American Journal of Biodiversity
https://biojournals.us/index.php/AJB
ISSN: 2997-3600

Study of the Causes of Soil Pollution with Heavy Metals

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Received: 2024, 17, Jul
Accepted: 2024, 21, Aug
Published: 2024, 20, Sep

Annotation: Soil pollution caused by heavy metals has received extensive attention due to its accelerating severity and potential threat to environmental and human health. Determining the primary sources and causes of heavy metal pollution in soil is urgent and plays an important role in assessing the eco-environmental and human health risk. Soil is the primary reserve and supplier of water and nutrients for crops and, thus, the most viable indication of stress induced by heavy metals in the environment. Heavy metal pollution in soil can not only reduce the quality and yield of agricultural products and threaten human health but also undermine ecosystem services. Thus, the research of heavy metal pollution in soil is not only economically meaningful but also important for the sustainable development of agriculture, environmental safety, the protection of public health, and ecosystem health.

"soil pollution" refers to damages caused by mixing foreign substances with soils, which in turn cause physical, chemical, or biological changes to the soils and adversely affect normal physical, chemical, and biological activities. Although researchers have slightly different definitions of "organic pollution" and "soil pollution" in terms of specific vocabulary, the essence of both definitions is the same. "soil pollution" as losses caused by human activities that deteriorate, degrade, destroy, and lead to the unavailability of the lands, and in which the agricultural production of these lands is affected to an extent. "soil pollution" as the presence in or on the soil of chemical substances in quantities that exceed natural background levels and thus may have direct or indirect adverse effects on humans and other biological species.

1. Background and Significance

Since the Industrial Revolution, soils around the world have gradually been polluted due to a variety of human activities. Heavy metals have been significantly accelerated, especially in recent decades. Urbanization and industrialization have been increasing alongside heavy metal pollution. The consumption of fuel, energy, and raw materials has been rising, which has led to the release of various types of waste into the atmosphere, covering the soil surface. Nutrient-rich ecosystems on Earth and habitats can be contaminated; heavy metals are introduced into soils, sediments, and water bodies. Minerals are chemical elements and have a density value between 5 g/cm^3 and 7 g/cm^3. About 1% of the Earth's crust contains iron, manganese, and zinc. The processing of mineral resources for metals can extract and concentrate these pollutants at low concentrations. These metals are not limited to but are used in mining, ore processing, iron, steel, non-ferrous metals, metallurgy, ceramics, paint, electronics, alloys, functional material additives, soil treatment chemicals, and pesticides. Human activities have resulted in a significant enrichment of metals in soils and sediments, particularly in dam reservoirs in rivers or estuarine environments. If these metals are cumulatively deposited, they can even be transported over time. [1][2]

Research has shown that heavy metal accumulation can continue to occur in the soil, aquatic ecosystems, and a variety of organisms, including humans. Within the context of long-term heavy metal poisoning of human and environmental health, soil pollution has been identified. Polluted arable soils can have long-term impacts on agricultural commodity quality, wild plant biodiversity, and soil microbial communities. Approximately 30% of agricultural soils have been found to be contaminated worldwide. In the 1990s, a survey showed that 20% of farmland in Denmark was contaminated with lead, and approximately 80% of organic soils in Great Britain were contaminated with nickel. Additionally, 25% of children in Great Britain had elevated levels of copper. Excessive absorption has been noted, and in the last 20 years of the 20th century, 35% of China’s soils contained levels of copper, arsenic, mercury, and other heavy metals. Excess concentrations are too high to ignore and can be measured. Fifty percent of Hungary and Romania contain excessive copper and zinc and are also contaminated with heavy metals due to potential toxic compounds and radioactive hotspots. Awareness of heavy metal risks, soil pollution, water pollution, and food safety hazards continues to increase in society, and studies have been carried out at national and regional levels. Biodiversity, ecosystem services, and the potential danger to humans and animals if heavy metals accumulate in abundance in the environment must be addressed. We must work scientifically and enact policies while promoting reform measures to study the movement of heavy metals and their effects. [3][4]

2. Heavy Metals in Soil

Heavy metals are defined differently by geologists and biochemists. Based on the abiotic properties of heavy metals and the health status of organisms, researchers have divided heavy metals into many groups. Dividing heavy metals into several classifications according to biotoxicity and metal behavior in the sediments is a hotspot in studying heavy metals in marine sediments. The toxicological properties of metals often determine their behavior. Heavy metals can be divided into toxic and potentially toxic categories. Depending on their availability to biological organisms, they can also be divided into mobile metals and immobile metals.

Heavy metals are of great ecological significance due to the possibility of being transferred along the food chain and gradually accumulated in the bodies of organisms. Heavy metals are widely used in agricultural production, especially in pesticides, chemical fertilizers, and so on. In many regions, the utilization rate of chemical fertilizers is only 50%, while the other 50% are mostly transformed into soluble and insoluble compounds of heavy metals, which pollute agricultural land and become the origin of soil heavy metals. Heavy metals cannot be degraded in natural soil, and some of them have the characteristics of hyperaccumulators, which can be enriched in plants, animals, and the human body through biogeochemical transformation and then affect crops and ecosystems in vivo and in vitro, causing various degrees of damage. Compared with organic pollutants, the removal of heavy metals in soil has become a focus because of their high persistence in soil, and the existence of heavy metals in soil has brought a series of problems. [5][6]

2.1. Types of Heavy Metals

Of the distinctly separate groups of heavy metals existing in nature, the first to consider are those of the inert group. These metals do not undergo chemical changes and are thus very persistent. The downside of their long life in soils is their long resistance and the time in which they can express their negative effects on living organisms and thus on soil. The metal-regulating mechanisms in living microorganisms do not efficiently address these metals. Examples of heavy metals that are part of this group are lead, cadmium, and mercury, but also silver, bismuth, and vanadium. Hydrogen, iridium, platinum, and zirconium are considered dangerous, but this is only the case in the metal form, which is found very rarely in nature, mainly because of their common presence in the form of anions. The harmful group of natural heavy metals can be divided mainly into those of primary (igneous and high-metamorphic) and those of secondary (sedimentary) origin.

