MANAGEMENT OF HEAVY METALS IN TROPICAL SOIL ENVIRONMENT

Abdul Kadir Salam University of Lampung

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ABDUL KADIR SALAM
UNIVERSITY OF LAMPUNG

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Abdul Kadir Salam

Director of GM Press : Liza Alvia
Cover Design : Sahroni

Jl. Kavling Raya XIV No. 1, Pramuka, Rajabasa,
Bandar Lampung 35144, Indonesia
Telephone : (0721) 8011325
Faximile : (0721) 8011329
Website : www.globalmadani.sch.id
E-mail : ypgm@globalmadani.sch.id

Abdul Kadir Salam
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Dedicated to my son and daughter
Fiqi and Rahma
~ with a sincere love

Abdul Kadir Salam – 2017

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PREFACE

Management of Heavy Metals in Tropical Soil Environment deals with the behaviors of heavy metals in tropical soils under the management of some key soil properties. Various parts of discussion are completed with some research results mostly in tropical soils and complemented with those from other parts of the world. The management is mainly related to the manipulation of tropical soil heavy metal retention capacity employing some soil ameliorants like lime, organic composts and other biosolids, and phosphate fertilizers.

This book is organized into 10 chapters. Chapter 1 (Introduction) shows the existence of heavy metals in the environment including their variety, concentrations, origin, use for and effects on the living things, and their chemistry. Chapter 2 (Behavior of Key Soil Properties) deals with the roles and behaviors of some important soil properties related to the behaviors of heavy metals. These properties may include some physical, chemical, and biological soil properties, among which is the soil adsorptive capacity as influenced by soil ameliorants. Chapter 3 (Behavior of Heavy Metals in Soils) deals with the response of heavy metals to the changes in some key soil properties related to some soil chemical reactions involved such as complexation – decomplexation, chelation – dechelation, adsorption – desorption, precipitation – dissolution, oxidation – reduction, and movement as well as translocation. Chapter 4 (Heavy Metal Retention in Soils) deals with the single most important behavior of heavy metals in the environment related to the phenomenon of soil and ground-water contamination. This behavior may include the adsorption and/or precipitation of heavy metals that may immobilize heavy metals in the soil system.

The following Chapters of 5 and 6 include human manipulation on heavy metal retention. Chapter 5 (Heavy Metal Retention in Tropical Soils under Immobilization Capacity Management) deals mainly with the manipulation of soil adsorptive capacity towards heavy metals by employing ameliorants such as organic matters and other biosolids or phosphate fertilizers. Chapter 6 (Heavy Metal Retention in Tropical Soils under pH-Management) deals with the manipulation of the soil adsorptive capacity towards heavy metals indirectly by pH management through the effect of lime on soil pH.

Chapters 7, 8, and 9 deals with the consequences of the changes in the soil adsorptive capacity towards heavy metals i.e. the easiness of heavy metals to move into or to be removed from soil system. The movement and extraction may be more difficult if the heavy metals are strongly held by soils and/or precipitated. The extracted heavy metals are consequently lower if heavy metals are adsorbed more strongly by soil adsorptive surfaces and/or precipitated. Thus, the strength of heavy metal- soil bonding may determine the movement and translocation of soil heavy metals as well as the extraction of soil heavy metals both by bioaccumulator plants or extracting solution for heavy metal analyses.

This book is completed with 131 illustrations as figures and tables and supported by more than 400 technical papers. This book is a trial and therefore it may contain mistakes. Correction and suggestion from readers, colleagues, and students are expected. Gratitude is extended to all colleagues and students involved in the research related to heavy metal management in soils I conducted for more than 30 years between 1987 through 2017. Special thanks are also given to my family members for all the supports. I hope that this piece of work is useful in building science and technology on heavy metal behaviors in tropical soils.

Bandar Lampung, August 17, 2017

AXA

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Chapter I

Introduction

1.5 Heavy metals in the Environment
1.6 Heavy Metals as Toxic Elements and Plant Nutrients
1.7 Heavy Metals in the Chemistry of Soils
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Important Questions

Heavy metals are in general well-known for their dangers to the living things. A great deal of research reports related to heavy metals in the environment is found in current literature. Interesting reports may include those containing findings on their **toxicities** (Lagerwerff, 1982; Bohn et al., 1985; Tiller, 1989; Alloway, 1990d; Baker, 1990; Steinnes, 1990; Kabata-Pendias and Pendias, 1992; Daoust et al., 2006; Oporto, 2007; and Widowati et al., 2008), their **sources** (Lagerwerff, 1982; Kardoz et al., 1986; Leung, 1988; Hegstrom and West, 1989; Alloway, 1990c; Davies, 1990; Kiekens, 1990; Rivai, 1990; Dowdy et al., 1991; Boon and Soltanpour, 1992; Jing and Logan, 1992; Wang et al., 1992; Herrero and Martin, 1993; Sweet et al., 1993; Tsoumbaris and Tsoukali-Papadopoulou, 1994;

Schuhmacher et al., 1994; Cabrera et al., 1994; Nicholson et al., 1994; Bilski and Alva, 1995; Flegal and Smith, 1995; Vile et al., 1995; Gimeno-Garcia et al., 1996; Salam et al., 1996; Yeh et al., 1996; Salam et al., 1997a; Juracek and Ziegler, 2006; Biasioli et al., 2007; Benke et al., 2008; Berenguer et al., 2008; Lin et al., 2008; Hobara et al., 2009; Benn et al., 2010; Cakmak et al., 2010; Kien et al., 2010; Wang et al., 2010; Alloway, 2012; and Tu et al., 2012), their **emission into the environment** (Leung, 1988; Akhter and Madany, 1992; Flegal and Smith, 1992; Gimeno-Garcia et al., 1996; Hellmann et al., 1997; Pagotto et al., 2001; Juracek and Ziegler, 2006; Lin et al., 2008; Guo et al., 2009; Kien et al., 2010; and Hu et al., 2013), their effects on **soil-water-air contamination and pollution** (Dowdy et al., 1991; Wang et al., 1992; Markus and McBratney, 1996; Bendfieldt et al., 2001; Benke et al., 2008; Cakmak et al., 2010; Smolders et al., 2012; and Kargar et al., 2013), their **vegetation intakes** (Allaway, 1986; Boon et al., 1992; He and Singh, 1994; Brown et al., 1995; Sriyani and Salam, 1998; Salam et al., 1999c; Berenguer et al., 2008; Opporto et al., 2010; Kukier et al., 2010; and Adams et al., 2014), their **human intakes** (Allaway, 1986 and Flegal and Smith, 1995), and their **effect on soil microorganisms and enzymes** (Baath, 1989; Landmeyer et al., 1993; Hiroki, 1994; Huysman et al., 1994; Witter et al., 1994; Hellmann et al., 1997; Juma and Tabatabai, 1997; Kuperman and Carreiro, 1997; Salam et al., 1997n; Geiger et al., 1998b; Gutser and Erdogan, 2008; Luo et al., 2010; and Zhou et al., 2011). We can find also research reports on the science and technology developed to detect **the degree of heavy metal existence in the environment** (Yeh et al., 1996; Wang et al., 2010; and Adams et al., 2014) and **to ameliorate** their increasing concentrations and effects to the living things (Salam et al., 1997k; 2000; Salam, 2000; Tokunaga et al., 2003; Moseley et al., 2008; Brown et al., 2004; 2009; Ippolito et al., 2011; Richards et al., 2011; Buss et al., 2012; Guo et al., 2013; and Kambhampati and Vu, 2013). There are also research reports focusing on various heavy metals emitted by modern industries present at increasing quantities in the environment.

The available science and technology concerning the topics mentioned above are of great importance to manage heavy metal in the environment, particularly in the soil environment where heavy metals accumulate the most. The management of heavy metals in soil environment is important not only to manage heavy metals considered dangerous to the living things particularly at relatively high concentrations, but also to manage heavy metals classified as micronutrients in agriculture. The chemical principles employed to manage both classification of heavy metals in the soil environment are similar, comprising some chemical reactions existing in the soil-water system but the objectives are different. Concerning the environmentally toxic heavy metals, the management is objected to lower the concentrations of heavy metals to the levels not dangerous to the living things, while concerning the plant nutrient management is objected to maintain the availability of micronutrient metals. However, the similarity is to control the soluble heavy metals directly in contact with the living things.

The management of heavy metals in the soil environment is of utmost importance, in particular related to the more polluted environment with heavy metals in the last few decades. Several understandings must be fulfilled to perfectly successful in managing the heavy metals in the environment. The first is the knowledge on the environmentally safe levels of particular heavy metals. The second is the knowledge on the important potential sources of heavy metals and their emission into the soil environment. The third is the knowledge on the chemistry of heavy metals in the soil environment. This may include the major chemical reactions controlling the levels of heavy metals in the soil environment. The fourth is the knowledge and skill of using and developing computer program or incorporating all the chemical principles and relationships to perfectly manage heavy metals in the soil environment. These four knowledge and skill are very important to perfectly manage heavy metals in the soil environment based on science and technology in soil chemistry.

1.1 Heavy metals in the environment

Heavy metals exist in the environment. Their existence and magnitude are more significant for the last few decades. Heavy metals have silently accumulated in the environment from two different sources: natural or lithogenic sources, particularly from particular minerals containing high amounts of particular heavy metals, and anthropogenic sources, related to the production and uses of heavy metals in modern industries. The estimates of worldwide natural and anthropogenic emissions of some heavy metals are listed in **Table 1.1**.

The anthropogenic sources have now been the most important origin of heavy metals accumulating in the environment, particularly in urban areas where modern industries are established. However, both sources need more serious attention to avoid heavy metal related disasters like Minamata disease caused by Hg pollution, Itai-itai disease caused by Cd pollution, both occurred Japan in the late 50s, and Wilson disease caused by Cu (Alloway, 1990d; Steinnes, 1990; Baker, 1990). Similar disasters may happen in other areas like Indonesia where the production and uses of heavy metals significantly increase. The potential for the disaster is higher due to the fact that the awareness to this problem and law enforcement on environmental destruction is quite low.

Table 1.1. The estimates of worldwide natural and anthropogenic emission of some heavy metals[1)].

	lithogenic	Anthropogenic
Cd	0.83	7.3
Cu	18	56
Ni	26	47
Pb	24	450
Zn	44	310

[1)] Adapted from Nriagu (1979) as cited by Tiller (1989); in x 10^3 ton year^{-1}

Heavy metals are in general environmentally mobile. Therefore, once emitted to the environment, heavy metals may spread into soil, water, and air systems. Part of heavy metals may dissolve in soil water and, thereby, may spread easily. Heavy metals may enter the food chain, may directly enter the animal or human bodies through drinking water, or indirectly through soils which are, together with those already in the soil system, finally absorbed by growing plants. Similarly, heavy metals may also be emitted to the air by factories. These heavy metals may spread widely and may deposit somewhere due to rainfalls or gravitation. In soils, these heavy metals may also finally enter food chain. The estimate of global emission of heavy metals into soil, water, and air system are listed in **Table 1.2**. **Table 1.2** clearly shows that the amounts of Cr and Ni emission are higher in the soil system and lowest in the air system.

There are differences in the behaviors of heavy metals in soil, water, and air systems. Heavy metals are more mobile in air than are in water, and in water are more mobile that are in soil. Therefore, the management of heavy metals is easier to conduct in soil systems than in the other two systems. This means that polluting heavy metals must be hindered to not entering the air and water system. Wastes to be disposed in the water and air system must be managed so that it contains insignificant amounts of heavy metals.

Table 1.2. The estimates of heavy metal global emission into

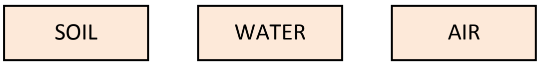
the environment1).

Environment Component	Cr	Ni
	…… 10^3 ton $year^{-1}$ …….	
Air	30	56
Water	142	113
Soil	896	325

1) Adapted from Nriagu (1979) as cited by Tiller (1989)

Soil system is principally similar to water and air systems. All these systems contain three similar phases, i.e. solids, liquids, and gases. However, as seen from **Fig. 1.1**, the soil system has more solid that water and air systems. Solid shows property to adsorb heavy metal cations due to their negative charges developed from different sources and by different mechanisms. Because containing more solids, soil system is expected to be able to immobilize more heavy metals than is water or air system. Therefore, soil system may act as an environmental sink for heavy metals. Heavy metals from different sources can be immobilized in soil system. By this means, it is expected that parts of heavy metals do not move freely and cause problem in the environment. It is obvious that the soil system may act as a sink for heavy metals.

However, the immobilization of heavy metals in soil solids is not permanent that can make heavy metal stay-still in the soil solid. In fact, the immobilization of heavy metals in soils is controlled by equilibrium constants. As long as the concentrations of the related species satisfy the equilibrium constants, heavy metals may be stayed adsorbed or precipitated, giving no danger to the environment. However, once the equilibrium constant is not satisfied, the immobilized heavy metals may release to the environment. Leak of heavy metals from sink is then probable. Keeping the concentrations of the related species in the soil environment at particular levels is expected to suffice the equilibrium constant.



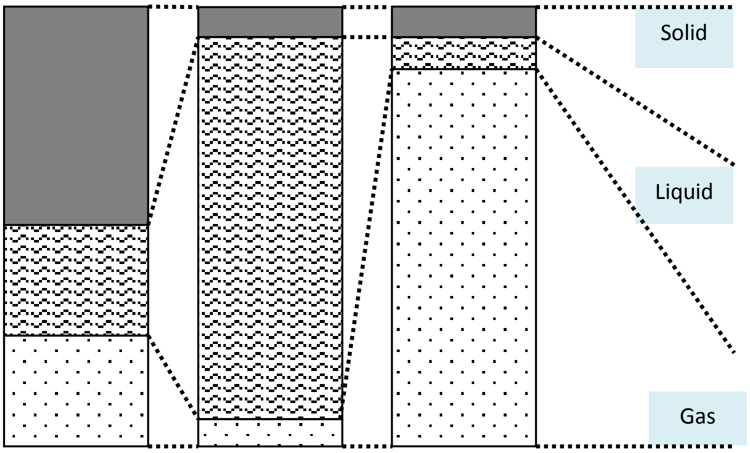


Fig. 1.1. The relative composition of soil, water, and air in the environment.

1.2 Heavy metals as toxic elements and plant nutrients

As mentioned previously, heavy metals are well-known for their toxicities to the living things. The toxicities of heavy metals to the living things including human beings have been documented in current literature (Alloway, 1990d; Baker, 1990; Steinnes, 1990; Daoust et al., 2006; Oporto, 2007). The toxicity levels of heavy metals are various (Lagerwerff, 1982; Bohn et al., 1985; Tiller, 1989; Alloway, 1990d; Steinnes, 1990; Widowati et al., 2008). Among heavy metals with high toxicities are Hg, Cd, Cu, and Zn; those with moderate toxicities are Cr, Ni, and Co; and those with low toxicities are Mn and Fe. However, there is a fact that different living thing shows different tolerance to toxic heavy metals; particular living things may show higher or lower tolerance.

The toxicities of some heavy metals on some living things are listed in **Table 1.3.** Heavy metals on the right side are less toxic than those on the left side; therefore, the heavy metals on the left side are toxic at lower concentrations than those located on the right side. This means that for algae, for example, Hg is more toxic than Cd and Cr, which are toxic at lower concentrations than Zn and Mn. Simlarly, for phytoplankton Hg is more toxic than Cu, Cd, Zn , and Pb; meaning that Hg is toxic at lower concentrations than the other heavy metals.

Table 1.3. Heavy metal toxicities[1).

No.	Organisms	Order of Toxicity
1	Algae	Hg > Cu > Cd > Fe > Cr > Zn > Co > Mn
2	Flower Plants	Hg > Pb > Cu > Cd > Cr > Ni > Zn
3	Fungi	Ag > Hg > Cu > Cd > Cr > Ni > Pb > Co > Zn >Fe
4	Phytoplankton	Hg > Cu > Cd > Zn > Pb

1) Adapted from Sposito (1989)

As mentioned previously, there are numerous heavy metal related disasters documented in literature. (Alloway, 1990d; Baker, 1990; Steinnes, 1990). Alloway (1990d) mentions the health disorder caused by an accumulation of Cd in human tissues, caused by the pollution of river and paddy field water in Jintsu Valley, Toyama, Japan in 1940s. The accumulation of Cd caused a fatal health problem called Itai-itai. In 1940s a similar case caused by Hg pollution was observed in Minamata Bay of Japan. The Hg was initially accumulated in the form of methyl mercury in fish consumed by Japanese (Steinnes, 1990). Baker (1990) also reports that accumulated Cu may cause heredity disease called Wilson disease.

However, as long as their concentrations are below the toxic levels, heavy metals are perceived safe for the living thing. For example, the total dissolved Cu in soil may not exceed 60 mg kg^{-1}, total dissolved Zn in soil may not exceed 70 mg kg^{-1}, and total dissolved Cd and Pb may not exceed 9 and 100 mg kg^{-1}, respectively (Ross, 1994). However, in fact the concentrations of heavy metals are affected by numerous input factors, both natural and anthropogenic (Juracek and Ziegler, 2006; Biasioli et al., 2007; Benke et al., 2008; Berenguer et al., 2008; Lin et al., 2008; and Cakmak et al., 2010). Land application of cattle manure was observed to significantly increase the total dissolved and available Cu and Zn in soils (Benke et al., 2008). The concentration of Cu, Ni, Hg, Pb, Cd, and As in sampled sediment from waste treatment unit of electronic waste in Guiyu, Guang Dong, China, increased significantly above the natural levels (Guo et al., 2009). Berenguer et al. (2008) also previously reports that long-term use of liquid waste of wine significantly increased the concentrations of Cu and Zn in soil. These mean that metal input from external sources may increase heavy metal concentrations above the toxic levels so that heavy metals are dangerous to the living things.

Some of the metal elements such as Cu and Zn, and also Fe and Mn, may be used as micronutrients for plants if managed at lower concentrations. Particular industrial wastes with heavy metal concentrations relatively low are possible to be used as fertilizer precursor to enhance soil fertility (Salam et al., 2000). Pereira et al. (2012) reports that the irrigation with reclaimed waste water increases the availabilities and total concentrations of nutrients and non-essential elements in soils, and also soil salinity and sodicity by two to three times compared to that the irrigated with well water. The major parts of nutrients in reclaimed waste water were free ionic species readily available for plant absorption such as: NH_4^+, NO_3^-, K^+, Ca^{2+}, Mg^{2+}, SO_4^{2-}, H_3BO_3, Cl^-, Fe^{2+}, Mn^{2+}, Zn^{2+}, Co^{2+}, and Ni^{2+}. More than 80% of Cu, Cr, Pb, and Al were complexed with CO_3^{2-}, OH^-, and/or organic matters.

1.3 Heavy metals in the chemistry of soils

As mentioned previously, heavy metals are abundant in the environment and one way to effectively manage their existence is to immobilize them in the soil environment. Soils are unique due to the fact that they comprise of solids and liquids that show complex and complicated chemistry caused by the interaction of substances in the liquids and those in the liquids with those on the surfaces and in the structure of solids. The most important substances in the liquids are the free ionic and complexed ions and those on and in the solids are the adsorbed cations and structural elements in minerals, both primary minerals such as feldspars and secondary minerals such 1:1 silicate minerals like kaolinite and 2:1 silicate minerals like montmorillonite, and organic matters. The relationship among these substances is shown in **Fig. 1.2**.

Shown in **Fig. 1.2** is that the central of the chemistry of heavy metals in soils is the free ion, which has been reported to be directly related to the plant root absorption and heavy metals toxicity. Free ionic heavy metals are controlled by equilibrium and non-equilibrium reactions. The equilibrium reactions controlling the free ions of heavy metals may include oxidation –reduction (Redox reaction), complexation-decomplexation, chelation-dechelation, precipitation–dissolution, and adsorption- desorption; while the non-equilibrium reactions are mineral weathering and organic matter decomposition.

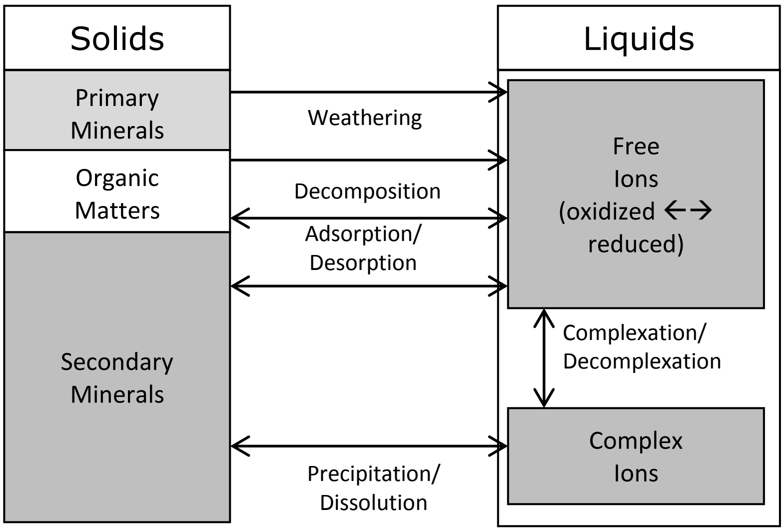


Fig. 1.2. The relationship between substances in the soil solids and liquids.

Oxidation–reduction (redox reaction) is related to the changes in the increase and decrease in heavy metal oxidation number. A very good example of this is the change in the oxidation number of Fe from Fe^{2+} to Fe^{3+} or from Fe^{3+} to Fe^{2+} due to the flooding and draining of paddy soils as shown in **Table 1.4**. When paddy soils are flooded, the redox potential decreases and, thereby, the system becomes reductive and causes the reduction of Fe. On the other hand, when paddy soils are drained, the redox potential increases and the system becomes oxidative which finally causes the oxidation of Fe. Therefore, the oxidation number of Fe can be manipulated by flooding and draining the soil environment.

Free ionic heavy metals are prone to other equilibrium reactions. When the complexing agents such as OH^-, CO_3^{2-}, and HPO_4^{2-} exist in soil water, the free ionic heavy metals may be complexed following **Eq. 1.1**, forming complex ion such as $Fe(OH)^+$, $Fe(OH)_2^0$, $Fe(OH)_3^-$ or $FeCO_3^0$, and $Fe(HPO_4)^+$, $Fe(HPO_{4)}^0$, etc., controlled by their respective equilibrium constant (**Eq. 1.2**). The complexing agents may be of inorganic origin such as OH^- ion or organic origin such as fulvic acid. Complexation involving organic ligands forms chelates. Similar to free ions, complex ions are dissolved in soil water. However, complex ions are less available and less toxic.

When the concentrations of their components are low, the reverse reaction may release the free ions back to the initial condition.

$$Fe^{2+} + A^{-} \leftrightarrow FeA^{+} \quad \text{.......} \quad \textbf{Eq. 1.1.}$$

$$K = \frac{[FeA^{+}]}{[Fe^{2+}][A^{-}]} \quad \text{.......} \quad \textbf{Eq. 1.2}$$

Table 1.4. The effect of flooding and draining on the oxidation number of Fe element in paddy soils.

Condition	Oxidation Number	Reaction
Flooding	+ 2	$Fe^{3+} + e \leftrightarrow Fe^{2+}$
Draining	+ 3	$Fe^{2+} \leftrightarrow Fe^{3+} + e$

Some of the free and complex ions common in soil water are listed in **Table 1.5**. Free ions of heavy metals do not exist at differing pH. For example Free Cu^{2+} only exists at acid condition. At higher pH, Cu^{2+} exists as complexes and chelates. On the other hand, Cd^{2+} and Fe^{2+} exist both at acid and alkaline conditions. This indicates that Cu^{2+} is more strongly bonded by anions and ligands. Ellis and Knezek (1982) has previously reports that the free Cu^{2+} in soil solution comprises only 2% of the total dissolved Cu, lower than other free ionic heavy metal such as Zn^{2+}, which comprises 40% of the total dissolved Zn. The reactions of free ionic heavy metals in soil solution are stronger than those of major cations like Na^{+}, K^{+}, Ca^{2+}, and Mg^{2+}, which comprises about 70-90% of their total dissolved elements in soil solution.

Table 1.5. Some free and complex ions of some heavy metals commonly found in soil water1).

Heavy Metals	Acid Condition		Alkaline Condition	
Cu	Cu^{2+}	Org*,	–	$CuCO_3^0$, $CuB(OH)_4^+$, $Cu[B(OH)_4]_4^0$, Org*
Cd	Cd^{2+},	$CdSO_4^0$, $CdCl^+$	Cd^{2+},	$CdCl^+$, $CdSO_4^0$, $CdHCO_3^+$
Fe	Fe^{2+}	$FeSO_4^0$, $FeH_2PO_4^+$	Fe^{2+},	$FeCO_3^o$, $FeHCO_3^+$, $FeSO_4^o$
Cr	–	CrO_4^{2-}	–	CrO_4^{2-}

1)Adapted from Sposito (1989)

Heavy metal free ions are also prone to the precipitation reaction, particularly when the concentration of free ions and complexing ions are relatively high following **Eq. 1.3**. For example, when the paddy soils are flooded and, thereby, the condition is reductive, Fe^{3+} and SO_4^{2-} in soil water are reduced to produce Fe^{2+} and S^{2-} ions, respectively. These chemical species may then react to produce FeS precipitate, which makes Fe and S are both not available to plants. However, when the paddy soils are drained, the condition is oxidative, FeS may dissolve in soil water due to the oxidation that converts Fe^{2+} to Fe^{3+} and S^{2-} to SO_4^{2-}. Fe^{3+} and SO_4^{2-} are available to plants. This process is called dissolution. It is believed that complexation and chelating processes by organic matters can also precipitate heavy metals if the molecular weights of the organic matters are relatively high (Keeney and Wildung, 1986; Kabata-Pendias and Pendias, 1992). The process of precipitation-dissolution in soil system controls several metals and the abundance of precipitating agents like OH^-, $H_2PO_4^-$, HPO_4^-, CO_3^{2-}, Cl^-, and SO_4^{2-}. Some experimental researches on the precipitation-dissolution of heavy metals have been reported (Lindsay, 1979; Brummer et al., 1983; Ma and Lindsay, 1990; 1995; Workman and Lindsay, 1990; El-Falaky et al., 1991; Stahl and James, 1991; and Salam, 2000). Some soil workers also report the use of this precipitating agent to immobilize heavy metals in soils (Ma and Lindsay, 1990; 1995; Workman and Lindsay, 1990; El-Falaky et al., 1991).

$$\mathbf{M^{2+} + A^- \leftrightarrow MA^2 \quad .... \quad Eq.\ 1.3.}$$

$$\mathbf{K_{sp} = [K]\,[A^-]^2 \quad .... \quad Eq.\ 1.4.}$$

In addition to oxidation–reduction, complexation-decomplexation, and precipitation–dissolution, free ions of heavy metals are also controlled by adsorption–desorption reactions. Some researchers suggest that this reaction dominates at low concentrations of heavy metals or low concentrations of precipitating agent. At high concentrations of free ions and high pH, precipitation–dissolution may dominate the controlling of free ion concentrations. Due to the fact that most soils contain low concentrations of heavy metals and the soil pH is generally acidic, the adsorption–desorption of heavy metals may dominate in most soils. This reaction, like all other reactions discussed previously, is important in controlling the free ion concentration in soil solution.

The concentrations of free ions in soil water are also affected by non-equilibrium chemical reaction i.e. mineral weathering and organic matter decomposition. These reactions may be significant when the contents of heavy metals in minerals and organic matters are high. Other factors that are very important in controlling the free ions of heavy metals are the easiness of minerals and organic matters to weather or decompose. Some minerals are easily weathered and some are not. Some of minerals such as Olivine, Apatite, and Albite are among the more easily weathered, while Titanite and Magnetite are among the more difficult to weather (Bohn et al., 1985). Some minerals containing heavy metals found in the environment are listed in **Table 1.6**. Likewise, not all organic matters are easily decomposed. Some organic matters such as soybean leaf and cassava leaf are among the more easily decomposed, while leaves of weed *Imperata cylindrica* is among the most difficult to decompose.

The weathering of minerals may occur usually in the presence of water and H^+ ions. The absence of enough water and lack of H^+ ions may inhibit the weathering process of minerals, and thus, the release of all structural elements. An example is the weathering of olivine shown by **Eq. 1.5**, the rate of which increases with the increase in water content and in H^+ ion concentration. The heavy metal ion Fe^{2+} may encounter several fates: absorbed by plant roots, complexed or chelated by any anions/ligands, precipitated, adsorbed by soil surfaces, etc. Any case may lower the concentration of Fe^{2+}, which may eventually speed up the weathering of Olivine.

$$\mathbf{(Mg,Fe)_2SiO_4 + H_2O + 5\,H^+ \rightarrow 2\,Mg^{2+} + 2\,Fe^{2+} + Si(OH)_4 + OH^-} \quad \text{……} \quad \textbf{Eq. 1.5}$$

Table 1.6. Some minerals containing heavy metal elements[1)].

Minerals	Heavy Metals
Olivine	Ni, Co, Mn, Li, Zn, Cu, Mo
Hornblende	Ni, Co, Mn, Zn, Cu
Augite	Ni, Co, Mn, Zn, Pb, Cu
Biotite	Ni, Co, Mn, Zn, Cu
Apatite	Pb, Cd
Anortite	Cu, Mn
Andesin	Cu, Mn
Oligoclase	Cu
Albite	Cu
Garnet	Cr, Mn
Orthoclase	Cu
Muscovite	Cu
Titanite	Sn
Ilmonit	Co, Ni
Magnetit	Zn, Co, Ni
Tourmaline	-
Zirkon	-
Quartz	-

[1)] Adapted from Alloway (1990c)

For weathering, the presence of H^+ ion is very important because H^+ ion is an attacking agent that may destruct the mineral structures. Higher H^+ ion concentration, which means lower pH, may cause more intensive weathering and higher free ions released into the soil water. This phenomenon is shown by weathering of soil minerals of an Oxisols from West Java and a Mollisols from Wisconsin, the United States of America (Salam, 1989, as shown in **Table 1.7**). The released Ca, Mg, K, and Zn increase with the decrease in soil pH buffered using resin method.

As previously mentioned, the concentration of free ionic heavy metals in soil water is also affected by the decomposition of organic matter, particularly those containing heavy metals. The decomposition of organic matters is speeded by the presence of water as the reactant and also by soil enzyme that act as a biocatalysator. The presence of these two substances may supply some free heavy metals that may interact with plant roots and also some equilibrium reactions i.e. oxidation-reduction, complexation-decomplexation, precipitation-dissolution, and adsorption-desorption. The easiness of organic matters to decompose also controls the amount of heavy metals released by organic matter decomposition.

Table 1.7. The release of some elements from Mollisol and Oxisol as affected by buffered soil pH[1].

pH	Mollisols[2]				Oxisols[3]			
	Ca	Mg	K	Zn	Ca	Mg	K	Zn
	.... mg kg^{-1}							
4	594	271	96	11	26	27	85	6.5
5	540	250	60	10	19	9	50	6.0
6	315	105	48	8.5	12	0	45	5.5
7	204	49	47	7.4	3.0	0	30	4.0

1)Adapted from Salam (1989); 2)from Wisconsin USA, 3)from West Java Indonesia

Organic matter decomposition is soil enzyme specific. The following are two examples of organic matter decomposition. The first is organic P that decomposes catalyzed by phosphatase (**Eq. 1.6**) and organic S that decomposes catalyzed by arylsulphatase (**Eq. 1.7**). As shown by **Eq. 1.6** and **Eq. 1.7**, the decomposition of organic matters needs water. Without water it is impossible for the process to happen. These reactions convert organic elements (elements bounded in the structures of organic matters) into inorganic elements as free ions of HPO_4^{2-} and SO_4^{2-}. The decomposition of organic matters may also release small amounts of heavy metals bound in the structure of or contained in organic matters.

$$\mathrm{RO{—}PO_3^{2-} + H_2O \rightarrow R{—}OH + HO\text{-}PO_3^{2-}} \quad \ldots\ldots\ \textbf{Eq. 1.6}$$

$$\mathrm{R{—}OSO_3^{-} + H_2O \rightarrow R{—}OH + SO_4^{2-}} \quad \ldots\ldots\ \textbf{Eq. 1.7}$$

1.4 Scope of *Management of Heavy Metals in Tropical Soil Environment*

This book is organized into 10 chapters. Chapter 1 (Introduction) shows the existence of heavy metals in the environment including their variety, concentrations, origin, use for and effects on the living things, and their chemistry. Chapter 2 (Behaviors of Key Soil Properties) deals with the roles and behaviors of some important soil properties, that are related to the behaviors of heavy metals. These properties may include some physical, chemical, and biological soil properties, among which is the soil adsorptive capacity as influenced by soil ameliorants. Chapter 3 (Behaviors of Heavy Metals in Soils) deals with the response of heavy metals to the changes in some soil properties related to some soil chemical reactions involved such as adsorption–desorption, precipitation–dissolution, oxidation– reduction, and movement as well as translocation. Chapter 4 (Heavy Metal Retention in Soils) deals with the single most important behavior of heavy metals in the environment related to the phenomenon of soil and ground water contamination. This behavior may include the adsorption and/or precipitation of heavy metals that may immobilize heavy metals in the soil system.

