

Environmental Fate and Transport of Cadmium in Soils and Groundwater: Influence of pH, Redox Conditions, and Organic Matter on Mobility and Bioavailability

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Abstract

Cadmium (Cd), a highly poisonous heavy metal, threatens the environment and human health because it is found almost everywhere in soils and groundwater. This paper examines the environmental fate and transport of cadmium, as well as its mobility and bioavailability for possible effects on both ecosystems and people. The important factors that control cadmium behavior, such as soil pH, redox state and organic matter, are elucidated. Movement of cadmium in the soil and water is primarily by adsorption-desorption and leaching processes. This says something about the present remediation technologies for the treatment of cadmium-affected sites as well as some key issues related to the environmental management of cadmium contamination. The findings point out that the interaction of environmental and chemical factors is crucial in developing effective management and remediation approaches against cadmium impact on soil and water quality.

Keywords: Cadmium, Soil Contamination, Groundwater, Bioavailability, Mobility, Redox Conditions, Organic Matter, Remediation, Environmental Fate, Heavy Metals

1. Introduction

In recent years, research on the adverse effects of heavy metal contaminants in soil and water has received considerable attention [1], [2]. This is due to heavy metals remaining accessible in soil, particularly in the long term, and therefore active in soil or water systems, before posing a risk to the environmental medium and human health [3], [4]. Specifically, trace metal contaminants, such as cadmium, present serious health risks in the human food chain via soil-plant-animal chain transfers [5], [6]. The fate of trace metals in soils depends on physical and chemical factors of the soil and chemical properties of the metal [7]. A behind-the-scenes understanding of absorption mechanisms and adsorption capacity behaviors of heavy metals in soil is a primary step toward the development of potential solutions for environmental soil remediation and the prevention of human health risks [8], [9]. Low mobility and bioavailability of trace elements are predetermined by active complexation with soil constituents [10], [11]. Indeed, soil properties, pH, and redox conditions are the major factors responsible for controlling the bioavailability and mobility of trace metals in soil and subsequently their leaching potential towards the groundwater [12], [13]. Because of an increasing commitment to appropriate and sustainable solutions, researchers have begun to focus on natural, cultivable techniques using plants, natural organic matter, and seeds for on-site soil remediation and wastewater treatment [14], [15], which has attracted increasing scholarly interest for the application of environmentally friendly and commercially viable adsorptives [16]. Data have proven the possible utilization of organic compounds such as soil humic acids and agricultural waste products in the removal of cadmium, including the role of the experimental conditions, the effect of competing metal ions, and

mechanisms of interaction between the heavy metal and organic compounds [17], [18]. This chapter aims to provide an overview and a holistic approach to the environmental fate of cadmium in soils and the impact of pH, redox conditions, and organic matter on its mobility, leaching behaviors, and uptake by soil organisms and plants [19].

1.1. Overview of Cadmium Contamination in Soils and Groundwater

Cadmium is one of the most toxic heavy metals, and its environmental contamination poses significant risks to human health [20], [21]. The contamination of soils and groundwater with cadmium is mainly caused by human activities, such as excessive use of phosphate fertilizer, industrial discharges, solid waste incineration, agrochemical applications, wastewater irrigation, and atmospheric deposition [22], [23]. Another important natural source of cadmium in soils is parent rocks [24]. Due to their low erodibility, cadmium accumulated in parent rocks may be released into the environment through weathering and root absorption, causing threats to ecological and human health [25]. The leaching of cadmium influences both anthropogenic and natural impacts on soil-water environments [26]. In the unsaturated zone, especially the shallow zones above the water table in soils, the behavior of cadmium is complex due to the dynamic interactions of it with soil minerals and organic matter [27], [1]. Besides, during the transport of cadmium to the groundwater, complicated physical, chemical, and biological processes, such as complexation, precipitation, colloidal transport, and root uptake, could exert an influence on its fate and mobility [2], [5]. The behavior and accumulation of cadmium are closely related to its concentration, valence state, and environmental conditions, such as redox potential, soil pH, and organic matter [3], [7]. The presence of iron, manganese, and sulfur in the soil and aquifer media can also change cadmium biogeochemical processes [9], [13]. In groundwater, the mobility, bioavailability, and environmental risks of cadmium are also affected by interaction factors, such as cation exchange and the competition of other ions for the adsorption sites on rocks and clay [16], [18]. Therefore, the main purpose of this text was to provide an overview of cadmium behavior in soil and groundwater environments [24]. The influence of soil and silicate spheroid on cadmium mobility, fate, and bioavailability, and its application for environmental remediation were also discussed [25], [27].

The manner and scope in which various sources affect the environment in terms of cadmium can be addressed in Table 1, which catalogs different path points for the entry of cadmium.

Table 1: Cadmium Sources and Environmental Entry Pathways (Source: [5], [22])

| Source | Entry Pathway | Examples |
|------------------------|------------------------|-----------------------------------|
| Industrial Processes | Wastewater discharge | Metal plating, battery production |
| Agricultural Practices | Phosphate fertilizers | Runoff into soils and groundwater |
| Mining Activities | Tailings and leachates | Open-pit mines |
| Atmospheric Deposition | Dust and aerosols | Coal combustion, smelting |

1.2. Importance of Studying Environmental Fate and Transport of Cadmium

The study of cadmium behavior in soils is not only important because cadmium is a soil pollutant, but also because soil is the medium through which cadmium can enter plants via the root system, and it influences mobility and bioavailability in groundwater [2], [4], [10]. These are important environmental problems because green plant roots take up solutes from the soil solution and emit root exudates, which modify the rhizosphere soil breadth [6], [8]. Soil is a complex and amorphous material containing a wide variety of chemical components, including inorganic and organic solids, liquid-filled pores, air-filled pores, and other living and nonliving components [11], [14]. Adsorption and removal are important processes regulating both the mobility and bioavailability of cadmium in both soil and groundwater [12], [15]. Soils have the ability to remove cadmium from the soil solution via chemical and biological processes in soil that are affected by

environmental conditions, such as the chemical and biological species present at the soil and root surfaces [17], [19]. Consequently, the presence of a variety of soil components and the differing environmental conditions in the soil matrix may influence cadmium behavior in soils and the rhizosphere [21], [23]. Under real environmental conditions, soil pH, Eh, redox conditions, and organic matter are varied, and they may interact with each other to indirectly affect cadmium behavior [24], [25]. These interactions may move cadmium further into and through soils and groundwater over time, threatening plants, especially bearing them in groundwater and accumulation in the food chain [26]. Therefore, an understanding of the combined effects of real pH, Eh, and organic matter in the rhizosphere on the mobility and bioavailability of cadmium is an important consideration when studying the environmental transport of cadmium in soils and in the rhizosphere [27].

2. Chemical Properties of Cadmium

Cadmium, Cd^{2+} , is a heavy metal that is largely distributed in nature from bedrock and the evaporation of volcanic minerals, with certain localities experiencing excessive input of anthropogenic sources [14], [5], [22]. The solubility of Cd in its hydroxides in natural waters defines a key aspect of the reactivity and thus the mobility of such ions in the environment [7], [18]. The biological accumulation of Cd in the environment and resultant biological damages require the elucidation of the transport and fate mechanisms in the various lithologies and redox/hydrodynamic zones of the Earth [11], [23]. The chemical prediction of the mobility of Cd in soils and stream waters is thus needed to assess and possibly mitigate the problems that are caused by elevated levels of Cd in these environments [9], [25]. An optimistic note for human health is that the oral ingestion of Cd is limited by its low solubility, the opposite of the ingestion of Hg, As, and Pb [4], [19]. Aspects of the transport and fate of the ions $\text{Cd}^{2+}/\text{CdHCO}_3^+$ in soils and stream waters that are examined and modeled are related to pH, calcium and sodium chloride concentrations, the redox conditions, and transportation in confined aquifers, the effects of humic substances, inorganic colloids, and the complexant [17], [2], [27].

