

Fate of some heavy metals in soils: a review

Ehi Robert Orhue* and Uzu Ogbonnaya Frank

Department of Soil Science, Faculty of Agriculture, University of Benin, Benin city, NIGERIA

*Corresponding author. E-mail: orhuerob@yahoo.com

Abstract: This review revealed that heavy metals are naturally components of the soil orchestrated by weathering processes and that the abundance of these metals in our soil environment nowadays is due to numerous anthropogenic activities. These heavy metals are in two major categories namely the essential and non-essential ones. The essential heavy metals are needed in trace amount by living things for their physiological processes. But at higher concentration, it is hazardous in plants and animals. On the other hand, the non-essential ones are dangerous to plants and animals even at low concentrations. This write-up further showed that soil pH, organic carbon, available P, oxides, effective cation exchange capacity, moisture content, oxidation-reduction state of the metals, ion exchange and sorption capacity of the metals are some of the soil factors influencing the fate and availability of the heavy metals. At lower levels of these soil factors, heavy metal ions are rendered free in the solution thereby making them available to plant and underground water. However, the most prominent soil factor influencing availability of these metals is the Soil pH. Raising some of these soil factors to appropriate levels have been discovered to reduce the availability of the heavy metals to mankind.

Keywords: Heavy metal, Soil, Contamination, Ion exchange

INTRODUCTION

Heavy metals are natural components of the earth's crust and have specific gravity of about 5gcm^{-3} (Duffus, 1980; Ademoroti, 1996 and Brady and Weil, 2002), and able to form sulphides (Atimanar and Aldoleya, 2004). Bond and Straub (1973) have earlier classified them as metals with atomic mass greater than the atomic mass of calcium. Heavy metals are classified into essential and non-essential metals. The essential metals are needed by living organisms in trace quantities for optimum performance of life processes and they include Zn, Fe, Co, Mo, Ni, etc. In the case of human body, Forstner and Prosi (1978) identified Fe, Co, Cu, Zn, and Mo as essential. Insufficient supply of these essential metals in an organism leads to problems associated with growth and ability to complete its life cycle, while sufficient supply results in optimum conditions and excess supply results in toxic effects and possibly death (Forstner and Wittmann, 1981; Young and Blevin, 1981).

The non-essential elements include As, Ag, Cd, Hg, Pb and the ability of numerous organisms to accommodate these non-essential metals are limited (Bryan, 1976). They may be tolerated at very low concentration but at higher concentrations, they become toxic. All heavy metals according to Young and Blevin (1981) are potentially harmful to most organisms at some levels of exposure and absorption. However the minimum tolerance levels for heavy metals concentration in plants, fish and man

have been published or computed by World Health Organization (WHO, 1984).

Metals are natural components in the soil brought about mainly by weathering of rocks, sometimes volcanic activity (Forstner and Prosi, 1978; Zollar, 1984 and Biney 1991). Contaminations of environment however, has resulted from industrial activities such as mining and smelting of metalliferous ores, electroplating, gas exhaust, energy and fuel production, fertilizer and pesticide application, and generation of municipal waste (Kabata-Pendias and Pendias, 1989). These heavy metals can be leached into surface water or groundwater, taken by plants, released as gasses into the atmosphere or bonded semi-permanently by soil components such as clay or organic matter. These artificial sources are known as anthropogenic sources. Therefore, the essence of this review was to identify some factors influencing the availability of heavy metals in soils.

FATE OF HEAVY METALS IN SOILS

In the environment, heavy metals are partitioned among the various environmental compartments such as water, soil, suspended solids and biota. Processes such as dilution, dispersion, sedimentation, adsorption and desorption govern their distribution (Biney *et al.*, 1994). Miller (1997) reported that heavy metals exist in colloidal ionic particulate and dissolved phases.