The following Chapters of 5 and 6 include human manipulation on heavy metal retention. Chapter 5 (Heavy Metal Retention in Tropical Soils under Soil-Adsorption Capacity Management) deals mainly with the manipulation of soil adsorptive capacity towards heavy metals by employing ameliorants such as organic matters and other biosolids or phosphatic fertilizers. Chapter 6 (Heavy Metal Retention in Tropical Soils under pH Management) deals with the manipulation of the soil adsorptive capacity towards heavy metals indirectly by pH management through the effect of lime on soil pH.

Chapters 7 (Heavy Metal Movement and Translocation), 8 (Heavy Metal Extraction by Bioaccumulators), and 9 (Heavy Metal Analysis) deals with the consequences of the changes in the soil adsorptive capacity towards heavy metals i.e. the easiness of heavy metals to move in or to be removed from soil system. The movement and extraction may be more difficult if the heavy metals are strongly adsorbed by soils or precipitated as relatively insoluble minerals. The extracted heavy metals are consequently lower if heavy metals are adsorbed more strongly by soil adsorptive surfaces or precipitated as insoluble minerals. Thus, the strength of heavy metal-soil bonding may determine the movement and translocation of soil heavy metals as well as the extraction of soil heavy metals both by bio-accumulator plant of by extracting solution for heavy metal analyses. Chapter 10 includes impotant conclusions and practical cosequences related to the behaviors of soils and heavy metals that controls heavy metal retention in the soil environment.

Important questions

1. How important is to manage heavy metal pollutants in the soil environment? Explain!
2. Explain why the management of heavy metal pollutants is better to be conducted in the soil system than in water system and air system!
3. What are the differences in the management of heavy metals as toxic elements and as plant nutrients?
4. Explain the lithogenic and the anthropogenic sources of heavy metals in the soil environment!
5. Explain the heavy-metal related disease disasters that ever happened in the environment!
6. Explain the pathways of heavy metal emission from their sources to reach the living things!
7. What are the similarities and differences of soil, water, and air system? Explain!
8. Explain the worldwide emission of heavy metals into the environment! Compare the relative amounts accumulated heavy metals in the soil, water, and air!
9. Explain the immobilization and release of heavy metals in the environment and their effects on the living things!
10. Explain the toxicity of heavy metas to the living things! What are the allowable limits of heavy metals?
11. Explain the various forms of heavy metals in the soil environment!
12. Explain the interactions of the various forms of heavy metals through equilibrium and non-equilibrium chemical reactions!
13. Explain the importance and occurrence of heavy metal oxidation-reduction reactions in the soil environment!
14. Explain the importance and occurrence of heavy metal complexation-decomplexation and chelation-dechelation reactions in the soil environment!

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15. Explain the importance and occurrence of heavy metal precipitation-dissolution reactions in the soil environment!
16. Explain the importance and occurrence of heavy metal adsorption-desorption reactions in the soil environment!
17. Explain the importance and occurrence of heavy metal containing mineral weathering in the soil environment!
18. Explain the importance and occurrence of heavy metal containing organic matter decomposition reactions in the soil environment!
19. Explain some factors affecting all chemical reactions controlling the chemical forms of heavy metals in the soil environment!
20. Explain the importance of H^+ ions, soil moisture content, and soil enzyme activities in affecting the weathering or decomposition of heavy metal containing minerals and organic matters!

Chapter 2

Behaviors of Key Soil Properties

Heavy metals are mobile. Once released to the environment, they will move from one place to another and endanger the living things. Therefore, one way or another is needed to immobilize heavy metals in the environment so that their existence does not interact directly with the living things. This way may be safe for the short run and the long run and may accommodate the everlasting heavy metal pollution occurring in the environment for the last few decades.

Even though containing solids, it is not possible for air and water systems to immobilize heavy metals. The air solids and water solids may actually immobilize heavy metals by adsorption processes, but these may not avoid the heavy metals to be in contact with the living things. The percentages of air solids and water solids are relatively small and are not adequate to immobilize huge amounts of heavy metals emitted to the environment. Air and water themselves are contained in mobile systems that may move easily from one place to another. The immobilized heavy metals in air and water solids may eventually be deposited somewhere and may directly or indirectly pollute the environment.

The only way to conduct the heavy metal immobilization is to use soil solids as “reservoir” for heavy metals. As previously shown, soil, water, and air are principally similar. They contain solids, liquids, and gases. However, different from water and air systems, soil system contains much higher solids. The huge part of solids in soils may enable soils to accumulate high amounts of heavy metals. Unlike water and air, soil is relatively stationary, may not easily move from one place to another. Therefore, soil system may then act as a heavy metal adsorber. Using soil to immobilize heavy metals may partially solve the problem of heavy metals in the environment.

2.1 Soil is a giant heavy metal adsorber

Soils are giant heavy metal adsorbers. They may adsorb huge amounts of drained heavy metals into the soil environment. This phenomenon is attributed to the fact that soils contain huge amount of various solids with two important properties: significantly large surface areas and huge amounts of surface negative charges contributed by colloids comprising secondary silicate clay minerals, non-silicate clay minerals (oxides and hydroxides), and organic matters. The existence of the huge amounts of negative charges on the very large areas of adsorptive solid surfaces may become a huge attracting force for positively charged cations including those of heavy metals. For secondary 1:1 silicate clay minerals, non-silicate clay minerals (oxides and hydroxides), and organic matters, the amounts of negative charges are higher at higher pH (Helling et al., 1964; Trehan and Sekhon, 1977; Elliott, 1983; Tan and Dowling, 1984; McGrath et al., 1988; Alloway 1990b; Parfitt et al., 1995; Rodella et al., 1995; Medonca and Rowel, 1996; Tack et al., 1996; Suryanto and Susetyo, 1997; Choi et al., 1999; Gagnon et al., 2013; Tokunaga et al., 2003; Quaghebour et al., 2005; and Schroder et al., 2008). As described in **Fig. 2.1** and **Fig. 2.2**, the positively charged heavy metal cations are easily attracted by the negative charges of soil solids developed by 1:1 secondary clay minerals and organic matters, respectively. To a lower extent, similar phenomenon must be observed by oxides and hydroxides (non-silicate clay minerals).

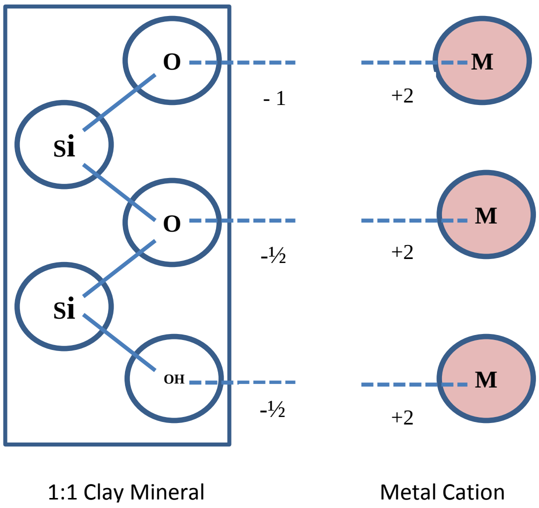


Fig. 2.1. The adsorption of heavy metal cation on a negatively charged 1:1 secondary clay mineral.

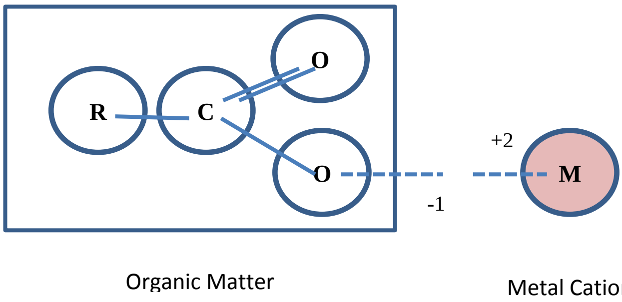


Fig. 2.2. The adsorption of heavy metal cation on a negatively charged organic matter.

Soils have not only solid negative charges that may immobilize heavy metal cations through attraction forces called adsorption, but also chemical species that might complex and precipitate heavy metal cations called precipitation. Adsorption immobilizes heavy metals from mobile fraction in soil solution so that they cannot move in and with water in the soil system. Precipitation is another probability of heavy metal immobilization mechanism in soil system particularly at high concentrations of heavy metals and precipitating agents. Some reports also mention that this reaction dominates the immobilization at high pH (Udo et al., 1970; Lindsay, 1979; Brummer et al., 1983; Ma and Lindsay, 1990; 1995; Workman and Lindsay, 1990; El-Falaky et al., 1991; Stahl and James, 1991; Salam, 2000). The precipitation reaction may occur as shown in **Fig. 2.3**, in which one heavy metal cation in soil water is initially complexed by any anion or complexing agent. If the concentration of heavy metal cation and anion are high enough, they will saturate the soil water and will finally precipitate forming a solid mineral. As a solid, both the heavy metal cation and anion are immobilized and cannot move in or with water.

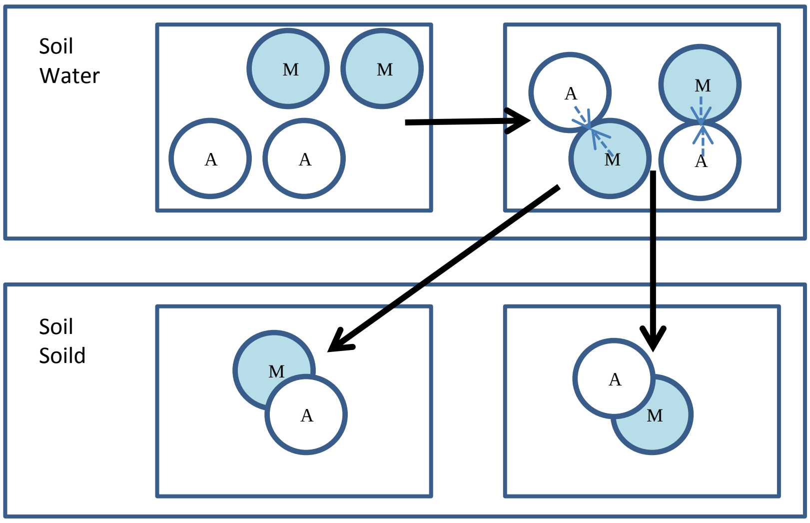


Fig. 2.3. Immobilization of heavy metal cation through precipitation reaction.

The above illustration suggests that the soil system possesses a power to immobilize heavy metal through two important chemical reactions i.e. adsorption reaction and precipitation reaction. By manipulating some important soil variable controlling these reactions, one may manage the immobilization of heavy metals emitted to the environment in the soil environment.

2.2 Soil negative charges and chemical properties

Soil negative charge is the single most important chemical properties. This soil property is responsible for the retention of cations of several origins in soils. Some of these cations are needed as essential nutrients for plants, that include macronutrients like Ca^{2+}, Mg^{2+}, and K^{+} as well as micronutrients like Cu^{2+}, Fe^{2+}, Mn^{2+}, Zn^{2+}, and Co^{2+}. These nutrients may come from fertilizers such as KCl (K^{+}) as well as dolomite and calcite (Ca^{2+} and Mg^{2+}) and from primary minerals such as K^{+} and Fe^{2+}. All these elements are temporary or permanently attached onto the soil surface charges. The rule is that when the concentrations of these elements in soil water are high, part of these elements may be adsorbed onto the soil negative charges. Conversely, when the concentrations in soil water are low, the adsorbed elements may dissolve from soil solids into soil water and become more mobile and ready for plant root absorption and other soil processes like leaching. Therefore, it is clear that the soil negative charges are very important in accumulating heavy metal cations in soil environment and must be increased. One way to accumulate more heavy metals is to increase the amount of the negative charges in the soil environment.

The soil negative charges are originated from the structure of the soil solids. These may include soil oxides and hydroxides, soil organic matters, 1:1 silicate clay minerals, and 2:1 silicate clay minerals. The first three solid structures are found abundant while the last is rarely found in tropical soils. Oxides and hydroxides are old mineral in the soil environment and, therefore, show low negative charges. The 1:1 silicate clay minerals also show low negative charges but higher than those of oxides and hydroxides and lower than those of the 2:1 silicate clay minerals. The 2:1 silicate clay minerals also show differences in CEC, generally the younger minerals show higher CEC. Vermiculite is younger that smectite and Illit. Therefore, to restore old soils with old soil minerals, organic matters are usually employed. Addition of organic matters has been repeatedly reported to increase the soil CEC. The 2:1 silicate clay minerals can also theoretically be added into the soil systems to increase the soil CEC. The negative charges as expressed as cation exchange capacity (CEC) are listed in **Table 2.1**.

Table 2.1. The soil solid negative charges as expressed by CEC[1)].

No.	Soil Solids	Type	CEC ($cmol_c\ kg^{-1}$)
1	Oxides of Fe and Al (pH 8)		0.5 – 1.0
2	Kaolinit	1:1	3 – 20
3	Illit	2:1	10 – 40
4	Smectite	2:1	60 – 100
5	Vermiculite	2:1	100 – 200
6	Allophane		50 – 100
7	Organic Matters/Humus		150 – 200
8	Humic Substances		200 – 750
	Fulvic Acids		500 – 750
	Humic Acids		300 – 500
	Humin		300

[1)] Adapted from Thomas and Hargrove (1984), Burns (1986)

Differences in CEC among soil solids (**Table 2.1**) indicate that the negative charges of every soil are dependent of the types and quantity of particular soil solids. Those containing higher organic matters may have higher CEC. Old soils with high quantity of oxides of Fe and Al may have lower CEC than those containing high amount of humic and fulvic acids. Most of the tropical soils like those in Indonesia may have low CEC because the soil solids are dominated by oxides and 1:1 silicate clay minerals, which possess low CECs. Therefore, tropical soils need proper CEC management to make them be able to accommodate high treatment with cationic elements.

However, soils with old soil solids may have higher CEC if treated with high CEC materials like organic matters. A good example is the old soils planted with grasses. Grasses have been reported to contribute high amounts of organic C (Studdert et al., 1997). Studdert et al. (1997) shows that organic C in soils planted with grasses are significantly higher than those planted with food plants. This phenomenon is also related to the higher N in soils planted with grasses that those with food plants. Salam et al. (2001) also report that soils in coffee plantation planted with *Paspalum conjugatum* show much higher organic C than the control only planted with coffee plants. Similarly, the organic C in coffee plantation with natural grasses is also significantly higher than those without grasses, even though lower that those with *P. conjugatum*. This trend is consistently observed for 4 years since 1996 – 1999. This effect is shown in **Table 2.2**.

Table 2.2. The effect of grasses on soil organic C in coffee plantation$^{1)}$.

	Control	Natural Grasses	*Paspalum conjugatum*
	……. g kg^{-1} …….		
1996	22.3	28.8	34.7
1997	14.7	17.1	29.1
1998	16.4	18.9	28.9
1999	21.1	23.0	50.0

$^{1)}$ Adapted from Salam et al. (2001)

The negative charges on the surface of organic matter colloids is originated from the dehydrogenation of some organic matter functional groups, such as hydroxyls (R – OH), phenolics (g – OH or C_6H_5OH), and carboxylics (R – COOH). These functional groups may lose their H to form R – O^-, $C_6H_5O^-$, and CH_3COO^-, respectively. The negative charges from organic matter functional groups increase with the increase in soil pH due to the more OH^- ion present in soils. This OH- ion may attract more H^+ forming H_2O molecules. This process dan its dependence on soil pH is shown in **Fig. 2.4**.

The development of negative charges of hydroxyl (R – OH) and carboxylics (RCOOH) functional groups are similar. Upon the increase in soil pH, the H on the functional groups is released and attracted by the increasing OH^- ions forming water molecules. The process is depicted in **Fig. 2.5**.

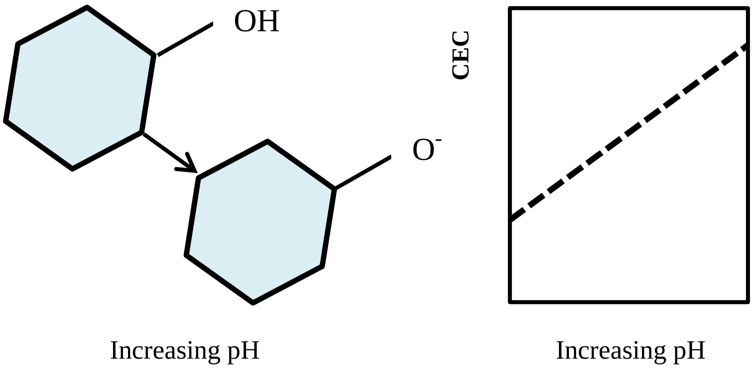


Fig. 2.4. The development of negative charges of organic matters origin with phenolic functional groups.

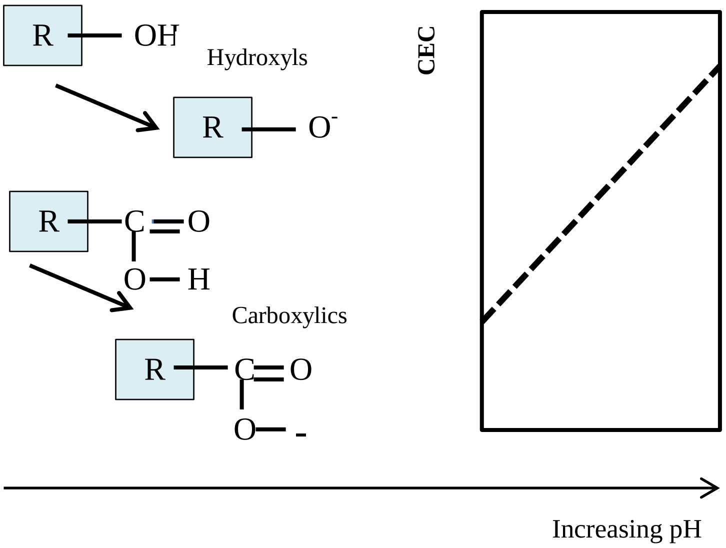


Fig. 2.5. The development of negative charges of organic matter origin with hydroxylic and carboxylic functional groups.

The negative charges developed on the surfaces of soil minerals are about the same with that occurs on the surface of organic colloids. The development of the negative charges of 1:1 silicate clay minerals occur on the edges of mineral surfaces by hydrogenation and dehydrogenation affected by the changes in soil pH (**Fig. 2.6**). When the pH is low, H^+ ions are attached on the edges of tetrahedral or octahedral structure causing the decrease in soil CEC. Conversely, the increase in soil pH may detach the attached H^+ ions and thus increase the negative charges of the CEC. As that of the organic matter, the negative charges are fairly pH dependent. In other words, the soil negative charges of soisl dominated by 1:1 silicate clay mineral can be manipulated by changing the soil pH.

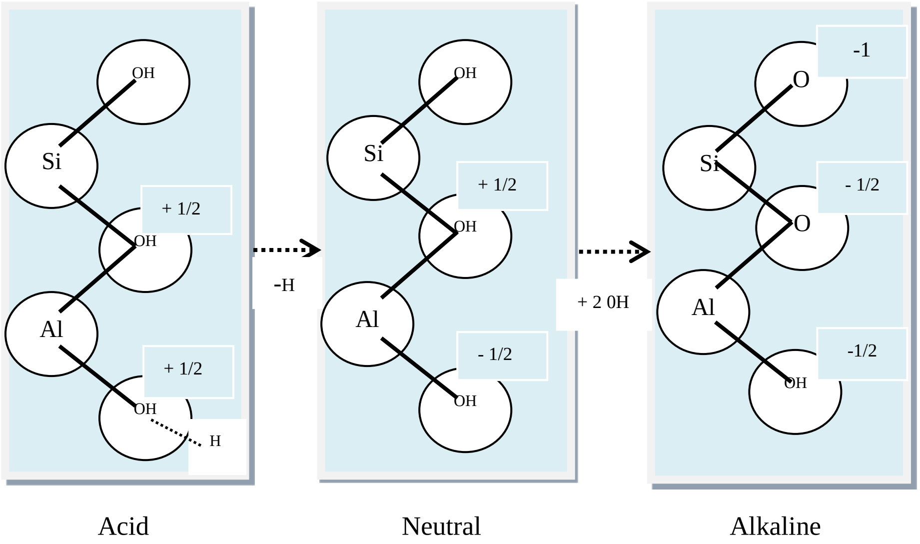


Fig. 2.6. The development of negative charges of 1:1 silicate clay minerals (Bohn et al., 1985).

Similarly, the negative charges of the non-silicate clay minerals such as Hematite (Fe_2O_3), Goethite (FeOOH), Buhmite (AlOOH), and Gibbsite ($Al(OH)_3$ developed on the surfaces of the minerals. Like those occurring in organic matters and in 1:1 silicate clay minerals, the negative charges on the surface of hematite is fairly dependent on soil pH (**Fig. 2.7**). The negative charges of hematite increase with the increase in soil pH. In this case, H is dehydrogenized from the hematite surface and then combines with OH^- ions forming H_2O molecules. The reverse reaction or hydrogenation due to low pH may decrease the soil negative charges or CEC. As shown in **Table 2.1**, the difference of oxides with 1:1 silicate clay minerals and organic matters is the magnitude of the negative charges, those on organic matters are the highest and then followed by the 1:1 silicate clay minerals and non-silicate clay minerals (oxides). The 1:1 silicate clay minerals and non-silicate clay minerals are both old minerals and, therefore, they show low negative charges. Using soils dominated by these minerals might consider the addition of organic matters to increase the soil negative charges and thus the soil CEC.

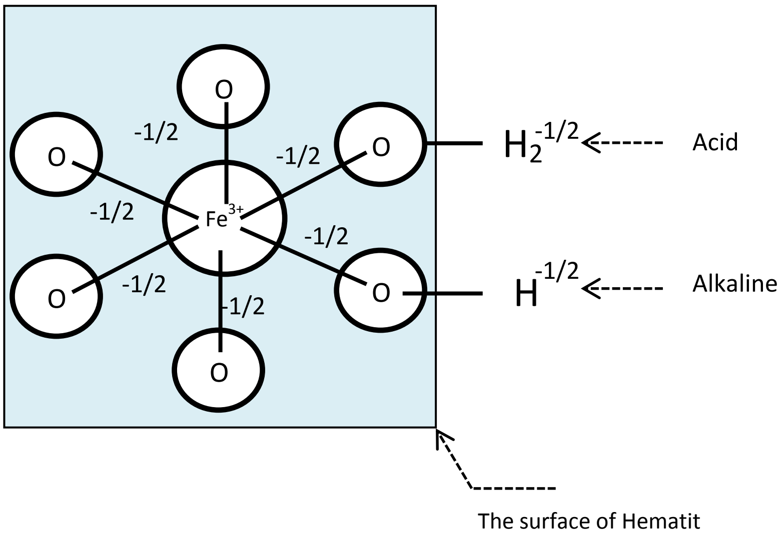


Fig. 2.7. The development of negative charges of oxides of Hematite (Fe_2O_3) (Bohn et al., 1985).

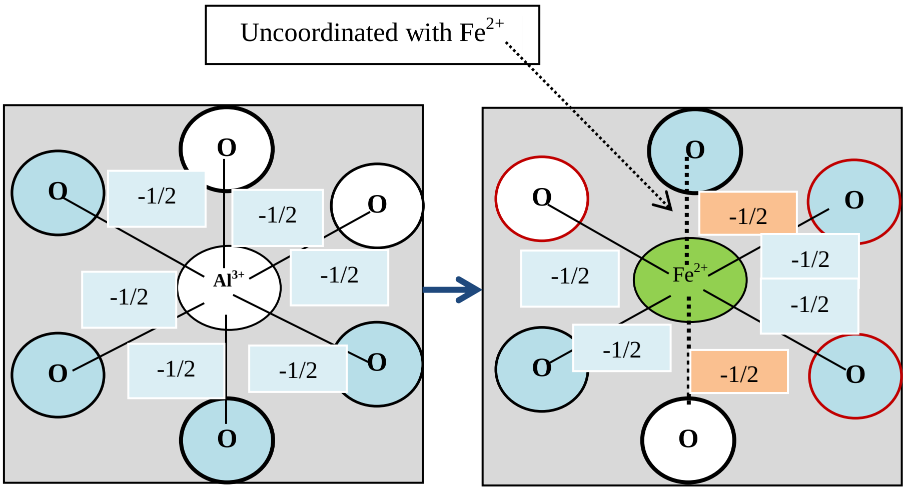
While the development of the negative charges on the surface of organic matter, 1:1 silicate clay minerals, and non-silicate clay minerals are pH dependent, the development of the negative charges on the surface of 2:1 silicate clay minerals is not pH dependent. The negative charges of these minerals arise from the substitution of metal elements in tetrahedral and/or octahedral structure of the minerals. The process called isomorphic substitution is described in **Fig. 1.8**, in which Al^{3+} in the aluminum octahedral is substituted by a similar size cation Fe^{2+}. Al^{3+} which have 6 coordination numbers each possessing charge + 0.5 is substituted by Fe^{2+} which have 4 coordination number each possessing charge +0.5. This process may fill only 4 positions each with charge – 0.5 previously filled by positive charges of Al^{3+} and leave 2 positions each with charge – 0.5. All together, the substitution of Al^{3+} by Fe^{2+} causes a net charge of 2 x -0.5 or -1 for each element. This process is not controlled by soil pH.

The type and amount of the emerging charges are dependent on the oxidation number of the substituting and substituted elements. Some of the possibility is listed in **Table 2.3**. The type of the net charge may be negative just like when Fe^{2+} substituting Al^{3+} in octahedral structure or when Mg^{2+} substituting Si^{4+} in the tetrahedral structure of silicate minerals. The type may be positive like when Al^{3+} substitutes Mg^{2+}. The amount of the negative charges can be found by subtracting the valence of the substituting element by the valence of the substituted element. For example, when Al^{3+} substitutes Mg^{2+}, the emerging net charge is the valence of the substituting element (3+ of Al) subtracted by the valence of the substituted element (2+ of Mg) or equals to + 1 (**Table 2.3**). Among the soil minerals, the 2:1 silicate clay minerals show the highest negative charges, as high as that of allophane, the amorphous primary minerals (**Table 2.1**).

Table 2.3. The development of surface charges on 2:1 silicate clay minerals.

Substituting Element	Substituted Element	Net Charges
Fe^{2+}	Al^{3+}	-1
Mg^{2+}	Si^{4+}	-2
Al^{3+}	Mg^{2+}	+1

The above explanations suggest that the negative charges in the soil environment are determined by the types and the amounts of soil solids. Soil containing high proportions of 2:1 silicate clay minerals or allophane may have high amounts of negative charges. However, old soils with high proportion of 1:1 silicate clay minerals and/or oxides and hydroxides may have low CEC. The presence organic matters may raise the soil negative charges. Therefore, to enhance the CEC of old soils like Oxisols and Ultisols that have low CEC, organic matter is usually employed.



Fe^{2+} (Coordination Number = 4) replaced Al^{3+} (Coordination Nunber = 6) producing negative charges = 2 x (0.5) = - 1

Fig. 2.8. The development of the negative charges of 2:1 silicate clay minerals through isomorphic substitution (Bohn et al., 1985).

The quantity orthophosphates added into the soil environment may also increase the soil negative charges. In addition to non-specific adsorption, phosphates in soil environment are specifically adsorbed by soil solids, particularly oxides. The phosphate ion may displace the structural element and cause the emergence of negative charges. This process is shown in **Fig. 2.9**. The OH position in the structure of oxides is displaced by $H_2PO_4^-$, after which the negative charges increase from -1 to -2. This may enable the increase in metal adsorption in soils by addition of phosphate.

In addition to soil CEC, that indicates the total soil negative charges, some other important soil chemical properties may include: soil organic C and organic matter contents, soil total N contents, activities of soil enzymes, soil pH, soil redox potential, and concentrations of competing cations and complexing/precipitating agents.. These soil chemical properties are directly or indirectly related to the process of adsorption and/or precipitation of heavy metals. These relationships are important to understand heavy metal retainment in the soil environment.

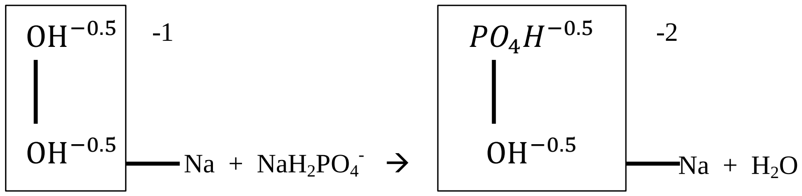


Fig. 2.9. The specific adsorption of phosphate by oxide in the soil environment (Bohn et al., 1985).

As previously explained, the total C is related closely to the content of organic matter content. It is well-known that the total organic matter content is related to the content of organic C by a factor of 1.5 – 2.0. Organic matter is one of the most important soil solids that have high negative charges. Organic matter content indicates not only the level of soil fertility but also the capability of the soil to adsorb cations. High contents of organic maters are expected to effectively immobilize metal cations in the soil environment. There are efforts have been made to increase the capacity of soils to adsorb heavy metal cations by organic matter incorporation into the soils system (Kukier et al., 2010). Some report show that the immobilization of heavy metals is enhanced by organic matter addition (Salam et al., 1997k; 1998f; Salam, 2000; 2001).

Organic matters in soils are originated from residues of plants and animals and dead as well as decaying plant roots. Organic matter decomposition changes their physical, chemical, and biochemical properties and also affects the soil physical, chemical, and biochemical properties and behaviors. The decay processes are accelerated by the presence of soil enzymes produced by soil microorganisms, soil macroorganisms, and plant roots, which function as biocatalysators. These processes release some inorganic constituents that can be absorbed by plants. These processes continue until the soil organic matters reach a stable form called humus, that cannot decay further.

In addition to by the presence of soil enzymes, organic matter decomposition is also controlled by the organic matters C/N ratios. Organic C is needed by soil microorganisms as energy sources (% Organic Matter Content = 1.5 – 2.0 times % C), while N is needed to build proteins required for the growth of soil microorganisms. By this reason, organic matters with high C and high N or low C/N ratios will decay more easily. Organic matter with low N or high C/N ratios will decompose more difficult because the available N will be used to build proteins for microorganisms. Therefore, low N organic matters must be enriched with Urea-N to decay faster.

Organic matters and humus in soils originated from decaying animal and plant residues are parts of soil solids. Structurally and chemically, organic matters and humus are different from mineral matters. Soil organic matters and humus are mostly composed of C chains completed with H and O atoms and possess functional sites. Mineral matters are mostly composed of Si, Al, and O. Organic matters are different from humus in the point of view that organic matters are the accumulation of animal and plant residues which are partially decomposed, while humus is organic matters that have been transformed by soil microorganisms to be more stable forms.

The contents of soil organic matters are different from one soil to other soils. The contents of organic matters in Peat and Muck were in general > 50%. The contents of organic matters in mineral soils range from 0% in desert soils to > 10% in forest soils. The general values of organic matter contents range from 1 – 3%, decreases with soil depth. Some reports showed that organic C of tropical soils ranges in values of 1.06 – 1.55% (Alfisols), 0.8 – 1.61% (Ultisols), 2.01 – 2.07% (Oxisols), and 2.44% (Mollisols) (Salam, 2014). The contents of soil organic matters are 1.5 – 2.0 times Organic C. According to Amelung et al. (1998), soil organic matter is related to the soil texture. Soil clay fraction is associated with 43% total Organic C, 56% of total N, and 62% or total S. The percentage decreases with the increase in soil temperature and the decrease in precipitation.

As described by Salam (2014), soil organic matters consist of Humic and Non-Humic Substances. Non-Humic Substances are plant residues that have not been decomposed. These materials are easy to indentify and consist of polysaccharides, lignin, and polypeptides. Conversely, humic substances are plant residues that have been decomposed. Humic substances consist of three fractions, each fraction is a mixture of several undescribed organic compounds. These fraction are Humin, Humic Acids, and Fulvic Acids (Tan, 1986; 1993). Humin is the humic substances not soluble in alkaline solution. Humic Acids are the humic substances not soluble in dilute acids, while Fulvic Acids are the humic substances soluble or do not precipitate in dilute acids after being separated from Humic Acids (**Fig. 2.10**).

Humic acids are the product of organic matter decomposition. These substances are relatively stable and, therefore, are accumulated in the soil environment. These substances enable soils to retain plant nutrient and heavy metal elements and, hence, can buffer their concentrations in soil water. According to Mackowiak et al. (2001), humic acids are also useful to buffer the soil solution H^+ and thereby the soil pH does not easily change due to acid or base additions.

Soil reaction (pH) is another very important soil properties related to the immobilization of heavy metal cations in the soil environment. As previously stated, soil pH is related to the pattern of heavy metal retainment in the soil environment. In general, the heavy metal retainment in the soil environment increases with the increase in soil pH. Some soil workers suggest that the ion exchange is the major chemical mechanism responsible for this pattern, while some others argue that precipitation is the responsible chemical mechanisms for this pattern, particularly at high pH and concentrations of heavy metal cations. The pattern of heavy metals retaiment as a function of pH is shown in **Fig. 2.11**.

The soil solid exchange site is affected directly by the increase in pH. The presence of more OH^- ion in soil solution may stimulate the release of H from the surfaces of organic matters, 1:1 silicate clay minerals, and oxides or hydroxides, which finally neutralized by OH^- ions forming water molecules. The sites left by H ions are then filled with heavy metal cations, the amount of which increases with the increase in soil pH. The presence of OH^- and other anions such as CO_3^{2-} may also complex and precipitate some of the heavy meals. The final result is as previous shown previously in **Fig. 2.11**. The soluble heavy metals decrease with the increase in soil pH.

