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A review of geo-chemical fractions of heavy metals in agricultural soils

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Abstract

Heavy metals are stable and persistence environmental contaminant of soils. The vast increase in population growth, urbanisation and industrialization leads to increase in use of chemicals, which results in total loads of pollutants being delivered to the soil. Heavy metal pollution in soil environment and subsequent uptake in food chain by aquatic organisms and humans put public health at risks. However, even at lower concentrations heavy metals like Cd, Hg, Cr and Pb may exhibit extreme toxicity under certain condition. Thus, this makes regular monitoring to be more imperative and necessary. Total levels of microelements provide no or little information about their chemical nature or potential mobility and bioavailability in the soil. The bioavailability mainly depends on chemical forms, fractions or phases in which an element occurs and is essentially a function of soil chemistry and mineralogy. This paper therefore, reviews the occurrence of heavy metals in various geo-chemical fractions in soil.

Keywords: agricultural soils, heavy metals, geo-chemical fractions

Introduction

Heavy metals are conventionally defined as elements with metallic properties (ductility, conductivity, stability as cations, ligand specificity etc.) and have higher atomic numbers with atomic densities greater than 5.0 g cm^{-3} (Adriano, 2001; Thomson, 2005) [3, 136]. Heavy metals can be divided into two groups: micronutrients (eg. Zn, Mn, Fe, Cu, Ni) which are required in low doses for plant nutrition and non-essential elements (eg., Cd, Pb, Cr, Hg) which have no known biological function. The latter ones have higher impact on organisms, but even the essential heavy metals can become toxic if a specific concentration level is exceeded (All oway and Jackson, 1991) [7].

Heavy metals are among the most serious environmental pollutants due to their high toxicity, abundance and ease of accumulation by various plant and animal organisms. The world has been witnessing serious environmental changes especially since the dawn of industrialization. Global industrial revolution has led to the release of unprecedented amount of toxic substances (pollutants) into the environment. This has posed serious threats to human health, flora, fauna, water, soil, air and the environment as a whole (Agamuthu and Al-Abdali, 2009; Manaf *et al.*, 2009; Kanmani and Gandhimathi, 2013; Ripin *et al.*, 2014; Dixit *et al.*, 2015) [5, 80, 68, 26]. Natural degradation of pollutants is becoming increasingly difficult due to the quantity, complexity and heterogeneity of pollutants released into the environment. One of such ubiquitous, toxic and recalcitrant pollutant of concern is heavy metals. Examples of heavy metals includes cadmium (Cd), iron (Fe), cobalt (Co), chromium (Cr), copper (Cu), mercury (Hg), lead (Pb), zinc (Zn), arsenic (As), manganese (Mn), nickel (Ni), selenium (Se) and the platinum group metals, which comprises platinum, palladium, rhodium, ruthenium, osmium, and iridium. Although, a number of studies on the prevalence of heavy metals in have been extensively reported (Agamuthu and Fauziah, 2010; Emenike *et al.*, 2012; Ismail *et al.*, 2015) [29, 56] and these studies have tended to focus on the distribution, total concentration and impact of heavy metals on surface and ground water, soils, plants, animals such as fishes and humans.

Sources of Heavy Metals

Heavy metals occur naturally in soils, and the primary minerals and parent material that make up the earth's crust are the original sources of these elements. The amount of these elements present in a given soil is dependent on several factors, including parent material composition,

biogeochemical processes and external contribution. The natural source of these metals is very small and the major contributing factor is anthropogenic activities which are potentially increasing their concentration in soils. Toxic heavy metals (Cd and Pb etc.) are environmental contaminants of great concern because they do not degrade in the soil due to their biochemical properties (Schulthess and Huang, 1990)^[114] and thus, accumulate in environmental media (Kabata-Pendias, 2011)^[65]. Risks associated with the presence of metals are varied and depend on their chemical forms (metal, oxide, salt and organo-metallic). The impact of these metals in soils is their possible transfer into water or plants, which is defined by the term of bioavailability. The mean concentrations of Cd in soils ranged from 0.37 mg kg⁻¹ in pedsols to 0.78 mg kg⁻¹ in histosols (Kabata-Pendias, 2001)^[64]. Studies of soils in remote regions suggest that baseline values for lead, without anthropogenic interference, should be about 20 mg kg⁻¹ (Gough *et al.*, 1988). The concentration of lead in soils generally varies from 10 to 40 mg kg⁻¹ (Kabata-Pendias, 2001)^[64]. Lead is ranked as the number one priority hazardous substance by the Agency for Toxic Substances and Disease Registry (ATSDR) and the EPA (Hoilett, 2006)^[50]. Most soil Pb is thought to be bound to the solid phases and is, therefore, insoluble. The major concern about Pb is its relatively long residence time in the soil, due to a low solubility and a high affinity for adsorption (Badawy *et al.*, 2002)^[12]. Specifically Pb may disturb the structure and function of soil ecosystems (Spurgeon *et al.*, 1994)^[127]. There are two major sources through which heavy metals enter into the environment namely natural sources and anthropogenic or man-made sources (Mohammad *et al.*, 2011; Park *et al.*, 2011; Bolan *et al.*, 2014)^[105]. According to Ripin *et al.*, (2014) and Ashrafi *et al.*, (2014), sources and fluxes of anthropogenically generated heavy metals have received significant attention worldwide. Much research has been conducted on heavy metal contamination in soils from various anthropogenic sources such as industrial wastes, automobile emissions, mining activity, added through use of organic and fertilizer impurities (Alloway and Jackson, 1991)^[7], pesticides (Yang *et al.*, 2002)^[145], irrigation in agriculture (Lombi *et al.*, 2006)^[76], agricultural practice (Mantovi *et al.*, 2003) and several other industrial processes. So, the pollution with heavy metals in particular has various sources, but the metallurgical industries are perceived to be the major anthropogenic ones (Kabata-Pendias, 2011)^[65]. The other major source is the waste materials. In addition to the potential beneficial components, some waste materials may also contain non-essential elements and persistent organic compounds that may be harmful to plants (Iwegbue *et al.*, 2006)^[57]. For the reasons above, soil heavy metal contamination has been documented worldwide, including China (Yang *et al.*, 2002)^[145], Italy (Bretzel and Calderisi, 2006)^[16], Korea (Lee *et al.*, 2006), Australia (Sultan, 2007)^[129] and India (Krishna and Goril, 2007)^[71].

Sequential fractionation

Heavy metals can be associated with several reactive components in soil. Although total metal concentration may indicate the overall level of metal in the soil, this provides no information regarding its chemical nature or potential mobility, bioavailability and potential environmental contamination (Vijver *et al.*, 2004; Powell *et al.*, 2005)^[140, 101]. Metal in soils can be divided into two fractions inert fraction, assumed as the non-toxic fraction and labile fraction, assumed to be potentially toxic. To assess the availability of

heavy metals, only the soil labile fraction is taken into account because this fraction is often called, by extension, the bioavailable fraction (Gray *et al.*, 1999)^[41]. It is the chemical form that determines metal behaviour in the environment and its remobilization ability. Therefore, it is more important to know the distribution of each metal in various forms, than just the total content (Lake *et al.*, 1984)^[73]. Measurement of different soil metal pools is required to quantify these pools both for metal availability and metal toxicity point of view (Ma *et al.*, 2006)^[31].

Sequential fractionation or speciation is a frequently used approach to evaluate metal distribution into different chemical forms present in a solid phase. It is defined by Tack and Verloo (1995)^[130] as the identification and quantification of the different, defined species, forms or phases in which an element occurs and is essentially a function of the mineralogy and chemistry of the soil sample examined. Methods used to characterize metals in soil solid phase include physical fractionation and chemical extraction. Chemical extraction schemes are most frequently used approach to fractionate metals in soils, composts and organic wastes (Iwegbue *et al.*, 2007)^[58]. Conceptually; this categorizes metals associated with chemically homogeneous fractions that, ultimately, affect metal bioavailability.

