

Micro-Scale Dynamics of Heavy Metal Speciation and Immobilization in Soils

Bijan Kumar Mondal¹, Veena Madhuri Ganjai², Jaydeep Panda³, Chandan Kumar Upadhyay⁴ and Koushik Ghosh⁵

Abstract:

Soil contamination by heavy metals (HM) is a significant ecological and environmental issue on a global scale. Prior research has concentrated on i) identifying the sources of pollution in soils contaminated with heavy metals (HMs), ii) investigating the adsorption capacity and distribution of HMs, and iii) evaluating the phyto-uptake of HMs and their ecotoxicity. Over the past ten years, however, only few papers have provided a systematic summary of HM pollution in soil-plant systems. Therefore, the key to successfully managing and remediating HM contamination is comprehending the mechanisms of interaction between HMs and solid soil components. Soil micro-domains with varying particle sizes and surface characteristics are created as a result of the heterogeneous spatial arrangements, complex structures, and varied compositions of solid soil phases. The speciation, transformation, and bioavailability of heavy metals (HMs) in soils are ultimately determined by the different soil constituents and how they interact. Our knowledge of the behavior of HMs in organic mineral assemblages has significantly increased over the last few decades due to the widespread use of sophisticated instrumental techniques and procedures. With a focus on the interfacial adsorption and immobilization of HMs, this review summarizes research on the immobilization of HMs by minerals, chemical compounds, microbes, and their related complexes.

Introduction:

Heavy metal (HM) contamination in agricultural soils poses significant global risks

*Bijan Kumar Mondal¹, Veena Madhuri Ganjai², Jaydeep Panda³,
Chandan Kumar Upadhyay⁴ and Koushik Ghosh⁵*

¹Ph.D Research Scholar, Department of Soil Science and Agricultural Chemistry, ICAR- Indian Agricultural Research Institute, New Delhi

²Ph.D Research Scholar, Department of Soil Science, Assam Agricultural University, Jorhat

³M.Sc Scholar, Department of Silviculture and Agroforestry, College of Horticulture and Forestry, ANDUAT University, Ayodhya

⁴Ph.D Research Scholar, Department of Soil Science and Agricultural Chemistry, Institute of Agricultural Sciences, BHU, Varanasi

⁵Ph.D Research Scholar, Department of Soil Science and Agricultural Chemistry, Uttar Banga Krishi Viswavidyalaya, Pundibari, Coochbehar, West Bengal-736165

to rice production and food safety. Anthropogenic activities like industrial processes, agriculture, and mining contribute substantially to HM pollution. Research indicates that over 10 million contaminated sites worldwide cover approximately 49.42 million acres, with more than half polluted by hazardous heavy metals. The behavior of heavy metals in soil environments is complex and influenced by multiple interconnected factors. These include soil pH, redox potential, mineral composition, organic carbon content, microorganisms, plant characteristics, and specific soil interface interactions. Soils are intricate ecosystems comprising minerals, organic matter, microorganisms, and fine particles that play crucial roles in determining heavy metal cycling and distribution. The speciation and bioavailability of heavy metals depend on their interactions with solid soil components, including binding mechanisms, ionic states, adsorption processes, precipitation, and chelation. These interactions occur through physical, chemical, and biological processes, forming complex mineral-organic compounds that significantly impact heavy metal mobility and fixation. Advanced analytical techniques such as Fourier transform infrared spectroscopy, X-ray photoelectron spectroscopy, and various microscopic methods have been employed to understand heavy metal reaction mechanisms

at soil interfaces. However, researchers acknowledge challenges related to low detection limits and the uneven distribution of heavy metals across soil components. Understanding these intricate interactions is critical for developing effective environmental risk assessments and pollution remediation strategies, ultimately protecting agricultural productivity and human health.

Speciation of HMs in soils

Sequential chemical extractions analyze heavy metal (HM) speciation in contaminated soils, revealing geochemical phases and potential ecological mobilization risks. While widely used for investigating HM chemical forms, the method's ability to accurately reflect HM bioavailability remains debated due to extractants oversimplifying complex soil environments.

Prominent methods like BCR, Tessier, and Sposito classify HMs into exchangeable, carbonate-bound, organic-bound, iron-manganese oxide-bound, and residual pools. However, variations in soil pollution levels and properties mean extraction rates differ between sites, limiting direct comparative analyses.

