Chapter 5
Organic Pollutants

Abstract Concerns on organic pollutants as threat to environment is increasingly perceived since later half of the previous century. Although initially focus was on some of the pesticides used in controlling insects in agriculture and disease spreading vectors in residential area, concerns on several other types of organic pollutants increased afterwards with activities of chemical and petrochemical industries and use of xenobiotics in many lifestyle products. Threat from organic pollutants arises many a times due to their extreme toxicity at very low level of exposure as well as their high persistency in the soil. Due to advancements in detection capabilities, researchers have generated considerable information on the source, routes of contamination to soil, interactions with soil constituents, degradability by and impact on soil microorganisms, uptake by plants and contamination of food etc. The impacts on agroecosystem are indicated as multidimensional like food contamination, reduced soil enzymes activity leading to disruption in nutrient transformation processes, diminished biodiversity, mutagenicity among microorganisms etc. Most common groups of organic pollutants in soil including polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), pesticides, dye pollutants, antibiotics are discussed for their sources, fate and impact on the ecosystem.

Keywords Soil • Food • Water • Pollution • Polycyclic aromatic hydrocarbons • Polychlorinated biphenyls • Persistent organic pollutants • Dye • Antibiotics

The soil quality is immediate concern for most people, because we all depend on this natural resource on a daily basis for food, fodder, fibre and fuel. Due to intense pressure on land resource from industrial and urban related activities, soil gets contaminated or polluted; as a result its quality is at greater risk to sustain plant, animal and human life on long run. Soil is contaminated with various organic pollutants from various sources like industrial effluents discharges containing toxic pollutants, improper disposal of urban and industrial solid waste, and accidental spillage of contaminants during transportation or handling of hazardous materials and indiscriminate use of pesticide and fertilizers. This chapter attempts to discuss in details about various potential organic pollutants particularly those, which contribute considerably to environmental pollution and their adverse impact on soil, plant and microbes. Organic pollutants can be both naturally occurring and

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synthesised compounds and may pollute agro-ecosystem either deliberately through crop management activities or accidentally through entry of industrial/urban wastes. Their behaviour and fate in the soil depend mainly on their chemical structure, which determines interactions with mineral particulates, organic matter, water, gas and biota of the soil.

Most common organic pollutants are pesticides, polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), BTEX (benzene, toluene, ethylbenzene, and xylenes), other persistent organic pollutants (POPs) trichloroethylene (TCE), and perchloroethylene, nitro-aromatic compounds, organophosphorus compounds, petroleum oil, etc. These organic pollutants must be investigated thoroughly and controlled as they cause life /life-style threatening diseases such as cataracts, kidney and liver damage, jaundice and cancer; as well as degrade immune system, reproductive system, nervous system, endocrine system of human beings. Beyond the potentially harmful effects on humans, these chemicals affect the biogeochemical cycle and the ecosystem conservation. These organic pollutants even at low concentration in soil may inhibit metabolic activities and growth of soil-associated microbes (Moore et al. 2006). The advanced research has also proved that the few azo-dyes cause bladder cancer, hepatocarcinomas and chromosomal aberrations in mammalian cells in human and animal system.

5.1 Organic Pollutants Entry in Soil, Its Uptake by Plant and Food Chain Contamination

Organic pollutants can reach the soil either by purpose, such as pesticides and other agricultural chemicals, or incidentally through a variety of materials commonly used in agricultural practices, e.g., fertilizers and amendments. Once on the soil surface, the organic pollutant can be partially photo-decomposed and/or volatilized, and partially enter the soil or be transported to surface aquatic bodies by runoff and/or erosion. When in the soil, the pollutant can be subjected to partial or total chemical decomposition and/or biodegradation. The original pollutant and possibly, its breakdown products may be adsorbed to soil organic and inorganic constituents, taken-up by plant roots, and/or leached through the unsaturated zone eventually reaching the groundwater. All these processes are controlled by several factors including the physical and chemical properties of the pollutant and its breakdown products, the nature and thickness of the soil, the amount of water applied to the soil, and the type and extent of interactions between the pollutant and soil components.

Different models for uptake of organic chemicals have been proposed (Trapp 2004; Dettenmaier 2008). Organic chemicals are generally taken up by plant roots via vapor or water phases of soil through active (phenoxy acid herbicides), passive and diffusive process (Bromilow and Chamberlain 1995) and transported to the above ground biomass. Uptake of organic compounds through plant transpiration stream is significant for slightly hydrophobic compounds, but may be severely restricted for soil-bound highly hydrophobic compounds in many higher plants (Bromilow and Chamberlain 1995; Briggs et al. 1982; Ryan et al. 1988). Recent evidence indicates that plants can also translocate some hydrophilic compounds. Such organic compounds likely to be translocated by plants more closely resemble those that can cross the blood − brain barrier as compared to the intestine (Limmer and Burken 2014). Experimental evidences have shown that PAHs, chlorobenzenes, PCBs, and polychlorinated dibenzo-p-dioxins/dibenzofurans (PCDD/Fs) are found accumulated significantly in plant roots (Duarte-Davidson and Jones 1996). In addition to the chemical properties of the contaminant, plant root anatomy plays a major role in uptake mechanism. The higher uptake of organic contaminants by barley plant root over beans root is probably due to higher lipid content in the root of former plant (Bromilow and Chamberlain 1995). Similar observation on organic contaminants uptake based on lipid content in roots has been reported by Fismes et al. (2002) and Wild and Jones (1992). Specific surface area and lipid content were found the most crucial factors for phenanthrene (a PAH compound) uptake with contribution of former being greater than that of lipid content (Zhan et al. 2013). However, no correlation was found between phenanthrene uptake and total root length, and root-water. Several pharmaceuticals compounds have also been found to be taken up by plants. For example diclofenac which has been held responsible for collapse of vulture population in south Asia, was found to accumulate in plant through root uptake (Carter et al. 2014). These evidences indicate that organic pollutants may be taken up by plants from soil and accumulate in above ground plant biomass. Another model was proposed for plant contamination with pollutants based on aerial deposition, soil volatilization, and systemic translocation pathway (Collins and Finnegan 2010). However, this pathway could be significant only in locations with pollutant concentrations >100 mg kg^{-1} in soil. If such organic contaminant accumulated biomass is used for feeding livestock, it consequently increases the probability of exposure of pollutants to humans. In the following sections of this chapter, some of the commonly found organic pollutants, their sources and its effect on soil, plant and human life have been discussed in details.

5.1.1 Pesticides

Pesticides are substances or mixtures of substances used in various terms like herbicides, insecticides, fungicides, rodenticides, molluscicides, and nematicides to prevent, destroy or control any pest, and these are widely used mainly in agriculture and in domestic sector. Based on the chemical constituents, pesticides are classified as organochlorine, organophosphate, carbamate, synthetic pyrethroides and inorganic pesticides. There is another class of pesticides which is produced from natural materials called as biopesticide. These various pesticide formulations have been extensively used for decades and have significantly increased food production.

Global insecticide use in 2007 has been estimated at 404000 t of active ingredient (Grube et al. 2011). The agricultural sector is the primary user of pesticides, consuming over four million tons (Mt) of pesticides annually. However, according to an estimate by Abhilash and Singh (2009), about 2 Mt. of pesticides are consumed every year throughout the world; and out of these 24% is consumed in USA, 45% in Europe and 25% in rest of the world. Among the Asian countries, pesticide consumption is the highest in China followed by Korea, Japan and India. The usage of pesticide in India is about 0.5 kg/ha, of which major contribution is from organochlorine pesticides. In global level, the consumption of herbicide is the highest, whereas in India and other tropical countries, the consumption of insecticides is more. This is due to increased insect pest attack caused mainly by the prevailing warm humid climatic condition.