Sequential fractionation techniques separate elements into different operationally defined soil fractions by subjecting the soil to a series of chemical reagents, each more destructive or using a different chemical reaction than the previous one (Tessier *et al.*, 1979; Morabito, 1995)^[133, 89]. Many of studies have demonstrated that metals are predominantly associated with operational soil fractions that are considered to be relatively unavailable for crop uptake (Sposito *et al.*, 1982; Chang *et al.*, 1984; Sloan *et al.*, 1997; Canet *et al.*, 1998)^[126, 122, 19]. Studies also have reported significant correlations between the amount of trace elements in chemical soil fractions and the amount in plant tissues (Qian *et al.*, 1996; Zhang *et al.*, 1998)^[103, 150]. The extraction profile of each element offers additional information about the kinetics of leaching processes and chemical association between elements in the solid materials (Shiowatana *et al.*, 2001)^[116]. Sequential extraction procedures are employed for measuring five chemical phases of heavy metals. Which include (i) water soluble (ii) exchangeable (iii) linked to organic substances (iv) occluded or co-precipitated with oxides, carbonate and phosphates, or other secondary minerals and (v) ions in the crystalline lattices of the primary minerals (Kashem *et al.*, 2007)^[69]. The first three chemical forms are considered to be balanced among themselves and to be most available forms for plant nutrition, each successive form representing less availability (Petruzzelli, 1989)^[99]. The different fractions of metals (water soluble, exchangeable, organically bound, carbonate bound, sesquioxide bound and residual) are in a state of dynamic equilibrium. They are briefly described below:-

Water soluble fraction

Water soluble fraction of heavy metals consists of non-adsorbed ions and can be extracted by water. This fraction is relatively labile and thus, may be potentially bioavailable (He *et al.*, 1995) as soil solution is a naturally dynamic medium for the transportation of metals from soil to plant (Fritioff and Greger, 2003)^[36] where exchange, adsorption, and complexation reactions take place (Harter and Naidu, 2001)^[45]. In general, plants readily take up the species of trace elements that are dissolved in the soil solution in either ionic

or chelated and complexed forms (Kabata-Pendias, 1992.)^[65]. It is first to be brought in process of fractionation. This fraction is usually negligible, except in areas where evaporites are present. Further this chemical species play important role in transfer of metals along the water, soil, plant, animal and human chain (Banerjee and Shrivastava, 1998)^[13].

Exchangeable or weakly adsorbed fraction

This fraction of microelements includes weakly adsorbed metals retained on the solid surface by relatively weak electrostatic interactions and can be released by ion exchange processes. Changes in the ionic composition, influencing adsorption-desorption reactions, or lowering of pH could cause remobilization of metals from this fraction (Ure *et al.*, 1993). A salt solution is commonly used to remove the exchangeable fraction (Tessier *et al.*, 1979)^[133]. The metals which are associated with the exchange sites on the soil solid phase can be considered as bioavailable (McLaughlin *et al.*, 2000)^[85]. Metals corresponding to the exchangeable fraction usually represent a small portion of the total metal content. Thus, this fraction generally accounts for less than 2% of the total metal present in the soil (Emmerson *et al.*, 2000)^[30].

Carbonate bound or acid soluble fraction

Carbonates are an important host of heavy metals (Yarlagadda *et al.*, 1995; Pichtel *et al.*, 1997; Cabral and Lefebvre, 1998; Maskall and Thornton, 1998)^[146, 100, 18, 83]. Carbonate bound or acid soluble fraction contains the metals which are precipitated or co-precipitated with carbonate. Carbonate can be an important adsorbent for many metals when organic matter and Fe-Mn oxides are less abundant. The carbonate form is a loosely bound phase and liable to change with environmental conditions. This phase is susceptible to changes in pH, being generally targeted by use of a mild acid (Filgueiras *et al.*, 2002)^[34].

Oxide bound or reducible fraction

The oxides and hydrous oxides of iron and aluminium are commonly found in soils in several mineralogical forms including hematite, goethite, gibbsite and hemite. Manganese oxides are also found in moderately high amounts in some soils. Scavenging of metals by these secondary oxides, present as coatings on mineral surfaces or as fine discrete particles, can occur by any or a combination of different mechanisms such as co-precipitation, adsorption, surface complex formation, ion exchange and penetration of the lattice (Filgueiras *et al.*, 2002)^[34]. In principle, the reducible fraction could be split into three fractions: easily reducible fraction (Mn oxides), moderately reducible fraction (amorphous Fe oxides) and poorly reducible fraction (crystalline Fe oxides). Due to the large surface area, iron and manganese oxides are one of the most important geochemical phases impacting the mobility and behavior of trace metals.

Organic matter bound or oxidizable fraction

This includes metals associated through complexation or bioaccumulation process with various kinds of organic materials such as living organisms, detritus or coatings on mineral particles (Tokalioglu *et al.*, 2000)^[137]. Organic substances exhibit a high degree of selectivity for divalent compared to monovalent ions. The composition of organic matter in the soil is highly complex consisting of organic residues, soil biomass, humus, humic acids and humin that play an important role in the distribution and dispersion of metals by mechanisms of chelating and cation exchange. The

most important of these with respect to metal interaction are the humic substances (humic and fulvic acids and humin) because of their stability in the soil and relative abundance (up to 80% of soil organic matter) (Sposito, 2008)^[125]. Degradation of organic matter under oxidizing conditions can lead to release of soluble trace metals bound to this component. The organic fraction released in the oxidizable step is not considered very mobile or available since it is thought to be associated with stable high molecular weight humic substances that release metals in a slow manner. Filgueiras *et al.* (2002)^[34] reported that this fraction was one of the smallest or even negligible in the surface soil horizons. To remove metals bound in the organic phase, the organic material must be oxidized (Tessier *et al.*, 1979)^[133]. Metals associations with organic fraction are not dangerous for environment because this fraction is less extractable. But when the environment becomes increasingly reducing or oxidizing, they can be mobilized (Yobouet *et al.*, 2010)^[147].

Residual Fraction

The residual fraction of microelements consists of primary and secondary minerals in which elements are associated with the mineral lattice. This fraction is the hardest to remove and requires the use of strong acids to break down silicate structures (Tessier *et al.*, 1979)^[133]. Often referred to as the inert phase, representing elements not likely to dissolve in conditions found in nature and, thus a worst case environmental scenario regarding element mobilization (Sims and Kline, 1991; Narwal and Singh, 1998)^[119, 90]. The residual fraction is a major carrier of metals in most environmental systems and can be taken as a guide to the degree of non-availability of metals (Horsfall and Ma, 2005)^[52]. As a result of weathering, a fraction of the trace element content is gradually transferred to forms accessible to plants (Hlavay *et al.*, 2004)^[49]. The equilibrium between this pool and water soluble, exchangeable and other fractions is extremely slow.

Fractionation of Heavy metals

Zinc

Zinc exists as Zn^{2+} , organic and $ZnSO_4^0$ under acidic conditions and Zn^{2+} , organic, Zn hydroxyl and carbonate species in alkaline soils. Water soluble Zn varied from 0.04 to 0.56 mg kg⁻¹ with a mean value of 0.25 mg kg⁻¹ in alkaline soils of Punjab (Thind *et al.*, 1990)^[135]. Razdan (1995)^[106] noticed that the amount of water soluble Zn varied from 0.00 to 0.08 mg kg⁻¹ with a mean value of 0.01 mg kg⁻¹ in soils of Ladakh. Ma and Roa (1997) found that the water soluble Zn varied from 0.15 to 7.00 mg kg⁻¹ in some contaminated soils of USA. Sakal (2000)^[110] reported that rice-wheat cropping system for 10 years on a calcareous soil in Bihar decreased the water soluble Zn content. Regmi *et al.* (2010)^[107] found that the water soluble Zn equals 0.32 and 0.36 mg kg⁻¹ under conventional and 0.2 and 0.1 mg kg⁻¹ under biological farming systems in Merredin and Dalwallinu areas of Australia.

Jalali *et al.* (1989)^[61] noticed that the exchangeable Zn was 0.35-0.65 mg kg⁻¹ in some bench mark soils of Kashmir. The exchangeable Zn varied from 0.08 to 2.24 mg kg⁻¹ with a mean value of 0.84 mg kg⁻¹ in alluvium derived alkaline soils of Punjab (Thind *et al.*, 1990)^[135]. Holmgren *et al.* (1993)^[51] found the exchangeable Zn ranged from 1.5 to 264.0 mg kg⁻¹ in agricultural soils of the United States of America. Razdan (1995)^[106] reported that the amount of exchangeable Zn ranged from 0.02 to 0.12, 0.01 to 0.16, 0.02 to 0.08, 0.00 to

0.18 and 0.00 to 0.08 mg kg⁻¹ with mean values of 0.06, 0.09, 0.03, 0.08 and 0.04 mg kg⁻¹, respectively in soils of Leh, Nobra, Nyoma, Khalsi and Durbug blocks of Ladakh. Mean value of exchangeable Zn expressed as percentage of sum of all fractions for the cultivated Ultisols of Malaysia was found to be 2.4 (Zauyah *et al.*, 2004) [149]. Dong-mei *et al.* (2002) [27] reported that about 75% of the total Zn existed in exchangeable fractions in the China soils.

