A Comprehensive Review of Remediation Strategies for Soil and Groundwater Contaminated with Explosives

Christiana Mystrioti * and Nymphodora Papassiopi

School of Mining and Metallurgical Engineering, National Technical University of Athens, 15780 Athens, Greece
* Correspondence: chmistrioti@metal.ntua.gr; Tel.: +30-2107724054

Abstract: This study offers an updated overview of the soil and water remediation strategies employed to address the widespread environmental and public health risks associated with explosive compounds, particularly TNT and RDX. Recognizing soil contamination originating from military activities, industrial accidents, and historical land use, this review delves into physical, chemical, and biological approaches to mitigating ecological and human health concerns. While physical methods like excavation and disposal are effective, their applicability is constrained by cost and logistical challenges for large contaminated areas. Chemical methods, such as oxidation and reduction, focus on transforming explosives into less toxic byproducts. Biological remediation utilizing plants and microorganisms emerges as a cost-effective and sustainable alternative. This review highlights challenges, including the persistence of explosive compounds, potential groundwater leaching, and the necessity for long-term monitoring. Emphasizing the need for site-specific strategies, considering the contaminant type, concentration, soil properties, and regulatory requirements, this study advocates for integrated and sustainable remediation approaches in pilot-scale applications. It concludes by evaluating the appropriate solution based on the advantages and disadvantages of the categories of soil and groundwater remediation methods. The duration, the effectiveness, and the cost of available technologies were estimated.

Keywords: soil contamination; explosives; 2,4,6-trinitrotoluene (TNT); rapid detention explosive (RDX); soil remediation; soil sustainability

1. Introduction

Soil pollution resulting from explosives represents a critical environmental challenge with far-reaching consequences for ecosystems and human health [1,2]. Explosives, commonly used in military activities, mining, and construction, release hazardous substances such as nitroaromatics and heavy metals into the soil, leading to long-lasting environmental degradation [3,4]. Explosives have the potential to cause extensive and varied soil contamination, necessitating substantial resources to delineate the contamination boundaries. It is important to note that the remediation of soil contaminated by explosives is not as advanced as the treatment of soil contamination caused by heavy metals and organic pollutants. The challenges in remediating soil contaminated by explosives can be attributed to the presence of decomposition products from energetic explosives and the emergence of new types of explosives with compositions that are difficult to define [5–7]. Moreover, most explosives have the capacity to bind to the organic matter in the soil and to coexist with other compounds as a mixture, creating difficulties in soil remediation [8,9].

Open burning and detonation were the most common treatment methods for waste explosives until the 1990s, when there was no safe alternative. These methods produce emissions and noise, and new regulations have restricted them [10,11]. In response to this environmental challenge, this study outlines contemporary remediation approaches and technologies that have been evaluated in pilot- and full-scale applications.

The explosive compounds that are commonly detected in polluted sites are 2,4,6-trinitrotoluene (TNT) and 1,3,5-Trinitroperhydro-1,3,5-triazine (RDX). TNT is a powerful
explosive compound commonly used in military applications, construction, and mining due to its low detonation velocity [12]. TNT is a yellow, crystalline compound with the chemical formula C\textsubscript{7}H\textsubscript{5}N\textsubscript{3}O\textsubscript{6} and remains relatively inert and does not pose an immediate danger of detonation under normal conditions, making it a suitable explosive for military and industrial applications [13]. It does not explode easily when subjected to mechanical shocks or high temperatures. Despite its stability, TNT is a powerful explosive when initiated by a detonator or heat. It releases a significant amount of energy upon detonation, producing a shockwave and heat that can cause destruction [12,14]. TNT is less soluble in water but more soluble in organic solvents like acetone and ethanol. This solubility affects its transport and potential for groundwater contamination [15]. When TNT is released into the environment, it can lead to soil contamination, which has a range of adverse effects. Soil pollution with TNT (2,4,6-trinitrotoluene) is a significant environmental concern with potentially serious consequences for both ecosystems and human health. The limit concentration of TNT is 51 mg/kg in soils for industrial uses and 0.98 µg/L in waters for domestic uses [16].

Hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) is an explosive compound widely used in military applications, mining, and industrial sectors. However, its persistence in the environment has raised concerns about soil pollution [17,18]. The compound’s resistance to decomposition and its limited solubility contribute to its long-term presence in soils. This soil pollution poses serious ecological risks, affecting soil quality, plant life (RDX has been shown to inhibit seed germination, root development, and overall plant growth), and microbial communities (leading to long-term soil degradation). Furthermore, RDX has been found to leach into the groundwater, posing a risk to nearby ecosystems and potentially affecting drinking water supplies. Efforts to mitigate RDX soil pollution involve a range of remediation strategies, including bioremediation, phytoremediation, and chemical treatment methods [19]. These techniques aim to degrade or remove RDX from contaminated soils, but their effectiveness depends on site-specific conditions and challenges [20].

Regulatory measures are crucial for preventing RDX soil pollution. Many countries have established guidelines and regulations to limit the release of RDX into the environment, promoting responsible handling, storage, and disposal practices. The monitoring and enforcement of these regulations are essential to safeguarding ecosystems and public health. Most of the explosive substances and their derivatives are included in the Table of Harmonized Classifications and Labeling of Hazardous Substances (Annex VI) of European Regulation 1272/2008 [21]. RDX and HMX have been registered as hazardous in the database of the European Chemicals Agency (ECHA) in accordance with the REACH Regulation ((EC) 1907/2006) [22].

