

Review

Factors That Determine the Sorption of Mineral Elements in Soils and Their Impact on Soil and Water Pollution

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Abstract: Soil is an essential ecosystem, delivering valuable services such as the provision of food, energy and raw materials, carbon sequestration, water purification and infiltration, nutrient regulation, pest control and recreation. Therefore, soil is crucial for fighting climate change, protecting human health, safeguarding biodiversity and ecosystems and ensuring food security. Pollution of the soil by organic and inorganic substances is, therefore, detrimental to ecosystem services and/or human health. Heavy metals at harmful concentrations are highly detrimental, and here, mining activities are one of the main sources of soil pollution. According to studies conducted, some of the major soil factors affecting mineral (including P) sorption are time, soil pH, soil organic matter and iron and aluminum oxides of soils. This paper looks at sources of mineral element pollution, including heavy metals, as heavy metals are toxic to all living organisms, including humans. This paper also reviews both cationic heavy metals and inorganic anionic pollutants, such as phosphate and arsenic, as well as cationic, non-heavy-metal pollutants such as nitrogen and potassium.

Keywords: minerals; soil; pollution water; sorption; heavy metals



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1. Introduction

Soil and water are polluted by numerous types of organic and inorganic compounds and ions that are hazardous to the environment and/or human health when present in excessive amounts. This review paper addresses only pollution of soils and water by inorganic compounds and ions. It aims to cover most of the major inorganic pollutants. Numerous research papers deal with a specific one or only few of these. Several review papers deal with a specific group of these, for example, pollution by potentially harmful or toxic cationic heavy metals [1–3]. Others deal with pollution by anionic ions, such as phosphates (e.g., Penn and Camberato [4]).

Soil is potentially an effective sink to remove potentially hazardous ions from the environment. Soils can do this by (i) reducing the bioavailability of the pollutant, i.e., the availability of the element for uptake by plants, thus preventing it from entering the food chain and/or (ii) reducing the mobility of the pollutant, thus preventing it from entering water bodies through leaching. The ability of a specific soil to do this efficiently depends essentially on the mineral composition of the soil and the influence of other factors on the physico-chemical reactions between specific soil minerals and specific pollutants. Soil pH, called the “master variable” in soil chemistry by Penn and Camberato [4], due to its huge impact on the chemical reactions of plant nutrients and pollutants in soils, is the most important of these factors.

In order to be able to identify how efficient a specific soil can potentially be to capture and immobilize pollutants and, thus, remove them from the environment, it is essential to understand the basic soil chemistry involved in the soil mineral–pollutant reactions.

“Soil chemistry” is emphasized, because it is different from and more complex than pure simple chemical reactions studied in a test tube. “Pollution” refers to the presence of a potentially harmful substance at a level at which is harmful to the environment, plants, animals and/or humans. Such a substance is called a pollutant. “Contamination” refers to the presence of a substance that is not potentially harmful to the environment, plants, animals and/or humans, even at high concentrations. It can also refer to the presence of a potential pollutant at a concentration that is so low that it is not harmful. All pollutants are contaminants, but not all contaminants are pollutants.

Regarding the abovementioned, some important soil “terms” play a role and are important to understand. As defined by Sposito [5], “any removal of a compound from solution to a solid phase we define as sorption, whereas the inverse process—the release of ions or molecules from soil solids into solution—we define as desorption. These definitions are universally applicable and useful when one has no knowledge of the actual sorption mechanism. When such knowledge is available, we can refer to the accumulation of chemicals at the solid–liquid interface as adsorption, the accumulation of molecules within existing solids as absorption, and the incorporation of substances within an expanding three-dimensional solid as precipitation. When discussing sorption processes, we call the adsorbing/absorbing solid phase the sorbent; solutes in the liquid phase that could potentially sorb are known as sorptives, and constituents that accumulate on or within a solid are termed sorbates” [5].

Most heavy metals are environmentally stable, non-biodegradable and toxic to living organisms. They affect human health through their accumulation in plants and animals [6]. According to Musa et al. [6], heavy metals are introduced into the soil through sources such as combustion, extraction processes, agricultural run-off and transportation of dissolved metals. In industrialized countries industries, especially metal processing industries, are the main sources of heavy-metal pollution of soils [7]. This has serious implications for the production of food crops on such polluted soils and, thus, on food security, since it may enforce withdrawal of such land from food crop production [7,8]. In less developed countries, with low levels of industrial activity, mining activities, especially gold mining and open-cast coal mining, are often the major, sometimes very large, sources of heavy-metal pollution [9]. Toxic levels of the metalloid arsenic (As) is often a serious pollutant [8] and is, for example, strongly associated with gold mining activities [9]. Moreover, regular use of heavy-metal-polluted water in irrigated agriculture leads to soil pollution, with toxic levels increasingly being built up in the soil.

Pollution of soils and water by excessive levels of elements, such as P and N, which are major essential nutrients for plants, animals and humans, is widespread and serious, in both highly developed and less developed countries. Eutrophication of water bodies is one of the major concerns related to these.

The aim of this paper is to highlight soil as sink for pollutants, which can minimize their negative impacts, emphasizing the role of different soil minerals and a factor such as soil pH in this. It concentrates on the situations in less developed countries and contrasts these with highly developed industrialized countries.

This paper intends to give an integrated interpretative review and not to just list topics on which research has been done without molding their findings into context.

2. Materials and Methods

Since this is a review paper, it does not report any new experimental work done especially for it. It, therefore, also does not report on any experimental procedures. An assessment was done of peer reviewed publications. A survey was also done of high-quality research that has not been reported in peer-reviewed papers, such as in theses or congress proceedings. The career of the second author started in 1962 when serious problems arose due to fast intensification of agriculture, industrial development and urbanization. Over many decades, he became aware of the fact that this “intensification” occurred during the peak period of basic soil chemistry research aimed at solving problems identified during

empirical field experimentation and by observations in the field (1950s to 1970s). Penn and Camberato [4] also recently pointed out that much basic soil phosphorus (P) chemistry research was, for example, carried out between the 1950s and 1970s. Good science does not become obsolete, but unfortunately, much of the valuable contributions in regard to soil chemistry from that period, and earlier periods, have become unknown or difficult to trace or access at present. In this paper, an attempt is made to also highlight some of that research again.

3. Results

3.1. Inorganic Pollutants That Are Not Heavy Metals

There are a number of inorganic pollutants that are not heavy metals. Only four of these are discussed here, namely, phosphorus (P), arsenic (As), nitrogen (N) and potassium (K).

3.1.1. Phosphorus

Phosphorus is a widespread and serious environmental pollutant. There are two main reasons why P pollution, despite being so widespread, does not receive the same prominence as heavy-metal pollution, namely:

- It is different from the other main pollutants by not being toxic to humans or animals at high concentrations.
- In nature, P is the plant nutrient of which deficiencies in soils are most widespread, and much research is focused on how to increase the plant-available P contents of soils and how to reduce the fixation of applied P into forms that are not available to plants.