Alvarez *et al.* (2006) [8] reported that the distribution of Zn content in the exchangeable fraction was in general the lowest and ranged from 0-0.05 mg kg⁻¹ in soils of Central Spain. Bashir *et al.* (2007) [14] found that the exchangeable Zn ranged from 0.0-0.8 mg kg⁻¹ in the soils of Lahore, Pakistan. Minkina *et al.* (2008) [87] showed that the exchangeable Zn was 0.4 mg kg⁻¹ in chernozem soils. Aydinalp *et al.* (2009) [11] found the exchangeable Zn in the cultivated Ultisols of northwestern Turkey averaged 2.2% and in cultivated Inceptisols 0.6%. Kumar and Babel (2011) [72] examined that the exchangeable Zn content ranged from 0.25-1.00 mg kg⁻¹ in soils of Orissa.

Lestan *et al.* (2003) [75] reported that in soils of Slovenia Zn bound to carbonates was 3.9 to 35.1%. Bashir *et al.* (2007) [14] found that the carbonate bound Zn ranged from 6.4-19.6 mg kg⁻¹ in soils of Lahore, Pakistan. Finzgar *et al.* (2007) [35] observed that the carbonate bound Zn ranged from 4.46 to 822.7 mg kg⁻¹ accounting about 5.0-44.7% of the total metal. Minkina *et al.* (2008) [87] obtained carbonate bound Zn content of 6.3 mg kg⁻¹ in chernozem soils of Russia. In Beijing soils of China, the carbonate bound Zn ranged from 2.00-4.54 mg kg⁻¹ with a mean value of 2.86 mg kg⁻¹ (Chen *et al.*, 2009) [103]. Olubunmi (2010) [94] reported that the carbonate bound Zn varied from 3.86-34.86 mg kg⁻¹ with an average value of 18.89 mg kg⁻¹ in soils of Agbabu, Nigeria. The carbonate bound Zn averaged 0.12 mg kg⁻¹ in conventional farming and 0.11 mg kg⁻¹ in biological farming systems (Regmi *et al.*, 2010) [107]. Adaikpoh (2011) stated that the mean content of carbonate bound Zn was 7.90-18.02% in soils of Nigeria. Kumar and Babel (2011) [72] examined that the carbonate bound Zn content ranged from 9.73-29.21 mg kg⁻¹ which accounted 23.84% of its total content in soils of Orissa. The carbonate bound Zn was 0.78-28.00 mg kg⁻¹ in Zambian soils (Mekichirwa *et al.*, 2012).

Research of Hazra *et al.* (1993) on red and lateritic soils of West Bengal revealed that amorphous sesquioxides have greater capacity to bind Zn followed by manganese oxides and crystalline sesquioxides. They found that manganese oxide bound Zn ranged from 0.3 to 1.2 mg kg⁻¹ and constituted 1.7% of the total Zn. Dhane and Shukla (1995) reported that the Mn oxide bound Zn ranged from 0.3 to 0.7 mg kg⁻¹ and constituted 0.5% of the total Zn in some bench mark soils of Maharashtra. Pal *et al.* (1997) examined that amorphous sesquioxide bound Zn ranged from 0.6 to 6.7 mg kg⁻¹ which constituted 1.6% whereas crystalline oxide bound Zn varied from 0.7 to 9.1 mg kg⁻¹ which constituted 3.2% the total Zn content in rice growing soils of Orissa. Lestan *et al.* (2003) [75] reported that in soils of Celje region of Slovenia, most of the Zn (1.4 to 25.4%) was found to reside in less labile forms bound to iron and manganese oxides. Zinc bound to iron oxides for the cultivated Ultisols was 64% (Zauyah *et al.*, 2004) [149]. Obrador *et al.* (2006) reported that the amorphous iron and aluminium oxide bound Zn content ranged from 13.0 to 51.2% in acid to neutral agricultural soils. Bashir *et al.* (2007) [14] found that the oxide bound Zn ranged from 8.32-27.00 mg kg⁻¹ in soils of Lahore. Shober (2007) [117] reported that the reducible fraction of Zn was in the range of 2.06-6.68 mg kg⁻¹ in soils of Pennsylvania, USA.

Wijebandara *et al.* (2007) reported that the manganese oxide bound Zn content varied from 2.18 to 7.65 mg kg⁻¹ in Gangavati taluk soils of Dharwad with a mean of 4.53 mg kg⁻¹. The contribution of this fraction to the total Zn was 0.50 to 4.20 mg kg⁻¹. Minkina *et al.* (2008) [87] reported that the amorphous iron and aluminium oxide bound Zn was 0.3 mg kg⁻¹ in chernozem soils. Aydinalp *et al.* (2009) [11] found that the Zn bound to amorphous iron oxides averaged 32.1% in cultivated Ultisols and 92.1% in Inceptisols. Chen *et al.* (2009) [103] reported that in soils of Beijing city, the oxide bound Zn varied from 7.94-20.29 mg kg⁻¹ averaging 12.25 mg kg⁻¹. Kumar and Babel (2011) [72] examined that the amorphous iron and aluminium oxide bound Zn content ranged from 23.99-108.93 mg kg⁻¹ in soils of Orissa constituting 7.08% of the total element.

Hazra *et al.* (1993) examined that in red and lateritic soils of West Bengal, organic bound Zn content varied from 0.5 to 3.0 mg kg⁻¹ constituting about 3.8% of the total Zn. Prasad and Sarangthem (1993) reported Zn-fulvic acid complexes with lowest stability constant adsorbed on soil colloids with electrostatic and co-ordinate covalent bonds and such complexes were less stable. In some bench mark and established soil series of Maharashtra, Dhane and Shukla (1995) observed that organic bound Zn comprised 0.5% of the total Zn. Hazra and Mandal (1996) observed that organically bound Zn fraction was comparatively more in Inceptisols than in Alfisols of West Bengal which was attributed to the higher content of organic matter in the former soils. The authors stated that though the organic matter content was fairly high, the organically bound Zn content was less in Howrah soils which was attributed to lower soil pH (4.3). They also observed that 94.9% variation in organically bound Zn content was due to the combined effect of the soil properties. Studies conducted by Pal *et al.* (1997) revealed that organically bound Zn content varied from 0.82 to 0.90 mg kg⁻¹ in Haplustulfs of Orissa and constituted about 2.0% of the total Zn. It was also showed that the variation in organically bound Zn was to the tune of 26.3% due to the combined effect of physico-chemical characteristics of soils.

Lestan *et al.* (2003) [75] noticed that in soils of Celje region, Slovenia, about 14.8 to 56.2% of the total Zn was bound to organic matter. The mean value of organic bound Zn for the cultivated Ultisols of Malaysia was reported to be 1.3% (Zauyah *et al.*, 2004) [149]. Alvarez *et al.* (2006) [8] showed that the organic fraction of Zn content was 0.55 mg kg⁻¹ in soils of central Spain. Obrado *et al.* (2006) observed that the fraction of Zn associated with organic matter ranged from 0.4 to 3.2 mg kg⁻¹ averaging 4.9% of the total content in acid to neutral agricultural soils. Bashir *et al.* (2007) [14] found that the organic bound Zn ranged from 8.32-27.0 mg kg⁻¹ in soils of Lahore. Wijebandara *et al.* (2007) confirmed that the organically complexed Zn in Gangavati taluk soils of Dharwad varied from 0.67 to 3.48 mg kg⁻¹ with a mean of 1.76 mg kg⁻¹ and its contribution to the total Zn varied from 0.26 to 11.6%. Aydinalp *et al.* (2009) [11] found that the organic Zn in the cultivated Ultisols averaged 1.1%. Olubunmi (2010) [94] reported that the organic bound Zn varied from 15.06-50.92 mg kg⁻¹ with an average value of 25.15 mg kg⁻¹ in soils of Agbabu, Nigeria. Regmi *et al.* (2010) [107] showed that the organic bound Zn averaged 0.35 mg kg⁻¹ in conventional farming and 0.58 mg kg⁻¹ in biological farming systems. Kumar and Babel (2011) [72] reported that the organic bound Zn content ranged from 0.45-3.89 mg kg⁻¹ accounting about 2.26% of the total Zn in Orissa soils.

