gases such as ethylenediaminetetraacetic acid (EDTA), citric acid, and calcium chloride, which are extracted later (Khalid et al. 2017). This procedure involves digging up polluted soil and treating it with the appropriate chemicals for a set period of time, depending on the kind of soil and pollutant (Khalid et al. 2017). Then pollutants are leached out from the soil to solvent via methods like ion exchange, adsorption, and chelation (Khalid et al. 2017). Chemical leaching is a competent and cost-effective technology for soil remediation. Chemical oxidation is a process of soil remediation which involves oxidation-reduction reaction to change hazardous compounds into nonhazardous and nontoxic form. Oxidizing agents commonly used for decontamination of soil are ozone, Fenton reagents, H_2O_2 , sodium persulfate, and permanganate (Ferrarese et al. 2008). Chemical oxidation has multistep processes that include formation of several intermediates which influences the activity of the oxidant (Kluck and Achari 2004). The physicochemical techniques used for remediation of soil are effective in reducing the level of xenobiotics in urban environment; however, these approaches are not sustainable and cost-effective. Therefore, switching to alternative and eco-friendly approach like bioremediation is prerequisite to manage xenobiotic pollution of urban agroecosystem.

5 Bioremediation

Bioremediation is a process whereby toxic and undesirable contaminants present in the environment are degraded or transformed into nontoxic compounds on action of living organisms and/or their enzymes (Sharma et al. 2018; Zhang et al. 2020; Usmani et al. 2021). Bioremediation is a safe, simple, effective, and low-cost technique that can restore contaminated urban soil into its original settings without compromising with the quality of the environment (Jobby et al. 2018; Letti et al. 2018). Bioremediation can be done either on-site or off-site. Bioremediation processes can be assisted by plants and/or microorganisms. Several plants and microbes, for instance, actinomycetes, bacteria, fungi, and algae, can catabolically degrade, immobilize, accumulate, or transform various xenobiotic compounds such as PAH, PCB, dyes, pharmaceutical compounds, heavy metals, petroleum products, and antibiotics present in urban soil (Usmani et al. 2021; Orellana et al. 2022). Microorganisms break down pollutants into metabolic intermediates or generate end products, which are utilized as substrates for their cell growth (Morsi et al. 2020). Plants and/or microorganisms can be applied either individually or in

consortia for bioremediation (Razmi et al. 2021). Selection of microbial strain and/or plant species for bioremediation depends on factors like their stress tolerance ability, density of indigenous microbial population, soil physicochemical properties, plant biomass, accumulation potential, prevailing environmental conditions (temperature, relative water content, redox potential), degrading potential, and bioavailability, quantity, and toxicity of contaminants (Sarwar et al. 2017; Razmi et al. 2021). For instance, increase in temperature increases bioavailability of PAH and metals, and optimum temperature condition promotes microbial bioremediation due to enhanced microbial metabolism and enzyme activities (Liu et al. 2017).

5.1 Microbial Bioremediation of Xenobiotics Contaminants in Urban Soil

Microbial bioremediation involves techniques like natural attenuation or bioattenuation, bioaugmentation, biostimulation, bioventing, and biopiling to clean contaminated soil (Dzionek et al. 2016; Jaiswal and Shukla 2020) (Fig. 2). Natural attenuation refers to the remediation process that uses native microorganisms (Dzionek et al. 2016). Due to the low population density of bacteria that degrade

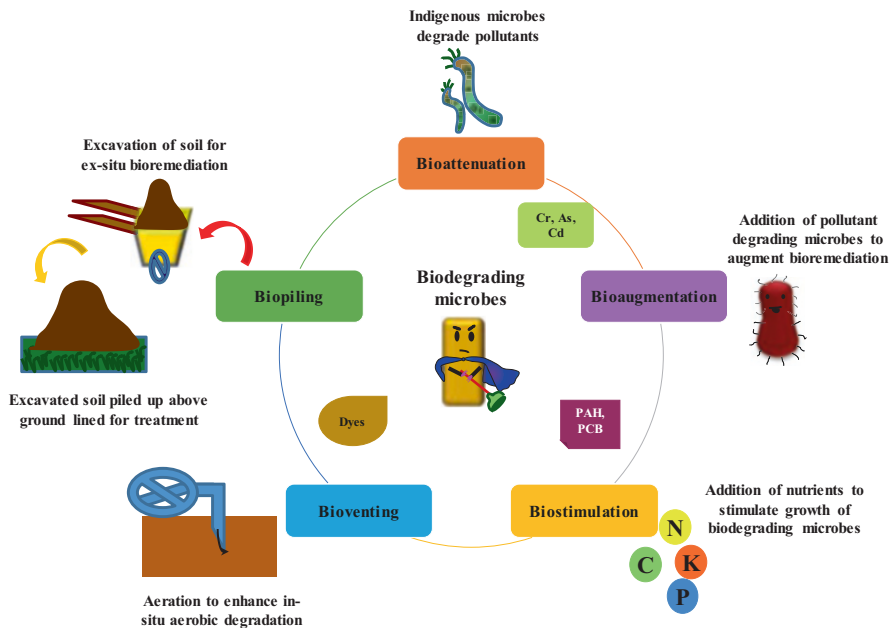


Fig. 2 Different in situ/ex situ methods for bioremediation of xenobiotics. Cr chromium, As arsenic, Cd cadmium, PAH polycyclic aromatic hydrocarbon, PCB polychlorinated biphenyl, N nitrogen, C carbon, K potassium, P phosphorus

contaminants, the process is slow and takes a long time (Dzionic et al. 2016). By modifying the physical, chemical, and biological features of the contaminated soil, biostimulation and/or bioaugmentation is used to hasten and improve the efficiency of microbial decomposition (Dzionic et al. 2016). Bioaugmentation entails adding effective pollutant-degrading bacteria, such as wild strains, while biostimulation involves changing the physical and chemical features of soil by adding nutrients and/or electron acceptors (Dzionic et al. 2016). Bioventing is an in situ technique which includes regulated aeration of soil to enhance activity of aerobic microorganisms (Abatenh et al. 2017). The techniques like land farming, biopiling, and composting are ex situ methods for microbial degradation that involve excavation of contaminated soil to aboveground lined treatment area, amendment of nutrients, and aeration to enhance the microbial growth and activity (Abatenh et al. 2017). In addition to direct utilization of microbes for bioremediation, application of their enzymes has demonstrated several folds more benefits than a living cell (Thatoi et al. 2014). The enzymes employed for bioremediation include oxygenases, dehydrogenases, laccases, reductase, and manganese peroxidases (Thatoi et al. 2014).

Bacteria (species like *Acinetobacter* sp., *Bacillus*, *Brevibacterium*, *Pseudomonas*), fungi (*Trichoderma* spp., *Pleurotus ostreatus*, *Aspergillus* spp.), and algae (*Chlorella vulgaris*) play an instrumental role in reclamation of polluted urban soil by removing toxic metal(loid)s, petrochemicals, and pesticides (Kapahi and Sachdeva 2019; Sachdev and Singh 2020; Orellana et al. 2022). Metal(loid)s are nondegradable contaminants, which can only be changed from one oxidation state to another, which reduces their toxic effect, solubility, and bioavailability (Chibuikwe and Obiora 2014). Several microorganisms have potential to alter metal speciation through production of enzymes and metal chelating ligands (siderophores, metallothionein, phytochelatin, porphyrins), and redox reaction, leading to change in metal solubility, mobility, and toxicity (Gadd 2010; Juwarkar and Yadav 2010; Balzano et al. 2020). Fungi like *Klebsiella oxytoca* can biotransform heavy metal(loid)s into less toxic compounds and utilize by-products for their own growth (Kapahi and Sachdeva 2019). Biotransformation includes redox conversion of inorganic compounds to organic form and vice versa through methylation/demethylation (Juwarkar and Yadav 2010). The enzymes biosynthesized by microbes reduce oxidized metals via electron transfer and transform them from soluble compound to insoluble form, thereby enhancing their precipitation and extraction from solutions (Juwarkar and Yadav 2010). The fungus *Pleurotus florida* has been reported to mitigate the metal pollution from urban sewage, used for agricultural purposes (Adhikari et al. 2004). Similarly, certain bacterial isolates are documented to reduce Cr (VI) and selenite (Se^{2-}) to Cr (III) and selenium (Se), respectively (Chibuikwe and Obiora 2014). In addition to enzymes, microbes secrete iron chelating siderophores that increase mobility and bioavailability of metals, thus, assisting in their removal from soil (Ojuederie and Babalola 2017). Microbes can also remove metals from soil by binding with them passively through biosorption or actively via bioaccumulation and/or by employing both mechanisms in combination (Juwarkar and Yadav 2010). Biosorption and bioaccumulation ultimately leads to immobilization of inorganic compounds (Francis and Nancharaiiah 2015; Shukla et al. 2017). Bioaccumulation

of Cd, Cr, Co, As, and Fe by algae *Chlorella colonialis* was reported by Jaafari and Yaghmaeian (2019). Microorganisms may sequester metals directly inside the cell or bind them on their surface through adsorption and then accumulate them inside cytoplasm (Balzano et al. 2020). Within the microbial cell, metals are detoxified by an intracellular detoxification system consisting of metal-binding protein like metallothioneins (Juwarkar and Yadav 2010).

Biodegradation of organic contaminants by microorganisms takes place through aerobic and anaerobic metabolism (Kang 2014). Anaerobic metabolism involves reductive dechlorination approach to degrade chlorine-containing compounds that can accept electrons (Kang 2014). Anaerobic bacteria belonging to *Dehalococcoides* genus have been reported to completely convert dechlorinate trichloroethylene (TCE) into harmless compounds (Wang et al. 2018b). At the same time, aerobic metabolism prompts degradation of organic compounds via catabolic enzymes (Kang 2014). For example, *Pseudomonas* spp. use toluene oxidases to oxidize chlorinated hydrocarbons into carbon dioxide and chloride ions (Shim and Wood 2000). Biodegradation of organic pollutants by microorganisms takes place after adsorption in two different ways (Ren et al. 2018). First includes desorption of pollutants in aqueous form with the help of biosurfactant after sorption from soil, which later followed by microbial degradation. Second method includes biodegradation of adsorbed organic materials directly by action of living cells or their extracellular enzymes (Ren et al. 2018). The extracellular enzymes produced by *Brevibacterium* sp. have been found to rapidly degrade insecticide fenamiphos after its immobilization through sorption by surfactant cetyltrimethylammonium-modified montmorillonite clay (CTMA-clay) (Singh et al. 2003). The enzyme manganese peroxidase extracted from fungus *Anthracoxyllum discolor* immobilized on nanoclay has been reported to degrade PAHs, namely, pyrene, anthracene, fluoranthene, and phenanthrene by >86%, > 65%, <15.2%, and < 8.6%, respectively (Acevedo et al. 2010).

Individual microorganisms can degrade or transform particular compound; however, mixed populations or consortia of microbes can enhance biodegradation process under multiple environmental cues (Villaverde et al. 2018). Therefore, bioaugmentation is required for a better remediation process. The biodegradation of pesticide phorate ranging 97.65–98.31% was achieved on inoculation of microbial consortia comprising three bacterial species, viz., *Pseudomonas fulva*, *Brevibacterium frigoritolerans*, and *Bacillus aerophilus* (Jariyal et al. 2018). Further, to speed up the rate of microbial remediation, biostimulation is often a requisite. It has been observed that in some cases, to improve degradation of poorly degradable hydrocarbons, co-substrates which can be easily accessed as carbon and energy source by microorganisms are added to contaminated soil (Liu et al. 2017). The PAH like anthracene, pyrene, and fluoranthene cannot be degraded as only carbon source by *Micrococcus* sp. PHE3; however, addition of naphthalene and phenanthrene has been observed to enhance the degradation of all PAHs at the rate >90%, over a 10-month incubation time period (Zhang et al. 2013). Analogously, addition of biosurfactants enhances the microbial degradation of PAHs from 57% to 86.5% after 45 days of incubation (Bezza and Chirwa 2016). Nevertheless, in some

instances, production of intermediates during the breakdown process negatively stimulated degradation rate ascribed to their intrinsic toxic effect on microbial population (Liu et al. 2017). For instance, accumulation of an intermediate phthalate ester (PAE) can hold back the degradation of pyrene (Wen et al. 2011). The microorganism-based bioremediation of contaminated environment is sustainable and less energy-intensive. Application of microbial bioremediation could alleviate array of xenobiotic compounds by implementing different mechanisms. Moreover, this method occurs naturally and do not require continuous monitoring. However, like other processes, microbial remediation suffers certain limitations. The process of microbial remediation is a slow process, it results in production of toxic intermediates, indigenous microbial population involved cannot remediate a wide range of xenobiotics, and augmented microbial species are sometimes unable to colonize the new ecological niche. Thus, there is a need to improve the potential of bioremediation by involving advanced scientific approaches.

5.2 *Phytoremediation of Xenobiotic Accumulating in Urban Soil*

Phytoremediation is an approach that harness plant potential to eliminate toxic compounds from environmental matrices (Tripathi et al. 2020). Plants derive nutrients and water from soil via roots, which also led them to release enzymes into the soil that assist in extraction, immobilization, degradation, and/or volatilization of contaminants (Santiago-Cruz et al. 2014). Phytoremediation can be done to remediate urban soil contaminated with metal(loid)s, petrochemicals, pesticides, POPs, and PAHs (Santiago-Cruz et al. 2014). Phytoremediation not only assists in cleanup of contaminated soil but also improves its physicochemical and biological properties by enhancing biological activities, organic matter content, nutrient level, etc. (Burges et al. 2018). Phytoremediation reclaims polluted soil through employment of various strategies including phytoextraction, phytostabilization, and phytodegradation (Nikolic and Stevovic 2015; Padoan et al. 2019; Razmi et al. 2021) (Fig. 3).

Phytoextraction is an in situ process, which include accumulation, sequestration, or absorption mechanism for treatment of soils, particularly, contaminated with metal(loid)s (Van Oosten and Maggio 2015; Sarwar et al. 2017). The plants that can extract metal(s) from soil and transport them to harvestable plant parts are generally used, which are later disposed of safely (Burges et al. 2018; Visconti et al. 2020). Phytoextraction includes employment of hyperaccumulators (plants that can accumulate metals 100–1000 times higher in concentration than non-hyperaccumulators without displaying any sign of phytotoxicity) (Suman et al. 2018) with low biomass or use of plants with high biomass and low contaminant-accumulating capacity (Dixit et al. 2015; Sarwar et al. 2017). *Noccaea caerulea* grown in urban soil contaminated with multiple trace metals was observed to remediate soil affected with moderate levels of Cd and Zn (Jacobs et al. 2017). *Noccaea caerulea* was

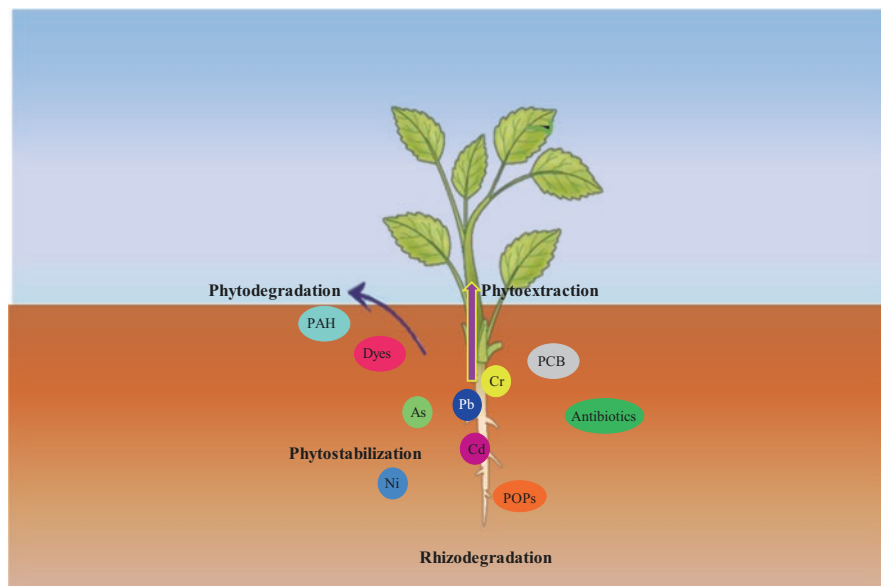


Fig. 3 Plant-assisted phytoremediation of xenobiotic compounds found in urban agroecosystem. *As* arsenic, *Cr* chromium, *Cd* cadmium, *Ni* nickel, *Pb* lead, *PAH* polycyclic aromatic hydrocarbon, *PCB* polychlorinated biphenyl, *POPs* persistent organic pollutants

reported to accumulate nearly 200 g/ha of Cd and 47 kg/ha of Zn. The phytoextraction ability of *Z. mays*, *B. juncea*, *Helianthus annuus*, and *Pteris vittata* was studied in urban soil of Turin city contaminated with heavy metals (Gaggero et al. 2020). The study revealed different plants had different metal uptake ability. Similarly, *Calamagrostis acutiflora* was observed to reduce heavy metal contamination from urban soil through phytoextraction (Rolka et al. 2022).

Phytostabilization or phytoimmobilization involves immobilization of pollutants by the root system through adsorption, complexation, precipitation, and/or metal valence change (Sarwar et al. 2017; Kumar et al. 2020). This process converts toxic compounds into nontoxic or less toxic form and reduces their mobility, thus, preventing entry to the food chain (Van Oosten and Maggio 2015; Kumar et al. 2020). By harnessing the phytostabilization mechanism, plants can easily be cultivated in contaminated urban soil, without leaving any toxic residue in food. Plants that are used for phytostabilization have translocation factor value less than 1, which indicates lower translocation of toxic elements from roots to aboveground parts (Visconti et al. 2020). For instance, maize and sorghum having low translocation factors for potentially toxic elements were reported to clean contaminated soil through phytostabilization (Razmi et al. 2021). Phytostabilization has been a well-established and proven technique for treatment of soil contaminated with different heavy metals (Yadav et al. 2018).

Phytodegradation/phytotransformation is a degradation process wherein organic contaminants like chlorinated solvents, PAHs, and pesticides are converted into

simpler and less toxic form after absorption by the roots (Yadav et al. 2018). Pollutants which are broken down by the plants are utilized by themselves to enhance their growth rate (Muthusarayanan et al. 2018). Phytodegradation of total petroleum hydrocarbons (TPHs) to 45, 54, and 66% has been reported by *B. camp-estris*, *Festuca arundinacea*, and *H. annuus*, respectively, in soil artificially spiked with TPH at concentration of 2300 mg/kg along with four heavy metals in different concentration. Further, addition of humic acid to soil augmented the process of phytodegradation resulting in 86, 64, and 85% degradation of TPH by *B. camp-estris*, *F. arundinacea*, and *H. annuus*, respectively (Park et al. 2011). Contaminants absorbed by plants are degraded or transformed by the action of enzymes involved in plant metabolism including dehalogenase, peroxidase, phosphatase, and oxygenase (Yadav et al. 2018; Khan et al. 2020). Analogous to microorganisms, plants have potential to remove toxic xenobiotics from environment by recruiting multiple mechanisms. Moreover, similar to microbes, bioremediation efficiency of plant is affected by several factors. To abridge these limitations, encouraging amalgamation of bioremediation mechanism of plants and microorganisms through rhizoremediation could be effective to eliminate xenobiotics from urban environment.

5.3 Rhizodegradation

Rhizodegradation or phytostimulation is a microbe-assisted phytoremediation (remediation approach which makes use of plants) process by which contaminants especially recalcitrant organic compounds are biodegraded at the root level, in a soil area called rhizosphere (Cristaldi et al. 2017; Abdullah et al. 2020) (Fig. 3). *Cymbopogon jwarancusa* and *H. annuus*, studied for their phytoremediation action in urban soil contaminated with PAH, were observed with rhizodegradation as the key mechanism for decontamination of soil (D'Souza et al. 2015). *Cymbopogon jwarancusa* and *H. annuus* are reported to degrade total PAH from 95 to 99% and 75 to 84% at 240 and 120 days after treatment, respectively. This technique depends upon activity of microorganisms (bacteria, yeast, and fungi) dwelling in the rhizospheric region in order to derive nutrition from root exudates (Cristaldi et al. 2017; Sachdev and Ansari 2022). Root exudates contain array of compounds, particularly, sugars and alcohol, that are utilized by microbes as energy and nutrient sources and to facilitate stimulation of microbial metabolic and degradation rate (Abdullah et al. 2020). Additionally, the increased surface area and oxygen provided by plant roots to microorganisms encourage their development in the rhizosphere (Abdullah et al. 2020). The plant-microbe symbiotic interaction in the rhizosphere further alters the physicochemical properties of soil, particularly, soil pH, which enhances bioavailability and contaminant uptake by plants (Yadav et al. 2018; Abdullah et al. 2020). For instance, chelating agents (citric and oxalic acid) exuded by *Echinochloa crus-galli* significantly increased translocation and bioaccumulation of heavy metals (Cd, Cu, and Pb) (Kim et al. 2010). C3 and C4 plants were reported to stimulate

microbial population which in turn promoted degradation of PAH (Sivaram et al. 2020). The efficiency of rhizodegradation depends upon compatibility of plant species and associated microbial population (Yadav et al. 2018). The significant difference in percentage of rhizodegradation of PAH by C3 and C4 plants was observed due to differences in root exudates produced by these plants, which demonstrated that specific plant species select peculiar microbial diversity in their rhizosphere (Sivaram et al. 2020). Coupling of phytoremediation with microbial remediation can improve the potential of biological remediation. Microbial community showing compatibility with plants colonizes them efficiently sustaining plant growth as well as remediation process.

6 Modern Approaches to Enhance Efficacy of Bioremediation Technology

Bioremediation is a preferable technique for decontamination of soil, although efficiency of this eco-friendly approach is limited. The activity of microorganisms and plants is greatly influenced by the nature of contaminants, i.e., their concentration, toxicity, and recalcitrance, as well as soil and environmental conditions. The rate of degradation determining duration of biological remediation is very slow, and none of the microorganisms or plants are capable of treating all types of contaminants. Therefore, there is a need for approaches such as nanotechnology, which enhance remediation potential (Song et al. 2017).

Several zerovalent metals particularly, Fe and palladium (Pd), in nanoscale form have shown tremendous potential in reclamation of urban soil contaminated with xenobiotics (Radziemska et al. 2021; Tripathi et al. 2022). Such nanomaterials exhibit capacity to stabilize transition metals like Cr and As and cause dehalogenation of POPs (Cecchin et al. 2017). Numerous studies evidently proved that collaboration of nanomaterials with biological methods of remediation can augment the process of bioremediation. Singh et al. (2013) in a study demonstrated the synergistic effect of integration of bimetallic nanoparticles (CMC-Pd/nFe⁰) with *Sphingomonas* sp. strain NM05 on degradation of chlorinated pesticide lindane (γ -HCH). Integration of nanoparticles and *Sphingomonas* increased the efficiency of the remediation process by 1.7–2.1 folds than individual treatment. Similarly, dechlorination of PCB with bimetallic nanoparticle Pd/nFe followed by microbial degradation using *Burkholderia xenovorans* LB400 resulted in higher efficiency with production of less toxic and innocuous compounds (Le et al. 2015). Moreover, remediation of urban soil contaminated with metal(loid)s by combined application of plants and zerovalent iron (ZVI) nanoparticles was reported by Majumdar et al. (2022). In the study *Cosmos bipinnatus* was reported as the most effective plant in removal of toxic elements from urban soil in the presence of ZVI at 20 mg/kg.

7 Conclusion and Future Prospects

Urban agriculture is an emerging approach to increase food production, and therefore, contamination of urban agricultural ecosystems with xenobiotics is a serious issue. Several chemical, physical, and biological approaches have been reviewed for decontamination of urban soils, among which bioremediation has been observed as the safest, socially viable, and eco-friendly measure. However, slow remediation process, continuous monitoring requirement in addition to high toxicity, recalcitrant nature, long persistence, and low bioavailability of xenobiotics are major drawbacks that reduce effectiveness of bioremediation. Therefore, new and novel approaches for sustainable remediation of urban agricultural soil are warranted every now and then. To improve the efficacy of bioremediation, the following points need to be focused:

- Coupling of biological methods with other approaches like nanotechnology could produce promising results with improved efficiency and effectiveness of remediation.
- To implement newly developed integrated approaches in urban areas, proper scientific validation, regulatory approval, cost-benefit analysis, and societal acceptance are needed.
- Acceptance of integrated approach can be achieved through the following: (1) in-depth scientific studies under controlled and noncontrolled urban conditions to assess safety and outcomes of use of nanomaterials, for societal as well as regulatory acceptance, (2) characterization of uncultivable microorganisms for their bioremediation potential to strengthen both natural bioremediation process and discovering new genes/enzymes for better result, and (3) developing risk mitigation plan to guarantee complete safety of humans and environment.

Conflict of Interest There is no conflict of interest.

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Potential Application of Bacteria in Degrading Xenobiotics for Sustainable Environmental Management



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1 Introduction

Urbanization is enhancing in developing countries and simultaneously urban ecosystem is highly exposed to huge xenobiotic compound, which have emerged as the environmental contaminants. Rapid increase in population, industry, transportation, building, and pollution in urban ecosystem is highly responsible for the increase in contaminants and xenobiotics, which is in turn affecting the soil, water, plant, animal, and human health. The effect of xenobiotics in modern urban system is affecting human health, animal, plant, and environment as they get accumulated in food chain and creates serious environmental issues (Mishra et al. 2021). This issue is one of the biggest threats to our society and ecosystem. The world of bacteria belongs to the large group of microorganisms that plays a major role in all parts of our ecosystems. High metabolic diversity and fitting adaptability preferred microorganisms to live in a varied natural ecosystem as well as in the artificial ecosystems created by anthropogenic activities (Chen et al. 2021). The importance of microorganisms is highly visible in the recent years, and it requires a greater platform and abled professionals to understand and implement the recent technologies to harvest the potential of bacteria in the everyday life of urban society (Singh et al. 2020). The demand for agricultural products has increased enormously with the increase in population. Thus, to combat the problem of food scarcity, implementation of plant growth regulators, chemical fertilizers, and pesticides are being used. Hence, the

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use of these chemicals has affected the soil and ground water quality especially in the urban society (Pérez-Lucas et al., 2019). Scientists and researchers have found a probable and safer solution to this by shifting their attention toward plant growth-promoting rhizobacteria (PGPR). The use of PGPR has promoted agriculture in a feasible manner. More workers need to be trained in this technique to eliminate the deposition of xenobiotics from chemical fertilizers (Gouda et al. 2018).

Today’s lifestyle is greatly occupied by the vast use of bacteria in the diverse field of human welfare, as represented in Fig. 1. For a long time, all bacteria were believed to have only negative effects of causing disease and illness to humans and other lifeforms (Lindahl and Grace 2015). However, new studies revealed large impacts of the diverse group of bacteria, and also the interactions between different groups of bacteria provide a broad area for resource utilization and sustainable production (Tshikantwa et al. 2018). Bacteria of various sizes, shapes, forms, and morphologies find a huge abundance in nature which create a complex web and offer multifarious roles in different fields of human benefaction (Tshikantwa et al. 2018). After the inventions of tools in the field of biotechnology, it became easier to manipulate microorganisms with efficiency, and it has helped researchers to utilize it on an industrial scale largely to produce a great variety of substances.