P pollution of soils in cultivated areas, from rain fed croplands to highly intensive vegetable and fruit production, is becoming a widespread serious problem in the form of excessive plant-available soil P levels [10–12]. Excessive P levels in soils are seldom referred to as the “pollution” of soil, because it is usually caused by deliberate application of P-containing inorganic fertilizers or organic amendments with relatively high P contents, such as dairy or chicken manure or compost containing large proportions of such manure [12]. Plant-available P levels build up in fertilized soils because P is immobile in the vast majority of soils and is retained where it is applied, even in soils with a low capacities to fix P into forms that are not available to plants, as seen in Table 1 [13]. These were all sandy soils with only between 7.8% and 11.4% clay in the topsoil and very little silt. Their pH (Water) levels were between 6.5 and 7, i.e., in the range where strong fixation of P is not expected. Soil 1 was a virgin soil that had never received any P application, having 3.5 mg·kg^{−1} Bray-2 extractable P in the topsoil (plough layer). The other sites were all in grain fields that had been fertilized and irrigated for about 30 years. Firstly, the build-up of plant-available P in the plough layer is clear from the plough layer Bray-2 P levels ranging between about 20 and 100 mg·kg^{−1}. Secondly, the lack of movement of P from the plough layer to the soil layer immediately below it is also clear.

The lack of leaching of P in these sandy soils may be a surprise to people who are not familiar with these soils. They are not highly leached and not highly weathered and are in a semi-arid area and do not have a high content of “free” sesquioxides (aluminum and ferric oxides). There are a few million hectares of such soils in the region (South African maize producing area). The explanation for the ability of the soils to bind P into non-soluble forms is found in their mineralogy: these were uniformly bright red sandy soils. Their color is due to a complete covering of the sand grains, which consist almost exclusively of quartz, an inert mineral, by an extremely thin layer of red ferric oxides, mainly hematite. This is proven by the fact that the sand grains have been found to be colorless quartz grains where the ferric oxides were removed with citrate–bicarbonate–dithionate (CBD) treatment. The phosphate ions are sorbed to the ferric oxides, but not by classic adsorption, and so are retained against leaching by water. This is supported by the findings of another study in the area [14,15]. In the region, there are also large areas with yellow-brown sandy soils, which have even stronger retention of P. Here, the main ferric mineral is goethite,

a ferric oxyhydroxy mineral in which exchange between hydroxide in the mineral and phosphate ions, a kind of ligand exchange, occurs additionally. In a rain-fed maize no-till field experiment in the area on a yellow-brown sandy soil with topsoil pH (KCl) of 6.1, Haarhoff [16] found that the Bray-1 extractable P content of the 0–15 cm soil layer was $64 \text{ mg}\cdot\text{kg}^{-1}$, that of the 15–30 cm layer was $36 \text{ mg}\cdot\text{kg}^{-1}$, and at 30–60 cm, it was only $4 \text{ mg}\cdot\text{kg}^{-1}$. Note that Bray-1 P figures are approximately 50% of those extracted by Bray-2. The significant value in the 15–30 cm layer can be related to the depth of P incorporation to about 25 cm under conventional tillage prior to changing to no-till.

Table 1. Bray-2 P levels of red sandy soils at Vaalharts irrigation scheme (extracted from Eloff and Laker [13]).

Site	Soil Layer	wt. %	Bray-2 P Content ($\text{mg P}\cdot\text{kg}^{-1}$ Soil)
1	Topsoil	9.5	3.5
	Subsoil	10.5	0.0
2	Topsoil	9.2	21.8
	Subsoil	8.2	0.8
3	Topsoil	8.2	29.6
	Subsoil	8.2	1.5
4	Topsoil	10.6	36.7
	Subsoil	13.1	5.6
5	Topsoil	7.8	38.5
	Subsoil	8.3	0.4
6	Topsoil	9.4	40.2
	Subsoil	12.7	5.3
7	Topsoil	9.5	49.3
	Subsoil	13.0	1.9
8	Topsoil	11.4	51.9
	Subsoil	9.9	1.5
9	Topsoil	8.4	61.3
	Subsoil	10.4	0.0
10	Topsoil	10.9	98.6
	Subsoil	11.9	2.3

Excessive P levels, which are harmful to plant growth and, thus, crop performance, are eventually built up in some soils. At Site 10 in Table 1, with a Bray-2 P content of $98.6 \text{ mg}\cdot\text{kg}^{-1}$, wheat yields were reduced relative to the optimum [17]. At a farm in the same area, a reduction of about 50% in wheat yields were found at a Bray-2 P level of $110 \text{ mg}\cdot\text{kg}^{-1}$. Bray-1 P values are about 50% of those of Bray-2, and the authors have found several incidences of yield reductions in various crops at Bray-1 P levels of above $50 \text{ mg}\cdot\text{kg}^{-1}$ [10,12]. Very high plant-available P concentrations in soils are not directly toxic to plants. They exhibit indirect toxicity, however, by inducing deficiencies of certain micro-nutrients, such as Zn, Fe and Mn, with serious negative impacts on plant growth [10,12]. In macadamias, several cases of even virtual death of plants due to induced Fe deficiencies caused by highly excessive P levels have been found [11,12].

Recent discussions from an environmental perspective on the fixation of P in soils almost exclusively treat it as a simple adsorption process (e.g., Vardhan et al. [1]. The reality is that fixation (sorption) of phosphorus in soils, especially strong fixation, entails much more than adsorption [18,19]. P in soils is present as the orthophosphate anions $\text{H}_2\text{PO}_4^{-1}$, HPO_4^{-2} , PO_4^{-3} , which, of these dominates, depend on the pH of the soil [1]. $\text{H}_2\text{PO}_4^{-}$ is

dominant in most soils and is even at high pH still present in significant quantities. At the pH values that predominate in the vast majority of soils, the soil minerals, mainly the layer lattice clay minerals, have negative charges. Cations are adsorbed to these negative charges, but anions such as the phosphate ions are repelled by them. At these pH levels, very little or no Cl^- or NO_3^- is adsorbed and retained in the soil. However, orthophosphates (PO_4 group) and arsenate (AsO_4) are bound in these soils, although not as strongly as at low pH.

Strong fixation of large quantities of P occurs in highly weathered, strongly acidic soils, such as those found in humid tropical and subtropical areas. In these soils, large quantities of P is fixed into forms that are not plant-available, unlike the situation in the red and yellow-brown sandy soils described above. This poses problems in regard to P nutrition of crops in such soils [10,20].

The mineralogy of the clay fractions of the highly weathered soils differs greatly from those of less highly weathered soils. The clay fractions of the latter are dominated by 2:1 layer lattice aluminosilicates such as smectites (mainly montmorillonite) or micas (hydrated mica/illite). These are characterized by significant amounts of isomorphous substitution, giving moderate (illite) to high (montmorillonite) numbers of permanent negative charges on the minerals. These are called permanent charges because they are not pH dependent.

In highly weathered soils, the contributions of the 2:1 layer aluminosilicate clay minerals to the clay fraction of the soils become minimal. The 1:1 aluminosilicate minerals, mainly kaolinite, become dominant in the soils. Little or no isomorphous substitution that leads to permanent negative charges occurs in the 1:1 minerals. Thus, kaolinite has only a small number of negative charges. It dominantly has variable charge that is pH dependent [4,18]. These charges originate from reactions at exposed hydroxyl groups of alumina octahedra at broken edges of the mineral [18]. It develops both negative and positive charges. The number of negative charges increases, and the number of positive charges decreases with increasing soil pH and the reverse as the soil pH decreases. Kaolinite is amphoteric, meaning that above a certain pH, negative charges dominate, and below that pH, positive charges dominate. Between these two is the “point of zero charge” (PZC). In strongly acidic soils, kaolinite is below its PZC, i.e., it is dominated by positive charges onto which the negatively charged phosphate ions are adsorbed.