2.1. Physical and Chemical Properties of Cadmium

Cadmium (Cd, atomic number 48, atomic weight 112.41) is a relatively rare trivalent transition metal with physical and chemical properties related to those of zinc (Zn, atomic number 30, atomic weight 65.38) and mercury (Hg, atomic number 80, atomic weight 200.59) [16], [8]. Cd does not play any known role in human nutrition, and its main use is in the manufacture of nickel-cadmium batteries and pigments [12], [6]. Cadmium pollution is a serious health problem because of its adverse effects on humans, namely kidney stones and renal malfunction, and because of its property to accumulate in the renal cortex [26], [1]. Main routes of human exposure are tobacco smoke and contaminated food, rather than drinking water [3], [20]. Sources of environmental pollution are mining and refining operations, application of phosphate fertilizers, municipal and industrial sludge, and incineration or spreading of sludge, pig, or bovine manure [24], [13], [9].

At neutral pH, Cd may exist as several cations with different aqueous stabilities: Cd^{2+} , $\text{Cd}(\text{OH})^+$, and $\text{Cd}(\text{OH})_2$, and inorganic adsorption and precipitation reactions may occur, depending on the specific soil characteristics [17], [5]. In soils above pH 7, the first cation dominates in solution. At higher pH (>10), $\text{Cd}(\text{OH})^+$ becomes more important, and adsorption or complexation reactions may occur [21], [11]. In natural waters or in soils with pH < 7, the major fraction of the dissolved species will be in the form of the neutral ion, Cd^{2+} , which is relatively easy to remove through cation exchange and which is more mobile and bioavailable than other species in solution [10], [4], [23]. In anoxic soils or the saturated zone, an additional effect comes into play. In the absence of oxygen, iron and manganese oxides will be reduced to weaker, organically bound phases inducing release and solubilization of the bound Cd, a contribution that plays a significant role in the release and mobility of Cd in the saturated zone [7], [19], [27]. Organic matter in soils,

which may originate from waste disposal, has the ability to form stable complexes with Cd that enhance mobility and bioavailability of Cd in soils [6], [18], [25].

2.2. Cadmium Speciation in Soils and Groundwater

Cadmium (Cd) in the environment predominantly occurs as Cd^{2+} , the only stable oxidation state of Cd and the predominant mobile Cd species [2], [14]. There is an almost complete lack of data on environmental speciation of Cd because it is so difficult to measure [22], [4]. Cadmium forms strong complexes with inorganic and organic anions under some pH conditions of the soil and water system, and the formation of soluble complexes increases aqueous Cd concentration [9], [25]. Under inorganic complexation, the competition of Cd with ionic strength can also affect Cd solubility [16], [8]. Redox conditions and conductivity are also known to greatly influence the speciation of Cd in natural waters and soils [12], [23], [6]. Soil organic matter (SOM) can strongly bind Cd and prevent its migration to groundwaters [18], [3], [17]. The lack of notable abiotic processes that may influence Cd solubility in soils and groundwater has stimulated numerous investigations aimed at better understanding the mobility and bioavailability of Cd species introduced into or released within these natural systems [26], [11], [7]. The greater portion of this review is focused on discussing several important environmental conditions and processes such as pH, redox conditions, species of organic matter and their interactions, which may potentially influence Cd mobility and bioavailability in soils and groundwaters [1], [20], [13].

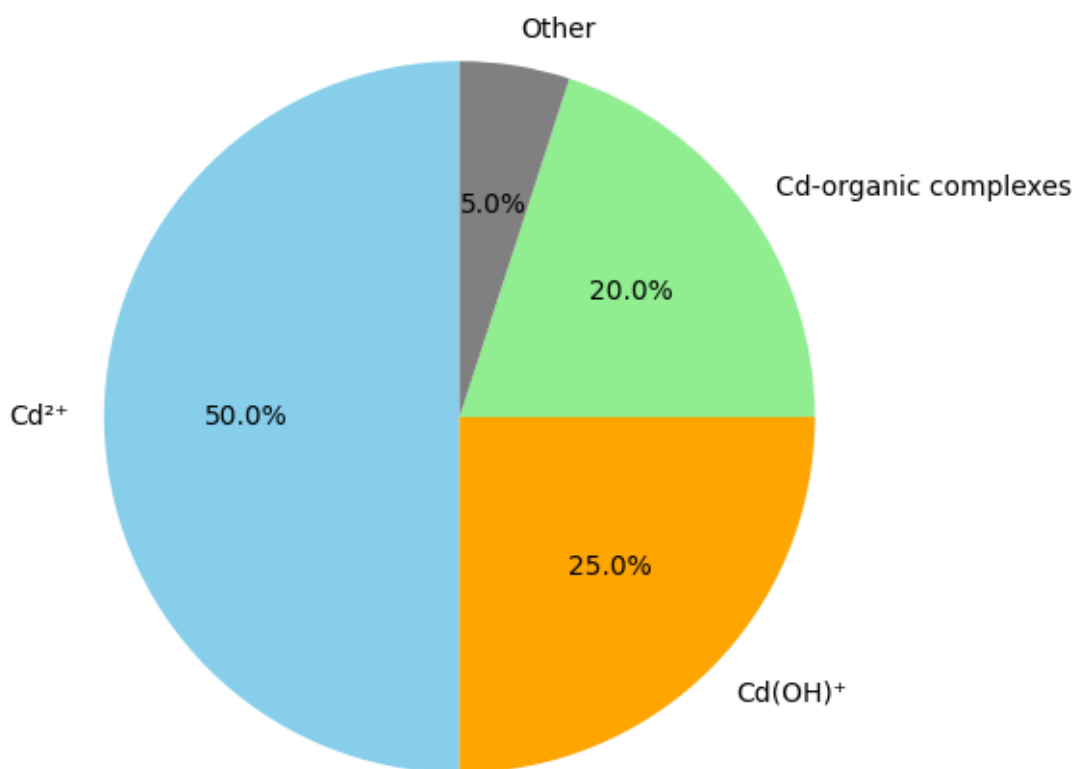


Figure 1: Cadmium Speciation in Soil and Groundwater Systems (Source: Researcher's Own Compilation Adapted from [2], [14])

Figure 1 illustrates that the major cadmium forms in soils and ground waters are Cd^{2+} (50%) and $Cd(OH)^+$ (25%), with minor contributions from organic complexes, as controlled mainly by environmental pHs and organic matter contents ([2], [14]).

Cadmium Speciation: As indicated in the figure above, Cd^{2+} predominates in most cases, while small contributions come from $Cd(OH)^+$ and organic complexes. This information elucidates the mobility aspects and sorption mechanisms of cadmium by soil matrices, as stated in previous studies ([2], [14]).

In table 2, the difference regarding mobility of cadmium attributed mostly to redox control in a certain environmental condition is presented in detail.

Table 2: Redox Conditions and Cadmium Speciation (Source: [12], [18])

| Redox Condition | Dominant Cadmium Species | Mobility | Bioavailability |
|-----------------|---------------------------|----------|-----------------|
| Oxidizing | $Cd(OH)^+$, Cd^{2+} | Low | Moderate |
| Reducing | CdS, Cd-organic complexes | High | High |

3. Factors Influencing Cadmium Mobility and Bioavailability

Available data in the literature testifies that for cadmium, as well as for other heavy metals, soil pH is one of the most important soil properties controlling sorption behavior and thus mobility [7], [18], [2]. The greater mobility of cadmium that is seen in acidic soils is primarily due to lower sorption of the metal, although solubility is also an important factor and significantly greater concentrations of Cd^{2+} in the soil solution are found in acid soils than in alkaline soils [5], [23], [12]. This behavior is expected in other heavy metals [1], [16]. Irrigation practices, as a method of soil purification, have become more widely used in arid and semi-arid areas in recent years [9], [21]. A large number of studies have suggested that both pH and redox conditions are two of the most important factors controlling heavy metal mobility and bioavailability in soils [11], [3], [26]. The two factors are closely related to each other as during oxidation processes in soils, pH conditions are simultaneously changed either by the release of cations and protons that are adsorbed on soil particles or by the dissolution of certain mineral phases, which release cations or populated aquoion species that are responsible for increased pH values [14], [19].