Some of the pesticides were banned several decades before due to longer persistence in the environment. Even after prohibition on use in most of the countries around the world, organochlorines are still found in agricultural soil, sediment and groundwater (Singh and Singh 2006, Matin et al. 1998; Singh 2001; Manirakiza et al. 2003; Gonçalves and Alpendurada 2005; Hilber et al. 2008). The organochlorine insecticides such as dichlorodiphenyl-trichloroethane (DDT) and hexachlorocyclohexane (HCH) were used widely previously in India due to their effectiveness in controlling malaria, locust and wide range of insects effectively. Presently, many organochlorine pesticides have been banned since 2003, except for DDT (permitted only for restricted use in disease spreading vector control) (Singh et al. 2007). However, some of these pesticides are still preferred by the small farmers because they are cost effective, easily available, and display a wide spectrum of bioactivity (Devi and Raha 2013). Intense and frequent use of these chemicals has led to accumulation of pesticides in soil due to lack of their speedy degradation. Low solubility and high structural stability of the pesticide limit their degradation in soil via chemical and biochemical processes by plants and microbes. Most of the hydrophobic pesticides are adsorbed to soil surface or to organic matter and get sequestrated into tiny pores of soil matrix, becoming less bioavailable. Soil microorganism generally degrades pesticides and converts them into less toxic form; but many a times, end products become more toxic than the original pesticide. Some of the factors that influence their persistency are microbial diversity, rainfall, soil temperature, exposure to sunlight, application rate as well as their solubility and mobility in soil.

5.1.1.1 Pesticides on Food Chain Contamination and Human Health

Generally less than 1% applied pesticides are used for the control of insect pest in crops (Arias-Estevez et al. 2008) and remaining unused pesticide contaminates soil, water and crop produce. Further, indiscriminate use of pesticides by the farmers' due to lack of awareness also results in their unwanted entry into soil with consequent adverse effects on the environment (Igbedioh 1991; Jeyaratnam 1985; Saiyed et al. 2003; Karunakaran 1958). Thus continued application of pesticides increases their concentration in soils and waters, which have adverse effect on different strata of organisms. The extent of these effects however, depends on the toxicity of the pesticides and degree of sensitivity of the organisms. This negative impact of pesticides is mainly due to the highly toxic, stable, less soluble active ingredients of pesticide. Among the various pesticides used, organochlorine pesticides pose serious health concerns. This group includes atrazine, DDT, benzene hexachloride (BHC), Lindane and Endosulfan. Humans are exposed to pesticides (found in environmental media such as soil, water, air and food) by different routes such as inhalation, ingestion and dermal contact, and such exposure results in acute and chronic health problems. Some of the chronic and acute toxicological effects of pesticides are chronic liver damage, endocrine and reproductive disorders, immune-suppression, various cancer, inhibition of choline esterases, Parkinson's and Alzheimer's diseases etc. (Ceron et al. 1995). Death and chronic illness caused by pesticide poisoning numbers about 1 million per year (Lorenz 2006).The World Health Organization has estimated that about 200,000 people are killed by pesticides worldwide every year. Even after ban, residues of organochlorine pesticides had been detected in edible crops, fruit, milk samples because of their transfer from soil through food chain (Jensen 1983; Banerjee et al. 1997). The incidence of pesticides contamination in the food chain is being reported regularly and is expected to increase in the future due to heavy dosage of pesticide use (Devi and Raha 2013). Organophosphate pesticides are generally regarded as safer as compared to organochlorine pesticides for use on crops and animals due to their relatively fast degradation rates.

Dieldrin and endrin residues in agricultural fields cause contamination of not only the aquatic environment but also of crops grown in contaminated soil. High levels of these pesticides have been detected in soils and in a variety of crops around the world. In spite of ban or restriction in use of organochlorine pesticides, their concentrations have been reported in soil of different countries (Table 5.1). Although use of pesticides in general is quite low in Africa, the presence of organochlorine pesticides in food crops have been reported from many countries in that continent. In Togo, West Africa, dieldrin and endrin residue levels of 39.50 and 13.16 ng g^{-1}, respectively, were found in cowpea and a dieldrin residue level of 18.09 ng g^{-1} was found in maize (Mawussi et al. 2009). In Nigeria, dieldrin residues of 6–80 ng g^{-1} were found in tubers (Adeyeye and Osibanjo 1999). Researchers from other countries have also reported residues of these pesticides in food; for example in cucumbers in Japan (Hashimoto 2005), winter squash in the USA (Johgenson 2001), in wheat in Serbia (Škrbić 2007) and vegetables such as spinach, garlic leaf, and pumpkin in China (Gao et al. 2005).

DDT and HCH concentrations in soils from India were lower and comparable with other locations of the world. Using the ratio of DDT/(DDD + DDE) for the contents in soils, Kumar et al. (2014) concluded that source of DDT in soils of Korba (India) may be from both ongoing and past applications. Also source of HCH in soil may be both lindane and HCH as indicated by ratio of α-HCH/γ-HCH. Cancer risk (ILCR) and non-cancer health hazard (HQ) were however lower than

Table 5.1 Levels of DDT and HCH in soils (μg kg^{-1}) reported after 2006

Country	ΣDDT	ΣHCH
China	ND – 663	ND – 654
Spain	126 – 316	1.8
Romania	20 – 50	–
Mexico	ND – 26980	–
Vietnam	BDL – 1538	BDL – 20.57
Pakistan	BDL – 1538	BDL – 119
India	BDL – 315	BDL – 104

Adapted from Kumar et al. (2014)

acceptable guideline values, suggesting low risk for adults and children residing in the area of study.

5.1.1.2 Effect of Pesticides on Biodiversity

Accumulation of pesticides may reduce number of macro- and micro-flora and fauna species like arthropods, earthworms, fungi, bacteria, protozoa, and other organisms in soil, which are responsible for several ecosystem functions related to soil fertility and soil formation. In a comprehensive review, Pelosi et al. (2014) concluded that pesticides had adverse impact on earthworms in soil at all organisation levels as these agro-chemicals disrupt enzymatic activities, increase individual mortality, decrease fecundity and growth, change individual behaviour such as feeding rate and decrease the overall community biomass and density of earthworms. Pesticides also affect other invertebrates in soil; although the impact varies with their types and accumulation levels as well as species of invertebrates (Frampton et al. 2006; Desneux et al. 2007). Exposure of birds to such toxic pesticides reduces the reproductive rate and biochemical reaction in the body, or even kills them directly at high doses (Wilson and Tisdell 2001).