Since the retainment of heavy metal cations in the soil environment is also affected by precipitation reaction, the presence of complexing and precipitating agents is very important. As a rule, the precipitation may occur when the concentrations of heavy metal cations and precipitating agents in the soil environment are high. This condition may suffice the requirement that the product of heavy metal cation and the precipitating agent surpasses the solubility constant

(K_{sp}). Some complexing or precipitating agents important in the alkaline soil environment are: OH^-, SO_4^{2-}, CO_3^{2-}, Cal^-, and PO_4^{3-}.

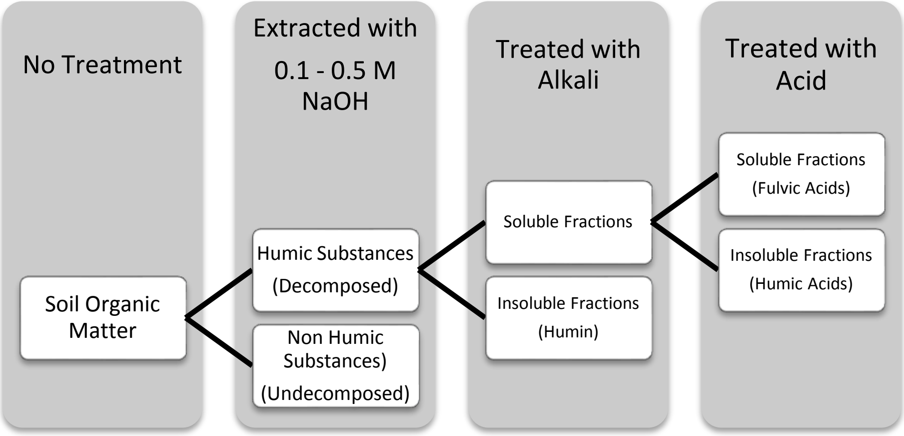


Fig. 2.10. Fractionation of humic substances in soil environment (Salam, 2012).

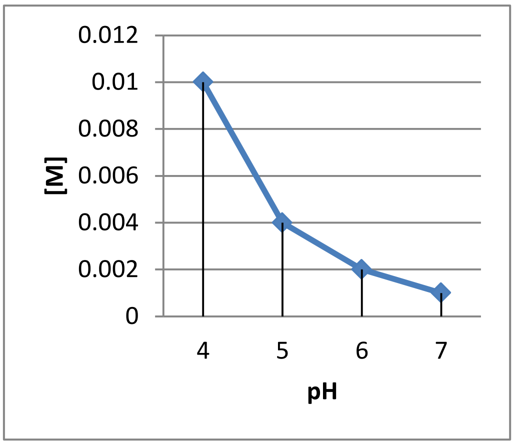


Fig. 2.11. The effect of pH on heavy metal retainment in the soil environment (Salam, 2012).

While the presence of precipitating agents may be very important to increase the retainment of heavy metal cations in the soil environment, the presence of other cations may give a negative effect on the retainment of heavy metal cations. Other cations may compete with the heavy metal cations. This may cause that the presence of other cations may hinder the adsorption of heavy metal cations. This may occur particularly when the competing cations show the following properties: higher oxidation numbers, lower radii, and high concentrations. With this condition as indicated by the Coloumbic Law, the attraction forces of heavy metal cations onto the surface active sites are higher. The competing cations may be those of major cations such as Ca^{2+}, Mg^{2+}, Na^{+}, and K+, or of the supplementary cations such as Al^{3+} and H^{+}, or heavy metals cations other than the heavy metal cation in question.

Some heavy metals such as Fe and Mn show different oxidation number. Fe may exist as Fe^{2+} or Fe^{3+} and Mn may exist as Mn^{2+} and Mn^{4+}, respectively. This difference is affected by the condition of the soil environment. When the soil condition is oxidative with high E, the Fe and Mn may exist as Fe^{3+} and Mn^{4+}, respectively. Conversely, when the soil condition is reductive or the soil is flooded with low E, Fe and Mn may exist as Fe^{2+} and Mn^{2+}, respectively The chemical reaction of each species is different. For example, the oxidized Fe or Fe^{3+} may precipitate with $H_2PO_4^{-}$. However, the reduced Fe^{2+} may precipitate with S^{2-} forming solid FeS. This means that the magnitude of E is very important in the soil environment. Together with pH, E may determine the form of elements and their reaction in soil system. This behavior is recorded in E-pH Diagram shown in **Fig. 3.4.**

2.3 Soil physical properties

Some of the soil physical properties and porcesses important for the management of heavy metals in the soil environment may include soil pore, porosity, and tortuosity; soil bulk density, compaction and tillage; soil moisture content; soil temperature, color, and cover, as well as water and element movement and disposition. These properties are important to understand the potential contamination and pollution of ground water and the living thing through the soil system, particularly when heavy metals are not strongly retained in the soil environment.

Soil pores are formed when the soil particles of sand, silt, and clay sizes stick together forming soil aggregates in which spaces are formed between the soil particles, or when spaces between aggregates are not filled with soil particles. Soil pores are filled with air, water, and/or microorganisms. Plant roots also grow and develop inside the soil pores. In fact, water and nutrients needed for plant growth and development are absorbed by plant roots from the soil pores. This indicates that soil pores play important roles in the cycles of plant growth. Soil pores are also important for heavy metal movement and transport because heavy metals may move through a connected soil pore water in pore channels.

Soil pores are of different sizes and in general are classified into three categories: micropores, mesopores, and macropores. In a normal condition or field capacity, water may fill micropores and part of mesopores while air fills part of the mesopores and macropores. However, in a wet condition like during and after raining, water may fill all categories of soil pores. All air initially fill the soil pore is displaced by the incoming water. Conversely, when the soil is dry, almost all soil pores are filled with air. Only a very thin film of water may exist around the soil particles when the soil is relatively dry. The existence of water and air in soil pores is very dynamic, may change from time to time depending on the condition of soil water. This phenomenon is described in **Fig. 2.12**.

The soil pores may be connected one to another making a channel of waterways in the soil body. This channel may go into any direction and is a channel for element movement in the soil system. Through this channel, heavy metals may move vertically through capillary force (in dry condition) or mass flow and/or diffusion (in wet condition). The connected soil pores may be long may be short, which may determine the degree of element translocation in the soil system. It is possible that the channels have the same straight distance but with different channel length; it is determined by the channel tortuosity. The tortuosity may determine the rates of water and element movement from one point to another point. Of course, water and elements may move slower when the tortuosity is high.

Not only the soil aggregation making soil pores and soil-pore channels in soil. Some other mechanisms may produce or affect the soil physical properties. Mesoorganisms may in fact make soil pores and soil-pore channels. These may include soil worms, ants, rats, and marmots. The resulted pores are in general large; therefore, these may accelerate the water infiltration and percolation in the soil body. The biopores implemented in the cities are of this principle, particularly to conserve water and avoid flood. However, in relation to heavy metals this practice may increase the ground water contamination and pollution.

The existence of soil pores control the soil porosity, that indicate the relative volume of soil pores to the total volume of soil, that is very important related to the existence of water in soil body available for element transport. The total soil porosity (f) can be calculated from the total soil bulk density (ρ_v) and the soil particle density (ρ_s) using **Eq. 2.1** or **Eq. 2.2** (Hillel, 1980).

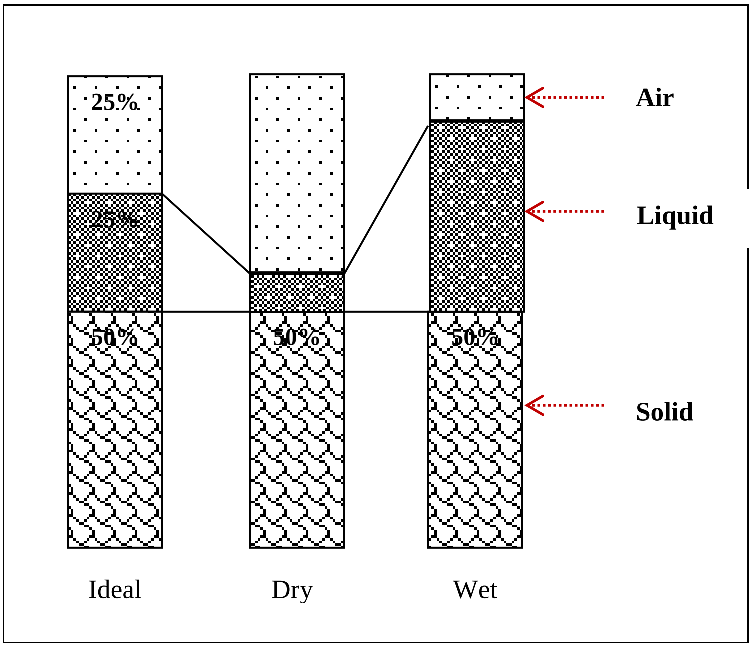


Fig. 2.12. The dynamics of the soil pore-water and air contents (Salam, 2012).

$f = (\rho s - \rho_v)/\rho_s$ .... **Eq. 2.1**

$f = 1 - \rho_v/\rho_s$ .... **Eq. 2.2**

The value of total porosity ranges between 0 – 1 or 0 – 100%. Clay soils with bulk densities 1.1 – 1.3 g cm^3 may have total porosity 0.58 – 0.51 or 58 – 51%. Sandy soils with bulk densities between 1.5 – 1.7 cm^3 may have total porosity between 0.43 – 0.36 0r 43 – 36%. Total porosity is determined by the soil bulk density as a variable while particle density is a constant.

The soil bulk density is the ratio between the total mass of soil and the total volume of soil (**Fig. 2.13**). The soil bulk density is calculated by **Eq. 2.3** (Hillel, 1980; Singer and Munns, 1987).

$$\rho_b = \frac{\mathrm{M_p}}{\mathrm{V_t}} \quad \text{....... Eq. 2.3.}$$

where ρ_v is the soil bulk density, M_p is the soil particle mass, and V_t is the total volume of soil. V_t is also the sum of the volume of soil mass and the volume of soil pores. The soil bulk density is in average 1.3 g cm^{-3}.

The soil bulk density is dynamic, may change with time. When soil is compacted, for example by the use of tractors in agricultural lands, the total porosity of soil decreases and thereby the soil mass per volume increases. On the other hand, when the total soil pore increases, for example by soil tillage, the soil mass per unit volume or the soil bulk density decreases.

The soil particle density is the ratio between the total soil mass and the volume of soil particle as shown in **Fig. 2.13** and expressed in **Eq. 2.4** (Hillel, 1980; Singer and Munns, 1987).

$$\rho_s = \frac{\mathrm{M_t}}{\mathrm{V_s}} \quad \text{....... Eq. 2.4}$$

where ρ_s is the soil particle density, M_t is the total soil mass, and V_s is the volume of soil solid (**Fig. 2.13**).

The soil bulk density is always lower than the soil particle density. The difference is higher with the increase in the soil total porosity. For soil with total porosity of 50%, ρ_v = 0.5 rs. For sandy soil, ρ_v may reach 1.6 g cm^{-3}, for loamy soils with good aggregation and clay soil may have ρ_v 1.1 g cm^{-3} caused by the high total soil porosity. Soil with no pores (massive) may have $\rho_v = \rho_s$. In general, mineral soils may have ρ_v 1.3 – 1.35 g cm-3 and ρ_s 2.6 – 2.7 g cm^{-3}.

As previously discussed, the soil bulk density is dynamic, depending on the soil porosity. A newly tillaged soil may have low bulk density and that encountered compaction may have high bulk density. However, the soil particle density is relatively constant except when other solids with different density are introduced in the soil system. This may include high amount of organic matters or biosolids or volcanic materials. The bulk density and porosity of soils may change due to several processes such as soil compaction and soil tillage (Afandi et al., 1997a; 1997b; Zhang et al., 1997; Gregorich et al., 2011). Soil compaction may increase the soil bulk density, and conversely, the soil tillage will decrease the soil bulk density. Structurally, the decrease in soil volume or the shrinkage of soil porosity by compaction is caused by a more closely packed soil particles in soil aggregates, and hence, causes more limited rooms between soil particles or between soil aggregates.

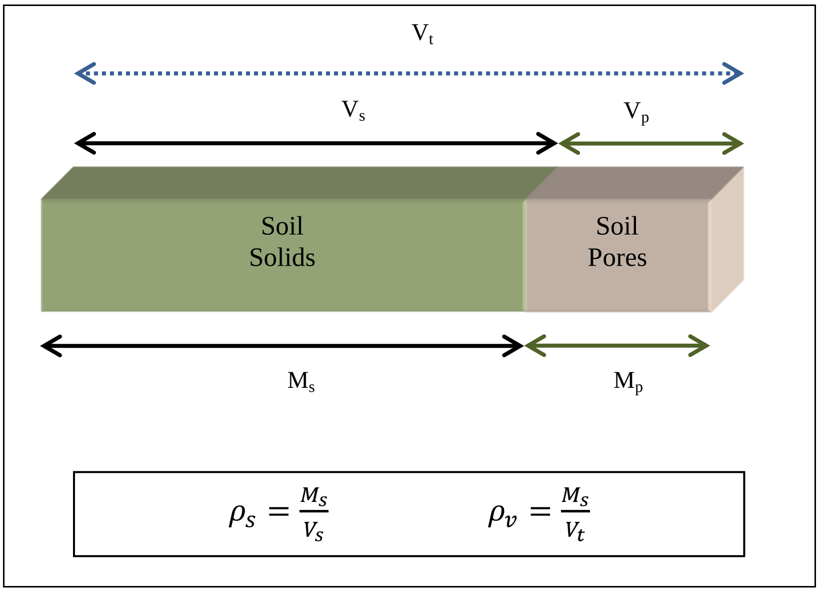


Fig. 2.13. The calculation of soil bulk density and soil particle density (Salam, 2012).

Soil pores and pore channels are very important for the management of heavy metal movement and translocation in the soil environment. However various anthropogenic activities may disturb their existence. The activities may include human activities walking back and forth in agricultural lands, tractors moving on the lands, the uses of other heavy vehicles and tools. Continuous anthropogenic activities like these may eventually compact soils and decrease the total porosity and increase the soil bulk density as a result of the increase in soil micropores and the decrease in soil macropore. These changes may alter the equilibrium related to soil water and air, which may result in the disturbance of heavy metal movement in soils. The soil compaction is more severe in clayey soils than that in silty and sandy soils.

One of the effort can be conducted to solve the problem of soil compaction is soil tillage. There is several method of soil tillage: no tillage and minimum tillage, both are referred to as conservation tillage, and conventional tillage. All of these techniques are useful to decrease the soil bulk density and increase the total soil porosity. Conservation tillages are reported to decrease the soil erosion and increase the soil particle aggregation, infiltration rates, and soil water deposit (Christensen et al., 1994; Baumhardt and Lascano, 1996; Kumari et al., 2011). However, long-term practice of no-tillage and/or minimum tillage may also increase the soil bulk density. Therefore, maximum tillage (conventional tillage) must be conducted in no tillage/minimum tillage soils after several seasons.

The soil pores are important to contain water in soils. As previously discussed, soil water is contained in micropores and mesopores. Therefore, it is easily understood that clayey soils may contain higher amount of water that do silty soils, and silty soil may have higher contents of water that do sandy soils. Therefore the amount of soil water may follow the sequence: clayey soils > silty soil > sandy soils assuming that the number of soil micropores and mesopores follow the same sequence.

The above sequence may change by soil particle aggregation and structure. Clayey soils with good structure might have been dominated by macropores, thereby, have lower retention on water and most of water is easily drained. As a result, the soil water content may change to be: sandy sois > silty soils > clayey soils, as shown in **Fig. 2.14**. As previously stated, the soil water content is dependent on the pore sizes. The percentage of micropore, particularly with increasing total porosity, may increase the soil water content due to the higher amount of pores that are able to retain water. On the other hand, the soil water content may decrease with the increase in total soil porosity dominated by macropores that may drain most of the soil water.

Soil pores, total porosity, and pore channels are important not only to pool water but also for the transportation of water and elements in soils related to the processes of water infiltration, water percolation, and elemental leaching. In fact, the incoming water to the soil surface by rainfalls may encounter these processes. Water on the surface of soils may enter the soil system through open pores (Water

Infiltration). The entering water, may then move downwards due to gravitation in the soil body (water percolation), part of which may enter groundwater. The dissolving elements may go with the moving water to move from one point to another, usually downwards (Elemental Leaching). All these physical processes may occur fast when the soil pores and pore channels are available. Good soil structure, high porosity, and good pore channels may accelerate these processes.

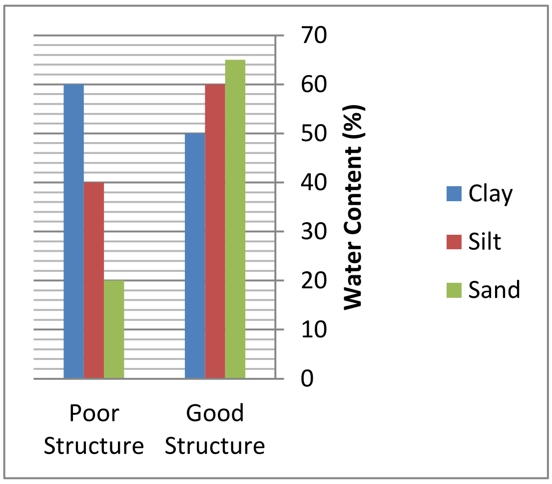


Fig. 2.14. Changes in soil water contents as affected by soil texture and structure (Salam, 2012).

However, when the soil pores are saturated with water due to some reasons, probably due to slower infiltration and percolation rates (lower than rainfalls) or low soil porosity or unavailable pore channels, part of the raining water may accumulate on the surface of soils. When occurred on tilted land surfaces, the accumulation may cause the water to move on the surface of soils (Runoff), which may cause destruction of soil structure and move the detached soil particles to lower position (Erosion). The slope of soil surface and gravitation may intensify the soil erosion. All these processes are depicted in **Fig. 2.15**.

All of the above processes are very important for environmental management. Infiltration is very important because of two reasons. First, water infiltration may avoid the occurrence of runoff and also erosion. Second, infiltration and percolation may increase the soil water pools, which is very important for the living things. Therefore, soil pore, porosity, and pore channels must be preserved to conserve water in the soil environment..

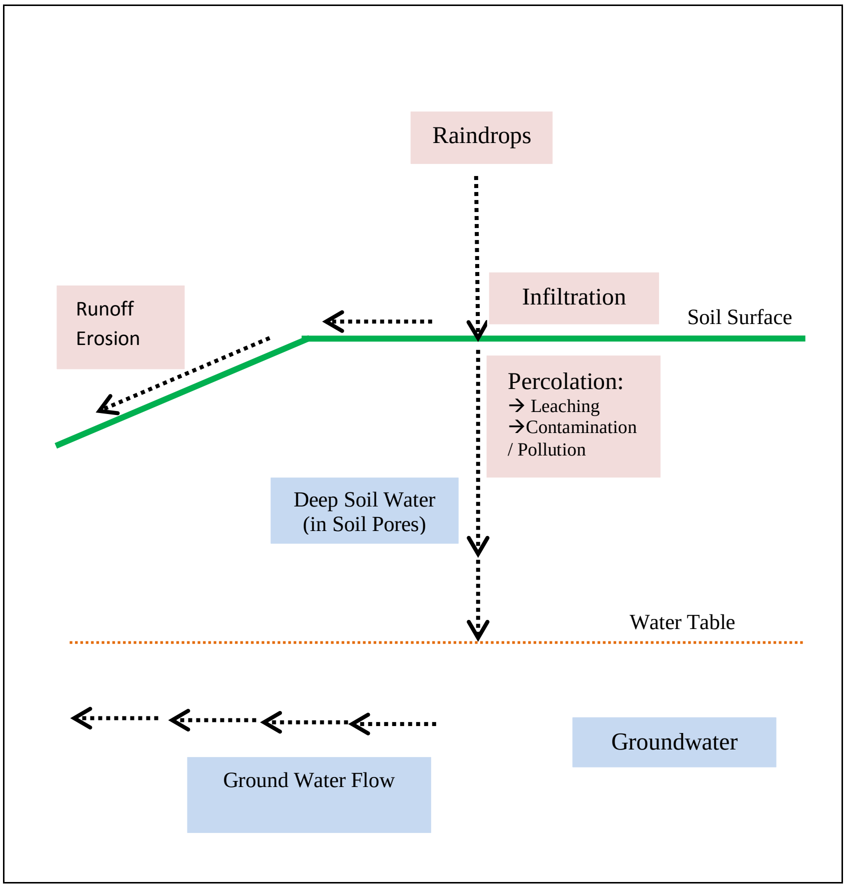


Fig. 2.15. The relationship between soil water, ground water, and all related processes (Salam, 2012)

However, if the percentage of macropores is high, the infiltration and percolation rates are too high and may cause faster elemental leaching. In addition to leach some essential elements for plant growth, this condition may cause high movement and translocation of heavy metal elements to deep soil water and ground water. This suggests that the proportion of soil pore sizes, including soil micropores, mesopores, and macropores must be carefully maintained. The distribution of pore size must enable part of the water to be contained in the soil pores and water movement in the soil body does not transport a great amount of essential and heavy metal elements.

The rates of infiltration are controlled by several factors, particularly of the soil physical properties like soil texture and structure. The rate of infiltration in clayey soils is about 5 cm per 24 hours while that in sandy soils is about 60 cm per 24 hours or 24 times higher. This phenomenon is due to the fact that the amount of the soil macropores in sandy soils is higher than those in clayey soils. However, the trend may change with soil structure, which definitely affects the distribution of soil pore sizes. The relationship between infiltration rates with soil textures and structures is described in **Fig. 2.16**.

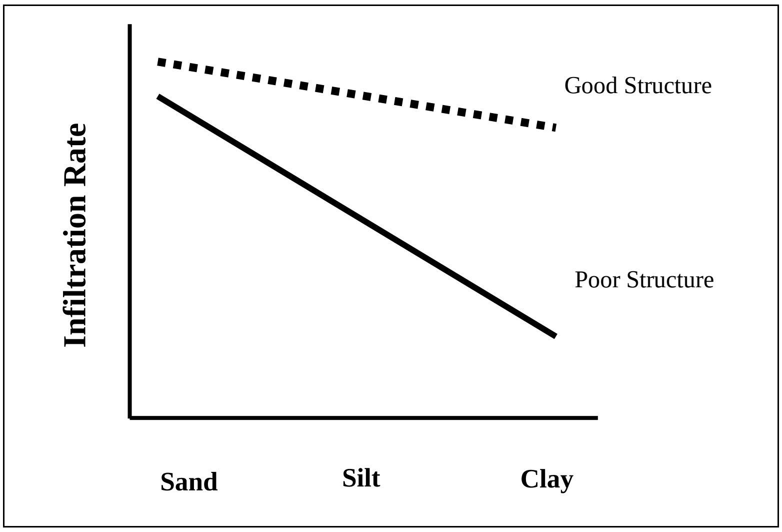


Fig. 2.16. The relationship between the rates of infiltration and soil texture and structures (Salam, 2012).

The rates of water infiltration are also affected by soil covers including plant covers and mulches. Soil covers may make the soil surface more stable, always porous, and thereby, water may enter and come out of the soils easily. Good soil aggregates are formed if organic matters are available and soils are not intensively tillaged. The decrease in organic matters through harvest may lower the rates of infiltration due to poorer soil aggregation. Low organic matter may also cause soil aggregates on the surface of soil weaker and are easily destroyed by raindrops and cause pore clogging.

After entering the soil system, water may encounter several possibilities. First, water may percolates in the soil body and may also transport some elements like heavy metals and enter the ground water and finally reach rivers or seas. Percolation is partially driven by gravitational forces; therefore, the excess water drained from the soils by percolation is called gravitation water. Second, through capillary forces water may reach the surface of soils and evaporate to the atmosphere. Third, water may move to the plant root surface and be absorbed, which may eventually transpired by plant leaves. Fourth, water may stay in soil micro and mesopore and be adsorbed by soil particles as the soil water.

Soil water is contained in soil pores by two forces i.e. adhesion and cohesion forces. Adhesion is attracting forces emerged between soil particle surface and water molecules while cohesion is an attracting forces emerged between water molecules. These forces are strong and cause strong bonding among water molecules and with soil particle surfaces. In general, clay particles adsorb more water molecules than do silt and sand particles due to the larger surface area of finer particles and also the higher negative charges of the clay particle surfaces. The surface area and the amount of the particle negative charges of soil particles follow the sequence of clay > silt > sand.

The soil water may eventually be absorbed by plants. Its availability varies depending on the soil texture and structure. After the gravitation water is drained out of the soil system, the rest of water in soil is the most easily available to plants. This level of soil water is called Field Capacity (Water potential about 10 – 35 kPa) (Singer and Munns, 1987). By absorption or evaporation, the soil water may deplete and become more difficult to absorb, and finally one condition is reached where the attraction force by soil particles is stronger than the absorption force by plant root causing plant root cannot absorb any water and plant encounter permanent wilting. This level of water content (Water Potential about 1,520 kPa is called Permanent Wilting Point (PWP) (Singer and Munns, 1987). The water contents in soils are depicted in **Fig. 2.17**. The water available for plant root absorption lied between FC and PWP, which is called Available Water (**Fig. 2.17** and **Fig. 2.18**).

Available water is different among soils, depending on the soil texture and soil types (**Fig. 2.18**), and also on several other factors like soil organic matter content. Clayey soils, which have large surface areas and high negative charges, may contain higher amount of available water. On the other hand, silty and sandy soils, which have lower surface areas and low negative charges, have low available water.

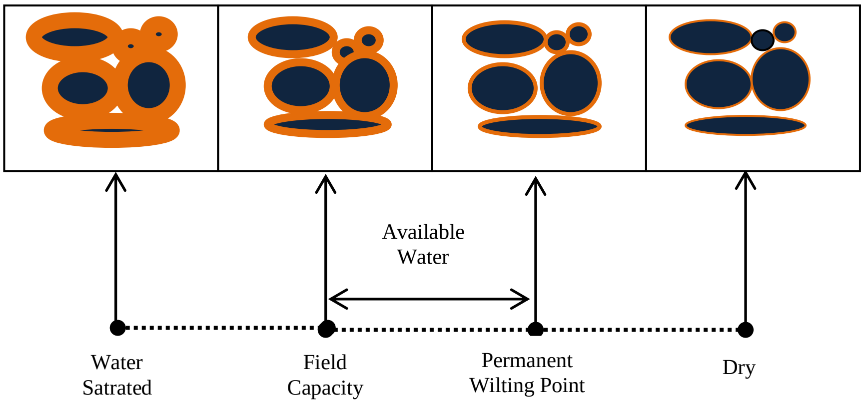


Fig. 2.17. The level of soil water contents (Salam, 2012).

In addition to water, the soil temperature may affect the movement and translocation of heavy metal elements in the soil environment. The soil temperature affects the metal elements by increasing the atomic vibration so that the increase in soil temperature may cause the higher rates of water and elemental movement in the soil environment. Moreover, soil temperature may also increase the rates of chemical reactions such as soil mineral weathering, organic matter decomposition (enzymatic reactions), and equilibrium reactions such as complexation/decomplexation, chelation/dechelation, precipitation/dissolution, adsorption/desorption, and oxidation/reduction. The equilibrium constants for the respective reactions increase with the increase in temperature (Sposito, 1989). The rates chemical reactions generally increase by a factor of 2-3 for a 10° increase in temperature. Therefore, every factor affecting the equilibrium constants may indirectly affect the chemical reactions and movement of heavy metals in the soil environment.

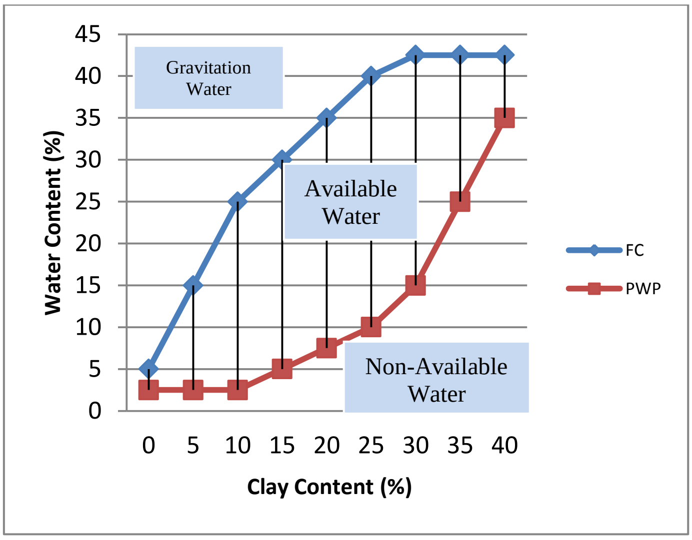


Fig. 2.18. The available water in the soil environment.

(FC = Field Capacity; PWP = Permanent Wilting Point; adapted from Harpstead et al., 1988).

As discussed in Salam (2012), soil temperature may encounter daily fluctuation. The soil temperature is lowest from the middle of the night until the early morning. The soil temperature begins to increase at sunrise when its radiation begins to touch the soil surface and reaches a maximum in the middle of the day. The soil temperature then begins to decrease at sunset and again reaches the minimum in the middle of the night. The average temperature also encounters monthly and yearly fluctuation, depending on the seasons and the position of the sun. The daily, monthly, and yearly temperature fluctuations also depend on the soil moisture content. Wet soils may encounter lower fluctuations than do dry soils. The presence of water may preserve soil heat that may buffer the decrease in soil temperature. This phenomenon is shown in **Fig. 2.19**.

Soil temperature is directly related to heat originated from sunlight, which is the main source of heat in the soil environment. Soil temperature is determined by the intensity of the sunlight reaching the surfaces of soils and also the properties of the surface of soils. The sunlight intensity reaching the surface of soil is known to also be affected by the angle of sunlight to the soil surface. The maximum heat absorption by soil surface is when the angle is upright on uncovered soil surfaces. A part of the sunheat reaching the soils is finally absorbed by soils and finally raises the soil temperature. Another part of it, however, is not absorbed but is reflected to the atmosphere.

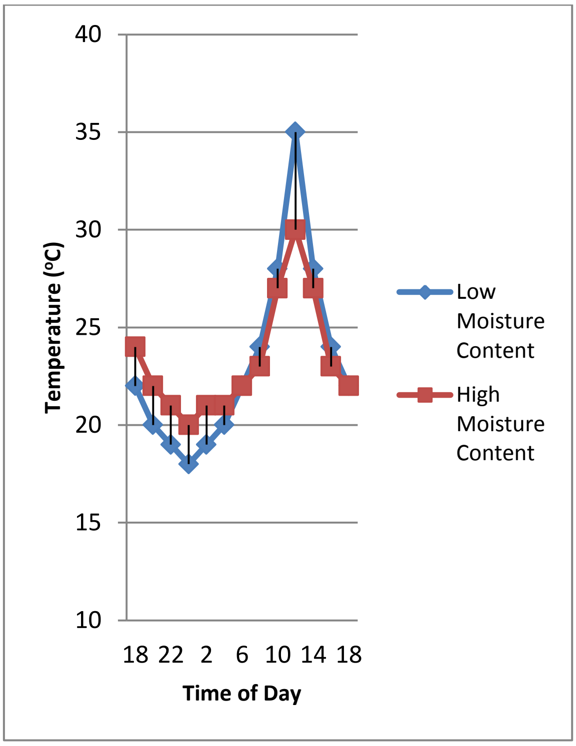


Fig. 2.19. The effect of water content on the daily fluctuation of soil temperature (Salam, 2012).

As pointed out by Salam (2012), the heat absorption by soils is affected by several factors, among which are: soil color, soil cover, soil water content, direction and magnitude of surface slope, and soil depth. Dark colored soil surfaces may absorb about 75% of the incoming sunheat and pale surface absorb only about 25%. The presence of cover vegetation, and also mulches, may decrease the heat absorption. The soil water content also determines the absorption of heat; wet soil may encounter slower rising of temperature that do dry soils. The direction and magnitude of surface slope also determine the heat absorption. The soil surfaces directly face the sunlight may absorb the highest sunheat. Because the heat may move through soil particles, the soil temperature may differ with soil depths. During daylight, the temperature of topsoils is higher than that of the subsoils while during the night the temperature of topsoils is lower than that of the subsoils (**Fig. 2.20**). The difference may also exist for the monthly and yearly soil temperature. Other soil properties affecting soil temperature is soil organic matter content. Douche et al. (2009) report that application of compost increased the soil temperature of bare Andosol in a cool climate region.

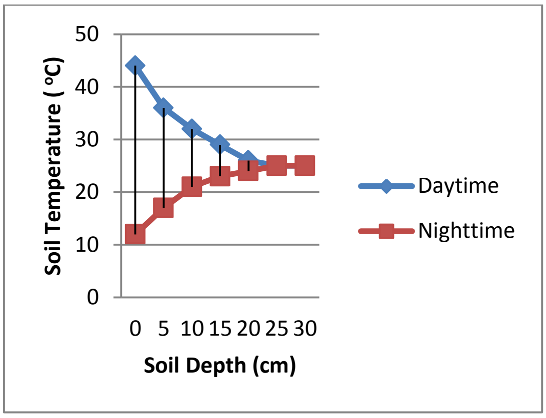


Fig. 2.20. The daily fluctuation of soil temperature as a function of soil depth (Salam, 2012).