The aim of this study is to conduct a comprehensive review of case studies conducted at both the pilot and full scales over the last decades, with a specific focus on technologies employed for the remediation of soil and water contaminated with explosive compounds. This investigation seeks to systematically summarize and evaluate the successes and challenges associated with these remediation technologies, providing a nuanced understanding of their practical applications. Through the synthesis of case-specific information, the study aims to identify the pros and cons of diverse approaches, shedding light on the effectiveness, limitations, and potential areas for improvement in the cleanup of explosive-compound contamination in soil and water environments.

2. General Categories of Technologies for the Restoration of Polluted Soils and Groundwater

2.1. Soils

Until 1990, in the USA and internationally, only thermal methods were used as on-site techniques for treating soils contaminated with explosives. With the aim of reducing processing costs and addressing other negative characteristics, such as high energy consumption, the need for the effective control of volatiles, etc., starting in the mid-1990s, there was a shift in the search for alternative treatment methods [23–25]. In Figure 1, the main
alternative methods for the restoration of soils polluted by explosives can be classified into four general categories: (i) containment, (ii) excavation and treatment or off-site disposal, (iii) in situ or on-site treatment, and (iv) monitoring of natural attenuation (Figure 1).

Figure 1. Remediation methods for soil contaminated with explosives.

(i) Containment

These methods aim to isolate the area where the contaminated soil is located so that there is no risk of transferring pollution to sensitive receptors through air, rainwater, or groundwater [23]. They usually involve creating impermeable surface covers or perimeter barriers, in combination with hydraulic control measures of groundwater and the collection of the leachate from the contained area. These technologies are typically applied to contaminated sites with large surface areas and large quantities of contaminated soil, particularly in remote areas (abandoned mines, uncontrolled landfills, etc.), far from populated areas and without other prospects for utilization.

(ii) Excavation and treatment or disposal of contaminated soil in facilities outside the area (off-site treatment or disposal)

In this category of methods, the excavation of the contaminated soil takes place, which is then transported to specialized facilities outside the area for the processing, cleaning, immobilization, or destruction of the pollutants (off-site treatment), with the aim of reusing it, or more commonly, for final disposal in specialized hazardous waste sites. These methods are usually feasible and economically advantageous only when the volume of contaminated soil is relatively small and is located at a shallow depth.

(iii) In situ or on-site treatment

This category includes methods that are applied in the area where the contaminated soil is located without prior excavation (in situ) or after excavation and transport of the soil to a neighboring area that has been prepared appropriately (on-site), with the aim of processing and restoring the soil to its original position. These methods involve a wide range of biological or physicochemical technologies and will be examined in more detail later.

(iv) Monitoring of natural attenuation

The monitoring of natural attenuation is usually selected in the case of organic pollutants if there are indications of their degradation, such as the detection of breakdown products. It is applied in areas with low concentrations of pollutants, and natural degradation can be monitored as a means of restoration. However, for areas with higher concentrations of pollutants, natural attenuation with in situ or on-site treatment technologies is employed. The monitoring process involves initial site characterization and the installation of monitoring wells for groundwater sampling (the samples are analyzed for concentrations of contaminants and their breakdown products, redox potential, and pH). Also, groundwater flow rates and microbial populations are recorded [26].
2.2. Waters

On-site treatment involves pumping groundwater to the surface and using biological or physical–chemical methods to clean it. In situ treatment of groundwater, on the other hand, has two main variations: the installation of a permeable reactive barrier containing materials that can absorb or degrade pollutants and the injection of suitable reactants into the aquifer to destroy or immobilize pollutants using biological or physiochemical processes.

3. Methods for Processing Soils and Waters Contaminated with Explosives

In this section, the methods that have been applied for the destruction or neutralization of explosives are presented and discussed in detail. These are methods that can be applied in situ or on-site and can be classified into two basic categories depending on the main mechanism of action: (1) biological and (2) physicochemical technologies.

In biological technologies, the breakdown of explosives can take place with bacteria under aerobic or anaerobic conditions, where the explosive compound serves as a source of carbon and/or nitrogen. Alternatively, degradation can result from metabolism, where an additional substrate serves as a source of carbon and energy. The dominant metabolites of TNT under aerobic and anaerobic conditions are 2-ADNT, 4-ADNT, 2,4-DANT, and 2,6-DANT (diamino-nitrotolouenes), while triaminotoluene can be formed under anaerobic conditions [23].

Physicochemical methods involve the addition of one or more chemical reactants (reductive, oxidative) to contaminated soils that alter their physicochemical properties, such as pH or redox potential (Eh). These methods outperform biological actions, as they are faster, can be applied to a wider range of compounds, and are more easily controllable.

Tables 1 and 2 compile information sourced from the international literature, highlighting the utilization of biological and physicochemical methods for treating soil and groundwater contaminated with explosives, respectively. The focus is on technologies implemented in pilot- or full-scale applications. The construction of Tables 1 and 2 is informed by recent studies evaluating agents and methodologies for remediating soil and water contaminated by explosives. The efficiency of these case studies is discussed in Sections 2 and 3.

Table 1. Efficient remediation case studies for soil contaminated with explosives in on-site or in situ environments: an evaluation of performance.