Heavy metals exist in many forms and can be categorized in different ways. They vary according to their mobility, behavior in the environment, and toxicity in some cases. Inert heavy metals comprise iron, copper, zinc, nickel, and manganese. Examples of heavy metals that are highly toxic and poorly mobile are arsenic and selenium. Some metals such as molybdenum, cobalt, and polonium are poorly mobile and hardly toxic to plants and other living organisms. Toxic metals such as lead, cadmium, and mercury, of which natural composition is scarce, can in particular be a result of anthropogenic activities. They can derive from a range of sources, and their diversity is closely linked to their origin and how they accumulated over the years in the environment. Some of these metals are dispersed all over the globe, and their traces can be found not only in rain and snow but also in the deep sea and even in the ice caps of the poles. Pollution with these types of heavy metals has proven possible to persist for a long time in some soils with low natural background contamination values. The persistence of such environmental pollution can be attributed to the presence of various mineral structures that bind the heavy metals more or less in their crystalline structure and the so-called colloid fraction. Retrogression of possible damage is often only possible by in-situ measures. [7][8]

2.2. Sources of Heavy Metals in Soil

Sources of Heavy Metals in Soil: Anthropogenic and natural processes usually determine the origin of heavy metals in soil. Anthropogenic sources of heavy metals in soils can be divided as follows: urban, industrial, agricultural, mining, and traffic. Modern activities generate large amounts of domestic and municipal waste, which are often disposed of carelessly with no consideration for the management of the waste. Prolonged pollutant discharge leads to their accumulation in the soil. Another significant contribution to heavy metal pollution in soil is a consequence of industry. Fuel and energy companies, smelting and processing plants, galvanizing plants, refineries, and chemical companies all emit pollutants along with regular and occasional production. Inorganic pesticides, synthetic fertilizers, and organic matter such as fertilizers and manures improve soil properties and production while depositing potential contaminants in the soil.

Agriculture is also responsible for soil pollution with heavy metals, particularly in ecosystems containing former mining areas. Intensely over-manured soil with organic and synthetic fertilizers alters soil properties and leads to the translocation of heavy metals to the food chain. Elevated heavy metal levels in crop plants raised in polluted soil will likely induce diseases in animals and humans. Accumulations of heavy metals are the natural and logical result of inadequate use of agrochemicals in a fertilizer-overdosed farmland scenario for several decades. Due to shoe wear and tear, construction, vehicular velocities, and weathering, paved roadways may generate airborne cement dust as well as elemental pollutants, such as heavy metals. The annual increase in the number of vehicles at a global level keeps particulate pollutants lofted in the atmosphere before eventually washing them down into receiving soil waters. Extensive vehicle use in and around developed and rural areas is linked to increased pollution on adjacent pavement. Expansive quantities of imported or native pavement crude oils, open-air break, detached tire fibers, accelerating erosion of the brake and clutch lining, exhaust gases liberated and resuspended, keep-off and deposit uninsurable contaminants on roadways. They slowly make their way to the lower trophic levels, store in tissue, and, in turn, enter the human population. Weathering results in the use or finding of usable elements from a single rock, mineral, or massive rock, or a mixture of all three as secondary materials. During the latter activity, heavy metals travel in the form of sediment and dust at varying distances downstream, often resulting in eventual deposition in natural surface waters and bank soils. But natural processes can also lead to heavy metal pollution in the soil without the direct or indirect involvement of human beings. Weathering of rocks and volcanic eruptions are examples of natural processes that contribute to the presence of heavy metals in the soil. [9][10]

3. Effects of Heavy Metal Pollution on Soil

Soil pollution with heavy metals has several negative effects on characteristics. The presence of heavy metals in soil can lead to a reduction in the number of microorganisms and, as a consequence, to a decrease in the intensity of soil-forming processes. Heavy metals can have a range of negative effects on colonization and bacteria. Heavy metal pollution changes the physical and chemical properties of the soil and destroys its trophic structure, which results in lower soil quality. Heavy metals are not fully metabolized in the soil ecosystem and can undergo a specific process through practically all soil components, disrupting the balance of natural cycles and key soil processes, such as decomposing lignin molecules and mineralizing organic raw materials. In general, heavy metals, which remain in the ecosystem for a long time, slow down the circulation of nutrients and reduce the turnover of zinc in soil by approximately 5%. In addition, the quality of the soil is also reduced because the presence of zinc in the soil ecosystem reduces the nitrification of ammonium nitrogen and phospholipids, which leads to a decrease in the number of phosphates in the soil and an increase in the degree of soil contamination. [11][9]

3.1. Impact on Soil Health and Quality

Pollution with heavy metals causes a number of negative effects in soils, namely the change of pH, reducing nutrients available for plants, and decreasing the productivity of soils. The change of soil pH can affect the mobility of heavy metals and their bioavailability. Due to their high reactivity, heavy metals change the structure of soil humus and accelerate the decomposition of its fractions. This causes the reduction of materials contributing to soil fertility. Moreover, heavy metals reduce the activity of soil microflora and cause changes in the balance of biogenic elements. While most soil bacteria are more tolerant to heavy metal toxicity, fungi can suffer dramatically; quite often, the respiration of fungi is significantly more sensitive. Because the decomposition of soil organic material is driven by bacteria and fungi, this difference means that heavy metals can have a profound impact on biological processes in soil and its fertility.