Soil color is one of the most easily recognized soil physical properties and useful to predict the environmental impacts occurring in the soil environment. In addition to indicating soil fertility, soil color is very important to predict the absorption of sunheat and its effect on soil temperature, which may affect the diffusion coefficients of heavy metal cations. For example, dark color of O Horizon may indicate not only the fact of the soil fertility, but also the probability of the soil good texture and structure as well as total porosity that is very important for heavy metal cation transport and translocation. The dark color is also closely related to the high content of organic matter that is important for the development of soil structure and pores. The opposite is what happen in red colored soils that indicate low organic matter content. However, to exactly determine the soil color a reliable tool must be employed. Soil scientist usually use Munsell Soil Color Chart to determine the soil color.

The color of soils is affected by the soil organic matter or humic substance contents and also the type of dominant soil minerals. If soils contain high amounts of humic substances, the soil color may be black. On the other hand, red colored soils indicate that unhydrated oxidized Fe is abundant. Yellow color indicates the Fe is hydrated and oxidized Fe is low. The grey color indicates that soils are flooded, in a reductive condition, thereby, Fe is reduced. The soil conditions affecting soil color are listed in **Table 2.4**.

Table 2.4. Conditions causing soil colors$^{1)}$.

No.	Color	Soil Condition
1	Black	Humic substances are very high
2	Red	Fe is oxidized, not hydrated
3	Yellow	Fe is lightly oxidized and hydrated
4	Grey	Soil is flooded; low O_2, Fe is reduced

$^{1)}$ After Salam (2012)

As discussed previously, heavy metals move to various directions in the soil environment through pores and pore-channels. The mechanism of heavy metal cation movement is of two types. The first is mass flow, in which heavy metal cations move together with the mass of water flowing in the soil pore channels controlled by the difference in soil matrix potential. The second is diffusion, in which heavy metal cations move in the soil pore channels controlled by the concentration gradients. With these mechanisms, heavy metal cations move in the water-filled pore channels. The movement of heavy metals by diffusion is independent of the water potential gradients. During diffusion, heavy metals may move either in the direction of water movement or in other direction other than the direction of water movement.

The movement of heavy metal cations by these mechanisms is of great importance to understand ground-water contamination or pollution by heavy metals. The high amounts of heavy metals in soil water may easily contaminate or pollute the ground water, particularly if soils and the incoming water contain significant amounts of heavy metals that may come from the adjacent industries or irrigation water contaminated by heavy metals. Avoiding heavy metal contamination or pollution can be conducted by heavy metal retention in soil solids. As long as heavy metals are dissolved in soil water, the contamination and pollution are difficult to avoid.

2.4 Soil biological properties

As pointed out by Alexander (1977), soil microorganisms plays some important roles, of which the most important is their roles in C-cycle (**Fig. 2.21**), particularly in decomposing organic matters. Organic matter decomposition may release the organic matter structural and functional elements and substances previously absorbed from the soil environment. The detached elements and substances may then be reabsorbed by plants or develop the soil colloidal system, structure, pores, and pore channels important for heavy metal cation retention and movement. As discussed previously, organic matter decomposition may develop the negative charges of the soil colloidal system and also strengthening the soil structure related to the roles of organic matter as cement in the soil structure. This suggests that the presence of microorganisms in soil indirectly affects heavy metal retention and movement.

Microorganisms are small size living things and, as usual, small size living things are abundant. There is a general rule that the smaller the size the greater the population. The smaller the size also means the greater their effects on the environment. There is a prediction that one million to 1 billion microorganisms live in a one gram soil sample. Therefore, microorganism may have great effects on soil dynamics. Some of the microorganisms are pathogen but a lot of them are useful in the soil environment. Nitrifying bacteria are among useful microorganism in the soil environment (Gopalakrishnan et al., 2009). Soil microorganisms produce soil enzymes. Some microorganisms are also useful for heavy metal management in the soil environment.

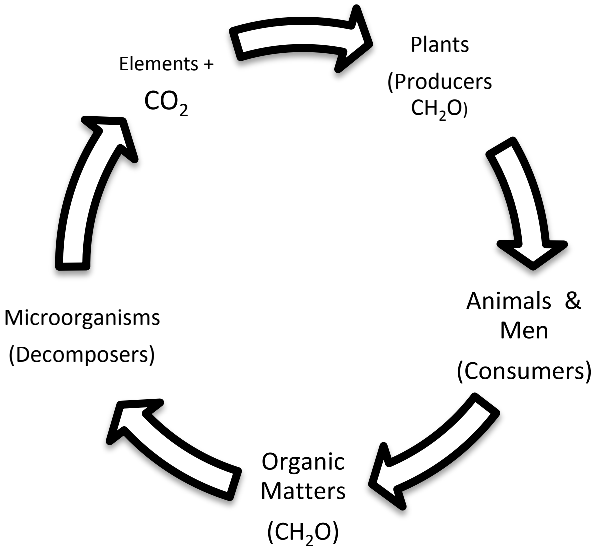


Fig. 2.21. The role of microorganisms as decomposers in the C-Cycle (Salam, 2012)

In addition to microorganisms, there are a number of macroorganisms live in soils. This includes nematode, earthworms, ants, mice, and marmots (Singer and Munns, 1987). Nematode is an arthropod that has no segmentation, colorless, and abundant in soils. This macroorganism is small in size; lives saprophytic on dead plant residues and part of them are also parasitic living in plant roots and endanger plants. The macroorganisms and their roles in soils are listed in **Table 2.5**.

Earthworms mix plant residues with soil mineral matters and move organic matters from the soil surface to the soil depths enriching soils with organic matters that are very important for developing soil structure, pores, and pore channels.

Earthworms also build holes in the soil environment, thereby, increase soil porosity and water infiltration and percolation. The role of earthworms at increasing soil porosity may include: (a) enlarging the soil pores by giving pressure and soil material movement, (b) developing new pores by making holes, and (c) filing the soil pores with materials from other places and, therefore, also decrease the soil pore sizes.

Table 2.5. Macroorganisms and their roles in soil environment[1)].

No.	Macroorganisms	Roles
1	Nematode	Decomposing organic matters
2	Earthworms	Mixing plant residues with mineral materials across soil horizons; developing soil macropores increasing soil porosity; producing enzyme of alkaline phosphatase; fertilizing soils
3	Ants	Fertilizing soils; transporting soil particles from subsoils
4	Mice	Mixing soil materials; increasing soil porosity;
5	Marmots	Mixing soil materials; Increasing soil porosity

[1)] After Salam (2012)

The soil macropores developed by earthworms are useful for water and element transport, including those of toxic chemicals like heavy metals and pesticides (Edwards, et al., 1993; Li and Ghodrati, 1997). It is reported that inoculation of earthworms into Ultisols in Amazone area, Peru, increases the macroaggregates (> 10mm) from 25.1 to 32.7% and decreases the soil microaggregates (< 2mm) from 33.2 to 26.1% (Alegre et al., 1996). However, this inoculation decreases the soil porosity and bulk density. In addition, earthworms may move residues (castings) to the soil surface. When earthworms are dead and decay, earthworms enrich soils with the results of decomposition from their dead bodies.

Earthworms are also very useful in biochemical decomposition of organic matters by producing alkaline phosphatase, an enzyme that accelerates the decomposition of organic P producing orthophosphates in the soil environment. Some researchers report that the activity of alkaline phosphatase is higher in soils inhabited by earthworms (Ross and Cairns, 1982; Satchell and Martin, 1984). One of the soil earthworms is *Lumbriscus terrestris* (Edwards and Lofty, 1977).

Ants are soil fauna, classified as arthropods. Ants move soil particles from soil depths and build soil “mountains” on the soil surface. Because ants are small-size, they move only small size soil particles and, therefore, there are no stone or gravel found in the ant “mountains”. This activity, therefore, increases the soil fertility. The resulted pores and pore channels are important for heavy metal transport in the soil environment.

Mice and marmots are vertebrates. These animals build a lot of holes by moving soil particles from soil depths to the soil surfaces. However, their activities are conducted in dry soils. Therefore, the transported materials in general are sands and gravels. However, by these activity mice and marmots till the soils and finally increase the soil fertility by organic matters and residues of these animals.

Other macroorganisms in the soil environment are plant roots, which are more important than animals. Plant roots may fill micro, meso, and macropores. Plant roots may also fill soil spaces made during their growth and development. After death, plant roots may leave all size pores. Plant roots are more important also due to the changes caused by their presence. The presence of plant roots may build soil aggregates making them to be more stable and stronger for physical forces like raindrops. Plant roots also excrete various ions and substances that may affect the soil chemistry. The production of CO_2 as a result of organic matter (CH_2O) respiration for energy may acidify the soil environment (**Eq. 2.5**). Plant roots also excrete H^+ ions that may lower the soil pH. The dead and decaying plant roots may contribute organic matters with several benefits. In addition to blacken the soil color, organic matters also strengthen the soil particle aggregation and become the C source for the living things (Emerson et al., 1986).

$$\mathbf{CO_2 + H_2O \leftrightarrow H_2CO_3 \leftrightarrow H^+ + HCO_3^- \quad \ldots\ldots\ Eq.\ 2.5}$$

In addition to the above roles, plant roots also produce various soil enzymes. Soil enzymes accelerate the decomposition of organic matters contaning particular plant nutrients not available to plants to inorganic plant nutrients that are available to plant root absorption. Some of the soil enzymes produced by plants are phosphatases, arylsulphatase, and urease, (Tabatabai, 1982), that accelerate the decomposition or Organic P, Organic S, and Urea, respectively. The production of enzymes is of course dependent of the plant types. Some researchers report that the activities of acid and alkaline phosphatase are high in the plant root zone and decrease towards those not filled with roots (Joner and Jacobsen, 1995). Forest soils are also reported to have higher activity of phosphatase than do the agricultural lands (Salam et al., 1997c; Salam et al., 1998d).

In addition to soil enzymes, soil organisms also produce various organic acids and other organic substances like allelophatic substances used to increase competition force towards other plant species (Sajise, 1980; Sriyani et al., 1996). Some of the organic acids produced by soil organism and the affected condition are listed in **Table 2.6**. The immediate effect of organic acid excretion into the soil environment is the decrease in soil pH that may affect other soil chemical properties including the solubility of heavy metal nutrients.

Table 2.6. Organic acid related to soil organisms$^{1)}$.

No.	Condition/Location	Organic Acids
1	Rhizosphere	CO_2, HNO_3, Protein, Amino Acids (Aspartic, Glutamic); Vitamin, Polysacharides (Polygalacturonic Acid); Sugar and Sugar Acids Phenolic Acids, Aliphatic Acids (Oxalic, Malic, Citric, Tartaric); Growth Inhibitors, Feromones, and Repelling Substances
2	Microorganisms	Oxalic, Citric, Formic, 2-Keto Glukonic, Laktic, Malic, Tartaric Acids, and Lichen Acids
3	Various Conditions	Oxalic and Citric Acids
4	Aerobic	Phenolic Acids
5	Anaerobic	Acetic, Butiric, Formic, Fumaric, Succinic, and Laktic Acids
6	Below plant residues and canopy	Alliphatic Acids (Oxalic, Citric, Malic); and Phenolic Acids (Galic, Vanilic, Hydroxybenzoic)

$^{1)}$ After Robert and Berthelin (1986)

Important Questions

1. Explain the meaning of “Soil system is a Great Metal Adsorber”! Why it is not applied to Water System and Air System?
2. Explain the two most important soil properties related to the soil capability to immobilize heavy metal cations!
3. Explain the different types of soil solids possessing immobilization properties towards heavy metals!
4. Explain the influence of soil pH on the soil negative charges!
5. Explain the roles of adsorption and precipitation reactions in controlling the immobilization of heavy metals in the soil environment!
6. Explain the origin of the soil negative charges as affected by soil pH!
7. Explain the modification of cation exchange capacity by high CEC materials like organic matters and 2:1 silicate clay minerals!
8. Explain the CEC of different soil solids in the soil environment! How the relation of CEC with organic matters and soil pH? How is the role of the organic matter functional groups?
9. Explain the origin of CEC of 2:1 silicate clay minerals! Explain the isomorphic substitution in 2:1 silicate clay minerals!
10. Explain the role of P-fertitilizers in affecting the soil CEC!
11. How does the soil organic matter content relate to the soil organic C content?
12. What is the relationship between soil organic matter, humus, decomposition, and enzymes? What is the difference between organic matters and humus?
13. Explain the factors affecting the soil organic C and organic matter content!
14. What is the difference between humic substances: Humin, Humic Acid, and Fulvic Acids?
15. Explain the effect of soil pH on the immobilization of heavy metals as related to the adsorption and precipitation!
16. Explain the effect of redox conditions on the presence of heavy metals!
17. Explain the effect of competing cation on the immobilization of heavy metals!
18. Explain the soil pores, pore channels, classification, content, and function, as well as their dynamics related to their water contents!
19. Explain the role of mesoorganisms in developing soil macropores!
20. What is the role of soil biopores? Explain roles and drawbacks of soil macropores!

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21. Explain the soil particle density, soil bulk density, soil porosity, and their relationship! How to calculate each of these soil properties! Compare the values of the soil particle density and the soil bulk density.
22. Explain the effect of soil compaction and tillage on soil pores and porosity! Why?
23. Explain the effect of different soil tillage techniques (Conventional and conservation tillages) on soil pores and porosity!
24. Explain the relationship between soil pores, porosity, and water contents! How does the water contents relate to the soil textures and soil structures? Explain!
25. Explain the roles of soil pores, porosity, and pore channels in water and metal element transport!
26. Explain the relationship between raining, infiltration, percolation, leaching, runoff, and erosion! How do these processes relate to the heavy metal contamination and pollution of ground-water, rivers, and seas?
27. Explain several important factors that control the water infiltration and percolation!
28. What forces control the attachment of water in soil pores? What is gravitation water?
29. Explain the relationships between soil water contents at soil field capacity and soil permanent wilting point!
30. What is the soil available water? How the soil texture and structure affect the amounts of available water?
31. Explain the role of soil temperature in affecting the chemical reactions and heavy metal movement in soils!
32. Explain the cause and pattern of daily and yearly fluctuation of soil temperature! What does the role of water in relation to the fluctuation?
33. Explain the sun and soil factors affecting the absorption of sunheat by soils! Explain the effect of soil water in controlling the raise and decrease of soil temperature!
34. Explain the factors affecting the soil colors! How do Fe redox reaction and organic matter contents affect the soil colors?
35. How is the soil color determined?
36. Explain the microorganisms useful and not useful in the soil environment!
37. How do the soil microorganisms affect the soil colloids and C cycle!

38. Explain the roles of earthworms in developing pore and porosity as well as soil fertility! Explain also the role of earthworms in producing soil enzymes and decomposing organic materials.
39. Explain the role of ants, mice, and marmots in the soil environment!
40. Explain the role of plant roots in affecting the soil reaction and the related chemical reactions that may affect several other chemical reactions in the soil environment!

Chapter 3

Behaviors of Heavy Metals in Soils

Heavy metals in the soil environment are present in various forms and are in dynamic equilibria. Changes in one form may affect the status and magnitude of any other forms. The most important of these forms is their free ionic forms due to its direct interactions with other forms and its interactions with the living things such as plant absorption. High concentrations of free ionic forms of heavy metals may also indicate their potential effects on environmental pollution.

Lowering the effects of heavy metals may be performed by lowering the presence of the free ionic forms by shifting them to form less "toxic" forms such as complexes and/or chelates or insoluble forms such as adsorbed forms or precipitates. Therefore, the process of complexation-decomplexation, chelation/dechelation, adsorption-desorption, and precipitation-dissolution play important roles in the soil environment. The dynamic equilibria of heavy metals present in soil-water system involving free ionic form, complexes, chelates, adsorbed forms, and precipitates in relation to these chemical mechanisms must be well-understood.

3.1 The dynamics of heavy metals in soil system

The existing equilibria between various forms of heavy metals in the soil environment are shown in **Fig. 3.1**. Free ionic form of heavy metals in the soil-water system is the central of heavy metal dynamics. As previously mentioned, this phenomenon is due to several reasons: (a) the availabilities of heavy metal elements to plant root absorption and heavy metal toxicities are related to this form (Allen et al., 1980; Checkai et al., 1987a; 1987b; Hernandez-Soriano et al., 2012), (b) the rates of heavy metal movement and leaching in the soil system are related to this form, (c) all chemical mechanisms controlling the solubilities of heavy metals (compelexation-decomplexation, chelation-dechelation, precipitation-dissolution, and adsoption-desorption processes) in the soil water system are also related to this form (Bowman and O'Connors, 1982; Sanders, 1982; Salam and Helmke, 1998; Hernandez-Soriano et al., 2012).

As shown by **Fig. 3.1**, free ionic form of heavy metals is in a direct relationship with their absorption by plant roots. The free ionic form is also in chemical equilibria with the processes of chelation-dechelation, complexation-decomplexation and precipitation-dissolution, as well as adsorption-desorption processes. In addition, the status of free ionic forms of heavy metals is also greatly affected by the emission of heavy metals from industrial wastes, fertilizers, and pesticides. A great deal of reports shows that these materials contribute a great amount of heavy metals in the soil environment (Lagerwerff, 1982; Kardoz et al., 1986; Leung, 1988; Hegstrom and West, 1989; Alloway, 1990c; Davies, 1990; Kiekens, 1990; Rivai, 1990; Dowdy et al., 1991; Boon and Soltanpour, 1992; Jing and

Logan, 1992; Wang et al., 1992; Herrero and Martin, 1993; Sweet et al., 1993; Cabrera et al., 1994; Nicholson et al., 1994; Tsoumbaris and Tsoukali-Papadopoulou, 1994; Schuhmacher et al., 1994; Bilski and Alva, 1995; Flegal and Smith, 1995; Vile et al., 1995; Gimeno-Garcia et al., 1996; Salam et al., 1996; Yeh et al., 1996; Salam et al., 1997a; Juracek and Ziegler, 2006; Biasioli et al., 2007; Benke et al., 2008; Berenguer et al., 2008; Lin et al., 2008; Hobara et al., 2009; Benn et al., 2010; Cakmak et al., 2010; Kien et al., 2010; Wang et al., 2010; and Tu et al., 2012). Similarly, the status of free ionic of heavy metals in soil water is also affected by absorption by plant roots and/or leaching by percolating water, which may cause the decrease in heavy metal free ionic form concentration in the soil water.

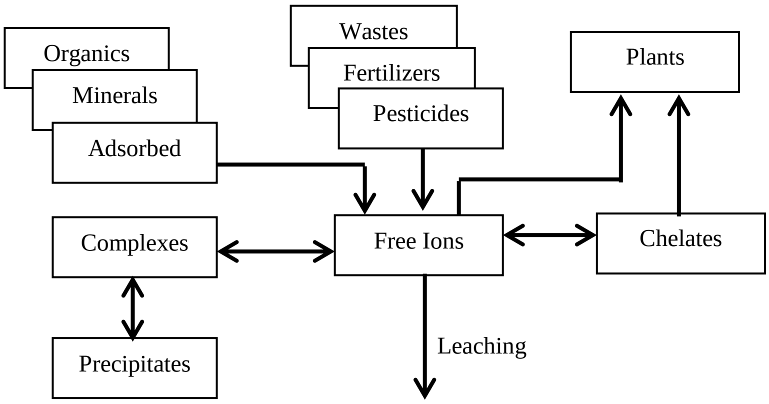


Fig. 3.1. The relationships between forms of heavy metals in the soil environment (Adapted from Salam, 1997a).

The dynamic equlilbria in **Fig. 3.1** means that whenever the concentration of free ionic heavy metals in soil water is lowered by some mechanisms such as plant root absorption or leaching, the heavy metals in complexes, chelates, adsorbed sites, or precipitates will be released to compensate the respective equilibrium constants through equilibrium processes. On the other hand, if the concentration of free ionic heavy metals in soil water is high enough due to external addition such as waste and fertilizer applications, parts of the free ionic heavy metals will be complexed, chelated, adsorbed, or precipitated, depending on the pertaining conditions to reach new equilibrium values. Through these processes, the heavy metals in compexes, chelates, adsorbed sites, and/or precipitates will buffer the concentrations of free ionic heavy metals based on the equilibration principles (Lindsay, 1979). This suggests that the related equilibrium constants are of great importance.

The importance of each chemical processes in controlling the concentrations of heavy metals in soil water is debatable, but are in general depending on the heavy metal cation concentration and soil pH. Cavallaro and McBride (1980) reports that the free ionic Cu^{2+} concentration in the soil system was greatly pH-dependent, but the concentration was below the levels needed for the precipitation processes to occur. Abd-elfattah and Wada (1981) also suggest that Zn^{2+}, Pb^{2+}, Cu^{2+}, Co^{2+}, and Cd^{2+} at concentrations 10^{-7} to 10^{-2} M in 10^{-3} to 10^{-2} M $CaCl_2$ are not precipitated as hydroxides but are adsorbed by cation-exchange sites. Salam and Helmke (1998) also report that the logarithmic of Cu^{2+} concentration is linearly related to the soil pH and is controlled by adsorption-desorption process (**Fig. 3.2**). However, in general soil workers agree that all mechanisms greatly depend on soil pH (Ma and Lindsay, 1990; Workman and Lindsay, 1990; Salam and Helmke, 1998; and Hernandez-Soriano et al., 2012).

It can be concluded that complexation, chelation, precipitation, or adsorption processes increase with the increase in soil pH. The soil adsorption capacities increase with the increase in soil pH due to H^+ ionization from various soil functional groups, both organic and inorganic and, thereby, the holding capacity of soil solids towards heavy metal cations also increases. By this process, the concentrations of heavy metals in soil water decrease with the increase in soil pH (Workman and Lindsay, 1990; El-Falaky et al., 1991; Salam and Helmke, 1998). Some other soil workers also believe that the heavy metal precipitation is important at high soil pH. The precipitation of heavy metals may increase at high pH with high concentrations of heavy metals, particularly if the concentrations of the precipitating agents like carbonate and sulphate ions in soil water are high (Singh and Sekhon, 1977; Brummer et al., 1983).

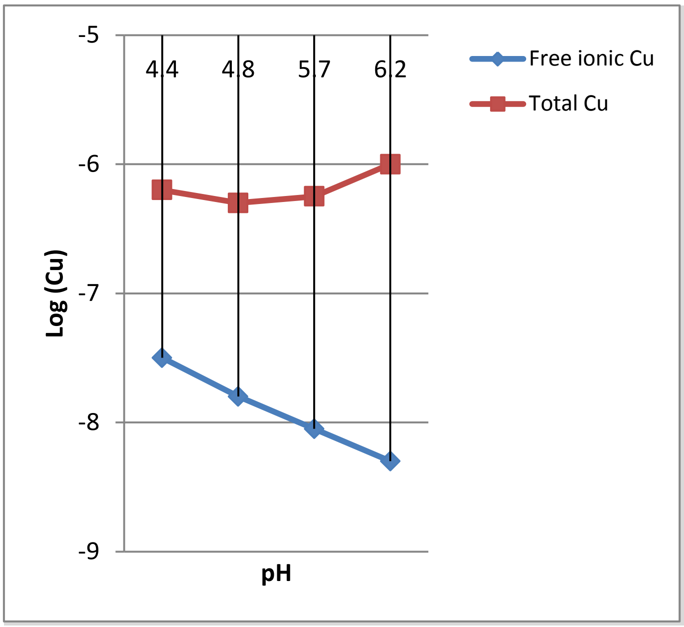


Fig 3.2. Relationship between logaritmic (Cu^{2+}) and total dissolved Cu (Cu_T) with soil pH (Adapted from Salam and Helmke, 1998).

3.2 Heavy metal adsorption – desorption

The adsorption-desorption process is suggested to be the major reaction controlling the concentration of free ionic form of heavy metals in soil solution at low pH (Cavallaro and McBride, 1980; Abd-el Fatah and Wada, 1981; Salam and Helmke, 1998), particularly at low concentrations of heavy metals. This reaction involves the presence of the soil exchange sites showing negative charges emerging from various sources, among which from the edges of soil 1:1 silicate clay minerals such as kaolinite, from isomorphic substitution among tetrahedral or octahedral structural cations of soil 2:1 silicate clay minerals, the edges of oxide/hydroxide non-silicate clay minerals, and the functional groups organic humic substances such as hydroxyls, carboxylics, and phenolycs. Some silicate clay minerals, non-silicate clay minerals are listed in **Table 3.1** and **Table 3.2**, respectively.

The adsorption-desorption processes in soil-water environment may occur through **Eq. 3.1**.

$$\text{X-M}_1 + \text{M}_2^{2+} \leftrightarrow \text{X-M}_2 + \text{M}_1^{2+} \quad .... \quad \textbf{Eq. 3.1}$$

where X is the soil exchange sites, M is heavy metal, and X-M is adsorbed heavy metal. This adsorption-desorption reaction is controlled by an equilibrium constant K shown in **Eq. 3.2**.

$$K = \frac{[M_1^{2+}]}{[M_2^{2+}]} \quad .... \quad \textbf{Eq. 3.2}$$

Under the initial condition, M_1 is adsorbed on the soil exchange sites and M_2 is dissolved in soil water as M^{2+} and under the final condition, after the cation exchange, M_1 is desorbed and dissolved to be M_1^{2+} in soil water and M^{2+} is adsorbed on the soil exchange sites displacing M_1^{2+} as the adsorbed M_2 or X-M_2. The exchange reaction may progress until the equilibrium suffices the values of the controlling K.

Tabel 3.1. Several silicate clay minerals in soil environment[1).]

	Mineralsh	Types	Chemical Formulas
1	Kaolinite	1:1	$Al_4Si_4O_{10}(OH)_8$
2	Haloisit	1:1	$Al_4Si_4O_{10}(OH)_8 \cdot 4H_2O$
3	Smectite:		
	Montmorilonite	2:1	$(Al_3Mg)Si_8O_{20}(OH)_4$
	Nontronite	2:1	$Fe_4(Si_7Al)O_{20}(OH)_4$
	Saponite	2:1	$Mg_6(Si_7Al)O_{20}(OH)_4$
4	Vermikulit	2:1	$Mg(Al,Fe,Mg_4)(Al_2Si_6)O_{20}(OH)_4 \cdot nH_2O$
5	Illit	2:1	$Al_4Si_7AlO_{20}(OH)_4K_{0.8}$
6	Chlorit	2:2	$Mg_6(OH)_{12} \cdot (Al,Mg_5)(Al_2Si_6)O_{20}(OH)_4$

1) Adapted from Singer and Munns (1987)

Table 3.2 Several non-silicate clay minerals in soil environment[1].

No.	Minerals	Chemical Formulas
1	Hematite	Fe_2O_3
2	Limonite	Fe_2O_3
3	Magnetite	Fe_3O_4
4	Fero Hydroxide	$Fe(OH)_2$
5	Feri Hidroxide	$Fe(OH)_3$
6	Goethite	FeOOH
7	Korundum	Al_2O_3
8	Gibbsite	$Al(OH)_3$
9	Buhmite	AlOOH
10	Anatase	TiO_2

[1] Adapted from Krauskopf (1982); Lindsay (1979); Bohn et al. (1985); Deer et al. (1992)

The adsorption-desorption reaction is controlled by various factors and is represented by the Coloumbic Law in **Eq. 3.3**.

$$F = \mathrm{k}\,\frac{q_1 q_2}{r^2} \quad \ldots\ldots \quad \textbf{Eq. 3.3.}$$

where F the force of adsorption of heavy metal on the soil exchange site, k is a constant, q_1 is the amount of soil negative charges represented by soil CEC, q_2 is the quantity of cationic charges adsorbed on the soil exchange sites, and r is the distance between the negative charges of soil mineral surfaces and the metal ion.

Eq. 3.3 clearly shows that the adsorption force is positively related to the amounts of soil surface charges and the charges of metal cation and is negatively affected by the distance between the soil mineral surfaces and the metal ions. The adsorption of a metal cation is stronger in a condition where the amounts of soil surface charges and the charges of cations are high and the distance of cation towards the soil exchange sites is low. Due to the ability to adsorb cations, the amount of soil negative charges of soils is called soil adsorptive capacity (SAC). The higher the SAC may indicate the higher ability of soil to adsorb cations. Because the adsorbed cations on the soil exchange sites are exchangeable, the soil SAC is generally termed as soil cation exchange capacity (CEC).

The CEC of some soil minerals and organic matters are listed previously in **Table 2.1**. It is clear that in general, organic matter shows higher CEC than do mineral matters. The 2:1 silicate clay minerals such as Illit, Smectite, and Vermiculite possess higher CEC than do 1:1 silicate clay minerals such as kaolinite, while oxides of Fe and Al shows the lowest CECs. The difference in soil CEC may suggest the difference in the ability of respective matters in adsorbing heavy metals cations.

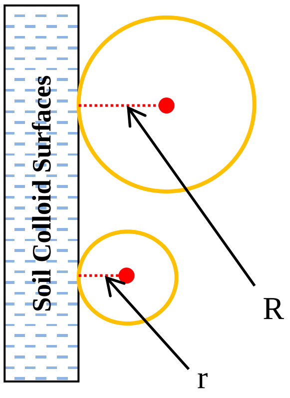
As shown previously, the soil CEC is pH-dependent due to the negative charges originated other than 2:1 silicate clay minerals i.e. organic matters, 1:1 silicate clay minerals, and oxides/hydroxides. The H of the functional edges of these sources may be dehydogenized at high pH increasing the soil CEC and hydrogenized at low pH decreasing the soil CEC. This behavior may cause the adsorption of heavy metal cation decreased with the decrease in soil pH, unadsorbed at PZC, and repelled at pH lower than PZC because the charges of the soil surface change to positive. The behaviors of heavy metal cations towards the changes in soil pH are shown in **Table 3.3**.

Table 3.3. The adsorption of heavy metal cation in differing soil pH.

Soil Reaction	Soil Surface Charges	Existence of Heavy Metal Cation Adsorption
Above PZC	• Negative Net, • Increase with the increase in soil pH	• Exists • Increases with the increase in soil pH
At PZC	• Zero Net	• Does not Exist
Below PZC	• Positive Net • Increase with the decrease in soil pH	• Does not exist

Heavy metal cations are in general of divalent type. Therefore, the adsoption selectivity is independent of heavy metal cation charges. In addition to the soil CEC, the heavy metal cation adsorption is dependent on the distance of heavy metal cation towards the soil negative surfaces. Because the positive charges of heavy metal cations are centralized in the heavy metal atoms, this indicates that the selectivity is then dependent on the heavy metal atomic radius. The smaller the radius, the stronger the adsorption force of any cation towards the soil surface negative charges as shown by **Fig. 3.3**.

This suggests that the adsorption forces of any soil adsorptive surfaces towards heavy metal divalent cations may follow the following sequence: Ca^{2+} > Pb^{2+} > Cu^{2+} > Mg^{2+} > Cd^{2+} > Zn^{2+} (for Na-Montmorillonite), Pb^{2+} > Ca^{2+} > Cu^{2+} > Mg^{2+} > Zn^{2+} > Cd^{2+} (Na- Kaolinite) or Cu^{2+} > Pb^{2+} > Zn^{2+} > Co^{2+} > Cd^{2+} (Goethite) (Alloway, 1990b). This sequence is logically in accordance with the increase in atomic radii However, in fact heavy metal hydration may increase the ionic radius. Therefore, the hydrated heavy metal cations may be more weakly adsorbed that those the unhydrated heavy metal cations. Part of the adsorbed heavy metal is exchangeable and another is so strongly adsorbed that it is not exchangeable. Mesquita and Viera e Silva (1996) report that, in a calcareous soils they used, more Cu and Zn was strongly adsorbed and only small amount of these elements were in the exchangeable form.



$$F = k\,\frac{q_1 q_2}{r^2}$$

$$F_r > F_R$$

Fig. 3.3. Control of ionic radii on the force of adsorption of heavy metal cations.

3.3 Heavy metal Precipitation – Dissolution

Heavy metal in soils may also be controlled by precipitation-dissolution processes related to the concentration of the heavy metal cations and the pertaining precipitating agents. Precipitation may occur at high concentrations of either or both the heavy metal cations and/or the precipitating agents controlled by the respective solubility constant shown in **Eq. 3.4** and **3.5**.

$$\mathbf{MP \leftrightarrow M^{2+} + P^{2-}} \quad \text{.......} \quad \textbf{Eq. 3.4}$$

$$\mathbf{K_{sp} = [M^{2+}][P^{2-}]} \quad \text{.......} \quad \textbf{Eq. 3.5}$$

where M is heavy metal, P is the related precipitating agent, and K_{sp} is the related solubility constant. The precipitation may occur if and only if the product of $[M^{2+}]$ and $[A^{2-}]$ is higher than K_{sp}. Otherwise heavy metal cations are dissolved in soil water.

Therefore, there is a possibility that the increase in soil pH may increase the heavy metal precipitation due to the increase in hydroxyl ion concentration, particularly at high concentration of heavy metal cation (Lindsay, 1979; Brummer et al., 1983; Ma and Lindsay, 1990; 1995; Workman and Lindsay, 1990; El-Falaky et al., 1991; Stahl and James, 1991; and Salam, 2000). This means that the precipitation process may also occur when the concentrations of heavy metals increase as long as the hydroxyl ion concentration or pH is high enough to suffice the value of the related K_{sp}. Udo et al. (1970) report that the Zn precipitation forming hydroxides does not occur at natural concentration of Zn^{2+}. If Zn^{2+} concentration increases above the maximum adsorption capacity, the product of the concentration of $(Zn^{2+})(OH^{-})^2$ is well correlated with the solubility product of $Zn(OH)_2$, which indicates that Zn precipitation occurs.