Besides the role as a decomposer of the food chain of our various ecosystems, bacteria also have various beneficent roles in agriculture and food production

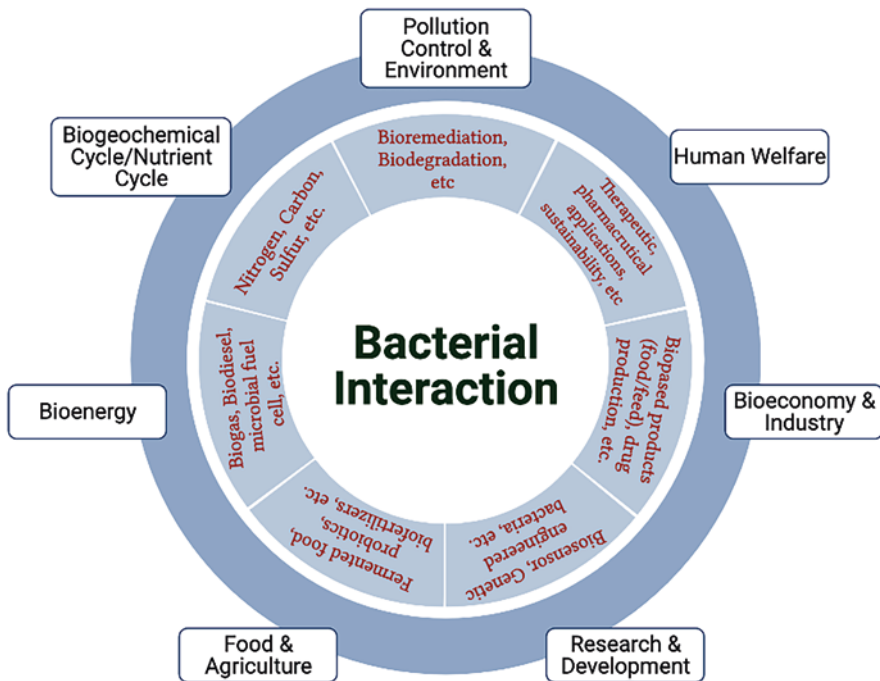


Fig. 1 Role of bacteria in welfare of human, environment, and society

system, disease and pest control, wastewater treatment, fermentations, antibiotic production, vaccine production, and bioenergy and biofuel production (Zaccaria et al. 2017). The world is now under the immense pressure of increased human populations, and the huge burden of waste generation contributes toward the formation of xenobiotics. The depleting state of natural resources focuses this generation to concentrate more on sustainable developments. Toward fulfilling the basic needs of increasing populations, some of the highlights are concerns on food, health, shelter, clothes, and energy utilization. The utilization of the renewable resources of our earth took our attention toward sustainable developments. The world is now in the era of development in terms of excessive resource utilization and resource manipulation that ultimately led to the pollution of the fundamental elements of our life as soil, water, air, etc. (Chu and Karr 2017). Various initiatives have already been taken by different agencies worldwide to study the effect of xenobiotics and to reduce the negative impact of xenobiotics in environment (Miglani et al. 2022).

The interaction between plants and bacteria can be significantly observed to tackle the concern of heavy metal toxicity in soil (Shabaan et al. 2021). Rhizobacteria act as a plant growth promoter, and it has the potential to grow in the presence of toxic metals (Efe 2020). Therefore, with proper education and with great intelligence, our society may find potential ways to utilize the bacteria for sustainable development. Sustainable development target toward the fulfillment of the needs of the present generation without affecting the natural resources in order for further use in future. It focused on protecting nonrenewable resources from getting extinction (United Nations 2016). The major beneficial impact of bacteria that can be observed very evidently on the environment is bacterial degradation of organic and inorganic waste materials for the normal growth and metabolism of the bacteria. This degradation of harmful waste substances helps to reduce the spread of diseases and maintains the quality of the soil and air by keeping the beauty of the environment (Ferronato and Torretta 2019; Atanasova et al. 2021).

Bacteria are taking a grip over the sector of food industries to make simple products like cheese, beer, bread, and many more food items that are required daily by the common people. Bacteria acting as gut flora help in the proper regulation and production of nutrients and vitamins that are strictly required for the proper functioning of the body. In recent scenarios, they play a crucial role in biofertilization and pest control that reduces the application of harmful artificial pesticides that are devastating for the health of the consumers in the long run (Dhuldhaj et al. 2023). A list of bacteria functioning as biocontrol and pest control agents is mentioned in Table 1. Moreover, the pharmaceutical sector is booming with the aid of bacterial application to manufacture life-saving drugs and chemicals. The lifestyle of humans has changed because of the advancement in research and technology by extracting the potential beneficial effect of bacteria to ease our day-to-day life. With the help of bacteria, bioelectricity is being generated and simultaneously waste management is also done (Han et al. 2021). The interaction between plants and microbes can be significantly observed to tackle the concern of heavy metal toxicity in soil. However, the implementation of bacteria also helps in reducing contaminations of harmful substances like plastic polymers. In the present scenario, we need to concentrate

Table 1 Influence of bacteria in the growth of plant products without using harmful artificial chemicals

Agriculture product	Bacteria name	Function	References
Wheat	<i>Pseudomonas fluorescens</i> (PSF)	Phosphorus solubilization	Chamani et al. (2015)
	<i>P. putida</i> (PSP)		
	<i>Arthrobacter protophormiae</i> (SA3)	Increased the drought tolerance	Barnawal et al. (2017)
	<i>Bacillus subtilis</i> (LDR2)		
	<i>Dietzia natronolimnaea</i> (STR1)		
	<i>Azorhizobium caulinodans</i>	Leaves and roots increase	Liu et al. (2017)
	<i>Rhizobium</i> sp.	Enhancement of shoot and root growth	Kamran et al. (2017)
<i>Azospirillum</i> sp.	Growth in wheat	Singh et al. (2017)	
Maize	<i>Klebsiella</i> sp.	Growth and hormone improvement in maize	Rodrigues et al. (2016)
	<i>Enterobacter</i> sp.		
	<i>Pantoea</i> sp.		
	<i>Azospirillum brasilense</i>	Nitrogen accumulations in the shoot	Picazevicz et al. (2017)
	<i>Rhizobium tropici</i>		
	<i>Funneliformis mosseae</i>	Improved the growth, N and P uptake	Ghorchiani et al. (2018)
	<i>Pseudomonas fluorescens</i>		
	<i>Azospirillum</i> sp. Az19	Improved shoot and root growth and increase drought tolerance	García et al. (2017)
	<i>Azospirillum</i> sp. Az3		
	<i>A. brasilense</i> Az39		
<i>Azospirillum</i> sp. Az63			
<i>Azospirillum</i> sp. Az8			
Soyabean	<i>Bradyrhizobium</i> sp.	Increase N, P, S content and improve the yield	Raj and Takankh (2018)
Cucumber	<i>Pseudomonas fluorescens</i>	Improvement of root and shoot, salinity tolerance	Nadeem et al. (2017)
Tomato	<i>Azotobacter chroococcum</i>	Improve plant growth, help in drought and salinity stress	Viscardi et al. (2016)

more on utilizing the bacteria for human welfare. Microbes contain various genes and enzymes that can degrade xenobiotic compounds present in different ecosystem. They utilize this compound as their nutrient sources for their growth and metabolic activities. Advance molecular studies along with in silico analysis can help in better understanding of the mechanism of microbial degradation in xenobiotics (Mishra et al. 2021). Hence, in this chapter, we are concentrating to find out the

beneficial role of bacteria in human welfare and xenobiotic degradation. We have explored the different groups of bacteria that provide a tremendous impact on our modern lifestyle on earth.

2 Category and Degradation Methods of Xenobiotics

There are various types of xenobiotics, and some of the major groups of xenobiotics are categorized under environmental pollutants, oil mixtures, synthetic polymers, hydrocarbons, carcinogens, antioxidants, pesticides, and drugs (Štefanac et al. 2021). Xenobiotics are the substances that are made up of chemical constituents and these are foreign to the animal life. Organisms getting exposed to factors that are foreign to the system and are hard to metabolize are considered as xenobiotics (Rathore et al. 2022). In absence of proper metabolism, xenobiotics reach to a toxic concentration. Components occurring naturally can also become xenobiotics when they are consumed by another organism (Croom 2012). Some of the examples are organisms imparting the phenomena of chemical defenses as a sign of protection against the predators. Another example is small fishes consuming human hormones and small organisms present in the sewage treatment plant outfalls. It has been studied that humans are exposed to millions of xenobiotic compounds throughout their life time via drinking water, diet, drug administration, and lifestyle choices (Higson 1991). To reduce the harmful effect of xenobiotic substances, bacteria degrade insoluble polymer lignin, nonrepeating and nonstereoselective polymers.

There are various physical and chemical methods like filtration, adsorption, and chemical precipitation for treating xenobiotics, but all these methods are costly and produce hazardous by-products. In this context, using microbes is the most suitable and potential approaches as they could survive in different extreme environment and is capable in stress tolerance. Microbes contain catabolic genes and enzymes and have degradation pathway that can degrade various xenobiotics compound and pollutants. The functionality of the microbes is also associated with the parameters of ecosystem like pH, soil characteristics, and temperature, along with their potential genes and enzymes. Thus, application of single microbe, microbial consortia, or genetically engineered microbes in any contaminated sites for degradation and transformation of pollutants is the most efficient method. But this method needs much more intensive research involving elaborative genetic analysis along with in-depth study on degradation pathways to combat with the problem of xenobiotics in urban ecosystem (Štefanac et al. 2021). Some of the key players to degrade lignin are extracellular ligninases or peroxidases that attack on lignin. The degradation of this ligninolytic-containing xenobiotic compounds into smaller particles has limited water solubility as a result of which they are not readily available in the soil (Zhang et al. 2020). This degradation of harmful chemical substances from the soil with the help of bacteria will enhance the quality of the agricultural land.

3 Bacterial Impact on Xenobiotic Remediation for the Betterment of Environment

3.1 Bacterial Remediation of Soil Xenobiotics

Regularly, soil is getting more and more polluted because of different hazardous materials like toxic compounds, radioactive materials, disease-causing agents, xenobiotics, and heavy metals, which is a threat for the health of human, animals, and plants (Alengebawy et al. 2021). Being the “universal sink” soil holds the highest load of environmental pollutants. The contamination of soil by pesticides, herbicides, chemical fertilizers, sewage sludge, heavy metals, solid waste seepage, petroleum hydrocarbons, industrial waste, and radioactive materials bring up the risk of terrestrial ecological factors, which in return affect the health of ecosystems negatively (Aqeel et al. 2014). Steps of conversion of xenobiotics and contaminants into beneficial products by the process of bioremediation have been mentioned in Fig. 2.

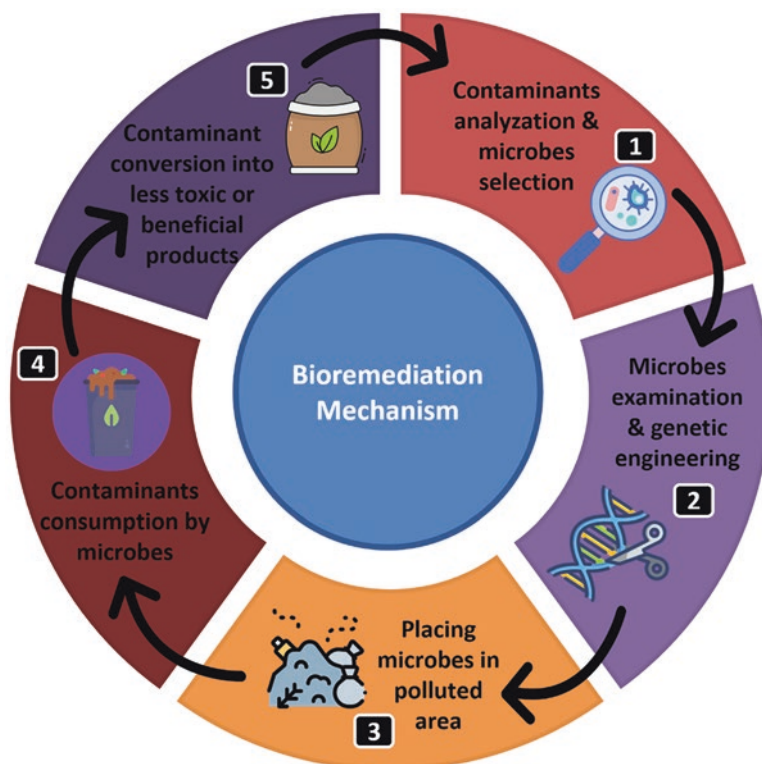


Fig. 2 Conversion of contaminants into beneficial products by the process of bioremediation

The long persistence of toxics and xenobiotic compounds and insoluble aromatic contaminants in the soil are harmful to agriculture, animals, and humans. Importance of bacteria to control biotic and abiotic factors in agriculture is presented in Fig. 2. Due to the metabolic diversity and modified adaptability, the bioaugmentation of different aromatics' contamination in the soil was utilized or degraded by a single strain as well as by different consortia of bacteria (Xu and Zhou 2017). Bioaugmentation of various nitroaromatics like nitrobenzene by *Pseudomonas putida* ZWL73 (Zhao et al. 2009), Fenitrothion by *Burkholderia* sp. FDS-1, para-nitrophenol (PNP) by *Arthrobacter protophormiae* RKJ100 (Labana et al. 2005), methyl parathion, and para-nitrophenol (PNP) by *Pseudomonas* sp. WBC-3 (Liu et al. 2005); various chloroaromatic like pentachlorophenol (PCP) by *Sphingobium chlorophenolicum* ATCC 39723, 4-chlorophenol (4-CP) by *Arthrobacter chlorophenolicus* A6L, and various chloronitroaromatics like 4-chloronitrobenzene (4CNB) by *Pseudomonas putida* strain ZWL73 and *Comamonas* sp. strain CNB-1 were extensively studied (Labana et al. 2005). The degradation of multiaromatic contaminations in the soil by consortia of different bacteria has helped to explain the improvised capacity of bioaugmentation of different xenobiotics and contaminants by bacterial interactions in the consortia (Chi et al. 2013). The emergence of xenobiotics imposes a great threat to the sewage treatment system as removing them is a very crucial task. Xenobiotic compounds like polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), and trichloroethylene (TCE) are very resistant to degrade, and they have the potential to get accumulated in the water bodies (Migiani et al. 2022). Some of the major sources of xenobiotics are fossil fuels, agriculture, pharmaceuticals, industries, and pulp and paper bleaching factories. To deal with this problem, bacteria could be the best solution for degrading xenobiotics (Rathore et al. 2022).

Bacteria play an immense role in sustainable development in agricultural fields. Their metabolic variability and biodegradability of numerous organic and inorganic contaminants in the soil provide a rich source of nutrients in the soil ecosystem. The mineralization of various types of pollutants in the soil by bacteria is used up by plants which enhanced the growth of plants (Kumar and Verma, 2018). The application of bacterial inoculants to the soil improved the nutrient availability and nutrient uptake by the soil, promotes plant growth, increased crop yields, and protect different crops and plants from various pests and diseases. Bacteria are used for the production of biofertilizers that replace chemical fertilizers and eliminate the harmful effects of chemicals in food and crops (Ahmad et al. 2018). A diverse group of microorganisms like algae, fungi, actinomycetes, bacteria, and protozoa was found in the soil as well as in the rhizosphere. Among them, the large availability of bacteria has a wide range of applications regarding plant productivity, growth, and protection. The diversity and metabolic functions of a different group of bacteria in situ and ex situ ground have found profound implications. Bacteria play a pivotal role in mineralization, nutrient uptake, plant growth, and stress management that in turn increase the agricultural productivity (Chamani et al. 2015). A list of bacteria and their influence on the growth of plant products are mentioned in Table 1.

3.2 *Bacterial Remediation of Xenobiotics and Water Contaminants and Their Role in Aquaculture*

The era of rapid industrialization along with dense population and uninterrupted urbanization has increased the utilization of water. The indiscriminate use of water leads to scarcity of water for consumption. The use of harsh pesticides and chemical applications in agriculture contributes to xenobiotics and increases the generation of waste that directly or indirectly contaminates the natural water bodies. As a consequence, the freshwater bodies, as well as the marine ecosystem, are now at great risk. Toxic substances, pollutants, and xenobiotics are responsible for the change in water quality and ecological balance of the aquatic ecosystems, which creates biomagnification, and becomes the potential cause and source of several diseases in humans as well as other animals (Dwivedi et al. 2018). Shortly, the scarcity of usable water will be going to be a major threat to the whole animal and plant kingdom as water is getting contaminated and polluted due to over utilization of chemicals and pesticides (Perron et al. 2021). Biomagnification is a major problem, especially in the urban society as lifestyle of urban people is more away from nature and people are exposed to more unnatural substances that contribute to xenobiotics. Humans are the most affected entity because of biomagnification, and as humans are holding the top position in the food chain, the accumulation of toxicity is highest at the top trophic level. Bioaccumulation of toxic elements in plants serves as the most potential risks for the human health in urban as well as in agro-environmental society. Consumption of these plant-based products that have accumulated toxic substances will be contributing more in terms of biomagnification (Correia et al. 2018). Individuals affected because of biomagnification had a great risk of suffering from cancer, heart disease, brain damage, and certain birth defects along with other health issues (Chowdhury et al. 2021). Although several bacterial contaminations in water indicate the pollution in water bodies and most of the bacteria create serious health issues, a diverse group of bacteria acted upon several contaminants of water and transform them into soluble and less toxic forms. Several aerobic and anaerobic bacteria in single and in groups degraded or oxidized the xenobiotics present in water.

Bacillus sp., *Nitrosomonas* sp., *Nitrobacter* sp., *Aerobacter* sp., and *Cellulomonas* sp. were found to be involved in mineralization, oxidation, and reduction of several harmful nitrogenous and organic compounds to harmless products (Wang et al. 2018). The wide range of denitrifying bacteria transforms nitrates into harmless nitrogen. Bacteria like *Rhodopseudomonas*, *Chromatium*, *Rhodospirillum*, *Chlorobium*, *Thiospirillum*, *Chloropseudomonas*, *Amoebobacter*, *Thiosarcina*, *Lamprocystis*, *Prosthecochloris*, *Clathrochloris*, *Ectothiorhodospira*, *Thiopedia*, *Pelodictyon*, and *Thiocystis* can decompose and mineralize organic matters and inorganic contaminants like NO_2 and H_2S in the pond ecosystems (Harman et al. 2021). This detoxification of water xenobiotics will lead to obtain fresh and contamination-free water for the use of rural and urban people.

The emergence of probiotics in aquaculture helps to promote good health of the fish, and it also imparts beneficial effects to the consumers by maintaining the enhanced microbial balance internally. The growth of pathogens is inhibited with the implementation of probiotics, as probiotics secrete lysozymes, bacteriocins, and proteases that help to destroy pathogens. Cellulase and protease enzymes are secreted by *Lactiplantibacillus plantarum*, *Bacillus subtilis*, and *Staphylococcus* (Ma et al. 2022).

Various enzymes are produced by bacteria, and these enzymes are being used in industries like pharmaceutical, food, paper, agro-based industries, and many more such sectors. Some of the enzymes along with their secretive organisms are mentioned in Table 2. The introduction of probiotics into aquaculture confers various health benefits and plays an essential function in developing disease-resistant, improved growth performance, improved quality of water, and enhanced immunity of organisms in the culture. Moreover, the application of antibiotics in the culture gets reduced and the side effect of antibiotic resistivity gets minimized. Promoting these applications in aquaculture has improved feed utilization and their productive performance to safeguard and boost human health (El-Saadony et al. 2021). Some probiotics such as *Carnobacterium*, *Lactobacillus*, *Vibrio alginolyticus*, *Pseudomonas*, and *Bacillus* act as biocontrol agents in aquaculture. It was found that in shrimp culture, the nonpathogenic isolates of *Vibrio alginolyticus* interact with pathogenic *Vibriosis* like *Vriesea splendens*, *Vibrio harveyi*, and *Vibrio parahaemolyticus* and suppresses the effects of pathogenic bacteria and reduce the invasion of opportunistic pathogens (Sanches-Fernandes et al. 2022).

Table 2 Role of different bacterial enzymes to degrade xenobiotic and related compounds in various industries

Enzymes	Bacteria Name	Role	References
α -amylase	<i>Bacillus subtilis</i>	Paper industries fermentation, starch degradation, polymer degradation	Balakrishnan et al. (2021)
Lipase	<i>Bacillus</i> , <i>Pseudomonas</i> , <i>Arthrobacter</i> , <i>Achromobacter</i>	Organic synthesis, detergent enzymes, biocatalyst	Chandra et al. (2020)
Beta-Lactamase	<i>Klebsiella pneumonia</i> <i>Serratia marcescens</i>	Antibiotic resistance	Gupta et al. (2012)
Protease	<i>Vibrio</i> sp.	Commercial importance, inhibit the growth of other bacteria, increase pathogenicity	Osei-Adjei et al. (2017)

3.3 *Bacterial Remediation of Xenobiotics and Heavy Metal Contamination*

Due to overexploitation of resources and a lack of strategic management system of the by-products, the land and water are at the greatest risk of xenobiotics. In low concentrations, some heavy metal performs a beneficial role in the human body such as iron, nickel, and copper. But in high concentration, it will create several toxic effects in the body (Valco et al. 2016). The functions of the brain, heart, kidney, lungs, blood constituents, spinal cord, and several organs can be destabilized due to heavy metal toxicity, and the biomagnification of several heavy metals can become the cause of cancers (Jaishankar et al. 2014). The high density of heavy metals was found to cause hazardous effects in minimum concentrations and became unfavorable to the environment as well as to the organisms (Jaishankar et al. 2014). Several heavy metal-reducing bacterial strains such as *Gemella* sp., *Micrococcus* sp., and *Hafnia* sp. (Rajasulochana and Preethy 2016), *Zooglea* sp., *Citrobacter* sp., *Chlorella vulgaris*, *Pseudomonas aeruginosa*, *Geobacter* sp., *Geobacter metallireducens*, *Geobacter sulfurreducens*, *Vibrio harveyi*, *Acinetobacter* sp., *Sporosarcina saromensis* (M52), *Bacillus subtilis*, *Desulfovibrio desulfuricans*, *Micrococcus* sp., *Stenotrophomonas* sp., *Bacillus cereus* were isolated, which were capable of reducing heavy metals in their nontoxic form in in situ contaminated ground. Several consortia of bacteria such as *Bacillus licheniformis*, *Acinetobacter* sp., *Arthrobacter* sp., and *Pseudomonas aeruginosa* were found to remove heavy metals more efficiently. Some biotechnologically engineered strains such as *Pseudomonas* strain K-62, *Acidithiobacillus ferrooxidans*, *Achromobacter* sp. AO22, *Deinococcus radiodurans*, *Escherichia coli* JM109, *Pseudomonas putida* 06909, *Bacillus subtilis* BR151 (pTOO24), *Caulobacter crescentus*, *Sphingomonas desiccabilis*, *Bacillus idriensis*, *Pseudomonas fluorescens* OS8, *Escherichia coli* MC1061, *Bacillus subtilis* BR151, *Staphylococcus aureus* RN4220, and *Klebsiella michiganensis* were also found to detoxify xenobiotics and reduce heavy metal contamination in efficient ways (Wang et al. 2020).

3.4 *Bacterial Remediation of Plastic Pollutants and Xenobiotics*

Today, the world is dependent on the use of synthetic polymer and their different forms in every sector of the world (Saha et al. 2022). A study reported that about 12,000 metric tons of plastic will be in landfills by 2050 (Geyer et al. 2017). Nonbiodegradability of polymer is a prime cause of pollution in lake, pond, river, ocean, and land ecosystems (Pauli et al. 2017). Xenobiotics containing polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), and trichloroethylene (TCE) lead to blockage problem in the drainage and affect human health and the natural ecosystem by overflowing the wastewater. The nonrecyclable plastic

in the wasteland and different water bodies was found to be the habitat of different groups of microorganisms.

In the natural ecosystem, diverse groups of bacteria in single and in consortia formed the biofilm on the surface of the plastic and can degrade various types of plastic in in situ and ex situ conditions (Puglisi et al. 2019). To date, diverse groups of bacteria in single and in consortia isolated from different ecosystems, such as *Bacillus megaterium*, *Azotobacter*, *Ralstonia eutropha*, *Halomonas* sp., *Pseudomonas putida* S3A, *Pseudomonas stutzeri*, *Comamonas acidovorans*, *Brevibacillus*, *Pseudomonas*, *Rhodococcus* spp., *Rhizobium tropici*, *Rhizobium fredii*, *Rhizobium loti*, *Rhizobium huakuii*, *Staphylococcus* sp., *Moraxella* sp., *Micrococcus* sp., *Streptococcus* sp., *Pseudomonas* sp., *Shewanella* sp., *Moritella* sp., *Pseudomonas* sp., *Psychrobacter* sp., *Vibrio alginolyticus*, *Vibrio parahaemolyticus*, *Pseudomonas* sp., *Alcanivorax*, *Tenacibaculum* sp., *Bacteroides*, *Proteobacteria* (De Tender et al. 2015), *Pseudomonas* sp. (Urbanek et al. 2017), efficiently degrade various forms of plastic and xenobiotics. One of the most important and key steps that is required for the breakdown of xenobiotic compounds is the cleavage of carbon and halogen bonds with the catalyzation of bacterial dehalogenases. Bacterial dehalogenases help in aerobic mineralization of halogenated compounds contributing in environmental pollutants (Janssen et al. 2005). Compounds that are not having halogen compound attached to it are easily degradable. To degrade xenobiotics, they are metabolized, and this process is majorly grouped into three phases. The first step includes modification of the xenobiotics into simpler components such as dehalogenation for efficient enzymatic activity to breakdown the xenobiotic compound. The next phase is conjugation, and it involves the attachment of various enzymes. The final step involves excretion that helps to remove and detoxify xenobiotics from the cells. As xenobiotics are acting as the potential threat to the urban society, it is very important to implement xenobiotic management techniques and find out the sources of xenobiotic generation and reduce its uses. Major contributors of xenobiotics are air pollutants, commercial and industrial wastes, agricultural wastes including pesticides and chemical fertilizers, water pollutants, and medical disposals. To get rid of these harmful components from the environment, five major steps are being followed, namely abiotic degradation, bioremediation, nanoremediation, phytoremediation and photo-remediation. A schematic representation is presented in Fig. 3 to highlight the major contributors of xenobiotic formation and their management techniques.

4 Xenobiotic Management Approaches

4.1 Biofuel Production by Microbial Metabolism

The indiscriminate use of fossil fuels and the depleting state of nonrenewable resources are the emerging concern that made scientists concentrate more on the technologies to achieve the sustainable development of biofuels. The potential

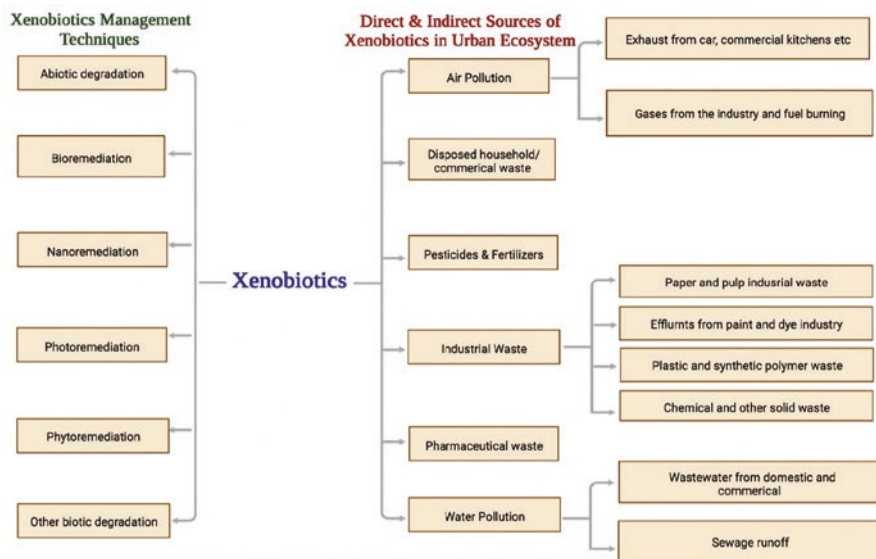


Fig. 3 Different direct and indirect sources of xenobiotics in urban environment and their management techniques

biofuel-producing microorganisms are now widely utilized in their wild type as well as in the recombinant strain. Butanol has high energy density and is one of the good sources of biofuel. Ethanol is also used as biofuel, and it is produced by utilizing the biomass of several plant materials. Biohydrogen is one of the promising sources of energy and hence has huge commercial potential in future. Several bacteria in a single and a community were found to generate biofuels like butanol, isobutanol, ethanol, and biohydrogen by utilizing different types of biomasses, which may provide an essential source in human welfare in the future (Yao et al. 2019). Rapid urbanization is highly associated with huge fuel consumption in commercial as well as domestic purposes, and this is related to pollution and emission of xenobiotics. Hence, biofuel or microbial fuel is considered as the most potent alternative sources of energy for sustainable and clean environment. This approach will not only help to reduce the load of xenobiotic toxicity in urban society as well as it will help to manage waste and reduce the use of nonrenewable sources of energy.