Soil—a thin, fragile layer of Earth made up of minerals, organic matter, air, and fluids—provides habitats for various organisms, from microorganisms to plants to large animals. The soil is a function of its materials, landscape position, climate, and time, and it forms a complex ecosystem. Soil pollution commonly leads to the degradation of terrestrial ecosystems due to the impacts it has on soil organisms and plant health. Furthermore, it can have impacts at a local, regional, or indeed global scale. Impacts at a global scale can include weathering and erosion of the land, increased flood risk, and atmospheric pollution. In soils, heavy metal pollutants can act as potent toxins to soil organisms or, as a result of their physical toxic effects, reduce soil structure, thus altering water flow and taking potential habitats.

The effects of the presence of heavy metals on soil quality, coupled with the implications of this for agricultural output, include the reduction of soil biodiversity and dissolved oxygen saturation, decreases in plant growth, seed production, and aboveground biomass via chelation of amino acids and dampened growth-initiating mechanical or hormonal cues. Reduced metabolic activity of bacteria and fungi results in a lower consequent magnitude of organic matter mineralization and rate of decomposition. As a result, the loss of available nitrogen for crop production and in situ phytoextraction results in lower plant NPK content and growth. Taken together, an investigation of soil health through an assessment of the processes that underpin the productivity of agricultural land can be effectively evaluated. These provide a reflection of diverse climates, soil, and management conditions. These indicators encompass the physical, chemical, as well as the biological speciation, mobility, and availability of heavy metals in soil. These can be used in combination to predict plant growth potential and productivity. The value of such monitoring approaches is to encourage policy and practice that serves to protect against current and historical soil pollution, minimizing potential crop losses as a result. [6][12]

3.2. Impact on Plant Growth

The presence of heavy metals in soil has a direct toxic effect on seed germination, root development, plant strength, stress tolerance level, and overall vigor. Certain heavy metals have a toxic impact on various physiological processes, which directly affect the metabolic pathways in plants. Metals in soil are considered to have an indirect negative influence on plants by altering soil physicochemical and microbiological properties. In addition, heavy metal accumulation in edible parts of plants may decrease the nutritional quality of the crops, which indirectly affects human food security. As a consequence, plant growth inhibition has profound consequences for ecosystems and agriculture. The large spread of heavy metal pollution in topsoil and its negative impacts on soil health closely link the biogeochemical cycles of nutrients and heavy metals.

Soil, as the most important factor directly determining the physiological function of plants, shows variations in the morphology, dry matter accumulation rate, bio-physicochemical responses of plants, and the growth and development of the root system induced by soil heavy metal pollution. Modern research provides ample evidence that heavy metals, alone or in combination, exert negative effects on physiological processes such as root growth and functioning, seed germination, water and energy metabolism, antioxidant enzymatic activities, cell division, and elongation. Thus, excessive concentrations of heavy metals with toxic effects in topsoil could result in decreased or even terminated root elongation and biomass allocation. Plants try to partially exclude heavy metals entering through the roots, and heavy metals are often accumulated in the aboveground part of plants, affecting the plants directly via the regulation of root length, weight, and vigor. [13][14]

4. Analytical Techniques for Detecting Heavy Metals in Soil

Assessment of the extent of contamination and the degree of heavy metals in soils is critically dependent on the specific detection techniques. Therefore, in addition to qualitative and quantitative research objectives, a deep knowledge of detection techniques is needed. Given the complexity and diversity of soil samples and the ever-increasing number of heavy metals, a standard detection method has not yet been fully developed. This section focuses on the analytical techniques for detecting heavy metals in soil.

A general classification of detection methods is based on the soil phases that are specifically tested, leading to indirect and direct methods. The former are performed on extractants resulting from dissolution or chemical treatment of soil samples, while the latter deal with the examination of intact soils or plant parts. Driven by different purposes and backgrounds, a wide range of indirect and direct detection techniques are applied in soil research. Indirect techniques are usually grouped into chemical analysis and instrumental analysis methods. Chemical analysis is further subdivided into colorimetric, titrimetric, vacuum fusion digestion, shipboard UV digestion, and microwave-assisted dissolution techniques, which are also called extraction procedures developed either for total metal or specific multielement analysis. Inductively coupled plasma is a combination method for metal analyses of either heavily contaminated soils or vegetation samples. The multielement capability of this method coupled to a high-resolution mass spectrometer can handle ultratrace level data for some heavy metals.

