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SOIL METALS AND SEDIMENTS: A REVIEW

Vivianne Lucia Bormann de Souza

Comissão Nacional de Energia Nuclear
–CNEN, Centro Regional de Ciências
Nucleares do Nordeste –CRCN-NE
Recife-PE

S. D. Barbosa

Comissão Nacional de Energia Nuclear
–CNEN, Centro Regional de Ciências
Nucleares do Nordeste –CRCN-NE
Recife-PE

L. C. D. da Silva

Comissão Nacional de Energia Nuclear
–CNEN, Centro Regional de Ciências
Nucleares do Nordeste –CRCN-NE
Recife-PE

Waldecy

Comissão Nacional de Energia Nuclear
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INTRODUCTION

The contamination of the soil by toxic chemical elements is of greater importance, in an attempt to avoid the compromise of water and food sources, taking into account the countless chemical substances used by the industries, waste disposal, pesticides, and chemical fertilizers used in agricultural activities [1]. Chromium contamination in the soil is often associated with electroplating, metal alloys, industrial sewage, tanneries, chemicals, paper, and cellulose-producing industries, and electricity generating units. Its addition to the soil can occur through atmospheric air, water, and through the application of phosphate fertilizers, limestones, and sewage sludge. The addition of Ni to the soil, per year on a global scale, corresponds to 106 thousand until 544 thousand tons, resulting from metallurgical activities, in the combustion of fossil fuels, and in the addition of sewage sludge and industrial compounds [2]. Metals in soil are retained by physical-chemical bonds and their lability is dependent on the binder, organic matter (OM) and oxides, and on the geochemical condition, especially the pH. The chemical adsorption of metals in the soil, results from the formation of stable molecules, with high binding energy, and has the consequence of the formation of complexes. According to Stevenson (1994) [3], OM has a great affinity for trace metals present in the soil, due to its configuration and profusion of phenolic and carboxylic groups. This behavior, being able to generate adsorption sites, acting via ionic bonding or as a chelating agent in the soil solution. Chelation can keep the metal in the solution, favor transport or make it unavailable due to the precipitation of the complex formed. Cu being the metal that most easily binds to OM [4]. The presence of OM plays an important role, whether in an aquatic or sedimentary compartment. Regarding the particle size,

the finer fractions (basically clay minerals) show high metal content. About the silt and fine sand fractions, the metal concentrations generally decrease as the fraction is composed mostly of quartz components. According to Kyziol et al. (2006) [5], the behavior of soil organic matter to trace metals depends on characteristics of molecular size, molar mass, structure and solubility characteristics, pH conditions, being the ability to solubilize or immobilize trace metals and its efficiency depends mainly on its colloidal shape.

The behavior of trace metals depends on the type of soil, that is, on the levels of oxides of Fe, Al, and Mn, of the interactions between factors such as pH, organic matter content, texture and composition of clays, redox potential, competition between metals by the adsorption sites, complexation reactions, temperature and microbial activity [6]. Among these properties, pH is among those that most affect the chemical distribution, mobility, and availability of trace metals in the soil. As, Se and Cr are elements that change their oxidation state with the change in the soil's redox potential, affecting its speciation, mobility, solubility, and toxicity. Pb, Cu, Zn, and Ni, although they do not change their oxidation state, may suffer indirectly from the change in the soil's redox potential due to the strong association with Fe and Mn oxides, which are susceptible to change in their oxidation state. In a reduction environment, the oxides of Fe and Mn become more soluble, releasing the metals adsorbed to them. In tropical soils, where oxidic mineralogy (mainly Fe, Al, and Mn) and kaolinitic clay predominates, there is great potential for the adsorption of metal ions. Another important aspect in the mobility of trace metals is the degree of crystallinity of the oxides since less crystallized oxides have a greater potential for adsorption of the metals. Concerning this topic, AlleonI and colleagues (2005) [7] found high positive correlations for