<table>
<thead>
<tr>
<th>Method</th>
<th>Level of Development</th>
<th>Area</th>
<th>Main Pollutants</th>
<th>Observations</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Windrow composting. Aerobic conditions mixing 30% soil, 70% organic material (manure, sawdust, etc.)</td>
<td>Full scale. 15,000 tons of soil</td>
<td>Umatilla Army Depot, Hermiston, Oregon, USA</td>
<td>TNT: 4800 mg/kg; RDX: 1000 mg/kg; HMX: 800 mg/kg</td>
<td>Processing in batches of 3000 tons within enclosed temporary structures for control of conditions. Duration: 10–12 days per batch. Reduction of pollutants below detection limits. Cost: 351 USD/t (1997).</td>
<td>[27,28]</td>
</tr>
<tr>
<td>Variations of aerobic composting with (a) horse manure (20% w/w), (b) Daramend (2% w/w) and ZVI (0.5% w/w), (c) only ZVI (0.5% w/w)</td>
<td>Lab scale</td>
<td>Bofors Test Center, Karlshoga, Sweden</td>
<td>Soil 1: RDX 1340 mg/kg; Soil 2: RDX 25,740 mg/kg</td>
<td>Soil 1. 94% removal of RDX with Darament + ZVI (75% with ZVI, 0% horse manure) after 26 weeks of treatment. Soil 2. The three variations were ineffective.</td>
<td>[29]</td>
</tr>
<tr>
<td>Land farming compared to bioreactor with addition of molasses</td>
<td>Lab scale</td>
<td>Louisiana Army, Ammunition Plant, USA</td>
<td>TNT: 400–10,000 mg/kg; RDX: 800–1900 mg/kg; HMX: 600–900 mg/kg</td>
<td>Removal of TNT after 182 days: 99% in the bioreactor and 82% with Techno-Agriculture. Lower effectiveness for RDX and HMX.</td>
<td>[23]</td>
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<tr>
<td>Soil-pile vaccination with white-rot fungi</td>
<td>Pilot scale</td>
<td>Construction Establishment of Finnish Defense Administration, Finland</td>
<td>NTD: 19,000 mg/kg mixing soil (14 kg) with fertilizer (271 kg), adding pine bark with fungi (10 kg)</td>
<td>Soil dilution with fertilizer (1:20) to reduce toxicity. TNT degradation: 80% on a laboratory scale (76 days) and 70% on a pilot scale (49 days).</td>
<td>[30]</td>
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Table 1. Cont.

<table>
<thead>
<tr>
<th>Method</th>
<th>Level of Development</th>
<th>Area</th>
<th>Main Pollutants</th>
<th>Observations</th>
<th>Reference</th>
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<tbody>
<tr>
<td><strong>Physicochemical technologies</strong></td>
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<td><strong>Chemical Reduction</strong></td>
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<tr>
<td>Addition of ZVI to soil piles.</td>
<td>Pilot scale</td>
<td>Los Alamos National Laboratory, New Mexico, USA</td>
<td>Soil 1: RDX: 2700 mg/kg, pH 9.9 Soil 2: RDX: 12,100 mg/kg, pH 7</td>
<td>98% removal of RDX                                                          [31]</td>
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<tr>
<td>Application to static soil piles.</td>
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<td>Soil pile 1: Mixing 70 kg soil, 3.5 kg ZVI, 1.05 L CH₃COOH. Soil pile 2: Mixing 70 kg soil, 3.5 kg ZVI, 2% w/w Al₂(SO₄)₃.</td>
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<td><strong>Adding sulfur compounds.</strong></td>
<td>Field scale</td>
<td>Ravenna Army Ammunition Plant, USA</td>
<td>TNT: 3347 mg/kg RDX: 5977 mg/kg HMX: 447 mg/kg</td>
<td>99.6% removal of TNT, 96.5% removal of RDX, and 97.1% removal of HMX 97.1% in 24 h (&gt;99% in two weeks)</td>
<td>[32]</td>
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<td>Commercial product: MuniRem</td>
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<td><strong>Alkaline Hydrolysis</strong></td>
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<tr>
<td>Mixing with Ca(OH)₂ solution at pH 11 and pH 12</td>
<td>Lab scale</td>
<td>Former German ammunition factories</td>
<td>Soil 1: TNT: 16,000 mg/kg; Soil 2: TNT: 116 mg/kg</td>
<td>93–98% removal of TNT in both soils within 7 days at both pH levels. DNT and ADNT showed more efficient removal at pH 12.</td>
<td>[33]</td>
</tr>
<tr>
<td>Mixing soil with dry Ca(OH)₂ 5% and moisture 0–200%</td>
<td>Laboratory and semi-pilot scale (2 kg)</td>
<td>Soils from Iowa, USA</td>
<td>TNT 60 mg/kg</td>
<td>Optimal moisture ~25% Laboratory tests: 82–92% TNT removal in 10 days. Pilot test: Slower degradation</td>
<td>[34]</td>
</tr>
<tr>
<td>Laboratory tests: Effect of soil chemistry, percentage of Ca(OH)₂, etc. Pilot tests: Type of alkali, application methods.</td>
<td>Lab scale and pilot scale (70 kg)</td>
<td>17 areas, Nebraska Ordnance Plant, USA</td>
<td>Pilot tests: RDX 38.4 mg/kg, HMX 4.4 mg/kg, TNT 10.8 mg/kg</td>
<td>Pilot tests: 82–83% removal of RDX in one week with calcium hydroxylapatite, and complete mixing. Slower kinetics with surface application and the use of fly ash.</td>
<td>[35]</td>
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<tr>
<td><strong>Bioremediation with nutrient addition</strong></td>
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<tr>
<td>Injection of soybean oil, lactic acid, Na, and surfactants</td>
<td>Full-scale 2008 installation, continuous monitoring</td>
<td>Pantex Plant, Amarillo, Texas,</td>
<td>RDX: 4000 µg/L,</td>
<td>42 injection wells on a surface area of 40,000 m². Depth of the aquifer horizon: 78 m. Thickness: 4.5–6.0 m. Cost: USD 190 per m³ of groundwater.</td>
<td>[38,39]</td>
</tr>
<tr>
<td><strong>Bioremediation with nutrient addition</strong></td>
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<tr>
<td>Injection of whey (4.7 m³) into an aquifer (400 m² × 2.5 m depth)</td>
<td>In Situ pilot tests</td>
<td>Czech Republic</td>
<td>TNT: 10 mg/L &gt; 90%</td>
<td>TNT removal over a period of 17 months</td>
<td>[40]</td>
</tr>
<tr>
<td><strong>Oxidation by Fenton Injection</strong></td>
<td>Field application</td>
<td>Pueblo Chemical Depot, Colorado, USA</td>
<td>RDX, HMX.</td>
<td>Injection, 16.6 m³ H₂O₂ (12.5%)/Fe²⁺ over a two-day period. After 26 days of treatment: 100% HMX removal, 60% RDX removal, and 72–100% removal of other nitroaromatic compounds</td>
<td>[41]</td>
</tr>
<tr>
<td><strong>Oxidation by NaMnO₄</strong></td>
<td>Pilot scale</td>
<td>Nebraska Ordnance Plant, USA</td>
<td>RDX 30–70 µg/L.</td>
<td>Problems with the uniform distribution of permanganate in the soil.</td>
<td>[36]</td>
</tr>
<tr>
<td>Injection of 70 m³ of NaMnO₄ (10 g/L) to create a reactive zone (9.2 m × 4 m × 6 m depth)</td>
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</tbody>
</table>