The choice of analytical technique depends on several factors such as the type of soil, expected concentration levels, the available infrastructure, and type of heavy metal elements. Total digestion procedures are usually appropriate for total heavy metal content quantification, while specific extraction methods that give a semi-quantitative and semi-specific resin extractable metal content are also widely referred to for metal quantification in plant tissues. A key parameter in methodology is the ability to evaluate and determine data accuracy. Given the crucial influence of correct detection results in remediation planning, more precise and more accurate techniques would be expected. With the future development of soil science, new detection methods and techniques are being continuously developed and tested for use in contaminated fields and for improving current techniques. [15][16]

4.1. Chemical Analysis Methods

In chemical analysis, there are several methods for heavy metal detection in soil. Among them, the most frequently used are spectrophotometry and titrimetric methods. The basic principle of spectrophotometry is the interaction between electromagnetic radiation and atoms, ions, or molecules. The measurement of the amount of light absorption is useful in determining the concentration of chemical substances in a given solution. Titrimetric methods are based on known chemical reactions. Complexometric, precipitation, and oxidation/reduction titrimetric methods already exist for heavy metal detection. Traditional spectrophotometry and titrimetric methods are two powerful tools for the analysis of solid particles in similar soil materials. If they are not combined with the extraction of the target metal, the spectrophotometric methods are used for the determination of heavy metals in a free state, while titrimetric methods use sequential extractions to determine heavy metals.

Generally, these two methods are simple, rapid, and easy to carry out with reasonable accuracy and precision, but they often seem time-consuming and require the raw samples to be destroyed before analysis. Moreover, ground information for many available methods can provide a good insight into the existing applicability of these tests to quantify heavy metal pollution. The spectrophotometric methods provide rapid and accurate results because all the solutions are automatically detected and produce the results directly, but an analysis using some of the above methods can be performed within 3 to 8 hours. However, some of the limitations of this method are the release of standard halos and other strong associations, and they will not detect the secondary minerals unable to release the target metals in the total extraction step, as well as sulfides and some secondary minerals that can slowly oxidize while acidifying. Another disadvantage of such methods is the interference from other metal or metalloid ions, macro- and micro-nutrients occurring in the original soil and sediment samples. Thus, in such a case, an error-free validation of either the selected standard method or the above-suggested method needs to be performed. Heavy metal analysis often requires validation and standardization of methods by relevant standards organizations. In particular, the aim of this analysis is to distinguish between new advanced and traditional methods for the rapid screening of soil samples. These methods are in agreement with the high demand for minimizing the costs of future research. [15][17]

4.2. Instrumental Analysis Techniques

In the last decades, a series of increasingly advanced instrumental analysis techniques have been developed to detect heavy metals in soil. Among these, there are two methods worthy of note, which are used because of their superior sensitivity and precision: atomic absorption spectrometry and inductively coupled plasma mass spectrometry. The basic principles and general operations of these methods are described below. The atomic absorption spectrometry involves using a certain flame to atomize a suspension or a solution of the sample to be analyzed. After the atomized particles are irradiated with a certain absorption light, the inside of the atomic absorption spectrometry instrument is adjusted and controlled. Each atom can freely pass through the medium; the magnitude of the absorption intensity can be determined or reduced according to the concentration of the element to be tested, thereby determining the concentration of the element to be tested in the solution. The equipment required is simple and easy to operate. Spectrometry has been widely used in various industries and fields. This method has the advantages of simple equipment, easy operation, and flexibility. It can be used for qualitative and quantitative analysis of various trace elements and is also suitable for a variety of environmental pollution and elemental analysis fields. The inductively coupled plasma mass spectrometry is a combination of the two techniques and has been widely used to determine heavy metallic elements in complex matrices because of its accuracy and excellent detection limits.

Most of the instrumental methods have not been applied in practical field detection because of sample pretreatment, expensive equipment, and challenging on-site analysis. Currently, most soil investigations are still completed by traditional chemical methods. Almost all instrumental methods require a high degree of calibration, testing, and quality, and a series of complicated calibration processes need to be followed to determine the content of the test monomers. Therefore, generally speaking, the content detected by instrumental methods is more accurate and reliable than that of traditional chemical methods. With the development of science and technology, increasingly sensitive and precise instrumental detection methods will also be easily applied to the detection of field soil heavy metal pollution. By comparing with traditional chemical methods, we can draw an initial conclusion that instrumental analysis techniques are the most important methods to study soil pollution in terms of complexity, selectivity, and problems. [7][18]

5. Regulatory Frameworks for Heavy Metal Pollution in Soil

5.1. National Regulations Each country has established due standards and regulatory frameworks for the soil environment and soil contamination according to its actual local conditions, which generally include the following three aspects. (1) Regulatory authorities have established guidelines and methods to monitor and control soil contamination and the level of heavy metals. (2) Local agencies supervise the application of these guidelines and pollution assessment works of enterprises and institutions. (3) Authorities regulate the legislative approval, standards, and assessment of site-specific soil quality. The main aims of soil prevention and regulations are to protect public health and guarantee the quality of agricultural, forestry, and recreational lands.

5.2. International Agreements These related pacts were developed according to the Rio Principles, which established funds for sustainable development and poverty alleviation, including support for the effective implementation and further development of international environmental agreements that are based on Rio principles and Agenda 21. The Medium Size Project - Implementation of the Reporting and Information System for Chemicals and Hazardous Waste frameworks. (1) The Basel Convention regulates the movable phenomenon that occurs under a state's regulatory sphere of influence and prescribes the requirement for prior informed consent before hazardous waste can be moved from one country to another or parties within an organization. International agreements and conventions. [19][20]

5.1. National Regulations

Since metals are addressed in the majority of soil contamination or environmental protection laws, we will focus on heavy metals when discussing soil contamination, specifically cadmium, lead, and mercury. In the U.S., both the primary federal regulations and other sector-specific actions have applied regulation to prevent soil contamination of heavy metals. Both site-specific and more general heavy metal soil contamination standards are included in these regulations. Other countries have established laws that address the management of heavy metal pollution and soil contamination. In Japan, the Soil Contamination Countermeasures Act was created to prevent and manage soil and underground water pollution. Additionally, a soil pollution standard for where children play or live was announced. The Swedish Environmental Protection Agency has reported that the use of substances has been reduced and soil levels are stabilizing. Switzerland has implemented a strategy that included a tax on kerosene with a high lead content to promote the use of clean aviation fuel. In the EU, the Integrated Pollution Prevention and Control Directive established internal controls for heavy metals released from industrial facilities into soil and water.