To address these limitations, Silveira et al. (2006) proposed refining the approach for Oxisols by:

- ⇒ Combining iron and manganese oxides

⇒ Subdividing into manganese oxide-bound, amorphous iron oxide-bound, and crystalline iron oxide-bound states

This method aims to more accurately capture HM distributions across different soil oxide environments.

Influence of active soil components and their interactions on HM distributions

Association of HMs with clay minerals and iron oxides

The primary constituents of solid soil matrices are minerals, and the most active constituents of soils are clay minerals, which mainly consist of layered silicate minerals, crystalline oxides, and amorphous oxides that have a major impact on the migration and fixation of heavy metals (HMs) within soils. According to Gupta and Bhattacharyya (2008) and Unuabonah et al. (2008), kaolinite (1:1) has a maximum adsorption capacity of 6.8–12.58 mg g⁻¹ for Cd and 7.75–13.32 mg g⁻¹ for Pb. Furthermore, the adsorption capacities of Pb and Cd on montmorillonite are 31.10–75.35 mg g⁻¹ and 30.70 mg g⁻¹, respectively. Both specific and non-specific adsorption methods can be used by heavy metal ions to bind the surfaces of silicate clay minerals. Weak non-specific adsorption mostly takes place at persistently charged locations on mineral surfaces, where electrostatic forces create outer ring complexes. On the other hand, specific adsorption is a really powerful

process that typically takes place at variable charge sites on mineral surfaces, such as Si-OH and Al-OH sites, and leads to the creation of inner ring complexes. The adsorption mechanisms of heavy metals (HMs) on the surfaces of layered aluminosilicate minerals have been the subject of numerous investigations. According to these investigations, Ni ions can form coprecipitates, outer ring complexes, and inner ring complexes on the surface of montmorillonite, whereas Pb²⁺ can form inner ring complexes with Al hydroxyl groups on the surface of kaolinite. While Cd²⁺ forms inner ring complexes at variable charge sites at high pH that are followed by surface precipitation, at low pH it forms outer ring complexes at constant charge sites on the surfaces of montmorillonite. In polluted soils, clay minerals are inexpensive and eco-friendly additives that can help effectively remediate heavy metals (HMs). For instance, a three-year in situ experiment by Sun et al. (2016) showed that the addition of sepiolite drastically decreased TCLP-Cd by 4.0% to 32.5%. Additionally, altering natural clay minerals enhances their adsorption capabilities, making them appropriate for use in remediating contaminated soil. A dosage of 5 weight percent humic acid modified-montmorillonite could successfully reduce the amounts of Cd and Hg in TCLP leachates by 94.1% and

93.0%, respectively. There are two potential processes to account for these findings. First off, humic acid is a naturally occurring organic substance with a range of functional groups that comprise nitrogen and oxygen. The long-term efficacy of metal immobilization is significantly increased by the complexation between these functional groups and metals. Second, adsorption is also facilitated by $C\pi$ -cation interactions between metals and the aromatic rings of humic acid. Adding mercapto-modified attapulgite to Cd-polluted alkaline soils similarly reduced TCLP-Cd concentrations by 16.3%. This suggests that surface complexation, not liming, was the primary stabilization mechanism at work in the soils. Therefore, attaining remediation objectives requires an understanding of the mechanisms and appropriateness of different clay mineral types in HM immobilization. In tropical and subtropical soils, iron oxides are significant secondary minerals. They are appropriate for the sorption and immobilization of various soil HM due to their greater specific surface areas and higher concentrations of surface hydroxyl groups. Goethite has a maximal adsorption capacity of 41.67 mg g⁻¹ for Cd and 67.83 mg g⁻¹ for pyrite. Moreover, several Pb inner ring complexes are visible on pyrite surfaces. When Pb and two Fe hydroxyl groups are on the same side, it generally forms bidentate

complexes at pH \geq 5. However, in addition to bidentate complexes, monodentate complexes with larger coordination distances can also form at pH \geq 4.5. Using X-ray absorption spectroscopy (XAFS), Boily et al. (2005) shown that Cd on goethite surfaces produces a common angle inner ring complex. Meanwhile, another study revealed that Cu and Pb on the surface of pyrite form bidentate inner ring complexes. In their study of 73 paddy soils, Yu et al. (2016) found a significant negative correlation between the content of amorphous iron oxide and exchangeable Cd ($r = -0.400$, $p < 0.01$) as well as carbonate-bound Cd ($r = -0.498$, $p < 0.01$), suggesting that amorphous iron oxide is crucial for Cd speciation.