Soil microbial diversity is important for maintenance of soil quality as well as for optimum ecosystem functions. The diverse groups of microorganisms commonly found in soil are mostly unicellular of prokaryotic or eukaryotic origin which include bacteria (eubacteria and archaebacteria), cyanobacteria, actinomycetes, fungi and algae. These soil microbes perform a variety of activities required for the proper functioning of the soil as a dynamic system. While soil enzymes released by soil microbes are responsible for many C and nutrient transformation processes important in crop production, microbial diversity plays important role in ecosystem multi-functionality, degradation of organic pollutants and resistance to invasion by pathogens (Kennedy and Smith 1995; He et al. 2009; van Elsas et al. 2012). Any change in their number or proportional distribution can potentially prohibit/enhance one or other soil biochemical processes important for soil fertility. Pesticides have been found to affect both soil enzyme activities and microbial diversity adversely and the effect depends on type of pesticides, their doses and time elapsed after application (Jacobsen and Hjelmsø 2014). Generally, impact on microbial diversity is more due to fumigant type of agro-chemicals like dithiocarbamate, organosulfur, organobromide etc. Glyphosate, an herbicide was found to impact negatively on the growth promoting bacteria in the rhizosphere (Zobiole et al. 2011).

Some pesticides (particularly non-organochlorine group) stimulate the growth of microorganisms, but other pesticides have either depressive effect or no effect. Organophosphorus pesticides are found less toxic to soil microorganisms (Digrak and Kazanaki 2001; Das et al. 2005). Soil microorganisms generally adapt initially to these pesticides and therefore, biodegradation is faster in soils that have had repeated applications of OPs compared to control soils which have never had OP applications (Ragnarsdottir 2000). Although half-life of OPs are generally 1–2 weeks, these may be detected in trace amount in soil years after application, probably due to their sorption on soil particles rendering these unavailable for microbial degradation (Das et al. 2005). Carbofuran (a carbamate compound) stimulated the population of *Azospirillum* and other anaerobic nitrogen fixers in flooded and non-flooded soil, but butachlor (acetanilide group) reduced the population of *Azospirillum* and aerobic nitrogen fixers in non-flooded soil (Lo 2010). Application of phorate (an organophosphorus compound) and carbofuran induced growth and development of several groups of microorganisms including N_2-fixing bacteria and phosphate solubilizing microorganisms (Das et al. 2005). In rice field agro-ecosystems of India, endosulfan and dichlorvos application at normal dose (@ 1 $mL\ L^{-1}$) did not show any adverse effect on soil micro flora; but showed a negative effect at double dose (Bhagabati and Sarma 2011). On the other hand, carbofuran showed an adverse effect on the growth of actinomycetes, bacteria and fungi even at recommended dose of application. Some pesticide compounds can severely limit the nitrogen-fixing capacities of blue-green algae, thereby affecting the overall nitrogen economy of soils in general (DaSilva et al. 1975). Application of aldrin, HCH, carbofuran, 2,4-D, and machette in higher dose lead to the reduction in the nitrifying bacteria population and in the concentrations of nitrate and nitrite in soil (Pandey and Rai 1993). Acid and alkaline phosphatase activities (responsible for phosphate mineralization) as well as the nitrification process (conversion of NH_4^+ to NO_3^-) were inhibited due to herbicide napropamide application (Cycoń et al. 2013). Pesticide application in paddy field soil decreased soil dehydrogenase activity with increasing doses and toxicity increased in the order insecticide > fungicide > herbicide (Subhani et al. 2002).

5.1.2 PAHs

The polycyclic aromatic hydrocarbons (PAHs) include more than 200 compounds with two or more fused benzene rings, the most significant of them are phenanthrene, anthracene, pyrene, fluoranthene, chrysene, benzo(a)pyrene, and benzo(a) anthracene. The differences in ring configurations lead to differences in chemical, physical, and toxicological characteristics of PAHs compounds. These are categorized as low molecular weight (LMW) and high molecular weight (HMW) PAHs based on molecular structure. The LMW PAHs include two and three rings structure while HMW PAHs comprise four and more rings structure and the aqueous solubility of PAHs decrease almost linearly with increase in molecular mass (Heitkamp and Cerniglia 1989).

5.1.2.1 PAH and Its Toxicity

The PAHs in environment are known to possess mutagenic, teratogenic, or carcinogenic properties and are widely associated with adverse effects on public health (Rost et al. 2002; Cerniglia 1993). A long back during 1791, the physician John Hill first linked nasal cancer with PAHs (Cerniglia 1984). The PAHs toxicity occurs mainly due to intercalation of the PAH aromatic ring system into the DNA molecule and this biochemical process is responsible for mutagenicity and carcinogenicity by this organic pollutant. The carcinogenicity of PAHs increased with increasing molecular weight. Human exposure to PAHs has been associated with an increased risk of developing cancer in the variety of organs (such as lung, bladder, stomach, skin, larynx, scrotum, breast, oesophageal, prostate, kidney and pancreas). Furthermore, they are known to suppress the immune system and are suspected of being endocrine disrupters. There are various industrial workplaces at which a significant increase of certain cancer diseases has been found that may be attributed to an unusually high exposure to PAHs. For instance, PAHs exposure is high in coke plants, coal tar manufacturing industries, asphalt, bitumen, aluminium plants, iron and steel industries, creosote, rubber, mineral oil, soot and carbon black-producing or manufacturing companies. As highly exposed occupational groups, chimney sweepers, road-men (involved in pavement-tarring) and roofers (involved in roof-tarring) are also under increased risk from these pollutants (Jacob and Seidel 2002). In a study, dermal absorption was found a major route of PAH entry in the body of coke-oven workers; where 75% of the total absorbed amount of PAHs (specifically pyrene) entered the body through the skin (VanRooij et al. 1993). United States Environmental Protection Agency has identified sixteen PAHs as priority pollutants due to their adverse effect on human health.

5.1.2.2 Sources of PAHs in Soil and Their Concentration Level

PAHs in soils may be generated from natural processes like biosynthesis (bacterial and algal synthesis, decomposition of vegetative liter fall) or geochemical reactions (forest fires or volcanic activity, erosion of sedimentary rocks containing petroleum hydrocarbons, fossil-fuel and mineral production). It is also believed that PAHs are produced during combustion of plant biomass, where these are synthesized during the chemical transformation of monomeric lignin components present in plant biomass (Medeiros and Simoneit 2008; Nussbaumer 2003). The species composition of burning biomass can influence the amount and nature of PAH compounds generated. Combustion of coniferous wood in fire place generated the maximum concentrations of hydrocarbons (Schauer et al. 2001). Also combustion of both pine and deciduous wood produced naphthalenes as the predominant PAH; however the amount being relatively smaller in case of deciduous wood. Combustion of herbaceous plants generated predominantly phenanthrene, pyrene and fluorene (Masclet et al. 1995). However, the amount of hydrocarbons produced in such case was comparable to that generated from the combustion of deciduous species, but smaller than during combustion of coniferous plants. These organic pollutants may also originate from anthropogenic sources such as burning of fossil fuels and biomass, industrial emissions, motor vehicle exhausts, abrasion of road surfaces and tires and petroleum processing (Masih and Taneja 2006). Contribution of anthropogenic sources in PAH introduction into the environment is much higher in comparison to their natural sources (Nam et al. 2003). Other potential sources of PAHs in soil include disposal from public sewage treatment, irrigation with coke oven effluent, and use of MSW compost (Santodonato et al. 1981; White and Lee 1980). In Brazil, Grossi et al. (1998) found increased concentrations of PAHs, PCBs, and PCDD/Fs in composts prepared from unsegregated MSW from metropolitan areas.