Table 2. Technologies for groundwater remediation in areas contaminated with explosives: evaluating their effectiveness in pilot- and large-scale applications.

<table>
<thead>
<tr>
<th>Method</th>
<th>Level of Development</th>
<th>Area</th>
<th>Contaminated soils, TNT and RDX &gt; 5000 mg/kg had contaminated the aquifer, RDX up to 300 µg/L</th>
<th>Observations</th>
<th>Cost</th>
</tr>
</thead>
<tbody>
<tr>
<td>Adsorption on activated carbon</td>
<td>Established</td>
<td>Nebraska Ordnance Plant, USA</td>
<td>15,000 m²/day. Installation cost: USD 30 million. Annual operating cost: USD 800,000.</td>
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<tr>
<td>Use of ZVI in permeable reactive barrier (PRB) (in situ chemical reduction)</td>
<td>Demonstration scale</td>
<td>Cornhusker Army Ammunition Plant (CAAP), Grand Island, Nebraska</td>
<td>RDX: 0.9 µg/L TNT: 130 µg/L</td>
<td>PRB dimensions: 15 m length, 4.5 m depth, and 1 m thickness. Content: ZVI (30%), sand (70%). Monitoring for 20 months. TNT below detection limits at the outlet PRB. Cost: USD 1940/m²</td>
<td>[37]</td>
</tr>
<tr>
<td>Bioremediation with nutrient addition</td>
<td>Full-scale 2008 installation, continuous monitoring</td>
<td>Pantex Plant, Amarillo, Texas,</td>
<td>RDX: 4000 µg/L,</td>
<td>42 injection wells on a surface area of 40,000 m². Depth of the aquifer horizon: 78 m. Thickness: 4.5–6.0 m. Cost: USD 190 per m³ of groundwater.</td>
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<td>[36]</td>
</tr>
</tbody>
</table>
3.1. Biological Methods

3.1.1. Composting

In the early 1990s, a series of laboratory and pilot tests were organized to evaluate biological decomposition methods for explosives. Five alternative biological treatment methods were assessed: (1) composting, (2) anaerobic, and (3) aerobic treatment in bio-piles, (4) inoculation with white-rot fungi in piles, and (5) agro-cultivation techniques [27]. The best results were obtained with composting, which achieved a removal of explosives greater than 99%. Composting was selected for the complete remediation of soils at the (1) Umatilla Army Depot Activity, Hermiston, Oregon, for 15,000 tons of soil contaminated with TNT, RDX, and HMX and (2) U.S. Naval Submarine Base, Bangor, Washington, for 2200 tons of soil contaminated with TNT. Initial cost estimates ranged from USD 206 to USD 766 per ton for quantities ranging from 1200 to 30,000 tons—40% to 50% lower than on-site incineration.

Composting is a biochemical process in which organic materials are biologically broken down, resulting in the production of organic or inorganic products and heat energy. The heat is trapped within the mass, leading to the phenomenon of self-heating, which is characteristic of the composting process.

Various types of composting and vermiculture systems exist, but static piles and windrow composting are the most used methods. In each composting system, an easily decomposable source of organic material, such as manure or vegetable waste, is mixed with contaminated soil, along with bulking agents, to improve its texture for optimal aeration. In highly contaminated soils, the addition of organic material effectively reduces the concentration of explosives and can mitigate toxicity in the microbial population. As a result, the breakdown of organic material occurs through aerobic and anaerobic processes, generating heat. The systems used differ in terms of how they aerate the pile, with some systems not using aeration.