The precipitation of heavy metal cations may follow the **Eq. 3.4** as shown in **Eq. 3.6** with the solubility constant described in **Eq. 3.7**.

$$\mathbf{M(OH)_2 \leftrightarrow M^{2+} + 2\,OH^{-}} \quad \text{.........} \quad \textbf{Eq. 3.6}$$

$$\mathbf{K_{sp} = [M^{2+}][OH^{-}]^2} \quad \text{.......} \quad \textbf{Eq. 3.7}$$

Processing the mathematics of K_{sp}, the the dependence of divalent heavy metal cations may follow **Eq. 3.8**, which shows that the logarithmic heavy metal cation concentrations decreases with soil pH with a gradient of 2.

$\text{Log } K_{sp} = \log [M^{2+}] + \log [OH\text{-}]^2$

Given that $K_w = [H^+][OH^-] = 10^{-14} \rightarrow [OH^-] = \frac{10^{-14}}{[H^+]}$, then

$\text{Log } K_{sp} = \log [M^{2+}] + \log (\frac{10^{-14}}{[H^+]})^2$

$\text{Log } K_{sp} = \log [M^{2+}] + 2 \log (10^{-14}) - 2 \log [H^+]$

$\text{Log } [M^{2+}] = \log K_{sp} - 2 \log (10^{-14}) - (-2 \log [H^+])$

$\text{Log } [M^{2+}] = X - 2 \text{ pH}$ ……. Eq. 3.8

where $X = \log K_{sp} - 2 \log (10^{-14})$, a particular value specific for heavy metal cations.

The relationship between the solubilities of several heavy metals and soil pH are listed in **Table 3.4**. These equations indicate that the solubilities of heavy metal cations in soil water decreases with increasing soil pH.

Table 3.4. The experimental relationships between Cd, Cu, and Zn solubilities with soil pH[1].

No	Heavy Metal	Equation
1	Cd	$\log (Cd^{2+}) = 6.50 - 2 \text{ pH}$
2	Cu	$\log (Cu^{2+}) = 2.80 - 2 \text{ pH}$
3	Zn	$\log (Zn^{2+}) = 5.80 - 2 \text{ pH}$

[1] Taken from Lindsay (1979), Workman and Lindsay (1990), Ma and Lindsay (1990), El-Falaky et al. (1991)

The solubilities of Cd^{2+}, Cu^{2+}, and Zn^{2+} are shown to behave similarly. Their logarithmic values are dependent on soil pH with a gradient of minus 2 but are different in the intercept values following the sequence of $Cd^{2+} > Zn^{2+} > Cu^{2+}$. This sequence indicates the difference in their concentrations in soil solution.

There are several precipitating agents that may react with heavy metal cations in the soil environment. Among the most frequently reported are hydroxyls, phosphates and carbonates. Santillan-Medrano and Jurinak (1975) show that in non-calcareous soils, the solubility of Pb is regulated by $Pb(OH)_2$, $Pb_3(PO_4)_2$, $Pb_4O(PO_4)_2$, or $Pb_5(PO_4)_3OH$ depending on soil pH. In calcareous soils, the solubility of Pb is controlled by $PbCO_3$. At high Cd concentration, the precipitation of $Cd_3(PO_4)_2$ and/or $CdCO_3$ regulated cadmium solubility.

3.4 Heavy metal oxidation - reduction

In some regions, particularly those with rainy season, soil water is found too much and may disturb plant roots and growth due to the lack of O_2 as a result of limited O_2 diffusion from atmosphere. In some region, the disturbance may be more severe because no oxygen diffuses into the soil system caused by a condition where the soil pore is saturated with water or flooded. This condition requires drainage of water so that some of the soil pores are freed from water and filled with oxygen.

One of the methods that can be accomplished to drain the saturated water is by using a number of drainage pipes constructed 0.3 meter apart under the plant root system about 0.6 – 1.8 meter from the soil surface tilted to the direction of rivers or reservoir where the water will be drained (Singer and Munns, 1987). Water in macropores may drain into the pipes through holes along the pipes and move in the pipes to the rivers or reservoirs. This way may drain the water and lower the water content around the plant root system to the values more suitable for plant growth and development.

Flooded water may raise problem (Moore and Patrick, 1989a; 1989b). Flooding may change the chemical reaction in the soil system, particularly related to the oxidation –reduction or redox reaction (Garrels dan Christ, 1965; Lindsay, 1979). Unlike the unflooded soils with abundant of O_2 and is therefore oxidative, the flooded soils are lack of O_2, which may cause the soil condition to be reductive. The changes in soil condition from oxidative to reductive may cause some elements to be reduced and cause some chemical consequences. For example, the reductive condition may cause the soluble Fe^{3+} and SO_4^{2-} to be reduced forming Fe^{2+} and S^{2-}, respectively. These reduced elements may form complex of FeS^0, which finally precipitates to form insoluble FeS.

A very good example where the oxidation-reduction reaction occurs intensively is in paddy soils, which are periodically being flooded and drained. When being drained, paddy soils are oxidative. The concentrations of Fe^{2+} and Mn^{2+} decrease, organic substances containing N, S, and C are oxidized. As one of the result, the solubility of P decreases because part of it reacts with Fe^{3+} and Mn^{4+} forming Fe-P and Mn-P precipitates. Conversely, when being flooded, paddy soils changes to be reductive, their redox potentials decrease, Fe^{3+} and Mn^{4+} are reduced, so are the N and S substances previously oxidized. As a consequence, Fe-P and Mn-P dissolved, P is soluble; while S^{2-} may complex Fe^{2+} and may precipitate forming FeS. The effects of flooding and draining the paddy soil water system on the soil chemical reactions are shown in **Table 3.5**.

Oxidation and reduction reactions that occur simultaneously are called Redox Reaction, in which one chemical species may act as electron donor and encounter oxidation reaction and another species may act as the electron acceptor and encounter reduction reaction. A summary of sample oxidation of Fe, in which Fe^{2+} is oxidized to be Fe^{3+} and O_2 as the electron acceptor, which is reduced from O_2 to be O^{2-}, is shown in **Table 3.6**.

Table 3.5. Effects of flooding and draining paddy soils on soil chemistry[1).]

Condition	Chemical Changes	Effects
Drying	• Redox Potential (E) increases • Oxidative • [Fe^{2+}] decreases • [Mn^{2+}] decreases	• Al-P precipitates • Fe-P precipitates • Mn-P precipitates • Fe, Mn, P insoluble
Flooding	• Redox Potential (E) Increases • Reductive • [Fe^{2+}] Increases • [Mn^{2+}] Increases • $SO_4^{2-} \rightarrow S$	• Al-P dissolves • Fe-P dissolves • Mn-P dissolves • P more soluble • FeS precipitates

1)Adapted from Bohn et al. (1985)

Redox reactions may occur on heavy metals which may change their oxidation number if the soil environment redox potential changes due to the changes in the availability of O_2. This may include for example Fe and Mn. The Fe species may change from Fe^{2+} at low redox potential to be Fe^{3+} at high redox potential. Likewise, Mn^{2+} which is stable at low redox potential may change into Mn^{4+} which is stable at high redox potential or oxidative condition.

Table 3.6. The redox reaction involving Fe and O_2.

	Fe (Lower E)	**O_2 (Higher E)**
Behavior	Oxidation	Reduction
Role	Reductor	Oxidator
Half-Cell Reaction	$Fe^{2+} + 2\ e \rightarrow Fe$ $E = -0.44\ V$	$O_2 + 4\ H^+ + 4\ e \rightarrow 2\ H_2O$ $E = +1.23\ V$
Redox Reaction	$2\ Fe^{2+} + O_2 + 4\ H^+ \rightarrow 2\ Fe^{2+} + 2\ H_2O$ $E = +1.67V$	

The existence of heavy metal species is actually not only controlled by redox potential (E) but also by pH of the soil environment. This phenomenon is shown by E – pH Diagram in **Fig. 3.4** showing the stability of Fe species under different values of E and pH of soil. This diagram clearly shows that Fe^{2+} and Fe^{3+} exist only at low pH. The difference is that Fe^{2+} exists at low E (reductive) and Fe^{3+} at high E (oxidative) condition. At high pH, both Fe^{2+} and Fe^{3+} may change into $Fe(OH)_3$ or $Fe(OH)_2$], depending on the values of E. Fe may form $Fe(OH)_2$ at low E value.

The redox reaction involving such element as Fe and Mn may be one of the important factors related to the vulnerability of soil minerals towards chemical weathering. Some minerals with this characteristic are the silicate minerals such as

Olivine, Amphibole, and Pyroxene. The changes in Fe of the silicate minerals may proceed through the oxidation reaction in **Eq. 3.9**.

$-Fe^{2+}-O-Si- \;+\; H_2O \;\leftrightarrow\; -Fe^{3+}-OH \;+\; HOSi^- \;+\; e^-$ ……. Eq. 3.9

This reaction may not occur in the absence of O_2 that act as the electron donor. This means that the redox reaction involved in the weathering of these mineral may occur in an oxidative condition or a high redox potential. Even though the presence of H_2O is needed, it clearly suggests that this reaction may not occur in a reductive condition. The solubility of Fe^{3+} in normal pH is low, therefore the release Fe^{3+} may be complexed by OH^- and precipitates as insoluble hydroxide or form oxides, among which goethite (FeOOH) is widespreadly found.

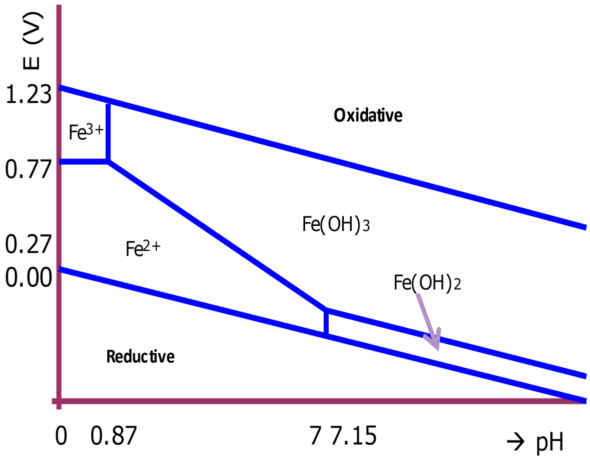


Fig. 3.4. E – pH diagram of Fe stability in soil water environment.

One other example of the chemical reaction involving redox reaction is the weathering of pyrite (FeS_2), which is generally observed in sulfate acidic peat soils.

Pyrite in peat soils is stable under reductive condition as a result of the inhibition of O_2 diffusion from the atmosphere to the pyrite minerals as seen in **Fig. 3.5**. Consequently, if peat soils are drained (water table is lowered by drainage), pyrite may become unflooded. Peat soils previously in a reductive environment with low redox potential may enter an oxidative condition with high redox potential because no inhibition for O_2 to diffuse into the peat soil system. This change may cause a redox reaction involving pyrite to occur as shown in **Eq. 3.10** (Nordstrom, 1982; Thomas and Hargrove, 1984) and as described in **Fig. 3.5**.

$$\mathbf{FeS_2 + \frac{15}{4}O_2 + \frac{7}{2}H_2O \leftrightarrow Fe(OH)_3 + 4\,H^+ + 2\,SO_4^{2-}} \quad \ldots\ldots\ \textbf{Eq. 3.10}$$

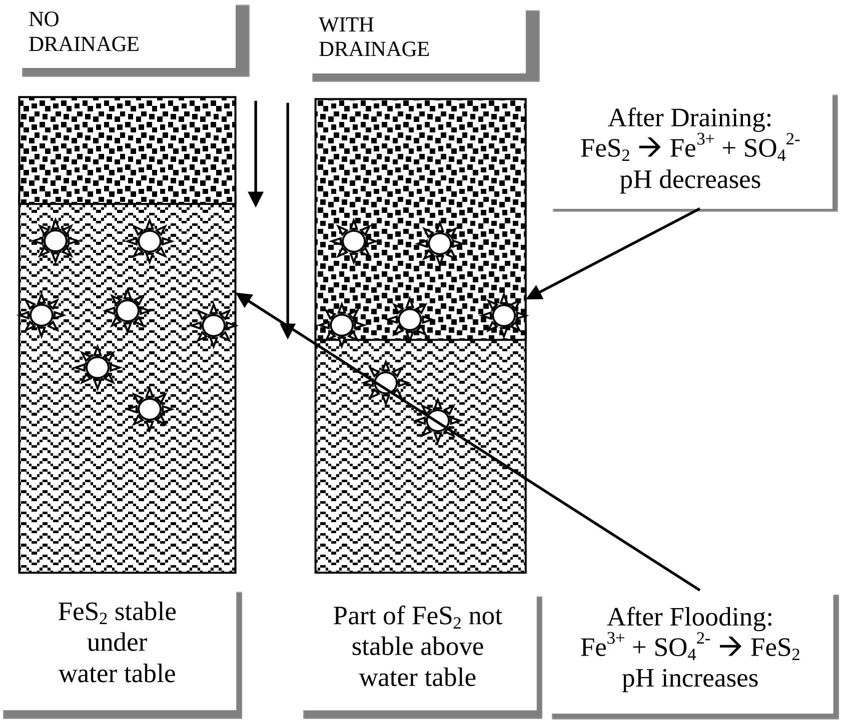


Fig. 3.5. Redox reaction involving pyrite in peat soils (After Salam, 2012).

Iron species previously in the pyrite mineral with an oxidation number of +2 is oxidized to form Fe with an oxidation number of +3 in the form of Fe^{3+}. In the presence of O_2, FeS_2 is destructured forming Fe^{3+} and SO_4^{2-} ions, which eventually significantly lower the peat soil pH.

The development of acid sulfate soils (cat clay) principally progresses through two steps. The first step is a reduction, which produce high pH and pyrite after the reduction of Fe and sulfate. The second step is an oxidation that dissolves pyrite and acidifies peat soils. Some required conditions for the first step are sources of Fe^{3+} and SO_4^{2-}, reductive condition with E <- 300 mV, the presence of reducing bacteria such as *Desulfovibrio spp*, energy source for microorganisms, and the mechanism to move HCO_3^- formed during the process. The reduction of Fe^{3+} (**Eq. 3.11**) dissolving this element may ease its reaction with sulfides (S^{2-}) produced by the reduction of SO_4^{2-} to form pyrite.

$$\mathbf{24\ FeOOH + C_6H_{12}O_6 + 6\ H_2O \leftrightarrow 24\ Fe^{2+} + 6\ CO_2 + 48\ OH^- \ \ldots\ldots\ Eq.\ 3.11}$$

In this reaction, different from that in silicate mineral weathering (**Eq. 3.9**), Fe acts as an electron acceptor (oxidator), that eventually become Fe^{2+}; while $C_6H_{12}O_6$ acts as the electron donor, of which its structural C changes its oxidation number from 0 in $C_6H_{12}O_6$ to +4 in CO_2.

A redox reaction of another element in the soil environment is exemplified by Cu in the weathering of Chalcopyrite ($CuFeS_2$) that releases Cu^{2+} into the soil solution. Copper is a micronutrient for plants. The redox reaction may progress as shown in **Eq. 3.12**.

$$\mathbf{4\ CuFeS_2 + 17\ O_2 + 10\ H_2O \leftrightarrow 4\ Cu^{2+} + 4\ Fe(OH)_3 + 8\ SO_4^{2-} + 8\ H^+ \ \ldots\ldots\ Eq.\ 3.12}$$

The redox reaction in **Eq. 3.12** clearly shows that Cu^+ in Chalcopyrite is oxidized to be Cu^{2+}, while S is reduced from S^{2-} in Chalcopyrite to be S-6 in SO_4^{2-}. In general, whatever the form in the primary minerals, Cu is generally released as Cu^{2+} through chemical weathering. As long as the soil environment is oxidative and not alkaline, Cu^{2+} may not precipitate. The lower the soil pH usually causes the higher concentration of Cu^{2+} ion (Salam and Helmke, 1998). This property is shown by most of the divalent heavy metal cations.

3.5 Heavy metal movement and accumulation

Heavy metal cations dissolved in soil solution may encounter also movement in soil body by mass flow and/or diffusion processes. Heavy metal cations are attracted by the dipole water molecules as shown in **Fig. 3.6**. This fact may drive heavy metal cations to move along the soil-pore channels by mass flow together with the mass movement of percolating water or with capillary movement of water. The amounts of heavy metals moved by water may be directly related to the amount of water moving and the concentration of heavy metal cation in the soil water (**Eq. 3.13**). When soil is unsaturated, heavy metal cation may move from the wet area to the dry area following the movement of water. When the soil is saturated, for example during or after raining, heavy metal cations may move downwards with the percolating water through the interconnected soil pores or soil-pore channels.

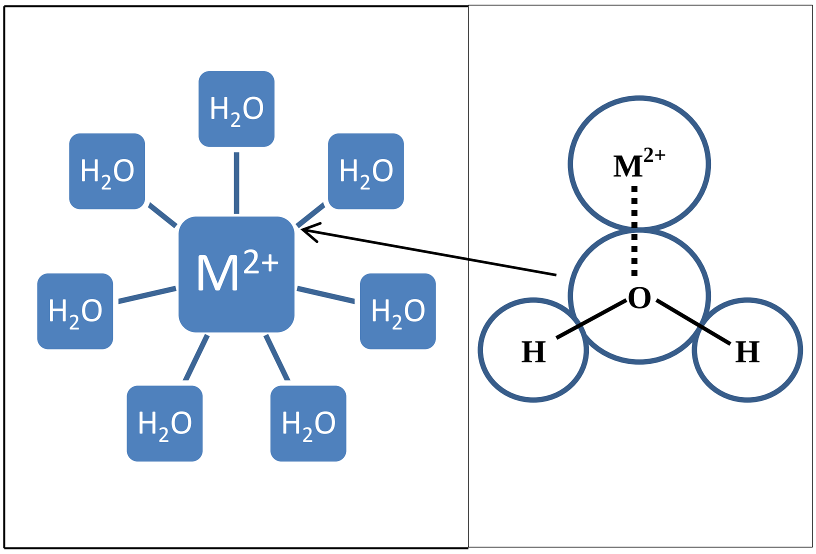


Fig. 3.6. The attraction of heavy metal cation by mass of dipole water molecules.

$$Q = VC \quad \text{.......} \quad \textbf{Eq. 3.13}$$

where Q is the amount of heavy metal transported, V is the volume of water transported, and C is the concentration of heavy metal in water. **Eq. 3.13** shows that the amount of heavy metal moving in soil is greater when the volume and concentration of heavy metal are greater. This suggests that heavy metal movement in the tropics where the rainfall is high is very significant. Accumulation of heavy metals deep in the soil body is probable. Because the rate of percolating water is high, entry of heavy metals into ground water is also probable.

The heavy metal cations may also move by diffusion, which is controlled by the gradient of heavy metal concentrations. Heavy metal may of course move from soil areas where the concentrations of heavy metal cation are high to those with low concentrations of the related heavy metal cations. The diffusion of heavy metal cations progress following **Eq. 3.14** (Barber, 1981)

$$\frac{\Delta Q}{\Delta t} = D_e \frac{C_1 - C_2}{L} \quad \text{.......} \quad \textbf{Eq. 3.14}$$

where $\frac{\Delta Q}{\Delta t}$ is the rate of heavy metal cation diffusion, D_e is the diffusion coefficient of heavy metal cations in soil water, C_1 and C_2 the concentrations of heavy metals at Area 1 and Area 2, respectively, and L is the distance between C_1 and C_2. As seen from **Eq. 3.14**, the rate of heavy metal cation diffusion, and thereby the quantity of heavy metal cation moving in the soil body, is controlled by the D_e, by the concentration difference between Area 1 and 2, and also by the distance between these areas. The rate is faster in a condition that the diffusion coefficient is high and the concentration difference of heavy metals with respect to distance is high.

The diffusion coefficients of heavy metals in soil water are related to those in water as shown in **Eq. 3.15** (Barber, 1981). This equation shows that the rates of heavy metal cation diffusion in soil is affected by heavy metal properties, soil volumetric moisture content, tortuosity factor, and buffering capacity of soils. In general, the rates of heavy metal diffusion are higher with the increase in soil moisture content, soil tortuosity, and soil buffering capacity.

$$D_e = D_w \theta f \frac{1}{b} \quad \text{......} \quad \textbf{Eq. 3.15}$$

where D_e is the diffusion coefficient of heavy metal cations in soil water, D_w is the diffusion coefficient of heavy metal cations in water, θ is the soil volumetric water content, f is the soil tortuosity factor, which is the reciprocal value of the length of continuous pore-channels, and b is the soil heavy metal buffering capacity.

Some heavy metals are transported in the soil body by mass flow, some other by diffusion, and some others by both mechanisms. The transport mechanisms of several heavy metal cations in soil are listed in **Table 3.7**.

Table 3.7. Mechanisms of transportation of several heavy metals in soil-water environment.

Transport Mechanisms	Heavy Metals/ Metaloids
Mass Flow	Cu, Zn, Fe, Mn, Mo
Diffusion	Zn, Fe

Movement may distribute the heavy metal cations in the soil body. The site and quantity of heavy metal accumulation depend on the availability of water (soil moisture) and the rates of mass flow and/or diffusion. The sites of accumulation may be close to the soil surface as that in the case when heavy metal movement is driven by capillary movement, particularly when the soil moisture content is low (unsaturated). The accumulation may also deep into the subsoil layers, particularly when the soil is saturated like during raining. When the percolating water is fast, the heavy metal may also enter ground water and cause contamination.

Since heavy metals may interact with the charges of the soil adsorption surfaces as shown in **Fig. 3.7**, which is generally negatively charged, the rates of heavy metal movement is soil-type dependent, particularly related to their CECs. The movement of heavy metal cations may be fast in soils with low CEC. On the other hand, the movement will be significantly retarded by negatively charged soil-pore surfaces in soils with high CEC as shown in **Fig. 3.7**. In a contrast condition, heavy metal cations may move freely in the soil environment with pH lower than PZC. In this condition, the colloid surface is positively charged. Consequently, the soil colloids are not able to attract heavy metal cations; heavy metal cations may then move in the soil without hindrance. In this case, heavy metal accumulation in soil body is unlikely. Fortunately, this phenomenon is rare.

The movement of heavy metal cations in soil body may be desirable or undesirable. In the point of view of agriculture, some heavy metal plant nutrients such as Fe, Mn, Cu, Zn, and Mo are expected to be available in the soil system. Therefore, particular heavy metal such as Cu and Mn are expected to be accumulated in soils. For this situation, the adsorption capacity must be increased by several mechanisms that are able to lower the heavy metal movement and to increase the heavy metal adsorption. By this reasoning, the same mechanisms are needed to lower ground water contamination by heavy metals. This also suggests that the negative charges of soil environment must be increased.

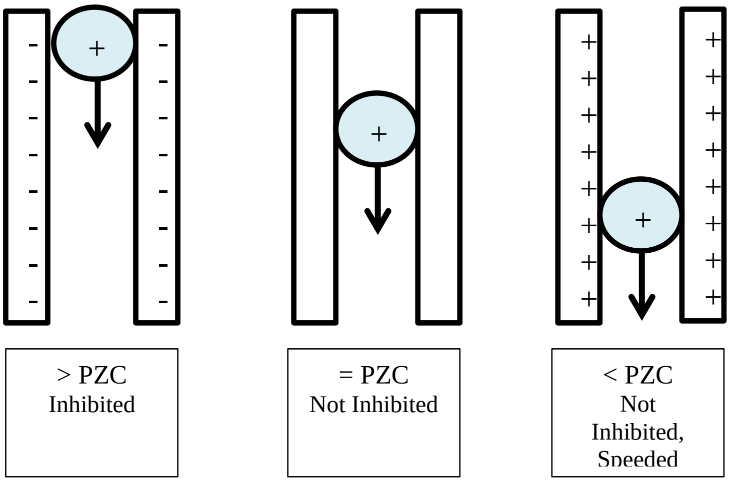


Fig. 3.7. The inhibition of heavy metal cation movement in negatively charged soil -pore channels.

However, in a condition that plants do not need these elements, one may let the heavy metal go with the percolating water through mass flow and enter ground water. This way may enable the concentration of heavy metals in the soil water system are maintained low and give no negative effect on plants and other living things depending on plants grown on the soils.

3.6 Heavy metal leaching and ground-water contamination

Percolating water containing heavy metal cations in the interconnected soil pores or soil-pore channels may significantly move heavy metal cations in the soil body. This mechanism is well-known as heavy-metal leaching. Leaching is percolating-water dependent, while the rate of percolating water is dependent on rainfall. The higher the rainfall and the faster the rate of percolating water the more severe the leaching process and the quantity of heavy metal losses.

The heavy metals leached from the soil system may enter ground water as shown by **Fig. 3.8**. The effect is depending on the amount of heavy metal entering ground water. If the amount is low, heavy metal may cause ground water contamination. If the amount of heavy metals entering grand-water is unexpectedly high, the leaching may cause ground water pollution. Ground-water pollution, and also ground-water contamination, by heavy metals is unwanted. Through ground-water contamination and pollution, heavy metals may spread to a larger area and may endanger the living things due to their carcinogenic consequence. This is because ground-water may supply the water for drinking water and probably for irrigation water. Ground water is also connected to rivers and seas that may also be affected by heavy metal contamination and pollution. Therefore, heavy metal contamination and pollution through leaching must be minimized.

As shown in **Fig. 3.8**, efforts to lower heavy metal contamination and pollution must be conducted in the soil-water system. The effort is by increasing the heavy metal retention in the soil body. As discussed previously and will be discussed in details in the following chapters, increasing the soil retention is related to several chemical mechanisms such as adsorption-desorption, complexation-decomplexation, and precipitation dissolution. By employing these mechanisms, some of dissolved heavy metals are immobilized in the soil body as adsorbed elements and/or precipitates. As long as the soil environment properties support, the reverse reaction, i.e. desorption and dissolution may not occur. This way, the heavy metals may accumulate in the soil body and may not drain into and contaminate and pollute ground-water.

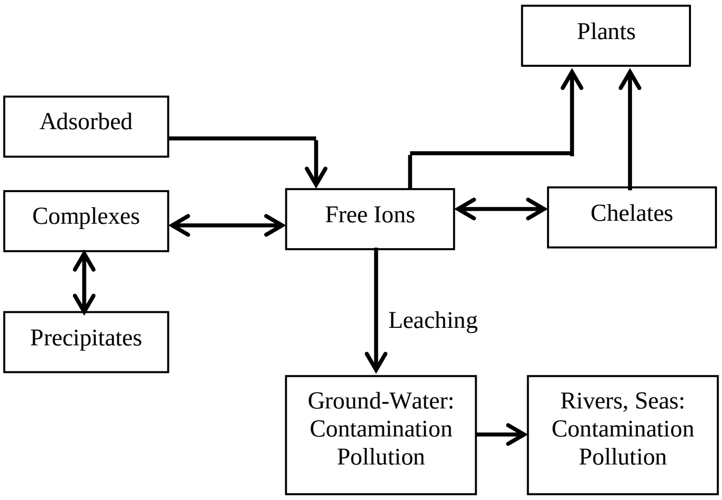


Fig. 3.8. The relationships between forms of heavy metals in the soil environment (Adapted from Salam, 1997a).

3.7 Heavy metal absorption by plants

As previously shown in **Fig. 3.1** and **Fig. 3.8**, heavy metal cations are also absorbed by plant roots. Since the heavy metals cations dissolved in soil solution are interrelated to some controlling mechanisms, the absorption of heavy metal cations from soil solution may disturb the equilibrium system. The decrease in the concentrations of heavy metal cations in soil water due to absorption by plant roots may cause the release of immobilized heavy metal cations in the adsorbed sites, precipitates, and primary minerals through desorption, dissolution, and weathering, respectively.

The adsorbed cations may probably the first to release through desorption process, followed by dissolution and weathering processes. However, each mechanism may supply the related metal cations in the rates influenced by several factors that also affect the immobilization process specific for each mechanism. For example, the desorption may depend on the soil CEC, charges and radii of cations, common cations, soil moisture content, and the related equilibrium constant. The desorption process may proceed more easily when the soil CEC is relatively low, the metal charge is low, the heavy metal radius is long, the common ion concentration is high, the moisture content is high, and the related equilibrium constant is low.

Absorption of heavy metal cations may be considered positive or negative in relation to agriculture and environmental management in the soil environment. From the point of view of plant nutrient management, high dissolved heavy metal cations may supply enough heavy metal micronutrients needed by plants. It is well-known that plants need some heavy metal micronutrients i.e. Cu, Zn, Fe, Mn, and Co. Thereby, the immobilized heavy metals easily released are desirable. Some heavy metal containing wastes may be used to avail the heavy metal elements. Some heavy metal containing wastes may also contain such macronutrients as Ca, Mg, K, and P. Salam et al. (2000) report a fertilizer called Limin LC formulated from a Cu and Zn containing waste, lime, and cassava leaf compost. This fertilizer was promising for providing a control supply of Cu and Zn and enough P, Ca and Mg. Novpriansyah et al. (2001) also report that chemical fertilizers formulated from metal-spoon industrial waste, lime, and peat soil increased the pH, exchangeable K and Ca, and available Cu and Zn, and decreased the availabilities of P, Fe, and Mn of Ultisol from North Sungkai North Lampung Indonesia

From the point of view of heavy metal emission to the living things through soil system, the absorption of heavy metal cations and so the release of immobilized heavy metal cations must be limited or even minimized. The release of immobilized heavy metal cations adsorbed on the surface of soil active sites, in the structure of secondary and primary minerals, may increase heavy metal cations absorbed by plant roots, and thus, may increase heavy metal emission to the living things through food chain. Sometimes, the negative effects are observed physically on plant growth. One example is observed on plant leaf areas in soil of Gedong Meneng Bandar Lampung (Ultisols) as shown in **Table 3.8**. Leaf-areas of Green Kyllinga and corn were unaffected and of amaranth were significantly depressed by Pb containing electronics industrial waste. Amaranth is known for its ability to accumulate heavy metals.

However, some plants are useful for environmental management due to their high accumulation of heavy metals absorbed from heavy metal contaminated or polluted soils. These specific plants may significantly absorb great amounts of heavy metals and lower heavy metal concentrations in soils polluted with heavy metals. Safe management of heavy metals accumulated in these plants may then help the efforts to solve problems with heavy metal pollution in the soil environment.

Table 3.8. The leaf-areas of some vegetations grown in Pb containing waste treated Ultisol at 4 weeks after planting$^{1)}$.

Waste Level	Green Kylinga	Corn	Amaranth
..... ton ha^{-1}	.... cm^{2}		
0	168	464	97.3
10	147	482	107
20	133	465	95.6
40	146	465	88.0

$^{1)}$After Sriyani et al. (1998)

Among the plants reported to behave as metalophytes is *Thlaspi caerulescens*, found as heavy metal hyperaccumulator in Belgium that may grow well in a medium with 25,000 mg Zn kg^{-1} and 1,000 mg Cd kg^{-1}. This plant is very tolerant towards heavy metals and absorbs Zn and Cd at extremely high amounts without the decrease in plant yield and can be employed in metal phytoextraction for Zn and Cd contaminated soils (Brown et al., 1995).

Some varieties of Indica paddy also show the ability to absorb Cd from Cd contaminated paddy fields. Ibaraki et al. (2009) shows that after planting with this paddy variety for 2 years, the concentration of Cd in contaminated paddy soils decreased as much as 18%, after which the soils are safe for non-accumulating paddy variety.

3.8 Heavy metal pollution and deposition

As pointed out in Salam (2012, 2014), heavy metals in the soil environment are emitted from two major sources i.e. the natural or lithogenic sources, such as heavy metal containing minerals, and the anthropogenic sources, such as various fertilizers, pesticides, and industrial wastes that contain heavy metals (Lagerwerff, 1982; Kardoz et al., 1986; Leung, 1988; Hegstrom and West, 1989; Alloway, 1990c; Davies, 1990; Kiekens, 1990; Rivai, 1990; Dowdy et al., 1991; Boon and Soltanpour, 1992; Jing and Logan, 1992; Wang et al., 1992; Herrero and Martin, 1993; Sweet et al., 1993; Cabrera et al., 1994; Nicholson et al., 1994; Schuhmacher et al., 1994; Tsoumbaris and Tsoukali-Papadopoulou, 1994; Bilski and Alva, 1995; Flegal and Smith, 1995; Vile et al., 1995; Gimeno-Garcia et al., 1996; Salam et al., 1996; Yeh et al., 1996; Salam et al., 1997a; Juracek and Ziegler, 2006; Biasioli et al., 2007; Arora et al., 2008; Benke et al., 2008; Berenguer et al., 2008; Lin et al., 2008; Hobara et al., 2009; Benn et al., 2010; Cakmak et al., 2010; Kien et al., 2010; Wang et al., 2010; Tu et al., 2012; and Li et al., 2014). Nriagu (1979) as cited by Tiller (1989) estimated that the anthropogenic emissions of heavy metals were much higher than those of lithogenic emissions (**Table 3.9**). Robinson et al. (2007) report that the concentrations of Zn, Pb, and Cu in soils were most strongly associated with highly developed land density and population density.

Heavy metals may spread to the environment through food chains, soils, rivers, and seas. Gimeno-Garcia et al. (1996) showed that Cd, Cu, and Zn from agricultural superphosphates entered the soil system at the rates of 1,322, 7,500, and 30,000 mg per hectare per year while those from pesticide Antracol were 7.79 mg, 20.00 mg, and 1,100 g per hectare per year for Cd, Pb, and Zn, respectively (**Table 3.10**). He and Singh (1994) show that application of high-Cd NPK fertilizer significantly increased DTPA-extractable Cd. The heavy metals spreading through the soil system are partly immobilized by adsorption and/or precipitation processes. Another part is absorbed by plants and another part may enter the ground water through water percolation, which then may enter the food chains through drinking water, while the rest may enter rivers and seas. Some parts of the emitted heavy metals may also directly enter rivers and seas.