Elliot *et al.* (1986) and Connel and Miller (1984) reported that metals have a high affinity for humic acids, organic

clays and oxides coated with organic matter. The soluble forms are generally ions or unionised organo metallic chelates or complexes (Warren, 1971). The solubility of metals in soil and groundwater is predominantly controlled by pH (Baker and Walter, 1990; Mcneil and Waring, 1992 and Henry, 2000), amount of metal (Biney *et al.*, 1994), cation exchange capacity (Martinez and Mottor, 2000), organic carbon content (Elliot *et al.*, 1986), the oxidation state of the mineral components and the redox potential of the system (Connel and Miller, 1984, Biney *et al.*, 1994). In general according to Ghosh and Singh (2005), soil pH seems to have the greatest effect of any single factor in the solubility or retention of metal in soils. Basta *et al.* (1993) recorded that greater retention and lower solubility of metal cations occurred at high soil pH. Both the concentration of trace metals and their speciation vary significantly, with the composition of soil solution and the amount of moisture content in the soil (Fotovat *et al.*, 1997).

ION EXCHANGE AND SORPTION OF HEAVY METALS IN SOILS

The concentration of trace and toxic metals in soil solution are explained by different authors in terms of adsorption - desorption or precipitation - dissolution reactions in soils. Sorption of heavy metals in soil may result in the release of proton or other metal cations (Doner *et al.*, 1982). According to Doner *et al.*, the addition of Ni, Cu, and Cd helped in the release of Mn in the soil and it is most probable that proton release with Ni and Cu sorption account for most of the Mn release.

The larger silicates in soil provide both permanent charges and pH dependent charges which retain trace metal cations by non-specific electrostatic forces. These trace elements compete with Ca and Mg for available exchange sites and trace metals are retained at higher concentration when in lower pH medium and at lower concentrations when in higher pH system. Metal hydrolysis is more prevalent and is the dominant reaction (Brady and Weil, 2002). The adsorption maximum was significantly high in soil high in pH, organic matter, calcium carbonate, cation exchange capacity and clay content and the binding energy constant however was dependent only on CaCO₃ and total iron content of soils (Rana and Kansal, 1983). According to Rana and Kansal, the release of adsorbed Cd decreased with increasing pH, organic matter, CaCO₃, CEC, and clay components and soils with high binding energy constant and adsorption maxima released smaller amount of Cd. Obukhovskaya (1982) reported that the magnitude of Hg sorption by clay minerals increased with increasing alkalinity of solution and reached maximum values at a pH > 6 and iron hydroxide adsorbed up to 96% of the mercury from the solution in the pH interval of 5-8 and

that the sorption of Hg (OH)₂ molecules plays the main role in mercury adsorption. Yudin *et al.* (1982) reported that the capacity of soils to adsorb Mn and Zn depends on the physicochemical properties of soils among which the reaction of the solution has the greatest effect on the magnitude of the sorption of micronutrients of nucleosides. Acid soils according to Yudin *et al.* fix Mn and Zn less strongly than soils with a weakly acid solution and soils with very acid solution have a higher content of mobile Mn than do weakly acid soils.

Girth *et al.* (1981) noted that Cd adsorption decreased with decreased pH and increase in Cl⁻ concentration from 151-152 Mol Cl⁻/l increased Cd adsorption and whereas the adsorption isotherms for Zn showed greater effects of pH than in the case of Cd and Ni, they were almost unaffected by the increase in Cl⁻ concentration. The total amount of Zn and content of its mobile forms were found to be higher (Berdinkova, 1982) in the soil of Volga flood plain and delta than semi-desert soils and that there were correlation between the amount of Zn and clay particles and the humus in the soil in Soviet Union. In a volcanic ash and an alluvial soil from Japan studied in the laboratory by Biddapa *et al.* (1982), it was observed that Cu, Pb, and Ni were the most mobile metal. Mokma *et al.* (1979) reported that Fe and Mn tended to increase with increasing clay content of soil and greater in poorly drained soils than well drained or somewhat poorly drained soils. Merha and Baser (1982) observed that the distribution of total Mn in saline alkaline soils is related to particle size distribution, pH, lime content and that water soluble Mn is higher in the surface layer of the soil in the rice field of West Bengal alluvial tract. The Mn content of the soil showed a highly significant positive correlation with clay content of the soils and the amount of Mn increased markedly after water logging for one month (Mitra and Mandel, 1983). Skripulchenko and Zolotarewa (1983) reported that Hg concentrations increased with decreasing diameter of the soil particles and that the accumulation of Hg in the clay and fine-silt fractions was shown to be caused by its stable fixation by main components of these fractions, that is humus and secondary clay minerals.