Concentration of total PAHs in soil may vary from 1 μg kg^{-1} to 300 g kg^{-1} soil, depending on the sources of contamination like combustion of fossil fuels, gasification and liquefaction of coal, incineration of wastes, and wood treatment processes (Bamforth and Singleton 2005). The high concentration of PAHs in the surface soil layer is observed especially in areas of municipal–industrial agglomerations, around roads/highways and fuel processing; and concentration of individual PAHs varies from below limit of detection to up to several hundred μg per kg of soil (Gąsecka et al. 2015). Coal-tar has been found a major source of PAHs in the environment particularly along roadside soils and water bodies (van Metre et al. 2009; Mahler et al. 2012). Median ΣPAH concentrations in dust from sealcoated pavement were 2200 mg kg^{-1}, which was almost 80 times higher than the similar concentration in dust samples received from unsealcoated roads (Van Metre et al. 2009). Such dust particles may be carried by air or storm water to contaminate nearby land. In India, most of the highways and city roads use coal-tar extensively as seal-coat and therefore, contamination of soils in the agricultural land alongside roads and highways with PAHs and their transfer to plant & food need to be investigated. High concentration of PAHs was observed in the atmosphere of Durg-Bhilai (India) city due to heavy vehicular traffic (Pandey et al. 1999). In an experiment at Jalandhar (Punjab), PAHs contamination in soil along the roadside was quantified. The average total PAHs concentration was found 4.04 μg g^{-1}, while 16 individual PAH concentration ranged between 0.008 and 28.4 μg g^{-1} (Kumar and Kothiyal 2011). The concentration of these pollutants was the highest within 1 m distance from road side. The ratio of noncarcinogenic and carcinogenic PAHs in all the soil samples was 1:2.95. In the most of the city locations, total carcinogenic PAHs concentration ranged from 60% to 80% of the total PAHs. The combined status of PAHs and metals in surface (0–5 cm) soils of three different land-use regions (industrial, flood-plain and a reference site) in Delhi was studied over a period of 1 year (Khillare et al. 2014). Mean Σ16PAH concentrations at the industrial and flood-plain sites (10.9 ± 2.8 and 3.1 ± 0.9 mg kg^{-1}, respectively) were ~15 and ~4 times respectively, higher than reference levels. Toxicity potentials (Benz[a]pyrene–equivalent concentrations, as a measure of carcinogenic potencies) of industrial and flood-plain soils were ~88 and ~8 times higher than reference levels.

$$\text{Benz[a]pyrene} - \text{equivalent concentrations} = \sum_{i}^{n} (C_i \times TEF_i)$$

where, TEF_i is Toxic equivalency factor of individual PAH relative to Benz[a]pyrene, as given by Tsai et al. (2004); and C_i is the concentration of an individual PAH. The values of TEF ranged from 0.001 (for Naphthalene, Acenaphthylene, Acenaphthene, Fluorene, Phenanthrene, Fluoranthene, Pyrene, Perylene, Coronene) to 1.0 (for Benzo(a)pyearene, Dibenzo(a,h)anthracene, Dibenzo(a,e)pyrene).

The identified sources of PAHs in the study were coal and wood combustion, vehicular and industrial emissions, and atmospheric transport. Health risk assessment (incremental lifetime cancer risk and hazard index) showed that flood-plain soils have potential high risk due to PAHs while industrial soils have potential risks due to both PAHs and Cr (Khillare et al. 2014). In another study to assess the health risk from PAH in Delhi, median concentrations of benzo(a)pyrene in soil was 0.029 (±0.002) mg/kg (Kumar et al. 2013a). Health risk from soil accumulated benzo(a)pyrene was low, as computed incremental life time cancer risk (ILCR) and index of additive cancer risk (IACR) values were much lower than the guideline values of $10^{-6} - 10^{-4}$ (ILCR) and <1 (IACR), respectively.

These organic contaminants have high environmental stability due to generally being resistant to microbial decomposition (Harrison et al. 1996; Zhang et al. 2009). Biochemical persistence of PAHs arises from dense clouds of π-electrons on both sides of the ring structures, making them resistant to nucleophilic attack. Their physical properties include low aqueous solubility and high solid-water distribution ratios, which decrease bioavailability for microbial utilization and promote their accumulation in the solid phases of soil mass. Bioavailability of the PAHs decreases almost logarithmically with increasing molecular mass. As a consequence of their low water-solubility, low vapour pressure and high degree of association with soil organic matter, PAHs tend to adsorb strongly onto soil particles (Kipopoulou et al. 1999; Orecchio 2010). In fact, most of the environmental burden of PAHs is considered to be due to their presence in soil (approximately 95%), as opposed to air (approximately 0.2%) (Smith et al. 1995). Once such PAHs seep into the soil, these get accumulated in horizons rich in organic matter and are likely to be retained for many years due to their persistence, hydrophobicity and slow degradation rate (Krauss et al. 2000).

5.1.2.3 Impact of PAHs on Soil and Crop Quality

While contaminated air and water are main routes of direct PAHs entry in human, their entry through contaminated soil is suspected only indirectly to food plant contamination or through grazing animals (soil ingestion). Soil system seems to be the important long-term repository for PAHs and is considered to be a steady indicator of the state of environmental pollution. PAHs with three rings or more tend to be very strongly adsorbed to the soil matrices (Knox et al. 1993), preferentially to small aggregates (<50 μm), which also contain the most humified organic matter (Quantin et al. 2005). Strong adsorption coupled with very low water solubility render PAH loss by leaching insignificant. The investigations have showed that assimilation of PAHs from soil into plants can be treated as an equilibrium process, where the accumulated PAHs are in equilibrium with available PAHs in soils. Available PAHs are only part of the total PAHs concentrations in soil. Therefore, the degree of bioaccumulation in plants, besides the physicochemical properties of organic pollutants and the plants' sensitivity to PAHs uptake, is closely related to the bioavailability of PAHs (van Bohemen and van de Laak 2003).

Absorption of PAHs from soil through roots and their transport into aboveground parts of the plant has been found possible mainly for low molecular weight (containing 2- and 3-ring) hydrocarbons due to their high solubility; whereas larger molecules (having >3 ring) of these are accumulated on the surface of the roots (Oleszczuk and Baran 2004). From a number of experiments, it has been concluded that contamination of crop plants via root absorption with PAHs is negligible (Ellwardt 1977; O'Connor 1996). Tao et al. (2006) determined the relationship among the contents of 16 PAHs (listed by EPA) present in cabbage, in air as well as in soil. The concentration of PAHs in cabbage was positively correlated with the concentration in the air, whereas dependence of the level of soil contamination was statistically insignificant indicating air pollution being major concern in respect food contamination. In another study, contamination of plants (trees, grasses, grain) including vegetables and fruits with PAHs depended on their contents in both soil and air (Liste and Alexander 2000). Only limited data are available on the toxicity of PAHs for plants; although it is generally opined that these pollutants do not produce any perceptible toxic effects in vegetation. PAHs did not have any adverse effect on the germination of several crops even at higher concentration (Ghanem et al. 2010). A study compared PAHs uptake by different plants in the vicinity of highway (Kluska 2005) and indicated that cabbage recorded the highest concentration (358 ng kg^{-1}) of total PAHs among studied vegetables, followed by cucumbers (71.3 ng kg^{-1}) and root of parsley (29 ng kg^{-1}). The concentrations in soil and plant decreased with distance away from highway. Aerial deposition of PAHs on leaves and their subsequent entry-translocation within plant are important mechanisms of their contamination of food. Leaf morphological features (cuticular wax, surface area, hairs, and stomata), leaf components (lipids) and contaminant molecular structure (low and high molecular weight PAHs) play important role in

PAH uptake and translocation by plant (Howsam et al. 2000). Many plants with relatively large surface area have greater potential to accumulate PAH from the polluted atmosphere through particle deposition on waxy leaf or by uptake in the gas phase through stomata (Kipopoulou et al. 1999; Lehndorff and Schwark 2004).