Phosphate is, furthermore, bound to kaolinite by ligand exchange with hydroxyls in the alumina octahedral layer of the mineral. Ligand exchange is a much stronger P sorption mechanism than simple anion adsorption [4]. This type of reaction is not possible in 2:1 aluminosilicate minerals, because there, the single alumino octahedral layer is sandwiched between two silica tetrahedral layers.

Very strong fixation of large quantities of P in strongly acidic highly weathered soils is due to the presence of large quantities of sesquioxide minerals, as outlined in the comprehensive review of the range of chemical processes and mechanisms involved in P fixation by these oxides/hydroxides by Penn and Camberato [4]. Sesquioxides are minerals with the general composition R_2O_3 , with R being Al^{+3} or Fe^{+3} (ferric iron). The most common Al mineral is gibbsite. The most common ferric minerals are hematite, magnetite and the two yellow ones, limonite (hydrated form) and goethite (having hydroxides as part of the mineral). These are often amorphous.

These oxides are more strongly amphoteric than kaolinite, thus having large numbers of positive charges at low soil pH onto which phosphates can adsorb. Secondly, ligand exchange of phosphates occur in them. These are followed by precipitation of P together with Al and Fe to form minerals of the variscite ($\text{AlPO}_4 \cdot 2\text{H}_2\text{O}$)-strengite ($\text{FePO}_4 \cdot 2\text{H}_2\text{O}$) series or non-crystalline Al and Fe phosphates [4], which all have very low solubilities. This occurs especially at high P solutions, as will happen during P pollution. Series of various equilibrium reactions occur over time between adsorbed and precipitated P and between P in different minerals by means of dissolution/decomposition and re-precipitation/recrystallization into less soluble forms [4,19]. From a point of using soil as a potential sink to trap P from pollution sources and prevent it from reaching water bodies,

the advantage of these shifts is that in these soils the adsorption capacity of the soil for P cannot actually be saturated with P, and very large quantities of P can be immobilized.

The huge impact of the difference between the mineralogies of the clay fractions of soils with predominantly 2:1 aluminosilicate clays and sesquioxide-rich soils on P sorption was very clearly shown in a comparative study by Ellis [21]. He compared several soils from Michigan, USA, with two highly weathered sesquioxide-rich soils from the eastern Highveld of Mpumalanga province in South Africa in regard to their adsorption maxima and the quantity of P required to bring the P concentration in the soil solution to an ideal level. A Griffin series soil [22] from Mpumalanga had a P adsorption maximum that was 10 times higher than that of a Parkhill soil from Michigan. However, 67 times more P would have to be applied to the Griffin soil than to the Parkhill soil to bring the P concentration in the soil solution to the desired level of $0.2 \mu\text{g P/cm}^3$ (Table 2). In practical terms, Ellis [21] explained that this would mean that a farmer would have to apply 0.26 metric tons (260 kg) of single superphosphate per hectare to the Parkhill soil to bring its P to the desired level, but on the Griffin soil, a farmer would have to apply 18 tons P to achieve the same. The same trend was observed for a Balmoral series soil compared with a Warsaw soil from Michigan, but here, the difference was not so big. A notable difference between the Griffin and Balmoral not highlighted by Ellis [21] was that the upper subsoil of the Griffin was yellow-brown and that of the Balmoral red. Thus, the mineralogy of the Griffin was predominantly goethite, having hydroxyls, and of the Balmoral hematite. Thus, it is logical that the Griffin would have a more extreme P fixing capacity, as is clear from previous discussions.

Table 2. Comparison between the P fixing capacities of upper subsoils of soils from Michigan, USA, and highly weathered soils from KwaZulu-Natal Province, South Africa (Adapted from Ellis [21]).

Soil Series	P Adsorption Capacity (mg P/100 g Soil)	Quantity of P Required to Increase the Activity of the P in Soil Solution to $0.2 \mu\text{g P/cm}^3$ (mg P/100 g Soil)
Munising ¹	23.8	8.9
Warsaw ¹	49.0	13.4
Parkhill ¹	8.8	1.1
Brookston ¹	16.0	4.8
Griffin ²	88.0	74.5
Balmoral ²	42.5	33.7

¹ Soils from Michigan. ² Soils from KwaZulu-Natal.

The concern of environmentalists regarding pollution with P is about its major role in the eutrophication of water bodies [23]. Eutrophication is the enrichment of a water body with plant nutrients above the normal background value. Eutrophication leads to excessive growth of harmful organisms, such as algae, or plants, such as water hyacinths, in water bodies. Phosphorus and nitrogen are the two main elements involved in the eutrophication of water bodies. Because a low P level is usually the most limiting nutrient in natural systems, increasing the P level through P pollution has the biggest eutrophication impact.

Pollution of P can be from point sources or from non-point sources [24]. Point sources include industrial sites, municipal sewage works and intensive agricultural practices such as feedlots, dairies, piggeries or chicken farming. Non-point sources include cultivated fields, informal settlements and runoff from urban areas [25,26]. The relative contributions of P by household and industrial detergents and agriculture are usually estimated as about $45.6 \text{ kt}\cdot\text{year}^{-1}$ (76%) and $12 \text{ kt}\cdot\text{year}^{-1}$ (20%), respectively. Four per cent comes from background sources [27]. The P from sewage works, urban runoff and industrial sites originates from P-containing household (former two) and industrial (latter) detergents [28,29]. In intensive agriculture, it originates from P-rich manures [11]. In informal settlements,

characterized by poor or no sanitary systems, it originates mainly from human excreta. In cultivated fields, it originates from fertilizer and/or manure applications.

Before 1945 detergents did not contain P, but after that, there was a sharp increase in the P contents of detergents, as so-called “builders” [30]. Eutrophication by P of important water bodies escalated and became a major environmental concern. In the USA, it was triggered by the eutrophication of the Great Lakes. So, in 1970, a movement towards reducing P in detergents started. By about 2010, total bans on the use of P in detergents were imposed in many countries, such as the United States, Canada, Australia and the European Union. According to Ngatia and Taylor [31], this control of point sources has led to the non-point sources agriculture and urban runoff becoming the drivers of eutrophication by P, with agriculture being the main source. According to them, application of fertilizers and manure are to be blamed for this.

Data collected by Van Puijenbroek et al. [32] during 1970 and 2010 and projections for 2050 give a rather different picture regarding P-free household detergents. Globally, P emissions from laundry detergents more than doubled from 241 million kg P·year⁻¹ in 1970 to 491 million kg P·year⁻¹ in 2010 (Table 3). A significant reduction from 69 million to 45 million kg P·year⁻¹ in North America and a major (70%) reduction from 108 million to 32 million kg P·year⁻¹ in Western and Central Europe were more than counteracted by a large increase in Central and South America and a huge (more than 40 fold) increase in the China region. In both 1970 and 2010, P emissions from laundry detergents were small in areas dominated by poor countries, increasing from 1970 to 2010.