The emission of heavy metals from industries is predicted to increase the relatively high intake of heavy metals in the Jakarta watershed and bay. For example, the prediction in 1983 alone showed that heavy metal intake of the Jakarta Bay was relatively massive as shown in **Table 3.11**. The heavy metals entering rivers may be used as irrigation water or fish ponds, etc., the products of which as agriculture products may enter the food chains. Similarly, the part of heavy metals entering seas may enter plankton and fishes, which then may enter food chains. Therefore, the problem of emissions of heavy metals must be solved. The spread of heavy metals from their sources to the environment is depicted in **Fig. 3.9**.

Table 3.9. The estimates of worldwide natural and anthropogenic emission of some heavy metals[1)].

	Natural	Anthropogenic
Cd	0.83	7.3
Cu	18	56
Ni	26	47
Pb	24	450
Zn	44	310

[1)]Adapted from Nriagu (1979) as cited by Tiller (1989); in x 10^3 Mg $year^{-1}$

Table 3.10. Estimates of some heavy metal additions to soil from agricultural activities[1)].

	Cd	Cu	Pb	Zn
Fertilizers				
Copper Sulphate	7.14	8,925[a]	385	749
Iron Sulphate	6.20	60.00	2,000	2,600
Urea	2.40	120	-	-
Superphosphate	1,332	7,500	-	30,000
Pesticides				
Antracol (Propineb)	7.79	-	20.00	1,100[a]
Saturn-G (Tiobencarb)	34.60	304	234	1.28[a]
Ordram (Molinato)	82.80	-	450	1.95[a]

[1)]Adapted from Gimeno-Garcia et al . (1996); [a]g ha^{-1} $year^{-1}$, others in mg kg^{-1} $year^{-1}$

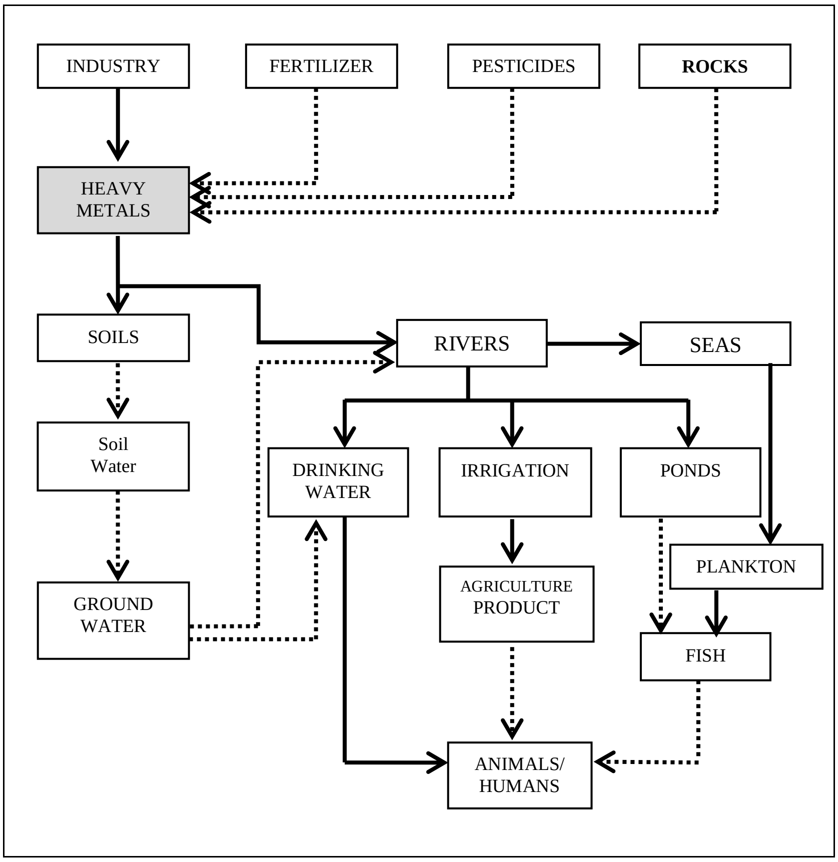


Fig. 3.9. The spread of contaminant heavy metals into the environment (After Salam, 2012).

The high contents of heavy metals in industrial wastes is listed in **Table 3.12**, obtained from several industrial wastes in Jakarta; while those in several fertilizers (McLaughlin et al., 1996; Salam et al., 1996; Salam, 1997a) are listed in **Table 3.13.**. The contents of Cu and Pb are relatively high in several industrial wastes, particularly in metal-spoon industry and jean laundry industry, and also Pb in electronical industry. Relatively high contents of heavy metals are also found in TSP (Fe, Zn, Cu, and Pb), SP-36 (Fe, Zn, Cu and Cd), and natural phosphatic rocks (Cd). McLaughlin et al. (1996) listed the concentrations Cd in some phosphate rocks around the world to be ranging from 0.2 to 340 mg kg^{-1} or from 1 to 641 mg kg^{-1} P.

Table 3.11. The heavy metal intake by Jakarta Bay as predicted by DPMA (1983).

No.	Heavy Metals	Daily Intake (kg day^{-1})
1	Cu	191
2	Cr	325
3	Hg	362
4	Ni	154
5	Pb	757
6	Zn	43,000

Table 3.12. The contents of Cu and Pb in several industrial wastes from Jakarta^1)^.

No.	Waste	Cu	Pb
		.... mg kg^{-1}	
1	Metal Spoon	23.4	2.44
2	Jeans Laudry	25.6	0.44
3	Laundry	0.93	0.88
4	Electronics	4.63	130.84
5	Metal Pipe	4,01	2.72
6	Food	1.11	0.36
7	Printing	0.79	0.88
8	Candy	0.77	2.72
9	Textile A	1.25	0.20
10	Textile B	2.58	3.40
11	Textile C	3.41	2.76
12	Textile D	0.68	1.92

1)After Salam et al. (1996)

Cadmium is a normal contaminant in phosphate fertilizers. Therefore, long-term application of phosphate fertilizers may result in a greater amount of Cd than those found naturally (Herrero and Martin, 1993). Nicholson et al. (1994) also report that the Cd concentrations in herbage are considerably greater in the phosphate treated plots. Arora et al. (2008) also report that the concentrations of Fe, Mn, Zn, and Cu in vegetables were higher in soils irrigated with waste water.

Table 3.13. The DTPA extractable heavy metals from dolomite and phosphate fertilizers[1)].

Metal Elements	Dolomite	TSP	SP-36	Natural Phosphatic Rock
	mg kg^{-1}			
Fe	2.40	383	272	1.40
Mn	1.16	15.1	7.12	0.16
Zn	0.64	152	153	9.75
Cu	0.04	16.6	17.8	0.38
Cd	0.04	3.56	1.72	1.38

[1)] After Salam (1997a)

Soils contaminated with Pb were also found in the lands adjacent to roads or highways with heavy traffics (Minami and Araki, 1975; Tiller, 1989; Akhter and Madany, 1992; Markus and McBratney, 1996). Lately, Kargar et al. (2013) found significantly higher concentrations of Cu, Cd, Zn, and Pb in soils from commercial streets, possibly as a result of heavier traffic as compared with residential streets. It is obvious that external inputs may increase the heavy metal concentrations higher than the safe levels. The general pattern of Pb distribution adjacent to the heavy traffic roads or highways is depicted in **Fig. 3.10** (Tiller, 1989).

Berenguer et al. (2008) reports that long-term uses of liquid wine industry significantly increased the concentrations of Cu and Zn in soils. Paddy fields around Cr mines in Vietnam (Co Finh) were also contaminated with Cr, Co, and Ni. The concentrations of Cu, Ni, Hg, Pb, Cd, and As in sediment samples from waste treatment unit in Guiyu, Guangdong, China, significantly increased above their natural concentrations (Guo et al., 2009). Benke et al. (2008) also show that the total concentrations and avalabilities of Cu and Zn significantly increased with long-term application of cow residues. These heavy metals may endanger human health through agricultural products and animals (Kien et al., 2010). As to other soil properties reported by Syam et al. (1997), Salam (1999) also report that the deforestation and land-use conversion in West Lampung Indonesia changed that extracted heavy metal elements.

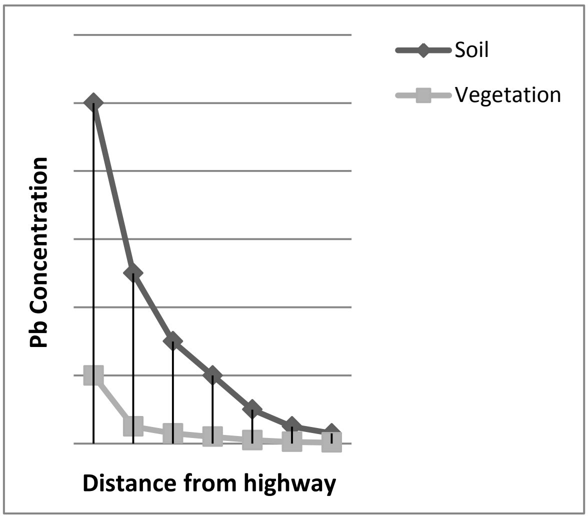


Fig. 3.10. Lead distribution in soil and vegetation adjacent to the heavy traffic roads or highways (After Tiller, 1989).

The increasing trend of heavy metal contamination is associated with the increase in the global production in heavy metals for various purposes. For example, the global production of Cu was 1,611,000 ton in 1930. The production significantly increased to 7,660,000 ton in 1980 or within 50 years. This trend increased the global emission of heavy metals into the soil system as high as 954,000 ton in 1980 (Alloway, 1990a).

As long as their concentrations in soils are below the allowable levels, the emission of heavy metals into the soil environment will not endanger the living things. Ross (1994) shows that the toxic levels of total Cu concentration in soils is

60 mg kg^{-1}, of total Zn concentration is below 70 mg kg^{-1}, and those for Cd and Pb are < 9 and < 100 mg kg^{-1}, respectively. In fact, some of the metal elements such as Cu and Zn may be used as micronutrients for plants if managed at lower concentrations. Particular industrial wastes with heavy metal concentrations relatively low are possible to be used as fertilizer precursors to enhance soil fertility (Salam et al., 2000). Pereira et al. (2012) reports that the irrigation with reclaimed waste waters increased the availabilities and total concentrations of nutrients and non-essential elements in soils, and also soil salinity and sodicity by two to three times compared with that irrigated by well water. The major parts of nutrients in reclaimed waste water were free ionic species readily available for plant absorption such as: NH_4^+, NO_3^-, K^+, Ca^{2+}, Mg^{2+}, SO_4^{2-}, H_3BO_3, Cl^-, Fe^{2+}, Mn^{2+}, Zn^{2+}, Co^{2+}, and Ni^{2+}. More than 80% of Cu, Cr, Pb, and Al were complexed with CO_3^-, OH^-, and/or organic matters.

3.9 Heavy metal effects on soil microorganisms

The presence of heavy metals in the soil environment indirectly affects the soil microorganisms. The effects of heavy metals on the populations and activities of soil microorganisms are not always unbeneficial. Mathur and Sanderson (1980) suggest that heavy metals were possible to be used to restrain the decomposition of organic soils. Copper, for example, may restrain the decomposition of organic soils, otherwise the decomposition may cause the subsidence of some organic soils. The Cu element is known to inactivate particular extracellular soil enzymes which normally facilitate the biochemical oxidation of non-humic soil organic matters. These soil enzymes may include cellulase, amylase, lichenase, and lipase.

The above indirect mechanisms have been reported by several workers (Baath, 1989; Hiroki, 1992; 1993; 1994; Landmeyer et al., 1993; Flieβach et al., 1994; Huysman, 1994; Witter et al., 1994; Brookes, 1995; Gutser and Erdogan, 2008; Nwuche and Ugoji, 2008; Zhou et al., 2011). Landmeyer et al. (1993) reports that the microbial biomass drastically decreased in soils treated with Pb. Mathur et al. (1980) previously report that the populations and activities of microorganisms in Histosols with high Cu concentration were lower than those with lower Cu concentration as indicated by the lower soil respiration rate of peat sample containing 797 ppm Cu, about half that of the peat sample containing 408 ppm Cu. Flieβach et al. (1994) also reports that high heavy metal contaminations of soils resulted in a substantial decrease in soil microbial biomass carbon. Zhou et al. (2011) also report that the increase in Cu concentration in citrus soils as a result of soil treatment with Cu containing fungicides lowered the soil microbial biomass and shifted their biodiversity. The decrease in the populations and activities of soil microorganisms lowered the activity of soil enzymes due to lower enzyme production. The effects of Cd, Cu, and Zn on the number of actinomycetes in an Andisol fallow paddy fields in Gunma Prefecture Japan are shown in **Table 3.14**. The effects of Cd, Cu, and Zn on the number of bacteria in an Andisol fallow paddy fields in Gunma Prefecture Japan is shown in **Table 3.15**. However, generally low metal concentrations showed beneficial effects on soil microbial biomass carbon.

Table 3.14. The effect of some metal elements on the number of actinomycetes in heavy metal contaminated soil$^{1)}$.

Heavy Metals Content	Cd	Cu	Zn
……. mg kg^{-1} …….	……. 10^7 CFU g^{-1} …….		
1	5.0		
2	3.1		
3	0.4		
250		5.15	5.2
500		3.30	1.95
750		1.95	0.00

$^{1)}$Adapted from Hiroki (1992)

Heavy metals may directly interact with soil microorganisms, which include those producing soil enzymes (Baath, 1989; Landmeyer et al., 1993; Flieβach et al., 1994; Huysman, 1994; Hiroki, 1994; Witter et al., 1994; Zhou et al., 2011). This interaction may lower the production of soil enzymes. Zhou et al. (2011) report that the increase in Cu caused by the use of Cu-containing fungicide decreases the soil microbial biomass and alters the microbial composition in orange plantation. It is also reported that the soil microbial populations decreased drastically in soils treated with Pb (Landmeyer et al. (1993)). Hiroki et al. (1994) found that the number of actinomycetes and bacteria decreased significantly by heavy metals. Actinomycetes were affected most strongly. The degree of tolerance to heavy metals follows the order of: fungi > bacteria > actinomycetes. In accordance with this findings, Huysman et al. (1994) report that in general bacteria were more sensitive to Cu than were fungi.

Table 3.15. The effect of some metal element on the number of bacteria in heavy metal contaminated soil$^{1)}$.

Heavy Metals Content	Cd	Cu	Zn
.... mg kg^{-1}	.... 10^7 CFU g^{-1}		
1	9.90		
2	7.50		
3	5.00		
4	2.10		
250		5.15	9.15
500		7.50	5.10
750		4,90	3.10
1000		2.50	0.00

$^{1)}$Adapted from Hiroki (1992)

3.10 Heavy metal effects on soil enzymes

Soil enzymes are biocatalisators in soils produced by microorganisms, mesoorganisms (for example earthworms), and plant roots (Hayano, 1973; Alexander, 1977; Ross and Cairns, 1982; Frankenberger, Jr. and Dick, 1983; Baruah and Mishra, 1984; Satchell et al., 1984; Satchell and Martin, 1984; Nasution, 1986; Tate III, 1987; Rao et al., 1990; Reddy et al., 1991; Jha et al., 1992; Park et al., 1992; Sakai and Tadano, 1993; Tarafdar et al., 1994; Joner et al., 1995; Salam, 1996; Joner and Jakobsen, 1995; Dharmakeerti and Thenabadu, 1996; Vinotha et al., 2000; Le Bayon and Binet, 2005; Supriatin et al., 2007; Wang et al., 2007; and Fang et al., 2010). The soil enzymatic properties are directly and indirectly affected by numerous environmental factors and practices such as pH, C, N, organic matter contents, temperature, water content, cropping practices, soil tillage, and soil compaction (Klein and Kohs, 1980; Speir et al., 1980; Frankenberger and Johanson, 1982; Moyo et al., 1989; Herbein and Neal, 1990; Neal, 1990; Fox and Commerford, 1992; Martens et al., 1992; Salam et al., 1997d; Salam, 1998; 1998d; Salam et al., 1998i; 1999a; 1999d; Sarapatka et al., 2004; Luo, 2010a; Curtin et al., 2012; and Garcia-Morote et al., 2012).

These biochemical substances are important in speeding up the alteration of organic nutrients in organic matters into inorganic nutrient element dissolved in soils water. For example, phosphatase may catalyze the alteration of organic phosphorus in soil organic P that is not available to plants, into orthophosphates, that are available to plants. Some of important soil enzymes in soils are phosphatases, sulphatases, ureases, and proteases.

Heavy metals may directly or indirectly affect the soil enzymatic activities. Heavy metals may directly interact with enzyme molecules and, hence, inactivate the active sites of enzyme molecules through the formation of complexes between heavy metal cations and enzyme molecules (Tate III, 1987). Heavy metals may also affect the soil enzymes indirectly through their effects on enzyme producers, i.e. soil microorganisms, soil macroorganisms, and plant root system. As a result, the presence of heavy metals may lower the soil enzymatic activities. Several soil properties related to the changes in heavy metal concentration, such as pH and organic matter content may also probably indirectly affect the activities of soil enzymes (Harrison, 1983).

A great deal of researchers report that heavy metals negatively affect the soil enzymatic activities (Juma and Tabatabai, 1977; Mathur and Sanderson, 1980; Mathur et al., 1980; Stroo and Jencks, 1982; Dick and Tabatabai,1983; Stott et al., 1985; Reddy et al., 1987; Reddy and Faza, 1989; Asthana et al., 1992; Landesmaki and Piispanen, 1992; Park et al., 1992; Joshi et al., 1993; Sakai and Tadano, 1993; Salam et al., 1997a; 1997e; 1997f; 1997n; Geiger et al., 1998a; Salam et al., 1999h; Gutser and Erdogan, 2008). Most of the researchers generally show that heavy metals decreased the activities of various soil enzymes such as acid phosphatase, β-glycosidase, dehydrogenase, and urease (Juma and Tabatabai, 1977; Stott et al., 1985; Reddy et al., 1987; Eivazi and Tabatabai, 1990; Park et al., 1992; Stott et al., 1992; Salam et al., 1997f; 1997n; 1999h). For example, Geiger et al. (1998a) found that the activity of β-glucosidase was inhibited by dissolved Cu concentration exceeding 0.2 mM. The presence of goethite reduced the inhibitory effect of Cu due to the strong affinity of Cu towards goethite. Reddy et al. (1987) found that soil dehydrogenase activity was inhibited by the presence of sludge borne Cu, Zn, Ni, Cd, Fe, and Mn. Salam et al. (1997f) also report the effect of Pb and Cd on the activity of phosphatase (**Fig. 3.11**). Similarly, Gutser and Erdogan (2008) report the negative effect of Mn and Pb on the activities of arylsulphatase, alkaline phosphatase, and urease.

Salam et al. (1997n) also report the negative effects of heavy metal on the activities acid phosphatase in an Indonesian and a Japanese soil. The activity of acid phosphatase was significantly reduced by Pb or Cd addition, but not reduced by Cu or Fe addition. Addition of Cd at 40 mg kg^{-1} reduced the acid phosphatase activity as much as 44% in the Japanese soil and 43% in the Indonesian soil; while Pb of the same level decreased the acid phosphatase in the Japanese and Indonesian soils as much as 54 and 39%, respectively. The effect of Cd and Pb in reducing the acid phosphatase is depicted in **Table 3.16**.

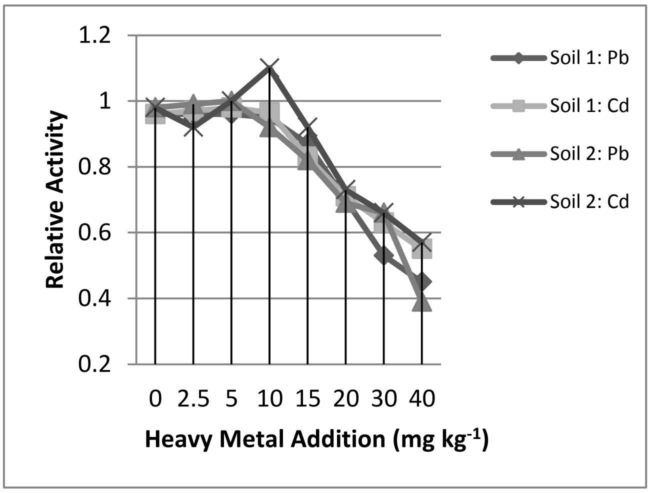


Fig. 3.11. The effect of Pb and Cd on soil phosphatase activity (Adapted from Salam et al., 1997f).

There is also a report that the activity of phosphatase in the root zones decreases with the increase in the level of electronical waste treatment independent of the growing vegetation, including corn, amaranth, and green kyllinga (Salam et al., 1999h). This pattern is related to the extracted Pb as a result of waste treatment. This phenomenon is depicted in **Table 3.17**. Liming was reported to decrease the extracted Pb from both soil of Gedongmeneng and soil of Banjaragung (Salam et al., 1999f), however it did not raise the activity of phosphatase. In this case the effect of soil pH is more dominant than Pb is. The activity of phosphatase was reported to increase below a the related optimum pH and decrease after which (Salam et al., 1998d).

Table 3.16. The effect of Pb and Cd on the activity of acid phosphatase[1].

Treatment Level	Relative Activity of Acid Phosphatase[2]	
… mg kg^{-1} …	Cd Effect	Pb Effect
Indonesian Ultisol:		
0	1.00	1.00
10	1.00	0.90
20	0.71	0.71
30	0.64	0.69
40	0.57	0.61
Japanese Ultisol:		
0	1.00	1.00
10	1.02	0.95
20	0.71	0.67
30	0.62	0.54
40	0.56	0.46

[1] Adapted from Salam et al. (1997n); [2] Relative activity is the activity at elevated heavy metal treatment divided by that at control treatment

Previously, Mathur et al. (1980) also observed lowered activities of amylase, invertase, protease, and acid phosphatase in the presence of high Cu. The activities of these soil enzymes were found lower in organic soils (sapric Histosol and fibric Histosol) from New Brunswick Canada treated with Cu. This phenomenon is listed in **Table 3.18**.

Table 3.17. The effect of industrial-waste Pb on the activity of phosphatase in soil of Gedongmeneng (Ultisol) and Banjaragung (Ultisol)[1).

Treatment	**Vegetation**		
	Corn	**Amaranth**	**Green Kyllinga**
	……. µg p-nitriphenol g^{-1} h^{-1} …….		
Soil of Gedongmeneng:			
Control			
Unlimed	121	105	132
Limed	112	81.0	98.3
Waste Treated			
Unlimed	89.8	86.7	75.4
Limed	48.2	40.0	53.1
Soil of Banjaragung:			
Control			
Unlimed	181	175	133
Limed	159	143	84.3
Waste Treated			
Unlimed	128	172	104
Lime	81.5	75.5	44.1

1)Adapted from Salam et al. (1999h); waste treatment at 40 mg kg^{-1}; lime at 5 ton $CaCO_3$ ha^{-1}

Table 3.18. The effects of Cu on the activities of some enzymes in organic soils1).

Soil	**Cu**	**Amylase**	**Invertase**	**Protease**	**Acid Phosphatase**
		... µmol glucose h-1 ...		nmol NH_4 h^{-1}	µmol phenol h^{-1}
Sapric	Low	6.86	11.5	264	19.7
Histosol	High	2.20	3.13	71.8	5.54
Hemic	Low	6.29	23.4	439	17.0
Histosol	High	2.25	14.1	144	6.57

1)Adapted from Mathur et al. (1980)

The effectiveness of heavy metal inhibition on the activities of enzymes is various. Comparing several heavy metals on the inhibition of pyrophosphatase, which catalyzes the hydrolysis of pyrophosphates to orthophosphate, with a 25 μmol/g soils, Stoot et al. (1985) grouped the metal elements into three categories: the most effective (average inhibition > 50%), moderately effective (average inhibition 30 – 50%), and weakly effective (average inhibition < 30%). The grouping of the metal cations is shown in **Table 3.19**.

Table 3.19. The grouping of heavy metal enzyme inhibitors[1].

1	Most Effective	Hg(II), As(V), Mo(VI), W(VI)
2	Moderately Effective	Cd(II), Cu(II), Fe(II), B(III), V(IV)
3	Weakly Effective	As(I), Cu(I), Mn(II), Ni(II), Pb(II), Sn(II), Zn(II), Al(III), As(III), Cr(III), Fe(III), Se(IV), Ti(IV)
4	Non Inhibitor	Ba(II), Co(II)

[1] Adapted from Stott et al. (1985)

Important questions

1. Among the various forms of heavy metals in the soil environment, free ion is the most important. Explain why!
2. Explain how to lower the toxicity of heavy metals in the soil environment!
3. Explain the role of various chemical reactions controlling the heavy metals in the soil environment! How is the relationship of each of the reaction with the concentration of free ionic heavy metal?
4. How do the chemical equilibria work in the soil environment? Explain the roles of equilibrium constants!
5. Explain the relationship of equilibrium chemical reactions with the pH of soil environment!

6. Explain the difference of adsorption-desorption and precipitation-dissolution of heavy metals in relation to the soil pH and the concentration of heavy metals!
7. Explain the various soil negative charges in the soil environment and how these negative charges develop!
8. Explain the sources of the soil negative charges both of silicate clay minerals and non-silicate clay minerals!
9. Explain the relationship between the soil negative charges with the changes in soil pH!
10. Explain the soil selectivity towards heavy metals with the Coloumbic Law!
11. Explain the soil adsorption capacity (SAC) and the soil cation exchange capacity (CEC)!
12. Compare the CEC of various matters in the soil environment!
13. Explain the role of precipitation-dissolution reaction in heavy metal retention in the soil environment!
14. How does the precipitation reaction work in relation to the solubility constant (K_{sp})?
15. Explain the precipitating agents in the precipitation-dissolution reactions! Describe their existence in the soil environment!
16. Describe the solubility equation! How is this equation developed?
17. Explain the solubility equations for Cu, Cd, and Zn! How is the role of pH in the precipitation reaction?
18. Make the graph of the solubility equations of Cu, Cd, and Zn!
19. Explain the similarities and differences between the adsorption and the precipitation reactions related to their dependence on soil pH!
20. Explain the chemical reactions related to the presence and the absence of O_2 in the soil environment!
21. Explain the changes in the soil chemical reactions when the soil environment is flooded!
22. Explain the soil chemical reaction when the flooded soil is drained!
23. Explain about what happens to Fe^{3+}, SO_4^{2-}, Fe^{2+}, and S^{2-} when the paddy soil is flooded!
24. Explain about what happens to organic C, N, and S when the paddy soil is flooded and when the paddy soil is drained!
25. Explain about what happens to P when the paddy soil is flooded and when the paddy soil is drained!
26. Explain the roles of redox potential (E) and pH in the soil environment!
27. What is the E – pH Diagram? Explain!
28. Explain the role of oxidation on silicate mineral weathering!
29. Explain the weathering of pyrite and its effect on the soil environment! What happens when pyrite is flooded or unflooded? Explain!
30. Explain the disturbance of plant absorption on free ions and the chemical reactions in the soil environment!
31. Explain the difference between heavy metal retention for plant nutrients and toxic heavy metals!
32. What is metalophytes? Is it important for heavy metal management in the soil environment? Explain!

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33. Explain the sources of heavy metals in the environment! Which one is very important? Explain!
34. Explain the pathways of heavy metal spreading from their sources to the environment!
35. Explain the P-fertilizers as Cd sources in the soil environment!
36. Explain the sources and distribution of heavy metals adjacent to heavy traffic streets and highways!
37. Are all heavy metal always dangerous for the living things? Explain!
38. Explain the mechanisms of heavy metal movement in the soil environment! How does the ground-water contamination and pollution occur?
39. What factors affect the mass flow and diffusion of heavy metals in the soil environment? Explain!
40. How does the diffusion coefficient affect the rates of diffusion of heavy metals in the soil environment?
41. Explain the relationship between the rates of heavy metal transport and point of zero charge (PZC) in the soil environment!
42. Explain the negative effect of heavy metals on the populations and activities of soil microorganisms!
43. Explain the effect of heavy metals on the decomposition of soil organic matters! How is its relation to the activities of soil enzymes?
44. Describe how the heavy metals directly and indirectly affect the activities of soil enzymes!

Chapter 4

Heavy Metal Retention in Soils

Heavy metal retention in the soil environment is an important issue from two stand of views. From the stand of view of nutrient management in agricultural lands, heavy metals must be temporally immobilized in the soil system for availability management. Some of the heavy metals in the soil environment that include Fe, Mn. Cu, Zn, and Co are micronutrients and hence are needed at small quantities. Therefore, in the soil system the big part of these elements must be immobilized and must be dissolved step by step into the soil solution where plant roots may absorb the dissolved species. When the concentrations of the dissolved heavy metal elements in the soil solution are relatively high, the big part of these elements must be temporarily immobilized. By this mechanism, most of the heavy metal micronutrients may not leach out of the soil system or highly absorbed so that they may not give negative effects to plants and the related living things including humans. Even though needed by plants, at high concentrations the heavy metal micronutrients can be viewed as pollutants.

From the stand of view of environmental management, all heavy metals are toxic at high concentrations, that may be elevated not only by natural sources such as heavy metal containing minerals but also by anthropogenic sources, which are reported to be more devastating from various sources such as various fertilizers, pesticides, and industrial wastes that contain heavy metals (Lagerwerff, 1982; Kardoz et al., 1986; Leung, 1988; Hegstrom and West, 1989; Alloway, 1990c; Davies, 1990; Kiekens, 1990; Rivai, 1990; Dowdy et al., 1991; Boon and Soltanpour, 1992; Jing and Logan, 1992; Wang et al., 1992; Herrero and Martin, 1993; Sweet et al., 1993; Cabrera et al., 1994; Nicholson et al., 1994; Schuhmacher et al., 1994; Tsoumbaris and Tsoukali-Papadopoulou, 1994; Bilski and Alva, 1995; Flegal and Smith, 1995; Vile et al., 1995; Gimeno-Garcia et al., 1996; Salam et al., 1996; Yeh et al., 1996; Salam et al., 1997a; Juracek and Ziegler, 2006; Biasioli et al., 2007; Benke et al., 2008; Berenguer et al., 2008; Lin et al., 2008; Hobara et al., 2009; Benn et al., 2010; Cakmak et al., 2010; Kien et al., 2010; Wang et al., 2010; and Tu et al., 2012). Since most of these heavy metal elements are not needed by plants and animals/human, their existence in the soil environment must be depressed. The most effective way to immobilize heavy metal elements in the soil environment is to elevate their retention by soil solids. To do this, two mechanisms can be employed i.e. adsorption and/or precipitation processes, by which the soluble heavy metal cations are adsorbed or precipitated permanently or at least for the time being to avoid their negative effects to the living things.

There are numerous factors that control the existence of heavy metal immobilized as adsorbed elements or precipitated elements. Among these factors the soil reaction (pH) is reported to be the most important. The immobilized heavy metal element is repeatedly reported to be negatively affected by soil pH; their dissolved species decreases with the increase in soil pH (Helling et al., 1964; Trehan and Sekhon, 1977; Elliott, 1983; Tan and Dowling, 1984; McGrath et al., 1988; Alloway 1990b; Parfitt et al., 1995; Rodella et al., 1995; Medonca and Rowel, 1996; Tack et al., 1996; Suryanto and Susetyo, 1997; Choi et al., 1999; Tokunaga et al., 2003; Quaghebour et al., 2005; Schroder et al., 2008; and Gagnon et al., 2013). Some authors (Lindsay, 1979; Brummer et al., 1983; Ma and Lindsay, 1990; 1995; Workman and Lindsay, 1990; El-Falaky et al., 1991; Stahl and James, 1991; and Salam, 2000) report that this phenomenon is caused directly by precipitation reaction, particularly at high concentrations on heavy metals; while others suggest that this phenomenon in an indirect effect of pH on the adsorption of heavy metal cations (Cavallaro and McBride, 1980; Abd-el Fatah and Wada, 1981; and Salam and Helmke, 1998). As previously stated, some soil workers suggest that adsorption may be dominant in controlling dissolved heavy metal cations at low concentration, while precipitation control heavy metal cation concentrations particularly at high concentrations and high pH due to the presence of some precipitating agents like OH^- and CO_3^{2-}.

4.1 Adsorption

As previously explained, adsorption process involves the presence of the soil negative charges emerged from the dissociation of H from some soil solids such as non-silicate clay minerals (oxides and hydroxyoxides), 1:1 silicate clay minerals, and organic matters' functional groups (first group) and isomorphic substitution in 2:1 silicate clay minerals (second group). Being positively charged, heavy metal cations are electrostatically adsorbed by the negatively charged soil solid surfaces. As explained by the Coloumbic Law, the force of adsorption increases with the increase in the negative charges of soil solids and in the positive charges of heavy metal cations. This means that the adsorption force of Ca^{2+} on a kaolinitic soils is higher that does K^+ on the same soils. Likewise, the adsorption force of Ca^{2+} on a kaolinitic soils is lower than does Ca^{2+} on montmorilonic soils.