4.2 Plant Microbial Fuel Cell (PMFC)

Implementation of a microbial fuel cell is considered as the potential source of bioenergy and treatment of wastewater at the same time. However, rapid substrate utilization by bacteria for generating electricity was the major drawback of this

research. Plant microbial fuel cell (PMFC) is one of the solutions to this problem, which can generate continuous energy without competition for food and can be operated at a large location. PMFC is the most effective alternative sources of energy due to green and clean energy production. PMFC arrests the root discharges from photosynthesis and converts them to bioelectricity with an aid of microbial metabolisms and degradation of contaminants (Maddalwar et al. 2021). This system will solve many issues related to food production, environmental preservation, economic development, and technological advancement.

4.3 Bioelectricity Generation in Microbial Fuel Cell

Numerous new methods and techniques have developed to compensate the needs of the present world through sustainable development for the welfare of the society. The increasing population of our planet requires more energy for their continuous upliftment. Electricity generation by solar panels, extraction of potable water from seawater, purification of wastewater for its subsequent use in irrigation, and many such sustainable technologies are already underway. Mass and energy are interchangeable, employing this concept, scientists have been working on developing systems that can convert waste and contaminants into electricity and recover other valuable resources. This is termed the bioelectrochemical system. Microbial fuel cell (MFC) converts the chemical energy of waste into electrical energy by the activity of microorganisms (Ebrahimi et al. 2018). The increasing demand of electricity can be fulfilled by the implementation of such alternative source of electricity produced by the bacteria. Such electrochemically active bacteria are known as exoelectrogens. MFC development brings conventional wastewater treatment toward a new direction with the simultaneous production of electricity that results into purification of wastewater in the urban sections of the society and stopping the spread of waterborne diseases. The MFC technology has evolved to clean up the pollutants and degrade xenobiotic components through microbial degradation with the simultaneous generation of electricity (Singh and Songera 2012). Several bacteria are already reported that show this exoelectrogenic activity and generate an efficient amount of electricity in the MFC. A list of bioelectricity generating bacteria from MFC is enlisted in Table 3.

Several rules and regulations have also been issued regarding disposal and use of toxic and pollutant in soil and water bodies by government organization, policy makers and stakeholders, but more measures need to be adopted in controlling the present situation immediately to make a pollutant-free environment in near future (Miglani et al. 2022).

Table 3 Production of bioelectricity with the help of bacteria by degrading wastes and xenobiotic components

Bacteria	Role	References
<i>Geobacter sulfurreducens</i>	Produce bioelectricity through a microbial fuel cell (MFC)	Szöllősi et al. (2015), Marassi et al. (2020)
<i>Shewanella oneidensis</i>		
<i>Clostridium butyricum</i>		
<i>Pseudomonas aeruginosa</i>		
<i>Escherichia coli</i>		
<i>Lactiplantibacillus plantarum</i>		
<i>Saccharomyces cerevisiae</i>		

5 Conclusions and Future Prospects

Degradation of xenobiotics in urban ecosystem must be a sustainable and eco-friendly method. Therefore, involving microbes in degradation and detoxification of pollutants is a very prominent approach. Anything that can perform a beneficial role in the improvement of the human lifestyle has been included in the platform of human welfare. In this chapter, we have explored bacterial diversity that finds large implications in agricultural, therapeutic, and industrial fields. The exponential population growth, blind use of nonrenewable resources, alarming rate of pollution, increasing waste products, xenobiotics, and large demand for food, medicine, and energy will lead scientists to focus on sustainable development, in which bacteria will be assumed to provide the great potential as a biocatalyst. In food chains, decomposer plays a critical role to maintain the balance of every ecosystem and protecting environments by depleting hazardous by-products and recycling the necessary components. Especially elements like nitrogen, carbon, and oxygen are recycled efficiently at a faster rate with the aid of the bacteria. This entire process contributes greatly to the overall sustainable maintenance of the environment. Bacteria can grow in every ecosystem even in extreme cold and extreme heat conditions. Their adaptability and metabolic diversity can perform an important role to utilize and bioaugmenting the xenobiotics that create several environmental pollutants and affect the health of different ecosystems. This chapter mainly focused on finding out the diversity of bacteria that colonizes different ecosystems in various environmental stress conditions, controls xenobiotics, and improves the quality of life in the urban society.

This chapter showed that different groups of bacteria in single as well as in consortia were found to degrade and detoxify various types of xenobiotics for the betterment of the rural health as well as for the urban society. More molecular research related to microbial remediation of xenobiotics involving genomics, proteomics, transcriptomics, and nanotechnology must be implemented along with more

policies and regulations regarding the use of xenobiotics must be initiated to achieve a pollutant-free urban ecosystem. The study will help to find out the organisms that take part to combat different environmental pollutants, by which we can further study the other beneficial activities of those bacteria and apply them to several grounds to remove environmental contaminants. Apart from obtaining benefits on environmental aspects, bacteria impart some well-known health benefits by providing probiotics and helping in manufacturing medicines and vaccines with the advancement in the field of biotechnology. The present need of the hour is to find out and analyze the potential role of bacteria in the good fare of society and human health. More research needs to be done to enhance and optimize the production of green energy as an alternative source of energy and to manage waste and xenobiotic production at the same time for the betterment of the urban society. Advanced and modern microbial and molecular methods are the key solution toward this issue. Finally, it can be concluded that exploring genetic features and molecular mechanisms of microbes using different “omics” approaches will be the most promising and relevant steps toward remediation of xenobiotics in urban system.

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Bioremediation Strategies for Microplastic Removal in Impacted Aquatic Environments



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1 Introduction

Plastic is an economical, convenient material and is widely used in industries and in everyday society around the world. However, along with this application in everyday life, it has recently emerged as a global environmental threat. The growing demand for the consumption of plastic products has caused this product to become a waste that contaminates the environment when disposed of incorrectly, since they are resistant in the natural environment, and cannot be degraded even in 100 years (Tiwari et al. 2020). For 2025, it is estimated that 11 million tons (MT) of plastic will be accumulating in different components of the environment; however, the recovery rate of this waste may not exceed 5% (Brahney et al. 2020). At this juncture, “white pollution” arises, which occurs due to various biophysical and chemical activities, being responsible for the formation of smaller plastic fragments, which are called microplastics (MPs) (Zhou et al. 2022).

Microplastics (MPs) are defined as the plastic particles having <5 mm size and originating from both primary and secondary sources. Primary MPs result from

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industrial manufacturing, while secondary MPs result from the fragmentation or breakdown of larger plastics, which are present in different environmental components. These are considered emerging contaminants for the aquatic environment, mainly urban, since their ubiquitous presence can lead to risks to the environment, particularly human health. In the urban environment, such dendrites have already been found in drinking water and wastewater treatment plants, sewage sludge, and solid waste treatment facilities (Viaroli et al. 2022).

Microplastics (MPs) have been detected more frequently in the urban environment, in the soil, and in rivers. The light weight and low density of these particles make them possible to float and exchange between different environmental components of the urban ecosystems (Qiu et al. al. 2020). Due to their ability to adsorb and accumulate with different types of environmental contaminants (e.g., metals and organic pollutants), it is clear that the negative effect of MPs is not only physical but also occurs at chemical levels. Furthermore, these can also provide long-term, stable habitat for a range of pathogenic microorganisms (Tong et al. 2020; Simmerman and Coleman Wasik 2020). Currently, several methods have been studied and developed in order to identify and treat plastic waste in the environment, through removal or degradation approaches. At this juncture, bioremediation using biological agents (e.g., algae, bacteria, and fungi) has been reported as an environmentally friendly technique for the sustainable degradation of plastics (Zamprougno et al. 2021; Auta et al. 2022).

Bioremediation can act in different ways and may be through the process of biostimulation, which is related to the addition of nutrients for stimulating the biodegradation process by the microorganisms, or even bioaugmentation, which is involved with the use of microorganisms capable of increasing the activities of biodegradation (Auta et al. 2022). In this context, bioremediation through the use of microorganisms is a promising technique, since it is considered beneficial to the environment, in addition to being capable of execution. The use of microorganisms can be very beneficial, since through them it is possible to manage plastic waste properly, and it is possible to observe a significant reduction when used for the removal and/or treatment of MPs from the environment (Muñio Sanjurjo 2022). In view of this, this chapter highlighted the approaches related to bioremediation in the treatment of microplastics in contaminated aquatic ecosystems.

2 Microplastics: Definition and Types

Plastics are classified as a varied group of synthetic polymeric materials. Based on this production, microplastics (MPs) can be defined as the plastic particles with <5 mm size (Yang et al. 2021). These are classified as primary and secondary. Primary MPs are intentionally manufactured due to their commercial viability, for example, for their use in the cosmetics industry, personal care products, pharmaceutical products, among others (Fan et al. 2021). Secondary MPs, on the other hand, are derived from the diminution of larger sized materials, such as plastic bags and

bottles, packaging lids, ropes, clothes, and tires, giving rise to the formation of smaller sized particles in the environmental systems (Reddy and Nair 2022).

Like plastics, MPs can be further classified into thermosetting plastics and thermoplastics. Thermosetting plastics include bakelite, polyesters, polyurethane, and epoxy resins, whereas thermoplastics include polyvinyl chloride (PVC), high-density polyethylene (HDPE), low-density polyethylene (LDPE), polystyrene (PS), polyethylene terephthalate (PET), polyamide (nylon) and acrylic, and polypropylene (PP) (Guo and Wang 2021). The degradation process of these polymers can occur in two ways, that is, biotic or abiotic measures in the environment. In the biotic degradation, the biodegradable materials break down into smaller pieces by the activities of different microorganisms, such as biofilms, bacteria, fungi, and insects. With regard to the abiotic degradation, this happens through different actions, including photooxidative, thermal, and mechanical forces. Additionally, MPs can also undergo the process of additional weathering, which leads to the changes in physicochemical properties, such as size, color, and surface area, a factor that is responsible for the release of additives derived from MPs, which are considered the toxic contaminants (Enfrin et al. 2020).

3 Microplastics in the Aquatic Environments

Microplastics (MPs) are ubiquitous water contaminants present in different aquatic ecosystems such as oceans, lakes, and even arctic ice. The first discovery of MPs in marine environments was dated 1997 by Charles Moore in the North Pacific Ocean, in which “strange pieces and flakes” were observed, denoted in his book “Plastic ocean” derived from the launching of bottles and fishing nets in this environment (Chae and An 2018).

Currently, it is estimated that approximately 10% of the plastic produced globally is released into the oceans. Many plastics found or used are discarded in water bodies, and it is predicted that by 2050 the amount will extend to a production of 32 million tons per year (Horton et al. 2017). A small fraction of MPs found in the aquatic environment are related to marine activities such as the fishing industry, while 80% are sourced from land-derived plastic wastes (Li et al. 2016). Aquatic environments receive MP particles as a result of terrestrial sources, including aging packaging, domestic sewage, tire abrasion, wastewater irrigation, illegal dumping of waste and landfills, and the use of personal care products. The transport of these fragments occurs in three ways, through wind, soil, and water itself (Boucher and Friot 2017; Wu et al. 2022).

Air transport is conditioned by storms and hurricanes, these factors being crucial for the transport process to occur over long distances. On land, dendrites reach the aquatic environment through rain, tidal washing with agricultural plastic films, dumping sites, and beaches. The watercourse is also configured as an important route, such as sewage water, sewage overflow, disposal of industrial effluents, rivers, and estuaries, which transport MPs to the ocean because of their low density of

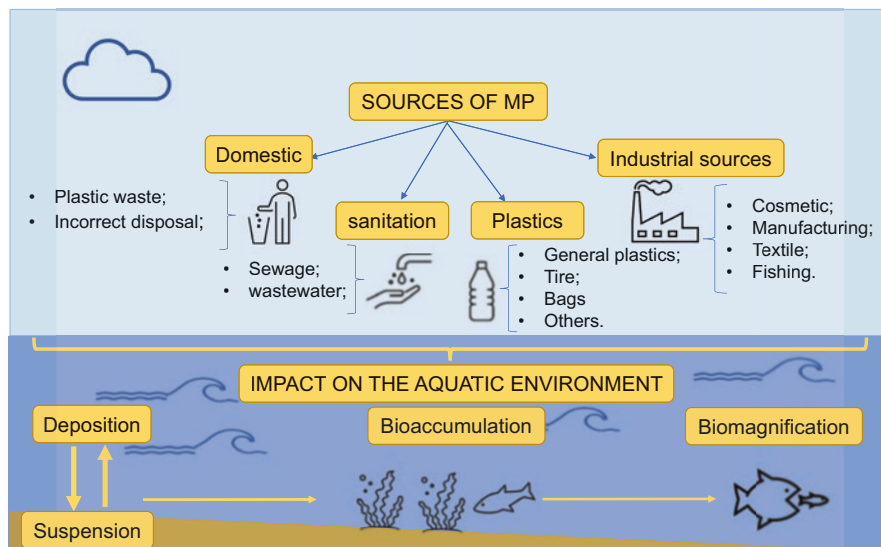


Fig. 1 Major sources of microplastics (MPs) in the aquatic ecosystems

plastic debris (Bhuyan et al. 2021). Primary MPs are introduced directly into the aquatic environment by direct discharges after using products containing these microspheres. These represent 19% of the total plastic contaminants present in the aquatic ecosystems, whereas the remaining 81% is the result of contamination by secondary MPs (Katare et al. 2021), as shown in Fig. 1.

In general, MPs have a low density and are initially released into rivers and lakes, followed later by the oceans. These are configured as a category of waste harmful to the aquatic environment, not only due to their ability to cross biological barriers but also due to the implications of the mechanisms of bioaccumulation and biomagnification of several other polluting compounds (Brennecke et al. 2016). Once released into the aquatic environment, MPs undergo changes in their physicochemical properties due to high exposure to sunlight, changes in temperature, and movement of the system. These particles become more fragmented and have a greater amount of oxygenated groups when exposed to ultraviolet radiation, thus demonstrating that environmental factors alter the surface of MPs, and consequently affect their interactions with contaminants (Gunes 2022).

4 Consequences of Microplastics (MPs) on Aquatic Organisms

The ubiquity of MPs in the aquatic systems has adverse effects on organisms residing there, overall ecosystems, and human health. This is a problem that raises concern, as organisms can ingest MPs and cause them to spread to cell boundaries and

accumulate, as they can translocate throughout the food chain (Veerasingam et al. 2020). MPs cause deleterious effects on algae, arthropods, bacteria, mollusks, and rotifers. Due to the hydrophobic surfaces of these organisms, they can adsorb and bioaccumulate the persistent toxic compounds (PBT), including the metals and persistent organic pollutants (POPs) (Bollinger et al. 2020).

As the marine life lies at the center of the food chain that human beings can utilize, the marine pollution by MPs is of paramount importance. The literature has shown that the MPs can accumulate in different tissues of the human body, including the kidney, liver, and intestine, which can alter metabolism and oxidative stress. Different organisms can mistakenly feed on these polymers instead of food, which can block the feeding organs and damage the digestive system (Ziajahromi et al. 2018; Liu et al. 2019).

The physical impacts caused by MPs in the aquatic ecosystems include the formation of webs in water bodies, mainly causing severe impacts on aquatic species, which are affected by the entanglement of these polymers. Some of these species are seabirds, mammals, sea turtles, and crustaceans. When these animals were trapped in these PM nets, they suffered from suffocation and starvation. Furthermore, the direct and indirect ingestion of PMs leads to the accumulation process at the most different trophic levels (Zhang 2017). Fish are one of the most affected organisms, in which the toxicity process can be observed mainly by the bioaccumulation mechanism. There are several ways in which humans can be affected by MPs, one of them being the ingestion of contaminated aquatic organisms (Wang et al. 2020).

Polyester, polyethylene, polystyrene, and polypropylene are the most commonly produced polythene-containing polymers around the world. These polymers more frequently occur in the digestive tract of the fishes. The adsorption of MPs by fish can occur directly, a factor that is due to the confusion of MPs with natural prey, or indirectly, through other contaminated organisms (Wang et al. 2017). According to Alomar and Deudero (2017), MPs were reported in the stomachs of cat sharks (*Galeus melastomus*) from the Mediterranean Sea, which can be attributed to the bioaccumulation of their prey that were contaminated.

Microplastics (MPs) may have the possibility to enter the circulatory system of the aquatic organisms via their intestinal tract. Particles of size 3.0–9.6 μm were reported in the hemolymph of the blue mussel *Mytilus edulis* (Peng et al. 2020). Different aquatic organisms, for example, bivalves, benthic invertebrates, zooplankton, small and large fishes, and mammals, ingest MPs as food. Such processes block and damage their digestive organs, which further resulted in the false satiety to the organisms (Su et al. 2016). Overall, the extent of the ecological disturbance in the trophic chain depends on how the exotoxicity of the MPs is transported and proliferated in the aquatic ecosystems. Since these processes interfere with the nutrients cycling in the environment, which causes physiological stress to the organisms, thus, threatening the composition and stability of the ecosystems (Tang et al. 2020).

5 Bioremediation of Microplastics (MPs)

The anthropic impacts on the aquatic ecosystem have generated worldwide concern. At this juncture, strategies have been developed, in which bioremediation appears as an alternative. However, it is important to emphasize that bioremediation techniques must be in consonance with the recycling pathways and biogeochemical cycles operating in the terrestrial and marine ecosystems for the ecologically sound remediation of the contaminated ecosystems (Dash et al. 2013; Masiá et al. 2020). The bioremediation technique is emerging in environmental biotechnology, as it applies some specific metabolic activities of the organisms including bacteria, fungi, microbial mats, microalgae, and yeasts for purifying the ecosystems. Thus, the activity of these microorganisms is crucial, as they are capable of mineralizing or transforming the organic contaminants into less harmful substances (Sayed et al. 2021). The bioremediation process can be carried out in different ways, as shown in Fig. 2, and may be through the addition of selected microorganisms, which is called “bioaugmentation” or the addition of nutrients, known as “biostimulation.”

There are different bioremediation strategies, such as bioaugmentation and biostimulation. The first acts through the introduction of variable microbial populations, while the second involves the stimulation of native microbial populations. In this way, the route chosen for the treatment of the contaminated environment must be based on detailed understanding of the biotic and abiotic factors that may have considerable impacts on the biodegradation process (Sayed et al. 2021). The use of living organisms for the bioremediation of MPs is still a great challenge, since it is important to take into account that the biodegradation process is influenced by

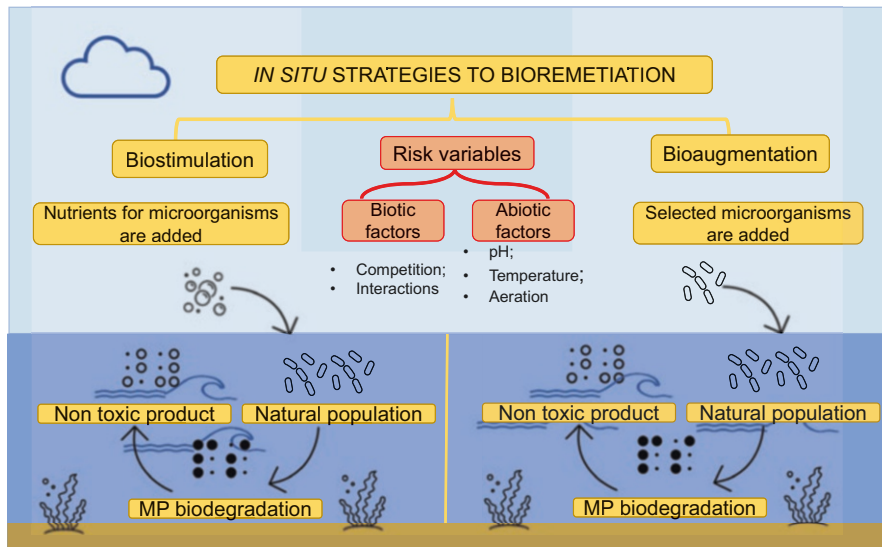


Fig. 2 Strategies for bioremediation of impacted environments

numerous factors, such as the type of polymer, its properties, type of organisms used, and nature of pretreatment (Tiwari et al. 2020).

The difficulty in control or regulation of microbial degradation processes is strongly related to the biotic and abiotic variables, particularly temperature, pH, and oxidative stress technology used for the degradation and/or elimination of MPs (Knott et al. 2020). Most researches showed the use of bacteria and lower eukaryotes and fungi as the major group of microorganisms that act in the bioremediation process of MPs (Silva et al. 2018; Ru et al. 2020). Different species of bacteria and fungi have been reported with the potential to degrade different types of plastic polishes. Some of the major examples include *Achromobacter* sp., *Acinetobacter* sp., *Alcaligenes* sp., *Amycolatopsis* sp., *Aspergillus* sp., *Candida cylindracea*, *Chromo-bacterium viscosus*, *Clostridium* sp., *Comamonas acidovorans*, *Curvularia senegalensis*, *Penicillium* sp., *Pseudomonas* sp., *Rhizopus arrizus*, *R. delemar*, *Roseateles depolymerans*, *R. ruber*, *R. eutropha*, *R. rubrum*, and *Thermobifida fusca* (Aliko et al. 2022).

The microbial degradation of MPs involves a series of biochemical reactions, which are divided into four stages, biodeterioration, biofragmentation, assimilation, and mineralization. Biodeterioration involves the formation of a biofilm around the plastic polymer, being the beginning of the degradation process. This is one of the most important stages, since it occurs when the microorganism has contact with the polymer to develop two hydrolytic activities (Rogers et al. 2020). The biofragmentation process is related to the secretion of the first extracellular enzymes, which allow the degradation of the polymer for the subsequent ingestion. The assimilation phase involves the assembly of oligomer/dimer/monomer on the surface of microorganisms and absorption can occur in two ways, simple or facilitated diffusion. Finally, mineralization concerns the production of secondary metabolites, for example, CO₂, CH₄, and H₂O after the degradation of organic contaminants (Nie et al. 2020; Lear et al. 2021).

According to Yang et al. (2020), the presence of MPs in the environment is responsible for triggering adaptation mechanisms of microorganisms to deal with their adverse impacts. Microorganisms respond to environmental stresses in different ways. For example, the microbial responses involve the decrease or increase in their growth pattern, metabolic rate, as well as biosynthesis of certain new bioproducts. According to Dey et al. (2021), bacteria can degrade MPs by producing enzymes with PETase and MHETase. Moreover, the quantification of CO₂ and CH₄ emissions during the mineralization process of MPs can be used to quantify biodegradation process and its efficiency. Some bacterial groups such as Alteromonadaceae and Burkholderiales have been involved in the biodegradation of poly(3-hydroxybutyrate-3-hydroxyhexanoate) (PHBH). Moreover, it was also demonstrated that the colonization and formation of biofilms by *Erythrobacter* sp. and *Alcanivorax borkum* are involved in the elimination of low-density polyethylene from the aquatic ecosystems (Yang et al. 2020).

According to Ru et al. (2020), the bacterium *Stenotrophomonas panacihumi* was able to break down polypropylene (PP) after 90 days, in low (Mn: 2800, 3600 Da) and high (Mn: 44,000 Da) forms. Similarly, Ariza-Tarazona et al. (2019) also

reported that *Rhodococcus* strains were able to degrade 6.4% of the PP polymer mass in 40 days. In addition to these microorganisms, some fungi such as *Achromobacter* sp., *C. cylindracea*, *R. arrhizus*, and *R. delemar* also have potential for the bioremediation, which are the sources of enzymes such as lipases and esters that are involved in the degradation of MPs (Iram et al. 2019).

6 Conclusion and Future Prospects

The high global production of plastics associated with the inadequate handling of waste generated by these materials is the main influencer in the diffusion of microplastics in the environment. Thus, new strategies have shown promise in the process of reducing and/or eliminating these microplastics, with bioremediation being a reliable, sustainable, and efficient method of converting these dangerous pollutants. The use of microorganisms such as algae, bacteria, and fungi is the most promising approach for using this technique. Thus, in addition to research aimed at new methods of analysis to identify and characterize microplastics, it is necessary to carry out more specific studies on the treatment of this waste, since it is a recurring problem that generates significant impacts on the human and environmental health. In this way, it is expected that with the use of this strategy to eliminate microplastics, it will be possible to reduce the process of environmental pollution in a more skillful and promising way.

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Part V
Analytical Tools and Techniques for
Assessment of Xenobiotics

Recent Advancements in Bioremediation of Xenobiotics Using Microbes



Anwasha Gohain, Rupak Sarma, and Pardeep Singh

1 Introduction

Existence of life is possible only when there is a healthy and safe environment pertaining around us. But revolution in the field of industries, urbanization, population growth, scientific and technological advancements, various anthropogenic activities are bringing change to our lives, affecting the environment by introducing toxic and hazardous pollutants such as Xenobiotics (Bhatt et al. 2020; Rodriguez et al. 2020). For example, the release of xenobiotics in the environment has a great impact on whole urban water cycle which becomes a cause of concern now a days. Moreover, halogenated and nitrated hydrocarbons are considered the most hazardous chemical substances that are generated from industrial processes (Jain et al. 2005). Manmade contaminants generally take longer time to degrade naturally. According to the study of Singh (2017), till date, there are no sufficient and applicable way out to eradicate these artificial pollutants. The term “Xenos’ means “stranger,” is a Greek word meaning stranger in living forms. Soucek (2011) defined xenobiotics as “chemicals found but not produced in organisms or the environment. Some naturally occurring chemicals (endobiotics) become xenobiotics when present in the environment at excessive concentrations”. These are chemical substances that are not produced naturally but are hazardous to the environment and refer to synthetic

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compounds that are produced in large quantities for agricultural, domestic, and industrial use (Embrandiri et al. 2016; Atashgahi et al. 2018; Dinka 2018). Introduction of xenobiotics into the environment, accidentally or deliberately, is a high-risk factor for all the living organisms. It is a growing public concern worldwide as it cannot degrade naturally (Hashmi et al. 2017; Zhu et al. 2017; Dinka 2018). Introduction of xenobiotics into the environment, accidentally or deliberately, is high risk factor for all the living organisms.

On the other hand, various wastewater treatment plants are not efficient in eradicating xenobiotics from wastewater, thus, entering public sewers and affecting human health as well as polluting water bodies (Gabet-Giraud et al. 2010; Roccaro et al. 2013; Karthiga devi et al. 2021; de Oliveira et al. 2020). Microbial community, although taking the responsibility to degrade individual xenobiotics, activated sludge, but it is not efficient and specific enough for the task. However, certain xenobiotics produced from pharmaceuticals companies and personal care products, shortly known as pharmaceutical and personal care products (PPCPs) can be degraded by application of advanced technologies (Lin et al. 2009). The revolution in the field of science and technology has led to many useful compounds such as antibiotics, pesticides, and dyes that can improve day-to-day life of mankind; however, these are not naturally occurring compounds (de Oliveira et al. 2020). Because of their physicochemical structures, it is difficult to identify as well as quantify them for degradation which is why they remain in the environment for a longer period of time (de Oliveira et al. 2020).