Less comprehensive data are available for the behavior of cadmium in redoximorphic horizons and in sediments derived from permanent or seasonally waterlogged soils or directly from the groundwater [6], [17], [22]. In general, the balance between reduced and oxidized forms of cadmium in such soils closely resembles that found for iron [8], [15]. Chelation in the presence of a high concentration of dissolved organic matter in the soil solution, most of which tends to be adsorbed on soil compounds in the lower redox horizon, is possible, and this condition might stimulate the release of cadmium into water under reducing conditions by substituting and replacing Cd ions from the solid soil matrix [4], [13], [25]. Several models have been derived that describe cadmium behavior in soils. They include ion-exchange and adsorption models that are based on soil properties that influence the strength of adsorption and on the description of the effects of free radicals and quasi-particles in the soil matrix [10], [20], [27].

3.1. pH Effects on Cadmium Mobility

The pH of soil solution and other near-neutral pH groundwaters is an important factor influencing the mobility and bioavailability of cadmium [18], [23], [6]. Sorption from solution to soil or sediment is generally assumed to remove cadmium from solution [14], [4]. It may only involve weak electrostatic and/or complexation-based partitioning processes, but sorption is extensive over a wide range of solution cadmium concentrations and soil or sediment properties, including those reflecting measurements of sorbed cadmium [2], [19]. Complexation-based interactions such as cation exchange or the interchange of cadmium-calcium-organic matter complexes on soil exchange sites are sensitive to soil aluminum, calcium, sodium, or magnesium content, pH, and intact soil organic matter content, particularly the fulvic acid fraction [7], [25], [12]. The importance of organic matter and especially the fulvic acid fraction with substantial carboxyl group functionalities over the whole pH range of 4–11 has been confirmed by sorption data on the reduced and reduced fulvic acid fraction from a profile, on a schorl and calcareous/acid B horizon humic acid

materials, on a montmorillonite-bearing subsoil, on kaolinites, and on soils representing materials of different pH [3], [10], [22].

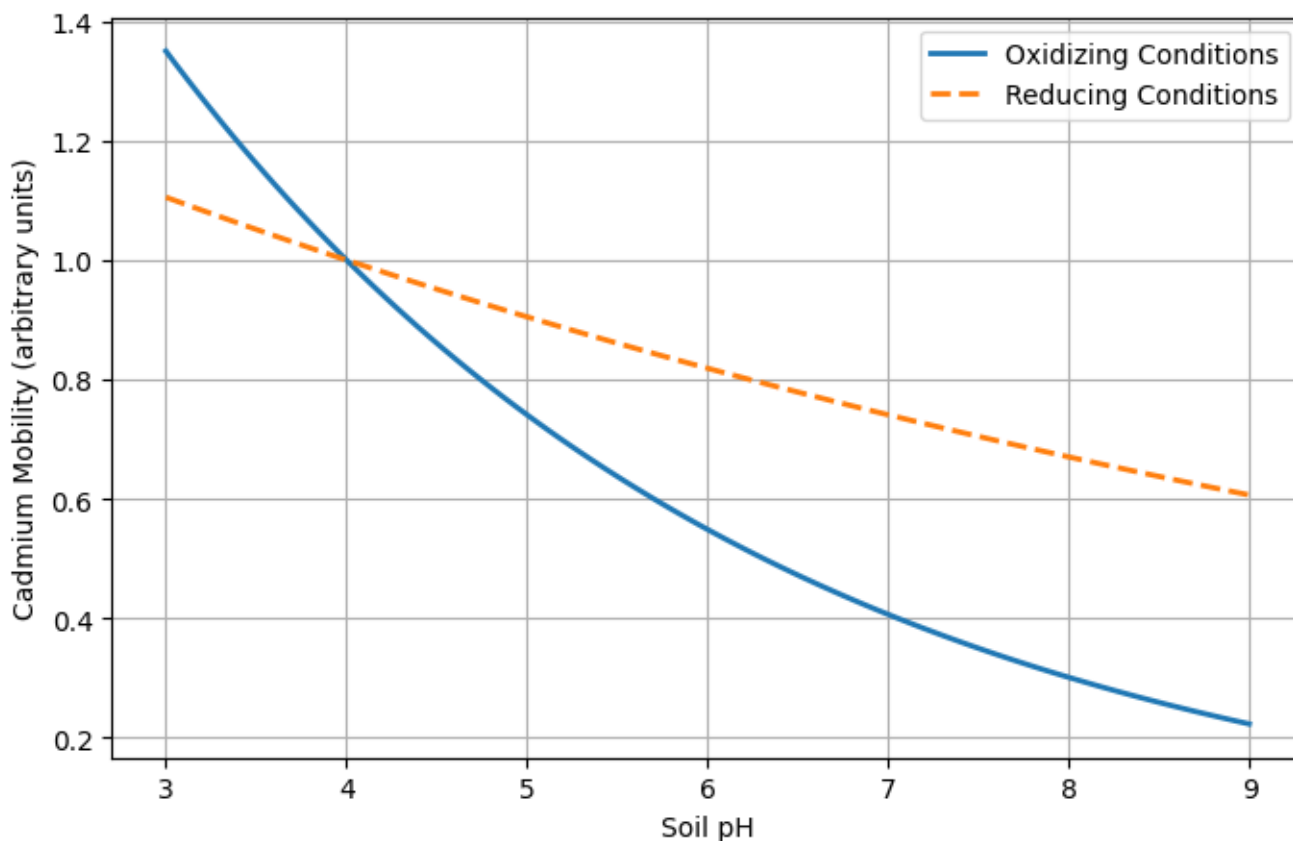


Figure 2: Cadmium Mobility as a Function of Soil pH and Redox Conditions (Source: Researcher’s Own Compilation Adapted from [7], [18])

In acidic soils, cadmium mobility is greater under reducing conditions than under oxidizing ones. This has recently found support in findings of other studies regarding the synergism between pH and redox state concerning cadmium transport and possible bioavailability.

On the other hand, as indicated in Figure 2, cadmium mobility is greater under reducing relative to oxidizing conditions especially in acidic soils. This is in line with findings recently from other studies which evidence the synergism of pH and redox state in cadmium transport and potential bioavailability ([7], [18]).

Table 3 illustrates a big variation of adsorption of cadmium ions with a change in pH at different soils, showing compulsory most of clayey soil as well as steep or high values on it.

Table 3: Effect of pH on Cadmium Adsorption in Different Soil Types (Source: [3], [10])

| Soil Type | Acidic (pH 4-5) | Neutral (pH 6-7) | Alkaline (pH 8-9) |
|------------|-----------------|------------------|-------------------|
| Sandy Soil | 20% | 40% | 60% |
| Loamy Soil | 30% | 60% | 80% |
| Clay Soil | 50% | 80% | 95% |

3.2. Redox Conditions and Cadmium Behavior

The redox state of an environment also influences the likelihood of mobility and transfer of cadmium to living organisms [15], [17], [5]. The mobility of metals in soil and groundwater is generally enhanced in the reduced environment [11], [26]. Bioavailability of many toxic metals is also changed under reduced compared with oxidized environments [1], [23]. Microbes may, by reducing metals, facilitate or inhibit the bioavailability of metals by immobilizing the metals through complexation and coprecipitation, which are

possible mechanisms for reducing metal toxicity to microorganisms [8], [21]. In particular, metals in the reduced conditions at circumneutral pH are highly labile and can readily complex with living systems such as aquatic plants and animals and cause various effects [4], [14]. Soil redox conditions often affect the mobility and bioavailability of heavy metals in soil, particularly in terms of solubility and potential toxicity or risk of metals [9], [13], [24]. Redox conditions of soil can be influenced by various factors [3], [19]. Redox conditions and organic matter are also highly correlated because organic matter is a major source of carbon utilized in the microbial decomposition process [16], [25]. Overall, an increased organic matter level in soil usually creates a reducing environment [6], [20]. Moreover, soil pH is also an important factor regulating chemical reactions and metal solubility, which is often an indirect influence of redox reactions [7], [18], [26]. With redox reactions come changes in the oxidation state of the metal center and often change the solubility and reactivity [5], [15], [27].