Table 3. Global and regional trends and projections for total emission of phosphorus by laundry detergents (106 kg P/year) (adapted from Van Puijenbroek et al. [32]).

Region	1970 *	210 *	2050B **	2050W ***
North America	69	45	3	159
Central and South America	13	83	11	180
Middle East/Northern Africa	6	51	23	149
Sub-Saharan Africa	3	12	283	111
Western and Central Europe	108	32	7	166
Russia and Central Asia	17	34	7	71
South Asia	2	22	125	258
China Region	4	167	6	410
Southeast Asia	1	5	41	82
Japan and Oceania	19	40	2	73
Global total	241	491	509	1658

* Actual values for 1970 and 2010; ** 2050B = projected best case scenario for 2050; *** 2050W = projected worst case scenario for 2050.

The 2050 projections by Van Puijenbroek et al. [32] show that economics is a very strong driver of the use of P-containing laundry detergents and not just the strength of environmental legislation. Thus, under strong environmental legislation, P emissions from laundry detergents are projected to drop to very low levels in areas where economies are projected to be fairly strong, such as, for example, North America, Central and Western Europe, Central and South America and the China region. However, the global emissions are projected to increase slightly above the 2010 value at 509 million kg P·year⁻¹, due to huge increases in regions that are expected to be dominated by countries with weak economies, namely, Sub-Saharan Africa, South Asia and Southeast Asia (Table 3). The worst case scenario projected by Van Puijenbroek et al. [32] would give a more than threefold increase in P emissions from laundry detergents by 2050, with high values all over the world (Table 3). The latter is described as a situation with weak environmental policy and use of P-containing detergents is allowed. It is inter alia projected that in countries

where P-free detergents are presently used its use will decrease by 50%, with P-containing detergents preferred instead.

The latter scenarios should be seen against the background that the P-free detergents are less effective than P-containing detergents, especially for heavily soiled (very dirty) garments [32], and are also harsher on fabrics and washing machines [33]. Heynike and Wiechers [34] estimated the loss in value of washing machines and fabrics in South Africa in 1983 would amount to USD 4.3 million and USD 70 million, respectively, at the then exchange rate of R1 = 1.12 USD. In addition, the P-free detergents are more expensive [33]. Thus, according to Pillay and Buckley [33], the best option scenario in their study was 35 to 1 in favor of not reformulating detergents to be P-free.

It is clear that reformulating detergents to be P-free would be feasible for rich countries, but not realistic or feasible for poor countries. A major problem in this regard is that scattered rural villages in the latter areas do not have efficient sewage systems or sewage treatment plants for the removal of P. The question then is to what extent soil can serve as an effective sink to remove P before it reaches water bodies, and how understanding the different mineralogies of different soils and their abilities to fix P will determine strategies in this regard. The paper of Ellis [21] then ends in a very important paragraph in this regard, namely that the results “would indicate that the Griffin or Balmoral soils would have a great potential for the removal of P if they were located near sources of wastewater. ___ Soils from Michigan, on the other hand, would require larger land areas to accomplish the same quantity of P removal.” This emphasizes the importance of soil mineralogy in regard to P removal and the potential mitigation of P pollution. The very big ability of the abundant highly weathered strongly acidic sesquioxenic soils to fix large quantities of P can be a very important asset in poor countries in the tropics and sub-tropics to counteract the fact that P-free detergents are not feasible for such countries. In the case of crop production, lime is applied to strongly acidic soils to reduce their capacities to fix P into forms that are not plant-available, in order to improve crop response to applied P. In the case of using soil to remove as much as possible P and fixing it into non-soluble forms so as to minimize P pollution, liming should not be done.

From the point of P pollution of water bodies, the red and yellow-brown sandy soils could act as an effective sink to trap P-rich effluents disposed on them, preventing the P from leaching into water bodies. From a crop production point of view, the negative aspect is that these soils do not fix large amounts of P into forms that are not plant available, and plant-available soil P levels are built up easily to levels that are excessive or even harmful to crops [10,11,20]. Thus, irrigating cropped areas with high amounts of P-rich effluents would not be wise. Where possible, designated disposal land would have to be identified.

Contrary to the red and yellow-brown sandy soils, sandy soils in which the inert primary minerals, mainly quartz and some others such as plagioclase, are not coated with amorphous ferric oxides or hydroxides do not have the ability to sorp phosphates. These are typically soils with light grey to white horizons, called albic horizons in international soil literature [35] or E horizons in the South African soil classification system [36]. In addition to not having a sorption capacity for P, these soils have low water storage capacities and high permeability. Thus, they are subject to intensive leaching of even P. They would consequently not be suitable for disposal of P-rich effluents. Mulidzi [37], for example, found major leaching of P from winery effluents disposed of by means of irrigating small areas of cultivated pasture in soils that do not have ferric oxide coatings. Some of these areas were near streams and posed potentially serious eutrophication hazards. The P in the effluents originated mainly from detergents used to clean wine tanks and equipment. Table 4 presents results for one such case, showing how the peak P content over time moves from the topsoil during the December tank cleaning period to the upper subsoil and then to the lower subsoil, before moving out of the soil by May.

Table 4. Changes in Bray-1 extractable P levels ($\text{mg}\cdot\text{kg}^{-1}$) with soil depth over time in a bleached (Albic/E) soil irrigated with winery effluent (extracted and adapted from Mulidzi [37]).

Month	Soil Depth (cm)		
	0–30	30–60	60–90
December	116	46	81
January	39	25	17
February	27	120	81
March	16	16	44
April	36	56	170
May	33	21	24
Unirrigated control	33	23	23

Organic compounds reduce the fixation of P in soils [19]. Two mechanisms in this regard mentioned by Kardos [19] are important:

1. Large molecule organic compounds are predominantly present as anions in soils and will, thus, compete with phosphates for adsorption sites. In other words, it blocks the first step in the series of P-fixing processes.
2. Small molecule water-soluble compounds, such as various organic acids, form chelates with Al and Fe and prevent them from reacting with phosphates.

A clear-cut example of the effect of the latter was found by Mulidzi [37] where a winery “ponded” effluent on a red sandy soil. Of course, ponding does not take place in a sandy soil—its permeability is too high and the effluent simply drains through. Winery effluents contain quite large quantities of water-soluble organic compounds (organic acids, phenols) that leach right through sandy soils, but with significant differences between wineries [37,38]. Studies to a depth of two meters in the case of the red sandy soil found that the organic compounds in the effluent leaching through the soil had stripped the thin iron oxide layer from the sand grains. The soil inside the pond was no longer red, but light grey, qualifying as an albic or E horizon. The winery effluent introduced a high amount of P at this site and also had an extremely high soluble organic matter content. The P content of the soil in the pond was found to be very high right through to the depth of 90 cm to which samples were taken for analyses, indicating little fixing of P in the soil and its leaching through the soil into water bodies (Table 5). This was in stark contrast to the virtually complete lack of P movement in red sandy soils similar to the unaffected soil outside the pond in the same region discussed earlier.

Table 5. Movement of P applied to the surface of a red sandy soil due to co-application of a very high amount of water-soluble organic matter (adapted from Mulidzi [37]).