Within the black peat zone both Cd and Pb metals showed differences in behaviour. Cadmium according to Kalcher *et al.* (1983) showed an increased affinity towards the high molecular phase whereas Pb showed an increased capacity to form complexes with smaller molecules. In relation to geochemistry of sediments of a harbour, an enrichment with heavy metals in the order Cd > Cu > Zn > Pb > Co more than Ni more than Cr were reported (Herms and Tent, 1982). Tang *et al.* (1983) recorded that yellow earths derived from quaternary red clay limestone and shale were richer in trace elements than those derived from granite, schist and sandstones in China. The alluvial

soils and soils derived or developed from calcareous shales tended to have Zn, Mn, Cu while the purple conglomerate soils and those developed over grandiocrites and quartz porphyry were low in available trace elements (Weir, 1980). The percentage of organically complexed form of Cu in calcareous soil was decreased by adjusting the soil pH downward and the concentration of uncomplexed Cu in soil solution increased with decrease in pH but the total soluble Cu was relatively insensitive to pH change (McBride and Bouldin, 1984). The solubility of Zn as reported by Jeffery and Uren (1983) in sandy loam was found to decrease markedly with increased soil pH with most of the Zn being present as free metal ions or labile complexes. In contrast, according to Jeffery and Uren, Cu species were largely moderately labile and non labile and the solubility of Cu varied only slightly with soil pH.

A great content of mineral particles and silicates in organic soils was not always accompanied by a higher content of Li (Sapek and Sapek, 1983). However, according to Sapek and Sapek soils developed from peat mud material of higher ash content were as a rule richer in Li than soils of low ash content developed from peat of greater deposits thickness. Scokart *et al.* (1983) reported higher amount of Cd and Zn in an acid loamy soil but with neutral loamy soil their availability was kept by adsorption onto clays and free oxides. The form and distribution of Mn and Fe in some soil of Garhwal hills showed that easily reducible Mn was positively correlated to organic carbon whereas the available Mn showed highly significant positive correlation with clay. (Tauchnitz *et al.*, 1983). The available Fe according to Tauchnitz *et al.* showed a significant negative correlation with pH and a positive correlation with clay and organic carbon content.

The potentiometric titration of humic and fulvic acids in the presence of metal ions indicated the formation of metal-complexes and the magnitude of the pH drops on the addition of metal ions in both humic and fulvic acids followed the order Cu more than Zn more than Mn more than Ca (Ram and Raman, 1983). Zvonarev and Zyrin (1982) reported that sorption of Hg from solution of humus horizon of a leached chernozem and alluvial horizon of leached Alpine-forest soil occur rapidly and equilibrium was reached between the Hg compounds in the solid and liquid phases within 30 minutes at pH between 4.75 and 6.5. In the exchange studies of N_1^{2+} , Cu^{2+} and Mn^{2+} with mixed (heteroionic) kaolinite clays in the presence of Mg^{2+} as complementary ion, Mukherjee *et al.* (1982) reported that the release percentages increased with increased concentration of H^+ added in the form of H-resin or H_2SO_4 and that for a particular amount of H-resin added, the release of the trace element cations present in the clay did not vary practically with the proportion of exchangeable trace element cations

present. The order of release according to Mukherjee *et al.* was $Co^{2+} > N_1^{2+} > Mn^{2+}$ and that the percentage releases of divalent cations from various clays were higher in kaolinite than bentonite. In an experiment conducted in Rajasthan using four texturally different soils ranging from loamy sand to clay loam Vyas *et al.* (1982) reported that total Mn was highest in heavy-textured black hilling soil and decreased as soil became higher in texture. They also reported that water soluble, exchangeable and available Mn also decreased with depth and that total, reducible and active Mn were highly correlated with clay as well as silt plus clay distribution irrespective of depth.