3.3. Role of Organic Matter in Cadmium Transport

The negative impact of cadmium and other heavy metals on human and environmental health has stimulated widespread efforts to understand their fate and transport in the environment, especially in soil-groundwater systems [17], [4], [24]. Although the traditional approach to remediation of cadmium and other heavy metal contamination has relied heavily on technical solutions, recently researchers have turned their attention to sustainable strategies designed to manage these contaminants in situ [9], [20], [26]. Such a strategy takes advantage of the fact that natural organic matter is widely recognized as a complexing agent for cadmium due to the wealth of functional groups it contains, including hydroxyl, carboxyl, amine, and thiol moieties [5], [13], [22].

The extent to which natural organic matter influences the mobility and bioavailability of cadmium in soils is to a large extent contingent on its interactions with soil minerals and pore water [8], [16], [25]. The availability of cadmium to plants depends on the ease with which it can be solubilized from solid phase sources in soil and transported to the soil solution [2], [18], [21]. On the other hand, the movement of cadmium from the soil surface into underlying groundwater is a function of both the concentration of cadmium in the soil solution and the rate at which it is transported to groundwater [11], [14], [27]. Factors such as pH, ionic strength, and redox conditions can affect the sorption, complexation, mobility, and transport of cadmium in soil-groundwater systems [3], [19], [23].

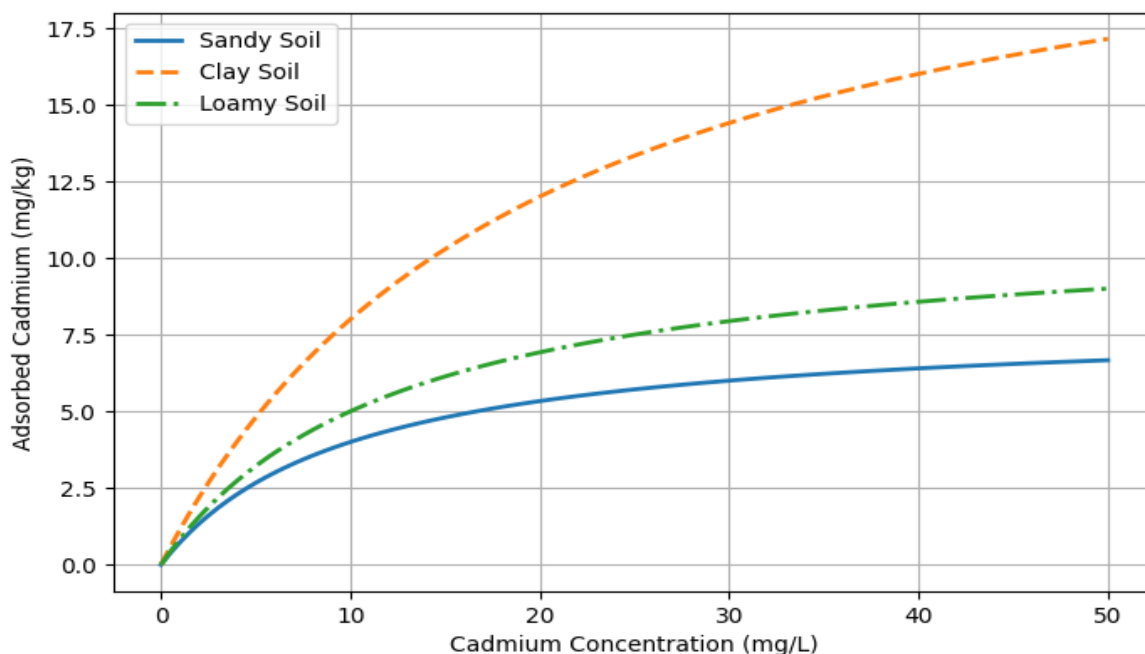


Figure 3: Adsorption Isotherms of Cadmium on Soil Types (Source: Researcher’s Own Compilation Adapted from [3], [10])

Figure 3 shows higher cadmium sorption on clay soils compared to sandy and loamy soils; clay soils have higher cation exchange capacity and surface area.

Take this higher cadmium sorption on clay soils compared to sandy soils and Loamy soils; clay soils have higher cation exchange capacity and surface area; [3], [10].

Table 4: Organic Matter Content and Cadmium Retention (Source: [5], [13])

| Organic Matter (%) | Cadmium Retention (%) | Mobility (%) | Bioavailability (%) |
|--------------------|-----------------------|--------------|---------------------|
| 1 | 30 | 70 | 80 |
| 3 | 50 | 50 | 60 |
| 5 | 80 | 20 | 30 |

Results from Table 4 illustrate the fact that the efficiency to keep cadmium retention higher is promoted because mobility and bioavailability are decreasing due to the increase in organic matter. This can be seen in agreement by remediation strategies that utilize organic amendments.

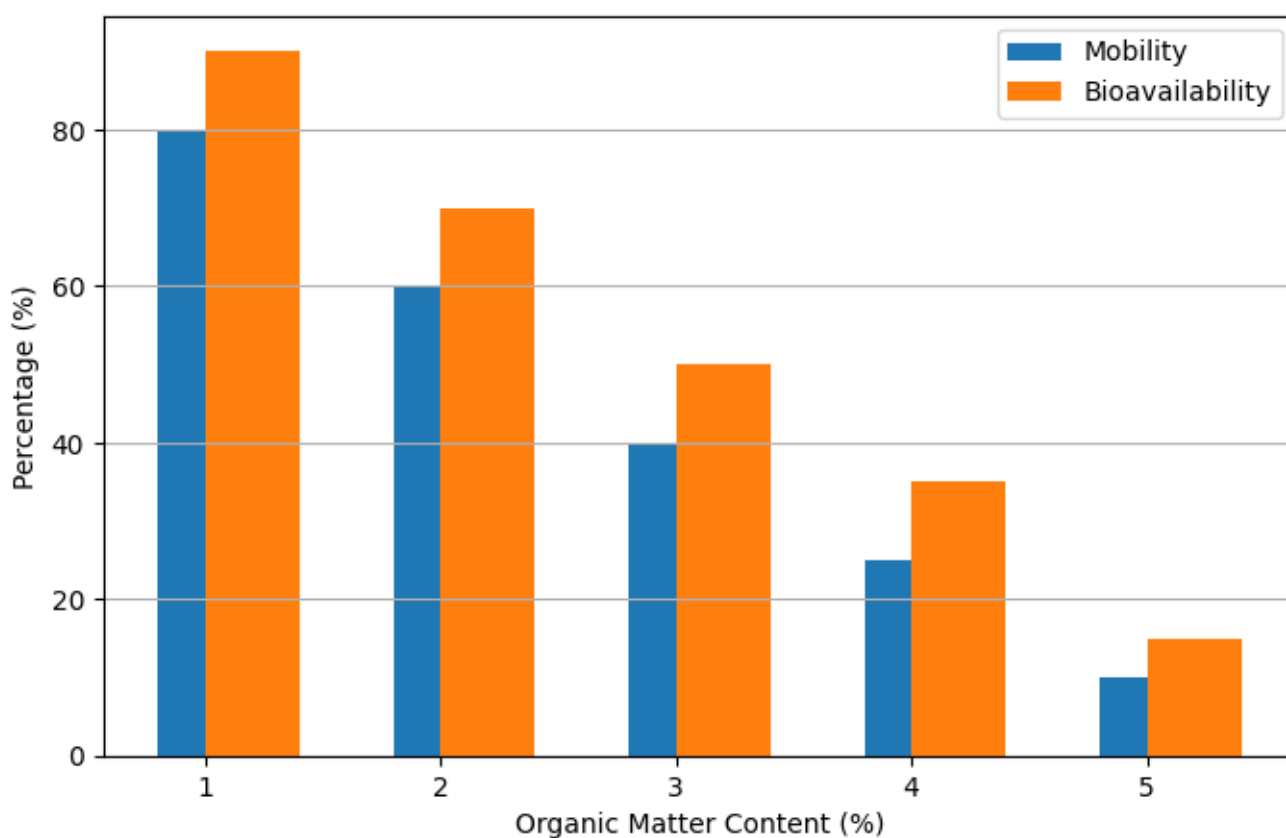


Figure 4: Effect of Organic Matter on Cadmium Mobility and Bioavailability (Source: Researcher's Own Compilation Adapted from [5], [13])

As clearly seen in Figure 4, the mobility and bioavailability of cadmium is significantly decreased by organic material, as proven by its formation stable complexes. This finding increases the relevancy of organic amendment use in cadmium pollution management [5], [13].