Changes in soil microbial activity and biodiversity have been reported due to accumulation of persistent and toxic organic pollutants. In the presence of PAHs, biomass-C, respiration, protease activity and heterotrophic counts were significantly enhanced, while urease activity was depressed. Mineralization of organic N in soil was initially, but reversibly inhibited in the presence of PAHs (Margesin et al. 2000). Adverse effect of these organic pollutants on enzymatic activity (dehydrogenase, phosphatase, urease and protease) was found influenced by soil physicochemical properties such as total organic carbon content and pH (Baran et al. 2004). Soil enrichment with organic matter considerably decreases the negative influence of PAH's on enzymatic activity (Kucharski et al. 2000; Baran et al. 2004). PAHs affected nodulation of alfalfa significantly and the effect was more in absence of humic matter (Wetzel and Werner 1995). In some of the soil samples, stimulating effect of PAH on dehydrogenase activity was also observed, which was attributed to an adaptation of the soil microflora and the use of the pollutant as a C and energy source (Baran et al. 2004).

5.1.2.4 Food Chain Contamination with PAHs

Accumulation of PAHs in soils and atmospheric pollution may lead to food chain contamination (Kipopoulou et al. 1999; Mueller and Shann 2006) and subsequently, cause direct or indirect exposure (ingestion, inhalation, and dermal contact) to human. Food appears to be the main source of PAH intake for humans who are not occupationally exposed to PAH. Raw foods should not contain high levels of PAH. In areas remote from urban or industrial activities, levels of PAH found in unprocessed foods reflect the background contamination. Generally, the average background values are in the range of 0.01–1 $\mu g\ kg^{-1}$ in uncooked foods. Such PAH usually originates from long distance airborne transportation of contaminated particles as well as natural emissions from volcanoes and forest fires. In the neighbourhood of industrial areas or along highways, the contamination of vegetation can be ten-fold higher than in rural areas. The waxy surface of vegetables and fruits can concentrate low molecular mass of PAH mainly through surface adsorption. PAH concentrations are generally greater on plant surface (peel, outer leaves) than on internal tissue. Careful washing may remove up to 50% of the total PAH. Particle bound PAH are easily washed off the surface; whereas those in the waxy layer are less efficiently removed. Sediments of lakes and sea also accumulate organic pollutants originated from anthropogenic activities like biomass & fossil fuel combustion, road construction, oil spill etc. (Magi et al. 2002; Perra et al. 2009). The main route of human exposure to sedimentary PAHs is through marine lives which make up part of the human diet. PAHs contained in sediments and pore water are taken in by benthic organisms such as lobsters, mussels, and clams which are either consumed directly by humans or are consumed by higher predators such as squid and fish which are also a part of the human diet. Therefore, knowledge on contamination in soil, groundwater, marine and atmosphere with PAHs is needed to avoid any food production risk and to restrict the deleterious effect of these contaminants on human.

5.1.3 Other Persistent Organic Pollutants (POPs)

Persistent organic pollutants (POPs) are toxic chemicals that adversely affect human health and the environment around the world. Some of the most well-known POPs are PCBs, DDT, and dioxins. PCBs and DDT were being produced chemically due to their usefulness. PCBs were extensively used as dielectric and coolant fluids in transformers and capacitors, lubricants, plasticizers, paints, etc. Dioxins result from some industrial processes and from waste combustion (for example, municipal and medical waste incineration and backyard burning of trash). A study on assessment of air quality of different potential sources in different cities of India indicated that the concentrations of both polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDDs/DFs) and dioxin-like PCBs from hazardous waste incinerators are much higher than those from some thermal processes (Thacker et al. 2013). A monitoring and toxicological study by Center for Marine Environmental Studies, Ehime University (Japan) revealed that municipal dumping sites were the major reservoirs and sources of terrestrial dioxins and related POPs, particularly PCDDs/DFs (Subramanian and Tanabe 2007). They also indicated that PCDD/DF homologue profiles of the dumpsite soils from India synchronized with the profiles reported for the soils representing environmental sources of these chemicals (municipal waste incinerator emissions) from United States. A decade after, the same group revisited the status of POPs in environmental samples of India and concluded that organochlorines such as DDTs and HCHs showed decreasing trend due to ban on the use of such chemicals, though their levels were still higher (Subramanian et al. 2015). Dumping site at Chennai (India) was estimated to receive 1400 mg of PCDD/DF annually (Minh et al. 2003). Use of polychlorinated biphenyls (PCBs) is more in Indian industries, but the production is totally contributed by other countries. Several experiments with increased sewage sludge application rates also demonstrated an accumulation of PCBs in the treated soils (Folch et al. 1996; Delschen 1999). Since 1966, PCBs and other organohalide compounds were identified in soil system and the sources of contribution were industrial effluent, sewage-sludge incinerators and biomass combustions. The discharged PCBs are adsorbed by the soil particles; affect the soil properties and persist for longer time. Exposure to these compounds is recognized as an important environmental risk factor for humans and animals because of the following effects: cancer; nervous system damages; reproductive and immune system impairments; and hormonal imbalance (Darnerud et al. 2001; Safe 2004). Presence of these organic contaminants however, has generally not been found to affect soil microorganisms

Table 5.2 Average concentrations of POPs in different environmental samples from various regions of India

Nature of sample	ΣDDT	ΣHCH/BHC	Period of sampling/ reporting
Surface water (ng L^{-1})	ND – 16,367,000	0.1 – 17,430,000	1988–2011
Groundwater (ng L^{-1})	ND – 75,000	88.43 – 400,000	2001–2011
Soil (ng g^{-1})	13.81 – 934	1.65 – 404,520.9	1996–2012
Sediments (ng g^{-1})	<0.01–128,600	<0.01 – –234,000	1998–2012
Aquatic organisms (ng g^{-1})	0.38 – 19,970	0.87 – 32,200	1995–2010
Human blood (μg L^{-1})	8 – 32,200	6 – 2633.7	1983–2012
Human milk (ng g^{-1} lipid wt.)	175.5 – 3210	127.25 – 4500	1981–2006

Adapted from Sharma et al. (2014)

and associated biochemical processes (Wild et al. 1994). However, their extreme persistence in the environment and ability to bioconcentrate in the food chain makes them great environmental and human health risks that need remedial action (Cousins and Jones 1998; Hickey 1999). Due to their high toxicity, many industrialized countries imposed regulations and bans on the production, use and discharge of these compounds. However developing countries are yet to initiate such actions due to the availability of limited baseline data.