The adsorption process is controlled by the adsorption equilibrium constant previously shown by **Eq. 3.2**. Taking an example of divalent heavy metal cation M^{2+} and the dominant cations in soil solution Ca^{2+}, the adsorption process in controlled by E**q. 4.1** with equilibrium constant K in **Eq. 4.2**.

$$\mathbf{X - Ca + M^{2+} \leftrightarrow X - M + Ca^{2+}} \quad \text{.......} \quad \textbf{Eq. 4.1}$$

$$\mathbf{K = \frac{Ca^{2+}}{M^{2+}}} \quad \text{.......} \quad \textbf{Eq. 4.2}$$

Where X – Ca and X – M are the adsorbed Ca^{2+} and M^{2+}, respectively, Ca^{2+} and M^{2+} are the dissolved Ca^{2+} and metal cation M^{2+}, respectively. Derivating **Eq. 4.2** may reveal a linear equation **Eq. 4.3**.

$$[M^{2+}] = \frac{[Ca^{2+}]}{K}$$

$$\text{Log}\,[M^{2+}] \;=\; \text{Log}\,(\tfrac{1}{K}) + \log\,[Ca^{2+}]$$

$$\textbf{Log}\,[M^{2+}] \;=\; k \;+\; \log\,[Ca^{2+}] \quad \text{…….} \quad \textbf{Eq. 4.3}$$

Plotting this equation with log [M^{2+}] on the Y axis and log [Ca^{2+}] in the X axis reveals a straight line in **Fig. 4.1**, with a slope of 1 and intercept of k = log [1/K]. This equation indicates that the adsorption of heavy metal cation M^{2+} is dependent on the controlling cation and not controlled by soil pH.

However, the change in soil pH may indirectly affect the adsorption of M^{2+}. The effect is due to the fact that the soil negative charges, particularly in tropical soils is of Group 1, which is dominated by non-silicate clay minerals (hydroxyoxides), 1:1 silicate clay minerals, and organic matters's functional groups. The negative charges are dependent on soil pH. The increase in soil pH may detach H from mineral and organic matter surfaces and leave more negative charges, which mean increase the soil adsorption capacity. The decrease in soil pH, conversely, may increase the hydrogenation of negative charges, neutralize the soil surfaces and decrease the soil adsorption capacity.

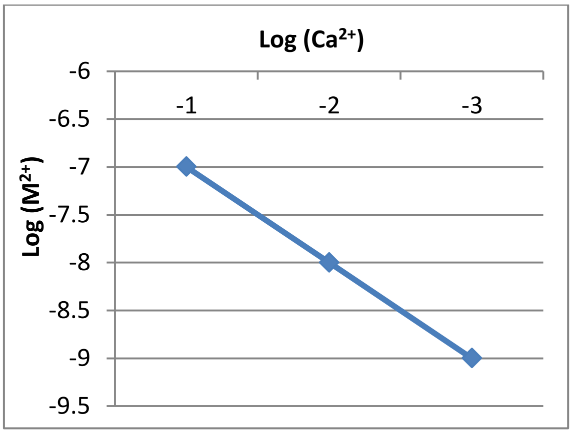

Fig. 4.1. The linear relationship between log (M^{2+}) and log (Ca^{2+}).

The magnitude of the changes in the soil negative charges is soil type dependent. The dependence of the soil adsorption capacity on soil pH is depicted in **Fig. 4.2**. This phenomenon is absent when the soil solid is dominated by the solid dominated by Group II or 2:1 silicate clay minerals such as montmorilonite. Therefore, the adsorption capacity of these soils is independent of soil pH. This phenomenon is shown in **Fig. 4.3**. This indicates that the heavy metal cation adsorption in soil with Group II sources, unlike those of Group I sources, cannot be managed by soil pH manipulation.

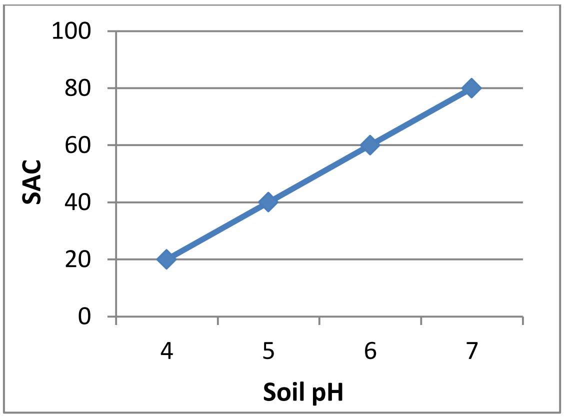

Fig. 4.2. The adsorption capacity (SAC) of soils dominated by pH-dependent negative charges.

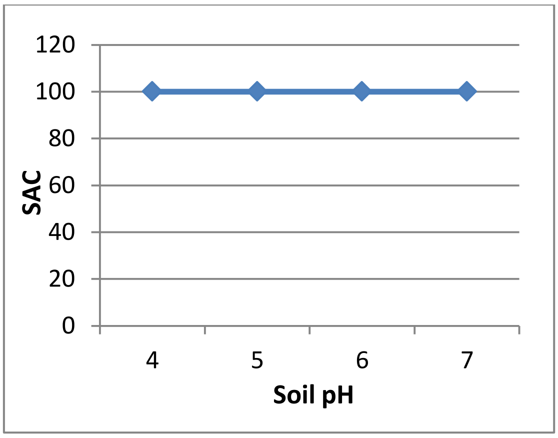

Fig. 4.3. The adsorption capacity (SAC) of soils dominated by pH-independent negative charges.

The quantities of adsorption of any substances are generally expressed by two major equations i.e. Langmuir Equation and Freundlich Equation. Both equations are also used to express the adsorption of heavy metals in the soil environment. However, each has its own good and bad sides that must be understood. Among the drawbacks of Freundlich adsorption isotherm is not including the adsorption maximum (Alloway, 1990b). Both equations give no information about the mechanism of adsorption reaction and assume that the distribution of soil adsorption sites is uniform. The adsorbed ions are also assumed to have no interactions each other.

The Langmuir equation is expressed in **Eq. 4.4**.

$$\frac{M}{x/m} = \frac{1}{Kb} + \frac{M}{b} \quad \text{.......} \quad \textbf{Eq. 4.4}$$

where M is the activity of the heavy metal cation, x/m is the amount of heavy metal cation per unit adsobate, K is a constant related to the bonding energy, and b is the maximum heavy metal cation that can be adsorbed by a given adsorbate (Alloway, 1990b). This equation is plotted in **Fig. 4.4** that shows a straight line with a gradient of 1/b and an intercept of 1/Kb. By this equation, the maximum adsorption capacity b and the bonding energy K are easily calculated from the values of the gradient and the intercept.

The values of b and K of a number of soils and heavy metals may enable the comparison of the adsorption capacity between soils and between treatments and also the strength of adsorption of various heavy metals cations. This comparison is often very important in determining any typical soils for any heavy metal retention to cope with heavy metal pollution in the soil environment.

The Freundlich Equation adsorption Isotherm is expressed by **Eq. 4.5** and **Eq. 4.6** (Alloway, 1990b).

$$X = kc^n \quad \text{.......} \quad \textbf{Eq. 4.5}$$

$$\text{Log } x = \log k + n \log c \quad \text{.......} \quad \textbf{Eq. 4.6}$$

where x is the amount of adsorbed heavy metal cation per unit adsorbent at concentration c of adsorbate while k and n are constants. This isotherm is plotted using **Eq. 4.6** in **Fig. 4.5**. The equation is a straight line with a gradient of n and intercept of log k. Using this plot, it is easy to calculate the values of k and n.

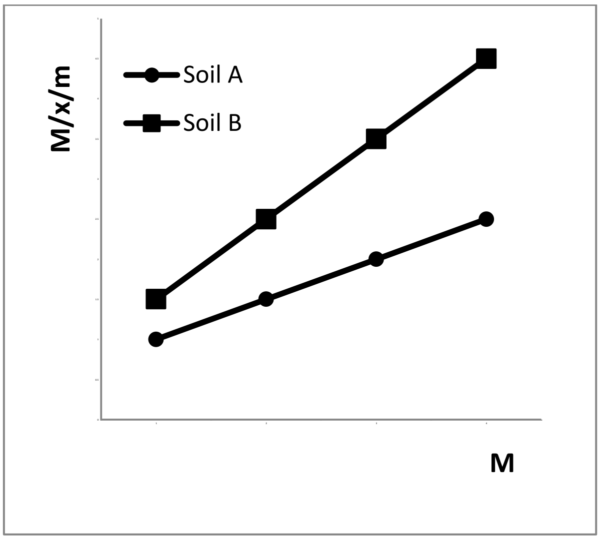

Fig. 4.4. Hypothetical plots of Langmuir Equations.

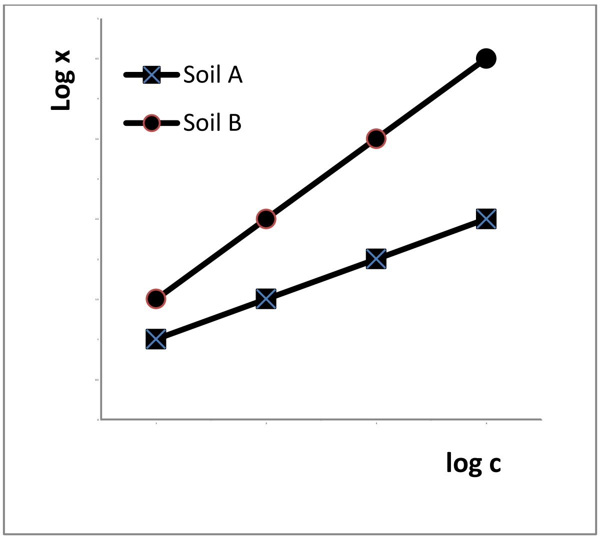

Fig. 4.5. Hypothetical plots of Freundlich Equations.

Regardless of their drawbacks, both isotherms are considered very useful (Alloway, 1990b). A great number of soil workers have uses these equations to study the adsorption of some elements including the heavy metal adsorption in the soil environment (Amuda et al., 2007; Peng et al., 2010). Among the important information is the study of the maximum adsorption capacity (b) and the bonding energy (K) among various soils and heavy metals. Amuda et al. (2007) report that the adsorption of heavy metals on a modified coconut shell carbon was best fitted to the Langmuir and Freundlich equations. Peng et al. (2010) also used Langmuir equation for Cu adsorption on the surface of chitosan-coated magnetic nanoparticles and found the maximum adsorption capacity for Cu (II) was 144.9 mg g^{-1} with Langmuir equilibrium constant of 0,0719 L mg^{-1} at 301 K.

4.2 Precipitation

Precipitation requires high concentrations of heavy metals and/or precipitating agents to occur. This phenomenon has been demonstrated by several researchers, particularly in calcareous soils with high pH where the concentrations of hydroxyl ions are high (Lindsay, 1979; Brummer et al., 1983; Ma and Lindsay, 1990; 1995; Workman and Lindsay, 1990; El-Falaky et al., 1991; Stahl and James, 1991). High concentrations of hydroxyl ions may complex heavy metal cations and finally precipitate some heavy metal cations. As expressed by **Eq. 3.6** and the reported equations for Cu, Cd, and Zn (**Table 3.4**), there is a characteristic of precipitation by hydroxyl ions, that is the gradients of the logarithmic concentrations of any heavy metal cations versus pH is minus 2. This phenomenon is depicted in **Fig. 4.6**. The difference is in their intercepts, which are 2.8, 6.50, and 5.80 for Cu, Cd, and Zn, respectively.

The decrease in the concentrations or activities of Cu^{2+}, Cd^{2+}, and Zn^{2+} is definitely as a result of the increase in the concentration on of OH^- ions as the increase in soil pH. As explained by **Eq. 3.4 and Eq. 3.5**, the precipitation may occur at varying soil pH depending on the concentrations of heavy metals. The precipitation may occur at lower pH if the concentrations of heavy metal cations are higher. On the other hand, low concentrations of heavy metal cations may shift the occurrence of precipitation reaction to higher pH values. Therefore, at low concentrations of heavy metal cations, the precipitation reaction may not control the concentrations of heavy metal and, instead, the adsorption may dominate.

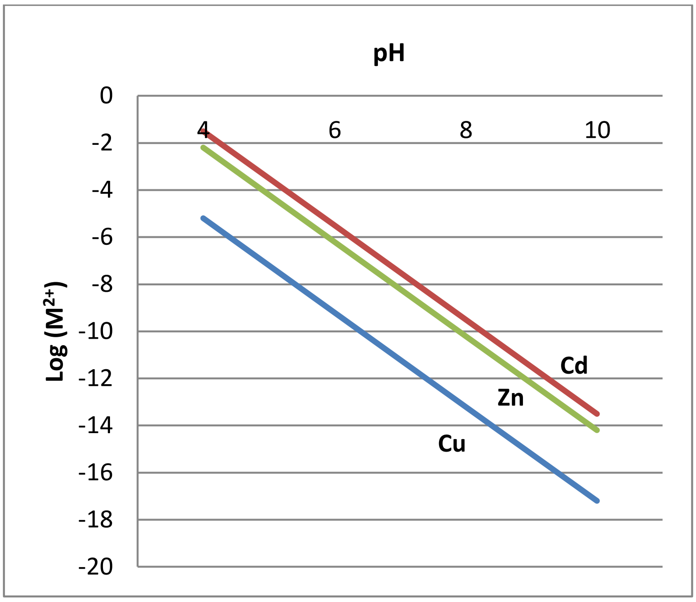

Fig. 4.6. The precipitation of some heavy metal cations by hydroxyl ions in calcareous soils.

The precipitation reaction does not depend only on the presence of OH^- ions, since there are various precipitating agents present in the soil environment. Among these precipitating agents are carbonates (CO_3^{2-} and HCO_3^-), sulphates (SO_4^{2-}), phosphates ($H_2PO_4^-$, HPO_4^{2-}, and PO_4^{3-}), and cloride (Cl^-). In case of CO_3^{2-} as the precipitating agent, particularly in alkaline soils, heavy metal cations may precipitate, for example, as $PbCO_3$, $CuCO_3$, $FeCO_3$, $ZnCO_3$, $NiCO_3$, and $MnCO_3$. The pattern of heavy metal precipitation with the increase in CO_3^{2-} concentration is just like the dependence of heavy metal precipitation on soil OH^- ion concentration, determined by **Eq. 4.7** with K_{sp} in **Eq. 4.8**..

$$\mathbf{MCO_3 \leftrightarrow M^{2+} + CO_3^{2-}} \quad \text{……… } \mathbf{Eq.\ 4.7}$$

$$\mathbf{K_{sp} = [M^{2+}][\,CO_3^{2-}]^2} \quad \text{……. } \mathbf{Eq.\ 4.8}$$

Processing the mathematics of **Eq. 4.8** (K_{sp}), the dependence of divalent heavy metal cations may follow **Eq. 4.9**, which shows that the logarithmic heavy metal cation concentrations decreases with the increase in CO_3^{2-} concentration with a gradient of minus 1.

$$\text{Log } K_{sp} = \log [M^{2+}] + \log [CO_3^{2-}]$$

$$\text{Log } [M^{2+}] = \log K_{sp} - \log (CO_3^{2-}) \quad \ldots\ldots. \quad \textbf{Eq. 4.9}$$

The dependence of the saturated concentrations of Pb^{2+} and Cd^{2+} on CO_3^{2-} concentrations are listed in **Table 4.1** and shown in **Fig. 4.7**. The dependence is straight lines with a gradient of minus 1.

Table 4.1. The dependence of Pb and Cd carbonates on CO_3^{2-} concentrations.

Heavy Metals	pK_{sp}[1)]	Equations
Pb	12.8	$\text{Log } [Pb^{2+}] = \log K_{sp} - \log (CO_3^{2-})$ $pPb^{2+} = pK_{sp} - pCO_3^{2-}$ $pPb^{2+} = 12.8 - pCO_3^{2-}$
Cd	11.2	$\text{Log } [Cd^{2+}] = \log K_{sp} - \log (CO_3^{2-})$ $pCd^{2+} = pK_{sp} - pCO_3^{2-}$ $pCd^{2+} = 11.2 - PCO_3^{2-}$

[1)] After Santillan-Medrano and Jurinak (1975)

As that for the precipitation by OH^- ions, the decrease in the concentrations or activities of these metal elements is definitely as a result of the increase in the concentration of CO_3^{2-} ions. As explained by **Eq. 4.8**, the precipitation of heavy metal carbonates may occur at varying soil solution CO_3^{2-} depending on the concentrations of heavy metals. The precipitation may occur at lower CO_3^{2-} concentration if the concentrations of heavy metal cation are higher. On the other hand, low concentration of heavy metal cations may shift the occurrence of heavy metal carbonate precipitation reactions to higher values of CO_3^{2-}.

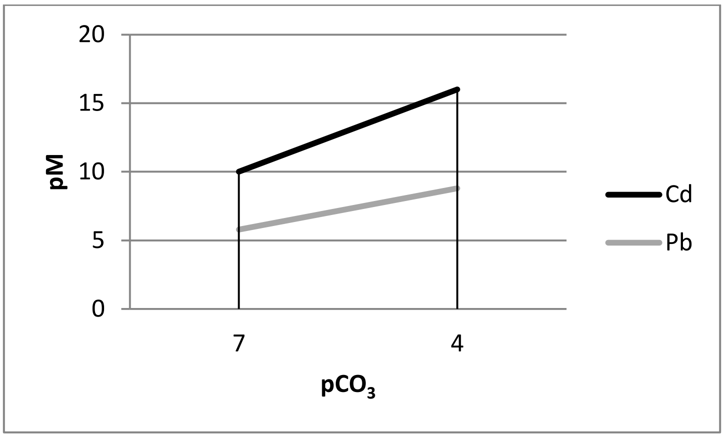

Fig. 4.7. The concentrations of heavy metals as a function of (CO_3^{2-}).

Similarly, the precipitation of heavy metal elements in the soil environment by other precipitating agents like SO_4^{2-}, S^{2-}, and Cl^- such as FeS in the paddy soils or FeS_2 in acid sulphate soils is dependent on the concentrations of the precipitating agent. In general, the precipitation may occur at high concentrations of the precipitating agents. However, the precipitation may also occur at lower concentrations of the precipitating agent provided that the concentrations of heavy metal cations are relatively high like in heavy metal contaminated soils.

4.3 Effect of pH on adsorption and precipitation

Soil pH is one of the major soil variables controlling the chemical reactions in the soil environment. The metal retention in the soil environment by adsorption and precipitation processes is fairly dependent on the soil pH. As shown previously, the metal retention is low at low pH and high at high pH, increases with the increase in soil pH. Some soil workers argue that the dependence of heavy metal retention on soil pH is related to the adsorption as the controlling mechanism for heavy metal cation concentrations. The increase in soil pH may develop new adsorption sites that may increase the heavy metal retention. Therefore, the extracted heavy metals in limed soils are lower than in unlimed soils.

However, the increase in soil pH may also increase OH^- ions that may react with heavy metal cations and cause precipitation reaction to occur. The increase in OH^- ion concentration may suffice the ionic saturation needed for the occurrence of precipitation reaction. This possibility is higher when the concentrations of heavy metals in the soil system are also high. Therefore, some soil workers suggest that the heavy metal retention in the soil environment is controlled by the precipitation reaction. This reaction is of course will not occur at low concentrations of both heavy metals and precipitating agent, at which the major mechanisms is the adsorption process.

The possibility of hydroxide precipitation at lower pH when the concentration of heavy metal cation is higher is shown in **Fig. 4.8**. **Fig. 4.8** shows that at high concentrations, heavy metal cations precipitate at lower pH (A) than those at low concentrations (B). A good example is probably exemplified by Fe^{2+} that may precipitates at lower pH when the concentration of $[Fe^{2+}]$ is higher. The calculation is shown in **Table 4.2**. At $[Fe^{2+}] = 10^{-6}$ M the precipitation of $Fe(OH)_2$ occurs at pH = 10.15 while at $[Fe^{2+}] = 10^{-3}$ M or 1,000 times higher, the $Fe(OH)_2$ precipitation occurs at pH = 8.65, about 1.85 unit pH lower. At $[Fe^{3+}]$ 1,000,000 times higher or $[Fe^{3+}] = 1$ M, the precipitation may occur at even lower pH i.e. pH = 7.15.

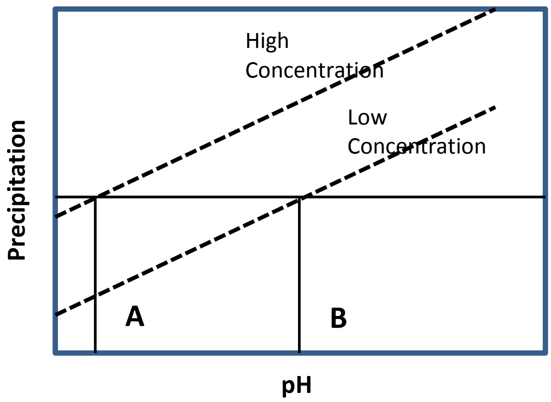

Fig. 4.8. The precipitation of heavy metal cation as a function of pH.

Table 4.2. The precipitation of $Fe(OH)_2$ at different concentration of Fe^{2+}.

$[Fe^{2+}]$ M	pH	Calculation
10^0	7.15	$K = [Fe^{2+}][OH^-]^2$ $K = 10^{-13.7}$ $[OH]^2 = K/[Fe^{2+}]$ pH + pOH = 14
10^{-3}	8.65	
10^{-6}	10.15	

In summary, generally the precipitation reaction may occur and control the concentrations of heavy metals in soils at high concentration of heavy metals and/or high OH^- ion concentration or high pH while the adsorption reaction may control the concentration of heavy metal cations at low concentration of heavy metals and/or low pH. The management of heavy metal cations in the soil environment must take this fact into account. Of course, the consideration of soil pH is very important to control the heavy metal concentration in the soil environment regardless of which mechanism that truly controls the concentration of heavy metal in the soil environment.

Important questions

1. Explain the importance of heavy metal retention in managing heavy metal elements as toxic elements in the soil environment! How?
2. Explain the importance of heavy metal retention in managing heavy metal elements as plant micronutrients in soil environment! How?
3. How is the importance of adsorption and precipitation reactions in heavy metal retention in the soil environment? Explain!
4. Explain the importance of soil pH in managing the soil heavy metals in the soil environment!
5. Explain the roles of soil negative charges in adsorption reactions!

6. Explain the adsorption reaction through cation exchange! Develop an adsorption equation to plot the logarithmic M^{2+} and Ca^{2+}!
7. Explain the direct and indirect effect of soil pH on the adsorption reaction of heavy metal elements in the soil environment!
8. Explain the soil adsorption capacity (SAC) in soil dominated by pH-dependent soil materials!
9. Explain the soil adsorption capacity (SAC) in soils dominated by non-pH-dependent soil materials!
10. Explain the general adsorption equations generally employed by soil scientists! Explain the good and bad sides of each equation!
11. Explain the Langmuir equation, including the development of the equation and the benefits of using the equation!
12. Explain the Freundlich equation, including the development of the equation and the benefits of using the equation!
13. Explain the way to calculate the maximum adsorption and the energy of adsorption using the adsorption equation! What are the benefits of this calculation?
14. Explain the equation of Cu, Cd, and Zn precipitation! What are the important factors affecting the precipitation reactions?
15. Explain the various precipitating agents present in the soil environment! Explain how the concentration of these substances affect the precipitation of heavy metals in the soil environment!
16. Explain using table or graph of how the precipitation of heavy metal carbonates is affected by the concentrations of CO_3^{2-}!
17. Explain the controlling factors of heavy metal adsorption and precipitation in the soil environment! Explain the roles of pH and heavy metal concentration to identify at what concentration these reaction may dominate!

Chapter 5

Heavy Metal Retention in Tropical Soils under Soil-Adsorption Capacity Management

Once released to the environment, heavy metals may flow to any directions and, when not immobilized, they may finally endanger the living things. One of the possibilities to immobilize the wandering heavy metals is to enhance their retention in the soil environment by adsorption onto the soil solid particle surfaces. As mentioned previously, this mechanism may immobilize a big part of heavy metals so that only a small part of them in contact with the living things. This suggests that the adsorption capacity of soil solids towards heavy metals is of great importance and must be maintained high and/or increased.

The soil solid adsorption capacity emerges from the soil solids that include non-silicate clay minerals (oxides and hydroxides), secondary silicate clay minerals, and organic matters which have been shown to be abundant in the soil environment and are fairly manageable. The management to increase the soil solid adsorption capacity can be theoretically accomplished at least by two options. The first option is by the addition of one or more of the three sources of the soil negative charges, either non-silicate clay minerals (oxides and hydroxides), secondary silicate clay minerals, or organic matters as well as other sources of negative charges, both of natural sources like zeolite and man-made sources like biochars and phosphates (Erdem et al., 2004; Shi et al., 2009; Penn et al., 2010; Ippolito et al., 2012; Buss et al., 2012; and Tang et al., 2014). The second option is by manipulating one or more soil properties that may affect the increase in soil solid adsorption capacity like soil pH, that has been repeatedly reported to increase the soil adsorption capacity (Helling et al., 1964; Trehan and Sekhon, 1977; Elliott, 1983; Tan and Dowling, 1984; McGrath et al., 1988; Alloway 1990b; Parfitt et al., 1995; Rodella et al., 1995; Medonca and Rowel, 1996; Tack et al., 1996; Suryanto and Susetyo, 1997; Choi et al., 1999; Tokunaga et al., 2003; Quaghebour et al., 2005; Schroder et al., 2008; and Gagnon et al., 2013;), which is shown in **Fig. 5.1** or P sources that are also reported to increase the soil adsorptive capacity towards heavy metals (Brown et al., 2004; Kilgour et al., 2008; and Moseley et al., 2008).

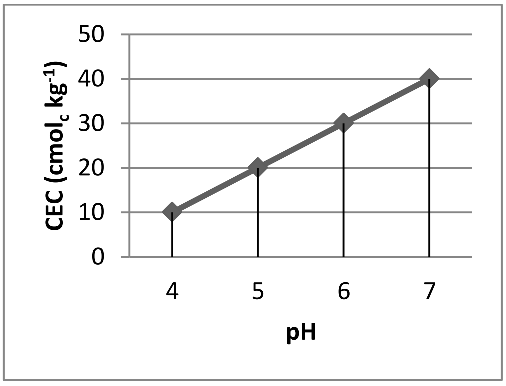

Fig. 5.1. The effect of pH on soil adsorption capacity (Salam, 2012).

However, low negatively charged solid minerals such as oxides and hydroxides and secondary 1:1 silicate clay minerals are not feasible to increase the soil adsorption capacity. The amounts of the negative charges of these minerals may not significantly increase the soil adsorption capacity. As shown in **Table 2.1**, the CEC of these mineral are relatively low i.e. 0.5 – 1.0 $cmol_c$ kg^{-1} for oxides of Fe and Al at pH 8.0 and 3 – 30 $cmol_c$ kg^{-1} for 1:1 secondary silicate clay minerals (kaolinite). However, Hartley et al. (2004) observed that the iron oxides amendment decreased the As and other heavy metal mobility in short and long-term leaching test. They found that the concentration of As in the leachates of iron-oxides amended soils were lower.

In contrast, organic matters and 2:1 silicate clay minerals are possible to accomplish the effort. The CEC of these materials are 10 – 40 $cmol_c$ kg^{-1} for Illit, 60 – 100 $cmol_c$ kg^{-1} for smectite, 100 – 200 $cmol_c$ kg^{-1} for vermiculite, and 150 – 200 $cmol_c$ kg^{-1} for organic matters (**Table 2.1**). Other materials that also show high CEC and are probably used are allophane with CEC 50 – 100 $cmol_c$ kg^{-1} and humic substances with CEC 200 – 750 $cmol_c$ kg^{-1} for fulvic acids, 500 -750 $cmol_c$ kg^{-1} for humic acids, and 300 $cmol_c kg^{-1}$ for humin. There are also several materials available to directly increase the soil adsorption capacity towards heavy metals. Among the materials are biosolids (Stuczynski et al., 2007) including organic matter composts and biochars (Salam, 2000; 2001; Amuda et al., 2007), minerals such as zeolite (Salam et al., 1998b; Shi et al., 2009; Setyawan, 2002; 2003; Erdem et al., 2004; Penn et al., 2010), and phosphatic rocks, and P-fertilizers (Rabinowitz, 1993; Ruby et al., 1994; Ma et al., 1993; 1994; 1995; Nicholson et al., 1994; Brown et al., 2004; Kilgour et al., 2008; and Moseley et al., 2008). Zeolite is the most popular among these materials. These minerals show high negative charges of which may increase the amount of negative charges upon their incorporation into the soil environment. Example of zeolites is Analcin ($NaAl_2O_6{\cdot}H_2O$) (Salam et al., 1998b; Setyawan, 2002; 2003; and Penn et al., 2010). Zeolites may be employed in adsorbing heavy metal contaminants in the soil environment. Erdem et al. (2004) report that zeolite of Clinoptilolite showed preference towards heavy metals as follows: $Co^{2+} > Cu^{2+} > Zn^{2+} > Mn^{2+}$.

Among those that indirectly affect the soil solid adsorptive capacity are lime and phosphatic fertilizers, that work actually by increasing the soil pH which indirectly related to the increase in soil adsorption capacity. For the tropical soils, managing the soil pH is possible to increase the negative charges, particularly because the tropical soils contain high amounts of oxides and hydroxides and 1:1 silicate clay minerals that show high pH dependent negative charges. Dehydrogenation of the mineral OH sites due to the presence of OH^- may possibly detach H from OH sites of these materials and increase the negative sites on their surfaces. The enlargement of the soil adsorptive sites is also possible in organic matters by the increase in soil pH, in which the increase in OH^- ions may detach H from the organic matter functional groups leaving the negative charges. Among the organic matters functional groups affected by the increase in pH are carboxylics (R-COOH), carbonyls (R-COH), phenolic OH (Aromatic Ring OH), imidazoles (Aromatic Ring NH), aminos ($R-NH_2$), alcoholic OH (R-OH), and sulfhydryl (R-SH) (Sposito, 1989) that upon dehydrogenation give negative charges.

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5.1. Effects of soil fractions

Soil solid comprises three different fractions i.e. sand, silt, and clay. Sand and silt contain high proportion of primary minerals while clay fraction contains clay minerals. In term of the negative charges, soil clay is more important than do sand and silt because soil clay contains higher amount negative charges. Therefore, soil clay is more important in the management of heavy metals in the soil environment (Bhattacharyya and Gupta, 2008). The higher the clay content of soils, the higher the adsorption capacity of the soils, which means the more effective for the soils to immobilize heavy metals in the soil environment. Several researchers report that metal retention in soils is closely related to the soil clay rather than to other soil fractions (Abd-elfattah and Wada, 1981), mainly related to their CEC values.

However, the adsorption capacities of soils as indicated by their CECs differ according to the dominance of clay minerals in soils (Abd-elfattah and Wada, 1981; Salam et al., 1998k; and Bhattacharyya and Gupta, 2008). Soils dominated by 1:1 silicate clay minerals such as kaolinite show relatively low CEC about 3-20 $cmol_c$ kg^{-1}, much lower than those dominated by Illit (10-40 $cmol_c$ kg^{-1}), Smectite (60-100 $cmol_c$ kg^{-1}), and vermiculite (100-200 $cmol_c$ kg^{-1}) (Bhattacharyya and Gupta, 2008). The non-silicate clay minerals oxides of Fe and Al show a much lower CEC (0.5-1.0 $cmol_c$ kg^{-1}). The relative comparison of the CEC of soil clays is shown in **Fig. 5.2**. These values indicate the soil clay effectiveness in adsorbing the heavy metals in the soil environment, of which the 2:1 silicate clay minerals (Illit, Smectite, and Vermiculite) are the most effective, while the non-silicate clay minerals are the least effective. Bhattacharyya and Gupta (2008) suggest that montmorillonite was more effective than kaolinite in removing heavy metals from contaminated soils. In addition to CEC, the surface areas also determine the clay mineral CEC. Vermiculite and montmorilonite show a greater surface area that does kaolinite. The BET surface areas of vermiculite, montmorillonite, and kaolinite are 21.7, 30,0, and 15.2 m^2 g^{-1}, respectively (Ziper et al., 1988).

The effectiveness of each clay mineral is different depending on the clay sizes. The smaller the size of the clay mineral the more effective in adsorbing heavy metals due to the higher CEC (Ziper et al., 1988). For example, the CEC of vermiculite are 11.2, 91.7, 69.9, 50.5, and 39.5 cmol kg^{-1} for those with size fraction <2, 2-20, 20-250, 250-500, and 500-1000 μm, respectively; while those for biotite are 12.3, 2.8, 1.7, 1.0, and 0.8 $cmol_c$ kg^{-1}, respectively.

Unlike those in the temperate regions, the tropical regions are dominated by old soils containing less or no 2:1 silicate clay minerals. Instead, the tropical regions are dominated by Ultisols and Oxisols, which are dominated by 1:1 silicate clay minerals and non-silicate clay minerals of oxide and hydroxide minerals, respectively. This means that the soils in the tropical regions are not effective in immobilizing the environmental heavy metals unless soil management is conducted by employing the two options previously mentioned. The first option is by addition of negative sources materials and the second option is by manipulating soil properties related to the soil negative charges. Conducting these options may significantly enhance the soil adsorption capacity and enable the use of tropical soils to effectively immobilize the environmental heavy metals.