The adsorption behaviour of Cd investigated in four soils, Elliot (1983) reported that Christiana silt (Typic Paleudulf) lima loam (Typic Hapludulf) and vergemes silt loam (glossque Hapludulf) showed low zero points of charge (ZPC) and thus they were negatively charged over the entire pH range typical of the soil system whereas Dorthan clay (Plinthic Paleudulf) in contrast had ZPC around pH of 6 indicating an electropositive surface at its field pH (4.7). When the Cd was complexed with EDTA according to Elliot, Cd was adsorbed by the positively charged Dorthan soil which suggested that strong Chelation does not necessarily produce substantial metal adsorption and in soils with high ZPCs complexed with EDTA, heavy metals become less mobile and available than their bound counterparts. Result of laboratory investigation by Liberati and Elliot (1981) with Cd solutions on surface and subsurface samples from eight soils from north eastern USA showed that sorption was in all cases lowest at low pH (4-5), increased to nearly 100% at the neutral pH range and leveled off or diminished slightly under more alkaline condition (8-9) and that by selective removal of organic matter and Fe-oxides from soils, it was reported that the importance of various soil components influencing retention followed the order of clay more than organic matter more than Fe-oxides. The consistent greater Cd uptake by surface over subsurface soils according to Liberati and Elliot was attributable to difference in organic matter and there was no evidence of any strong correlation that existed between Cd uptake and soil CEC. Kurdi and Donar (1983) reported that Zn or Cu sorption differences among different soils were more related to equilibrium pH than to CEC and that Zn or Cu sorption resulted in the release of H and Mn. The release of H and Mn increased with increased metal ion sorption and was higher with Cu than with Zn. Naidu *et al.* (2003) reported that the amount of Cd retained by oxisol commonly found in northern Australia at natural soil pH values, (5-6) was significantly less than that retained by vertisol (pH 6-7) a soil type common to southern Australia and at any given total metal concentration, the metal fraction is higher in oxisol relative to vertisol unless the

pH of the oxisol are increased (to >6) to enhance their binding capacity.

Due to low negative charge densities at common pH values (4-5), highly weathered tropical soils (oxisols, utisols, andisols and acid alfisols) may exhibit relatively low affinities for heavy metals (McBride, 1994). The persistence and mobility of Cd and Pb in these ultisols, oxisols, andisols as well as acid alfisols are dictated by the extent to which the metals sorbs to solid phase which is a function of reactions affecting surface charge (that is pH and ionic strength) (Naidu *et al.*, 1997). Increased ionic strength and the pH to greater than ZPC (Zero point of charge) in tropical soil system increases negative surface charge. (Marcano-Martinez and McBride 1989; Van-Olphen, 1977; Van-Reji and Peech, 1972). Bruemmer (1999), Davis and Leckie (1978), Dzombak and Morel (1986), Kinneburgh *et al.* (1976), Naidu *et al.* (1994), Puls *et al.* (1991), Rose and Bianchi-Mosquera (1993) and Tiller *et al.* (1984) reported increased Cd and or Pb sorption in tropical soils and or in pure oxide mineral system (goethite) with increased pH due mainly to increased negative surface charge. Appel and Ma (2002) recorded that Pb sorption was greater than Cd sorption in the Oxisol and utisol samples at an initial metal concentration of >0.1mM while Molisol soil sample sorbed roughly equal amount of Cd and Pb due in part to their mineralogical properties, higher pH and generally greater amount of sorption sites compared with highly weathered tropical soils (McBride, 1994). The preference exhibited by oxisol and ultisol Pb over Cd observed by Gao *et al.* (1997), Phillip (1999) and Pardo (2000) may be attributed to Pb's smaller hydrated radius (Nightingale, 1959), greater affinity of Pb for most functional groups in organic matter as well as its higher electronegativity making it better candidate than Cd for electrostatic and inner sphere surface complexation reactions (Hugheey, 1983).