Tagwira *et al.* (1993) reported that in sandy loam acidic soils of Zimbabwe derived from different parent rocks, the residual Zn content was 6.5 mg kg^{-1} and constituted 66.5% of the total Zn. They also stated that in the acidic soils derived specifically from granite, the residual Zn content was 3.44 mg kg^{-1} and constituted 60.4% of the total Zn. Dhane and Shukla (1995) studied the distribution of different forms of Zn in benchmark and other established soil series of Maharashtra and noticed that the residual fraction of Zn was a dominant constituent (95.9%) in these soils. Soumare *et al.* (2003) found that residual Zn varied from 25% for Kgba to 60% for Bgda soils of West Africa. Zauyah *et al.* (2004) ^[149] reported that Zn was mostly concentrated in the residual fraction in cultivated Ultisols. Obrado *et al.* (2006) observed that the residual fraction of Zn content ranged from 4.2 to 13.9 mg kg^{-1} in acid to neutral agricultural soils. Bashir *et al.* (2007) ^[14] found that the residual Zn ranged from 11.2-138 mg kg^{-1} in soils of Lahore, Pakistan. Han *et al.* (2007) concluded that most of Zn (60-70%) was present in the stable residual fraction in selected Vertisols of the Mississippi River Delta. The higher percentage of Zn in the residual fraction probably reflects the greater tendency for Zn to become unavailable once it was in the soils. Shober (2007) ^[117] examined that the residual fraction of Zn was in the range of 36.97-69.72 mg kg^{-1} in soils of Pennsylvania, USA. Wijebandara *et al.* (2007) reported that the residual Zn content of Gangavati soils of Dharwad was in the range of 242.8-564.2 mg kg^{-1} . Minkina *et al.* (2008) revealed that the residual Zn was 55.9 mg kg^{-1} in chernozem soils. Aydinalp *et al.* (2009) ^[11] found the residual Zn in the cultivated Ultisols of northwestern Turkey averaged 32.1% and in Inceptisols 92.1%. Study of Kamali *et al.* (2010) indicated that the amount of the residual Zn fraction was almost 80% of the total Zn in soils of Iran. Kumar and Babel (2011) ^[72] reported that the residual Zn content ranged from 2.4-11.19 mg kg^{-1} in the soils of Orissa.

Copper

Copper exists as Cu^{2+} and organic in acidic soils and Cu hydroxyl, CuCO_3^0 and organic forms under alkaline conditions. The Cu (II) is its most common oxidation state in the environment and is classically thought to exist as the free cupric cation $[\text{Cu}(\text{H}_2\text{O})_6^{2+}]$ in solution. Knowledge of the chemical forms of Cu in soils and the relationship of these forms with Cu availability are important for predicting the Cu behaviour in the soil-plant system. Jalali (1976) ^[60] reported that the water soluble Cu was higher in forest (0.06 mg kg^{-1}) compared to Karewa (0.04 mg kg^{-1}) and lower belt (0.01 mg kg^{-1}) soils of Kashmir. Perveen *et al.* (1993) studied micronutrient status of thirty soil series of Pakistan, the results revealed that the water soluble Cu ranged from 0.51-7.92 mg kg^{-1} and was sufficient in all the series.

Exchangeable Cu is generally low in soils. It is expected that the primary sorption mechanism is inner-sphere adsorption. The retention of Cu in soils is predicted to be through the specific adsorption of Cu^{2+} and CuOH^+ on most functional groups (Agbenin and Olojo, 2004). Copper is sorbed through Al-OH on aluminum oxides and is specifically adsorbed, possibly through bidentate structures on allophane and imogolite (Clark and McBride, 1984). The formation of bonds by direct coordination and the functional oxygen's of organic substances often occurs, which is mainly dependent on soil pH (Kabata-Pendias, 2001) ^[64].

Holmgren *et al.* (1993) ^[51] found the exchangeable Cu ranged from 0.30 to 4.95 mg kg^{-1} in agricultural soils. Ma and Roa (1997) confirmed that the exchangeable Cu varied from 0.5 to

3.0 mg kg^{-1} in some soils of USA. Sequential extraction of a soil treated with biosolids showed that only a small amount of Cu was associated with the exchangeable fraction (McLaren and Clucas, 2001). Zauyah *et al.* (2004) investigated that the mean value of exchangeable Cu expressed as percentage of sum of all fraction for the Ultisols was 1.3. Shober (2007) ^[117] revealed that the proportion of Cu that is potentially bioavailable was quite small in unamended soils of Pennsylvania, USA. Gondek (2006) reported that the exchangeable Cu was 0.17-2.64 mg kg^{-1} in soils of Poland. Minkina *et al.* (2008) found 0.3 mg kg^{-1} of Cu in the exchangeable fraction in chernozem soils. Aydinalp *et al.* (2009) ^[11] stated that exchangeable Cu in the cultivated Ultisols and Inceptisols of northwestern Turkey varied between 1.1% 4.7%.

While Cu sorption is mainly controlled by organic matter and oxides in soils, it has been showed to be enhanced by calcite (Rodriguez-Rubio *et al.*, 2003). Precipitation of Cu occurs through its retention by calcium carbonate forming copper hydroxide and carbonate precipitates. Ma and Roa (1997) found that the carbonate bound Cu was 1.1 mg kg^{-1} in the Mollisols of northern China. Guerra *et al.* (2007) noticed that the mean value of 1.6 mg kg^{-1} of the carbonate bound Cu was reported in chernozem soils by Minkina *et al.* (2008) ^[87]. While working with the soils of Agbabu, Olubunmi (2010) ^[94] examined that the carbonate bound Cu varied from 0.00-0.38 mg kg^{-1} with an average value of 0.38 mg kg^{-1} . Wang *et al.* (2010) registered approximately 10-25% of Cu associated with carbonate minerals in northeast China. Adaikpoh (2011) reported that the mean carbonate bound Cu was 3.00-7.74% in the soils of Nigeria. Guan *et al.* (2011) reported that the carbonate bound Cu was 0.66-0.76 mg kg^{-1} in Mollisols. Kumar and Babel (2011) ^[72] revealed that the carbonate bound Cu content ranged from 1.00-4.49 mg kg^{-1} contributing 9.67% to its total level in the soils of Orissa.

Metal oxides are a significant source controlling Cu distribution in soils. The removal of amorphous oxides from a soil decreases the fraction of sorbed Cu/soluble Cu 100 times (Agbenin and Olojo, 2004). Although organic matter is the main component affecting sorption of Cu, especially at neutral pH, oxides control the distribution in soils containing a lower content of organic matter (Vega *et al.*, 2007). Through fractionation it was determined that 15% of Cu was extracted by oxalate, the portion sorbed to free oxides. This shows that amorphous iron oxide provides an important sink for Cu but may not lower Cu solubility in the soil.

Falatah (1993) explored that Cu in the oxide bound fraction was higher, but in its occluded form was lower for conservation tillage systems compared to conventional systems. Ma and Roa (1997) found that the oxide bound Cu was 27.5 mg kg^{-1} in Mollisols. Nikola *et al.* (2001) ^[92] reported that the oxide bound Cu was 2.61 mg kg^{-1} in serpentine soils of Serbia. The Cu distribution corresponded to 11% in iron oxide fraction, 8% in aluminium oxide fraction and 3% in manganese oxide fractions in soils of Brazil (Williams *et al.* 2003). Gondek (2006) revealed that the oxide bound Cu was 2.63-41.07 mg kg^{-1} in soils of Poland. Shober (2007) ^[117] showed that the reducible fraction of Cu was in the range of 0.49-3.92 mg kg^{-1} . Minkina *et al.* (2008) ^[87] found that the amorphous iron and aluminium oxide bound Cu was 0.2 mg kg^{-1} in chernozem soils. Chen *et al.* (2009) ^[103] reported that in soils of Beijing, the oxide bound Cu varied from 8.24-15.09 mg kg^{-1} with a mean value of 11.64 mg kg^{-1} . Kumar and Babel (2011) ^[72] noticed that the

amorphous iron and aluminium oxide bound Cu content ranged from 3.50-11.49 mg kg⁻¹ (4.91%) in soils of Orissa.

Copper is known to have a high affinity for organic matter (Chlopecka *et al.*, 1996) and its preference for organic matter is supported by high stability constant of Cu complexes with organic matter (Ramos *et al.*, 1999). CuOH⁺ retention on humic substances rises as pH is increased. It has been found that dissolved organic carbon sorption can block Cu sorption sites. For treatments without liming, Cu distribution corresponded to 17% in the organic fraction (Williams *et al.*, 2003). In general, dissolved organic matter controls Cu solubility through the formation of dissolved organic carbon Cu complexes and by lowering Cu retention by competition (Martinez-Villegas and Martinez, 2008).

Ma and Roa (1997) found that the organic bound Cu was 0.6 mg kg⁻¹ in Mollisols. Gondek (2006) reported that the organic bound Cu was 1.72-26.98 mg kg⁻¹ in soils of Poland. Minkina *et al.* (2008)^[87] revealed that the organic bound Cu was 4.2 mg kg⁻¹ in chernozem soils of Russia. Chen *et al.* (2009)^[103] noticed that in Beijing soils of China, the organic bound Cu varied from 25.51-43.64 mg kg⁻¹ with a mean value of 37.32 mg kg⁻¹. Olubunmi (2010)^[94] reported that the organic bound Cu ranged from 4.06-38.68 mg kg⁻¹ with an average value of 14.40 mg kg⁻¹ in soils of Agbabu, Nigeria.