HMs and organic-mineral composites

Based on both particular and non-specific adsorption mechanisms, SOM is frequently bonded to the exterior surfaces of minerals or between mineral layers. However, the ways that different minerals adsorb chemical molecules vary. Metal-O-C covalent connections can be formed when the carboxyl groups on the surfaces of organic matter and the hydroxyl groups on metal oxide surfaces coordinate. Conversely, the primary binding mechanisms of organic molecules on the surfaces of negatively charged clay minerals include van der Waals forces, hydrogen bonds, and cation bridges (Uddin, 2017; Qu et al.,

2018a). The development of mineral organic complexes alters the minerals' crystal structures, specific surface areas, porosity, surface charges, and surface chemical functional groups. These changes have an impact on the complexes' environmental effects, particularly on the HM ion adsorption behavior. HAs can create outer ring or forinner complexes on clay minerals and oxides by means of hydrophobic contacts, hydrogen bonds, and carboxyl and hydroxyl functional groups on the surface. The connection of HMs may then be considerably impacted by these intricate interfacial interactions. The adsorption of Cu on hematite rose by around 30% when fulvic acid (FA) was present. Pb adsorbed onto goethite-humic and γ -Al₂O₃-FA composites, as well as Cu adsorbed onto goethite-HA complexes and HA-coated gibbsite, likewise showed comparable increases. This phenomena is explained by alterations in HA's affinity for HMs, the creation of ternary complexes, or the lowered surface potential of oxides brought on by HA.

Immobilization of HMs in mineral-microbial complexes

Since clay minerals and microbes have small particle sizes and high surface charges, they are crucial for the binding of heavy metals. As a result, clay mineral-microorganism complexes' ability to

immobilize HMs has continuously drawn attention. When compared to the sum of the individual complex components, the adsorption capacity of mixes of montmorillonite and *Bacillus thuringiensis* and *Pseudomonas putida* increases by approximately 30.6% and 16.4%, respectively.

Additionally, one investigation revealed that the amounts of cadmium adsorption on binary complexes of montmorillonite with *Pseudomonas putida* and *Bacillus subtilis* were marginally higher than those anticipated by component additivity (CA) estimates (Du et al., 2017). Additionally, the adsorption capacity and rate of Pb, Cu, and Zn adsorption are improved by the extracellular polymeric substance (EPS) coating on bentonite. The creation of cation bridges between microbes and minerals is thought to be the cause of the capacity to facilitate adsorption. There have also been reports of decreased adsorption capacity for (hydr)oxide-bacteria composites, which is in contrast to the commonly reported decreased HM adsorption onto clay mineral-bacterial cell systems. According to Alessi and Fein (2010), the additive model determined the cadmium adsorption by Fe hydroxide bacterial composites at varying mineral and organic matter ratios. The composition addition rule also applies to the adsorption of antimony by bacterial goethite complexes. Furthermore, it

has been found that the bacterial iron(hydrogen) oxide complexes' adsorption capability for Sr, Cd, Pb, and Cu ranges from 17% to 193%, which is lower than what additivity would predict. The composite system's decreases could be ascribed to place masking of hydroxyl, carboxyl, and phosphoryl groups on the surfaces of iron (hydrogen) oxides and microorganisms. The adsorption behavior of metal ions on binary mineral-organic or mineral-microbial composites has been the subject of numerous investigations. Nevertheless, only individual determinations of the molecular-scale binding processes and adsorption properties of HMs to ternary mineral-HA-bacteria composites have been made. The fates of metal contaminants are influenced by the addition of active elements (such as minerals, organic matter, and microbes) to natural soils. These uses are typical agricultural techniques or remediation methods to support the preservation of soil fertility, food safety, and soil quality. Nevertheless, little is understood about how metal connections at organic-mineral interfaces are impacted by multi-component interactions. The impact of soil constituents such as minerals, organics, and microorganisms on the adsorption, immobilization, and availability of heavy metals has been covered in numerous reviews, but their distribution-focused analyses have

mostly assessed macro-level dynamics. To provide an overview of the distribution of heavy metals (HMs) at the micro-scale interface from the standpoint of interactions between various soil components, reviews are necessary. This viewpoint is essential for correctly forecasting the fate and distribution of heavy metals (HMs) during pollution cleanup in soils and related environments, as well as for better understanding the features of HM distributions at the micro-interface.