Information about the full-scale implementation of composting at the Umatilla Army Depot Activity can be found in a USEPA informational pamphlet (1997) [28]. The processing took place in an improvised facility constructed for this purpose. Each batch consisted of approximately 2000 m³ of soil, which was mixed with organic materials in proportions of 30% soil, 21% bovine manure, 18% sawdust, 18% alfalfa, 10% potato waste, and 3% poultry manure. Long rows (windrows) of the mixture were created, which were turned three times a day to achieve aeration; release heat, moisture, and generated gases; and break up aggregates.

The processing duration for each batch was 10–12 days, achieving the complete removal of explosives at concentrations below detection limits. The cost amounted to USD 351 per ton of soil. An important advantage of composting is that the final product is soil rich in organic matter. Once the cleanup levels are achieved, the composted material can be returned to the site, mixed with healthy soil, and used to support plant growth. However, it should be noted that composting for certain types of pollutants may require extended processing periods, and composting unknown contaminants may create toxic byproducts.

3.1.2. Composting under Anaerobic Conditions

Elgh-Dalgren et al. (2009) conducted laboratory-scale variations of composting under anaerobic conditions with significantly lower mixing rates [29]. They examined soils from the Bofors Test Center, Karlskoga, Sweden, with two different pollution levels, for instance, RDX at 1340 mg/kg and 28,740 mg/kg. The variations they examined were the mixing of soils (1) with horse manure 20% (w/w), (2) with the commercial product Daramend (organic components, 2% w/w) and zero-valent iron (ZVI) (0.5% w/w), and (3) with ZVI alone (0.5% w/w). The treatment with Daramend and ZVI was highly effective in low-pollution soil, with 94% RDX degradation after 26 weeks (72% with ZVI alone, 0% with manure). This study highlighted the critical importance of pollution levels concerning the effectiveness of biological treatment methods. In heavily polluted soil, all three treatment methods were entirely ineffective.
3.1.3. Land Farming Technique

The land farming technique has been extensively used for the remediation of soils contaminated with petroleum hydrocarbons and could potentially be used for the remediation of soils with low to moderate concentrations of explosives. In the land farming technique, soils are excavated and placed in processing areas with impermeable liners, creating a thin layer about 30–40 cm thick. They are periodically tilled to mix nutrients and moisture and to achieve aeration. However, this method usually achieves very slow remediation rates and may take many years to achieve remediation goals.

Kalderis et al. (2011) compared the effectiveness of land farming techniques with treatment in a pilot-scale bioreactor. They used soil from the Louisiana Army Ammunition Plant, USA, with the following concentrations of explosives: TNT 4000–10,000, RDX 800–1900, and HMX 600–900 mg/kg. Treatment was performed by adding molasses. After 182 days, TNT removal was 99% in the bioreactor and 82% with the land farming technique. Lower effectiveness was observed in the case of RDX and HMX with both techniques [23].

The Federal Remediation Technology Roundtable (FRTR, 2022), US DoD, reports that the land farming method was evaluated through pilot-scale tests at a site with explosive residues in Hercules, California [42]. The specific method failed to reduce concentrations to the desired levels of 30 ppm TNT, 5 ppm DNT, and 5 ppm DNB. However, reductions of around 30 to 40% in concentration were observed. Further details about the application conditions of the method were not provided.

3.1.4. Vaccination of Soil with White-Rot Fungi

Anasonye et al. (2015) investigated the potential degradation of TNT through the action of fungi in laboratory- and pilot-scale experiments [30]. They used contaminated soil from a site in Finland (Construction Establishment of Finnish Defense Administration) with very high pollution levels of 19,000 mg/kg. Preliminary laboratory tests found that soil dilution by approximately 20 times was necessary to reduce its toxicity to fungi. In other words, the non-toxic concentration of TNT was around 1000 mg/kg. Pilot-scale tests were conducted by mixing 14 kg of soil with 271 kg of fertilizer and 10 kg of pine bark for fungal cultivation. They achieved 80% TNT degradation on the laboratory scale (in 76 days) and 70% on the pilot scale (in 49 days) [30].

3.2. Physicochemical Methods

Physicochemical methods evaluated for the removal of explosives from soils are based on two main mechanisms of action: (i) adding a reducing agent to the contaminated soil and (ii) increasing alkalinity.

3.2.1. Reduction with Zero-Valent Iron (ZVI)

Comfort et al. (2003) studied the effectiveness of using zero-valent iron (ZVI) for the breakdown of explosives in soil from the Los Alamos National Laboratory, USA [31]. They conducted laboratory- and pilot-scale tests on two soils. One soil had an RDX concentration of 2700 mg/kg and a pH of 9.9, while the second soil had an RDX concentration of 12,100 mg/kg and a pH of 7.0. They found that reducing the pH of the soil using the appropriate chemical agent was necessary for effective RDX removal, with different agents used for each soil. They achieved a 98% removal of RDX in both soils in 120 days, using CH$_3$COOH in the first soil and Al$_2$(SO$_4$)$_3$ in the second soil.