Nikola *et al.* (2001)^[92] investigated that the residual Cu was 69.42 mg kg⁻¹ in serpentine soils of Serbia. Soumare *et al.* (2003) found that the residual Cu was less than 35% of the total Cu in soils of West Africa. Gondek (2006) reported that the residual Cu was 1.6-25.0 mg kg⁻¹ in soils of Poland. Guerra *et al.* (2007) observed that in biosolid treated soils, the microelements were predominantly bound to the residual fraction and the residual Cu was 60% of the total Cu. Minkina *et al.* (2008)^[87] reported that the residual Cu was 36.9 mg kg⁻¹ in chernozem soils of Russia.

Nemati *et al.* (2009) indicated that Cu had stronger capacity to associate with the crystalline structures of the minerals. Olubunmi (2010)^[94] examined that the residual Cu varied from 4.70-13.2 mg kg⁻¹ with an average value of 7.95 mg kg⁻¹ in soils of Agbabu, Nigeria. Kumar and Babel (2011)^[72] reported that the residual Cu ranged from 3.5-11.49 mg kg⁻¹ in soils of Orissa.

Iron

Iron exists in low amounts in water soluble fraction probably due to the fact that it is easily absorbed and utilized by plants and other organisms in the soil environment. Jalali (1976)^[60] reported that the water soluble Fe was higher (0.41 mg kg⁻¹) in forest soils of Kashmir as compared to Karewa (0.3 mg kg⁻¹) and lower belt soils (0.3 mg kg⁻¹). Razdan (1995)^[106] found that the amount of water soluble Fe varied from 0.00 to 1.00 mg kg⁻¹ with a mean value of 0.02 mg kg⁻¹ in soils of Ladakh. Sharma (2005) reported that the water soluble Fe ranged from 3.10 to 30.5 mg kg⁻¹ in Alfisols of Punjab. Osakwe (2012)^[96] examined that the water soluble Fe ranged from 0.00 to 1.28 mg kg⁻¹ with an average percentage of 0.08 in soils of south-eastern Nigeria.

Jalali (1976)^[60] obtained contents of exchangeable Fe as 3.7, 3.9 and 2.9 mg kg⁻¹ in valley basin, Karewa and high altitude Kandi soils of Kashmir. Perveen *et al.* (1993) reported that the exchangeable Fe varied between 3.08-51.00 mg kg⁻¹ in North West frontier province of Pakistan. Soumare *et al.* (2003) reported that the readily available Fe was less than 1.5% of the total Fe in soils. Olubunmi (2010)^[94] found that the exchangeable Fe varied from 2.04-46.02 mg kg⁻¹ with an average value of 24.03 mg kg⁻¹ in the soils of Agbabu,

Nigeria. Ibrahim *et al.* (2011) confirmed that the available Fe ranged from 10.31 to 20.17 mg kg⁻¹ in soils of Billiri.

Carbonate fraction of Fe is relatively stable (slowly labile, poorly leachable), hence the high percentage of Fe in carbonate form is an indication that it will not be readily available for uptake by plants (Graham and Stangoulis, 2003). Olubunmi (2010)^[94] found that the carbonate bound Fe varied from 1.90-3.24 mg kg⁻¹ with an average value of 2.69 mg kg⁻¹ in soils of Agbabu, Nigeria. Wang *et al.* (2010) reported only a small fraction of Fe (1.3-2.1%) associated with carbonate minerals. The carbonate bound Fe was 11.74-21.37% in soils of Nigeria (Adaikpoh, 2011). Jelic *et al.* (2011) indicated that the carbonate bound Fe was 2.62 and 4.00 mg kg⁻¹ in field and meadow soils of Serbia. Osakwe (2012)^[96] reported that the carbonate bound Fe ranged from 128-217 mg kg⁻¹ in soils of south-eastern Nigeria.

Nikola *et al.* (2001)^[92] examined that the oxide bound Fe was 8.9 mg kg⁻¹ in serpentine soils. Olubunmi (2010)^[94] reported that the oxide bound Fe varied from 337-803.8 mg kg⁻¹ with an average value of 479.55 mg kg⁻¹ in soils of Agbabu, Nigeria. Adaikpoh (2011) investigated that the oxide Fe was 12.95-32.66% in soils of Nigeria. Jelic *et al.* (2011) concluded that in Vertisols of Serbia, the oxide bound Fe was 4024 and 4094 mg kg⁻¹ in field and meadow soils, respectively. Osakwe (2012)^[96] reported that the oxide bound Fe ranged from 15.4-98.4 mg kg⁻¹ in soils of south-eastern Nigeria.

A very low content of Fe (1.09%) in the organic fraction was reported by Horsfall and Spiff (2005)^[52]. An average of 6.44% of Fe in this fraction was observed by Iwegbue *et al.* (2007)^[58]. Olubunmi (2010)^[94] reported that the organic bound Fe varied from 239.5-1149.00 mg kg⁻¹ with an average value of 569.00 mg kg⁻¹ in soils of Agbabu, Nigeria. Adaikpoh (2011) showed that the organic bound Fe was 28.27-44.39% in soils of Nigeria. Jelic *et al.* (2011) while investigating the Vertisols of Serbia revealed that the organic bound Fe was 221 mg kg⁻¹ in field and 231 mg kg⁻¹ in meadow soils. Osakwe (2012)^[96] reported that the organic bound Fe ranged from 58.7-140.3 mg kg⁻¹ averaging 5.63% in soils of south-eastern Nigeria.

The metals in the residual form are not available to the biota as it is considered to be held within the mineral matrix. Nikola *et al.* (2001)^[92] examined that the residual Fe was 83 mg kg⁻¹ in serpentine soils of Serbia. Soumare *et al.* (2003) registered the greatest amount of Fe in the residual fraction which varied between 75 and 87% of the total Fe in Kgba and Bgni soils of West Africa. Han *et al.* (2007) revealed that most of Fe (50-60%) was present in the stable residual fraction in Vertisols. Olubunmi (2010)^[94] confirmed that the residual Fe varied from 767-3686 mg kg⁻¹ with an average value of 2257 mg kg⁻¹ in soils of Agbabu, Nigeria. Adaikpoh (2011) reported that the residual form of Fe was 26.01-42.64% in soils of Nigeria. Jelic *et al.* (2011) indicated that in Serbia, the residual Fe was 32552 and 31970 mg kg⁻¹ in field and meadow soils of Serbia. Osakwe (2012)^[96] stated that the oxide bound Fe ranged from 993-1462 mg kg⁻¹ with an average percentage of 74.43 in soils of south-eastern Nigeria.

Manganese

Manganese exists as Mn²⁺, MnSO₄⁰ and organic form in acidic soils and Mn²⁺, MnCO₃ and MnSO₄⁰ ions under alkaline conditions. Jalali (1976)^[60] reported that the water soluble Mn was 0.44 mg kg⁻¹ in forest soils and 0.21 mg kg⁻¹ in Karewa and lower belt soils of Kashmir Himalayas. Gondek (2006) reported 0.28-4.3 mg kg⁻¹ of Mn in the water soluble fraction in soils of Poland.

Perveen *et al.* (1993) revealed that the exchangeable Mn ranged from 0.23-23.75 mg kg⁻¹ in some soils of Pakistan. Razdan (1995) ^[106] noticed that the amount of exchangeable Mn had average values of 0.90, 1.98, 1.45, 1.30, 1.81 mg kg⁻¹, respectively in Leh, Nobra, Nyoma, Khalsi and Durbug blocks of Ladakh. Moja (2007) stated that the content of exchangeable Mn was 8.43 mg kg⁻¹ in soils of South Africa. Afifi *et al.* (2011) found that the exchangeable Mn was 16.95 mg kg⁻¹ in soils of Egypt. Sharma and Mukherjee (2011) examined that the soil solution plus exchangeable Mn content ranged from 0.04-0.30 mg kg⁻¹ in arid zone soils of Punjab. Bashir *et al.* (2007) ^[14] examined that the carbonate bound Mn ranged from 12.5-19 mg kg⁻¹ in soils of Lahore. Moja (2007) reported that the content of Mn bound to carbonates was 81.87 mg kg⁻¹ in soils from South Africa. Olubunmi (2010) ^[94] showed that the carbonate bound Mn ranged from 3.96-9.42 mg kg⁻¹ with an average value of 6.47 mg kg⁻¹ in soils of Agbabu, Nigeria. Nearly half (46%-54%) of the total Mn was in the carbonate bound fraction in soils of northeast China (Wang *et al.* 2010). Adaikpoh (2011) reported the mean carbonate bound Mn content of 6.21-18.04% in soils of Nigeria.