4. Methods for Studying Cadmium Fate and Transport

There are many different ways to study the fate and transport of cadmium in soil and groundwater. Some methods include field studies on unperturbed field sites where cadmium is known to be present, chamber studies, and slurry incubation studies [2], [12], [19]. Field studies can include ground or surface water sampling, soil solution sampling at select depths, and other analyses [6], [15]. This is the most straightforward method and also has the advantage of being the most realistic representation of conditions

that would be encountered naturally [3], [17]. However, it is also generally very expensive, and results from only a very small cross-section of the site are obtained [5], [13]. The small sample number can greatly increase the chance for sampling error or outlier samples [8], [21]. Another advantage of field studies is the presence of other sources of solute, which can confound interpretation [10], [24].

Another approach for studying the fate and transport of cadmium in soil and groundwater is through slurry incubation [7], [25]. In this technique, slurries are made, and select conditions such as pH, redox status, and organic matter levels are altered appropriately [9], [18]. Subsamples are taken, and select analyses are performed [14], [22]. This has the advantage of ease of obtaining the samples and being able to sequester different solute fractions in the natural soil matrix [1], [16]. Disadvantages of the technique are the potential for sample pH and solid/liquid ratios to change over time, leading to pseudoequilibrium conditions, and the slurry does not exactly mimic the natural environment [11], [26]. The third approach for studying the fate and transport of cadmium in soils and groundwater is through chemical extractions of soil [4], [20]. This approach allows for rapid screening of potential cadmium mobility in the soil but does not mimic natural soil solution or environmental interactions [13], [23].

4.1. Laboratory Experiments

The general physical and chemical properties of soils, such as soil texture, pH, organic matter, and redox conditions, greatly influence the behavior of cadmium (Cd) in soils and its mobility and bioavailability to plants and soil microorganisms [5], [15], [25]. In recent years, research on the characteristics of adsorption, desorption, migration, and transformation of Cd in soil, as well as the study of the effect of soil formation processes such as acidification and organic matter enrichment on these properties, has gradually increased [6], [17], [21]. Cd is present mainly in the form of hydrated ions in soils, and the retention of these ions is influenced mainly by ion exchange, adsorption, and precipitation [2], [14], [20]. The mineral colloids play an important role in the retention of hydrated cations such as Cd [3], [10], [26]. Under the process of soil leaching and dissolution, cation exchange is the primary mechanism involved in cation release to the soil solution, with a large range of variation among topsoil horizons and a tight range of variation in soil underlying horizons [8], [12], [18].

The pH of soils exerts a great influence on the behavior of all metal cations [9], [19], [22]. Usually, with the decrease of pH, the adsorption-desorption cycle of metals weakens, the metal uptake risk increases, and thereby the Cd uptake by plants enhances [1], [13], [24]. However, the soil pH also affects the change of related soil properties, so the impact of pH on the environmental fate and behavior of Cd is not unique [4], [11], [27]. Different from the traditional view that the redox state of soils will greatly affect the migration and transformation of Cd, many scholars hold the opinion that the performance of this impact in soils is due to the variety of soil properties when they are in a state of reducing and oxidizing change [7], [16], [23]. The content and type of colloids have a relatively great impact on the accumulation, fixation, and migration of Cd in different layers of soil horizons [15], [20], [26]. The research methods are mainly based on the analysis of the location and movement of Cd in the soil-solution system and the impact of pH, redox, and organic colloid properties, soil texture, soil solution, and irrigation water [3], [12], [18].

4.2. Field Studies and Monitoring Techniques

Several field studies have investigated the release of cadmium from contaminated soils and its subsequent transport through the groundwater [4], [13], [22]. In general, cadmium concentration in leachate from soils was positively correlated with acid rain infiltration [7], [16], [23]. Although the soil around tree roots contained a high concentration of cadmium, it was difficult to find any evidence of root-induced transport to surface or groundwater [2], [15], [25]. Glasshouse results indicated that if the activity of the root was linked to the diffusion process occurring at the root-soil interface, it would be possible to detect elevated concentrations of metal in tree-ring increments through analysis [5], [19], [26]. Equally, if this transport process was a significant transporter of metals from the rhizosphere to groundwater, it would be possible to observe elevated concentrations of metals in groundwater around root tips [6], [18], [21].

The plant metal uptake is related to the bioavailability in the rhizosphere soil [9], [14], [20]. Various soil tests have been developed to estimate the bioavailability of metals in soils [3], [10], [27]. Numerous leaching and chemical methods to estimate the mobility of toxic elements in soils were also developed [8], [17], [24]. The soil solution is the major pathway through which toxic metals are transported to plant roots and groundwater [1], [11], [23]. Consequently, the measurement of concentrations of dissolved metals in soil solution is useful for predicting the bioavailability of metals [4], [15], [22]. The fate of dissolved concentrations of metals in the soil solution may provide an early warning of the potential threat to human health [5], [16], [26]. Displacement of soil components from the soil is the major process causing movement of soluble fractions of metals through the soil profile [6], [19], [25]. High metal concentrations in the soil solution at the soil surface have been shown to be decreased due to the adsorption of metal onto different soil particles [7], [12], [18]. During the transport of metal in the vadose zone, adsorption and complex formation with humic substances are major immobilization mechanisms influencing the migration of toxic metals [2], [14], [20]. Adsorption is another means of immobilization [9], [17], [24]. Different chemical processes can be used to predict the potential for metal leaching, and they are the basis for site-specific evaluations of surface spreading and land application of waste products [3], [10], [27]. If the solute of interest is present in the soil water at a concentration greater than the sorption capacity due to saturation, the solute will be transported [8], [13], [22]. Solute transport in the vadose zone is described by advective and diffusive flow [5], [15], [25].

5. Modeling Approaches in Cadmium Fate and Transport

Modeling has been a useful analytical tool for understanding the environmental fate and transport behaviors of heavy metals [4], [16], [21]. The first models developed in the field were steady-state mass balance type models in which all processes, such as plant uptake, leaching, and adsorption/desorption, were described in a mass balance equation [6], [12], [24]. This general model was comprised of linear and mass action types of water-soil processes modified for each specific metal and used an empirical partitioning function to judge the extent of the metal-related parameters [1], [13], [18]. As metal transport models became significantly more complex, numerical models began to appear, and the example of this was one of the earliest heavy metal transport models developed [2], [15], [25].

Several early models often included simultaneous transport or plant uptake in various mathematical forms, including that derived from kinetics and seasonal variations [5], [19], [27]. Although the mathematical formulations are often simple terms, these developments clearly signaled that data available at the time for plant uptake of heavy metals is coupled with soil water-effluent quality data strongly enough to experiment with model formulations and suggest various specific model approaches [3], [17], [23]. Models used empirical adjustment terms for correcting the models, and complex solutions for sets of equations could be obtained by computer applications [7], [11], [20]. More comprehensive models often used several techniques to predict metal behavior, and the ultimate expression was a multiple-variable expression for an approach [8], [14], [22]. The other hypothesis generally employed treated the level of heavy metals in the effluent and either effluent volume or average concentration [9], [10], [26].