Several studies reported elevated levels of persistent organic pollutants (POPs) in various environmental and biotic samples from India (Kumari et al. 2008; Devanathan et al. 2009; Someya et al. 2010; Sharma et al. 2014) (Table 5.2). In a study, large number of environmental samples (fish, dust and human milk) from different locations of India were analyzed for PCBs and other organohalide compounds (Devanathan et al. 2012). High levels of PCBs were found in human milk from surrounding municipal waste dumping site indicating higher risk for infants living near these sites. Significantly higher levels of organohalide compounds were found in dust samples from e-waste recycling locations, suggesting that the crude e-waste recycling/dismantling activities are the major emission sources of these contaminants. The hazard quotients values of PCBs were above one for the infants and toddlers living near the municipal dumping and e-waste recycling areas indicating high risk, which warrants regular monitoring and regulations to reduce the pollution levels. Dietary intake values of PCBs and polybrominated diphenyl ethers (PBDEs) through farm-raised fish were far lower than the guideline values indicating less risk through fish consumption. Soil samples from agricultural land near pesticide manufacturing industry at Lucknow contained very high concentrations of HCH (Jit et al. 2011; Abhilash and Singh 2009). Concentrations of DDTs and HCHs were generally lower in urban areas than in agricultural soils indicating higher use of these POPs as pesticides in agriculture (Sharma et al. 2014). Meta-analysis on time trend of data did not indicate a general decline in DDT and HCH residues in the environment and human body in India in spite of ban on their use; whereas, such samples from China showed a tendency towards decline in POP contamination (Sharma et al. 2014). In urban soils of Kurukshetra city, average of 28 PCBs and dioxin-like PCBs were 11.57 ± 2.00 $\mu g\ kg^{-1}$ and 2.58 ± 0.34 $\mu g\ kg^{-1}$, respectively. However, analysis of incremental life time cancer risk indicated that these contaminated soils were not likely to pose any health risk to adults and children (Kumar et al. 2013b).

5.1.3.1 Impact of POPs on Soil and Produce Quality

Persistent organic pollutants are lipophilic /hydrophobic in nature and hence, these are strongly adsorbed to soil organic matter restricting their uptake by plant root. Availability of organic pollutants for plant uptake is governed its solubility in water which are generally determined by octanol-water partition coefficient (K_{ow}). Concentration of organic pollutants in soil and that in aboveground plant parts were found to be related by the equation below (Travis and Arms 1988):

$$\log B_v = 1.588 - 0.578 \log K_{ow}$$

where, B_v is the ratio of conc. of organic in aboveground plant to that in soil.

Contaminants with values of K_{ow} ranging between 0.5 and 3 are considered moderately hydrophobic and are most likely to be taken up by plants (Ryan et al. 1988; Wenzel et al. 1999). Hawker and Connell (1988) determined K_{ow} values for 13 PCB congeners and found its strong relationship with total surface area. Transfer of PCBs from contaminated soil to plant root is generally low; and higher chlorinated congeners are further less preferentially absorbed (Suzuki et al. 1977; McCrady et al. 1990; Wild et al. 1994). Several researches have also concluded that uptake and translocation of PCBs to aboveground biomass is very small with bioaccumulation factor of about 0.0045 (Webber et al. 1990; Gan and Berthouex 1994). However, some PCBs (like 2,3,7,8-Tetrachlorodibenzodioxin, TCDD) are likely to be absorbed by plant leaves via volatilization from soil surface (McCrady et al. 1990). In a study on a highly contaminated soil (0.6–200 $\mu g\ g^{-1}$ total PCBs in terms of Aroclor 1254/1260), sedge (*Carex normalis)* showed significant accumulation of PCBs in shoot with bioaccumulation factors up to 0.29 indicating its potential for phytoremediation (Whitfield Aslund et al. 2007). Turrio-Baldassarri et al. (2007) found significant level of contamination in forage crop nearby PCB manufacturing plant in Brescia, Italy which was assumed to be from air-borne PCBs.

POPs are highly stable chemicals that resist the natural processes of degradation. Once introduced into the environment, they can persist for a long time. These are readily absorbed in fatty tissue and accumulate in the body fat of living organisms; and become more concentrated as they move up the food chain, especially into larger, longer-living organisms. Long-term consumption of contaminated forage plants led to their build-up in the body of bovines and human population residing in the contaminated area (Turrio-Baldassarri et al. 2008, 2009). Soil contamination with PCB (Aroclor1248; tetrachlorbiphenyl) resulted significant reduction in root growth of several plants (Chekol et al. 2004). This group of organic pollutant, particularly higher-chlorinated congeners has considerable adverse effect on soil microorganisms (Cámara et al. 2004; Correa et al. 2010). Soil ingestion during grazing has been found to play key role in toxic POPs transfer into livestock which in turn increases risk of their exposure to human (Wild et al. 1994).

5.1.4 Dye Pollutants

Several textile, pharmaceutical and printing industries use large volume of azo-dyes, which is a group of synthetic organic colorants (generally derivatives of benzene, toluene, naphthalene, phenol and aniline) containing N as azo group –N=N. Due to the extensive use of these dyes in industries, they have become an integral part of industrial effluent. A considerable fraction (about one-tenth) of azo-dyes used by textile industries does not bind the fabrics, and therefore is released through wastewater (Puvaneswari et al. 2006). In fact, of the one million ton of organic dyes annually produced worldwide, more than 11% is lost in effluents during manufacture and application processes (Forgas et al. 2004). The presence of dyes in water imparts color to it which can block sunlight penetration and oxygen dissolution, both of which are essential ingredients for aquatic life (Pereira and Alves 2012). Thus, there is a considerable need to treat these colored effluents before discharging them to various water bodies. Further, some azo dyes are bonded with heavy metals like Cr and Cu in order to impart shades and resistance to washing. As a result, wastewaters from textile industries, unless treated properly, pose considerable threat to environment from both organic and metal pollutants. Groundwater of several villages near industrial area of Ratlam and Bichhri (India) has been turned red due to contamination from dye industry effluents (DTE 1999; Saha and Sharma 2006) (Fig. 5.1). Several types of azo-dyes and their breakdown products are toxic (lethal, mutagenic and carcinogenic) to terrestrial and aquatic organisms including mammals (Brown and De Vito 1993; Puvaneswari et al. 2006). Many of these dyes are resistant to degradation and remediation under natural conditions and through conventional treatment methods (Tahir et al. 2016). Reported half-life of hydrolyzed Reactive-Blue 19 is 46 years (Hao et al. 2000).

5.1.4.1 Impact of Dye Pollutants on Soil Quality

Dyes show different degree of stability in soils from days to several weeks depending upon the nature of chemical compounds. Direct-Red 81 was more resistant to microbial degradation as compared to Reactive-Black 5 and Acid-Yellow 19 (Imran et al. 2015). As a result of irrigation with effluent from dye industries, considerable accumulation of total organic dyes in cultivated soil had

Fig. 5.1 Groundwater near Ratlam industrial area has turned *red*, suspected to be due to contamination with azo-dyes

been observed and such accumulation has also been transported in plant tissue (Zhou 2001). Phytotoxicity of dyes has been reported by some workers (Kalyani et al. 2008; Ayed et al. 2011). There are evidences of plant uptake of dye compounds by plants (Uera et al. 2007; Muthunarayanan et al. 2011). Different azo dyes have expressed toxicity to soil microorganisms and toxicity is more on Gram-negative bacteria than Gram-positive bacteria (Imran et al. 2015). Certain azo-dye had been found to affect adversely on growth of atmospheric N fixing cyanobacterium *Anabaena* sp. (Hu and Wu 2001). Sulfonated azo dye had significant adverse effect on urease activity, ammonification and nitrification rates in soil and therefore reduces nitrogen use efficiency in crop production (Topac et al. 2009). Ammonia oxidizing bacteria population and rate of nitrification process was depressed considerably in presence of reactive-black 5 dye (Batool et al. 2015). These results show dye pollutants show considerable toxicity to soil microorganisms and agriculturally important nutrient cycling processes.