The development of national policy for addressing the problem of heavy metals in soil is a national problem, and there can be no one-size-fits-all solution to an international problem that can be taken on by such a variety of nations. Ultimately, the efficacy of any regulations related to heavy metal contamination, including those related to phosphorus-containing fertilizer and uses of biosolids, is a policy decision that depends on a wide range of policy considerations, including economics, health issues, public policy, and other societal issues. Regulation has been established as the most effective means for minimizing environmental contamination from point sources. Ineffective policies for heavy metals include inconsistent international regulations, as in this situation a push to the bottom can result, while countries do not want to advance stringent rules if similar neighboring countries do not. Some countries have shown positive approaches and solved contamination issues across boundaries—although international legal obligations were not available, good practices included cooperation on transitional means with respect to industry and other relevant issues. Preventive policies for heavy metal pollution were regulatory related in design for the Superfund Risk Management Program and Effluent Facilitative Action. Cooperation is needed in order to ameliorate heavy metal issues, share experiences, and exchange information on heavy metal pollution standards for soil and other environmental media.

European laws require a coordinated approach to the most dangerous chemicals as a group of toxicants. Criticisms of existing policies for managing heavy metal pollution from organic environmental chemicals have taken place, and global agreements are being signed even prior to agreements or regulations existing at the time, based on changing transnational norms, values, and social organizations resulting from an active civil society and a lively local regulatory community. The regulation of mercury emissions under international law followed from a proposal made for the very first time in Europe in terms of policy. Therefore, policy to address a health, safety, and environmental problem, including heavy metal pollution, results in part from pressure driven by proving unacceptable social costs. Controlling the sources of pollution can be more economically viable compared with treating the negative effects of soil pollution. [21][22]

5.2. International Agreements and Protocols

5. Information on the treatment of heavy metal pollution is in interest. There is a clear link between the Stockholm Convention and the Minamata Convention. During an evaluation of the approved reports of the Secretariat of the Convention on Biological Diversity, I did not find reliable data on the total number of protocols and their coverage in Section D. Report on Protocols and Coordination in the thematic section of the conference. Consequently, I cannot estimate the total number of international instruments on heavy metals and their coverage at the international level. The Minamata Convention on Mercury is a concerted effort by countries to reduce transboundary mercury pollution and the physical resource centers. The Stockholm Convention reviewed global efforts to reduce mercury emissions and concluded that continued international efforts were needed to tackle deadly mercury pollution around the globe. It was stated that the Minamata Convention should move from the upstream to the downstream phase of the mercury trade and supply chain, which will allow the market space to move from mercury-based products to non-toxic alternatives. Based on the information and materials presented in the topic of this conference, I could not find a direct link between the cost of scaling up in these three identified functions and the Global Mercury Assessment. One of the objectives of the Convention is to make it easier for technologies designed to reduce emissions and production from mercury-containing products to transition to less emission-intensive technologies. [23][24]

6. Case Studies of Soil Pollution with Heavy Metals

After many, sometimes contradictory studies concerning the subject, it became clear that polluted soil can lead to the pollution of agricultural products and the appearance of harmful effects on human health. Among all the existing soil pollutants, heavy metals are among the most important, given that they are not biodegradable and bioaccumulate. With this in mind, the following detailed case studies examine current heavy metal content in some soil types and make proposals for amelioration. CONTENTS: The Southern Part of the Mining Site of Cu–Au of Rosia Poieni. Methods of Amelioration in the Rehabilitation Plan of the Rosia Poieni Mine. Pollution Severity by Heavy Metals. Remedial Measures for the Rehabilitation Plan for the Rosia Poieni Mining Site. The Impact of Mining Activities on the Role of the Soil in the Local Plant Communities. The Importance of Establishing the Characteristic Edaphic Profile. The Case of South-Western Romania. The Hoghiz Area. The Retezat–Peștu Retezat Mining Area. The Regions and Ecosystems in and near Industrial Areas. Aquatic Ecosystems. Compaction. Subsurface Minerogenic Horizon. Rasekaro case study: situation in June–August 2017. The Zlatna Area. Conclusions. General Conclusions. General proposals. Socioeconomic consequences. Perspective. Case Studies: The specific case studies were selected to fit into two main categories: simple examples, describing one heavy metal parameter, and more complex case studies, describing a multispectral approach to environmental pollution. Examples of simple case studies in Romania are examples right from the former industrial area—the lead smelter from Copșa Mică, which was closed in the middle of 1993 after more than 50 years of technological activity. Moreover, in 2000, near the Copșa Mică Lead Smelter, the first Romanian ferronickel industrial facility emerged in Zlatna. Another example refers to the emissions of the 22 coal thermal power plants constructed along the Jiu Valley in 1950, as well as an example of biogeochemical anomalies upwind and downwind of the Fetiți Communal Top. Overall Soils: Here several pedosystems were analyzed: the Edins and the Buso Arc in the mining town of Maramureș; the soils developed on iron ore wastes and room storage in the Abrud–Horea mining areas, and in Tău Bistra, situated on the former Fe-Au mine. The Zoos sedges and Zeit trans-humus pedosystems were detected. The aim of these studies was to observe and discuss, in small details, dead smearists in contrast to life smearists. The Impact of Mining Activities on the Scaun Basin (Maramureș County, North-Western Romania): Maramureș County, rich in minerals, was affected by the processes of mining exploitation. The implications of mining activities are reflected in the microbiological populations of different soils. Mixtures of residual pre-growing soils, mounting orchid; pre-black mountain black soil have been studied at greater depths. Ecotope with mixed domination of four spruce stands with the admixture of deciduous species and a block of two tumenets were selected—all in transhumance. The following microbiological properties have been highlighted: the number of microorganisms, as well as the content of the following enzymes—amylase, cellulase, phosphatase, urease, catechol-1-oxidase, while multivariate statistics were performed to differentiate the analyzed sites. Analysis of the contents of heavy metals in the Fe ore and pyrite from some chimneys is also intended as an informative study. [25][26]