Cu and Cd with Fe and Al oxides in Oxisols B horizons, thus indicating the low mobility of metals in these soils. The literature has shown chemical adsorption as the main mechanism of Zn retention in soils [8]. Contrary to the behavior of trace metals in soils in temperate climate regions, where silicate clays of type 2:1 associated with the high pH value of poorly weathered soils, have a great capacity to retain these metals [9]. According to Kabata-Pendias and Pendias (2001) [10] when the pH is more alkaline, the metal preferably precipitates with Mn. That is the degree of acidity/alkalinity influences the formation of Fe and Mn oxides. The Fe content in the soil reflects the nature of the source material and processes that have occurred. Pb and Cd have high chemical activity in the soil, which translates into easy absorption by plants and, finally, threatens human health through the food chain. Although it is well recognized that trace metal contamination is spatially variable in urban districts [11] studies indicate that the extent of trace metal contamination in the soil increases with the age of urbanization.

Digestion with hydrofluoric acid (HF) is usually used to assess the total content of metals in the soil together with other strong acids. Based on the retention of metal in the soil and its translocation in the plant, metals are classified as: of low environmental risk, as they present low solubility and/or high retention in the soil (Ag, Cr, Sr, Ti, Y, and Zr); minimal risk, strongly adsorbed to soil colloids and low plant mobility (As, Hg and Pb); little risk to human and/or animal health, as the "soil-plant barrier" prevents entry into the food chain (B, Cu, Mn, Ni, and Zn) and high risk for damaging human and/or animal health, due to the possibility of accumulation in the food chain (Cd, Co, Mo, and Se). The sources of Ni, As, Cr and Cu were attributed to the metallurgical industries for water samples analyzed in soil of Wuhan, China. The sources

of Cu, Pb and Cr came from transport [12]. Concentrations of Cd and Sb in surface soils of the eastern and western slopes and Pb on the western slope of Ailao Mountain in Yunnan Province of China had altitude distribution trends, which showed their concentrations increased with the increasing elevation. The elevation trends of Cd and Sb were mainly controlled by the effects from atmospheric input and soil organic matter absorption, and there was a "cold trapping" effect in high altitude areas. The distribution variations of As and Cr were mainly derived from the weathering difference of soil parent material, while the variations for Pb were controlled by the weathering of bedrock minerals. Pb, Zn, and Co present a zonal distribution pattern, while Cr, Cu, Ni, V, Cd, and Hg present a point-like distribution pattern, and the physicochemical properties affecting heavy metal content in latosolic red soil [13].

SEDIMENTS

The contamination of sediments by metals can originate from diffuse and punctual sources. Typical diffuse sources are caused by the atmosphere and solid depositions. Typical point sources are emissions from industrial dumps, domestic sewage, garbage dumps, and mining dumps, which cause metal pollution on a local scale. The presence of metals in sediments is due to chemical, biological, and physical processes that occur in rivers, estuaries, and the coastal region. The spatial variation of trace metals in sediments is the result of the combination of these processes. Metals precipitate into the bottom sediments as a result of changes in pH, oxidation, and changes in their chemical composition. The metals in the bottom sediments do not always remain immobilized and can be released as a result of chemical changes in the aquatic environment. According to the Agency for the Registration of Toxic Substances and