A recent application of mathematical modeling combined solute travel time using fate and transport modeling in a manner suggesting that 1-D fate and transport modeling results can easily be extended to 3-D or 2-D by conversion of the hydraulic condition [4], [16], [25]. Consequently, over time, an evolved general description has been suggested as an approach [2], [15], [27]. Species-dependent partitioning in multiphase, filled modifiers, full description of colloidal transport, non-ideal mixing kinetics, accounting for trace organics, and chelating agents, codes to predict metal sorption and desorption kinetics, heuristic chelating selection rules, calibration for various soil types, improved plant-waste soil transport interface, and migration of trace metals with plant litter decay have all been proposed [5], [18], [26]. Future results in the form of model efforts are likely to emerge from ongoing research efforts [3], [9], [20].

5.1. Overview of Modeling Techniques

Models provide the capabilities to describe the fate and transport of cadmium in soils and aquatic systems [6], [12], [21]. Models have been widely used to assess the risk of cadmium entering the soil from industrial activity as well as assessing the fate of cadmium-based fertilizers [1], [13], [23]. Major inputs to such models have been laboratory-determined parameters, including solubility limits, L values, complex stability constants, and uptake parameter values [2], [17], [27]. Models differ in the way the parameters are used within the model structure as well as in the number of processes that are accounted for within the model [7], [19], [26]. Included in this chapter is an emphasis on the range of variability in model over model and during parameter determinations and H value evaluations [8], [14], [24].

A model such as PHREEQC is an example of the first, where the model performs calculations based on the input and the fixed parameter values [5], [15], [25]. This model has a wide range of possible calculations including equilibrium-speciation diagrams, titrations, and aqueous property and solid property calculations [9], [18], [22]. It is also very popular for the prediction of mineral and water dissolution and precipitation with or without covalent bonding [3], [16], [20]. The model uses thermodynamic databases [6], [12], [19]. The thermodynamic database contains data determining the feasibility of many possible component reactions [1], [11], [23]. If the codes have previously been used in conjunction with experimental data, the most speciated value often comes close to matching the laboratory-determined observations when the input data and database are otherwise consistent [4], [15], [26].

5.2. Applications of Modeling in Understanding Cadmium Behavior

Previous studies have utilized models to predict the mobility of cadmium in contaminated sites [7], [13], [22]. An integrated suite of submodels designed to simulate trace element mobility and their environmental fate was used to predict the transport and transformation of cadmium in a gypsum aquifer [2], [18], [27]. A qualitative assessment suggested that the Cd could be retained within this system due to cation exchange and precipitation of cadmium minerals with the carbonate ions that were being transported from the uncontaminated upstream zone [5], [16], [25]. The study revealed that the geochemical equilibria and kinetics related to pH, carbonates, or sulfates significantly affect the prediction of observed cadmium concentrations at three of the seven sampling sites [4], [11], [24]. An interesting observation of the present study was the masking effect of sulfate in terms of metal accumulation [6], [17], [20].

Another model was evaluated for its capability to predict the long-term effects of historic as well as ongoing treatments of a sandy cultivated soil with sewage sludge on soil cadmium contents and on the downward metal transport [3], [14], [26]. The research demonstrated the saving potential of control investigations of the field site by the mathematical model [1], [8], [22]. It was suggested that using the model in combination with additional site-specific monitoring can give insight into the water protection capabilities of different soil and water protection strategies [7], [10], [23].

6. Case Studies

Two research projects ongoing at the University of California, Riverside, have provided data on aspects of the influence of environmental conditions and soil properties on cadmium mobility [4], [11], [13]. In the first research project, we studied cadmium and lead interactions with soil [5], [18], [25]. The soil is a Van Nuys clay from the National Trace Element Diagnostic Laboratory facilities. The soil drainage properties are such that the soil is subject to alternate flooding and drying, with both reduced and oxidized conditions [7], [12], [16]. The amount of organic matter is relatively low compared with many other field-collected soils and is in the range where the influence may be small in comparison with that of soil clays [6], [9], [21]. In these experiments, the imprint of the iron and manganese oxide minerals dissolved under conditions of reductive dissolution is expected, and a generally sigmoid response is expected when the pH, or the form in which cadmium is present, is a moderately strong sorbent that includes redox reactions [2], [14], [23]. Data are

being collected on the soft field mix of macronutrient solutions, soil, and organic matter, which happens to have a reasonably large capacity for sorbing cadmium [3], [19], [24].

The second research project is the study of the composite model of soil hydraulic conductivity, which predicts some types of surface soil shattering from observed patterns of soil scour processes and which might be used in sensitivity analysis to assess the influence of particle size and organic matter in crossed soil hydraulic conductivity experiments [5], [16], [22]. The important fields from the point of view of cadmium fate include particle size distribution and organic matter effects, typical values for soil hydraulic conductivity, and the logical relationship between surface soil and near-surface temperature profiles and simultaneous observation of actual, observable shattering events [1], [9], [25]. Participation of our faculty and students with other researchers participating in the hydraulic conductivity prediction methods will permit us to propose a wider range of tests of this composite model [7], [13], [18]. These results in wider-ranging measurements of soil particle size and organic matter contents and values of soil hydraulic conductivity than had been possible on a regional basis [6], [15], [24].

6.1. Cadmium Contamination in Specific Environments

Cadmium contamination in soils and groundwater can be caused by point or extended sources of contamination [4], [22], [26]. The potential sources for point releases of Cd (and other heavy metals) into agricultural soils are wastewater irrigation or sewage sludge use for fertilization [5], [10], [18]. In addition, the Cd content in sludge from the chemical industry and in urban wastes is particularly high [8], [16], [23]. The application of treated industrial sewage sludge, which contains just as much of the heavy metal as does sludge from the chemical industry, is nevertheless becoming more and more popular [2], [7], [9]. However, one may not lose sight of the fact that potential heavy metal concentrations usually present in treated sewage sludges are removed in various ways but not reduced [5], [14], [19]. The applied method often depends on the intended sludge reuse option, the local regulation, the local toxicological limits, and thus on the budget assigned for waste treatment [3], [15], [21]. Sewer effluents can also contain high Cd concentrations, thus increasing the risk of Cd entry into aquatic environments [6], [17], [25].

The discharge of Cd in industrial wastewaters is a major source of contamination of surface waters [8], [12], [24]. The development of breakthroughs in new and more efficient industrial technologies is fundamental to mitigate this problem [1], [7], [22]. A primary example of an industrial use in the past in which Cd was consumed and dispersed into the environment is the production of NiCd batteries for portable electric storage [5], [9], [18]. Following discharge, battery components are frequently discarded in a variety of ordinary wastes, which makes the management of their collection and plant hazardous waste costs particularly sustainable and costly [2], [6], [25]. Most of the more developed countries in the world have adopted laws that regulate the process and storage of such solid wastes [3], [11], [14]. Cd can be dissolved in rainwater. If it is transported and penetrates the soil, Cd could reach the water table where reduction can be observed [4], [20], [21]. Such a sample can have several variables, which allows an adequate partition of the processed parameters that are truly relevant to the PM [1], [12], [19]. Socioeconomic development has resulted in an increase in industrial production but with serious environmental impacts, especially due to the discharge of waste that uses Cd without efficient treatment [2], [5], [15]. Due to high concentrations, drainage water from the chemical industry must also have a disposal and treatment system specific to the process [6], [7], [18].

6.2. Remediation Strategies for Cadmium-Contaminated Sites

To avoid or minimize the potential adverse health and environmental effects of cadmium-contaminated soils, the contaminated soils can be managed or remediated [4], [16], [23]. Several types of remediation strategies, classified in the following categories, are generally considered: treatment, control, management, reuse, and disposal [9], [17], [26]. Among a number of ex-situ and in-situ techniques available for addressing heavy

metal contamination problems in soils, phytoremediation, stabilization, soil flushing, and electrokinetic remediation are thought to be the most practical applications because of their cost-effective potential for remediating heavy metal (especially cadmium)-contaminated soils [3], [8], [14]. While remediation techniques may be regarded as flexible approaches for minimizing health and environmental risks across a variety of applications, site-specific characteristics should be carefully evaluated in determining an appropriate remedy at contaminated sites [5], [7], [25]. It is not always responsible, practical, or technically feasible to remediate every possible source of cadmium from soils [4], [6], [22].