6.1. Industrial Areas

Most heavy metals found in urban soils have industrial origins. High values for Pb, Zn, Cd, Cu, Ni, and so on were found. The pollution has many sources including heavy traffic, industrial activities, careless waste disposal, and the use of agrochemicals. High Pb values were found in certain areas.

Air quality monitoring also showed a high level of urban air pollution. Considerable enrichment of Hg, Tl, and Cd in street dust was observed. This is not surprising due to the existence of several industries and extensive traffic all over the city. A very high Hg concentration factor was found in the close vicinity of the gold processing factory. In another mining city, heavy metals pollution of the surroundings was studied in some detail. Large quantities of liquid mercury were used in the area. Mercury had been emitted from the mine to the environment over the years.

The industrial area of Baia Mare, in the northwestern part of Romania, is known as one of the most important sources of a series of significant heavy metals and sulfur pollution. Soil contamination with heavy metals and, consequently, soil acidification are the main environmental and ecological pressures upon large urban and rural areas close to the town and have been emphasized by the pollutant impact assessment approach. Improper activities consisting of mining and the associated metallurgical industry, processing of large proportions of fast creation and accumulation of huge quantities of mining wastes, their careless storage or deposits without previous or expected recycling were and are the main technical processes responsible for the important environmental, ecological, and human health impacts in this area. [27][28]

6.2. Mining Sites

Mining activities are a very common activity overall, which poses a threat regarding soil pollution with heavy metals. In mining, rock is removed from the ground in two steps and prepared for further processing. This mineral processing, which includes crushing, milling, flotation, heating, and smelting in high-temperature furnaces, is necessary to convert the initial mineral to the end product. This type of processing is known to release arsenic, lead, and dust into the air and soil. In this way, heavy metals are released into the environment and life ground through physical, chemical, or biological processes. If soil strata are affected by the extraction and tailings from mining, heavy metals can become part of the soils that plants and animals depend on. Several mining activities have been identified as arsenic sources. Mining activities also have other environmental impacts such as habitat destruction, alteration of surface materials, soil profiles, vegetation, soil degradation, and alteration of natural land surfaces. In some mining sites, mining activities have jeopardized the integrity of the land, urged relocations, and cut off traditional land-use properties without compensation. In fact, they create an impact on local communities, long-lasting grazers, and resource gatherers who harvest minerals and other resources. For example, in some developing countries, due to gold mine mercury pollution, a significant portion of the population has been reported to suffer from mercury pollution. The historical mining sites include some important risks, the transformation of hydraulic balance, and alterations on an earth perennial time scale. Remediation and risk management can protect people, ecosystems, and critical drinking water supplies. In Finland, many approaches, such as landscaping, phytoremediation, and excavation with replacement, have been successfully employed in the treatment of contaminated land areas. Therefore, designing, implementing, and enforcing measures to prevent negative impacts in advance is based on international treaties and is an important part of the environmental permitting process. Despite various projects and numerous pilot and research initiatives, there are still some challenges and openings, including exaggerated legislation and low standards, mining in environmentally sensitive areas, and an adequate assessment of various management and rehabilitation measures. In Gyttorp, Sweden, the sulfide-rich mineral lands are covered by several detailed sites. Many sites have devastating land damage and are seriously polluted. All these sites have undergone restoration or remediation. Today, major sources of arsenic contamination are heat-tolerized uphill dump sites and sulfide waste rock dumps. Whether the engineered flood-path dams will withstand future catastrophic rainfall or not is unknown. The ability of the dam to maintain the lime flow from the internal waste rock alone is also uncertain, as the adverse oxidation effect of the wastewater on the internal waste rocks has not been studied, and this may result in pH values dropping below 4.5, causing negative arsenic remobilization effects. [29][30]

7. Mitigation Strategies for Heavy Metal Pollution in Soil

The confined soil, which was heavily polluted with heavy metals, remains an urgent contemporary problem. Different approaches are used to deal with heavy metals. There are two main strategies for dealing with heavy metal pollution in soil, which can be associated with the reduction of pollutants at source by implementing cleaner technologies and changes in production and consumption modes, as well as site remediation and restoration. Site remediation and restoration processes undergo a critical factor for the reduction of heavy metal pollution, including natural and artificial strategies.