Soil pH plays a major role in the sorption of heavy metals as it directly controls the solubilities of metal hydroxides, as well as metal carbonates and phosphates (Appel and Ma, 2002). Soil pH also affect metal hydrolysis, ion-pair formation, organic matter solubility as well as surface charge iron and aluminum oxides, organic matter and clay edges (Bruemmer *et al.*, 1986; McBride, 1994; Sauve *et al.*, 1988a,b). Increasing soil pH increases cationic heavy metal retention to soil surfaces via adsorption, inner-sphere surface complexation and or precipitation and multinuclear type reactions (Kinneburgh *et al.*, 1976, Rose and Binache-Mosquera, 1993; Basta *et al.*, 1993; Yong and Phadungehewit, 1993 Spark, 1995 and Altin *et al.*, 1999).

Hanafi and Sjaola (1998) observed that CEC was highly positively correlated to sorption of Cd²⁺ and Zn²⁺ in acid tropical soils. Naidu *et al.* (1998) found Cd sorption to depend strongly on surface charge density in tropical

soils while Zachara *et al.* (1992) found that sorption of Cd on the edges of layer silicates and on Fe and Al oxides was controlled by the CEC (at pH<6.5). Yong and Phadungehewit (1993) found that metal sorption occurred over a wider pH range on montmorillonite than on Kaolinite or illite. They also observed lower pH values for Pb and Cd in clayey soil. Heavy metals are less available in soil containing high clay % and with basic pH (Miner *et al.*, 1997). The neutral to mild alkaline (6.6-8.1) conditions appear to have resulted in low solubility of cerussite (Mole *et al.*, 2004). The different amount of metals retained by different soil types may be attributed to the different clay content and mineral composition of the soils, their pH, organic matter content and soil composition which is the medium of reaction in soils (Naidu and McConet, 2003). Miner *et al.* (1997) reported that heavy metals are less available in soil containing high clay percentage and with basic pH.

HEAVY METALS AND OXIDATION-REDUCTION REACTIONS IN SOILS

The presence of hydroxides and oxides such as Fe (III), Mn (III/IV) Cr (III)/(IV) are common in soils and sediments as suspended particles and as coating on clay mineral surfaces. These hydroxides are thermodynamically stable in oxygenated systems at pH 7. Under anoxic conditions, reductive dissolutions of oxides/hydroxides by reducing agents occur. Under anoxic and/or acidic conditions Mn (IV) and Mn (III) oxides and hydroxides are reduced to the more soluble manganous form (Moore and Patrick 1989). Adams and Wear (1957) stated that Mn solubility in aerated soils was extremely pH dependent with appreciable amounts being brought into solution below pH 5.0. Patrick and Turner (1968) noted that an increase in water soluble and exchangeable Mn was one of first measureable effects of reducing conditions brought on by water-logging. They found that the easily reducible Mn fraction decreased by approximately 80% in less than 40 days after submergence. Mitra and Mandal (1983) showed that water soluble plus exchangeable Mn increased at the expense of reducible Mn following flooding. Gotoh and Patrick (1972) found that below pH 5 almost all the reducible Mn was converted to water soluble and exchangeable. Barrlet and James (1980) and Fendorf and Zasoski (1992) reported that Cr(III) can occur as Cr³⁺ and its hydroxide products as CrO₂⁻ and Cr(III) can be oxidized to Cr(IV) by Mn(III)(V) oxides and that Cr (IV) is mobile in the soil environment and found as Cr₂O₇²⁻ and CrO₄²⁻ anions. Iron (II) oxides such as magnetite (Fe²⁺, Fe₂³⁺)O₄ and ilmenite (Fe²⁺, Ti) O₃ have been reported by White and Peterson (1998) to play a significant role in the reduction of inorganic contaminants. They reported that Cr (IV) can be reduced to Cr (III) by a generic Fe²⁺ oxide. However, according to

them, under field conditions and at longer times, the effectiveness of reduction of contaminants such as heavy metals is affected by the reductive capacity of the oxide minerals, the impact of surface passivation and competition effects and poisoning by other aqueous species.