1.1 Classification of Xenobiotic Substances

According to Kumar and Chopra (2020), xenobiotics can be categorized into pharmaceutical products, personal care products (PCPs), pesticides, illicit drugs, nuclear waste and other industrial products (Kumar and Chopra 2020). They are again subdivided into an array of different compounds. However, Directive 2013/39/EU of the European parliament and of the council amending Directives 2000/60/EC (Water Framework Directive (WFD) and 2008/105/EC identified 17 groups based on their priority (herbicides, polyaromatic hydrocarbons, organophosphorus and organochlorine insecticides, chlorinated solvents, aromatic organochlorine compounds, dioxins, metals, phthalate, anti-fouling biocide, alkylphenols, pyrethroid insecticides, perfluorinated surfactant, benzene, quinoline fungicide, chloroalkanes, and hexabromocyclododecane). Eight groups in watch list substances and pyrethroid insecticides, sulfonyleurea herbicide, organophosphorus insecticides, and metals and nonmetal trace elements are grouped into candidate substances. On the other hand, Mathew et al. (2017) gave another classification of xenobiotics. It is based on the characteristics of xenobiotics. This encompasses nature of xenobiotics, its uses, physical state, and pathophysiological effects. Xenobiotics, however, also classified based on the sources (Fig. 1 and Table 1).

As this chapter has already defined xenobiotics as foreign compounds but simultaneously Kumar and Chopra (2020) described them as the natural substance for

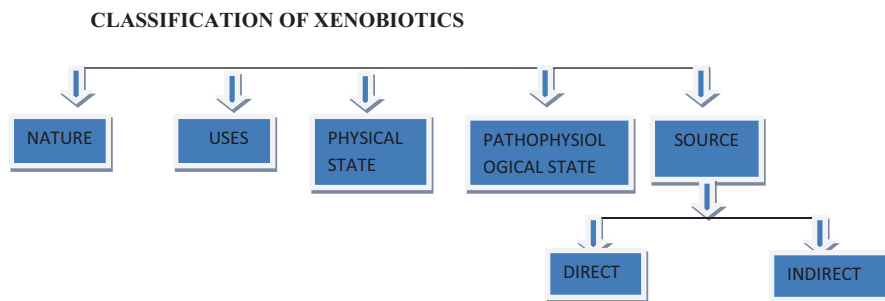


Fig. 1 Categorization of xenobiotics based on the characteristics and sources

Table 1 Categorization of xenobiotics with the examples

Serial No.	Characteristics	Categories	Examples
1.	Natural	Natural	Produced by living organisms, namely, bacteriotoxins, zootoxins, and phytotoxins
		Manmade	Toxic substances, namely, pesticides
2.	Uses	Active uses	Used in day-to-day life such as pesticides and dyes
		Passive Uses	Use as additives, carrier molecules
3.	Physical state	Gaseous	Vapor, aerosol
		Solid	Dust-form xenobiotics
		Liquid	Dissolved chemicals in water
4.	Pathophysiological effects	Tissue or organ	Kidney toxins
		Biochemical Pathways	Methemoglobin producing toxin
5.	Source	Direct	Direct release chemicals such as phenols and hydrocarbons from pharma companies Plastics, paint including emulsifiers
		Indirect	The substances which affect the environment indirectly such as the discharge from the medical stores, pharmaceutical companies, and herbicides

other organisms based on the organisms' metabolic activity to degrade it, i.e., xenobiotics can be natural as some of the organisms can produce some chemical substances for their self-defense, e.g., bacteriotoxins, zootoxins, or phytotoxins; active amines such as serotonin. On the contrary, manmade chemical substances can be called as synthetic xenobiotics as it becomes toxic for living organisms due to their slow degradation or their ability to transform to other hazardous compounds that are more toxic to the environment. Based on uses, xenobiotics are categorized into active and passive xenobiotic compounds such as pesticides, paints, dyes, and additive compounds or carrier molecules, respectively. These passive compounds

generally, facilitate the working of active xenobiotic compounds in a better way (Donner and Eriksson 2010).

The physical state of xenobiotic compounds can make them more easily spreadable. Xenobiotics are found in gaseous form, i.e., either in vapor or aerosol form and can be easily spread in environment. Solid form of xenobiotics is mainly available in dust form (asbestos powder) which is minute and light, and hence, can easily be carried away by air or water. Nonetheless, liquid form of xenobiotics has the ability to dissolve in water (Kumar and Chopra 2020).

Another way of classifying xenobiotics is their physiological characteristics, i.e., targeted tissue or organs by xenobiotics and the biochemical pathways of affecting the target sites can also be the way of classifying xenobiotics (Mathew et al. 2017). Sources can also be the important factors for classifying xenobiotics as these can be released in the environment directly. Emission or the influence of these xenobiotic compounds can be minimized by unfolding the sources of emission. Based on direct or indirect sources, xenobiotic compounds can be categorized, as some of the chemicals are released directly in the environment. Mostly, phenols and hydrocarbons emitted from pharma companies are considered the direct sources. In addition, the substances that degrade slowly and persist in the environment for a longer period of time can be grouped under direct source of xenobiotics (Mathew et al. 2017).

2 Effect on Environment

There are various human practices due to which xenobiotics enters into the environment. These anthropogenic activities include human consumption and excretion, wastewater management and sewage treatment plants, livestock management, various industries and production plants, and different agriculture practices (Kumar and Chopra 2020). Direct application of pesticides in soil causes water pollution as these are carried by rain into rivers as well as groundwater. PPCPs enter the environment indirectly as human consumption. These products cannot be metabolized completely. The process involves conversion into other metabolites which might be more toxic as compared to the original compounds. Thus, these excretory products ultimately treated in sewage or wastewater treatment plants and end up in soil, rivers, lakes, oceans, etc., affecting the aquatic ecosystem (Kumar and Chopra 2020).

2.1 Soil

Nature provides balanced constituents for Earth's crust which make it stable, but undesirable activities of mankind significantly altered the biogeochemical cycle. This results in the accumulation of metals and ultimately leads to the formation of synthetic xenobiotics (Singh et al. 2011). In this regard, human activities adversely affect soil in various ways. Microbes are ubiquitous. The microbial community of

soil is responsible for various degradation activities which help to maintain a healthy environment. But various human activities make drastic changes in the environmental factors such as pH, temperature, pollution, and production of synthetic xenobiotics, which is why the degradation process becomes slower or sometimes does not take place at all (Armstrong et al. 1967; Häggblom 1992; Boussu et al. 2007). The ability of these compounds (chlorinated aromatic herbicides (triazine) and pesticides) to transform itself into more stable form make them more persistent in the environment, thus polluting the environment and affecting the health of living organisms (Gavrilescu 2005; Couto and Herrera 2006).

2.2 Water

The water bodies, on the other hand, are also getting contaminated due to the direct release of various industrial wastes into the water bodies. Along with it, various pesticides, organic solvents, some of which are hydrophobic in nature, remain in un-dissolved state and set as sediments in the water bodies. Because of their tendency to dissolve only in lipids (hydrophobic nature) rather than water, biomagnification causes severe effect on the lower tropic levels (Mathew et al. 2017).

3 Bioconversion of Xenobiotic Compounds

Bioconversion is a process of transforming compounds from one form to another so that the toxic or unwanted compounds can be eliminated from the body. In this process, fat-soluble compounds will convert to water-soluble compounds, and thus, can be excreted from the body in the form of urine and bile. These will be called as xenobiotic compounds and are not soluble in water (Oesch and Arand 1999). That is why before excretion it is essential to make them soluble in water. There are three phases in bioconversion of these compounds. In phase I, functional groups such as $-OH$, $-SH$, $-NH_2$, or $-COOH$ are exposed or added so that further transformation can be processed. In the next phase, the product of phase I or parent molecule is conjugated with polar molecules. In phase III, these soluble compounds are eliminated from the body (Vasiliou et al. 2000). That is the transformation of the compounds takes place in phase I followed by transportation and finally elimination of these compounds in phase III.

Currently, biological techniques play crucial role for the removal and degradation of xenobiotic compounds. They gain popularity because they are cost effective as compared to the physicochemical techniques which were used initially. Moreover, the resultant products produced in physicochemical techniques is toxic and is risky to the environment, and thus, need further treatment (Sethy et al. 2011). Thus, the xenobiotic remediation technique can be classified further as biotreatment, bioreclamation, and biorestitution. In this technology, microbes and their enzymes are

manipulated and play a vital role for transforming xenobiotic compounds such as methane and carbon dioxide (Das and Chandran 2011). According to some reports, bacteria are useful in absorbing large quantities of metals and minerals so that they can ensure a satisfactory binary fission. On the other hand, algae and plants play vital role in absorbing nitrogen, phosphorus, sulfur, and many minerals as well as metals from the environment, and thus, helps in bioremediation of these toxic elements (Caplan 1993). Bioremediation process is influenced by some of the factors such as the concentration of pollutants in the environment, population of microorganisms, and their ability to degrade xenobiotic compounds. However, some physical parameters such as temperature, pH, and activity of microbial enzymes also play crucial role in this degradation process (Vidali 2001), and proper optimization of these parameters may enhance the bioremediation of xenobiotic compounds (Cunningham et al. 1996). Effective bioremediation can be performed out in two different ways: ex situ and in situ bioremediation of xenobiotics.

3.1 In Situ and Ex Situ Bioremediation

Microorganisms are used directly at the site of pollution such as soil and ground water in case of in situ bioremediation. Furthermore, the method is divided naturally where the current condition of the pollution has not been changed. Another one is enhanced bioremediation, which is done by adding additives such as nutrients and oxygen. Though the method is cost effective, it is time consuming and the specific nature of microorganisms is that their behavior to change according to different environmental factors (Saldana et al. 2005; Farhadian et al. 2008). Then again, a better controlled method is applied in ex situ bioremediation that includes transfer of waste and toxic substances to a designated place and then carry out the bioremediation process. Application of this method is done via excavation in soil and pumping in case of water. Ex situ bioremediation is a time efficient and high-yielding technique; however, this is an expensive process as compared to in situ bioremediation (Atlas 1981).

3.2 Microbial Bioremediation of Xenobiotics and Its Compounds

Gadzała-Kopciuch et al. (2004) reported an array of microorganisms that are helpful in degradation of xenobiotics. Totally, 50 different microbial strains were isolated and identified, capable of decomposing xenobiotics and its compounds, such as *Pseudomonas*, *Mycobacterium*, *Alcaligenes*, and *Nocardia*. Microbial degradation of xenobiotics is getting importance because of its effectiveness as well as its economic advantages while decomposing toxic pollutants, especially environmental

pollutants. Diversified bacterial strains participate in xenobiotic degradation process, although the mechanism of action will vary depending upon the type of organisms. For example, aerobic bacteria (*Pseudomonas*, *Escherichia coli*, etc.) require oxygen to actively participate in degradation and anaerobic bacteria (*Syntrophobacter*, *Syntrophus*, and *Desulphovibrio*) perform its jobs without the presence of oxygen (Chowdhury et al. 2008). On the other hand, production of methane gas along with carbon dioxide is evolved in the process of degradation of xenobiotic compounds. Methanogenic bacterium carries out this process via methanogenic process (Jha et al. 2011). Cyanobacterium, another specific bacterium in microbial community, have the ability to degrade the oil derivatives due to its plasmid-borne mechanism (Genovese et al. 2014). They are also responsible for degrading synthetic polymers such as sphingomonads (Kawai 1999). In spite of these microbes, genetically modified organisms (GMO), such as “super bugs” of *Pseudomonas* spp., play key role in degrading hydrocarbons present in oil spills in a large amount (Furukawa 2003). Fungus, achlorophyllous, and unicellular or multicellular organisms also play significant role in bioremediation of xenobiotic compounds. This method is known as mycoremediation, which include the degradation of heavy metals, hydrocarbons in oil pills, and pesticides (Bhadouria et al. 2020). Fungal bioremediation can be further classified as fungal biosorption, micorrhizal fungal degradation, and ligninolytic fungal degradation.

Biosorption is a better way of bioremediation than bioaccumulation, as in fungal biosorption, structure of biosorbents is not affected (Gurel et al. 2010). Volesky (1990) reported that fungal bioremediation is mostly common in the areas where industrial effluents and biomass are dumped. In these areas, xenobiotic compounds are attached to the cellular structure of fungus. Mycorrhizal fungal degradation, on other hand, leads to a symbiotic association of fungi and actinomycetes. This association increases the soil organic carbon. Symbionts such as *Morchella conica* and *Tylospeno fibrilnsa* (fungus) protects soil nutrients by degrading organic xenobiotic compounds that are present in the soil (Kumar and Chopra 2020). There are some species of fungus that are capable of degrading lignocellulose present in paper and pulp effluents. These species produce lignolytic enzymes, which help in lignin degradation. Furthermore, some other species (*Trichoderma harzianum*, *Basidiomycetes*, *Ascomycetes*, etc.) also help in degrading synthetic dyes (Hammel 1996; El-Bondkly et al. 2010).

Algae, a diverse group of photosynthetic life forms also play a significant role in degrading xenobiotic compounds because of their ability to resist heavy metals. The process of bioremediation with the help of algae is called phycoremediation. Different algal species were reported by Cerniglia and Gibson (1977), which have the ability to absorb and degrade polyaromatic hydrocarbons. Those algal species include *Stigeoclonium tenue*, *Anabaena inaequalis*, *Chlorella*, *Westiellopsi sprolifca*, *Synechoccus* spp., and certain other fresh algae such as *Chlorella vulgaris*, *Scenedesmus platydiscus*, *S. quadricauda*, and *S. capricornutum*. However, practical application of these algae is somewhat challenging because of the operational conditions (Dwivedi 2012). Adsorption of the xenobiotic compounds through algal species, next step is the application of chelating agents, namely, unicellular algae.

Chelating agents have the ability to bind with the toxic compounds and form complex structures, thus removal of these compounds becomes easy either from intracellular or extracellular spaces (Davis et al. 2003). Researchers/scientists observed that algal species have the ability to oxidize many toxic hydrocarbons to less harmful metabolites, and thus, degrade the crude oil in oil spills (Ibraheem 2010). In this degradation process, carbon dioxide and less harmful metabolites are produced as by-products (Abdelkader et al. 2011), which can be utilized by algae as nutrient source.

Besides, phytoremediation is also a unique method for removal of xenobiotics and contaminants in situ in soil, sludge, ground water, etc., where direct use of living organisms is carried out (Utmezian and Wenzel 2006). Wenzel et al. (1999) used the term “green remediation” or “agroremediation” in this context when higher plants are used for xenobiotic remediation. Although phytoremediation is eco-friendly and cost effective, it is a time-taking process which is why the full-scale application is yet to be applied (Zhai 2011; Singh et al. 2023). Further, phytoremediation can be categorized as: phytoextraction, phytostabilization or phytoimmobilization, rhizofiltration or phytofiltration, rhizodegradation, phytodegradation, as well as phytovolatilization (Tripathi et al. 2020).

Phytoextraction or phytoaccumulation helps in translocation and uptake of metal impurities present in soil (Shukla et al. 2010). Plant species such as *Brassica juncea*, *Berkheya coddii*, *Allysum bertolonii*, *Thlaspi caerulescens*, and *Thlaspi goesingense* are regarded as hyperaccumulators as they can absorb a large quantity of metals from soil (Pivetz 2001). Certain plant species are also useful in this context. The process of absorption and accumulation of contaminants in the soil through root helps in removal of soil contaminants. This method is known as phytostabilization or phytoimmobilization (Saharan 2011). On the other hand, in plant root zone, rhizofiltration or phytofiltration is the technique used by certain plants to adsorb and precipitation of the xenobiotic compounds. Another term, rhizodegradation is also used when natural biodegradation process is enhanced by plant roots uptake and detoxification of organic compounds in the soil is observed. This process is enhanced due to the rich microbial activity near plant rhizosphere.

Another method to remove the soil contaminants is phytoremediation or phytotransformation where breakdown of contaminants takes place by the plants through metabolic process. It can be within the plant body or external to the plant body by the use of the enzymes secreted by plants (Shukla et al. 2010). Uptake of soluble contaminants from soil and release those as volatile compounds into the atmosphere also help detoxification of soil. This process is called as phytovolatilization (Pilon-Smits et al. 1999). Some examples of plant species which help in phytovolatilization are Water ferns such as *Azolla filiculoides* and water hyssop such as *Bacopa monnieri* which have the ability to accumulate metals; *Canna flaccida* (Golden canna), *Carex pedula* (Drooping sedge), *Miscanthus floridulus* (Giant miscanthus), *Miscanthus sacchariflorus* (Amur silver-grass) helps in removal of heavy metals from constructed wetland area; Algae (*Chara*, *Nitella*, *Ulothrix*, etc.) could provide a simple, long-term solution for radionuclides removal (Gadzała-Kopciuch

et al. 2004). Xenobiotic compounds have a high affinity toward photon (light). They absorb light (i.e., ultraviolet, infrared, and visible radiation) and helps in degrading the xenobiotic compounds. This method is photoremediation, which is also used to eradicate pesticides, heavy metals such as Pb, Cr, Fe, and dyes (Zhang and Shahbazi 2011).

4 Recent Advanced Technologies Employed in Bioremediation

VBNC, i.e., viable but nonculturable bacteria, is a very popular term in modern era of science these days. These communities of bacteria help in biodegradation of environmental pollutants like xenobiotics. Molecular techniques, at this present time, are revolutionizing, and there are a lot of practices, including metagenomics, proteomics, transcriptomics, and metabolomics, which give deeper insights into genes, proteins, mRNA expression, metabolic pathways, and enzymes. The use of an integrated approach in the field of bioremediation is termed as “omics approach” to unfold the biological macromolecule characterization along with specific genetic and molecular structures and their mechanisms among the species of microbial communities (Desai et al. 2009; Yang 2013; Godheja et al. 2014; Franzosa et al. 2015; Chandran et al. 2020). This “omics approach” increases the knowledge in the field of “viable but nonculturable (VBNC)” bacteria along with their novel chemical pathways for degrading xenobiotics and their compounds (Bodor et al. 2020).

Although Su et al. (2013) reported that these VBNC bacteria are different from cells and cannot be cultivated conventionally, a few details are available regarding these. Other studies said that due to the specific metabolic and respiratory activities, they participate in gene expression and transcription. This characteristic allows them to revive under favorable culturable conditions in an autoinducer (Bari et al. 2013; Li et al. 2015; Zhao et al. 2017). Selection of VBNC bacteria is performed by several culture-independent molecular-based techniques, such as next-generation sequencing technology that captures almost all terms that are used in sequencing and is used to thrive all the information about the structural and gene composition of uncultivable microorganisms (Zhao et al. 2017; Bodor et al. 2020). To detect viable cells, Zhong et al. (2016) used a high affinity photolysis DNA nucleic acid dye to detect VBNC. They combined this dye with real-time fluorescence and developed a real-time fluorescence LAMP technique. Thus, a combined approach of advanced molecular technologies along with bioinformatics approaches amplify the researcher’s understandings and knowledge and create a new horizon to unravel microbial communities and their role in biodegradation of environmental pollutants such as xenobiotics and their compounds (Dangi et al. 2018; Pandey et al. 2019; Pinu et al. 2019).

4.1 Genomics and Proteomics

In the modern era of science and technologies, genomics and proteomics play a significant role to interpret and analyze biological data at the genomic and proteomics level. Researchers take various microbial samples directly from contaminated environments for better understanding of genetic variability of unculturable bacteria (metagenomics) and reveal the detailed information about particular degradation process of microbes (Awasthi et al. 2020), which entails directly the whole genome sequencing technique. Several reports are available regarding metagenomics and its techniques which unleash conventional ways of exploring uncultured microorganisms (Nascimento et al. 2020). Remarkable discoveries were identified in the field of metagenomics by sequencing the whole genome sequence of certain microbial strains such as *Pseudomonas aeruginosa* KT2440, *Shewanella oneidensis* MR-1, *Deinococcus indicus* R1, and *Dehalococcoides mccartyi* WBC-2 (<http://www.tigr.org>). These whole genome sequence data are valuable in the successful application of bioremediation of environmental pollutants, as this technique specifies new genes and thus provides comprehensible knowledge about the utility of microbes in biodegradation (Zhu et al. 2020).

Metagenomics approaches highlight the vital novel genes that are attributed to code degradative enzymes of microbial community indentified through whole genome sequencing (Zhu et al. 2020). The metagenomics techniques involve the manufacturing of metagenomics libraries based on sequence-based analysis using high-throughput sequencing as well as functional analysis using phenotypic characteristics (Handelsman 2004). However, Kumar and Chopra (2020) emphasized recent sequence-based metagenome analysis (SOLiD system of Applied Biosystems, Roche 454 sequencing). The construction of cloned libraries is not necessary in these techniques. To explore the diversity of protein families, function-driven metagenomics is an effective method. Exploring the widely distributed novel genes having specific functions involves the construction screening of metagenomics libraries (Kumar and Chopra 2020).

Ngara and Zhang (2018) in their study reported several novel antibiotic resistant genes, which were identified directly from environmental source using functional metagenomics approach. Hydrolytic enzymes such as mainly esterases and glycoside hydrolases have been isolated and characterized by applying functional metagenomics (Taupp et al. 2011). However, Rabausch et al. (2013) developed metagenome extract thin-layer chromatography (META) system for rapid identification of glycosyltransferase (GT) and other flavonoid-modifying enzymes from metagenomic clone libraries. Monooxygenase, a toluene degrading enzyme, was reported where they used function-based metagenomics approaches to explore these diverge genes among microbial community (Bouhajja et al. 2017).

Although metagenomics paves a new way of discovering novel genes which are quite reliable, even then these techniques are costly. However, data interpretation is a challenging task in this respect. An experiment was conducted by Zafra et al. (2016) to degrade PAHs utilizing soil microorganisms. They utilized metagenomic

approach and demonstrated the efficacy of soil microbial consortium for degrading xenobiotics. During this bioremediation process, the microbes synthesized enzymes and metabolites. Auti et al. (2019) investigated an *in silico*, i.e., next-generation sequencing (NGS) approach to reveal the capability of microbes that are isolated from refined- and crude petroleum-contaminated soil for bioremediation of hydrocarbons. They also investigated their role in plant growth promotions. The study sequenced 16S rRNA amplicons on the Illumina MiSeq platform and PICRUSt and proves that microbes isolated from both types of samples (refined and contaminated) have excellent metabolic activity to degrade petroleum hydrocarbon (PHC).

Presence of 61 enzyme-encoding genes (alkane monooxygenase, alcohol dehydrogenase, and aldehyde dehydrogenase) is reported, which are involved in degradation of hydrocarbon. On the other hand, 16S rRNA sequencing gives insights of evolutionary origin of microorganisms as well as taxonomic identification. Studies revealed that the 16S rRNA gene consists of several conserved regions interlinked with variable regions. Presence of these conserved region along with nine variable regions make 16S rRNA gene suitable for sequencing of bacterial DNA (Gursoy and Can 2019). Microbial community analysis has evolved after the introduction of NGS approach as it gives temporal as well as spatial data (Hidalgo et al. 2020). Several studies validated, elucidated, and documented the efficacy of NGS technologies in interpreting microbial data from diverse environmental samples (Zhou et al. 2015; Niu et al. 2016; Scholer et al. 2017). For example, 16S rRNA in prokaryotes (Bacteria), and 5S or 18S rRNA genes, or the internal-transcribe-spacer (ITS) region (fungus) in eukaryotes was validated (Luo et al. 2012).

4.2 Transcriptomics

Transcriptomics provides full insights of genome, proteome, and cellular phenotype with the help of mRNA transcriptional profiles. In this approach, mRNA is directly extracted from microbial communities (Bashiardes et al. 2016). It is a remarkable tool to understand transcribed genes of organisms, which is known as transcriptome. Gene expression analysis revealed that under stressful conditions microbial community showed significant changes in their gene expression level and regulation. Deep insights of a wide range of diverse expressed genes of microbial community can be elucidated using the techniques of transcriptomics and meta-transcriptomics. Diaz (2004) reported DNA microarrays and RNA seq as the most powerful techniques to elucidate and validate the mRNA expression level of every gene of entire genome. In another study, Xie et al. (2011) carried out one experiment based on geochips of functional gene diversity and metabolic potential of microbial communities isolated from acid mine drainage areas and spotted microbe-mediated mechanism of different biogeochemical cycles, biodegradation pathways of xenobiotics, as well as reason of resistivity against heavy metals. In the same way, for stable isotope probing, RNA-SIP and DNA technologies are

considered valuable and significant for uncovering varied microbial and catabolic genes responsible for biodegradation of polluted environments (Lueders 2015).

On the other hand, dominant bacterial communities of diverse bacterial taxa such as Acidobacteria, Cyanobacteria, Bacteroidetes, Ascomycota, as well as Firmicutes were identified and analyzed using meta-transcriptomics, which play crucial role in bioremediation of various xenobiotics and its compounds (Singh et al. 2018). In another study, yet again, Singh et al., in 2016 identified an array of enzymes and 21 different pathways, which are helpful in degrading compounds such as benzoates, aromatic amines, phenols, bisphenols, and other xenobiotics. A significant discovery was made in this field when a gram-negative bacterium, *Sphingobacterium multivorum* was isolated from activated sludge. This bacterial strain was capable of degrading hexaconazole (85.6%) in just 6 days. Three different metabolites, M1, M2, and M3, were identified from this bacterial strains that are later recognized as (2-(2,4-dichlorophenyl)-1-(1H-1,2,4-triazol-1-yl) hexane-2,5-diol), (2-(2,4-dichlorophenyl) hexane-1,2-diol), and (1H-1,2,4-triazol), respectively. Another bacterial strain, *Rhodococcus* sp. BUPNP1 was identified to degrade 4-nitrophenol (4-NP). Genomics and transcriptomics approaches gave deep insight of genome of this strain where the study found a cluster of 43 genes named as nph. This cluster of genes facilitate the important gens to breakdown of 4-NP into acetyl co-A and succinate by nitrocatechol. It is also responsible for degrading other aromatic compounds (Sengupta et al. 2019).

In a synergistic approach using meta-transcriptomics, *Cryptococcus* fungal species and their in situ mock communities were studied and found strain-level inconsistency (Marcelino et al. 2019). Thus, a wide and new idea arose in microbial community regarding potential gene information for degrading environmental pollutants that are turned on in extreme and stressed environmental conditions for proper adaptation in that stressful environment (Marcelino et al. 2019).

4.3 Proteomics

Along with transcriptomics and metagenomics, proteomics is also became known as a fascinating and fruitful technology to get a deep insight of proteins of living organisms. The term proteomics was put forwarded to understand the entire set of expressed proteins during the metabolic and catabolic activities of all living organisms (Hettich et al. 2013). Proteomics with respect to omic technologies is a fruitful approach in microbiological field and helpful to investigate the entire protein profile of microbial population retrieved from contaminated environment (Wang et al. 2016). On the other hand, Arsene-Ploetze et al. (2015) reported meta-proteomics to decode the protein profiling of two ecologically diverse units.

Introduction of proteomics decipher new information regarding protein synthesis, gene-expression stability, mRNA turnover, and protein-protein networking in microbial communities under stress environments (Aslam et al. 2017). However, enzymes identification for bioremediation of xenobiotics can be easily performed

using proteomic approach (Wei et al. 2017). In a study, Nzila et al. (2018), performed proteomic analysis of *Achromobacter xylosoxidans* PY4, capable of degrading pyrene. In this study, they reported a total of 1094 proteins among which 95 proteins were spotted in glucose supplementation, while 912 were identified in presence of pyrene. However, 25 more upregulated proteins were recognized that become active in stressed condition. Furthermore, lower degradation pathway of pyrene was implicated by two upregulated proteins, 4-hydroxyphenylpyruvate dioxygenase, and homogentisate 1,2-dioxygenase.