In well-drained and well-aerated soils at pH above 6.0, much of Mn exists as manganese oxides (Moja, 2007). However, when soils are waterlogged for two or three days, the oxygen is lost from the soil and microorganisms use the chemically combined oxygen in manganese and iron oxides for their respiratory needs. This process releases Mn from non-available (MnO₂) to available (Mn²⁺) forms and increases the pool of available Mn in the soil (Sims and Wells, 1985) ^[118]. Thus, excessive moisture and readily available organic matter results in high levels of available soil Mn by reduction of manganese oxides.

Nikola *et al.* (2001) ^[92] notified that the oxide bound Mn was 13.96 mg kg⁻¹ in serpentine soils of Serbia. Alvarez *et al.* (2006) reported that the amorphous iron and aluminium oxides bound Mn content was 72 mg kg⁻¹ in soils of Spain. Obrado *et al.* (2006) found that the oxide bound Mn content ranged from 4.0 to 28.2 mg kg⁻¹ (3.4 to 20.9%) in acid to neutral agricultural soils from Central Spain. Bashir *et al.* (2007) ^[14] found that the oxide bound Mn ranged from 2.2-6.0 mg kg⁻¹ in soils of Lahore. Olubunmi (2010) ^[94] confirmed that the oxide bound Mn varied from 9.05-37.00 mg kg⁻¹ with an average value of 17.19 mg kg⁻¹ in soil of Agbabu. Adaikpoh (2011) concluded that the mean oxide bound Mn content was 16.42-31.06 mg kg⁻¹ in soils of Nigeria. Sharma and Mukherjee (2011) revealed that the Mn adsorbed on to oxide surfaces ranged from 28-173 mg kg⁻¹ in arid zone soils of Punjab.

Nikola *et al.* (2001) ^[92] reported that the organic bound Mn was 6.12 mg kg⁻¹ in serpentine soils of Serbia. Alvarez *et al.* (2006) revealed that the organically bound fraction of Mn was 14 mg kg⁻¹ in soils of Central Spain. Bashir *et al.* (2007) ^[14] found that the organic bound Mn ranged from 2.2-6.0 mg kg⁻¹ in Lahore soils of Pakistan. Moja (2007) indicated that the organic bound Mn was 185.6 mg kg⁻¹ in some soils of South Africa. Olubunmi (2010) ^[94] examined that the organic bound Mn varied from 5.82-24.6 mg kg⁻¹ with an average value of 13.47 mg kg⁻¹ in soils of Agbabu, Nigeria. Adaikpoh (2011) found that the organic bound Mn was 21.33-35.91% in soils of Nigeria. Sharma and Mukherjee (2011) revealed that the Mn bound to organic sites ranged from 14-56 mg kg⁻¹ in arid zone soils of Punjab.

Nikola *et al.* (2001) ^[92] concluded that the residual Mn was 27.18 mg kg⁻¹ in serpentine soils of Serbia. Soumare *et al.*

(2003) found the residual Mn was more than 51% of the total Mn in soils of West Africa. Obrador *et al.* (2006) reported that the residual fraction of Mn ranged from 4.2 to 13.9 mg kg⁻¹ (26.4-56.8%) in acid to neutral soils. Bashir *et al.* (2007) ^[14] found that the residual Mn ranged from 77-168 mg kg⁻¹ in soils of Lahore.

A case study conducted on Vertisols of the Mississippi River Delta alluvial plain revealed that Mn in catfish pond soils was greater in labile and lower in potential labile fractions compared to paddy and forest soils which had higher Mn in potential labile fraction (Han *et al.*, 2007). Moja (2007) reported that the residual Mn was 908.7 mg kg⁻¹ in soils of South Africa. Olubunmi (2010) ^[94] reported that the residual Mn varied from 11.90-35.80 mg kg⁻¹ with an average value of 27.40 mg kg⁻¹ in soils of Agbabu. The mean residual Mn was 20.14-30.99% in soils of Nigeria (Adaikpoh, 2011).

Cadmium

Cadmium exists as Cd²⁺, CdCl⁺ and CdSO₄⁰ in acidic soils and Cd²⁺, CdCl⁺ and CdSO₄⁰ ions under alkaline conditions. Sauve *et al.* (1997, 1998) reported that the phytoavailability of trace metals including Cd is more strongly correlated to the free metal ion activity in soil solution than to total metal content of soils. Water soluble Cd can easily move and may be considered as highly bioavailable.

Organic matter plays an important role not only in forming complexes, but also in retaining Cd in exchangeable form (Zalidis *et al.*, 1999). Gondek (2006) investigated that the exchangeable Cd was 0.13-18.4 mg kg⁻¹ in soils of Poland. Bashir *et al.* (2007) ^[14] found that the exchangeable Cd ranged from 0.0-0.3 mg kg⁻¹ in soils of Lahore, Pakistan. Kashem *et al.* (2007) ^[69] showed that the mobile fraction of Cd varied from 22 to 64%, with higher values in contaminated soils compared to the non-contaminated soils. Aydinalp *et al.* (2009) ^[11] observed the exchangeable Cd in the irrigated vertisols was 1.03 mg kg⁻¹. Ibrahim and Al-Hawas (2009) found that the exchangeable Cd ranged from 0.25-1.00 mg kg⁻¹ in calcareous soils of Al-Hassa at Saudi Arabia. Abioye *et al.* (2011) concluded that the exchangeable Cd was 0.69-12.1 mg kg⁻¹ in shooting range soils of Florida. Rahmani *et al.* (2012) reported that the exchangeable Cd was 0.22 mg kg⁻¹ in some of the calcareous polluted soils of Iran.

Ma and Roa (1997) noticed that the carbonate bound Cd was 3.9 mg kg⁻¹ in Mollisols of northern China. Chen *et al.* (2009) ^[103] found carbonate bound Cd below detection limit in Beijing soils of China. Olubunmi (2010) ^[94] reported that the carbonate bound Cd ranged from 0.98-1.26 mg kg⁻¹ with an average value of 1.09 mg kg⁻¹ in soils of Agbabu, Nigeria. Wang *et al.* (2010) observed that 10-25% of Cd was associated with carbonate minerals in northeast China. Adaikpoh (2011) reported that the carbonate bound Cd was 8.10-20.72% in soils of Nigeria. Rahmani *et al.* (2012) pointed out that the carbonate bound Cd was 0.5 mg kg⁻¹ in some calcareous soils.

It has been proposed that hydrous oxides of iron and manganese furnish the principal control on the fixation of Cd in soils. This fraction could be considered relatively stable, but could change with variations in redox conditions of the soil (Horsfall and Spiff, 2005) ^[52].

Ma and Roa (1997) noticed that the oxide bound Cd was 17.8 mg kg⁻¹ in Mollisols. Gondek (2006) reported that the oxide bound Cd was 0.32-45.42 mg kg⁻¹ in soils of Poland. Bashir *et al.* (2007) ^[14] found that the oxide bound Cd ranged from 0.08-0.45 mg kg⁻¹ in soils of Lahore. Olubunmi (2010) ^[94] reported that the oxide bound Cd varied from 2.25-2.75 mg

kg⁻¹ averaging 2.44 mg kg⁻¹ in soils of Agbabu. Osakwe (2012) ^[96] found low levels of Cd associated with iron and manganese oxides ranging from 3.93 to 21.51% with an average of 15.86% in soils of Nigeria.

Fernandez *et al.* (2004) reported that the organic bound Cd content averaged 0.10 mg kg⁻¹ in Haplic and Luvic calcisols. The organic bound Cd was 0.13-18.14 mg kg⁻¹ in soils of Poland (Gondek, 2006). Chen *et al.* (2009) ^[103] observed that in soils of Beijing city of China, the organic bound Cd was below detection limit. Olubunmi (2010) ^[94] explored that the organic bound Cd varied from 0.18-0.40 mg kg⁻¹ with an average value of 0.31 mg kg⁻¹ in soils of Agbabu. Yobouet *et al.* (2010) ^[147] examined less than 6% of Cd in amorphous organic bound form. Adaikpoh (2011) reported that the organic bound Cd was 2.55-11.05% in soils of Nigeria. Rahmani *et al.* (2012) showed that in some calcareous soils, the organic bound Cd was 0.18 mg kg⁻¹.