3.2.2. Reduction with Sulfur-Based Compounds (MuniRem)

The University of Georgia developed a reduction reactor based on sulfur-based compounds with the trade name MuniRem, which has been successfully used for the breakdown and neutralization of various explosive substances that remain as solid residues in buildings, industrial facilities, storage areas, etc. [32]. This reactor has also been used at a pilot scale for treating contaminated soils at the Ravenna Army Ammunition Plant in Ohio, USA.
Field tests were conducted in an area with concentrations of TNT at 3347 mg/kg, RDX at 5977 mg/kg, and HMX at 647 mg/kg. Within 24 h, the TNT, RDX, and HMX removal rates reached 99.6%, 96.5%, and 97.1%, respectively. After 2 weeks, the removal rates were 99.9% for TNT and >99% for RDX and HMX.

Another advantage of this method is that, in addition to breaking down explosives, it simultaneously stabilizes metallic pollutants in the form of insoluble sulfur compounds.

3.2.3. Alkaline Hydrolysis

Increasing the pH value leads to the alkaline hydrolysis of most explosive compounds. Alkaline hydrolysis does not result in the complete inorganicization of explosives but rather converts them into less hazardous forms. Specifically, for TNT, it is reported that raising the pH to alkaline levels leads to the removal of nitro groups, followed by the breakdown of the aromatic ring and subsequent polymerization reactions. It has been observed that the polymeric products of hydrolysis are retained in soil particles (possibly incorporated into chemical constituents), resulting in reduced mobility and toxicity [34,35].

The most common variation studied on both laboratory and pilot scales (up to 50 kg of soil) involves the use of calcium hydroxide (Ca(OH)$_2$). Emmrich (1999) applied this treatment to two soils with different pollution levels, TNT concentrations of 16,000 and 116 mg/kg, and two pH values, 11 and 12, in laboratory-scale tests using soil columns (5 g/50 mL) [33]. TNT removal was equally effective in both soils and at both pH values (93–99% in 7 days). The removal was more effective at pH = 12 for various degradation products of TNT, such as 2,4-DNT, 2A-DNT, and 4A-DNT.

Hansen et al. (2003) conducted laboratory tests using dry soil and studied the effect of the mixing method of Ca(OH)$_2$ (5% w/w addition) and moisture content [34]. They found that hydrolysis can occur at low moisture content levels ≥25%. In laboratory tests, TNT was removed at rates of 82–92% within 10 days. The lowest removal rate (82%) was recorded in the experiment where the mixture was kept static, and the highest (92%) was obtained when the vials were rotated. In a pilot test conducted with 2.8 kg of soil (static conditions, 5% Ca(OH)$_2$, 35% moisture content), the kinetics of TNT degradation were slower, with a half-life of approximately 7 days.

Brooks et al. (2003) conducted laboratory tests on soils from 11 different regions in the USA and pilot-scale tests on soil from a former munitions plant in Nebraska, USA [35]. The pilot-scale tests were conducted with approximately 70 kg of soil per test. Alternative alkaline materials, such as lime, hydrated lime, and fly ash, were evaluated at a 5% addition rate. The addition was made with either complete mixing or surface application. The fastest kinetics of RDX removal were observed with the addition of lime and hydrated lime using the complete mixing method (removal of 82–83% in one week). Kinetics were slower in the case of surface application and the use of fly ash.

Of the methods presented in Table 1 on a full scale, only the windrow composting method with the windrow technique has been applied, for which cost data range from USD 206 to USD 766 per ton of soil, depending on the scale of implementation. As for other treatment methods, there are prospects for the application of techniques involving piles with the addition of ZVI/Al$_2$(SO$_4$)$_3$ or the addition of calcium hydroxide. Both methods have shown encouraging results in soils with low and high contamination levels.

4. Groundwater Remediation Technologies

4.1. Pump and Treat

The prevailing method for treating groundwater involves pumping the water and treating it at the surface. There is a wide range of technologies available for treating water at the surface, relying on processes such as adsorption, oxidation, or transforming organic pollutants into less hazardous forms. The dominant surface treatment method involves adsorption onto activated carbon, as exemplified by the Nebraska Ordnance Plant case discussed below [36].
At the former Nebraska Ordnance Plant, USA, contaminated waters from facility runoff were discharged without prior treatment, resulting in significant soil contamination in the disposal area (TNT and RDX > 5000 mg/kg). With rainwater infiltration, the contaminants were transported into groundwater, with RDX as the dominant pollutant at concentrations up to 300 µg/L. To prevent further transport of contamination toward nearby residential well fields, continuous groundwater extraction from an array of 11 extraction wells is employed. The extracted water is then directed to a treatment unit using granular activated carbon (GAC). The quantity of water pumped and treated is approximately 15,000 m$^3$ per day. Albano et al. (2010) reported that the construction cost of the entire facility was USD 33 million, with an annual operating cost of approximately USD 800,000, and the estimated duration of operation for complete pollutant removal exceeds 100 years [36].

4.2. In Situ Methods

Due to the high cost associated with pump-and-treat technologies, efforts are being made to develop on-site groundwater treatment techniques. In situ methods come in two variations: (a) the installation of permeable reactive barriers (PRBs) placed perpendicular to the groundwater flow, containing suitable sorption or degradation materials for pollutants, and (b) the injection–extraction of appropriate reactants into the aquifer for the destruction or immobilization of contaminants through biological or physicochemical processes. Below are examples of in situ methods, with an emphasis on those applied at the pilot or full scale for explosives, discussed in more detail.