Another study of proteomics analysis demonstrated the characteristics of bacterial isolate *Spingobium chungbukense* DJ77, which was found to exhibit exceptional ability of degrading various aromatic compounds (Lee et al. 2016). The study carried out 2-DE and MALDI-TOF/MS analysis to describe the degradation mechanism of three xenobiotic compounds (phenanthrene, naphthalene, and biphenyls (PNB)) and their related proteins. Besides, proteomics technique was utilized to uncover the mechanism of biodegradation tetrabromobis-phenol A(TBBPA) in *Phanerochaete chrysosporium*. A total of 2224 proteins were recognized through iTRAQ analysis in three different biological samples. In order to control TBBPA, stressed conditions were applied to *P. chrysosporium* which activated 148 differentially expressed proteins. In this case, 90 proteins were found to be upregulated, while 58 proteins were downregulated, and this expression of genes was responsible for biotransformation of TBBPA by means of oxidative hydroxylation and reductive debromination (Chen and Zhan 2019).

4.4 *Metabolomics and Bioinformatics*

Metabolomics is the profiling of metabolites in cell and tissues, biofluids, etc., and are of low molecular weight, approximately <1000 Da. Because of the inherent sensitivity, subtle alternations in biological pathways can also be detected (Withers et al. 2020). Thus, the relationships between organisms and environment can be explored and provide insight of metabolic activities (Mallick et al. 2019). Degradation mechanism of carbonyl and other N-methyl carbamates pesticides was investigated in *Burkholderia* sp. strain C3 utilizing metabolomics approach (Seo et al. 2013). The metabolomic study gave insight bacterial adaptation as the presence of different environmental pollutants, toxic pesticides, chemicals, etc., causes alternations in their synthesis and metabolic pathways. Another study undertaken by Wang et al. (2019) utilized comparative metabolic approach to observe the biodegradation of cyfluthrin in *Photobacterium ganghwense*. Totally, 156 metabolites were identified through metabolomics approach during the biodegradation process of cyfluthrin.

In modern era of technology, bioinformatics has also been regarded as the blooming subject where a new array of computational technologies helps in determining relationship among organic molecules, biochemical and metabolic pathways, protein expression, structures, and metabolites (Shekhar et al. 2020). There are a

number of reports that explain the significance of bioinformatics to understand the mechanisms of bioremediation of toxic pollutants in the environment. It provides in-depth information regarding molecular, cellular, as well as genetics of xenobiotic degradation and detoxification (Kumar et al. 2016, 2020; Huang et al. 2020). Moreover, a number of bioinformatics tools are available to investigate the biodegradation process. For example, University of Minnesota Biocatalysis/Biodegradation Database (UM-BBD) provides information regarding microbial catabolism and related biotransformation and biodegradation pathways for xenobiotics and other hazardous pollutants (Ellis et al. 2006). Another good example is Biodegradation Network-Molecular Biology (Bionemo), which provides information about the structure and function of biodegradative genes and proteins at molecular level (Carbajosa et al. 2009).

In recent times, a number of databases (CAMERA, MG-RAST, and IMG/M) have been developed and used to provide information for in-depth analysis and understanding of genome of diverse microbial community, their intra and interrelationship. Utilization of microbial community for bioremediation of xenobiotic compounds is considered the most proficient and accepted remediation technology. In this regard, there is no such source available where one can find all the information with respect to environmental pollutants, microorganisms, and their potentiality of biodegradation. Thus, bioinformatics (biological databases, softwares, and tools) can coalesce all the well-defined information such as bioremediation pathways using microorganisms, enzymes, genes, type, and nature of pollutants. This will help the researchers to do more investigation in the field of bioremediation.

5 Conclusions and Future Recommendations

Our environment is surrounded by chemical and natural compounds that can become potential pollutants when produced in an uncontrolled manner. Eventually it will be accumulated in the environment, and thus, causing harm to the natural ecosystem including biotic and abiotic components. Successful bioremediation can be achieved by manipulating the microbial population. The microbial community has tremendous potential to degrade xenobiotically contaminated biological resources such as soil and water. Although there are a number of unidentified microorganisms that can be better source for bioremediation. This is due to the fact that all the microbial community can never be cultured in artificial conditions, besides metagenomics might be a solution for all those nonculturable (VBNC) organisms. Hence, advanced and recent technologies, such as advancements in omic technology including metagenomics, genomics, proteomics, and metabolomics, will be useful to enhance and understand the genetics and metabolic alternation in microorganisms in stressed environments, i.e., in the presence of pollutants. Various studies proved that the degradation of xenobiotic compounds can be enhanced by exploiting microorganisms, and photodegradation has shown much capability. Moreover, the limitations of biodegradation of xenobiotics by using microorganisms can be overcome by use

of genetically modified organisms (GMOs). Thus, interdisciplinary applications in biodegradation process will pave a new way of understanding and deciphering knowledge for bioremediation of xenobiotics and its compounds by exploiting the microbial community.

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Advancements in the Analytical Techniques for Precise Xenobiotics Assessment: A Special Emphasis on Pesticides Detection



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Abbreviations

ELISA	Enzyme-linked immunosorbent assay
FUSLE	Focused ultrasonic solid–liquid extraction
GC	Gas chromatography
HPLC	High-performance liquid chromatography
LC	Liquid chromatography
MS	Mass spectrometry
OCs	Organochlorine
OPs	Organophosphorus
PAHs	Polycyclic aromatic hydrocarbons
PCBs	Polychlorinated biphenyl
QuEChERS	Quick, easy, cheap, effective, rugged, and safe
SBSE	Stir bar sorptive extraction
SPE	Solid-phase extraction
SPME	Solid-phase microextraction

1 Introduction

Nowadays, owing to the advanced industrialization, urbanization, and different human actions are the main causes for the additions of lethal and harmful pollutants in the environment (Embrandiri et al. 2016; Bhatt et al. 2021). Advancement in

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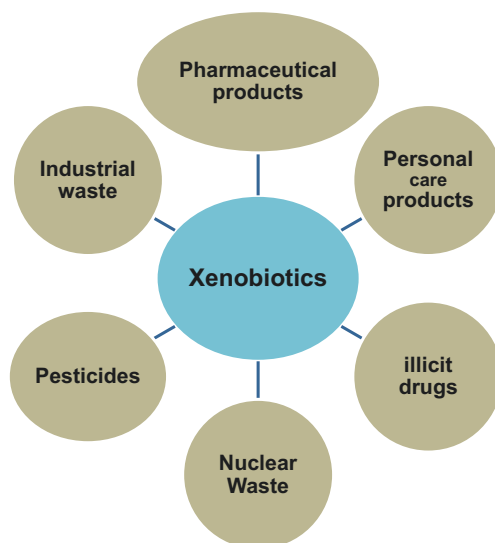
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technology, longer life, and improved access to medicine for humans as well as animals, inevitable uses of pesticides, and daily uses of personal care products commence new substances enter into the environment is called xenobiotic. The word “xenobiotic” generally used in the context of synthetic pollutants produced by industries and used for domestic and agricultural purposes (Embrandiri et al. 2016; Atashgahi et al. 2018). Xenobiotics are chemically synthesized compounds, which are not generated naturally but may present in the living organisms as a foreign substance (Sharma et al. 2016). Xenobiotics consist of polycyclic aromatic hydrocarbons (PAHs), pesticides, pharmaceutical active compounds, personal care products, illicit drugs, chlorinated compounds, phenolics, and more industrial waste (Fig. 1). The word xenobiotics derived from the Greek “*xenos*” (foreign) and “*bios*” (life), denoting the foreign things present in living forms. Further, xenobiotics can be classified based on their properties and structural characteristics. Xenobiotics are insoluble in water and are extremely stable in nature. Microorganisms cannot take them as a substrate and are mostly nonbiodegradable in nature. Due to its large molecular weight, they cannot enter easily into the microbial cells and are extremely toxic. For instance, the fish exposed with the effluent of the sewage treatment plant will be harmed substantially.

Due to the presence of halogen molecule instead of hydrogen in xenobiotic compounds, it requires extra energy for cleavage. Moreover, the groups like amino, methoxy, nitro, and sulfonate also exist in xenobiotic compounds. Xenobiotics are recalcitrant in nature due to the presence of cycloalkanes, aromatic compounds, and heterocyclic compounds. Branched linear chains of xenobiotics are nonbiodegradable in nature (Foti and Dalvie 2016). Likewise, hormones produced by human beings can be entering into the water bodies and for fish they act as foreign substance (Llorca et al. 2016). Wide range of xenobiotic compounds are intentionally or accidentally being introduced into the environment, poses lethal effect on

Fig. 1 Different types of xenobiotic compounds present in the environmental matrix



humans, as well as animals health (Jacob and Cherian 2013; Zhu et al. 2017; Dinka 2018). Synthetic pesticides are the main xenobiotics that are used worldwide extensively for a long duration of time in agricultural as well as domestic purposes. Highly toxic nature, long persistence in the environment, and bioaccumulative property pose potential human health risk (Jayaraj et al. 2016; Pang et al. 2020). To circumvent and reduce the adverse effect of xenobiotics in the environment, thus it is imperative to find precise xenobiotics assessment analytical techniques.

Due to the presence of xenobiotics in ultralow concentrations, their detection in environmental samples is a tedious task (Salem et al. 2017). Efficient extraction and determination methods of analytes with fast, accurate, and at acceptable cost-effective methods are of utmost importance (Priyanka et al. 2022). In chromatographic analysis, mostly efficient and precise methods include pretreatment of samples before the extraction of the compounds, and purification requires interferences removal. In recent times, certain advancement has been developed to prepare quick, easy, cheap, effective, rugged, and safe (QuEChERS) samples for analysis, stir bar sorptive extraction (SBSE), solid-phase microextraction (SPME), solid-phase extraction (SPE), and focused ultrasonic solid-liquid extraction (FUSLE) methods (Juliano and Magrini 2017). QuEChERS technique is involved in the extraction of antibiotics, mycotoxins, multiresidue pesticide analysis, hormones, persistent organic pollutants, and PAHs in environmental samples.

Conventional extraction methods namely solid-phase extraction (SPE) and liquid-liquid extraction (LLE) follow multisteps, consume toxic solvents and are also time-consuming method to carry out. Notwithstanding advancement in analytical technology, efficient sample preparation methods for pesticide and their residue in environmental samples are still required. Moreover, these detection methods must be suitable with latest analytical techniques. The main objective of this chapter is to give an outline of the current technologies employed for the precise assessment of xenobiotic in the environmental samples. This chapter specially focuses on the current approaches for the assessment of pesticides in the environment.

2 Methods Used in the Detection of Xenobiotics

Xenobiotics detection in the environment is a tedious task since the compounds mostly exist in ultralow concentrations that are challenging to assess and also the heterogeneity of them in various sample variety (Salem et al. 2017). Efficient extraction and determination methods of mixtures of xenobiotics compounds with fast, accurate, and at acceptable cost-effective methods are of utmost importance (Juliano and Magrini 2017; Priyanka et al. 2022). Mostly efficient and precise analytical methods for xenobiotics determination include pretreatment of samples before the extraction of the compounds, and purification requires for interferences removal. In recent times, certain advancement has been developed to prepare QuEChERS samples for analysis, SBSE, SPME, SPE, and FUSLE methods (Juliano and Magrini 2017). QuEChERS technique is used for the extraction of antibiotics, mycotoxins,

multiresidue pesticide analysis, hormones, persistent organic pollutants, and PAHs in environmental samples. On the contrary, SPME can simultaneously prepare and analyze pesticides, polycyclic aromatic hydrocarbons (PAHs), phenols, amines, and polychlorinated biphenyl (PCBs) in the environmental samples (Lashgari et al. 2019). Further, SBSE is employed to detect pesticides, bisphenol A (BPA), PAHs, phenols, and pharmaceuticals present in the environment (David and Sandra 2007). FUSLE can analyze organic and inorganic substances such as PCBs, PAH, hydrocarbons, esters, phthalate, and phenols in different environmental samples (Errekaxto et al. 2008).

The QuEChERS technique is generally coupled with gas chromatography and liquid chromatography-mass spectrometry (GC-MS) and (LC-MS) analysis, respectively (Kim et al. 2019). Xenobiotics detection includes highly sensitive and specific techniques, which includes chromatographic methods including gas chromatography (GC), high-performance liquid chromatography (HPLC), ultrahigh-performance liquid chromatography (UPLC), and multidimensional chromatographic techniques, mostly coupled with latest analytical techniques such as high-resolution mass spectrometry (HRMS) (de Oliveira et al. 2020).

Chromatographic techniques involved in the investigations of xenobiotics following the separation and detection of analytes have similar chemical structures in environmental samples. GC methods analyze the volatile and semi-volatile compounds, which includes xylene, toluene, and acetaldehyde. HPLC analyzes the PCBs, PAHs, and phenols, namely pyrene, chrysene, fluorine, and acenaphthene in water samples (Oros et al. 2012). UPLC analyzes the mycotoxins, pesticides, and pharmaceuticals and in a short time (Narváez et al. 2020). HPLC and UPLC are often coupled with MS or MS/MS. Multidimensional chromatography increases the separation and resolution power. With the coupling of HRMS, multiple numbers of xenobiotic compounds can be detected concurrently, as the full-scan data generated to overcome the problem with preselected ion transition which attune to specific compounds (Tuzimski and Sherma 2019).

Further, for the analysis of pharmaceutical compounds in the water samples, a suitable method is the enzyme-linked immunosorbent assay (ELISA) (Deng et al. 2003; Jaria et al. 2020). This method is also appropriate for the analysis of diethylhexyl phthalate, BPA, dibutyl phthalate, carbamates, organochlorine (OCs) and organophosphorus (OPs) compounds for qualitative analysis. This method can help in the detection of a large number of samples, simultaneously (Estévez-Alberola and Marco 2004). Sensors are innovative devices used for the detection and monitoring of xenobiotics compounds made up of nanomaterials and transmit signals during detection of analyte. Biosensors sense pesticides, PAHs, pharmaceuticals, perfluorinated compounds, personal care products, and disinfection by-products in the environment (Mohamed 2020). They are convenient, sustainable, and economical (Kimmel et al. 2012). Acetamiprid, atrazine, fenitrothion, and paraoxon are pesticides that can be detected by biosensors. Bhattacharyya et al. (2022) have found and applied modified QuEChERS-GC-MS-LC-MS/MS method for the screening of some group of pesticides from the environmental matrix.

3 Pesticides Determination Methods in Environmental Samples

Artificially synthesized (synthetic) pesticides, mainly the organochlorine pesticides (OCPs), are the examples of xenobiotics that are broadly used for a long duration of time in agriculture, worldwide. Many OCPs, including aldrin, dieldrin, benzene hexachloride (BHC), and hexachlorocyclohexane, are very hazardous due to their bioaccumulative nature and stability (Jayaraj et al. 2016; Pang et al. 2020).

3.1 Detection and Quantification of Pesticides

In the past few decades, the uncontrolled usage of pesticides results in significant concerns of human health effects. It is necessitating to tightly control and monitor the excessive usage of pesticides. Highly sensitive, accurate, and rapid analytical methods should be regulated to ensure the determination of pesticides in water, vegetable, and food (Wahab et al. 2021). Different conventional to sophisticated methods have been established for the efficient extraction and detection of the pesticides, which include extraction, cleaning the target analytes, and detection process (Prodhan et al. 2017). Still, there is no standard method approved for the pesticide extraction in laboratories (Narendran et al. 2019).

3.2 Pretreatment and Pesticides Extraction Methods

Solvent separates the pesticide and their residue from the samples during extraction procedure. A standardized extraction technique involves in the recovery of the target analyte from the sample. The designed extraction method should recover the pesticides from the sample efficiently without changing the chemical structure. Further, the co-extracts can be eliminated using physical and chemical methods. Extraction of pesticides belongs to different classes can extract using different types of solvents. Multiple approaches like QuEChERS, SPME, SPE, and liquid–liquid extraction (LLE) are employed for the extraction of target analytes from the samples (Narendran et al. 2020). Accuracy, sensitivity, and selectivity are the most important necessities for the analysis of a particular analyte. The pesticides and their residues can be extracted from different matrices. But the selection of the extraction method completely relies upon the type of pesticide. Acetonitrile, dichloromethane, ethyl acetate, methanol, and toluene are mainly used for pesticides extraction from fruits and vegetables. Moreover, the solvent with good solubility and does not alter pesticides chemically should be selected only. Sometimes a mixture of different solvents can be used to ramp up the recovery of the pesticides (Andrade et al. 2015; Boyapati 2021). The extraction procedures start with the preparation of the samples

further follows the cleaning and homogenization of the samples. The homogenized sample weighed for the extraction of target analyte. Liquid–liquid extraction (LLE) and solid-phase extraction (SPE) procedures have been employed first, owing to its simplicity. Further, during the past decade, microscale extraction efficacy with QuEChERS method has expanded its application, significantly (Lehotay et al. 2010). The QuEChERS method saves the extraction time, stages, and reagents with efficient recovery of the analyte. Mustapha F. A. Jallow and his colleagues in their study extracted 34 pesticides by using QuEChERS multiresidue extraction kit from 150 fruits and vegetables samples and further detected precisely through GC/MS or liquid chromatography-tandem mass spectrometry (LC/MSMS) (Jallow et al. 2017). Comparatively less studies revealed the excellent recovery of the target analytes using QuEChER, method, in contrast to ethyl acetate, and Luke extraction methods. Overall, comparative analysis exhibits that QuEChERS method made the extraction procedure easier, cut the time, and utilization of less toxic solvents.

3.3 *Liquid–Liquid Extraction*

Liquid–liquid extraction (LLE) is also referred as partitioning method that facilitates in transfer of a solute from one solvent to another (Berk 2018). The solubility of the analyte depends upon two immiscible solvents. In LLE method, organic solvents, like acetonitrile, chloroform, hexane, and 1,2-dichloromethane, are widely used for pesticide extraction from the food and environmental sample since their potential to dissolve in different types of immiscible solvents. Medium-polarity solvents (ethyl acetate) reduce the polarity of a polar solvent, whereas it increases the polarity of a nonpolar solvent. Aldicarb, carbaryl, and carbofuran were extracted with LLE method where low temperature and HPLC coupled with an ultraviolet-visible detector were used to improve and confirms the efficacy of this method (Goulart et al. 2012). In a study, atrazine, carbaryl, ametryn, and chlorothalonil extracted using LLE method and detected by high-performance liquid chromatography coupled with an ultraviolet-visible (UV) detector. Further, this study concluded that LLE approach is an efficient and highly selective for target analyte extraction prior to its quantification using HPLC using ultraviolet-visible (UV) detector (Bedassa et al. 2017; Amir et al. 2022). In another study, mebendazole and its metabolites were extracted using an LLE method, and the extract was examined using liquid chromatography-tandem mass spectrometry (LC–MS/MS) (Lee et al. 2017; Ahmad et al. 2022). Hence, from the previous studies, it has been concluded that LLE is one of the best approaches for the extraction of pesticide, but a variety of extraction solvents are required for the recovery of most commonly used pesticides such as carbendazim (CB), thiabendazole (TB), and 6-benzyl aminopurine (6-BA) (Cho et al. 2013). Moreover, LLE is compatible with a wide range of equipment. However, in LLE procedures, a large amount of hazardous leftovers, difficult task to make the process automated, laborious, time consuming, and expensive makes this approach inefficient.

3.4 *Solid-Phase Extraction*

Among all extraction procedures, the solid-phase extraction (SPE) method uses most extensively due to its simplicity, rapid and efficacy in the extraction of a wide range of target analytes. This method uses packing column or cartridge in extraction procedure (Sabik et al. 2000). In SPE extraction procedure, the analyte passed through the cartridge and absorbed on solid-phase material, further prepared and activated by water and organic solvent. First, the analyte is absorbed on an appropriate material through their interaction. A specific organic solvent is used for removal of the interferences further a different solvent used for the elution of target analyte (Else et al. 2010). The solvent to be used in the SPE method is selected based on the molecular properties of the pesticides. Some solvents like acetone, acetonitrile, cyclohexane, ethyl acetate, ether, dichloromethane, hexane, methanol, and toluene are widely used in SPE (Khalid et al. 2022). Different types of cartridges are used for the pretreatment of pesticides and their residues in different samples. In a study, bispyribac sodium residues in rice samples were extracted using solid phase and determined coupled with high-performance liquid chromatography with a diode array detector (DAD) (Wu and Mei 2011). From the above, it is concluded that pH plays an essential role for the stability of the analytes, and it also ensures the good retention on the absorbent. As a result, for maintaining pesticide stability and increasing absorption in the solid phase necessitates the use of an adequate pH (Ravelo-Pérez et al. 2008).

3.5 *Chromatographic Techniques*

Various conventional analytical techniques have been utilized for the analysis of pesticides in different environmental samples. Exclusive techniques include gas chromatography (GC), liquid chromatography (LC), high-performance liquid chromatography (HPLC), GC coupled with mass spectrometry (GC-MS) and liquid chromatography (LC-MS), etc. More advanced techniques are coupled with tandem mass spectrometry such as ultrahigh-performance liquid chromatography-tandem mass spectrometry (UHPLC-MS/MS). Practically, due to the interference of the matrix, it is tedious to detect actual concentration of the pesticides. Nevertheless, owing to high sensitivity, separation, and detection ability GC and LC have turned out to be the prominent methods for the quantification of pesticide residues in samples. Apart from this, several techniques are also utilized to detect pesticide and their residue in samples through enzyme-linked immunosorbent assay (ELISA) and capillary electrophoresis (CE) (Chen and Fung 2010).

3.6 Gas Chromatography

Gas chromatography is an advanced separation method employed in the detection of various volatile and readily vaporized pesticides. GC is mostly coupled with detectors like a flame ionization detector (FID) for the measurement of OPs and pyrethroid pesticides (Farajzadeh et al. 2014; 2016). It has been reported that analysis of large number of pesticides through GC only can be accomplished when combined with different detectors. Nitrogen phosphorus detectors (NPD), flame photometric detectors (FPD), electron capturing detectors (ECD), and mass selective detectors (MSD) are employed due to their high sensitivity (Bakırcı and Hı 2012; Łozowicka et al. 2017). Different types of detectors have been employed for the analysis of different class of pesticides in different matrices. For instance, the flame photometric detector (FPD) used to detect OCPs pesticide and the electron capture detector (ECD) are utilized for the analysis of fenitrothion, chlorpyrifos-methyl, procymidone, and vinclozolin (Balinova et al. 2006; Sapahin et al. 2019)). MS and tandem MS detectors are alternatively used in pesticides analysis (Stoytcheva 2012). In the past two years, the usage of polar pesticides due to their high toxicity and short persistence has been increased making GC tool less suitable for its detection. Since polar pesticides are highly volatile and with low thermal stability.

3.7 Liquid Chromatography

In pesticides and their residues detection process, different kinds of liquid-chromatography based approaches mostly coupled with ultraviolet (UV), photodiode array (PDA), diode array detector (DAD), and mass (MS) detectors have been proposed (Chung and Lam 2012). Otherwise, HPLC analysis is considered as the most efficient method for the separation of compound having high polarity and nonvolatile nature (Bagheri et al. 2016; Timofeeva et al. 2017). At present, time-of-flight mass spectrometry (TOF-MS) is employed with ultrahigh-performance liquid chromatography (UHPLC) for the detection of more than 60 pesticides in fruits and vegetable samples. Therefore, the higher separation efficacy of UHPLC than HPLC now becomes the most suitable option for the separation of multicomponent mixtures in the samples (Swartz 2005).

3.8 Liquid Chromatography–Mass Spectrometry

Pesticide and their residue analysis through LC–MS is one of the most progressive analysis tools. It has been tested and implemented in this area in almost every form of ionization source and mass analyzer. LC–MS system routinely conducts the analysis of multiclass and multiresidue simultaneously broadly in fruits and vegetables.

Furthermore, there are some LC-ESI-MS/MS applications for pesticide residue analysis. Besides, LC-QqQ-MS/MS tool has facilitated to analyze above 50 pesticides in a lot concurrently (Blasco and Picó 2007).

Presently, GC-MS and LC-MS/MS with electrospray ionization (ESI) are the two frequently used methods for multipesticide residue analysis in samples. Since they have high sensitivity, selectivity can be employed to assess various pesticides of different chemical classes in a single run. Significantly, it can differentiate volatile, nonvolatile, thermolabile, and underivatized compounds in LC/MS analysis. In contrast to GC-MS, LC-MS can analyze large number of compounds. Tandem mass spectrometry (MS/MS) is an expeditious separation technology that is coupled with same or different kinds of two analyzers (Blasco and Picó 2007). Furthermore, in LC-MS/MS, it is possible to integrate various kinds of analyzers in different ways. Quadrupole-time-of-flight systems (Q-TOF), quadrupole-linear ion trap systems (Q-Trap), and triple quadrupole systems (QQQ) are the commonly used analyzers mass spectrometry for the identification of pesticide and their residues in various samples (Hałas 2003).

4 Pesticide Determination with Optical Screening Methods

In the light of aforementioned chromatographic and mass spectrometry methods which are expensive, lengthy, and need highly skilled staff, alternatively researchers invented easy, economical, quick, and onsite methods. Microplate assay such as ELISA; a biochemical test has been employed for the detection of antibodies and enzymes. ELISA has been employed to determine pesticides in various samples (Esteve-Turrillas et al. 2016; Watanabe and Miyake 2018). The innovations in nanomaterials have uplifted the fluorescence determination more notably and help in the detection of organophosphorous pesticides, particularly dichlorvos, malathion, paraoxon, and triazophos (Korram et al. 2020). Colorimetry is the primary and easily accessible optical detection technology; on the other hand, fluorescence (FL), surface-enhanced Raman scattering (SERS), and surface plasmon resonance (SPR) regularly produce sensitive result because of their high selectivity and conjunction with nanomaterials. With portable SERS, it does not require prior sample preparation. In view of escalating globalization especially in the food industry, pesticides detection through smart phones becomes the important tool for inspections in field testing (Tsagkaris et al. 2021).

5 Conclusion and Future Prospects

This book chapter briefly provides the negative impact of xenobiotics on humans as well as animals. Various advanced assessment methods for precise determination of xenobiotics in environmental samples have been discussed in detailed. This chapter

mainly focused on to provide detailed information of pesticides assessment methods in the environmental samples. Xenobiotics extraction methods such as QuEChERS, SPME, SPE, HPLPME, SBSE, FUSLE, and DLLME are also included. Furthermore, xenobiotics assessment involves accurate and precise techniques, like HPLC, UPLC, LC–MS, and GC–MS, multidimensional chromatographic methods, mostly coupled with latest detection tools which includes high-resolution mass spectrometry (HRMS) has also been discussed. Detection methods help in detecting precisely even in ultralow quantity of xenobiotics in environmental samples, although the difficulty is the multiplicity and mixtures of xenobiotics compounds existing in the environment and their additive effects are not known. Thus, this necessitated the improvement of various detection approaches for the monitoring and assessment of xenobiotics. So, in this chapter, it has been concluded that universally, there is not even a single authentic method to evaluate all xenobiotics in a single run. The list of xenobiotics compounds should be updated time to time with the development and advancements of precise assessment methods which can detect ultralow concentration of xenobiotic compounds.