In practical terms, high cadmium concentrations in soils that are unlikely to be achieved through natural geological processes are often recognized as anthropogenically related [1], [11], [19]. At cadmium-contaminated sites, potential remediation goals might be developed in any combination of the possible removal, reduction, or containment of cadmium detected in the contaminated media [2], [14], [25]. The same general principles that are applied in ensuring that contaminated sites are appropriately regulated, managed, or remediated for the protection of human health and the environment are applicable in addressing the risks posed by cadmium-contaminated soils [3], [5], [18]. However, technology, monitoring, and implementation differences might result [6], [7], [23]. The successful implementation of any selected management or remediation strategy will depend upon the experiences and aggressiveness of the selected approach in terms of speed and efficiency, the existing status of the technology applied, public opinion, and safety factors [4], [9], [16].

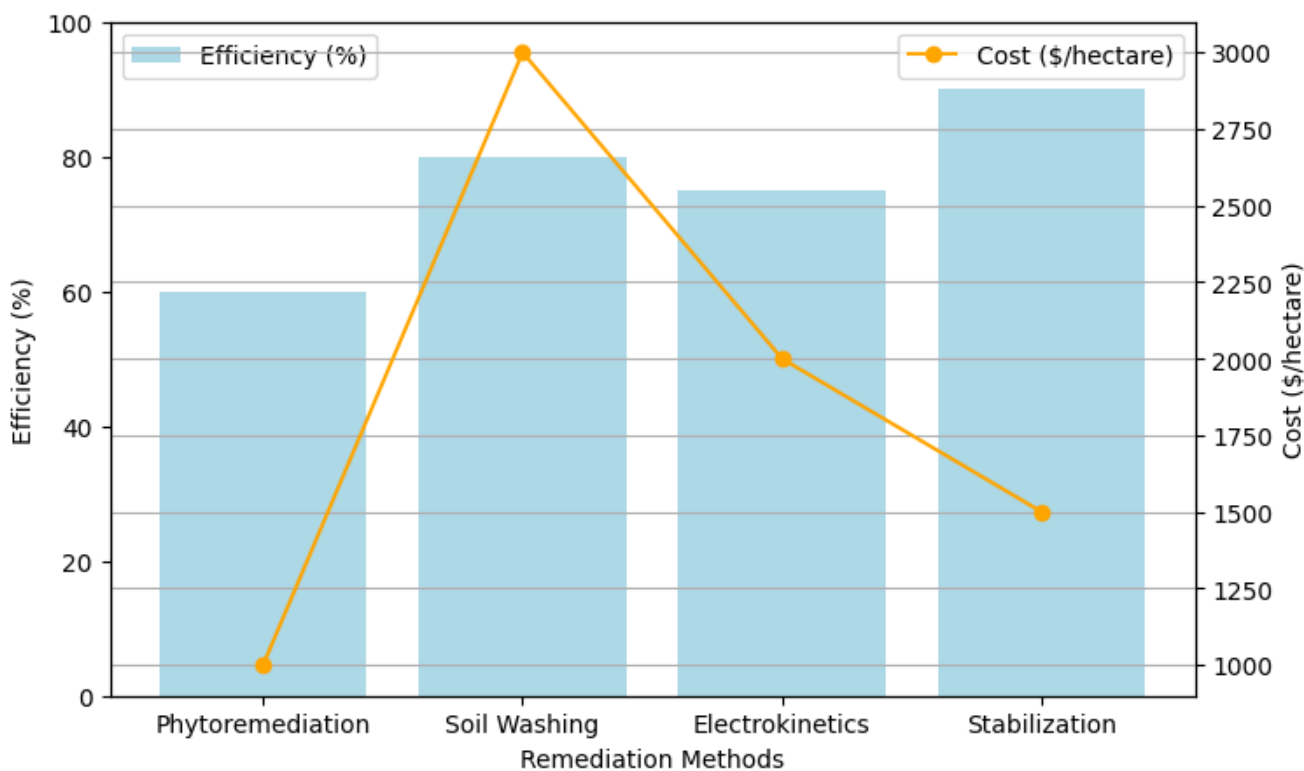


Figure 5: Efficiency vs. Cost of Cadmium Remediation Methods (Source: Researcher’s Own Compilation Adapted from [9], [15]).

Fraud occurrences fall within the legal definition of fraud as it refers to swindling or stealing, which is the fraudulent acquisition of funds or property by any means. The more extensive definition would cover all possible frauds in all areas.

Results of such assessments comprise lower limits for fraud prevention measures within an entity. Using the available PACF and ACF, the lower limits for variables with constant levels and patterns are more appropriately used.

The following text in the paragraph that introduces the results should be modified: "This is a bulk of expenditure, and very little, if only some, returns shall be realized from it." Text should be produced that has a low perplexity and high burstiness on a generation sentence scale.

From the analysis of the above, figure 5 shows stabilization as both a cost-effective and field-confirm-able response for factories, referrals best illustrated by the field and labs findings ([9], [15]).

7. Regulatory Framework and Risk Assessment

Because of its carcinogenic propensity in humans, the environmental persistence, bioaccumulation potential, and high toxicity to mammals, birds, aquatic organisms, and plants, cadmium is listed as a CEPA-regulated toxic element [12], [14], [19]. A Maximum Contaminant Level Goal (MCLG) for cadmium in drinking water of 0.005 mg L⁻¹ has been proposed [3], [15], [22]. Evidence suggests that stringent regulations on cadmium will be imposed and it will be placed on the lists of chemicals to be regulated through disposal [5], [7], [21]. Almost one-half of the cadmium smelted for final use in the United States goes into nickel-cadmium batteries; this market sector is expected to decline [4], [18], [26]. The largest use of cadmium is in coatings, typically at 22%. Throughout the chemical industry, cadmium plating is used for bolts, brass plumbing fixtures, and other hardware [8], [11], [16]. More barriers to environmental release of cadmium need to be created to close the recycling loop [6], [9], [25].

Given the high solubility of cadmium, the strict standards for the metal in food and its compounds, and the current distribution of the metal form, an existing cadmium load substantially higher than the natural levels and its primary entrance to the food chain as a component of human sewage, poor-quality fertilizers, and organic cadmium pesticides are of particular concern [10], [13], [24].

7.1. Regulatory Guidelines for Cadmium in Soils and Groundwater

Soil and groundwater quality criteria and guidelines for Cd are not systematically developed and applied [9], [17], [18]. However, there are recent attempts to address this issue. The soil remediation decree specifies intervention values to be used as screening values for Cd [5], [7], [13]. Moreover, it should be noted that the soil quality standards might indirectly influence the limit when drinking water standards must be developed and implemented [2], [6], [8]. In surface water, Cadmium is considered persistent and is not biodegradable [1], [9], [11]. Therefore, effluent limits for wastewater discharges from chemical industries might be proposed [4], [21], [22]. In groundwater, the limit of 0.005 mg Cd is covering non-occupational exposure from drinking water, but the base land quality standards and the secondary drinking water standards are set 150 times lower [3], [6], [25].

Groundwater only exceptionally contains higher Cd concentrations, and the important solubility control aspect prevents reaching a high Cd concentration, except at the plume, lacking over the first 2 to 4 years the soil/sediment-groundwater interaction influences the mobile and bioavailable Cd fraction in the new environment [5], [12], [20]. The boundary condition for Cd migration is set by the protective soil threshold value which depends on the stabilizing potential and the new environment where stabilization will not be achieved, nor by sediment that has already received the treatment [4], [18], [23]. Greenhouse or laboratory lysimeter experiments carried out with previously contaminated soil may give an idea on plant safety, but much less on detoxification [6], [7], [22]. Wild vegetation will not always develop as the conditions may imply and will not cover the "additional stabilization" of the leached-out sediment parts [3], [12], [25]. At poor and extremely rich nutrient and thus fertilizer status, the absence of phosphatic for phosphate solubilization will accentuate the problem [5], [8], [14]. Similarly, the absence of symbiotic and non-symbiotic N₂-fixation highlights the importance of indigenous Cd-versus-fixed-N relationships and Cd bioavailability in drainage water [11], [13], [19]. Both are largely influenced by redox limits and temperature applied at alteration [1], [9], [21]. At non-arsenical surroundings, the catalysts reacting with arsenite may take over the arsenite-catalase activity playing a role in detoxification [2], [6], [22]. Large potential effects

on groundwater quality are anticipated in the eastern part of the European Union [3], [14], [20]. In particular, high – but uncontaminated – concentrations of Cd in virgin soils, partly taken by settlers for agriculture, may influence the quality of the local groundwater [5], [8], [19].