Future challenges and prospects

Previous studies have advanced our understanding of HM behavior at mineral-organic interactions. Although these investigations were carried out in simulated systems, they have shown the impacts of ternary complex formation and mineral organic interfacial reactions on HM fixation. As a result, these connections have not been confirmed in organic settings. Therefore, in order to better understand these systems, soil mineral organic complexes must be used. The low concentration of HMs in natural samples makes it difficult to detect them with EXAFS and NanoSIMS, which is one problem with in situ investigations. For instance, medium- and low-polluted soils had a Cd concentration of 0.3 to 0.8 mg kg⁻¹. Therefore, to precisely assess the interactions between HMs and soil constituents in natural settings, in-situ analytical techniques must be developed.

Specifically, natural soils can gradually restore the availability of immobilized metals to plants. The features of amendments and soil environmental parameters, particularly pH and redox potential, which significantly regulate the possible release of immobilized metals, are the main determinants of a soil's immobilizing capacity. It is crucial that immobilized metals remain stable over time. However, because these studies necessitate lengthy experiments, few studies have assessed the durability of immobilized metals over longer time scales. Therefore, to address the existing HM-contaminated soils, long-term, economical solutions are required. More significantly, long-term field tests are ideal for investigating the lingering impacts of different amendments on diverse soil types in a range of environmental circumstances. Furthermore, it's important to clarify the risks that cleanup techniques pose to the environment and human health. Both mineral-bacterial composites and soils have undergone qualitative characterizations of HM transformations under varied redox settings and aging in the presence of organic matter and microorganisms. Nevertheless, there aren't enough mechanical models to forecast HM speciation under these dynamic soil processes. Therefore, when taking into account microbial activity and comprehending the dynamics of mineral-organic interactions with HM speciation, these

results are far from quantitative and accurate. When characteristics are properly taken into account, the involvement of various soil components in HM fixation may be ascertained from the standpoint of the SOM model for metal fixation, which includes Fe/Al/Mn (hydr)oxides and clay minerals. Although the majority of earlier research has been on abiotic factors, it is important to remember that microbes might be the most active soil constituents involved in HM stabilization, particularly at low metal concentrations. The substantial drops in active heavy metal concentrations brought about by microbial application suggest that microbial activity plays a part in stabilizing contaminants in natural settings. Despite making up a small percentage of the SOM pool, microbial biomass may be responsible for over 50% of the extractable SOM components. According to this review, research on the relationships among microbes, organic matter, different clay minerals, and (hydr)oxides is still in its early stages. Therefore, more research is still needed to fully understand the related mechanisms in metal cycling, particularly in rhizosphere habitats that are abundant in microbial variety and abundance.

References

1. Burgos, P., Madejon, E., Perez-De-Mora, A., Cabrera, F., 2006. Spatial variability of the chemical

- characteristics of a trace-element-contaminated soil before and after remediation.
2. Geoderma 130, 157–175.
 3. Buurman, P., Roscoe, R., 2011. Different chemical composition of free light, occluded light and extractable SOM fractions in soils of Cerrado and tilled and untilled fields, Minas Gerais, Brazil: a pyrolysis-GC/MS study. Eur. J. Soil Sci. 62, 253–266.
 4. Chen, C., Dynes, J.J., Wang, J., Karunakaran, C., Sparks, D.L., 2014. Soft X-ray spectromicroscopy study of mineral-organic matter associations in pasture soil clay fractions. Environ. Sci. Technol. 48, 6678–6686.
 5. Chen, W., Habibul, N., Liu, X.Y., Sheng, G.P., Yu, H.Q., 2015. FTIR and synchronous fluorescence heterospectral two-dimensional correlation analyses on the binding characteristics of copper onto dissolved organic matter. Environ. Sci. Technol. 49, 2052–2058.
 6. Christl, I., Kretzschmar, R., 2001. Interaction of copper and fulvic acid at the hematite-water interface. Geochim. Cosmochim. Acta 65, 3435–3442.
 7. Cui, Y.S., Du, X., Weng, L.P., Zhu, Y.G., 2008. Effects of rice straw on the speciation of cadmium (Cd) and copper (Cu) in soils. Geoderma 146, 370–377.