Month	Soil Depth (cm)		
	0–30	30–60	60–90
December	692	872	572
January	227	395	Nd
February	457	3173	Nd
March	313	138	126
April	549	858	Nd
May	133	626	124
Unfertilized control	23	33	Nd

Nd = not determined.

3.1.2. Arsenic

Mobilization of arsenic from rocks and soils into water bodies is of concern because it is a highly toxic element that poses serious threats to human and ecosystem health [39]. According to McBride [40] an element like As, which is more toxic to humans than to plants, poses a very insidious hazard to human health, as it may accumulate in crops to concentrations that are toxic to humans, while the crops do not show any signs of phytotoxicity.

Arsenic is often an important component of gold deposits, and gold mining is frequently associated with arsenic pollution [39,41]. Processing of gold-bearing minerals that contain arsenopyrite or other arsenic-containing sulfide minerals can lead to the As pollution of water bodies. Aucamp [9] pointed out that in South Africa, gold mine slime, deposited as slimes dams, is a source of toxic element pollution, since the soluble salts that precipitate on the surface of slimes dams contain highly soluble concentrations of various toxic elements, including As. This is because in South Africa, gold mining is done from the so-called Black Reef formation. Determination of the “average maximum trace element content” of pyrite of the Black Reef formation showed that As was the element with the second highest concentration out of 22 elements. As was absent in white precipitate on paddocked tailings at a Machavie gold mine that had been abandoned 60 years earlier near Potchefstroom in South Africa but had a much higher water-soluble concentration than any of Co, Cr, Cu, Ni, Pb or Zn in the yellow precipitate [9]. He found that in 97% of the tailings samples and in 82% of the polluted top soils around the tailings, As exceeded the permissible Dutch A values, but noteworthy, less (60%) in ferruginized soil samples (i.e., samples containing ferric oxides). Furthermore, 83% of the tailing samples had As levels exceeding the Dutch B values, but for topsoil, it dropped to between 19% and 33% and for the soil containing ferric oxides to 0%. The latter is very significant in view of further discussions. As was identified as a priority pollutant according to the Dutch C screening values.

In rural household gardens in Limpopo Province, South Africa, soils were found that were heavily contaminated with As. The specific site is located in the Giyani Greenbelt Zone, characterized by abandoned mines and artisanal mining activities [42].

Use of arsenic compounds as insecticides also pose As pollution hazards. Ramudzuli and Horn [43], for example, studied the situation at an abandoned cattle dip tank in a rural area in the far north of Limpopo province, South Africa. The previous government used arsenic-based dip solutions for the control of East Coast fever, a tick-borne disease, in cattle. Numerous such dip tanks were constructed in deep rural areas all over the country for the control of tick-borne diseases. It was compulsory for people to take their cattle regularly for dipping. Ramudzuli and Horn [43] found that significant proportions of soil samples from around the former dip tank site contained As levels above $2 \text{ mg}\cdot\text{kg}^{-1}$ and a few even more than $30 \text{ mg}\cdot\text{kg}^{-1}$. It must be kept in mind that a lot of dip solution drips from cattle onto the soil around a dip tank. Ramudzuli and Horn [43] are concerned about the fact that houses are now being built to within 50 m from the abandoned dip tank. Rural people also usually grow vegetables for home consumption around their homes.

Aucamp [9] summarized the discussions of McBride [40] and Alloway [44] on the chemistry of As in soils. In aerobic soils, as the vast majority of soils are, arsenic is mainly in the form of As (5+), as arsenate, i.e., AsO_4^{-3} . From this, it is not surprising that the chemical behavior of arsenate in soils is very similar to that of phosphate. Arsenate is most strongly fixed by sesquioxides and most effectively fixed at low pH values. It, therefore, has low mobility in strongly acid soils with high clay or sesquioxide contents. In neutral to alkaline soils, i.e., at higher pH, As becomes more mobile, especially if it is a sodic soil. This is a problem where As is one of the toxic pollutants together with a range of toxic cationic heavy-metal pollutants, as is often the case with gold mine tailings [9,41]. As is discussed later, those cations become very mobile in strongly acid conditions, and the pH must be increased to lower their mobility. However, by doing that, the mobility of arsenic will be increased.

The pH of the paddocked tailings was very low, with an average of 3.4 [9]. It is, thus, not surprising that As did not move vertically downward into the soil below the tailings. However, As-containing tailings were distributed from the paddock in the direction of a nearby stream through erosion. There was a very sharp spike in the concentration of As in the overlying distributed tailings at a seepage line formed at the contact between the sandy colluvium soil near the paddock and clayey alluvial soil towards the stream.

Because of the similarities between phosphate and arsenate, they compete for the same adsorption sites and other fixation mechanisms in soils. Phosphate outcompetes arsenate for adsorption and fixation, especially on ferric oxides [41]. Thus, the application of high P levels to soils causes less arsenate to be fixed and leads to a higher mobility of As. This causes more leaching and transport of As to water bodies. As from As-rich mine tailings or from other potential polluting sources could be effectively fixed in soils with low pH and high contents of ferric minerals. However, the addition of high P levels to such soils must be avoided for this to be effective.

3.1.3. Nitrogen

High N and P levels are the main causes of eutrophication of water bodies (e.g., Lee [45]). Nitrogen is present mainly in inorganic forms in water, representing 60–100% of the total N. These are predominantly nitrate (NO_3^-), nitrite (NO_2^-) and ammonium (NH_4^+), with nitrate being the most important. Nitrate is not only a cause of eutrophication, but elevated nitrate levels in drinking water also have very serious human health implications [46]. The longest and the best known of the latter is methemoglobinemia (“blue disease”) in infants. Diseases that are aggravated by nitrate in adults include colorectal, bladder and breast cancer and some other diseases. If nitrate reduction in the human body is not fully completed, N-nitroso compounds (nitrosamines) accumulate and these are carcinogenic. It was found that anti-oxidants prevent the accumulation of nitrosamines in the stomach [47]. The second author of this paper developed an integrated model describing the interrelationships between environmental factors (with geology and soils key components), agricultural practices and esophageal cancer incidence rate [48].

There are various sources of high nitrate levels that enter water bodies. Excessive application of inorganic nitrogen fertilizers to croplands is often believed to be the main source of nitrate that reaches water sources [45]. This is in many areas an important source, especially in intensive cropping systems, such as irrigation schemes. It is, however, not nearly the only source and, in some areas, not nearly the most important source, however (e.g., Zhao et al. [49]). In or near urban areas, nitrate pollution is mainly from leaking sewage systems and septic tanks, industrial spillages, leachates from landfill sites and fertilizers which are applied in gardens and parks [50]. In areas with highly intensive livestock production systems, such as dairy farming, land application of excessive amounts of manure is the main source of nitrate pollution of water bodies [50].

Contrary to phosphate, nitrate is not sorbed in soils at the pH levels prevailing in most soils of large parts of the world [18]. Furthermore, the clay fractions of these soils are dominated by clay minerals, such as illite and montmorillonite, with moderate to high amounts of negative charges and virtually no positive charges. Apart from not being adsorbed, nitrate is subject to “negative adsorption” [18], i.e., being repelled by the negative charges and pushed into the soil solution. Nitrate is consequently highly mobile in soils, and a large proportion of it is leached out of the soil, leading to eutrophication of water bodies and N deficiencies in crops. This is especially the case in sandy soils, which have low water storage capacities and very high permeability. Thus, the mineralogical make-up of the vast majority of soils is such that it is not conducive to using land application of nitrate-rich effluents to prevent nitrates from polluting water bodies.