4.2.1. Use of ZVI in Permeable Reactive Barriers (PRBs)

This method, along with the injection of reductants into the aquifer, represents specific applications of the broader category of techniques often referred to as in situ chemical reduction (ISCR). In the case of a PRB, the reducing agent is placed within the permeable reactive barrier constructed vertically across the flow of contaminated groundwater. PRB technology using zero-valent iron (ZVI) was applied at a demonstration scale at the Cornhusker Army Ammunition Plant site in Grand Island, Nebraska, USA [37]. In this area, the groundwater level was relatively close to the surface, ranging from 4.5 to 6.0 m, which is a prerequisite for the application of this technology. The dimensions of the barrier were 15 m in length, 4.5 m in depth, and 1 m in thickness, with the filling material consisting of a mixture of ZVI (30%) and sand (70%). The monitoring program lasted for 20 months, and it proved to be effective. TNT concentrations remained below detection limits at the downgradient side of the barrier throughout the monitoring period, with levels ranging from 100 to 150 µg/L at the upgradient side of the barrier. The estimated cost for the construction and operation of a full-scale PRB in this area was approximately USD 2000 per square meter.

4.2.2. Bioremediation by Nutrient Injection

This method was implemented on a full scale at a specific location in the Pantex Plant, Amarillo, Texas, USA. In this area, extensive contamination of the perched aquifer was observed, with the main pollutant being RDX (up to 4000 µg/L). This aquifer is located at a significant depth, approximately 78 m below the surface of the soil, with a thickness of 4.5–6.0 m, and the plume of RDX contamination covers an area of approximately 550 acres. It was considered that there was a risk of the contaminated waters infiltrating the lower Ogallala aquifer, from which neighboring settlements draw their water supply.

The remediation intervention was decided to be carried out in the upstream area of this hazardous zone by creating a reactive barrier perpendicular to the flow of underground waters with the injection of suitable reactants. Various alternative solutions were explored through pilot field tests, such as in situ reduction by injecting sodium dithionite (Na$_2$S$_2$O$_4$) and calcium polysulfide (CaS$_x$), in situ oxidation by injecting potassium permanganate (KMnO$_4$), and in situ bioremediation by injecting nutrients. The bioremediation solution
with the addition of soybean oil, sodium lactate, and surfactants was selected. From the pilot tests, it was found that a reduction in RDX below environmental limits was achieved within a few days.

The intervention was carried out in 2008 with the installation of 42 injection wells covering an area of approximately 40,000 m² (550 m × 73 m). According to the data presented in the relevant study [38], the treatment cost was approximately USD 190 per m³ of contaminated groundwater. The process of installing the wells and adding nutrients took only a few weeks. However, due to the extensive contamination, a continuous water quality monitoring program is expected to last at least 30 years. From the study data, the average monitoring cost per well per year is approximately USD 6000 [38,39].

Innemanová et al. (2015) studied the effectiveness of in situ bioremediation of contaminated groundwater by nutrient injection [40]. Laboratory tests were conducted to evaluate alternative nutrient sources, and whey was selected as the preferred option. Pilot-scale tests were carried out in the Czech Republic. The contaminated aquifer was located at a depth of 1 m below the ground surface and extended to a total depth of 3–4 m. Approximately 4.7 m³ of whey was injected into three injection wells covering an area of approximately 400 m³. The initial TNT concentration in the groundwater was around 10 mg/L, and a reduction of >90% was achieved at most monitoring points.

4.2.3. In Situ Chemical Oxidation by Fenton Injection

In situ chemical oxidation (ISCO) is a category of technologies primarily applied to groundwater for the breakdown of organic pollutants by injecting suitable oxidizing agents into the aquifer. There are fewer examples of applications in soils. Common oxidants include hydrogen peroxide (H₂O₂), either alone or in the form of the Fenton reagent (H₂O₂ + Fe(II)), ozone (O₃), permanganate (MnO₄⁻), and persulfate (S₂O₈²⁻). In the case of groundwater contaminated with explosives, field pilot tests have been conducted mainly using the Fenton reagent and potassium permanganate.

Geo-Cleanse International conducted field tests using a mixture of Fenton reagent for the remediation of groundwater at the Pueblo Chemical Depot, Colorado, USA [41]. Approximately 16.5 m³ of H₂O₂ solution (12.5%)/Fe²⁺ was injected. After 26 days, HMX was completely removed, and RDX concentrations were reduced by 60%. Furthermore, other nitroaromatic compounds were reduced by 72–100%.

A pilot test using sodium permanganate was conducted at the Nebraska Ordnance Plant, USA, where groundwater contained RDX (30–70 µg/L). The contaminated aquifer was located at depths ranging from 16.8 to 22.9 m. The goal was to create a reaction zone approximately 9.2 m × 4 m × 6 m in depth, using a system of three injection wells spaced 4.6 m apart. Approximately 70 m³ of sodium permanganate solution (10 g/L) was injected into two end wells. The pumping of water from the central well and reinjection into the two end wells was performed for 42 min to achieve a better distribution of permanganate within the reaction zone. RDX concentrations near the injection wells were reduced by 70–80%, but problems with the uniform distribution of permanganate due to aquifer heterogeneity resulted in reduced treatment effectiveness.

4.3. Evaluation of Available Techniques for Soil Remediation

The advantages and disadvantages of the four general categories of soil remediation methods are summarized in Table 3. This table was constructed to select a suitable remediation technique based on the site characteristics, decontamination cost, and estimated duration of remediation.
Table 3. Pros and cons of broad categories of remediation approaches for soil contaminated by explosives [23,42,43].