HEAVY METALS AND SOIL ORGANIC MATTER

The soil organic fraction affects the physical, chemical and biological conditions in soils. Chemically, it increases the cation exchange capacity and water holding capacity of soils and cation exchange capacity far exceeding that of clay mineral and sand. It is the reason for high soils buffer capacity. Harmful elements and compounds are detoxified by interaction with soil organic matter (Tan, 1996). Soil organic matter has many functional groups contained in it that can serve as exchange sites and most of this functional group are high in oxygen and are mostly –COOH or OH groups. They can aid to drive the complex reactions in the organic matter and the highly reactive oxygen groups that hold the metals in place tie up metal compounds (Brady and Weil, 2002). The binding of metal ions to abiotic surfaces and ligands like soil organic matter is influenced by pH, quantity of soil organic matter, metal ion content of soil and possibly the concentration of metal ions present which may compete for the same binding site (Brady and Weil, 2002).

Haynes and Swift (1984) reported that Co, Fe, Mn, Zn and Cu were significantly correlated with organic matter content and that the cycling of nutrients and build-up of organic matter which characteristically occurred under grassland condition in New Zealand were the major factors influencing the trace elements status of the soil. Results of trials by Saviozzi *et al.* (1983) showed that added organic residues to soil restricted heavy metal movement and that various organics behaved in different ways. According to Saviozzi *et al.*, association of Pb with organic matter was observed to be greater in samples of soil solution with a higher initial pH and thus was related to increased stability constants for Pb - organic complexes at higher pH.

Garate *et al.* (1983) recorded that an organic soil from North East Spain had a high capacity to absorb Cd, Co, Cr, Cu, Ni and Zn. Sapek and Sapek (1983) found that upper layers of organic soils profile were generally enriched in Li. It was recorded by Scokart *et al.* (1983) that Cd, Zn Cu, Pb were found to be associated with organic matter migration in podzolic soils near zinc smelters. In the studies of the mobility of heavy metals such as Cr, Pb, Zn through major Indian soils namely pellustert (black soil), an oxisol (Laterite soil) and Haplaquent (alluvial soil) D'souza *et al.* (1983) recorded that more than 98% of the surface - deposited pollutants were retained in the top 0 – 2.5 in layer with high doses of

added organic matter when compared with control. Friedland *et al.* (1984) observed that in the forest floor in the green mountains of Vermont Pb, Cu, Zn, Ni as well as Cd increased with increased organic matter for about 14 years. The distribution of total Pb concentration levels in 3944 samples from 896 Scottish soil profiles revealed that Pb concentration in organic soils was generally higher and more variable than that in mineral soils. In a pot trial to determine the effect of organic matter combined with puddling, no-puddling and moisture regimes, Mitra and Madal (1983) however, reported that application of organic matter significantly decreased Cu and Zn content of soil. The composting process was reported by Pitchel and Anderson (1997), Shuman (1998) Pare *et al.* (1999) to have reduced heavy metal availability in the raw material possibly due to adsorption on or complexing by humic substances. The mobility of certain metals such as Mn, Zn, Cu and Fe investigated as affected by soil organic matter and its humic acid fraction revealed that the increasing concentration of soil organic matter caused a decrease while the increasing concentration of humic acid caused an increase in their mobility and that the mobility order was Mn>Zn>Cu>Fe (Khan *et al.*, 1997).

Conclusion

The present review has shown that heavy metals are not only naturally produced by weathering but also enhanced in the soil environment by numerous anthropogenic activities. In the soil environment, these heavy metals availability is highly dependent on some soil factors such as soil pH, organic matter, organic clays and oxides coated with organic matter, amount of heavy metals, cation exchange capacity, clay, silt, available P, etc. with the soil pH having the greatest effect of any single factor in the solubility and retention of heavy metal ions in the soil. At lower levels of these soil factors, the heavy metal ions are freely made available to plants and underground water. Therefore, for the amelioration of soils heavily laden with heavy metals raising some of these soil factors to higher levels may help to reduce their availability and deleterious potentials to mankind.

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