On the other hand, several researchers have found that clayey acid tropical soils can retain substantial amounts of nitrate despite high water fluxes through these soils [51]. These soils are highly permeable [51]. This is due to their stable micro-structure causing them to act like “pseudo sand”. Furthermore, rainfall is very high. Cahn et al. [51] found

that 25% to 50% of the nitrate in the subsoil of such soil was sorbed by the soil. This is ascribed to adsorption of nitrate to the positively charged sites on the kaolinitic clay minerals and protonated aluminum and ferric oxides that prevail under acid conditions in these soils. Nitrate sorption was found to increase with decreasing pH.

“Ammonium-ions wastewater pollution has become one of the most serious environmental problems of today” [52]. Ammonium (NH_4^{+1}) also occurs in significant to high quantities in cropland due to:

- Its application in ammonium fertilizers.
- Its formation being the first step in the conversion of urea applied as fertilizer to soil.
- Its formation being the first step in the mineralization of organic nitrogen compounds in soil.

Since ammonium is a cation, it adsorbs to the negative charges that dominate most soils. It is together with potassium (K^{+1}) special in the sense that they differ from all other major cations in soils in respect to becoming fixed by 2:1 layer lattice aluminosilicate clay minerals into forms that are not easily exchangeable [19,53]. The same mechanism is responsible for the fixation of both NH_4^{+} and K^{+} . They are the only two cations among the major cations that are small ions that fit exactly into the hexagonal holes in the basal oxygen plane of 2:1 clay minerals [19,53,54]. Penetration of these cations into the clay mineral interlayers causes the clay layers to collapse, and the NH_4^{+} and K^{+} ions are trapped between silicate sheets and largely withdrawn from exchange reactions [53]. Therefore, both cations when held in the interlayers of collapsed 2:1 clay minerals are said to be “fixed”.

There are important differences between different 2:1 clay minerals in regard to their ability to fix NH_4^{+} and K^{+} into non-exchangeable forms [53,54]. Montmorillonite can do it, but to a limited extent and only upon drying. The two main minerals that are capable of strongly fixing large quantities of NH_4^{+} and K^{+} into non-exchangeable forms, even under moist conditions, are illite and vermiculite [19,53,54]. Since the fixed NH_4^{+} is not in quick equilibrium with the soil solution, this NH_4^{+} will not leach in large amounts from soils in which the latter two clay minerals dominate, especially where the soil has a relatively high clay content, and thus, not cause serious eutrophication of water bodies.

This effect of clay mineralogy was, for example, clearly illustrated in the study of Snyman et al. [55] at the Vaalharts irrigation scheme. Farmers obtained good results by using ammonium sulphate as a nitrogen source on the sandy soils (about 10% clay) under heavy flood irrigation. Then, advisors decided that the farmers should change to a different N source, namely, limestone ammonium nitrate with about a 50/50 ratio of ammonium and nitrate. The second author and A.J. van der Merwe warned that this would lead to a disaster. In the first season after the change, this indeed happened with tremendous typical N deficiency symptoms, which were confirmed by the same two gentlemen, due to nitrate leaching. Snyman et al. [55] then did field crop experiments and leaching studies in columns on a typical sandy soil of the area with 9% clay and an otherwise similar soil from the area with 20% clay. On the sandy soil, wheat yields were statistically significantly higher where all N was applied in the ammonium form than where it was applied as 50:50 ammonium: nitrate. In the soil with 20% clay, there was no statistically significant differences between the N sources. In the leaching studies, very little NH_4^{+} was lost from both soils, i.e., even from the sandy soil with less than 10% clay. The clay fractions of the soils of this region contain a major proportion of vermiculite. In contrast, considerable amounts of nitrate were leached from these soils, with much more from the sandy soil than from the other soil.

The fixed NH_4^{+} is in slow equilibrium with normally adsorbed NH_4^{+} . In crop nutrition, it will, thus, act as a slow-release nitrogen source. Thus, the irrigation of crops with NH_4^{+} -polluted effluent on soils that are dominated by illite and/or vermiculite clay minerals can both trap NH_4^{+} from leaching into water bodies and provide a slow-release N source. These are, for example, over large areas the dominant clay minerals in the soils of the central parts of South Africa.

In sandy soils elsewhere, NH_4^+ is not fixed, and there is large leaching of NH_4^+ from such soils [53]. Likewise, kaolinite does not fix NH_4^+ , and consequently, large quantities of it will leach from soils in which the clay fraction is dominated by this mineral. This will even more so be the case in highly weathered soils where sesquioxide minerals dominate the clay fraction. The positive charges that develop in these minerals will further reduce NH_4^+ sorption and increase its leaching because the positively charged NH_4^+ will be repelled by the positive charges on the minerals and pushed into the soil solution. This makes management of the nitrogen nutrition of crops in those permeable soils under high rainfall even more difficult. Land application of ammonium-rich effluents to avoid eutrophication of water bodies is also not a viable option in soils with such mineralogy and low pH.

3.1.4. Potassium

Potassium is one of the three primary macro plant nutrients, together with nitrogen and phosphorus. Yet, a high K level is not seen as a direct cause of eutrophication of water bodies, unlike the case with N and P. Since K is not toxic to plants, animals and humans, it does not seem as if there is concern about potential K pollution of the environment. In situations where concern about potential pollution by K-rich effluents may develop, then all the arguments in regard to ammonium above would also be applicable to potassium.

A study on land application of winery effluents at 10 wineries in South Africa revealed high K levels in the effluents in most of the effluents [37,56]. Analyses of the soils on which the effluents were disposed revealed highly elevated K levels above the control levels, even deep into the soil profiles at most sites and strong indications that quite high amounts of K were leaching into close-by streams and other water bodies [37,57]. The researchers consequently expressed concern that the high K levels leaching into the water bodies may contribute to eutrophication of the water bodies.

3.2. Toxic Heavy Metals as Pollutants

The term heavy metal refers to any metallic chemical element that has a relatively high density and is toxic or poisonous at low concentrations. Examples include mercury (Hg), cadmium (Cd), chromium (Cr), thallium (Tl) and lead (Pb).

Heavy metals of concern to human and animal life include Hg, Pb, Cd and Cr [6]. Heavy metals accumulate in the soil to toxic levels due to the application of wastewater, amongst others [29,58]. It has been shown that toxic amounts of heavy metals such as Pb and Hg reduce soil fertility as well as crop yields. South African studies found that in suburban areas, the use of municipal and industrial wastewater for the irrigation of vegetable gardens exceeded the maximum permissible concentrations [42,59].