5.1.5 Antibiotics Contamination in Soil and Their Impact

Antibiotics inhibit the activity of microorganisms, viruses, and eukaryotic cells and are commonly used in human and veterinary (bovines, swines and birds) medicines for treating infections. Their benefits have been recognized in agriculture, aquaculture, beekeeping, and livestock as growth promoters. A significant quantity of these is also routinely used as a feed supplement to promote growth of food and milch animals to inhibit subclinical infections and to reduce growth-depressing microbial metabolites (Kumar et al. 2005a, b). There are several different kinds of antibiotics and these can be classified based on their chemical structure, action mechanism, action spectrum, and the route of administration. Although antibiotics are designed to perform effectively at very low concentration, they are administered in the body at larger dose because of lower efficacy in reaching the targeted pathogens. Most antibiotics administered in human or fed to animals are poorly absorbed in the gut and as a result a substantial amount of these are excreted through urine and faeces, which in turn end up in municipal sewage effluent and manure.

5.1.5.1 Antibiotics Release into Environment and Their Entry into Agroecosystem

It is estimated that as much as 90% of some antibiotics may be excreted as parent compound, thereby contaminating the environment (Phillips et al. 2004). Tetracyclines (oxytetracycline and chlortetracycline), tylosin, sulfamethazine, amprolium, monensin, virginiamycin, penicillin, and nicarbazine are the most common antibiotics present in swine, beef, and poultry/turkey manures. The concentration of these antibiotics varies from traces to as high as 216 (mg L^{-1}) of manure slurry (NAAS 2010). Soil, sediment, sludge, groundwater, wastewater, tap water, surface water (lakes, streams, rivers, sea), plants, and aquatic animals have been reported for contamination with antibiotics by several researchers (Hirsch et al. 1999; Hamscher et al. 2002; Fick et al. 2009). Pharmaceutical industries in Hyderabad (India) have been reported to contaminate surface, groundwater and drinking water severely with antibiotics like ciprofloxacin, ofloxacin, cetirizine. Wastewater from a common effluent treatment plant receiving process water from approximately 90 bulk drug manufacturers contained several antibiotics in very high concentration (Fick et al. 2009). Mutiyar and Mittal (2013) found concentration of amoxicillin in the untreated raw sewage in Delhi (India) in the range from “not detected” (ND) to 172.6 ng L^{-1}. In another study by this group, significant concentrations of ampicillin (23.5–263.3 μg l^{-1}), ciprofloxacin (9.7–45.4 μg l^{-1}), sparfloxacin (ND to 63.2 μg l^{-1}) and gatifloxacin (ND to 8.4 μg l^{-1}) had been found in wastewater influents from Delhi (Mutiyar and Mittal 2014). Removal efficiencies of the STP varied between 55 and 99%. Thus significant amounts of antibiotics in the effluents were discharged in Yamuna River. The Yamuna River also receives effluents from 17 STPs and also carries sewage and industrial discharges from 17 stormwater drains. The concentration of the antibiotics in the river varied from ND to 13.75 μg l^{-1} ampicillin, ND to 1.44 μg l^{-1} for ciprofloxacin, ND to 0.48 μg l^{-1} for gatifloxacin, and ND to 2.09 μg l^{-1} for sparfloxacin. Similarly, significant levels of antibiotics had been detected in different river-water in different countries (Munoz et al. 2009; Feitosa-Felizzola and Chiron 2009; Watkinson et al. 2009; Lin and Tsai 2009). As use of treated and untreated sewage effluent for irrigation is quite prevalent in urban and peri-urban areas, soil contamination with antibiotics may be widespread.

Animal derived manure, an important soil amendment in Indian agriculture is also considered as another source of antibiotic contamination in soil. Most of the antibiotics fed to animals are poorly absorbed in the animal gut and consequently, a substantial amount of these is excreted with the urine and faeces within a few days of medication (Aust et al. 2008). In general, 72% of the active ingredients initially dispensed in animals were recovered in the animal wastes within 2 days of application (Winckler and Grafe 2001). Tetracyclines, tylosin, sulfamethazine, amprolium, monensin, virginiamycin, penicillin, and nicarbazine are commonly observed antibiotics in pig, cattle, and turkey manures (Webb and Fontenot 1975; De Liguoro et al. 2003; Kumar et al. 2005a). Antibiotics were found to degrade during composting of animal dung and the extent of degradation is highly variable among different antibiotics (Dolliver et al. 2008). At the end of the composting period, degradation of chlortetracycline was >99%; whereas monensin and tylosin degraded to the extent of 54–76%. Sulfamethazine, however, didn't degrade significantly during composting.

Composting methods (passively aerated composting or frequently turned aerobic composting, or vessel composting) did not have significant impact on degradation of antibiotics (Mitchell et al. 2015). Thermophilic stage (with ≥ 60 °C) during composting process has been found to enhance degradation kinetics of antibiotics, with greater degradation in cattle dung manure as compared to biosolids from wastewater treatment plant. However, most of the composting in India is not properly managed to impart thermophilic treatment for whole feedstock due to infrequent turning (Saha et al. 2010). Therefore certain antibiotics can still persist in the manure being prepared in the country. A review by Kumar et al. (2005a) indicated that antibiotic concentrations in manure ranged from trace levels to >200 mg kg^{-1}, with typical concentrations in the 1–10 mg kg^{-1} range. Although there is very few data available on veterinary antibiotics use in various food-producing animals in developing countries such as India (WHO 2001), their amount may be considerable due to huge livestock population (more than 33% of the world) and lack of regulatory mechanism with antimicrobial drug use in animals intended for food. Antibiotics have been detected in soils amended with livestock manure, with periods of detection ranging from days to months after application, depending on the antibiotics type and their degradation kinetics (Hamscher et al. 2002; De Liguoro et al. 2003). Sustained elevated levels of externally added antibiotics in the environment may contribute to the development of antibiotic-resistant microbial populations; and even very low quantities of antibiotics encourage the selection of antibiotic-resistant bacteria (Boxall et al. 2003). Contact of such antibiotic-resistant bacteria in the soil and water with human-associated microbiota has been suspected to be a cause in development of multi-drug-resistant human pathogens, a concern among medical practitioners (Baquero et al. 2008).

For sustainable agriculture, maintenance of soil organic matter is of paramount importance under different land use management systems and this necessitates regular incorporation of organic matter into the rhizosphere from external sources. Indian soils are generally deficient in organic matter due to high mineralization rate under prevalent climatic condition and therefore, frequent application of animal manure in crop land is advocated for improving and sustaining soil quality. Data from long-term experiments have revealed that additional yields of different crops can be realized over and above soil test based optimum NPK rates, only if 10–-15 tonnes of FYM per hectare are annually supplemented (Swarup and Wanjari 2001). Similarly scarcity of irrigation water for agriculture is prevalent in India due to erratic rainfall and stiff competition for this resource with industry and municipality. As a result, farmers in the peri-urban area who live nearby such water sources divert this untreated wastewater for irrigation whenever needed as it proves to be low-cost alternative to conventional irrigation water. It supports livelihood and generates considerable value in urban and peri-urban agriculture of India, despite the health and environmental risks associated with this practice. Conclusions based on the considerable research worldwide, limited studies in Indian context and available related secondary information indicates that presence of antibiotics in manure and wastewater (both being important inputs for agriculture) may be widespread across India and their regular use may be contaminating the soil.