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Part VII
Socio-economic Aspects, Livelihood Status
and Policy Regulations

Impacts of the Pesticides on Urban Aquatic Ecosystems and Their Regulation Measures



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1 Introduction

Nowadays, pesticides play a major role and considered as fundamental for the agro-system, since, due to world population growth, there has consequently been an increase in food production, which has made the use of pesticides a type of necessity. To ensure a certain availability of food for the population, chemicals such as pesticides are used as controllers and exterminators of pests, and pests that affect plantations (Clark and Tilman 2017; Tripathi et al. 2020). According to the Food and Agriculture Organization of the United Nations (FAO), pesticides are considered any type of substance or even mixture of substances whose main objective is to prevent, destroy, and control any type of pest, such as vectors of human and animal

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diseases, unwanted species of plants or animals that cause damage in the production, processing, storage, in addition to the commercialization of food products (Souza et al. 2022).

The high social, demographic, and economic demands have generated a great demand for water, so that reservoirs are the main aquatic systems that guarantee good water availability, as well as good quality, especially in urbanized regions. Therefore, this high water demand is also linked to the increasing pollution of aquatic ecosystems, especially with pesticides, which, in turn, has provided changes in the supply of clean water to people (Doval et al. 2017). Over the years, there has been a gradual increase in pesticide residues in the environment, which have caused contamination in different ecosystems and consequently significantly compromised water and food resources. Thus, it is extremely important that these toxic substances such as pesticides are applied correctly to avoid exacerbated and incorrect use, which can pose risks to consumers and handlers (Carvalho 2017).

In view of this, the main objective of this chapter is to approach and discuss through the scientific literature about the impacts caused by pesticides on the environment, particularly in urban aquatic ecosystems, in addition to addressing the regulation of the use of these pesticides.

2 Classification and Use of Pesticides

Pesticides comprise a comprehensive group of organic compounds that effectively help the agrosystem, which have been used since the last century, and over the years their use has increased, mainly due to increased crop productivity (Carvalho 2017). Historically, the fight against pests and diseases through pesticides has been carried out for decades, specifically starting approximately 50 years ago, especially shortly after the world wars, when these respective poisons were used as chemical weapons (Gomes et al. 2020). One of them, for example, DDT (dichlorodiphenyltrichloroethane) had its insecticidal properties discovered in 1939, which in turn became one of the best known, with regard to the class of organochlorines. The erroneous use of DDT made possible the commercial prohibition of this pesticide in the 1970s and 1980s, since it led to extreme concern among governments worldwide (Solivo 2022).

However, even with characteristics of being harmful, DDT was one of the main chemicals responsible for the reduction of malaria cases until the 80s in the world, which the World Health Organization (WHO) recommended its use in the fight against the mosquito, the causative agent of malaria, by spraying houses in regions considered epidemic or even with high rates of malaria transmission. Therefore, it is verified that the use of pesticides also helps to increase agricultural production, especially in combating the action of pests, which are responsible for approximately 30% of losses in this respective production (Gomes et al. 2020).

Worldwide about three billion kilogram of pesticides are used every year, since only 1% of this total is used effectively to control pests in target plants. In this way, a large amount of remaining pesticides reach the environment and non-target plants, which causes contamination and pollution of the environment and makes it possible

to generate major negative impacts on the entire ecosystem (Tudi et al. 2021; Dhuldhaj et al. 2023).

Pesticides can be used as fungicides, insecticides, herbicides, rodenticides, molluscicides, and nematocides, which in most cases are considered substances that play an essential role in the development of the agroecosystem, so that, in addition to reducing the pests, there is an improvement in the yield and quality of the food produced (Strassemeyer et al. 2017). Thus, pesticides can be classified in different ways, such as chemical class, working group, mechanism of action, in addition to their toxicity (Dhuldhaj et al. 2023). For example, with regard to targeting pests, fungicides are vehemently used to kill fungi, insecticides are used to kill insects, and herbicides are used to kill weeds (Tudi et al. 2021).

Pesticides classified according to their chemical class can be divided into organic and inorganic ingredients, since the inorganic ones have copper sulfate, ferrous sulfate, copper, lime, and sulfur. Organic pesticides are considered more complex, since they are also classified according to their chemical structure, such as chloro-hydrocarbons, organophosphates, carbamates, synthetic pyrethroids, synthetic urea herbicides, as well as metabolite herbicides and hormone analogues, triazine herbicides, metalaldehyde molluscicides, benzimidazole nematocides, metal phosphide rodenticides, in addition to rodenticides based on vitamins specifically from group D (Kim et al. 2017; Zhang et al. 2018).

In addition, the classification of pesticides according to the degree of toxicity is conditioned according to the results of studies or tests previously carried out in laboratories. In Brazil, this classification is established by ANVISA (Health Surveillance Agency) through Ordinance No. 3/MS/SNVS, of January 16, 1992, which is vehemently the responsibility of the Ministry of Health (Anvisa 2014). Thus, the Ministry of Health determines that pesticide products contain on their respective labels a colored band with their toxicological class, which is considered the lethality indicator (LD 50) as an indication of the colors on the pesticide labels. This indicator comprises the ability of a dose to kill about 50% of individuals in a test population, therefore, each color has a certain intensity of lethal toxicity, namely: class I – red band (extremely toxic); class II – yellow band (highly toxic); class III – blue band (averagely toxic); and class IV – green band (little or very little toxic) (Mendes et al. 2019).

In view of this, the widespread use of pesticides around the world has resulted in biotic and abiotic changes in the environment, which have led to potentially hazardous products. Therefore, even though it is difficult to predict the extent and respective degradation pathways of pesticides, science is increasingly trying to provide opportunities for identifying processes of degradation of pesticides in the environment (Carvalho 2017).

3 Pesticides in the Environment

The exacerbated use of pesticides has generated several problems, such as damage to human health, contamination of water, soil, food, and even bioaccumulation. The contamination of ecosystems and the demonstration of the inefficiency of the

maximum residual limit (MRL), which in turn defines the legally accepted level of concentrations for pesticide residues in food, considering that it is urgent that there be changes with regard to the perspectives on the use of pesticides by agriculture, given that both population growth and environmental protection are significantly affected (Alencar et al. 2020).

Pesticides are used vehemently to kill pests and control weeds, which in turn become toxic to other organisms, such as the environment, nontarget plants, birds, fish, beneficial insects, water, soils, and humans (Mingo et al. 2017). It is extremely important to understand the effects and degradation of pesticides in the transformation processes of their substances, which are mediated through microorganisms, plants, as well as abiotic processes, such as photochemical and chemical reactions. In this sense, the transformation processes in pesticides are arranged through the structural affinity of different types of transformations, as well as the environmental condition to which it is exposed, especially with regard to its transport and distribution (Carvalho 2017).

The entry of pesticides into the environment can both undergo movement processes, that is, transfers, as well as degradation, so that this degradation generates new products or chemical substances. This movement from destination to other places in the environment can be carried out through adsorption, leaching, volatilization, spray drift, and surface runoff (Liu et al. 2015; Tudi et al. 2021). Thus, different chemicals which are produced by the disposal of pesticides in the environment also point to differences with regard to the behavior of these compounds in the environment (Kim et al. 2017). Figure 1 corresponds to the examples of behavior of pesticides exposed to the environment.

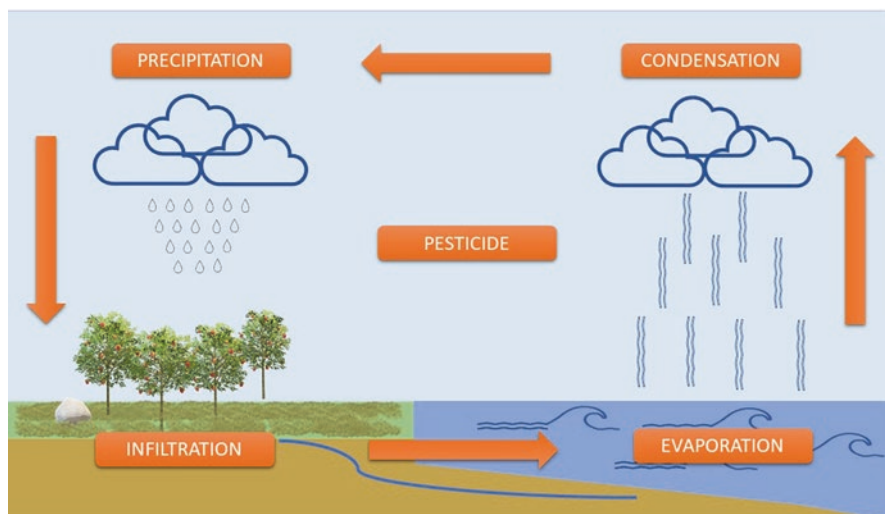


Fig. 1 Different behaviors of pesticides exposed in the environment

4 Pesticides in Urban Aquatic Ecosystems

Pesticides can be present in bodies of water and consequently reach aquatic organisms, mainly through dermal exposure, in addition to ingestion of water and food that are contaminated with these chemical compounds. Thus, according to the physicochemical characteristics of pesticide residues in the aquatic ecosystem, it can be strongly linked to suspended material, be absorbed by the organisms that inhabit there, in addition to being deposited in aquatic sediments and transported through diffusion in water currents (Doval et al. 2017). In this context, pesticides can be derived from both agricultural and human sources and are vehemently ubiquitous in urban surface waters as well. Even so, most of the time the occurrence of anthropogenic contaminants such as pesticides in urban surface waters is due to the mediation of transport from external sources to these aquatic ecosystems (Bradley et al. 2020).

As a result, the increase in industrial development and even the modernization of agricultural sectors worldwide has led to a reduction in the availability of drinking water for urban areas and contributed to the serious pollution of aquatic ecosystems. This type of pollution of water resources is mainly due to the exacerbated release of organic pollutants into the environment, such as polycyclic aromatic hydrocarbons (PAHs), organophosphate esters (OPEs), and pesticides containing chlorine/phosphorus (Peng et al. 2021). Therefore, when compared to industrial emissions in urban aquatic ecosystems, they are considered easier to control due to the fact that they have more punctual origins. The concentration of pesticides in urban surface water is often below 1 $\mu\text{g/L}$, of which it demonstrates that the risk of exposure is mainly long term (Zhang et al. 2022).

Thus, pesticides that contain chlorine in their composition are the main candidates for long-term application, both because of their high effectiveness and stability, so that organochlorines are relevant in studies of urban surface water, in which they gain greater attention by researchers due to the serious risks it can pose to human health, such as nervous diseases (Dhuldhaj et al. 2023). In addition, endocrine-disrupting and carcinogenic effects have already been reported in laboratory experiments on animals, with a view to also demonstrating high toxicity and long-term half-life when compared to other organic pollutants (Li et al. 2020; Aceves et al. 2021). Therefore, pesticides widely used are not always present in high concentrations and urban surface waters, so that, if not detected, risks to both the aquatic ecosystem and human health, especially urban aquatic ecosystems, increase. It further reduces its portability significantly and can bring long-term risks (Zhang et al. 2022).

5 Regulation of Pesticides in Brazil

Environmental standards mostly do not have specific regulations that are understandable or even clear for water glasses, especially in urban areas, thus, becoming a type of obstacle to ensure the safety of human health and the environment (Zhang

et al. 2022). Pesticide legislation is globally different, which creates major problems with regard to the commercialization of products internationally. As a result, nations that are more developed tend to ban certain pesticides considered dangerous, so that they bar the import of food products from countries that do not have adequate care regarding the regulation of pesticides (Handford et al. 2015).

The impediment of these products based on dangerous pesticides is rejected, since most of the time they are above the limits established by the MRL. Thus, developing countries suffer from the rigorous standards established for food safety in developed countries, which in most cases generates higher costs for producers and even higher food prices. Therefore, each nation has its pesticide residue control program, which are considered independent according to each legislation, so that many are also under development (Gomes et al. 2020).

In Brazil, the regulatory framework for pesticides was passed in 1989 by the National Congress, through Law 7802, known as the Pesticides Law, replacing Decree 24,114 of 1934, which was, therefore, regulated by Decree 98,816 of January 11, 1990, and replaced in 2002 by Decree 4074. This advancement allowed stricter rules to be established for granting pesticide registration and even a possible challenge and cancellation of registration (Pelaez et al. 2010).

In this context, for a greater possibility of tracking infringements due to the inappropriate use of pesticides, the obligation to contain an agronomic prescription for the sale of pesticides was instituted, which also established norms and standards on packaging. With the modernization of the pesticide registration structure, it was shared by the Ministries of Agriculture, Health and Environment (Silva 2007).

Another regulatory framework was Decree 5981 of 2006 in Brazil, which simplified the process of toxicological and ecotoxicological analysis of candidate products for registration in just three successive stages in degrees of demand, so that the registration became simplified and concomitantly generated a conflict of interests which facilitated the release of pesticides in the Brazilian market and significantly expanded the market of foreign chemical industries (Pelaez et al. 2010).

Currently, Brazil is the largest global consumer of pesticides, considering that from 2007 to 2015 there were about 84,000 cases of pesticide poisoning, which has grown annually. In 2019, about 474 new products were duly authorized by the government in Brazil, totaling about 4644 pesticides are released for use, both in agricultural and other related activities (Moreira 2019). In the same year of 2019, ANVISA (National Health Surveillance Agency) approved a milestone which is considered innovative with regard to the regulation of the use of pesticides, specifically in the classification of pesticide toxicity (class I – red band; class II – yellow band; class III – blue belt; and class IV – green belt). This approval is mainly related to the fact that the old toxicological classification that Brazil advocated was not associated with the Globally Harmonized System of Classification and Labeling of Chemicals – GHS, which in turn is a classification used globally (Moreira 2019; Gomes et al. 2020). However, even this classification did not prevent the unbridled use of pesticides in Brazil, estimating that thousands of liters of pesticides are released every year into the environment, causing water supply problems and even sick individuals resulting mainly from the contact with the active ingredients of these pesticides (Gomes et al. 2020).

6 Conclusion and Future Prospects

Pesticides comprise a huge group of compounds or toxic substances, which have contributed comprehensively to the agricultural system today. However, its rampant use has been vehemently caused by the significant increase in food production, above all, by the increased demand for food due to high population growth. It is noticeable that pollution by pesticide residues in urban aquatic ecosystems has become increasingly serious and has required specialized attention since it has reduced water quality and has generated harmful consequences for human beings, water resources, and food in the air and on the ground. In this way, the regulation for its use in a conscious and adequate way is fundamental. In view of this, it is suggested the need to reassess the employability of pesticides in the agrosystem, from which, increasingly innovative ways are sought to achieve food production in a more sustainable way.

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Xenobiotics in Urban Soils and Water: Remediation Strategies, Socioeconomic Impacts, and Regulatory Provisions



Sharda Bharti and Awanish Kumar

1 Introduction

Since a few decades ago, the occurrence and prevalence of xenobiotics in water bodies and soil in urban system are rising continuously. Xenobiotic compounds (xenobiotics in short) are the chemical substances that are not produced naturally or are not expected to be found in the natural ecosystem (Štefanac et al. 2021). Xenobiotics include personal care products, bactericides, pesticides, heavy metals, halogenated chemical compounds, and persistent organic pollutants (POPs) (Godheja et al. 2016; Štefanac et al. 2021). Now, concern over the effects of xenobiotics is increasing due to presence of a few substances for which extensive data are currently unavailable. Their concentrations are found to be increasing in urban water and soil system nowadays (Tambosi et al. 2010; Lapworth et al. 2012; Chander et al. 2016). Xenobiotics in drinking water and wastewater have a major impact on public health, and research is being conducted to determine their fate in water bodies (Fatta-Kassinos et al. 2011). Moreover, due to possible adverse impacts on public health as well as environment, governing authority is also actively involved in their management. Public behavior has a major influence on the amount of wastewater contaminated by industrial activities, unlike in the past when industrial activities were the primary cause of water contamination (Bester et al. 2008).

Urban water is particularly problematic since it fulfils the need of potable water supply and treated wastewater from storm water, and combined sewer is used for recreation. Xenobiotics can damage human health by altering cellular communication networks that regulate development, growth, and physiological activities (Godheja et al. 2016). These substances have a high level of toxicity and can have an impact on the survival of both lower and higher eukaryotes. These substances

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cause bioaccumulation or biomagnification because they are tenacious and last for a longer duration in the environment (Hassaan and El Nemr 2020; Vasilachi et al. 2021). They also enter food chains, and it has been discovered that these substances are present in high amounts in creatures that do not directly interact with xenobiotics (Godheja et al. 2016). Even though most of them are resistant by nature, some microorganisms can breakdown xenobiotics over time after undergoing mutations in response to repeated exposure (Donner et al. 2010). The active site of enzymes in microorganisms has changed because of mutations, increasing their affinity for xenobiotics. They are typically found to be recalcitrant; however, they can change into other chemicals mostly by microbial biodegradation (Bento et al. 2005).

This chapter focuses on an overview of the fundamentals and types of xenobiotic compounds in urban water and soil, their sources, and environmental effects. This chapter introduces xenobiotics in urban water and soil, their origins, and their environmental impacts. This chapter also discusses the properties, destiny, and ecosystem dispersion of xenobiotics and their effects on public, animal, and environmental health. The importance of various xenobiotic degradation/removal methods is also emphasized. These methods include physicochemical techniques, microbial bioremediation, and hybrid techniques, as well as the benefits and drawbacks of various methods. Also covered are the xenobiotics' fate and biotransformation. Finally, various socioeconomic and technical mitigation strategies are presented, followed by certain xenobiotics-related policies.

2 Sources and Classification of Xenobiotics

Up until the early 1960s, industrial activities like the production of steel and coal as well as the chemical industry were the leading contributors to the introduction of xenobiotics into surface and ground waters. However, there are more sources available now than ever before. The cumulative effects of the daily use of the goods and products produced by industries such as cleaning supplies and personal care products like laundry detergent and dishwashing liquid which are directly discharged into sewers (Bester et al. 2008). Plasticizers, flame retardants, and perfluorinated compounds from a variety of materials, such as flooring, carpeting, and wall coatings, evaporate or leak into the indoor environment (Vasilachi et al. 2021). Additionally, pollution is a result of the use of construction materials including paint, concrete, metals, and plastics. Vehicle exhaust, catalysts, and tyres release metals, PAHs, and other pollutants into the environment (Kümmerer 2004; Bester et al. 2008).

In general, there are two categories of sources—direct and indirect—for the appearance of xenobiotics in the environment. The wastewater discharges from industries including chemical companies, pharmaceutical industries, plastics, paper and textile mills, and biocides used in agricultural fields are the direct sources of xenobiotics (Kiyasudeen et al. 2016). Phenol, hydrocarbons, various colors, paint effluents, herbicides, insecticides, and other related substances are among a few

remaining substances frequently found in wastewater and other discharges. Nonsteroidal anti-inflammatory medicines, pharmaceuticals, fertilizers, biocide residuals are some examples of indirect sources of xenobiotics (Roccaro et al. 2013; Ahmad et al. 2020). Pharmaceutical industries or hospital effluents immediately dump pharmaceutically active chemicals, an indirect entry of xenobiotics into the environment after they have had their biological effects in either their original or fragmented state (as illustrated in Fig. 1). These mostly consist of substances like hormones, anesthetics, and antibiotics that bioaccumulate in an individual and are transferred to other organisms via the food chain (Kumar et al. 2017). Pesticide bioaccumulation and biomagnification processes lead to damaging behavioral impacts in higher organisms (Tahar et al. 2013; Kumar et al. 2017; Dhuldhaj et al. 2022).

Xenobiotics can be released intentionally or unintentionally into the ecosystem, which includes personal care compounds (PCPs), flame-retardants, pharmaceuticals, steroid hormones, biocides, polyaromatic hydrocarbons (PAHs), and pesticides (Roccaro et al. 2013; Hassaan and El Nembr 2020). Surfactants, oils and waxes, perfumes, biocides, dyes, and pigments are all ingredients found in personal care and cosmetic goods (Bester et al. 2008). Because cosmetics frequently contain significant amounts of water, preservatives, or biocides like triclosan are usually added into them to extend the shelf life of the products. It has been demonstrated that biocides, perfumes, and UV-blockers are released into receiving streams (Bester et al. 2008). These modifications in how different substances are used partly result from environmental concerns, but they also reflect changes in fashion. The discovery of personal care products (PCPs) in the aquatic ecosystem is matter of worry

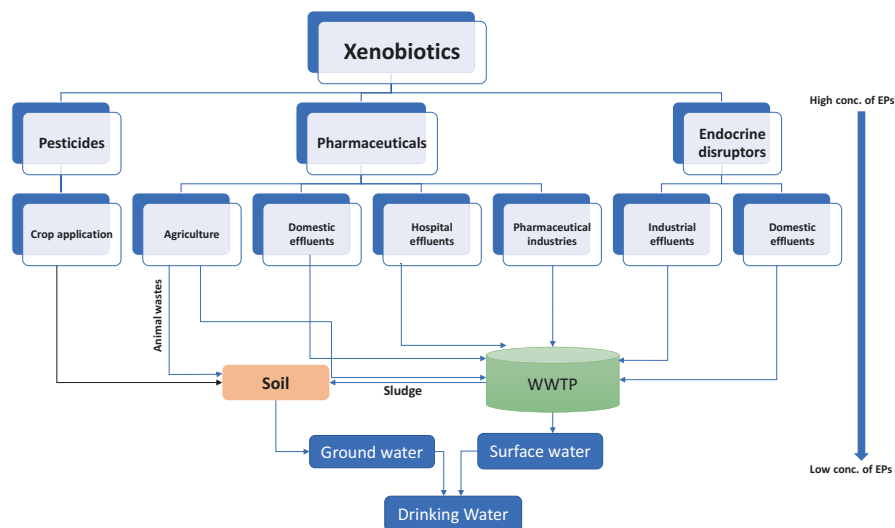


Fig. 1 Sources of xenobiotics and their pathways to aquatic bodies and soil. *WWTP* wastewater treatment plant

despite some improvements in usage trends. Another most important group is pharmaceuticals. Drugs leave the body as metabolites or in original form when people take them (Bester et al. 2008; Tahar et al. 2013; Ahmad et al. 2020). Pharmaceuticals are not effectively eliminated by current wastewater treatment methods, making it difficult to prevent their entry into wastewater (Hussain et al. 2022). Wastewater contains steroid hormones because of typical human excretions (Semião and Schäfer 2010). Biocides, used for extending the shelf life of products like cosmetics (triclosan) and paints (isothiazolinones), are a major group of pollutants which are also found to be recalcitrant in nature (Donner et al. 2010; Miglani et al. 2022). The PAHs typically emitted by coal-processing facilities, car exhausts, and tyres are also recalcitrant in nature (Fetzner 2002; Miglani et al. 2022). According to the traits, fate, and distribution of xenobiotics in the ecosystem, major source types are categorized into six classes (Donner et al. 2010; Štefanac et al. 2021), as shown in Fig. 2.

Halocarbons (mixtures of molecules that have halogen atoms in place of H molecules) are used as solvents, charges, sprays, and insecticides (Arava 2021). The polychlorinated biphenyls (PCBs) are utilized in plasticizers, transformer protector coolants, and hotness trade fluid. Chlorine substitution affects how inactive it is, both biologically and synthetically. Due to their halogenation and cyclic design and water insoluble nature, they are persistent in nature. Alkyl benzyl sulfonates, due to presence of sulfonate ($-\text{SO}_3^-$) cluster on one side, resist microbial degradation and become refractory (Donner et al. 2010; Kiyasudeen et al. 2016; Vasilachi et al. 2021). Oil is stubborn due to its insolubility in water, and it contains harmful chemicals. Xenobiotic substances have increased complexity and water insolubility, depending on structures of aliphatic and cyclic rings with replacements for nitro-,

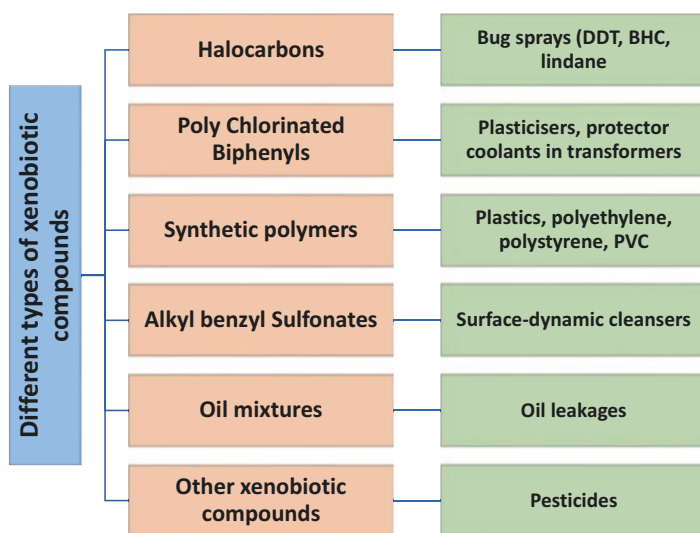


Fig. 2 Classification of xenobiotics based on major characteristics

sulfonate, carbonyl groups, etc., which make them resistant to biodegradation (Kumar et al. 2017; Arava 2021).

3 Impacts of Xenobiotics on Human and Environment

Pollutants can be released from a single source into one or more distinct environmental compartments and many of their metabolites are discharged into the environment, and finally they reach to water bodies through infiltration (illustrated in Fig. 3). Emerging pollutants may be discharged into the environment via the point or diffused resources followed by their transportation to different environmental compartments via a variety of pathways or mechanisms (Donner et al. 2010; Arava 2021; Vasilachi et al. 2021). The specific release processes and their relative release rates are mainly determined by the chemical and physical characteristics such as their solubility in water and their volatility and usage pattern, i.e., in free form or bound form and their location. These mechanisms largely depend on the characteristics of the environmental compartments and the attributes of environmental pollutants' (EPs') (Vasilachi et al. 2021; Miglani et al. 2022). Where insufficiently treated effluents from the treatment plants are released, such emerging pollutants can rapidly contaminate the river ecosystems. This may adversely affect the human and animal health and environmental system (Illustrated in Table 1).

4 Treatment and Remediation of Xenobiotics

Microbes are responsible for most of the xenobiotic chemical modification and degradation on Earth. Aerobic xenobiotics-degrading bacteria are great models for understanding how bacteria adapt and evolve as the microorganisms consume them as food and energy source (Kiyasudeen et al. 2016). Xenobiotics can be completely mineralized or stabilized as their parent compound or degraded to simpler compounds. However, xenobiotics are difficult to break down due to their sorption and entrapment in soil micropores (Kumar et al. 2017; Chakraborty et al. 2020; Bala et al. 2022). Xenobiotics get accumulated in water, soil, and other living organisms due to their stability, low rate of biodegradation, and degradation (Štefanac et al. 2021). Pollutants naturally biodegrade, and as the investigations are typically carried out in the lab, which may not accurately reflect environmental conditions. Hence, more research is needed as their application on large scale is still unknown. The scientists need to explore the enormous potential of microbial populations adapted for certain xenobiotics at larger scale (Sayara et al. 2011; Miglani et al. 2022).