Gondek (2006) found that the residual Cd was below detection limit in soils of Poland. Bashir *et al.* (2007) ^[14] reported that the residual Cd ranged from 0.78-4.2 mg kg⁻¹ in Lahore soils. Olubunmi (2010) ^[94] revealed that the residual Cd varied from 8.7-10.20 mg kg⁻¹ with an average value of 9.33 mg kg⁻¹ in Agbabu soils. Osakwe (2012) ^[96] examined that the residual Cd ranged from 16.67 to 76.94% with an average of 37.69% in soils of Nigeria. Rahmani *et al.* (2012) reported that the residual Cd was 2.85 mg kg⁻¹ in some of the contaminated calcareous soils of Iran.

Lead

Lead exists as Pb²⁺, organic and PbSO₄⁰ ions in acidic soils and Pb hydroxy, organic and carbonate species in alkaline soils. Although the total Pb concentration in many contaminated soils may be high, the bioavailable Pb fraction (water soluble and exchangeable) is usually very low due to its strong association with organic matter, Fe-Mn oxides, clay and precipitation as carbonates, hydroxides, and phosphates (McBride, 1995). Howard and Jeffrey (1993) reported that the water soluble Pb ranged from 0.0 to 1.9 mg kg⁻¹ in soils of southeastern Michigan. Several researchers found a very small fraction of the total Pb in soil solution (Ramos *et al.*, 1994; Chlopecka *et al.*, 1996; Maiz *et al.*, 2000).

Lead accumulates in the upper soil horizons and is highly immobile. Contamination is long-term without remedial action, high soil Pb levels will never return to normal. As observed by several authors (Ramos *et al.*, 1994; Chlopecka *et al.*, 1996; Maiz *et al.*, 2000), a small portion of the total Pb (0.01-6.40%) was exchangeable from the soil colloids to the soil solution.

Holmgren *et al.* (1993) ^[51] found the exchangeable Pb varied from 0.5 to 135 mg kg⁻¹ in agricultural soils. Howard and Jeffrey (1993) examined that the exchangeable Pb ranged from 0.0 to 3.1 mg kg⁻¹ in soils of southeastern Michigan. Gondek (2006) reported that the exchangeable Pb was 1.2-4.81 mg kg⁻¹ in soils of Poland. Finzgar *et al.* (2007) ^[35] explored that the exchangeable Pb ranged from 0.02 and 27.1 mg kg⁻¹ in Mezica Valley and Celje region of Slovenia. Golia *et al.* (2007) researched that 75-89% of the total Pb was present in exchangeable fraction. Guerra *et al.* (2007) showed that the exchangeable Pb was 1.1% of the total metal in Mollisols of Chile. Kashem *et al.* (2007) ^[69] found that mobile fraction of Pb varied from 8-15% in the contaminated soils. Minkina *et al.* (2008) ^[87] reported that the exchangeable Pb was 0.4-0.6 mg kg⁻¹ in chernozem soils of Russia. Aydinalp *et al.* (2009) ^[11] confirmed that exchangeable Pb in the irrigated vertisols of northwestern Turkey was 2.78 mg kg⁻¹. Atkinson

et al. (2010) investigated that the exchangeable Pb was 1.42, 0.00, 1.75 and 0.07% of the total Pb in an arable fenland, an uncultivated grassland site, a sewage sludge processing farm and a grassed roadside location, respectively. In all the cases, there was a very low proportion of Pb in the exchangeable fraction. Yobouet *et al.* (2010) ^[147] reported less than 5% of total Pb in exchangeable fraction in the soils of Cote d'Ivoire. Abioye *et al.* (2011) reported that about 10% of the total Pb in exchangeable form in soils of Florida. Afifi *et al.* (2011) examined that the exchangeable Pb was 2.25 mg kg⁻¹ in Egyptian soils.

Howard and Jeffrey (1993) reported that the carbonate bound Pb ranged from 0.4-196.7 mg kg⁻¹ in soils of southeastern Michigan. Ma and Roa (1997) found that the carbonate bound Pb was 2.5 mg kg⁻¹ in Mollisols. Teutsch *et al.* (2001) investigated that the carbonate bound Pb ranged from 0.2 to 291.0 mg kg⁻¹ which accounted 1.5-52% of its total concentration in the vicinity of a major highway (Jerusalem-Tel-Aviv) in Israel. In contrast to natural Pb, largest fraction of anthropogenic Pb in the studied soils was associated with pedogenic carbonate. Badawy *et al.* (2002) ^[12] revealed the solid phase control of Pb in soil solution and concluded that it was most likely governed by a mixture of Pb minerals comprising Pb carbonates. Lestan *et al.* (2003) ^[75] reported that Pb was found to reside in less labile form bound to carbonate (2.04 to 43.5%). Finzgar *et al.* (2007) ^[35] stated that the carbonate bound Pb constituted about 5.0-67.1% of the total Pb. Atkinson *et al.* (2010) reported that the carbonate bound Pb was 6.35, 0.19, 19.4 and 6.28% of total in an arable fenland, an uncultivated grassland site, a sewage sludge managed processing farm and a grassed roadside location. Nearly 10-25% of Pb was associated with carbonate minerals in northeast China (Wang *et al.*, 2010). Abioye *et al.* (2011) noticed 36.34 mg kg⁻¹ of Pb associated with carbonates which accounted 82% of the total Pb in shooting soils of Florida. Osakwe (2012) ^[96] showed that carbonate bound Pb ranged from 128-217 mg kg⁻¹ averaging 16.29% in soils of southeastern Nigeria.

Iron and manganese oxides normally provide the most important adsorption surface for Pb, particularly at higher soil pH (7.9) (Sauve *et al.*, 2003; Terzano *et al.*, 2007). Sequential extraction of soils have shown that Pb is often associated with iron and manganese oxide minerals and organic/sulphide fractions (Burt *et al.*, 2003; Wilson *et al.*, 2006; Strawn *et al.*, 2007).

Teutsch *et al.* (2001) reported that the oxide bound Pb ranged from 3.3 to 232.0 mg kg⁻¹ which accounted about 20-40% of the total Pb in the vicinity of a major highway (Jerusalem-Tel-Aviv) in Israel. Lestan *et al.* (2003) ^[75] observed that in soils of Celje region, most of the Pb (0.0 to 16.1%) was found to reside in less labile form bound to iron and manganese oxides. Fernandez *et al.* (2004) reported that the amorphous iron and aluminium oxide bound Pb content was 3.93 mg kg⁻¹ in Haplic calcisol and Luvic calcisol soils. Gondek (2006) revealed that the oxide bound Pb was 8.44-33.83 mg kg⁻¹ in soils of Poland. Jaradat *et al.* (2006) concluded that the Pb mostly existed in the Fe-Mn oxide fraction. Finzgar *et al.* (2007) ^[35] examined that the oxide bound Pb ranged from 0.18 to 74.2 mg kg⁻¹ which accounted about 0.11-8.3% of the total element. Guerra *et al.* (2007) investigated that the oxide bound Pb was 15.3% of the total metal in Mollisols. Research conducted by Shober (2007) ^[117] revealed that the reducible fraction of Pb was in the range of 11.48-19.39 mg kg⁻¹. Minkina *et al.* (2008) ^[87] reported that the amorphous iron and aluminium oxide bound Pb was 0.7 mg kg⁻¹ in chernozem

soils. Aydinalp *et al.* (2009)^[11] found that the Pb bound to amorphous iron oxide averaged 48.7% of its total concentration in the cultivated Ultisols and 88.6% in Inceptisols. Atkinson *et al.* (2010) found that the organic bound Pb was 23.00, 1.84, 33.4 and 57.2% of the total Pb in an arable fenland, an uncultivated grassland site, a sewage sludge processing farm and a grassed roadside location. Olubunmi (2010)^[94] reported that the oxide bound Pb varied from 0.00-1.35 mg kg⁻¹ with an average value of 0.88 mg kg⁻¹ in soils of Agbabu.

Teutsch *et al.* (2001) revealed that the organic bound Pb ranged from 0.3 to 71.0 mg kg⁻¹ which accounted about 1.2-20.0% of the total Pb in the vicinity of Jerusalem-Tel-Aviv highway in Israel. In soils of Celje region of Slovenia, about 35.8 to 71.1% Pb was bound to organic matter (Lestan *et al.*, 2003)^[75]. Gondek (2006) found that the organic bound Pb was 8.44-33.83 mg kg⁻¹ in soils of Poland. Finzgar *et al.* (2007)^[35] examined that the organic bound Pb accounted 31.5-74.7% of the total soil Pb. Guerra *et al.* (2007) revealed that organic bound Pb was 5.5% of the total metal in Mollisols of Chile. Minkina *et al.* (2008)^[87] reported that the organic bound Pb was 6.5 mg kg⁻¹ in chernozem soils of Russia. Olubunmi (2010)^[94] reported that the organic bound Pb varied from 0.64-1.58 mg kg⁻¹ with an average value of 1.09 mg kg⁻¹ in Agbabu soils. Abioye *et al.* (2011) registered 44, 46 and 13% of the total Pb associated with organic fraction in three shooting soils of Florida.