5.1.5.2 Antibiotics Persistence and Its Effects on Soil Properties

Antibiotics concentration in soil has been reported by researchers across the world to vary widely in the range of ND to 1534.4 μg kg^{-1} (Du and Liu 2012). Impact of antibiotics in soil depends on their persistence and solubility. Distribution coefficients (K_d), a measure of contaminant activity retardation, for the adsorption to soil constituents of different groups of antibiotics vary from 0.6 to 4.9 for sulfonamides, from 290 to 1620 for tetracyclines and from 310 to 6310 for fluoroquinolones (Thiele-Bruhn 2003). Sorption of antibiotics to soil minerals is weaker than to soil organic matter and is governed by pH, ionic strength, and type of ions in the medium. Adsorption of most of the antibiotics is fast and reduces their antibiotic potency; though the process does not completely eliminate their antimicrobial activity. Most of the antibiotics have low solubility and therefore, their mobility in soil is mainly facilitated by their association with mobile soil colloids and dissolved organic matter (Thiele-Bruhn 2003).

Soil microorganisms play important role in several nutrient transformation processes in soil like nitrogen fixation, nitrification, ammonification, phosphate solubilisation etc. As antibiotics are meant to kill mainly microorganisms, their entry is expected to have harmful effects on agriculturally important soil microorganisms. Repeated contamination through livestock manure application and wastewater irrigation during cropping can accumulate antibiotics in the soil, which may reach beyond the level of the threshold inhibitory concentrations for agriculturally important microorganisms in the soil ecosystem. A comprehensive review by Thiele-Bruhn (2003) indicated that effects of antibiotics in soil are diverse and are generally microorganism and dose specific, which tend to cause shift in microbial community. Antibiotics on the soil have been found to reduce microbial population including soil enzyme activities (Kotzerke et al. 2008; Akimenko et al. 2015). For example, sulfonamides affected activities of dehydrogenase (responsible for organic matter mineralization) and urease (responsible for hydrolysis of urea) as well as structural diversity of the soil microbial community (decrease in bacterial biomass and increase in proportion of fungal biomass) even at a relatively low concentration (Gutierrez et al. 2010). In another study, six antibiotics (chlortetracycline, tetracycline and tylosin; sulfamethoxazole, sulfamethazine and trimethoprim) inhibited soil phosphatase activity during the 22 days' incubation; while sulfonamides (sulfamethoxazole and sulfamethazine) inhibited total microbial activity as indicated by reduced soil respiration (Liu et al. 2009). The effective concentration doses (EC_{10}) for soil respiration in the first 2 days were 7 mg kg^{-1} for sulfamethoxazole, 13 mg kg^{-1} for sulfamethazine and 20 mg kg^{-1} for trimethoprim.

5.1.5.3 Effect of Antibiotics on Plant

The presence of antibiotics in surface water, groundwater, seawater, soil and sludge opened their entry into biota. The contaminant transfer usually takes place from contaminated soils to the plants, via retention by root surfaces, root uptake, translocation and foliar uptake. There are some reports available which indicate adverse effects of antibiotics on plant growth and yield; although their toxic doses are several folds higher in plants as compared to soil microorganisms. Phytotoxicity depended on plant species and antibiotic types (Batchelder 1982; Jjemba 2002; Farkas et al. 2007; Liu et al. 2009). For example, significant gentamicin (but not streptomycin) uptake was observed in radish, while carrot roots or lettuce leaves didn't uptake these two antibiotics (Bassil et al. 2013). Experimentally determined phytotoxicity doses for different antibiotics are generally much higher than the reported range of antibiotics in different contaminated sites, which indicates that phytotoxicity due to antibiotic contamination is rare in agroecosystem (Thiele-Bruhn 2003). High-level accumulation of antibiotics in food crops may raise potential human health concerns through food chain. A recent review indicated absorption of antibiotics by crops from contaminated soils and detected concentrations in different plant parts ranged between 0.9 and 6.1 mg/kg (Du and Liu 2012). A greenhouse studies with plants grown in antibiotic contaminated manure-applied soil indicated that corn, green onion and cabbage absorbed chlortetracycline but not tylosin antibiotics present in manure (Kumar et al. 2005a). The concentrations of chlortetracycline in plant tissues were small (2–17 ng g^{-1} fresh weight), but these concentrations increased with increasing amount of antibiotics present in the manure. Antibiotics with large molecular weight are generally not taken up easily by plants (Kumar et al. 2005b). Although the maximum residue value for antibiotics in animal-based products has been established, the limit for antibiotics in plant-based products is absent. Antibiotics present in plant materials ingested by humans may provide resistance to human pathogens thus resulting in illnesses that may be difficult to cure with currently available antibiotics. This can be a serious threat, as has been proved in many animal studies.

5.1.5.4 Antibiotic Resistance in Microbes

The most obvious risk of antibiotic release into the environment is related to the development of antibiotic-resistant microorganisms which has resulted in the reduction of therapeutic potential against human and animal pathogens. Residues of antibiotics can induce resistance in pathogens either directly or indirectly by transfer of plasmids from non-pathogens to pathogenic microorganisms. The detection of antibiotics residues (even at sub-nanogram per liter) is alarming for ecosystem sustainability. These compounds are specially engineered to show their effect at trace levels. There are no reports of direct effect on human beings from contaminated water but effects on other organisms have been documented. Kummerer (2004) reported the development of various resistant bacterial strains associated with discharges of antibiotics. A study on archived long-term soil-series from different locations in The Netherlands showed a significant accumulation of antibiotic resistance genes in agricultural soils sampled since 1940, postulated to be due to decades of increasing use of antibiotics (Knapp et al. 2010). Three Indian soil samples irrigated with wastewater (from Aligarh, Kanpur and Ghaziabad) contained the antibiotic resistance genes (*ampC)*; while it was absent in the samples from groundwater irrigated soils (Malik et al. 2008). Similarly, *E. coli* resistant to cefotaxime, ciprofloxacin, and cefoxitin was present in treated effluent (originated from hospital) samples (Galvin et al. 2010). These observations indicate that antibiotic resistant genes might have been transferred from the sewage system to soil. Therefore, anthropogenic activities such as manure/biosolid application, wastewater irrigation, and agricultural application of antibiotic compounds are supposed to be responsible in transmitting antibiotic resistance to the environment.

Studies have also found that highly diverse and abundant levels of antibiotic resistant bacteria are already present in soils. Rhizosphere comprises large populations of different microorganisms and some of these naturally produce antibiotics which are lethal to susceptible rhizobial populations in the soil. Therefore, intrinsic resistance to antibiotics is a desirable trait for the rhizobial population. It increases the rhizobia's chances of growth, multiplication and persistence in the soil (Naamala et al. 2016). Hollowell et al. (2015) genotyped more than 400 isolates from plant roots and soils across California and assayed 98 of them for resistance traits against 17 clinically relevant antibiotics. However, resistance to certain group of antibiotics had been found to reduce symbiotic effectiveness of *Rhizobium sp.* and that affect biological nitrogen fixation (Pankhurst 1977; Turco et al. 1986). Thus, there is a need for detailed investigations on assessing impacts antibiotics of anthropogenic origin on soil biodiversity, development of multidrug resistant organic organisms and transfer to human through food chain contamination.

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