This approach is distinguished into four different groups, including phytoremediation, which is the use of growing plants in contaminated soil for the stabilization, extraction, or volatilization of heavy metals; soil amendment, which is the application of different materials such as the addition of organic matter to enhance soil properties; solidification and stabilization; and pre- and post-treatment.

The role of plants in the remediation of polluted soils is of great importance. It is very complex in its potential phytoremediation offers and strategies that could be used to cope with heavily contaminated soils. Phytoremediation is a potentially cost-effective technique for cleaning up a site whose economic value has been limited by heavy metal contamination. It can be performed in situ, i.e., on the location of the contaminated site, which is advantageous as it economizes on the cost of heavy transportation of valuable topsoil, and ecological risks are reduced because there is no displacement or just minimal transport of pollutants. The main advantage of phytoremediation is that it utilizes naturally occurring biological processes. [31][32]

7.1. Phytoremediation

Phytoremediation: Lightweight Technology for Cleaning Heavy Metal-Polluted Soil

Soil is a main incubator of metal pollutants, such as Cd, Pb, and Cr, originating from different natural and anthropogenic sources. Metal-contaminated soil will severely inhibit the growth of crop plants, endanger human health, and disrupt organic homeostasis. Therefore, the rapid remediation of contaminated soil has been of great concern. As for phytoremediation, one of the most innovative cleanup methods involves growing specific plants with root systems that have significant metal absorption and accumulation capabilities, and then utilizing the potential of transferring and sequestering metals to purify the substrate or water. Hyperaccumulators are used to remediate the contamination. Reports have documented figures such as bioaccumulation in root, as well as translocation factor and bioconcentration factor to evaluate the metal profiles in a number of wild or greenhouse crop species, including tobacco, kenaf, bird's foot clover, sunflower, borage, pumpkin, and dwarf beach plum.

Since first being adopted in the phytoremediation of heavy metal-contaminated soil in 1978, over 400 plant species with general accumulation abilities and at least 438 hyperaccumulators have been identified throughout the globe. The advantages and disadvantages of phytoremediation include:

Advantages of phytoremediation

Phytoremediation is effective and environmentally friendly in situ remediation, where plants or natural features can take over any follow-up tasks where contaminant exposure may reoccur long after active remediation beneath a cap or cover. Most phytoremediation utilizes plants that voluntarily uptake heavy metals via their root systems and are natural metal accumulators, although this is not true for the generation of genetically engineered plants designed to increase the uptake of heavy metals or improve metal tolerance in plants. This innovative remedy can be cost-effective due to the low renovation costs of the contaminated sites; some don't require any human intervention. This method of removing metals is fast; it is a total solution, as metals can be removed from soil and groundwater for recycling in plants. It is a good idea in theory and can serve as a research link to remedy metal-deficient soils by adding required nutrients. [33][34]

7.2. Soil Amendment Techniques

Soil amendments, including organic amendments, chemical additives, and biochar, are promising materials to reduce heavy metal pollution. Soil amendment methods impede the availability and mobility of metals in soils due to stronger sorption, chelation, complexation, or precipitation of organic compounds on the surfaces of inorganic particles. Potentially toxic elements are immobilized in resistant compounds, which can transform from the bioavailable fractions; this increases soil fertility and the biological, chemical, and ecological functioning of soils and reduces environmental risks. Different techniques have been used to amend soils; these included amendments, lime, phosphate rock, organic amendments, and biological processes. Also, other techniques for managing heavy metal pollution have been proposed, considering non-target effects, uncertainties regarding their long-term effects, the natural sequestration abilities of carbon in soils, the effects of soil properties, and the scale and subject of field experimental investigations.

Empirical studies have confirmed that the treatment of soil with biochar and soil amendments can immobilize metals by improving the soil properties and stabilizing the organic carbon after being introduced into soils. In the context of soil pollution, amendments are promising materials in ameliorating polluted soils and increasing the use of waste products as an approach to minimizing environmental risks. However, several challenges have been brought about because pure soils were used in the research that investigated amendments in soils, and the feasibility of producing agricultural products on amended soils remains unknown. Economic aspects are critical for considering remediation alternatives, but the long-term risks remain unknown. Integrated alternative management solutions for waste treatment have been recently proposed to combine biochar and composting. This delivers enriched substrates that can be used in various agricultural fields—e.g., a combination of soil amendments and adapted biochar to immobilize waste in order to grow energy that can be utilized in one year. Carboxyl and alkyl were used to immobilize copper in the compost and biochar; for example, one global warming potential of 6000-copper load of 2000 per kilogram was immobilized in the enriched substrate after treatment with the organic amendment biochar.

The immobilization of metals is particularly important for biogeochemical cycles and maximizing productivity and resistance against natural stresses such as drought, high temperatures, and other adverse effects. Alternative management methods for the immobilization of metals, via chelative and complexing processes, are now under consideration to address the potential immobility and biodegradability of substrates in the long term. Future research will use these technologies to grow specific plants and test the immobilization methods. To have a positive effect on productivity, this research will help restore soil health and promote the use of substances as "feeds" for polluted sites. The aim of recent research on processing waste was to look for "substances for feeding" that are mainly characterized by immobilizing the metals leaching from waste compost when they are applied to clean soils. The small part of studies on the remediation of polluted soils resulted in chelating and complexing metals to increase the amelioration of soil properties and promote superior plant growth. Biological investigations were conducted via the use of selective plant species and a trial experiment as well as an empirical study. [35][36]

8. Future Research Directions

From the discussion in the preceding section, it is apparent that significant progress has been made in the identification of research needs for heavy metal soil pollution. The development of advanced technology for the detection of pollution sources, the identification of hotspots of soil metal contamination, and the exploration of processes and mechanisms of metal accumulation in plant and animal products are important areas for future research. Research on the development of suitable management options to rehabilitate polluted soils is also urgently required, including the potential of employing currently available and novel technologies for the in-situ management of soil heavy metal contamination. Nanotechnology is an emerging area with great potential to deliver new options in the detection, monitoring, and remediation of environmental pollution. Recent developments in biotechnology and the use of the emerging field of bioremediation may provide opportunities for novel methodologies to effectively rehabilitate metal-contaminated sites. Preliminary research on the potential for bioremediation to remediate heavy metal contaminated soils is also recommended.