Howard and Jeffrey (1993) stated that the residual Pb ranged from 6.2-70 mg kg⁻¹ in soils of southeastern Michigan. Teutsch *et al.* (2001) reported that the residual Pb ranged from 11-51 mg kg⁻¹ which accounted 8.0-61% of the total element in the vicinity of Jerusalem Tel-Aviv highway in Israel. Lestan *et al.* (2003)^[75] showed that in soils of Celje region, Slovenia, a major portion of Pb was found to reside in less labile residual fraction (10.4-53.4%). Gondek (2006) reported that the residual Pb was 2.7-10.82 mg kg⁻¹ in soils of Poland. Finzgar *et al.* (2007)^[35] confirmed that the residual Pb ranged from 12.9 to 606.0 mg kg⁻¹ accounting 5.9-23.8% of its total content in Mezica Valley and Celje region of Slovenia. Minkina *et al.* (2008)^[87] reported a residual Pb level of 14.3 mg kg⁻¹ in chernozem soils of Russia. The dominant fractions of Pb in Ultisols were residual and exchangeable whereas in Inceptisols it was mainly bound to residual and Fe/Mn oxide fraction (Aydinalp *et al.*, 2009)^[11]. Atkinson *et al.* (2010) concluded that the residual Pb was 28.1, 98.0, 25.2 and 21.4% in an arable fenland, an uncultivated grassland site, a sewage sludge processing farm and a grassed roadside location, respectively.

Nickel

Ma and Rao (1997) found that the water soluble Ni was below detection limit in some soils of USA. Shober (2007)^[117] showed that the proportion of Ni that is potentially bioavailable is quite small. Osakwe (2012)^[96] reported low levels of Ni (0.03-0.13 mg kg⁻¹) in water soluble fraction. Holmgren *et al.* (1993)^[51] found the exchangeable Ni averaged 0.70 to 269.0 mg kg⁻¹ in agricultural soils of the United States of America. Ma and Roa (1997) found that the exchangeable Ni varied from 2.8 to 3.9 mg kg⁻¹ in soils of U.S.A. Onianwa (2001) observed that about 3% of the total Ni was associated with this fraction. Golia *et al.* (2007) stated 41-69% of Ni in the exchangeable fraction. Guerra *et al.* (2007) reported that exchangeable Ni was 9.3% of the total metal in Mollisols. Fractionation results indicated that the proportion of Ni that is potentially bioavailable is quite small

(Shober, 2007)^[117]. Khurana and Bansal (2008)^[70] reported that the exchangeable Ni was 0.64-0.16 mg kg⁻¹ in sewage treated soils and 0.07-0.018 mg kg⁻¹ in tube-well irrigated soils of Punjab. Afifi *et al.* (2011) found that the exchangeable Ni was 0.74 mg kg⁻¹ in Egyptian soils. Osakwe (2012)^[96] registered low levels of Ni in exchangeable fraction ranging from 0.38-0.83 mg kg⁻¹ in soils of Nigeria.

Guerra *et al.* (2007) reported that carbonate bound Ni was 16% of the total metal in irrigated Mollisols. The carbonate bound Ni was in the range of 0.58-1.32 mg kg⁻¹ in soils of Pennsylvania, USA (Shober, 2007)^[117]. Khurana and Bansal (2008)^[70] investigated that the carbonate bound Ni was 0.80-2.02 mg kg⁻¹ in sewage irrigated and 0.52-0.98 mg kg⁻¹ in tube-well irrigated soils of Punjab. Olubunmi (2010)^[94] reported that the carbonate bound Ni varied from 1.34-3.28 mg kg⁻¹ with an average value of 2.07 mg kg⁻¹ in soils of Agbabu, Nigeria. Adaikpoh (2011) and Osakwe (2012)^[96] found very low levels of Ni in carbonate bound fraction.

Nickel might be hosted by goethite, [FeO(OH)], and/or hematite, [Fe₂O₃]. These two oxides of iron are common minerals found in soils and both are capable of incorporating a variety of elements including Ni as impurities in their crystal structures, via substitution for Fe (Singh and Gilkes, 1992). Singh *et al.* (2000) found that up to 6% of Ni can substitute for Fe in the hematite structure. In a study on a laterite soil, Som and Joshi (2002) quantified the degree of substitution in goethite, finding Ni:Fe ratios ranging from 1:26 to 1:50. Drysdale (2008) confirmed that Ni was primarily hosted by Ni ferrite, also known as trevorite, a mineral with the formula NiFe₂O₄.

Ma and Roa (1997) found that the oxide bound Ni varied from 0.4 to 0.8 mg kg⁻¹ in contaminated soils of USA. Nikola *et al.* (2001)^[92] reported that the oxide bound Ni was 10.32 mg kg⁻¹ in serpentine soils. Fernandez *et al.* (2004) reported that the amorphous iron and aluminium oxide bound Ni content was 7.7 mg kg⁻¹ in Haplic calcisol and Luvic calcisol soils. Guerra *et al.* (2007) reported that the oxide bound Ni was 15.3% of the total metal in Mollisols. Shober (2007)^[117] reported that the reducible fraction of Ni was in the range of 0.8-1.19 mg kg⁻¹ in soils of Pennsylvania, USA.

Khurana and Bansal (2008)^[70] reported that oxide bound Ni was 9.44-27.62 mg kg⁻¹ in sewage treated soils and 5.72-12.25 mg kg⁻¹ in tube-well irrigated soils of Punjab. The relative higher value of oxide fraction in sewage treated compared to the tube-well irrigated soils was most likely due to predominance of free iron and manganese oxides in the former case. Olubunmi (2010)^[94] found that the oxide bound Ni varied from 8.00-12.85 mg kg⁻¹ with an average value of 9.98 mg kg⁻¹ in soils of Agbabu. Osakwe (2012)^[96] reported that the oxide bound Ni ranged from 0.17-0.29 mg kg⁻¹ in soils of south eastern Nigeria.

Cunningham *et al.* (1975) indicated that since Ni appears to be organo-philic, therefore, its chemical association was more favorable for the formation of strong organic complexes. Nikola *et al.* (2001)^[92] reported that the organic bound Ni was 14.83 mg kg⁻¹ in serpentine soils of Serbia. The average content of organic bound Ni expressed as percentage of sum of all fractions for the cultivated Ultisols of Malaysia was 1.3 (Zauyah *et al.*, 2004)^[149]. Khurana and Bansal (2008)^[70] reported that organic bound Ni was 1.34-2.64 mg kg⁻¹ in sewage irrigated and 0.16-0.54 mg kg⁻¹ in tube-well irrigated soils of Punjab. Olubunmi (2010)^[94] noticed that the organic bound Ni varied from 2.10-0.5 mg kg⁻¹ with an average value of 2.82 mg kg⁻¹ in Agbabu soils. Osakwe (2012)^[96] observed

low levels of Ni in organic fraction ranging from 0.13-0.28 mg kg⁻¹.

It has been indicated that Ni is commonly occluded by silicates during soil weathering (Horsfall and Spiff, 2005)^[52]. Narwal and Singh (1998)^[90] observed that the Ni was mostly associated with residual fraction. Ma and Roa (1997) concluded that the residual fraction was by far the most important fraction for Ni in soils ranging from 57% to 94%. Nikola *et al.* (2001)^[92] reported that the residual Ni was 48.96 mg kg⁻¹ in serpentine soils of Serbia. Shober (2007)^[117] reported that the residual Ni was in the range of 7.5-16.23 mg kg⁻¹ in soils of Pennsylvania, USA. Khurana and Bansal (2008)^[70] revealed that residual Ni was 13.4-38.42 mg kg⁻¹ in sewage treated soils and 8.5-19.8 mg kg⁻¹ in tube-well irrigated soils of Punjab. The higher proportion of Ni in this form might be due to the fact that as a result of irrigation with sewage water for many years, conditions would have become conducive for the diffusion of Ni into silicate minerals and other resistant materials. Olubunmi (2010)^[94] reported that the residual Ni varied from 38.20-62.30 mg kg⁻¹ with an average value of 46.75 mg kg⁻¹ in Agbabu soils. Osakwe (2012)^[96] showed that the residual fraction of Ni ranged from 3.15-4.63 mg kg⁻¹ in Nigerian soils.

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