Current wastewater treatment plants, in short WWTPs, are not able to degrade the emerging contaminants, so treatment facilities must be improved to degrade such contaminants. Most endocrine-disrupting substances (EDS), persistent organic

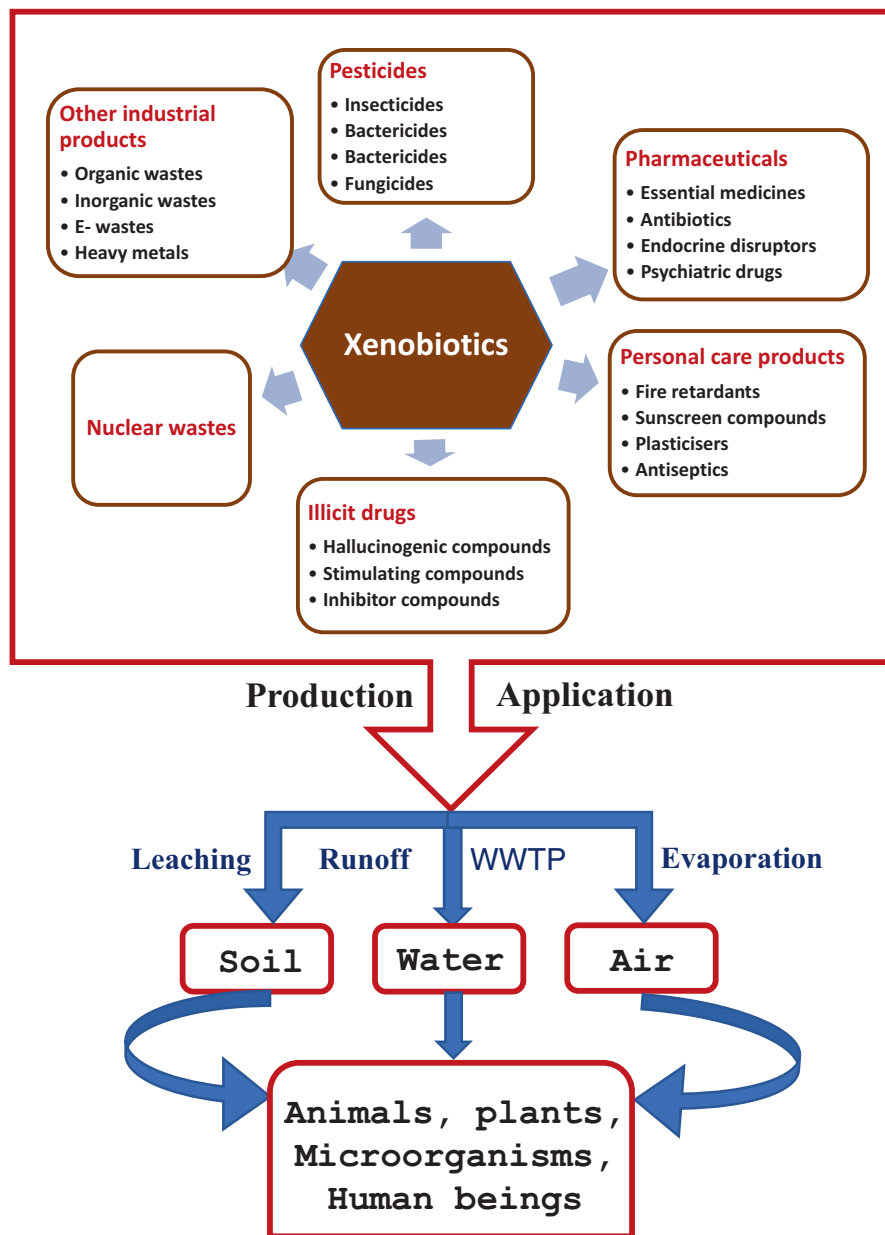


Fig. 3 Origins of xenobiotics in the environment and their release and fates

pollutants (POPs), and personal care products (PCPs) are resistant to wastewater treatment due to acidic or crucial functional groups, making them to treat (Lapworth et al. 2012; Roccaro et al. 2013; Karthigadevi et al. 2021). There are several methods that are being used for treatment of xenobiotics, as illustrated in Fig. 4. Physical

Table 1 Major impacts caused due to exposure to such xenobiotics on human, animal, and environmental health

System affected	Xenobiotics	Sources	Impacts
Soil	Pesticides, PCBs, chlordane, polycyclic aromatic hydrocarbons, and nitroaromatics	Industrial processes, burning of fossil fuels, use of insecticides, fertilizers.	Negatively impact the soil's physicochemical characteristics, the amount of soil organic matter (SOM), the microbial community, and have an ecotoxicological impact on the soil
Water	PAHs, phthalates, and pesticides	Surface water flowing from highways and land surfaces; sewage effluents from sewage treatment; as well as products from fossil fuel; airborne particulate deposition; burnt solid waste.	Suppression of the antioxidant system, eutrophication alters the homeostasis of fish and causes oxidative stress, as well as biomagnification.
Plants	Phytohormone analogs, particulate matter, and heavy metals (Pb, Cd, Hg, and As)	From the automobile sector.	Affects the photosynthetic pigments, proteins, cysteine contents, and foliar surface of plants; induces DNA damage in plants because of free radical generation leading to oxidative stress; and disrupts signaling cascades.
Aquatic lives	Pesticides and herbicides, dyes and paints, insecticide such as β -cypermethrin	Chemicals employed in agriculture and daily life, e.g., organophosphorus, nitrophenols, and carbamates.	Defects in morphology and function, death-causing growth retardation, fish death, altered body form, physical defects, delays in hatching, neurotoxicity, and developmental issues
Terrestrial animals and Human being	Pharmaceuticals or other compounds. pharmacologic drugs, steroid hormones, antibiotics, pesticides from contaminated water/foods	Chemicals, exposure to drugs and nonessential exogenous substances through ingestion, inhalation, skin contact, or other exposure route.	Modify immunological processes, oxidative damage, including low glutathione levels and significant lipid peroxidation, increased allergic reactions, organism mortality, genetic polymorphisms, metabolic diseases, as well as changes to the human gut microbiome that cause dysbiosis, chronic illnesses, and DNA damage, cancer, neurological disorders, and hormonal imbalances.

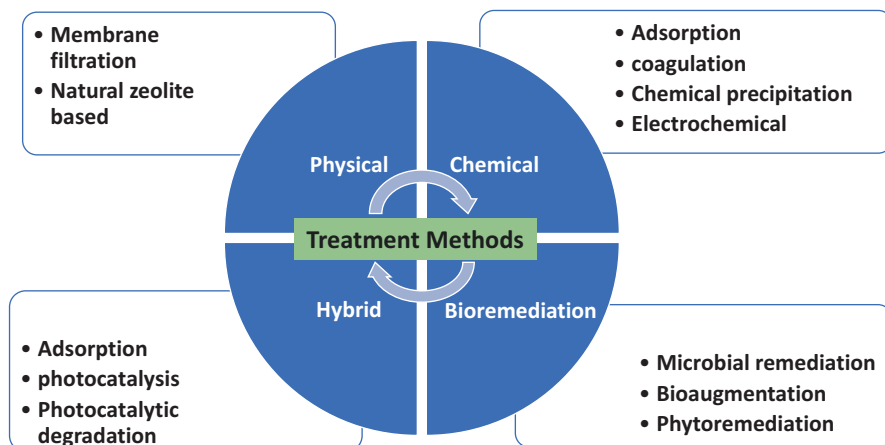


Fig. 4 Treatment and removal of xenobiotics from water

and chemical techniques to breakdown xenobiotics in water have been developed over time; however, they cannot get rid of chronic organic contamination. Major solutions for eliminating POPs are provided by contemporary methods for characterizing and analyzing compounds based on their molecular dimensions, water solubility, polarity, and volatility (Vasilachi et al. 2021).

There is a rise in potential analytical treatment techniques that can detect complicated substances even when they are stored in very low concentrations. Biotreatment technologies, a low-cost wastewater treatment solution in ecosystem with microbial abundance, have emerged. Since they are catabolic and either degrade or modify the molecules, aerobic bacteria utilize xenobiotic compounds as a carbon source. Most simple organic pollutants can be degraded using these remediation techniques, but POPs like polyhydroxyalkanoate, polychlorinated biphenyls (PCBs), heterocyclic compounds, and phosphorus containing pesticides have been entering the environment for decades due to their high biomagnification and bioaccumulation. Microorganisms are unable to effectively handle effluents when chemical concentrations are extremely high, so new hybrid techniques, for example, chemical oxidation and nanoparticle-based treatment techniques, are developing to reduce toxicity before biological method to reduce the concentration (Karthigadevi et al. 2021; Vasilachi et al. 2021; Bhatt et al. 2022).

4.1 Membrane Technology

Membrane technology is a type of physical treatment method where the unwanted components are taken out of water by a specific membrane. Barriers like membranes allow certain molecules to pass through while blocking others. Surface water, groundwater, and wastewater are cleaned by water treatment plants using a

variety of membrane types and procedures to create water for use in industry and drinking. Depending on the impurities that need to be eliminated and the desired water quality by the end user, various types of membranes can be employed to treat water. The various membrane types include those used in membrane filtration, including micro- and ultrafiltration, reverse osmosis, nanofiltration, and membrane softening (Romanos et al. 2013; Nqombolo et al. 2018; Singh et al. 2020). Membrane filtration purifies water by removing impurities using membranes. While dissolved solids are typically not removed, the procedure is comparable to that of traditional sand or media filters in that suspended solids are removed. Both pressure and vacuum are possible operating conditions for membrane filtration. To treat wastewater and get rid of bacteria and some viruses, membrane filtration is frequently utilized. Membrane technology includes all engineering and scientific methods used to remove the pollutants through or by membranes. Several sectors employ this technique extensively to cleanse water for home and industrial uses, including chemical industries, biotechnological applications, pharmaceutical, and food sectors, as well as other separation processes (Nqombolo et al. 2018).

Municipalities and enterprises are turning to membrane treatment for process solutions as a result of the federal government's ever-increasing environmental laws. Membrane-based technique is a clean approach which have low energy requirement and hence can be used for various applications as an substitute to several traditional processes including filtration, ion exchange, and other chemical-based treatment systems (Cevallos-Mendoza et al. 2022). Additionally, it provides a simple upscaling hybrid processing, permits continuous separation under mild conditions, and allows for adjusting the membrane properties to the desired outcome. This approach, however, possesses several limitations, such as membrane fouling and concentration polarization, reduced membrane durability, and insufficient selectivity and flux. To overcome these difficulties, many membrane morphologies can be developed, each having unique biological, chemical, and physical properties depending on the usage (Saleh et al. 2020; Cevallos-Mendoza et al. 2022).

4.1.1 Membrane Technology for Removal of Pharmaceutical Compounds

The extensive application of pharmacological active chemicals (PhACs) by people and other creatures causes the aquatic environment to become contaminated, having a significant negative impact on human health. Although these substances are removed using the most cutting-edge techniques, their persistence in drinking water still exists. Numerous studies have discussed the creation of new focused techniques for the membrane filtration-based removal of these chemicals from water (Semião and Schäfer 2010; Ganiyu et al. 2015; Padmanaban et al. 2016). The removal efficacy of PhACs is dependent on various physical and chemical characteristics, pH, membrane composition, interactions with solute, and simultaneous occurrence of related compounds. Several researchers have shown that polymeric membranes may remove pharmaceutical residues from water in the past 20 years (Cevallos-Mendoza et al. 2022).

Microfiltration (MF), nanofiltration (NF), ultrafiltration (UF), reverse osmosis (RO), and combinations of membranes are used to remove PhACs in wastewater reclamation/reuse membranes (Singh et al. 2020). The use of MF and UF for the treatment of PhACs in aqueous circumstances is constrained because of their higher molecular weight cutoff (MWCO) relative to the molecular weight (MW) of bulk of PhACs. The PhACs are strongly rejected due to the significantly reduced MWCO that NF and RO display. The best methods for removing PhACs have been described as NF and RO separation. Microfiltration and ultrafiltration are often not completely successful at removing PhACs, according to the literature (Cevallos-Mendoza et al. 2022). NF- and RO-based technologies may be effective for removing drugs from wastewater, but other research finds unsatisfactory findings (Singh et al. 2020). A phase-inverted polyethersulfone (PES) nanofiltration membrane does not entirely eliminate pesticides carbamazepine, diclofenac, and ibuprofen from drinking water. One study investigated how a PES NF membrane rejected three PhACs. Ionic (diclofenac and ibuprofen) and neutral (carbamazepine) PhACs revealed total rejection rates of 31–39% and 55–61%, respectively. Since diclofenac and ibuprofen are negatively charged, electrostatic repulsion may have contributed to the experimental rejection of these PhACs over carbamazepine. These results were supported by literature, who demonstrated that negative surface charged membranes are more effective in removing negatively charged molecules than neutral and positive ones. However, the lower PhAC molecular size in comparison to these membranes' pore size can be used to explain the low overall removal effectiveness (Cevallos-Mendoza et al. 2022).

4.1.2 Membrane Technology for Pesticide Removal

Since pesticides are used on lawns, gardens, and agricultural land, they have the potential to contaminate drinking water supplies and can penetrate water resources. The Environment Protection Agency (EPA) created restrictions to safeguard the drinking water from the origin to the consumer's tap since they are typically highly hazardous to living things due to more exposure of these substances to human. As a result, pesticides can also be eliminated via membrane filtration methods, however, to a lesser extent than PhACs (Cevallos-Mendoza et al. 2022). The only use of nano-materials in this instance was to create ultrafiltration membranes utilizing a new cross-linked cyclodextrin polymer (-CDP) with a hierarchically micro-mesoporous structure and huge surface area. 2,4-Dichlorophenol and other organic micropollutants were also evaluated on this membrane (Bhatt et al. 2022). The authors claim that the combination of CDP's micropores and mesopores has a synergistic effect on the high 2,4-dichlorophenol removal efficiency. As the mesopores offer an open diffusion pathway and enhance the adsorption rate by increasing the rate of mass transfer, it significantly improves the total site for adsorption thereby increasing their adsorption capacity. Additionally, nanofiltration membranes have been proposed as a method for removing pesticides from water.

The majority of xenobiotics have been proven to respond better to sophisticated procedures including reverse osmosis (RO), nanofiltration (NF), and UV-based treatment, which have been reported to remove more than 90% of xenobiotics than standard WWTPs. However, unless we find a solution to the problems with the treatment of concentrate produced by RO/NF procedures, these techniques are not environmentally benign. Moreover, due to financial constraints, these sophisticated techniques cannot be successfully applied to WWTPs with population equivalents below 50,000, necessitating the development of additional research to examine the further treatment (Tahar et al. 2013).

4.2 Adsorption Methods for Treatment of Xenobiotics

Pharmaceutically active chemicals (PhACs) and pesticides are common xenobiotics found in water bodies (Fountoulakis et al. 2009; Kumar et al. 2017; Saleh et al. 2020; Karthigadevi et al. 2021). EU rules reduce xenobiotic discharge by prioritizing priority compounds. Due to insufficient xenobiotic treatment, discharge from WWTPs has been primarily recognized as point sources of xenobiotic transmission into the water bodies. Some xenobiotics are present in treated effluents due to incomplete biodegradation or high concentration in influents. One method to reduce their discharge into the aquatic system could be adsorption of xenobiotics using activated carbon (Tahar et al. 2013; Bala et al. 2022). The first physicochemical treatment procedure that can be used is activated carbon (AC) filtering. The AC has been treated to improve the surface area for adsorption while maintaining its small, low-volume pores. Pharmaceuticals and pesticides can be removed from water using activated carbon. The complex adsorption process of activated carbon is influenced by several characteristics of the adsorbents, including structure, surface chemistry, chemical characteristics (such as functional groups, polarity, and solubility), and reaction parameters, including pH, temperature, the existence of other species, and concentration of adsorbate (Marican and Durán-Lara 2018). Among various forms, granular- and powdered-activated carbon, i.e., GAC and PAC, are the most common types of AC for removing persistent pesticides from raw water (Marican and Durán-Lara 2018). Pesticides used together can lead to competing adsorption and lower removal rates. Hence, this method is occasionally preceded by a flocculation stage to lower the activated carbon filtration expenses and improve the efficacy.

Pesticides and medications are examples of xenobiotics that are becoming a bigger issue in water bodies. A fixed-bed adsorption filter as the tertiary step of wastewater treatment can further reduce xenobiotic concentrations (WWTPs). In batch testing, expanded clay (EC) and zeolite (ZE), two mineral adsorbent materials, were compared. For two initial xenobiotic concentration levels—concentrations below 10 g/L and concentrations between 100 and 1000 g/L—removal efficiencies and partition coefficients were computed. With greater partition coefficients, EC had the

best adsorption potential, while Zeolite demonstrated almost the same. This initial batch analysis suggests that ZE and EC could be employed in WWTPs as alternatives to AC as absorbent materials (Tahar et al. 2014).

4.3 Advanced Oxidation Processes for Treatment of Xenobiotics

Advanced oxidation processes (AOPs) are a group of treatment methods that use highly reactive oxidants, including H_2O_2 , ozone, or ultraviolet light, to degrade or remove xenobiotics (i.e., synthetic chemicals) from water or air. AOPs can be effective in breaking down diverse pollutants, including pesticides, herbicides, pharmaceuticals, and personal care products (Khan et al. 2014; Ganiyu et al. 2015; Saleh et al. 2020; Syafrudin et al. 2021). These chemical treatment techniques involve the oxidation of organic contaminants in response to powerful oxidants (e.g., hydroxyl radicals). Radicals can be produced using chlorine, ozone, hydrogen peroxide, UV radiation, or other substances. The inclusion of additional organic compounds may impair efficiency. Additionally, transition products with unidentified toxicity can be formed. These physicochemical treatment techniques are all very efficient, need less space, and can treat large amount of wastewater. However, they are more expensive and technologically sophisticated (Verhagen 2015).

4.4 Coagulation-Flocculation for Treatment of Xenobiotics

Coagulation-flocculation is a method for the treatment of xenobiotics, or foreign substances, in water. The process involves the addition of chemicals, called coagulants, to the water to destabilize the pollutants and cause them to clump together, or flocculate. These flocs can then be easily removed from the water through filtration or sedimentation. This technique is commonly used in water treatment plants to remove contaminants such as heavy metals and suspended solids. Chemical approaches are difficult to remove hazardous sludge components and inorganic metal complexes, making it difficult to scale the use of inorganic coagulants to treat pollutants. POPs and xenobiotics are removed through coagulation and flocculating processes due to velocity gradient, pH, temperature, and retention time. Halogenated chemicals, petroleum hydrocarbons, and phthalic acid esters can be treated with this approach. The electro-coagulation technique eliminates endocrine-disrupting compounds by employing amorphous aluminum oxide as a coagulant and using sweep flocculation mechanisms to absorb organic pollutants (Ahmad et al. 2020; Karthigadevi et al. 2021; Miglani et al. 2022). For instance, Bakraouy et al. (2015) used a mixed ferric chloride coagulant and polymer flocculant to remediate intermediary landfill leachate of Rabat city. The best removal rates for turbidity were 88%,

phenol was 98%, and surfactant was 82%. According to this study, the optimal doses were 13.2 g/L and 62 mL/L (Bakraouy et al. 2015).

4.5 Chemical Precipitation Method for Treatment of Xenobiotics

Chemical precipitation is a method for the treatment of xenobiotics, or foreign substances, in water. The process involves the adding chemicals, called precipitants, to the wastewater to cause the pollutants to form solid particles that can be easily removed from the water through sedimentation or filtration. The chemical reaction between the precipitant and the pollutant creates a solid compound, which is known as precipitate. The phenolic compounds or other aromatic compounds commonly reported in industrial wastewater frequently used this technique. Heavy metals can be isolated by selectively altering the pH of a solution, but this requires chemicals to modify solubility, making it expensive to produce pure goods (Karthigadevi et al. 2021).

4.6 Biological Methods/ Bioremediation

Biosynthetic processes in animals, plants, and microbes produce organic chemicals, which are biodegradable by microorganisms. Microorganisms are primarily responsible for the biodegradation of all kinds of contaminants (Singh et al. 2019). Microorganisms are essential for the Earth's biogeochemical cycles, and biological treatment is an affordable and effective alternative to on-site remediation of pesticide waste streams (Kiyasudeen et al. 2016). Bioremediation is the process of using biological organisms to remove chemical contaminants through biodegradation, mineralization, or biotransformation. Biodegradation is the process of transforming organic compounds to water, carbon dioxide, and other elements. It is often referred to as "ultimate/complete" biodegradation, even though it also involves the creation of biomass and inorganic chemicals. Incomplete (partial) biodegradation refers to the breakdown of an organic component into a simpler organic substance. The organic compound's solubility, movement in the environment, or toxicity may change as a result of biotransformation (Marican and Durán-Lara 2018). Microbes use endo- and exo-enzymes, metabolic pathways, and biodegradation to combat environmental pollution and remove toxins. Microorganisms use two different mechanisms to breakdown xenobiotic compounds: aerobic and anaerobic biodegradation. Aerobic degradation uses surplus oxygen for mineralizing or degrading the pollutants. In anaerobic habitats such as sludge digesters, groundwater, sediments, water-logged soils, digestive tracts, livestock waste, and landfills, anaerobic bacteria can change or mineralize various substances (Kiyasudeen et al. 2016).

Bioremediation or treatment at wastewater or water treatment facilities, respectively, are two options for dealing with xenobiotic-contaminated water. Bioventing, bioslurping, biosparging, phytoremediation, permeable reactive barriers, and similar in situ procedures are used to extract harmful substances from polluted soil and water (Hussain et al. 2022). Ex situ remediation is the process of transporting contaminated soils or groundwater from their original site to another area for treatment. Farming on cultivated ground, windrows, bioreactors, and biopiles are all examples of ex situ methods. Compared to its ex situ counterparts, in situ procedures are less expensive. Therefore, heavy metals, pigments, chlorinated solvents, and hydrocarbon-polluted settings have been treated with in situ bioremediation methods. This has been shown by multiple groups of researchers (Chakraborty et al. 2020; Hussain et al. 2022). The proximity of an electron acceptor, the amount of moisture present, the ease with which a supplement can be obtained, the pH level, and the temperature are all important considerations for successful bioremediation.

4.6.1 Microbial Bioremediation

Enzymes and biological processes play crucial roles in the biotransformation of xenobiotics by soil microorganisms, sediment microorganisms, and aquatic organisms. Co-metabolism occurs when a microbial community breaks down a pollutant into a simpler material that can be used as a carbon or energy source. Small adjustments or breakdown of a molecule through co-metabolic transformation are possible, but they are of no service to live organisms. The consequences of a xenobiotic that has undergone partial biodegradation or co-metabolic conversion can range from being much less dangerous than the original chemical to being on par with its toxicity to being significantly more detrimental (Satish et al. 2017). Xenobiotics like tetrachloroethene and trichloroethene can be metabolized by microbes into vinyl chloride, which is known to cause cancer, in anaerobic conditions. When released into their natural surroundings, the released products might be altered or subsequently degraded microbially, leading to mineralization. Persistent organic pollutants and metabolic products, on the other hand, can accumulate in the environment, combine with humus in the soil, or lead to biomagnification (Hussain et al. 2022). Microorganisms have a remarkable ability to catabolize, although only a few of enzymes are involved in the reclamation of xenobiotics. These enzymes have multiple mechanisms for breaking down halogenated compounds, dyes, and aromatic hydrocarbons. Table 2 shows that only a subset of microbial enzymes, including cytochrome P450s, laccases, cellulases, phytases, proteases, and lipases, are involved in the detoxification of xenobiotics (Kumar et al. 2017; Satish et al. 2017).

Table 2 Various microbial enzymes involved in the bioremediation of xenobiotics

Microbial enzymes	Bacterial source	Fungal source
Cytochrome P450s	<i>Streptomyces griseus</i>	<i>Fusarium graminearum</i>
Laccases	<i>Streptomyces cyaneus</i>	<i>Corilopsis gallica</i> , <i>Scytalidium thermophilus</i>
Cellulases	<i>Komagataeibacter xylinus</i> E-89370	<i>Phanerochaete chrysosporium</i>
Phytases	<i>Pseudomonas aeruginosa</i>	<i>Pleurotus ostre</i> , <i>P. pulmonaris</i>
Lipases and Proteases	<i>Bacillus subtilis</i> , <i>Chromobacterium viscosum</i>	<i>Aspergillus niger</i> , <i>Acremonium murorum</i>
Amylase and keratinase	<i>Bacillus megaterium</i> , <i>Bacillus pumilus</i>	<i>Phanerochaete chrysosporium</i> , <i>Pleurotus ostreatus</i>
Pectinases	<i>Bacillus</i> sp.	<i>Aspergillus niger</i> , <i>Pichia fermentans</i>
Phenol oxidase and Mn peroxidase	<i>Serratia marcescens</i>	<i>Aspergillus fumigatus</i> , <i>Taloromyces thermophilus</i>

4.6.1.1 Parameters Affecting the Biodegradation of Xenobiotics

Microorganisms can only degrade a portion of a water-soluble xenobiotic pollutant, depending on diversity in microorganisms present, chemical composition, concentration, and physical and chemical attributes of the surrounding (Fernando et al. 2019). Bioavailability of xenobiotics is influenced by their physical state, water solubility, and propensity to attach to soil particles/sediments. In soil systems, sorption, immobilization, and micropore entrapment are the main reasons for their recalcitrance/persistence. The “aging” process of contaminants also affects the bioavailability, as they become increasingly inaccessible to microorganisms due to their low water solubility and immobilization by the soil matrix and sedimentary material (Shukla et al. 2013).

Biodegradation is impacted by “unphysiological” substituents and stable chemical bonds, as well as high concentrations of xenobiotics. When a chemical is present in a concentration that is ineffective for inducing catabolic genes, catabolic enzyme synthesis may not take place (Štefanac et al. 2021). The rates of metabolism and growth, as well as the thermodynamics of the transformation reaction, dictate the minimum threshold concentration for biodegradation of contaminants. Biodegradation is affected by environmental factors including temperature, pH, moisture content, salinity, chemical inhibitor, nutrient supply, presence of electron donors, and availability of oxygen. Microbes that compete with them or predators that graze on the microbial communities also play a role (Štefanac et al. 2021).

Pesticides degrade in soil due to five prerequisites: a xenobiotic molecule-metabolizing organism must exist in or be capable of existing in soil, a chemical and physical form of xenobiotic compound must be suitable for degradation, the molecule must be present in the same form as the active agent, the enzyme must be able to trigger the production of the enzyme or enzymes necessary for detoxification, and the environment’s pH, temperature, and organic matter must be favorable (Fernando

et al. 2019). The characteristics of the soil, microorganisms, and pesticide molecule all affect how quickly pesticides degrade in soil, so reliable assessments of the ecological effects of pesticides in soil can be produced (Arava 2021) (Fig. 5). The observed disappearance of xenobiotics from an ecosystem may not always be an indication of biodegradation, as it may be due to incomplete degradation, biotransformation, or chemical conversion. Monitoring a chemical's environmental fate requires keeping an eye on both the by-products it generates and the breakdown of the parent component. Rates of environmental xenobiotic biodegradation can change over time (Nguyen et al. 2021).

4.6.2 Phytoremediation

Phytoremediation is a plant-based technique that combines microbes and plants to clean up a contaminated environment (Singh and Pant 2023). It involves using plants to remove toxins, while bioremediation involves using live organisms to degrade, detoxify, transform, immobilise, or stabilize environmental contaminants. The main targets are organic pollutants and heavy metal poisons, and stationary contaminated soil or water situations are treated (Tripathi et al. 2020; Hussain et al. 2022). Examples include removing PCBs and mitigating coal mines can reduce the effects of xenobiotics, such as pesticides, explosives, and crude oil (Yan et al. 2020; Rezoqi et al. 2021; Hussain et al. 2022). Numerous plants have demonstrated success at hyperaccumulating chemicals at toxic waste sites, including mustard plants, alpine pennycress, hemp, and pigweed (Rezoqi et al. 2021; Hussain et al. 2022). Different plant varieties have different abilities to acquire pollutants, even within the same species (Tripathi et al. 2020; Yan et al. 2020).