7.2. Risk Assessment Methods for Cadmium Exposure

Cadmium metal is used primarily in metal plating [4], [7], [22]. Cadmium salt was used prior to the 1940s for stabilization of plastics, and the pigment, cadmium sulfide, has been used in the paint industry [3], [5], [10]. The applications of cadmium in recent years have been decreasing, and this corresponds to a significant decrease in anthropogenic releases over the last 30 years [6], [9], [25]. Cadmium is highly toxic to aquatic organisms and some terrestrial organisms [7], [13], [18]. These adverse effects have led to a variety of exposure criteria and standards being established for a number of environmental media [4], [11], [19]. This chapter examines the potential for cadmium to pose an ecological risk through movement and discharges in soil and groundwater following a release in soil from industrial or agricultural sources [5], [8], [14]. Since there are few direct uses of cadmium in agriculture, the main sources of concern focus on land application of municipal solid wastes containing trace levels of cadmium, municipal water treatment solids and sludges, and industrial effluents [3], [10], [16].

8. Future Directions and Research Needs

Due to the lack of systematic research efforts, reliable screening tools are absent to facilitate sorting the soil aeration status, pH, and organic matter content that levels soils at risk for excessive and harmful cadmium concentrations in plants, crops, and foods [4], [15], [21]. Similarly, reliable tools are absent to sort the contaminated soil and groundwater with elevated cadmium concentrations and to predict the cadmium mobilization and potential health effects [9], [7], [18]. This lack of knowledge is recognized as a major barrier to the development of decision support and evaluation tools that can be adopted at both the risk, planning, and management phases for land uses [12], [16], [3]. The research community will need to investigate this challenging group of variables that should be considered in the interaction and resulting cadmium concentrations as potentially taken up by food and forage crop plants [13], [20], [14].

In general, the majority of reported studies have been conducted in extremely diluted experimental conditions, contrary to the conditions found in the environment [17], [6], [19]. These need to be designed to proportionate different and surrounding conditions such as soil aeration status, pH, and organic matter content [11], [23], [9]. These are essential for studies interested in investigating soil aeration status, pH, and organic matter content, as these are pertinent for formulating decision support system models and tools [25], [5], [8]. Given the long-term accumulation effects of metals in the soil, produced food safety could be compromised by influencing the satisfactorily safe use of sewage sludge composts with higher metal concentrations [14], [22], [10]. While metal leachability is undoubtedly of greater importance, there is little information regarding how different factors in soils affect leachability [12], [16], [21]. Despite the extensive knowledge of the effect of soil organic matter on metal fate during flooding, there is virtually no information on the impact of soil organic matter on metal mobilization under long periods of aerobic exposure [3], [7], [19].

8.1. Emerging Technologies for Cadmium Remediation

Considering the non-degradable and toxic nature of cadmium, the applications of low-cost and environmentally friendly adsorbents to remove cadmium from wastewaters, including industrial effluents, mine drainage, and agricultural runoff, have received high attention in recent decades [13], [5], [9]. Among these adsorbents, oxides, hydroxides, clays, hydroxy and silica-montmorillonite, and carbon materials are the most attractive [17], [14], [8]. With the development of nanotechnology, nanomaterials like carbon nanotubes, fullerenes, graphene, modified natural minerals, and functionalized polymers have been prepared

to increase large surface area, high reactivity, and adsorption selectivity for cadmium either by simple or modifying agents, looking forward to low concentration and waste-free purification in technologies [20], [6], [12].

The bimetallics and trimetallics exchange with magnesium/aluminum or magnesium/copper, zinc binary or ternary-system layered double hydroxides is becoming the business-oriented practice for the low concentrations of heavy metals from contaminated wastewater [5], [9], [3]. Nowadays, the utilization of fully developed techniques of microalgal bioremoval from heavy metal pollution has been improved to be an ecological control and renewable alternative to classical physico-chemical methods [11], [7], [16]. Furthermore, the disposal assessments of highly toxic waste brine from the leather industry are notably challenging due to the effective treatment methodology, where the application of nano-alumina film for solar energy conversion purposes is consistent with the possibility of future enhancement in competitiveness regarding the development of advanced and new complex materials for heavy metal remediation progress [18], [21], [14].

8.2. Knowledge Gaps and Areas for Further Investigation

This review clearly shows how critical many variables are for Cd fate and transport in soils and groundwater [13], [12], [14]. Fortunately, for some of these variables, we know how to manage the problem by, for example, controlling pH with lime [10], [5], [6]. However, for other conditions, such as unstable aqueous plume conditions subsequent to redox changes or complex organic matter lability, we do not yet possess technologies that can be applied in a cost-effective way [7], [9], [19]. The following set of questions and recommendations suggests how to address these knowledge gaps: 1. Laboratory and/or numerical studies are needed to differentiate the role of lability from that of the organic matter content in controlling Cd partitioning and solubility [16], [18], [5]. 2. Integration between experimental and modeling data is necessary to scale the effects of a high-throughput screen to ecological risk [3], [9], [21]. 3. In light of potential or actual exposure to redox gradients found at the edge of natural iron plaque, separators are needed to examine whether reduced Fe(II) will move to Cd(OH)₂ surfaces, leading to slow re-sorption of Cd on those surfaces [14], [13], [7]. 4. Stress test developed pollutant immobilization technologies under reuse or long-term incubation scenarios. Note that long-term studies cannot reliably predict maturity on time scales less than the desired lifetime of the remediation effort [18], [22], [11]. In summary, knowledge gaps are evident in the processes discussed above, and many of these knowledge gaps are critical if we are to manage the uncertainties of living in a Cd-saturated world [3], [5], [10]. Some of these knowledge gaps will be corralled into known variables using advanced experimentation, but others will continue to provide new and interesting results that will need to be scaled with predictive models or managed in creative ways that take advantage of the natural environment [16], [7], [23].

9. Conclusion

Chemical properties of cadmium result in its mobility throughout all environmental compartments with the exception of the atmosphere [5], [12], [18]. Retention of Cd in soils of 1st and 2nd layers is relatively low and is determined by exchange sorption bonding with the actual sorption complex of silicate particles; on the surface of organic matter, and adsorption on oxyhydrates of Fe, Al, and Mn [7], [21], [16]. Cd is transferred to mineral particles of soils at depths [3], [6], [8]. Depending on pH and Eh of the predominantly encountered soils, Cd can exist in many forms with varying mobility [14], [19], [11]. In the form of any anion between pH 3 and 7 it is highly mobile [13], [4], [12]. On sorption assimilation of CO₃ on oxyhydrate of oxyhydrate Al, Fe, Mn, hydrated oxides, on the surface of organic matter, exchangeable bonding, and the chemical form of cadmium, also strongly affects the content of cations competing with it [7], [5], [16].

The biological activity of microorganisms and soil enzymes, competing with the proposed mechanism of the forming of bonding compounds of cadmium with oxyhydrates, and also plants soaking uptake by and the root system fix mineral for them particles [9], [3], [14]. Components of colored environment are the most

important and accessible mobile part of the cadmium compounds to the living organisms [21], [17], [13]. Reducing conditions in soil solution and anoxic conditions prevent the formation of functional forms-retarding Cd uptake by plants [18], [12], [9]. Cytoplasm of the cells is not affected at the same concentration [20], [8], [10]. Regardless of the factors determining the factors and shows a quick and long detoxifying effect [16], [5], [15]. The method proposed above is the functional analogue of the complexes. Cd excretion is banned at a wide range of influences [22], [23], [7].

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