To develop a comprehensive understanding of heavy metal soil pollution, interdisciplinary approaches may also provide significant insights into the potential for interaction between metals and soil biota, the bioavailability of heavy metals, and develop a framework for assessing and managing heavy metal soil pollution impacts. It is recommended that there be more frequent assessments of the status of heavy metal soil pollution and a greater appreciation of the long-term changes in metal contaminant quality guidelines. This will require a cooperative approach involving research institutions, government, non-government, private industry, public participation, and markets in driving innovative solutions for the effective management of heavy metal soil pollution. In view of recent developments in metal risk assessment, metal properties, and innovative remediation technologies, the review identifies potential directions for future research that are required to most effectively develop innovative solutions to a suite of heavy metal soil pollution scenarios. Finally, it is essential to foster a greater understanding of the economics and social issues related to heavy metal soil pollution in order to develop a suppression management approach. The inherent challenges of managing a heavy metal soil pollution issue require that this research be proactively targeted to develop a comprehensive assessment of the nature and scale of the issue, the impacts associated with pollution events, and the susceptibility of vulnerable systems to minimization practices. Given that heavy metal soil pollution occurrence makes it impossible to return to pre-pollution conditions, there is a particularly serious need for a consistent and efficient research policy. It is therefore recommended that long-term research should focus on the relationship between heavy metals in soil and plant uptake and hence transfer further potential impacts in animal and human health. Future research priorities must also identify ways to reduce public health costs associated with heavy metals in soil, and further consideration is needed to identify any other areas where further improvement can be realized. It is important that future research not only assesses the longer-term benefits to plants and soils but also investigates other potential sources of exposure that may contribute to increased health costs associated with heavy metals in soil. [37][38][39]

8.1. Emerging Technologies for Soil Remediation

provide a comprehensive overview of novel and emerging solutions for the potential remediation of heavy metal-affected soil. While some of these treatments show only the early signs of promise, such as phytoremediation enhancements using mycorrhizal symbioses and designer plants, the technology is considered to be approaching maturity for other methodologies such as the use of nano-zero valent iron nanoparticles to remove arsenic from heavily contaminated soils. Likewise, bioremediation, which typically involves the use of microorganisms to bind, break down, and transform environmental contaminants, is a fast-growing field, with recent innovations focusing on improvements of existing methods such as three-dimensional structure-based electro bioremediation and the development of enzymatic assays to detect and degrade pesticides. This change of approach is driven by recent advances in microorganism characterization tools including metagenomic and single-cell techniques, leading us to better understand and bypass the limitations of state-of-the-art bioremediation technologies.

This approach could then be scaled up in the future to the application of enzyme mixes to wastewater reservoirs and sites affected by agricultural, industrial, or military contamination, thus introducing a new green economy for the treatment of water and sewage. Some systems have been integrated to offer cost-effective and efficient heavy metals removal such as improved chelator-assisted phytoremediation and biological remediation. The latter technology typically involves the use of microorganisms to bind, take up, and transform environmental contaminants, and therefore reduce their availability and mobility. While some methods effectively apply naturally occurring soil bacteria and plants, other novel technologies are applied in a variety of human-engineered systems such as natural wetlands. The articles included in this Special Issue therefore address relevant gaps in the long sequence of practices and technologies that could be combined with conventional approaches. [40][41]

9. Conclusion

Now the problem of soil pollution is the main problem in the field of agro-industrial complex and environmental protection. The objectives of the ecosystems chemical safety improve and the full land resource turnover promotion for the agricultural sector necessitate intensifying studies of heavy metals entry to soil. It is obvious that one of the main tasks is to establish the causes of their penetration into the soil environment. The most important of them are that metal pollutions form ecotrophic areas with high anthropogenic load on the ecosystems. An effective system is needed from scientific substantiation of regulatory support that ensures the safety and full functioning of soils, accompanied by rapid re-profiling in areas of tourist, recuperative and industrial infrastructure. Our analytical studies are of a unique nature because they have combined the efforts of specialists from several scientific units with implementers in regulating soil quality. The issue of soil pollution with heavy metals is extremely relevant; therefore, its study is the most important task for the scientific staff. The main purpose of the research is to study the conditions of the transition of the inorganic form of heavy metals in the territory of the Petrovsky district of the Saratov region and to establish the main causes of soil contamination. Today, it is necessary to carry out a number of studies in this direction. It is extremely important to create regulatory support ecological and hygienic, which will ensure the safety of the process of changing the functional purpose of soil objects, for agro-tourism and agricultural landscapes used in the construction and development of industrial infrastructure along with the implementation of valuable tourist and recreational activities. Scientists and soil science need to feel the pulse of ongoing changes in agriculture and environmental management.

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