Diseases (ATSDR), linked to the American government, trace metals such as As, Pb, and Hg are among the three most toxic substances, requiring priority monitoring and control of these metals in food [14]. The binding of Zn and Cd to carbonates at acid pH is common, which leads to the co-precipitation of these elements with calcium carbonate. Copper and Ni can also form sulfides, influenced by the concentration of sulfur and organic carbon in the aquatic environment. Nickel and chromium evolution in the three cores is similar to that previously reported by Essoni (1998) [15] to the north of the the Mejerda outlet and throughout the Gulf of Tunis, except for offshore sediments (beyond 50 m depth). Enrichment of these metals in the delta sediments is found to be to the same degree as for Pb and Zn. Ni, Cr, and Co also appear to be of human origin, though levels are not sufficient to cause any pollution. For example, the nickel content in the Persian Gulf exceeded 100 mg/kg [16] and attained nearly 50 mg/kg in the Gulf of Gabes [17] and the Gdansk Basin in Poland [18]. Similar values have been recorded in Monastir Bay in Tunisia [19] and Cardiff Bay (25 to 30 mg/kg) [20]. The cobalt content in the Mejerda Delta is even lower, as observed in other similar marine environments: 15 to 21 mg/kg in the Gediz Delta [21] 8 mg/kg in the Rhône Delta [22], and 16 to 24 mg/kg in the Pearl River Estuary in China [23]. Only chromium levels appear to be slightly higher as only 20 to 25 mg/kg are observed in the Rhône Delta [22] and in Monastir Bay and 44 mg/kg in Cardiff Bay.

In general, lead is bound to all five of the sediment fractions. Like lead, copper is also bound to the five fractions, but only at lower depths. The bioavailability of copper in the sediments appears to be more pronounced at depth than on the surface. At greater depths (below 20 cm) copper is bound to

the exchangeable fraction (10 to 20%) and carbonates, making it bioavailable in these fractions. Only 40 to 50% of copper is bound to the residual fraction and this part of copper is highly sequestered in the sediment. Zinc and iron are even more sequestered in the sediment, except for surface levels where Zn is bound to the exchangeable fraction (20%), to oxyhydroxides (40%), and organic matter (5 to 10%). In the deeper layer of the cores, Zn is essentially bound to the residual fraction; zinc is of limited toxicity as more than 90% of it is not bioavailable. Iron is also among the metals whose concentrations are high but with limited toxicity: only 20 to 25% of it is bound to oxyhydroxides and more than 80% bound to the residual fraction Cadmium is one of the most toxic metals for marine biotas, and in the case of the Mejerda Delta, it is the most polluting. However, it is bound only to the sediment's residual fraction (100%) in the cores and at all depths. This trend confirms the latest studies of cadmium speciation in surface sediments in the western Gulf of Tunis [24]. With its abundant mining activities and high Cd values in the catchment, and though theme era Delta has a high level of cadmium in comparison to other coastal areas, the offshore cadmium accumulation is nevertheless so deeply sequestered in the sediment that it is not bioavailable. Organic matter shows that the shallower areas are more prone to detrital accumulation than the deep areas. The potential ecological hazard index for heavy metals in Mejerda (China) was determined following the order of $Cd > Pb > Cu > As > Ni > Zn > Cr > Mn$. Generally, Cd, Pb and Cu presented moderate potential ecological risk, and the others presented low potential ecological risk. Cd, Cu, Cr, As, Ni, Pb and Zn can be derived from artificial factors like fertilizers, road aging, tire wear, exhaust emissions and so on, whereas Mn was derived from natural factors [25].

CONCLUSIONS

It seems that despite of soil contamination by heavy metals, crops have not yet suffered as much impact and the consumption by the population is still viable. Note that sequential extraction can be performed for both soils and sediments. It is also observed that air pollution by heavy metals that precipitate into the soil has been reported as a future concern, especially for children and the elderly, who suffer a greater influence on their health. Copper has also been reported as the element with the highest correlation with organic

matter and this has been a collaborative grid to prevent greater contamination of soils and sediments by heavy metals, confirming the importance of mangroves for the purification of sea and ocean water. It is also notorious that, in general, Mn contamination is due to natural factors, while elements such as: Cd, Cu, Cr, As, Ni, Pb and Zn originate from fertilizers, exhaust emissions and tire wear. Cd, Pb and Cu are generally have a moderate potential risk by environment. Soil weathering is capable of releasing As and Cr, while mineral weathering is capable of releasing Pb.

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