There are mainly three different kinds of phytoremediation. In situ phytoremediation is a method of remediation that involves placing living plants in

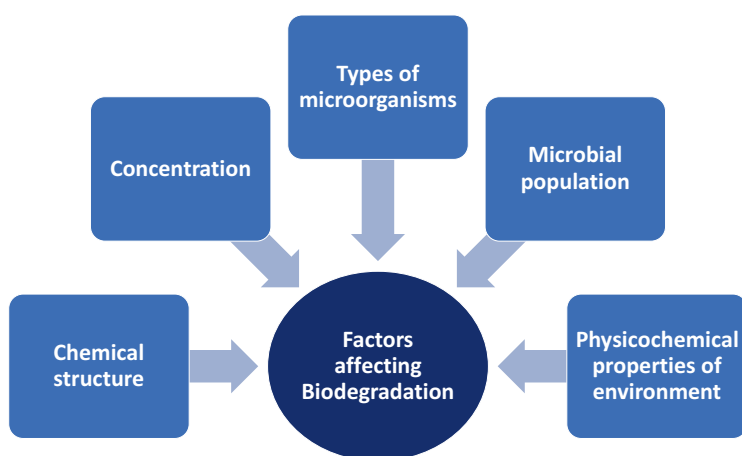


Fig. 5 Factors affecting biodegradation of xenobiotics

contaminated areas. It is cost effective and conserves natural resources, but it only considers shallow groundwater, soils, and sediments, making it vulnerable to dangerous compounds and products from biodegradation. Additionally, it can lead to contamination of groundwater due to mass transfer constraints. Whereas, *in vivo* phytoremediation involves growing plants in a controlled environment and transplanting them to the contaminated area. This process is eco-friendly and cost effective and can be used to remove heavy metals, pesticides, and other pollutants from the environment (McCutcheon et al. 2002). *In situ* and *in vivo* phytoremediation are both eco-friendly and cost-effective methods of remediation, but *in situ* is considered more effective as it allows the plants to grow in the natural environment where the contaminants are present. Enzymes from bacteria, fungi, and plants are used to remove toxic xenobiotics, proving them a sustainable solution (Karigar and Rao 2011; Almeidaa et al. 2017; Hussain et al. 2022), as listed in Table 2.

Mechanisms of phytoremediation to clean up contaminated sites use natural processes such as absorption of xenobiotics, mineralization, metabolism, volatilization, release of chemicals, and raising soil carbon and oxygen content to promote microbial and fungal activity (Mukherjee et al. 2021). Based on mechanism, phytoremediation is classified into several methods, such as phytostabilization/phytosequestration, phytoextraction/ phytoaccumulation, hyperaccumulation, phytovolatilization, phytodegradation, and rhizofiltration, as illustrated in Fig. 6 (McCutcheon et al. 2002; Yan et al. 2020; Hussain et al. 2022).

4.6.3 Hybrid Techniques

Hybrid techniques for the removal of xenobiotics involve combining multiple treatment methods to remove or breakdown the pollutants from water or soil (Singh et al. 2017). These methods may combine physical, chemical, and biological methodologies. Some examples of hybrid techniques include (a) Adsorption-biodegradation, where pollutants are first adsorbed onto a solid material and then broken down by microorganisms, (b) chemical oxidation-biodegradation, where pollutants are first oxidized using chemicals like hydrogen peroxide or ozone, and then further broken down by microorganisms, (c) membrane filtration-biodegradation, where pollutants are first filtered out of the water using a membrane, and then broken down by microorganisms, (d) photocatalysis-biodegradation, where pollutants are broken down combinedly by chemical and biological methods with the use of light energy, and (e) nanomaterial-based method where nanomaterials are also used in addition to traditional physicochemical techniques. The choice of technique is based on the specific pollutant and the physicochemical attributes of the water or soil, as well as the availability of resources. Hybrid techniques such as bioelectrochemical method and nanomaterials in various forms can be more effective at removing pollutants than traditional methods, but they also tend to be more expensive (Hussain et al. 2022), as explained in the following section.

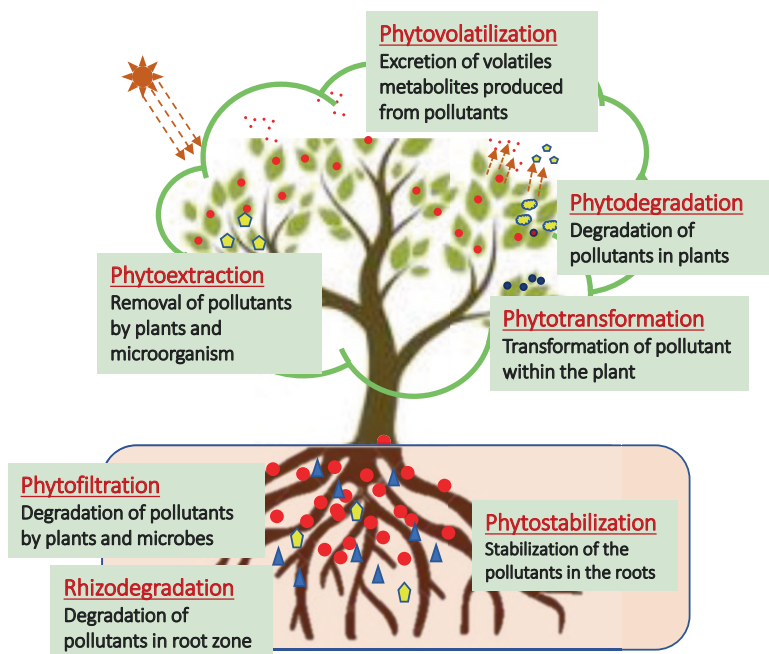


Fig. 6 Mechanism of phytoremediation of xenobiotic compounds

4.6.3.1 Bioelectrochemical Method for the Removal of Xenobiotics

Several methods, such as electrochemical oxidation/reduction, electrocoagulation/flotation, electrodialysis, electrochemical advanced oxidation processes, and bio-electrochemical systems (BES), can effectively remove or transform most environmental contaminants into nontoxic compounds. Depending on the characteristics of the pollutants, several electrochemical techniques are used to remove and recycle various types of pollutants (Fernando et al. 2019).

Modern technology, the bio-electrochemical system (BES), has been thoroughly researched recently to remove contaminants. BES is a collection of devices that may convert organic waste into either hydrogen, methane, or electricity through microbial oxidation. The anode of a typical two-chamber microbial fuel cell (MFC) is submerged in a substrate solution, while the cathode is placed in a liquid (Vinayak et al. 2021). A proton exchange membrane (PEM), which is an ion exchange membrane, separates these two compartments (Chakraborty et al. 2020). An external load is connected to a conductive metal wire that connects the positive and negative electrodes. The anaerobic sludge containing exo-electrogenic bacteria produce electrons are introduced into the anodic compartment of the MFC (Chakraborty et al. 2020; Yaqoob et al. 2021). Exo-electrogenic bacteria transmit electrons

exogenously, requiring a mediator such as conductive pili or nanowires. The BES's anodic chamber has robust microbial communities that can withstand greater changes in organic load (Chakraborty et al. 2020).

Researchers are investigating the use of BES to treat wastewater-containing xenobiotics. The MFC and microbial electrolysis cell (MEC) are two prominent BES modifications. Renewable MFC and MEC transform chemical energy into electrical energy. Due to its ability to convert substrate chemical energy into electrical energy and low sludge generation, MFC can cleanse wastewater and generate renewable energy. Depending on the cleaving mechanism, the dual-chambered MFC's cathodic or anodic chamber can degrade xenobiotic substances (Chakraborty et al. 2020). Table 3 provides a summary of the use of MFC for the degradation of dyes, antibiotics, and several refractory chemicals, based on review by Chakraborty et al. (2020).

Table 3 Removal of xenobiotics using bio-electrochemical system (BES)

Arrangement	Xenobiotics type	Examples	Initial concentration (mg/ L)	Removal efficiency (%)
Air cathode single-chambered MFC	Antibiotics	Penicillin, ceftriaxone	50	91-98
Double-chambered MFC	Antibiotics	Sodium metronidazole, Chloramphenicol, Tetracycline	30-50	75-85
Graphene-modified biocathode and bioanode in double-chambered MFC	Antibiotics	Oxytetracycline	12-16	91
Single chambered air cathode MFC	Antibiotics	Neomycin sulfate	20	54
Microbial fuel cell (MFC)	Heavy metals	Chromium [Cr(VI)]	40-80	100
		Arsenic [As (III)]	0.2-1	98-100
		Nickel (Ni)	25-50	95-99
		Cadmium (Cd)	20-60	60-93
Microbial electrolysis cell (MEC)	Heavy metals	Lead (Pb)	100	98-100
MEC	Dyes	Orange G	400	100
Double chambered MEC	Aromatics and chlorinated compounds	Nitrobenzene	50	98
MEC-Fenton process	Aromatics and chlorinated compounds	Aniline	4460	98

Based on Chakraborty et al. (2020)

4.7 *Nanomaterials for the Degradation of Xenobiotics*

Recently, a dramatic increase in the number of pollutants have been reported in environments, increasing the risk to human health. Nanomaterial has been explored as an efficient material for the removal of xenobiotics and persistent organic pollutants (POPs) from the environment (Karthigadevi et al. 2021) and some examples of nanotechnology-based treatment methods include

1. Nanofiltration: This involves using nanoparticles or nanostructures to filter contaminants from water or air.
2. Nanocatalysis: This involves using nanoparticles to catalyze the breakdown of contaminants into less harmful substances.
3. Nanosorbents: These are materials with an enhanced specific surface area for absorption and removal of the contaminants from water or air.
4. Nanoparticles: These are tiny particles that can be engineered to specifically target and remove contaminants from the environment.
5. Nano-membrane filtration: The nanoparticles are used to filter pollutants out of water using a membrane.
6. Nano-bioremediation: The nanoparticles are utilized to augment the action of microorganisms that break down pollutants.

There are many different approaches that have been studied for the use of nanomaterials in environmental remediation (Bhatt et al. 2022). Adsorption is a process in which contaminants are removed from a liquid or gas by binding to the surface of a solid material. With photocatalytic degradation, dangerous pollutants are transformed into less hazardous by-products using light energy. The membrane in membrane filtration acts as a filter, letting the liquid pass through yet trapping the impurities. The special physicochemical features of nanomaterials make them applicable in many fields, including environmental remediation. Water, air, and soil can all benefit from the usage of these materials since they can be treated to eliminate pollutants even when they are present in minute quantities, whereas conventional techniques often fail to eradicate such traces of pollution (Singh et al. 2020). One example of a nanomaterial that is being used for environmental remediation is graphene, which has a high surface area and excellent conductive properties. Other nanomaterials that have been used for environmental remediation include carbon nanotubes, metal nanoparticles, and clay nanoparticles. These materials have the potential to significantly improve current treatment methods and help to protect the environment from the negative impacts of pollutants (Ganie et al. 2021; Karthigadevi et al. 2021).

Nano-based treatment methods can also be used as hybrid methods for the removal of xenobiotics. These methods involve combining nanoparticles with other treatment methods to remove pollutants from water or soil (Hussain et al. 2022). For example, a combination of nanoparticle adsorption and microbial degradation is known as nano-adsorption-biodegradation. The combination of nanoparticle-

based photocatalysis with microbial biodegradation is known as nano-photocatalysis-biodegradation. Nanoparticle membrane filtration followed by biodegradation, in which contaminants in water are first removed by means of a membrane and subsequently degraded by microorganisms. When nanoparticles are employed to catalyze chemical processes that degrade pollutants, and then the advanced oxidation process (AOP) is performed to further degrade the pollutants, the technique is known as nano-catalysis-advanced oxidation process (AOP).

Nanomaterials have the potential to be employed in remediation techniques like adsorption of contaminants and photodegradation of pollutants, but further study is needed to fully understand their efficacy and long-term implications. Each contamination requires a unique nanomaterial, as some nanomaterials may be more efficient at eliminating certain types of toxins than others due to their unique modes of action (Karthigadevi et al. 2021).

4.7.1 Nanomaterial as Adsorbent for Removal of Xenobiotics

Adsorption is a process in which contaminants are removed from a liquid or gas by binding to the surface of a solid material. It can be used to remove xenobiotics, such as pesticides, pharmaceuticals, and industrial chemicals, from water, air, and soil. Factors such as surface area, chemical structure, pH, and temperature and humidity may affect the effectiveness of adsorption (Chowdhury and Balasubramanian 2015). Some commonly used adsorbent materials for the removal of xenobiotics include activated carbon, clay minerals, graphene oxide, and metal oxides (Srivastava et al. 2006; Abhishek et al. 2014; Ganie et al. 2021). Adsorbent nanomaterials for xenobiotic removal are characterized by a large surface area and tailorable chemical characteristics that allow them to bind to and remove specific xenobiotics. Graphene, carbon nanotubes, and metal nanoparticles are just some of the nanomaterials put to use in the adsorption of xenobiotics (Karthigadevi et al. 2021).

Microporous pores in activated carbon increase the effectiveness of the adsorption process for eliminating POPs, reducing the rate of absorption by the soil. The surface load density varies with the type of material used, and the removal is enabled by their electrostatic response with the contaminant (Ganie et al. 2021). Removal efficiency has increased interest in this technology, but the adsorption process is expensive, which slows its adoption. To remove aromatic hydrocarbons from salty wastewater, alternative resources with superior adsorption capacities and component regeneration are required (Ganie et al. 2021). Adsorption remains a possible option because of the characteristics of the process involved. Recently, biosorbents have gained popularity as a means of purifying pharmaceutically active compounds. Due to its high regeneration capacity and ability to bioaccumulate and biomagnify wastes, the sorption process is economically viable (Ganie et al. 2021).

4.8 Photocatalytic Degradation for Removal of Xenobiotics

Photocatalytic degradation involves the photocatalyst absorbing light energy and then using that energy to form free radicals, which interact with the contaminants, reducing them to less harmful molecules in the process. This process is often employed as an environment-friendly and effective method for the treatment of wastewater (Singh et al. 2017). Organic chemicals, heavy metals, and microbes are just a few of the contaminants that can be effectively removed from various systems by employing photocatalytic degradation. Photocatalysis typically employs irradiation to generate photocharges, which can then transfer to any surface and lead to the mineralization of organic contaminants (Ibhadon and Fitzpatrick 2013; Martínez et al. 2013). Several distinct semi-conductive materials are utilized as photocatalysts because of their affordability, chemical stability, and structure-dependent electronic characteristics. Researchers experimented with altering material crystal structures and surface characteristics to increase the degrading qualities of such semiconducting materials. TiO_2 is the widely accepted semiconductor material for POP destruction (Nsib et al. 2013; Wang et al. 2017). Modified structures can be made by combining different semiconductor materials with methods for boosting photocatalytic activity through hydrothermal and electronic deposition. Heterogeneous photocatalysts are used to detoxify super-hydrophilic water of xenobiotics, with features such as size, surface, pore structure, and pore volume increasing catalysis (Klementova 2018).

4.9 Metal–Organic Framework in Pesticide Removal from Wastewater

“Metal–organic frameworks” (MOFs) are a class of porous materials that are made up of metal ions or clusters held together by organic ligands (Safaei et al. 2019). MOFs are employed for variety of applications such as the treatment of wastewater. The pollutants are attracted to and retained on the surface of the MOF through adsorption, proving them efficient at removing xenobiotics from wastewater. Organic chemicals, heavy metals, and microbes are also pollutants that MOFs may efficiently adsorb because of their high surface area and variable porosity (Saleh et al. 2020).

MOFs can be employed as a potential alternative to wastewater treatment technologies due to their topological structure, functional groups, tuneable porosity, and unique catalytic capabilities. The secondary building unit, i.e., SBU of MOF coordinates metal/metal oxides with polytopic linkers with a variety of functions. Different types of MOFs with tailored physicochemical properties are conceivable via engineering. These porous materials undergo controlled structural changes at elevated temperatures (Bagheri et al. 2021). Their various applications range from energy storage and gas sensing to water purification and catalysis, all of which

depend on their unique features (Liu et al. 2018; Sun et al. 2018; Bagheri et al. 2021; Huang et al. 2021; Wei et al. 2021; Sohrabi et al. 2022). In place of zeolites, MOFs are now being used in gas separation, ion exchange, and catalytic exchange processes. With larger and more numerous holes than zeolite, it may be used in a variety of processes that previously required the use of smaller molecules. MOFs may be unstable in aqueous solution due to the mutual attraction of metal ions and organic ligands. By altering their structures, MOFs are able to harvest more light, and their optical characteristics are fine-tuned to facilitate photocatalysis (Bagheri et al. 2021).

There are numerous ways in which MOFs and target analytes like insecticides interact. The relationship between MOFs and target analytes is essential for understanding how each entity responds in each situation. MOFs can engage through multiple interactions, including electrostatic, H-bonding, and acid–base reaction. Acid–base interaction is based on the fact that the MOF or analyte has both acidic and basic groups on its surface. Using MOFs in this way to clean up pesticides in water and soil has been investigated (Bagheri et al. 2021). MOFs can be used as adsorbents for the elimination of pesticides in the natural environment. To do this, MOFs can be added to polluted water or soil, where the pesticides will then bond to their surface. After the pesticides have been attached to the MOFs, they can be desorbed and removed from the environment. Alternatively, MOFs could be used as catalysts to break down pesticides into less dangerous chemicals. MOFs can be engineered to have the catalytic capabilities necessary to degrade pesticides via chemical processes. Due to the MOFs' ability to convert the pesticides into innocuous by-products, this strategy may prove very useful for the total elimination of pesticides from the environment. MOFs have been applied to the identification and sensing of pesticides in wastewater and soil, in addition to their usage in removal and degradation. For instance, MOFs can function as sensors to detect trace amounts of pesticides, or for the quantification of pesticides (Bedia et al. 2020; Russo et al. 2020; Huang et al. 2021).

Using the metal–organic framework ZIF-8/magnetic multiwalled carbon nanotubes (M-M-ZIF-8) as functional adsorbent, Liu et al. (2018) were able to remove eight distinct P-containing pesticides from both the soil and water (Liu et al. 2018). Static adsorption of organophosphorus pesticides is enhanced by M-M-high ZIF-8's specific surface area and high porosity. The eight organophosphorus pesticides were effectively removed from environmental water and soil samples by M-M-ZIF-8 under optimal conditions. Adsorption of organophosphate pesticides on to the M-M-ZIF-8 may be driven by valence electrons, with the molecules of the pesticides exchanging or sharing electrons with those of the protein's inactive sites. Thus, M-M-ZIF-8 shows potential as a hybrid adsorbent for detoxification due to organic pollutants (Liu et al. 2018).

To get rid of diazinon, an organophosphate pesticide, from water, Diab et al. (2021) used bio-based zirconium-based metal–organic frameworks (Zr-MOFs) called MIP-202. To increase performance, however, we must develop a better and more cost-effective alternative approach for using these materials in their immobilized state on a suitable substrate, as the powdered form is ineffective. They showed

that Bio Zr-MOF beads could be made with the same degree of reactivity and in the same conditions as those achieved by dissolving powdered material in water. They disclosed an essential part of an integrated technique for the elimination of organophosphates from wastewater by the use of MIP 202/CA Composite Beads, or bio-based MOFs (Diab et al. 2021).

Numerous types of nanomaterials have demonstrated enormous potential for pesticide removal from contaminated water and soil, as the nanomaterials can help to break down the contaminants into harmless by-products that can be absorbed or used by the plants or microbe (Hussain et al. 2022). Research is being done to use nanomaterials in combination with plants or microorganisms to degrade the pollutants from the contaminated zone. Nanomaterials can help to convert the pollutant into harmless form that can be taken in or used by the plants (Hussain et al. 2022). Therefore, multiple methods can be utilized efficiently for the total removal of toxins from the ecosystem, and this includes using nanomaterials in a variety of forms, either alone or in combination with other strategies. More study is needed to understand the possible benefits and hazards of these approaches, as well as to further understand and optimize the management of xenobiotics in the ecosystem employing nanomaterials for the elimination of xenobiotics and POPs (Saleh et al. 2020; Bagheri et al. 2021).

5 Socioeconomic Mitigation Measures for Removal of Xenobiotics from Wastewater and Soil

Xenobiotics, or synthetic compounds, can be removed from wastewater and soil by a variety of technical and socioeconomic techniques. Physical, chemical, and biological treatment procedures are frequently employed to get rid of xenobiotics in wastewater. The negative effects of xenobiotics on the environment can be lessened by the application of both technical and social countermeasures. These can include public education initiatives to raise knowledge of the risks and effects of xenobiotics, research and development programs to create new technologies and methodologies for remediating xenobiotics from wastewater and soil, and legislation and policy changes to reduce xenobiotic releases (Fatta-Kassinos et al. 2011). There are several socioeconomic measures that can be taken to mitigate the impact of xenobiotics, or synthetic chemicals, on the environment. These measures can be organized into a “socioeconomic mitigation model” that outlines the steps that can be taken to address the problem of xenobiotics in the environment, as depicted in Fig. 7 (Štefanac et al. 2021).

One potential socioeconomic mitigation model for the removal of xenobiotics from wastewater and soil might include the following steps:

1. Identification of the problem: The first step in the model is to identify the problem of xenobiotics in the environment. This may involve collecting data on the sources and types of xenobiotics that are present in the environment, as well as the impacts of these chemicals on human health and the environment.



Fig. 7 A potential socioeconomic mitigation model for removal of xenobiotics from wastewater and soil

2. **Risk assessment:** Once the problem has been detected, the subsequent stage is to evaluate the consequences posed by the xenobiotics in the environment. This may involve evaluating the potential health and environmental impacts of the chemicals and identifying the populations or ecosystems that are most vulnerable to these impacts.
3. **Risk management:** Based on the results of the risk assessment, the next step is to develop and implement risk management procedures to alleviate the impacts of xenobiotics on human health and the environment. These measures may include technical measures, such as the use of treatment technologies to eradicate xenobiotics from wastewater and soil, as well as socioeconomic measures, such as regulations and policies to control the release of xenobiotics into the environment.
4. **Monitoring and evaluation:** The final step in the model is to monitor and evaluate the effectiveness of the risk management measures in reducing the impacts of xenobiotics on the environment. This may involve collecting data on the concentrations of xenobiotics in the environment, as well as monitoring the health of exposed populations and ecosystems. Based on the results of the monitoring and evaluation, the risk management measures may be adjusted as needed to ensure their ongoing effectiveness in mitigating the impacts of xenobiotics.

Thus, the socioeconomic mitigation model is a viable tool for safeguarding both public health and the ecosystem from xenobiotics. Several societal and economic strategies can reduce the negative effects of xenobiotics, or man-made chemicals, on the natural world (Norton et al. 1992). Some examples of these measures include

1. **Regulations and policies:** Governments can implement regulations and policies to control the release of xenobiotics into the environment. These measures can include limits on the number of xenobiotics that can be released, permit requirements for the discharge of xenobiotics, and penalties for noncompliance.
2. **Public education programs:** Public education programs can help to increase awareness of the risks and impacts of xenobiotics and can encourage individuals and organizations to adopt practices that minimizes the possibility of their direct discharge in the atmosphere.

3. **Research and development programs:** Governments and private organizations can invest in research and development programs to develop new technologies and approaches for the remediation of xenobiotics from wastewater and soil. This can include research on the effectiveness of different treatment technologies and development of novel materials and methods to remove xenobiotics.
4. **Economic incentives:** Governments and private organizations can also provide economic incentives, such as grants, subsidies, and tax credits, to encourage the adoption of technologies and practices that reduce the discharge of xenobiotics in the atmosphere.

Overall, these socioeconomic measures can help to decrease the adverse effects of xenobiotics by encouraging the development and adoption of technologies and practices that prevent or mitigate their discharge (Donner et al. 2010).

6 Existing Policies for Xenobiotics Management

There are a number of policies and regulations that have been implemented to manage xenobiotics, or synthetic chemicals, in the environment (UNEP 2012). Some examples of these policies include the following:

1. **The Stockholm Convention on Persistent Organic Pollutants:** It is an international agreement, adopted in 2001 with the stated goal of reducing people's exposure to harmful levels of POPs and keeping ecosystems healthy (POPs). Parties to the Convention are obligated to take steps to minimize the discharge of POPs in the ecosystem, and the treaty also includes a list of POPs that are subject to global restrictions or bans (URL-1).
2. **The Rotterdam Convention on the Prior Informed Consent Procedure for Certain Hazardous Chemicals and Pesticides in International Trade:** The goal of this international pact, which was ratified in 1998, is to reduce exposure to harmful chemicals and pesticides, thereby protecting human and environmental health. The Convention requires Parties to the treaty to take steps to ensure the safe and responsible use of certain substances, as well as to share information regarding the risks and hazards associated with their use, with the other Parties to the Convention (URL-2).
3. **The European Union's REACH Regulation:** To better safeguard people and ecosystems from chemical hazards, the European Union (EU) enacted this legislation in 2007. The REACH Regulation mandates that businesses in the European Union (EU) register the chemicals they produce or import, as well as give data on the risks and hazards posed by those chemicals (Donner et al. 2010) (URL-3).
4. **The United States' Toxic Substances Control Act (TSCA):** This US regulation, originally passed in 1976 and updated in 2016, is meant to limit the adverse impacts of chemicals on people and the ecosystem. Under the Toxic Substances Control Act (TSCA), the US Environmental Protection Agency (EPA) conducts chemical risk evaluations and implements regulations to address concerns (URL-4).

There are many other policies and regulations at the national and international level that address the management of specific chemicals or groups of chemicals and the application of these chemicals in specific industrial sectors. In India, the management of xenobiotics, or synthetic chemicals, is governed by a number of policies and regulations at the national and state level. Some examples of these policies include the following:

1. The Manufacture, Storage, and Import of Hazardous Chemical Rules, 1989: These rules, which are administered by the Ministry of Environment, Forest, and Climate Change, regulate the manufacture, storage, and import of hazardous chemicals in India. The regulations set out requirements for the registration, handling, and transportation of hazardous chemicals and specify the duties and responsibilities of manufacturers, importers, and users of these chemicals (URL-5).
2. The Water (Prevention and Control of Pollution) Act, 1974: The Central Pollution Control Board (CPCB) is responsible for enforcing this law, which has as its stated goal the reduction of water pollution in India. Industries and other dischargers are required under the act to get permission from the appropriate pollution control board before discharging pollutants into water bodies (URL-6).
3. The Air (Prevention and Control of Pollution) Act, 1981: The Central Pollution Control Board (CPCB) is also responsible for enforcing this law, which was enacted to reduce air pollution in India. Emissions of air pollutants are regulated by the legislation, which mandates that polluters, such as factories, must first receive permission from the appropriate pollution control board (URL-7).
4. The Hazardous and Other Wastes (Management and Transboundary Movement) Rules, 2016: These rules, which are administered by the Ministry of Environment, Forest and Climate Change, regulate the management and transboundary movement of hazardous and other wastes in India. The guidelines set out requirements for the generation, collection, transportation, treatment, and discarding the hazardous and other wastes and specify the duties and responsibilities of generators and handlers of these wastes (URL-8).

These are just a few examples of the policies and regulations that have been implemented to manage xenobiotics in the environment. Overall, these policies and regulations aim to protect public and environmental health from the threats caused by xenobiotics in India.

7 Conclusion and Future Prospects

Xenobiotics are chemicals and substances that are foreign to living organisms and can have harmful effects on living systems. As the quantity of manmade chemicals and other substances in the environment rises, xenobiotics research has become increasingly vital. Studies on the effects of xenobiotics have led researchers to the conclusion that these chemicals can have serious consequences for human health

and the environment. They have the potential to disrupt the entire food chain and environment, with consequences ranging from immediate toxicity to decades of problems. The study of xenobiotics has intriguing future prospects. Better methods for detecting and reducing the impacts of these compounds, as well as better understanding of the mechanisms by which they interact with living systems, require the development of new technologies and procedures. Research into the effects of xenobiotics on the environment is likely to expand due to the current emphasis on sustainability and environmental health. Research into xenobiotics has the potential to significantly advance our knowledge of the environmental effects of human activity and the creation of long-term answers to the problems posed by these chemicals. The public health and the environment can both be protected from xenobiotics with the help of the socioeconomic mitigation approach. Implementing regulations and policies to control the release of xenobiotics into the environment, public education programmes to raise awareness of the risks and impacts, research and development programmes to create new technologies and approaches, and economic incentives to encourage the adoption of technologies and practises that prevent or mitigate their discharge are all part of this process.

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