Studies of environmental pollution in Africa (2000–2010) showed that toxic metal pollution has reached unprecedented levels over the past decade. Human exposure to these has lately become a major health risk on the continent and is the subject of increasing attention from national and international environmentalists. Africa was previously considered to be safe from heavy-metal pollution. Heavy-metal pollution of water, sediment and/or soil has been reported in many African countries [60]. Prominent heavy metals that have been reported include Pb, Cd, Hg, Cu, Co, Zn, Cr, Ni, Mn, Fe and vanadium (V). Accumulation of these in fish and food animals as well as impacts of heavy-metal pollution on humans are also described [60].

The degree of contamination and the mobility of heavy metals in abandoned mine tailings were determined in a study by Aucamp and van Schalkwyk [61]. They found that fine-grained material distributed by wind and water from tailings dams at the abandoned Machavie Gold Mine, South Africa, was deposited over an area of more than 1 km². The low pH (average 3.4) of the tailings caused by oxidation of the abundant pyrites (sulfide minerals) in the tailings led to the formation of water-soluble heavy-metal-rich leachate. Comparisons of the trace element content of the tailings and underlying soils with the Dutch-B soil standards indicated potential pollution with Co, Cr, Cu and Ni. The

degree of contamination and mobility of trace elements was determined by extraction with ammonium nitrate as the leaching agent. Mobility was calculated by comparing total trace element concentration with extractable trace element concentration. The average trace element mobility was generally higher in the tailings than in the underlying sandy colluvium and clayey alluvial soils and also showed an increase where the pH values of soils and tailings were lower than 5 and 3.5, respectively [9]. This indicated that the tailings were a source and cause of heavy-metal pollution, even 60 years after the mine had been abandoned.

Heavy metals reaching toxic levels were also found in the soils in the Witwatersrand Gold Mining Basin (South Africa). Samples were collected from two mine villages and 15 from mine tailings dams. The samples were analyzed for Pb, Hg, Cd, Cr, Co, Ni, Cu and Zn [62]. Their concentrations were in the order $Cr > Ni > Zn > Cu > Co > Pb > Hg > Cd$. Cr and Ni were higher than permissible levels, when calculating their individual health risks for adults and children. This showed a critical need to put mining regulations in place to protect residents, and especially children [62]. Opencast coal mines in South Africa have the same polluting effects [63]. A study to assess the enrichment of heavy metals in surface soil and plant (*Digitaria eriantha*) around coal-fired power plants receiving their coal from opencast mines, in the Mpumalanga Province, South Africa, found that soils were moderately enriched with heavy metals, with the exception of Pb, which had significant enrichment [63]. The heavy-metal distribution also showed that the concentrations of Pb, Ni, Cr and Cu were higher than the maximum allowable limits (MALs) specified for most countries. The average total concentrations of heavy metals in the plant (*Digitaria eriantha*), for Fe, Ni, Cr, Mn and Cu, were also found to be higher than permissible limits set by the Food and Agriculture Organization (FAO) of the United Nations and the World Health Organization (WHO) for edible plants.

With regard to the copper-mining pollution reported by Weissenstein and Sinkala [64], an important finding was that the concentration of heavy metals such as Cu, Co, Ni, Pb and Zn is peaked at 100 m distance from the edge of the mine dump. Minimum heavy-metal levels were found in the dump material itself and often at the edge of the dump. Since in the Copperbelt in Zambia, these dumps are often situated in the flood plains of river basins, there are high inputs of suspended solids such as toxic heavy metals into the streams and rivers. The increase in siltation processes is a known fact of environmental degradation due to water erosion of mine dumps. Since there are sensitive land uses such as townships in the impact area, the serious impacts on human health are predictable [64].

It is important to note the contrasting situations in developing countries and those in developed industrialized countries. In the vicinity of gold mine slimes dams, soils are acidified strongly due to the oxidation of the abundance of pyrite minerals in the gold mining ores, leading to the production of sulfuric acid [9]. The same is found in the case of open-cast coal mining. The consequence is sharp increases in the mobility and bioavailability of heavy metals, causing serious environmental and health problems, as discussed earlier. In the vicinity of the sites of mining and processing of metal ores in countries such as those in Western Europe and Great Britain, the opposite is commonly found, namely, an increase in pH and, thus, a reduction in the mobility and bioavailability of potentially toxic heavy minerals, often to very low, safe limits. This was, for example, clearly illustrated by Kicinska [8] and Kicinska and Wikar [7] in case studies in Poland. Total heavy-metal concentrations were increased strongly, even up to 20-fold in some cases, over a 20-year period in the vicinity of metal ore mines and processing plants. However, there were positive trends in terms of mobility and bioavailability in of these elements in surrounding soils, due to reduction in these over time. This was due to a large increase in the pH of the soils from the original 5.4–5.7 to a very high 7.6–8.4, thus immobilizing the elements. It has for nearly a century been known that so-called “basic slag”, a by-product of the steel industry, can be used effectively as a liming material to increase the pH of strongly acid soils in order to overcome problems such as P fixation and, thus, P

deficiencies in crops, Al toxicities to crops, etc. This has recently been confirmed clearly again by Mamatha et al. [65].

4. Potential Mitigative Measures

It is clear from the above review that there are indeed several environmental problems in the abovementioned study areas due to mining activities (past and present), as well as municipal and industrial waste and agricultural waste. In the past decade (2000–2010), there has been a steady accumulation of heavy metals in the African environment. Pollution levels in many African countries are at critical points, as the current levels of many metals and inorganic pollutants in water, fish, soils, edible vegetables and food animals exceed international limits. Toxic heavy metals such as Pb, Cu and Cd are widespread, while Hg and As are reported in limited places. Regular monitoring is essential to prevent excessive build up in the soil and water resources and the food chain as well as widespread metal toxicity in animals and humans.

During recent years, many physical, chemical and biological remediation treatment techniques have been applied to address heavy-metal contamination in soil, water and sediments. In situ and ex situ remediation techniques have been developed to rectify heavy-metal-contaminated soil sites, including surface capping, encapsulation, landfilling, soil flushing, soil washing, chemical extraction, adsorption, electro-kinetic extraction, stabilization, solidification, vitrification, phytoremediation and bioremediation [66]. These techniques are discussed below. The use of these techniques should be evaluated against their practicality, effectiveness and costs (Table 6). Remediation costs do differ, and the right technique for each specific situation should be chosen:

- Bio-accumulation, also called phytoremediation or phyto-extraction, by means of growing plant species that are super-accumulators of, for example, P and heavy metals and remove large quantities of these without being impacted on negatively: Different researchers suggests different plants for different heavy metals under the concept of phytoremediation. Such plants take up large quantities of heavy metals and make them part of their bodies. However, some researchers think that in this philosophy of treatment of waste, we are only changing the form of pollution. Phytoremediation can avoid the high cost of soil disposal or other cleaning methods. If you use energy crops (especially wood), incineration will decrease the mass of contaminated material (ash) to 1–3% of the original dry mass. It means you need to dispose of a very small mass of hazardous material compared to the soil. Growing plants can help contain or reduce heavy-metal pollution.

Table 6. Comparison of different methods of heavy-metal soil remediation (adapted from Schnoor [67]) (relative costs as during 1997).