<table>
<thead>
<tr>
<th>Method</th>
<th>Advantages</th>
<th>Disadvantages</th>
<th>Estimated Duration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Encapsulation</td>
<td>A relatively cost-effective solution when limited to surface coverage with impermeable material. Does not allow for immediate water infiltration and significantly restricts further movement of pollutants from the unsaturated zone to the groundwater.</td>
<td>It is a passive solution that encapsulates the soil rather than decontaminating it, especially only from the surface. No further use of the site is feasible. The problem of groundwater pollution is not solved as long as it exists.</td>
<td>2–4 months</td>
</tr>
<tr>
<td>Excavation and treatment or disposal of contaminated soil outside the area</td>
<td>Immediate solution, especially for small quantities of contaminated soil. Complete removal of pollution from the site. The site is suitable for any use after decontamination.</td>
<td>Particularly high decontamination costs. Risks of pollutant dispersion in the atmosphere during excavation. Need for site re-filling with clean fill material (cost increase) if deemed necessary.</td>
<td>4–6 months</td>
</tr>
<tr>
<td>In situ or on-site remediation techniques</td>
<td>A relatively cost-effective solution. Involves relatively limited earthmoving operations with a lower risk of pollutant dispersion into the atmosphere. Causes fewer disturbances in the area. Regular activities can continue during the remediation process. The site is suitable for any use after remediation.</td>
<td>Does not provide an immediate solution; it takes time.</td>
<td>10–14 months</td>
</tr>
<tr>
<td>Natural attenuation</td>
<td>A particularly cost-effective solution.</td>
<td>It is a passive solution, and the environmental risk at the site may not be addressed at all, making it suitable only for low-environmental-risk contaminated sites. Requires intensive and systematic monitoring of the situation. No further use of the site is feasible.</td>
<td>20–40 years (in cases where there will be no additional source of contamination at the site)</td>
</tr>
</tbody>
</table>

In general, on-site and in situ remediation techniques offer significant advantages over other alternative solutions. They address pollution problems fundamentally by destroying, removing, or neutralizing contaminants; eliminate risks to potentially sensitive receptors; and allow the site to be returned to any use once the prescribed low concentration limits for pollutants are achieved. In situ applications have no risks of airborne pollutant dispersion during earthworks, loading, and the transport of contaminated soil, because no excavations are involved. In on-site applications, related disturbances occur near the polluted area without adversely affecting the wider area. Finally, their costs are usually significantly lower compared to excavating and processing soil off-site. In most cases, contaminated soil is classified as hazardous waste, and its management, when transported off-site, is subject to all hazardous waste management regulations [44,45].

4.4. Evaluation of Available Techniques for Groundwater Remediation

The pump-and-treat methods for water extraction and treatment on the surface are well established, offering effective control of operational conditions. Surface treatment using granular activated carbon (GAC) or zero-valent iron (ZVI) filters is common. However, international experience indicates that these units require extended operation times, especially in areas with high concentrations of trapped pollutants (hotspots), leading to the continuous dissolution and re-contamination of water. This is particularly evident with non-water-soluble organic fluids like petroleum, which can remain trapped in the unsaturated or saturated zones as droplets. In situ processing methods, such as the permeable reactive barrier (PRB), extend water cleanup times but significantly reduce operational
costs by requiring only monitoring of the barrier’s upgradient and downgradient water quality. For areas with trapped pollutants, on-site injection of reactive agents is preferable for destroying pollutants both at the contamination source and in groundwater [46,47].

5. How to Select a Suitable Remediation Technique for a Contaminated Site

A remediation project in a contaminated site must address the identified risks in the risk assessment, specifically (1) eliminating the potential for mass explosion accidents, (2) ensuring the protection of the health of workers in the area, and (3) minimizing the wind and water dispersion of pollution to neighboring areas and sensitive receptors [48,49]. In choosing the appropriate solution, in addition to the effectiveness, maturity, and cost of available technologies, many other parameters and data must be considered, such as the following factors:

- The physicochemical characteristics of the pollution;
- The extent and intensity of existing soil and groundwater pollution;
- The geological and hydrogeological characteristics of the area;
- International practices for the application of remediation technologies in similar cases;
- The simplicity of the methods, equipment availability, and technical expertise in each country based on experience with similar remediation technologies, especially in similar or identical hydrogeological conditions;
- Possible secondary environmental impacts and how to address them;
- Wider social acceptance to ensure the highest possible efficiency of measures with the least possible disruption;
- Economic, technical, and time constraints.

6. Conclusions

This review study has focused on case studies of in situ and on-site remediation applications for soil and groundwater contaminated with explosives. The challenges inherent in addressing explosive-induced contamination were thoroughly examined, highlighting the complexities arising from the stability of explosive compounds, their mixture formations, and the difficulties in precisely defining pollution hotspots. The exploration of various remediation approaches, from chemical treatments to biological interventions, underscores the diversity of strategies available. To successfully navigate these challenges, it is evident that a multidisciplinary approach is essential. Thorough hydrogeological field investigations and meticulous field tests emerge as crucial prerequisites before undertaking full-scale remediation projects. The selection of reactive agents, tailored to the specific biogeochemical environment, determines the success of interventions, whether through direct chemical reduction, the oxidation of pollutants, or the augmentation of endogenous microorganism activity. The application of effective and sustainable remediation techniques ensures a cleaner, safer, and sustainable environment.

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