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-trinitrotolune 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.

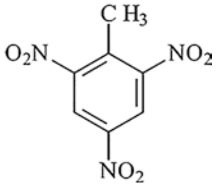
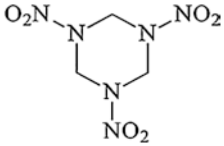
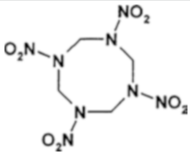
2 Explosives: General Chemistry and Classification

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 (-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)	$C_7H_5N_3O_6$		227.13	0.15
RDX (hexahydro-1,3,5-trinitro-1, 3,5-triazine, hexogen)	$C_3H_6N_6O_6$		222.12	0.015
HMX (octahydro-1,3,5,7-tetranitro-1, 3,5,7-tetrazocine, octogen)	$C_4H_8N_8O_8$		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, cyclotrimethylenetrinitramine, 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

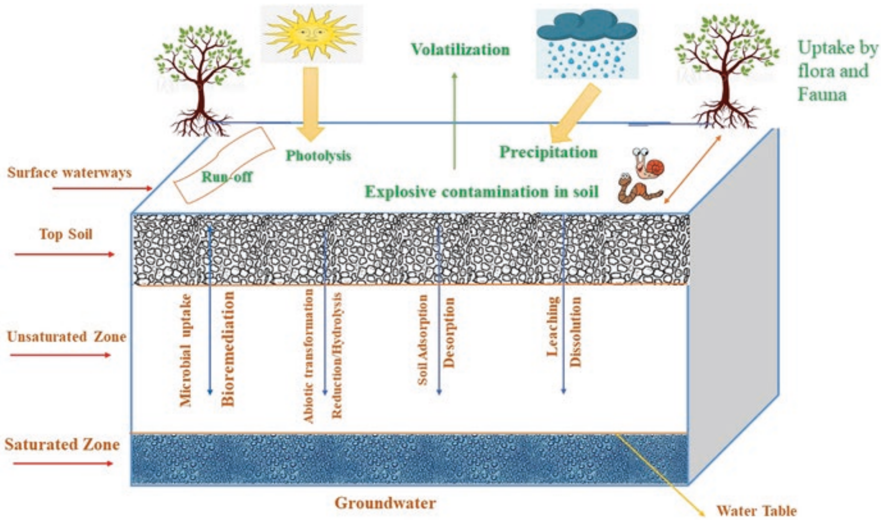


Fig. 1 Distribution, fate, and transport of explosives in soil (Based on Celin et al. (2020))

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

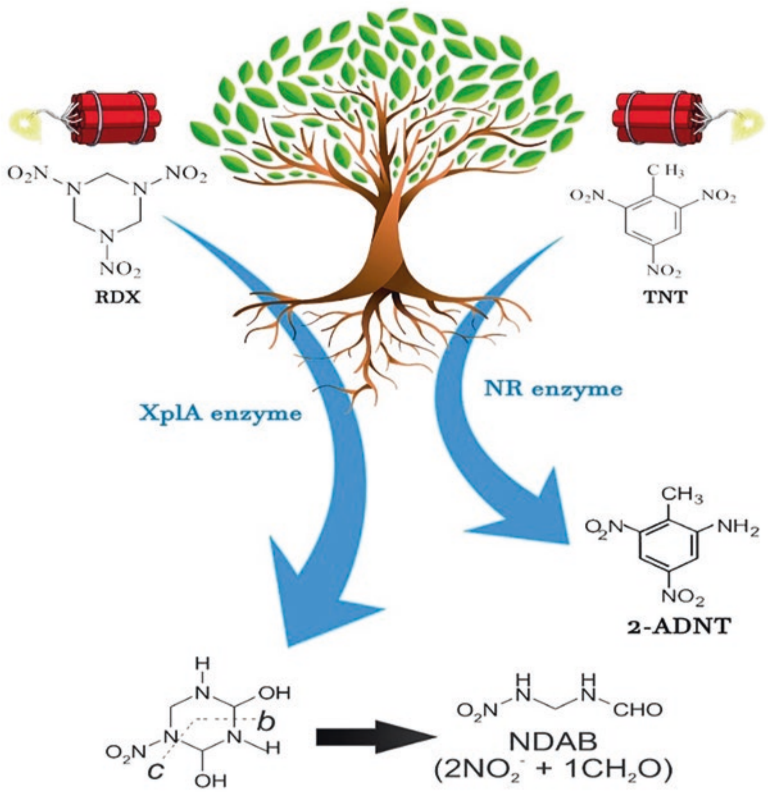


Fig. 2 Phytodegradation of explosives

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 (*Circium 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 (-NH_2) (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

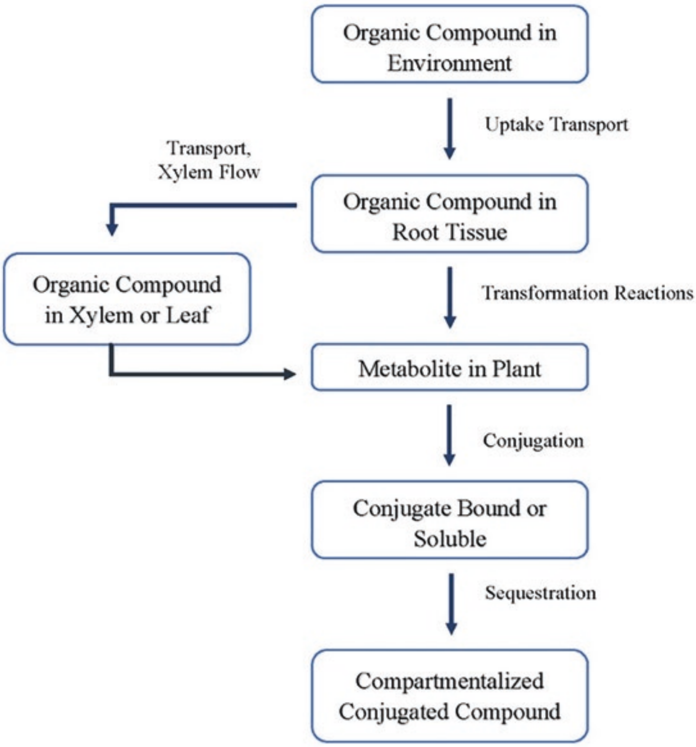


Fig. 3 Metabolism of explosives in plants (Green Liver model) (Based on Burken et al. (2000))

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
Lolium perenne	HMX	30*	77	8.1	Groom et al. (2002)
Populus deltoides	HMX	1.77**	21	45	Yoon et al. (2002)
Brassica rapa	HMX	30*	77	5.2	Groom et al. (2002)
Abutilon avicenna	TNT	120*	50	n.a.	Chang et al. (2004)
Oryza sativa	TNT	500*	40	0.8	Vila et al. (2007a)
Triticum aestivum	RDX	138*	42	64.54	Vila et al. (2007b)
Oryza sativa	RDX	138*	42	3.71	Vila et al. (2007a)
Vetiveria zizanioides	TNT	80*	12	n.a.	Das et al. (2010)
Zea mays	*RDX*	100*	28	1.21	Chen et al. (2011)
Arabidopsis thaliana (Arabidopsis)	RDX	250*	49	1.34	Rylott and Bruce (2009)
Pascopyrum smithii	RDX	40**	12	3	Zhang et al. (2019)
Pascopyrum smithii	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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