Method	Type of Remediation	Cost/Cubic Meter (US Dollars)	Time Required (Months)	Comments
Physical	Excavation, removal and soil flushing	100–400	6–9	Laborious and costly, but can be applied to highly contaminated sites
Chemical (sources: natural and anthropogenic—agriculture, mining, smelting industries)	In situ fixation (including soil amendments), vitrification, elektro-kinetics	90–200	6–9	Rapid and effective, but depends on the type of soil, chemical and metal
Biological (bio-remediation)	Phytoextraction	15–40	18–60	Economical, eco-friendly, but time consuming and limited to moderately contaminated sites

This is often called phytoremediation [68]. It has the advantage of relatively low cost and wide public acceptance [67]. It can be less than a quarter of the cost of excavation or in situ fixation. Phytoremediation has the disadvantage of taking longer to accomplish than other treatment. Plants can be used in different ways. Sometimes, a contaminated site is simply revegetated in a process called phyto-stabilization. The plants are used to reduce wind and water erosion that spread materials containing heavy metals. In one example, grass or tree buffers could reduce sediment loss from the chat piles at a contaminated site in Galena, Kansas, anywhere from 18% to 25% [69]. If all of the ground could be revegetated, sediment loss could be cut by approximately 70%. However, it would be necessary to find plants that could tolerate high levels of heavy metals. Another way plants can be used to clean up heavy-metal-contaminated soil is called phyto-extraction. Some plant species can take up heavy metals and concentrate them in their tissue. The plants can be harvested, and the contaminated plant material disposed of safely. Sometimes soil amendments are added to the soil to increase the ability of the plants to take up the heavy metals. One type of plant used for this purpose is called Indian mustard.

This plant has been used to extract lead from soil and reduce lead contamination at various contaminated sites. Other plants that may be used for phyto-extraction include alfalfa, cabbage, tall fescue, juniper and poplar trees. Another way plants are used to treat heavy-metal contamination is called rhizo-filtration [70]. In this method, heavy metals are removed directly from water by plant roots. The plants are grown directly in water or in water-rich materials such as sand, using aquatic species or hydroponic methods. In field tests, sunflowers on floating rafts have removed radioactive metals from water in ponds at Chernobyl, and other plants removed metals from mine drainage flowing through diversion troughs [70]. Plants used for phyto-extraction may accumulate high concentrations of metals. Fences or other ways to limit access to people and animals and disposal of plant matter as special waste is sometimes necessary.

- Excavation and removal: Excavation and physical removal of the soil is perhaps the oldest remediation method for contaminated soil. It is still in use at many locations, including residential areas contaminated with lead in southwestern Missouri. Advantages of excavation include the complete removal of the contaminants and the relatively rapid cleanup of a contaminated site [71]. Disadvantages include the fact that the contaminants are simply moved to a different place, where they must be monitored; the risk of spreading contaminated soil and dust particles during removal and transport of contaminated soil; the relatively high cost. Excavation can be the most expensive option when large amounts of soil must be removed or disposal as hazardous or toxic waste is required.
- In situ fixation (including soil amendments): Heavy metals can be left on site and treated in a way that reduces or eliminates their ability to adversely affect human health and the environment. This process is sometimes called stabilization. Eliminating the bio-availability of heavy metals on site has many advantages over excavation. One way of stabilizing heavy metals consists of adding chemicals to the soil that cause the formation of minerals that contain the heavy metals in a form that is not easily absorbed by plants, animals or people. This method is called in situ (in place) fixation or stabilization. This process does not disrupt the environment or generate hazardous wastes. Instead, the heavy metal combines with the added chemical to create a less toxic compound.

The heavy metal remains in the soil, but in a form that is much less harmful. One example of in situ fixation of heavy metals involves adding phosphate fertilizer as a soil amendment to soil that has high amounts of the heavy-metal lead. Chemical reactions between the phosphate and the lead cause a mineral to form, called lead pyromorphite. Lead pyromorphite and similar minerals called heavy-metal phosphates are extremely insoluble. This means the new minerals cannot dissolve easily in water [72]. This has two beneficial effects. The minerals (and the heavy metals) cannot be easily spread by water to pollute streams, lakes or other groundwater. Additionally, the heavy-metal phosphates are

less likely to enter the food chain by being absorbed into plants or animals that may eat soil particles. Table 5 shows the cost of treating the soil by in situ fixation may be about half the cost of excavation and disposal of heavy-metal-contaminated soil. This method is relatively rapid and takes about the same amount of time as excavation.

Vitrification is the transformation of a substance into a glass. This is usually achieved by heating to a high temperature and rapid cooling. In geo-environmental engineering, soil vitrification is a method that embeds the waste into a glassy matrix so that hazardous waste will not leak out. It requires a high temperature to melt the soil. The melted soil is then refrozen into a glass-like solid. The contaminants are incorporated into the waste glass either through chemical bonding or through encapsulation [68]. Therefore, soil vitrification is a method that has been widely used to treat hazardous and radioactive waste. Soil vitrification is also effective for organic waste because the high temperature will make organic compounds inactive.

In general, in situ soil remediation techniques are more cost effective than ex situ treatments, and contaminant removal/extraction is more favorable than immobilization and containment. Electrokinetic extraction, chemical stabilization and phytoremediation are at the development stage, while the other techniques have been practiced at full field scales. Wide-ranging assessment indicates that chemical stabilization serves as a temporary soil remediation technique, phytoremediation needs improvement and some more research regarding efficiency, and surface capping and landfilling are applicable to small, serious contaminated sites. Solidification and vitrification are the last applied remediation options in practice.

5. Concluding Remarks

Pollution of soil and water with various toxic heavy metals or with non-metal pollutants, such as P, As and N, pose serious problems in many areas in many countries. Different pollutants pose different challenges, with dominant challenges differing between rich industrialized countries, on the one hand, and poorer countries, on the other hand.

The pollution hazard of any element to the environment, agriculture and/or human health is not determined by its total concentration in the environment and/or soil, but by its mobility and/or bioavailability. If the mobility of an element is low, it cannot be transported in hazardous amounts to agricultural land or water bodies, even if its total concentration is very high. If the bioavailability of an element is low, it cannot enter the food chain in hazardous levels and, thus, cannot pose a hazard to agriculture and/or human health, even if its total concentration is highly excessive.

The pH of the source of pollution or the polluted soil, is the major factor determining the mobility and/or bioavailability of potentially toxic heavy-metal pollutants. This is well illustrated by the following two extremes. Ore mining and processing in Europe is associated with production of strongly alkaline by-products, which cause polluted soil to become strongly alkaline. In these conditions, the mobility and/or bioavailability of the heavy metals are very low and within acceptable limits. Thus, they do not pose hazards. On the other hand, very strong acidification of mine tailings and soils around gold mine tailings and opencast coal mines occur due to the oxidation of pyrites contained in the ores. At the resultant very low pH levels, the mobility and/or bioavailability of the potentially toxic heavy metals become very high. Thus, they pose very serious hazards to agriculture and/or human health.

The situation with non-metal elements such as P and As, which are present as large anions, is opposite to that outlined for metals above. At low pH, they become fixed into forms with low mobility and/or bioavailability. Highly weathered strongly acidic soils with an abundance of ferric and/or Al oxides or hydroxides, as found abundantly in humid tropical and subtropical areas, are especially able to fix extremely high amounts of these elements into forms that are not mobile and/or bioavailable.

Various potential remedial measures to overcome problems of pollution with potentially toxic elements are listed.

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