The adsorptive sites of the 1:1 silicate clay minerals and non-silicate clay minerals, unlike the 2:1 silicate clay minerals, are pH-dependent. Their CECs are dependent on the soil pH, which increase with the increase in soil pH. This relationship is useful to enhance the soil adsorption capacity and heavy metal immobilization in tropical regions. This relationship is not observed in soils dominated by 2:1 silicate clay minerals. Therefore, it is possible to highly immobilize the heavy metals in tropical soils better that in temperate regions when soil pH is managed properly. The theoretical relationship between the CECs of soils differing in this property is depicted in **Fig. 5.3**.

The mineralogical properties cause differences of soil capacity to adsorb heavy metals in the soil environment. The order of adsorption capacity of the three soils employed in experiment on heavy metal adsorption was Soil of Banjaragung > Soil of Cihea > Soil of Gedongmeneng (Salam et al., 1998k), which was related to their clay contents 56.8% in Banjaragung > 47.8% in soil of Cihea > 34.8% in soil of Gedongmeneng (Salam et al., 1997k). Abd-efattah and Wada (1981) report that the adsorption capacity of cation-exchange materials decrease following the order of: montmorillonite >humus, kaolinite > allophane, imogilite >

halloysite, iron oxides. Raising the soil pH increased the amount and affinity of adsorption of heavy metals. Selectivity towards cations also increased in the following order: Mg, Ca < Cd, Co < Zn < Cu, Pb.

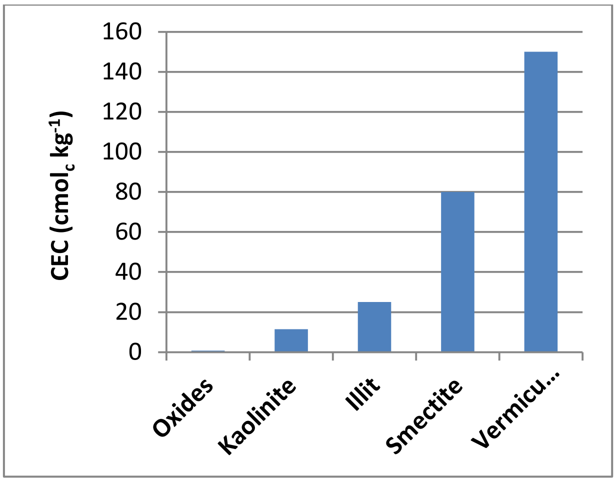


Fig. 5.2. The relative comparison of soil clay CECs.
(Adapted from Thomas and Hargrove, 1984 and, Burns, 1986).

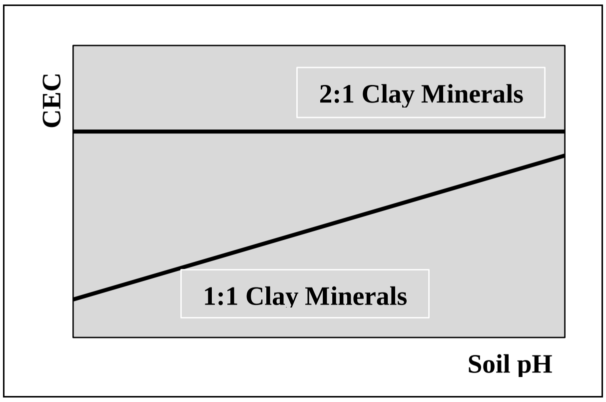


Fig. 5.3. Theoretical relationships between CECs of soils differing in clay minerals.

5.2. Effect organic matters

Organic matters and humic substances show the highest CEC among the soil solids (**Table 3.1.**). Humic substances are reported to have CEC about 200 – 750 cmol$_c$ kg^{-1}, while fulvic acid, humic acid, and humin about 500 – 750, 300 – 500, and 300 cmol$_c$ kg^{-1}, respectively (Thomas and Hargrove, 1984; Burns, 1986). These values are higher than those of 2:1 silicate clay minerals that are abundantly found in the temperate regions. Therefore, incorporating organic matters into the soil environment may increase the amounts of the soil solid negative charges that are very important for heavy metal retention in the tropical soils. This means that choosing the Option 1 in enhancing the soil CEC by organic matter incorporation is promising. Smolders et al. (2012) showed that Cu derived from long-term amendment with sewage sludge was significantly less labile about 5.9 fold compared to freshly added Cu.

The uses of organic residues as organic sources in agriculture have been reported by several workers (Allaway, 1986; McCalla et al.,1986; Banuwa et al., 2003a; 2003b; Banuwa and Damai, 2003; Amuda et al., 2007; Yusnaini et al., 2007; Bintoro, 2008; Diaz et al., 2011). Banuwa et al. (2003a; 2003b) and Banuwa and Damai (2003) used 'night soils' (human residues) in corn culture. They showed that 'night soils' significantly increased the soil Total N, Available P, Exchangeable K as well as corn heights and corn dry and wet weights. Yusnaini et al. (2007) substituted commercial fertilizers with green manure and chicken manure and found that these materials increased the organic C, total N, and available P. They showed that chicken manure was more effective in enhancing these plant nutrients**.** These observations indicate that even though organic residues in the environment possess some problems, they also have potentials as nutrient sources for plants and as soil amendments for heavy metal amelioration. Wise uses based on research data may enable the use of organic residues to lower the use of commercial fertilizers as well as heavy metal problems significantly. In addition to use their potential contents, their uses in agriculture may also solve the environment and social problems.

The negative charges of organic matters emerge from the various functional groups like phenolics and carboxylics which may release their H ions and leave negative sites when the soil pH increases (Helling et al., 1964; Trehan and Sekhon, 1977; Elliott, 1983; Tan and Dowling, 1984; McGrath et al., 1988; Alloway 1990b; Parfitt et al., 1995; Rodella et al., 1995; Medonca and Rowel, 1996; Tack et al., 1996; Suryanto and Susetyo, 1997; Choi et al., 1999; Tokunaga et al., 2003; Quaghebour et al., 2005; Schroder et al., 2008; and ; Gagnon et al., 2013). The presence of organic matters, therefore, may lower the concentration of heavy metal cations in soil solution through adsorption reactions. Rodella et al. (1990) report that the CECs of A and B horizons in several soils from New Zealand were originated from organic matter carboxylics. Alloway (1990b) reports that the maximum of heavy metals that can be adsorbed by soil organic matters was about the same as the amount of carboxylics in organic matters. Saidy and Badruzsaufari (2009) also report the decrease in the concentration of Cr (VI) with the increase in soil organic C content. Some soil organic matter functional groups are listed in **Table 5.1**.

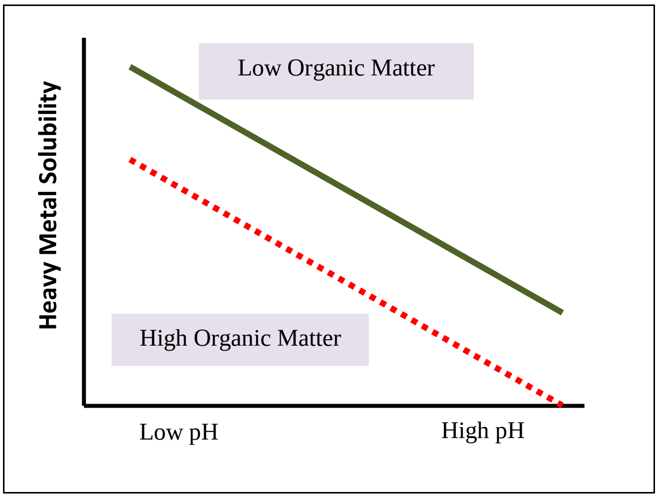
Table 5.1. Some functional groups of soil organic matters[1).]

No.	Functional Group	Chemical Formula
1	Carboxyl	R-COOH
2	Carbonyl	R-COH
3	Amino	$R\text{-}NH_2$
4	Imidazole	Aromatic Ring NH
5	Phenolic OH	Aromatic Ring OH
6	Alcoholic OH	R-OH
7	Sulfhydryl	R-SH

[1)]Adapted from Sposito (1989)

The effect of organic matter on the soil negative charges is more significant at high pH. It is reported that the soil organic matters contributed only about 32% of the soil solid CEC (Rodella et al., 1995). However, the negative charges of soil organic matter functional groups are pH-dependent, which may increase with the increase in soil pH. Therefore, by considering the soil pH factor, the contribution of organic matter on soil CEC significantly increased to 78%. This fact strengthens the suggestion that soil pH is also an important factor in heavy metal retention in the soil environment. The importance of soil pH is not only related to non-specific adsorption involving the electrostatically bonding between the soil negative charges and the cationic positive charges but also related to the specific adsorption that involve covalent bonds in the mineral crystals. The mechanism of specific adsorption is more important because the soil capacity for the adsorption with this mechanism is higher than that with non-specific adsorption (Bohn et al., 1985). The importance of organic matter is adsorbing heavy metal is shown in **Fig. 5.4**.

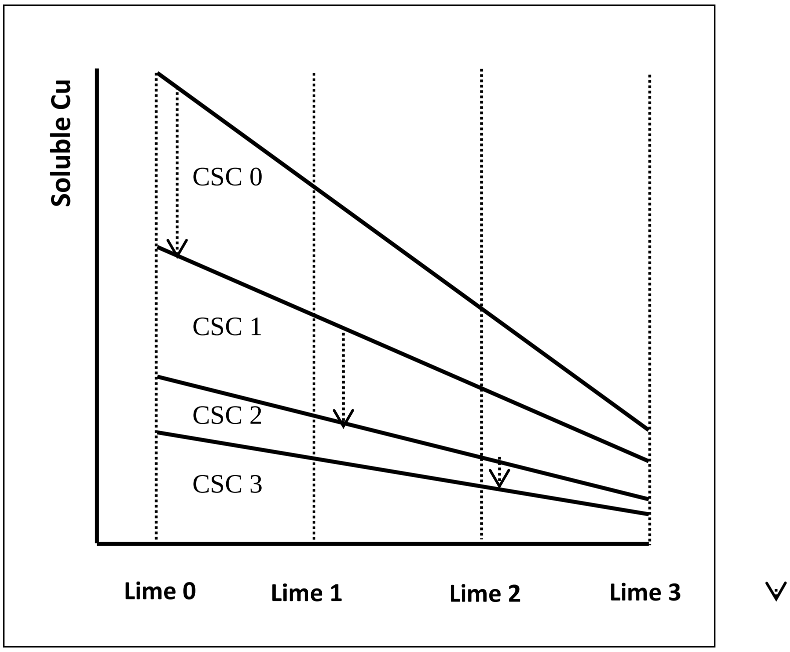
Fig. 5.4. suggests that the availabilities of heavy metals in contact with and absorbed by plant roots are lowered by organic matter treatments because part of the soluble heavy metal cations are adsorbed by soil solid negative charges of organic matters, the adsorption capacity of which increases by the presence of organic matters. The absorption of heavy metals is even lower when the soil pH is higher, caused by the higher soil adsorption capacity at high pH. The decrease in heavy metal solubility caused by soil differing in organic matter and pH treatments is demonstrated by Cu as shown in **Fig. 5.5**. This figure clearly shows that the solubility of Cu significantly decreases in the presence of higher amounts of cassava-leaf compost and also by the increase in pH caused by lime treatment.



Adapted from Salam et al. (1998a; 1998f)

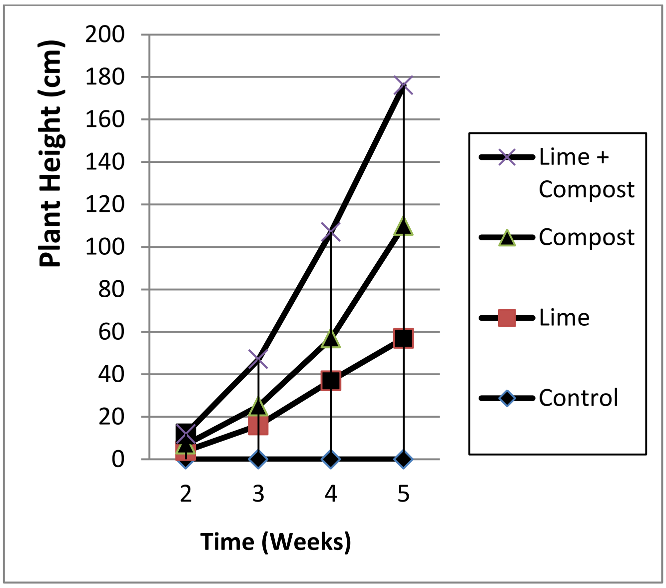
Fig. 5.4. The decrease in heavy metal solubilities in soil treated with organic matter and lime.

The decrease in solubilities of heavy metals of industrial waste origin caused by the presence of organic matters in limed soils is also observed in plant growth indicators like plant height (Salam et al., 1999b; 1999g), shown in **Fig. 5.6**. This figure shows that the addition of 15 ton of heavy metal containing industrial waste per hectare significantly decreased the growth of corn planted in Sri Bawono, East Lampung, Indonesia (Control). The presence of organic matter added by treatment with 5 ton ha^{-1} cassava-leaf compost significantly increases the corn growth as indicated by its height. The height improvement is much better when only lime is added to the soil (Salam et al., 1999g). The decrease in the accumulation of heavy metals by the presence of cassava-leaf compost at higher pH is also observed for Cu and Pb in spinach shoots and several weed plants in soils polluted with heavy metals (Sriyani and Salam, 1998; Salam et al., 1998g; 1999b). Tang et al. (2007) also showed that organic matter as manures reduced the toxicity f Al in acid soils. Bendfeldt et al. (2001) also showed that organic amendment may ameliorate mine soils.



*Adapted from Salam et al. (1998a)

Fig. 5.5. The decrease in solubility of Cu of industrial origin by cassava-leaf compost in limed soils (L = Lime, CLC = Cassava Leaf Compost).



Adapted from Salam et al. (1999g)

Fig. 5.6. The growth improvement of corn in heavy metal polluted soil of Sri Bawono, East Lampung, by cassava-leaf compost.

Organic matters show some drawbacks. One of the drawbacks is that organic matter is prone to decaying process. The soil organic matter content may decrease with time through decomposition process and this may decrease the amount of the negative charges important for heavy metal retention in the soil environment. Based on their researches, Bendfeldt et al. (2001) report that organic matter incorporation is useful to retain part of heavy metal in mine soils, but they suggest that the decomposition organic matter by soil microorganisms may cause the release of heavy metals to more readily available in the future. This may finally endanger the living things. It is reported that the oxidation of soils with dilute H_2O_2 significantly decreased Cu and slightly decreased the adsorbed Zn onto organic substances (Stietiya and Wang , 2011). In fact, the oxidation also increases the Cu-dd and Zn-dd. However, organic matter decomposition may in general increase Cu and Zn mobilities and availabilities but does not affect Pb and As.

As explained by Qureshi et al. (2003) peat soil in general contain elevated concentrations of heavy metals. These metals are gradually released following soil drainage for agriculture. The elemental losses are related to the microbial activity and temperature. They found that the elemental losses for heavy metals increased in the following order of temperature: 28 > 16 > 4 > 37 ^oC, related to the cumulative respiration. The elemental losses from acidic peat soils at 28^oC were 15 to 22% for As, Cd, Ni, and Zn, and Cu about 1% and Ni about 19%, respectively.

One of the efforts to combat with the drawbacks of organic matter related to the relatively quick decomposition to employ more resistant materials in the soil environment. Some researchers have developed new biosolids called biochars. Biochars was reported to adsorb several substances, ranging from herbicides to plant-inhibiting allelochemicals such as heavy metals (Buss et al., 2012). Buss et al. (2012) report that the presence of biochars in the soil environment decreased the Cu entering the plant tissues in the order of roots, shoots, and leaves. The most probable ameliorating mechanisms were the adsorption of Cu onto the negatively charged biochar surfaces. Thereby, application of biochars may lower the Cu toxicity to plants. Ippolito et al. (2012) also report that biochars adsorbed increasing amounts of Cu as the soil solution pH decreased from 9 to 6.

5.3. Effect of phosphates

In addition to by manipulating the soil pH, enhancing the amounts of the soil negative charges can be conducted by manipulation with phosphate addition. Phosphates are reported to indirectly increase the soil negative charges, hence, may decrease the solubilities of some heavy metals (Rabinowitz, 1993; Ruby et al., 1994; Ma et al., 1993; 1994; 1995; Nicholson et al., 1994; Brown et al., 2004; Kilgour et al., 2008; and Moseley et al., 2008). It was reported that the soil CEC is not only affected by soil pH but also by P-fertilizers. Several workers reported that phosphates may react with the soil colloids and may increase the soil adsorption capacity towards cations, including heavy metals cations (Saeed and Fox, 1979; Xie and McKenzie, 1990). Addition of 1 mmol pyrophosphate increased the soil CEC as high as 0.52 – 0.89 $cmol_c\ kg^{-1}$ (Xie and McKenzie, 1990). This process was related to increased Zn adsorption equivalent to 0.3 – 12% of the pyrophosphate-induced increase in soil CEC. This explains why plant roots were not able to absorb P and may induce deficiency symptom in plants (Friesen et al., 1980; Norvell et al., 1987).

This process may also result in the decrease of the availabilities of heavy metal micronutrients (Brown et al.,1970; Saeed and Fox, 1979; Kuo and McNeal,1984; Xie and McKenzie, 1990). The decrease in heavy metal availabilities, however, may also be attributed to the increase in soil pH as affected by addition of P and the increase in soil CEC induced by pH increase. As shown previously, phosphate addition is observed to increase the soil pH (Salam et al., 1997b). Thus, phosphate incorporation into soils may in general help the management of heavy metals in the soil environment.

The soluble heavy metals cations in the soil environment may also decrease due to the precipitation reaction by soluble orthophosphates, both the primary orthophosphates ($H_2PO_4^-$) and the secondary orthophosphates (HPO_4^{2-}) with chemical reactions shown in **Eq. 5.1** and **Eq. 5.2**, respectively.

$$\mathbf{M^{2+} + 2\,H_2PO_4^- \leftrightarrow M(H_2PO_4)_2} \quad \text{....... } \mathbf{Eq.\ 5.1}$$

$$\mathbf{M^{2+} + HPO_4^{2-} \leftrightarrow MHPO_4} \quad \text{....... } \mathbf{Eq.\ 5.2}$$

Thus, when the soluble orthophosphates and the soluble heavy metals cations are relatively high, the product of the concentrations may exceed the related solubility constant of each mineral and may cause the precipitation of heavy metal cation by the soluble phosphates. This phenomenon is observed in paddy soils. Upon drying, the metal elements like Fe are oxidized from Fe^{2+} to be Fe^{3+}. The trivalent Fe^{3+} is then precipitated by $H_2PO_4^-$ producing precipitates of $Fe_2(H_2PO_4)_3$ or $Fe_2(HPO_4)_3$ or $FePO_4$ at higher pH values (Bohn et al., 1985). McGowen et al. (2001) also report that addition of phosphates of $(NH_4)_2HPO_4$ lowered the solubilities of Cd, Pb, and Zn due to metal-phosphate precipitation.

The resulted phosphate precipitates are determined by the forms of the precipitating P anions, which are dependent on the soil pH. The forms of phosphates follow the sequence of $PO_4^{3-} > HPO_4^{2-} > H_2PO_4^-$ with the decrease in soil pH. Therefore, the phosphate precipitates in **Eq. 5.2** may occur at higher pH than that in **Eq. 5.1**. The distribution of phosphate ions with pH is shown in **Fig. 5.7**. This figure clearly shows that the presence of H^+ as affected by H^+ dissociation is closely related to the P forms. Therefore, soil pH is of great importance for precipitation reactions, not only related to OH^- ions but also the phosphate ions.

Ruby et al. (1994) suggest that, for example, lead phosphates are the most stable environmental soil lead form and may form rapidly when enough phosphates are present in the soil environment. The Pb-phosphates may form for example Chloropyromorphite ($Pb5_(PO_4)_3Cl$), Hydroxypyromorphite ($PB_5(PO_4)_3OH$), Fluoropyromorphite ($Pb_5(PO_4)_3F$), and Bromopyromorphite ($Pb_5(PO_4)_3Br$). Geochemical modeling indicated that phosphate addition to Pb-bearing soil may result in the formation of Pb Phosphate when the estimated aqueous lead solubility of 0.1 μg per liter in soils. Ma et al. (1994) suggest that hydroxyapatite showed the potential to be employed for in situ immobilization of Pb in Pb contaminated soils and waste.

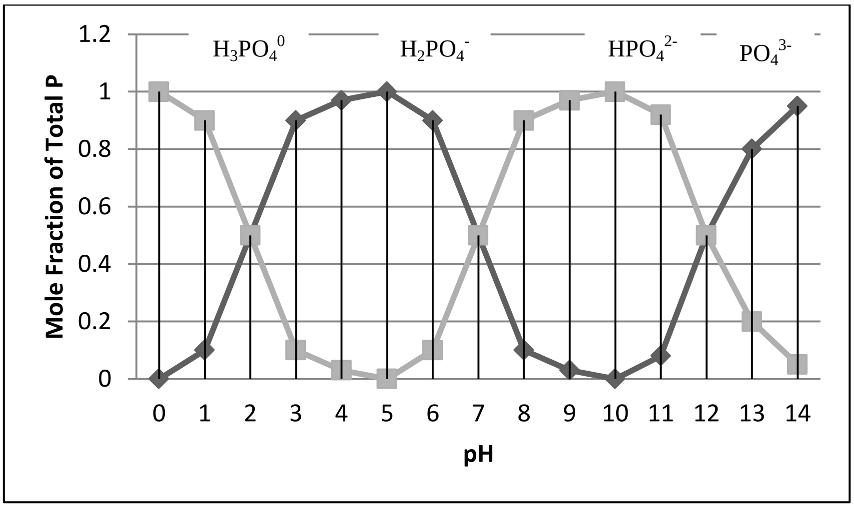


Fig. 5.7. The distribution of soluble P species as a function of pH (After Lindsay, 1979).

However, the use of P substances needs more researches considering numerous factors. Moseley et al. (2008) states that even though the reduction in Pb bioacessability with P amendments is technically possible, it requires large amendment masses to achieve relatively modest reductions in bioaccessability. More economical techniques to employ P amendment in reducing heavy metal solubility must be devised.

Important questions

1. How dangerous are the increasing concentrations of heavy metals in the soil environment? Explain!
2. How important is the soil adsorptive capacity for the management of heavy metals in the soil environment? Explain!
3. Explain the two options to overcome the heavy metal polluting the soil environment!
4. What can be done to do Option 1 in coping with the heavy metal problems in the soil environment?
5. What can be done to do Option 2 in coping with the heavy metal problems in the soil environment?
6. Explain the roles of soil fractions in heavy metal retention in the soil environment!
7. Explain the adsorption capacity of differing silicate clay minerals in the soil environment!
8. Explain the adsorption capacity of non-silicate clay minerals towards heavy metals in the soil environment!
9. Explain the adsorption capacity of high CEC soils!
10. Explain the relationship between the soil CEC and soil pH of 1:1 silicate clay minerals and 2:1 silicate clay minerals!
11. Explain the effects of soil organic matters on the adsorptive capacity of soils! How is the effect of soil pH on this?
12. Describe the drawbacks of using organic matters to increase the soil CEC in the soil environment!
13. What are the advantages of using biochars compared to organic matters if used to increase the soil adsorptive capacity towards heavy metals?
14. Explain the effects of phosphates on the soil adsorptive capacity!
15. Explain the indirect effect of P-fertilizers on the soil adsorptive capacity towards heavy metals!
16. Explain the possibility of the occurrence of heavy metal precipitation when phosphates are used in the soil environment!
17. Explain the improvement of plant growth planted in heavy metal polluted soils treated with organic matter and/or lime!

Abdul Kadir Salam – 2017

Chapter 6

Heavy Metal Retention under Soil pH Management

AS previously stated in Chapter 5, the danger of heavy metals in the soil environment can be alleviated by soil solid management with two options. Assuming that the major mechanism controlling the concentration of dissolved heavy metal cations is adsorption/desorption processes, the first option (Option 1) is possibly conducted by increasing the quantity of negative charges responsible for heavy metal retention through incorporation of any materials with high amounts of negative charges. These materials may include clays, zeolites, organic matters, and biochars. These materials may increase the amounts of the negative charges in the soil environment and increase the metal retention.

Thereby, the soluble heavy metals in contact with the living things can be minimized to lessen their dangers. Some of these materials have been investigated and the good effects of clays have been reported (Abd-elfattah and Wada, 1981; Ziper et al., 1988; and Salam et al., 1998k), organic matters and biochars (Salam, 2000; 2001; Stuczynski et al., 2007), and zeolite (Salam et al., 1998b; Setyawan, 2002; 2003; and Penn et al., 2010).

The second option (Option 2) to increase the soil adsorption capacity towards heavy metal cations is to indirectly increase the amount of the soil negative charges. This option can be conducted by raising the soil pH by liming. As explained previously, the increased soil pH may stimulate the dissociation of H in several soil solids such as organic matters, 1:1 silicate clay minerals, and non-silicate clay minerals (hydroxides and oxides) as well as biochars and/or zeolites. This indirect effect of increasing pH may finally increase the adsorption sites on the soil solid surfaces.

Like that with lime amendment, the soil adsorptive capacity may also increase with phosphate amendment (Rabinowitz, 1993; Ruby et al., 1994; Ma et al., 1993; 1994; 1995; Nicholson et al., 1994; Brown et al., 2004; Kilgour et al., 2008; and Moseley et al., 2008). The specifically adsorbed P is reported to increase the soil adsorption capacity towards heavy metals. However, phosphate also gives indirect effects on the soil adsorptive capacity towards heavy metal cations since any phosphate addition is observed to increase the soil pH. Although the influence of phosphates on soil pH is slight, the effect may be great to the adsorption of heavy metals.

The increase in soil pH may also actually enable the precipitation reaction to occur since the high amounts of OH^- ions at high pH may form hydroxides with any divalent heavy metal cations. This process is not related to the increase in the soil solid adsorption sites but become more important at high pH. Some researchers report the existence of this process at high pH (Udo et al., 1970; Lindsay, 1979; Brummer et al., 1983; Ma and Lindsay, 1990; 1995; Workman and Lindsay, 1990; El-Falaky et al., 1991; Stahl and James, 1991; and Salam, 2000). At low pH, the precipitation reaction may not present except when the heavy metal cation concentrations in the soil solution are extremely high. As that of liming, phosphates may also cause metal-P precipitation, particularly at high concentration of dissolved heavy metals. There are similarities between lime and P-fertilizers in affecting the heavy metal retention in the soil environment, both directly increase the soil metal adsorption capacity; both indirectly increase the soil adsorption capacity through the increase in pH by the materials (Salam et al., 1997b); and both indirectly cause the occurrence of heavy metal precipitation.

6.1 Changes in soil pH

As it is well-known, soil pH is one of the two master variables controlling the soil environment. Along with the soil pE, a variable indicating the concentration of electrons in the soil environment – usually also indicated as redox potential, soil pH may greatly influence other soil chemical properties including the soil adsorption capacity towards heavy metal cations. The shifting of soil pH due to one or more of the various soil internal and external factors may change the amounts of the soil solid negative charges. The presence of high concentration of OH^- ions in the soil water caused by increasing soil pH may detach the H ion from the surface of soil colloids and increase the soil CEC. Some of the soil solids responsible for this pattern have been shown to include the soil organic matters, the 1:1 silicate clay minerals, and non-silicate clay minerals (oxides/hydroxides). Other solids i.e. biochars and zeolites also show the same behaviors. Some scientific evidences on the influence of soil pH on the soil adsorption capacity or CEC have been published. The pattern of this effect has been shown in the previous chapters.

The soil pH is shifted by some natural or anthropogenic acidification or alkalization processes. Among the natural soil acidification process is the formation of carbonic acid as a result of the reaction between water and carbon dioxide molecules produced in the respiration of hydrocarbon in plant roots, soil macroorganisms, and soil microorganisms. The reaction is shown chemically in **Eq. 6.1.**

$$\mathbf{CO_2 + H_2O \leftrightarrow H_2CO_3 \leftrightarrow H^+ + HCO_3^- \quad \ldots\ldots . \quad Eq.\ 6.1}$$

Carbonic acid (H_2CO_3) is not stable in the soil environment and, therefore, it easily dissociates to produce H^+ ions. The increase in H^+ concentration will acidify soils and decrease the soil pH. The higher the production of CO_2 during the respiration, the higher the H^+ ion is produced in the soil environment, and so the higher the decrease in soil pH.

This acidification is very common in the rhizosphere soils. The acidification of the soil rhizosphere is intensified by the excretion of H^+ ions by plant roots during absorption of nutrient cations to preserve the electrostatically balance in the soil system (Tisdale et al., 1985). Yang et al. (1996) report that the soil pH in the soybean rhizosphere of Alfisols was lower than that in the bulk soil in the extent of 0.07 – 0.65 units. Long-term soil culture with cassava (*Mannihot utilisima*) was also reported to lower the soil pH (Salam et al., 1999e).

Acidification of the rhizosphere is dependent on the types of vegetations. Salam et al. (1997e) observed in Oxisol Gedongmeneng that the root zones of *Alang-alang* (*Imperata cylindrica* L.) showed a higher pH value than those of pigweed (*Amaranthus spinosus* L.), Green Kyllinga (*Cyperus kyllingia* L.), and Amaranth (*Amaranthus tricolor* L.). The pH in the root zones of these vegetations were 6.25, 5.03, 5.01, and 5.64, respectively. The significant difference in the pH measurement (0.64 – 1.24 units) indicates that *Alang-alang* possesses an extraordinary adaptability. Its adaptability is also observed by the higher activities of enzyme phosphatases in *Alang-alang* root zones than those in the other vegetations (**Table 6.1**).

Table 6.1. The soil reaction and enzyme phosphatase activities in the root-zones of some vegetations$^{1)}$.

Soil Property	IC	AT	AS	CK
Soil pH	6.25	5.03	5.01	5.64
Acid phosphatases*	179	170	112	155
Alkaline Phosphatase*	62.5	45.8	32.3	41.0

$^{1)}$Adapted from Salam et al. (1997e), IC = *I. cylindrica* = , AT = *A. tricolour*, AS = *A. Spinosus*, CK = *C. Kyllingia;* *in µg *p*-Nitrophenol g^{-1} h^{-1}

As explained in Salam (2012), the example of anthropogenic acidification is related to the use of Urea in agricultural fields. Urea is an important commercial source of N commonly used, particularly in Indonesia. Since it contains one of the major plant nutrients, the use of Urea is huge, and in greater amount than those of other major nutrients such as P and K. However, the use of Urea may cause acidification as seen chemically in **Eq. 6.2** and **Eq. 6.3**. The Urea molecule is hydrolyzed to produce carbon dioxide and ammonia molecules. The carbon dioxide molecules will then react with water molecules to produce H^+ ion as indicated by **Eq. 6.1**. After being protonated to be an ammonium ion, ammonia molecules will encounter nitrification to produce H^+ ions. This reactions change NH_4^+ to NO_2^- with *Nitrosomonas* as the oxidizing agent and of NO_2^- to NO_3^- with *Nitrobacter* as the oxidizing agent (Bartlett, 1981).

$$NH_2CONH_2 + H_2O \rightarrow CO_2 + 2\ NH_3 \quad \text{.......} \quad \text{Eq. 6.2.}$$

$$2\ NH_4^+ + 2\ O_2 \rightarrow NO_3^- + 2\ H^+ + H_2O \quad \text{.......} \quad \text{Eq. 6.3.}$$

These processes may eventually decrease the soil pH. A long term effect of the use of Urea on soil pH is shown in **Table 6.2**. The soil pH is shown to decrease with the increase in the amounts of Urea treatments. For example, a long-term use of Urea at 200 kg N ha^{-1} lowers the soil pH from 5.09 to 4.66. Greater decrease occurs when the Urea treatment is done in the field with intensive soil tillage.

Table 6.2. The decrease in soil pH as affected by long-term use of Urea in some soil tillage systems conducted in Lampung Indonesia$^{1)}$.

Soil Tillage	Urea N (kg ha^{-1})		
	0	100	200
Intensive Soil Tillage	5.03	4.83	4.44
Minimum Soil Tillage	5.18	4.96	4.78
No Tillage	5.06	4.89	4.75
Average	5.09	4.89	4.66

$^{1)}$Adapted from Salam et al. (1998c)

According to Boulman et al. (1995), the decrease in soil pH with Urea treatment is attributed to two reasons: (a) the production of H^+ ions due to Urea hydrolysis and (b) the decrease in exchangeable Ca and Mg due to the replacement by NH_4^+. The decrease in soil pH due to long-term application of Urea has been reported to increase the soil exchangeable Al and Al saturation and also to decrease the exchangeable Ca and Mg (Schroder et al., 2011). Because Al^{3+} is a potential source of acidity, this condition will worsen the soil pH. However, Boulman et al. (1995) reported that the decrease in pH by Urea treatment was lower than that by the use of ammonia (NH_3.

In some cases, soil acidification may also happen intentionally in response to the need of agriculture management. For example, soils in the pineapple plantations owned by PT Great Giant Pineapple in Central Lampung, Indonesia, are acidified by using sulfur powder to manage particular plant deseases at low pH. This practice has acidified the soils to relatively low values (Salam et al., 1999e).

As mentioned in Salam (2014), one example of alkalination is liming, which may significantly increase the soil pH (Barber, 1981; 1984; Kamprath, 1984; Thomas and Hargrove, 1984; Liu et al., 2004). The liming materials may encounter a series of chemical reactions in soil water and may end with the increase in soil pH. For example, $CaCO_3$ in soil water may dissociate to form Ca^{2+} and CO_3^{2-} ions. Ca^{2+} ions will displace exchangeable H and Al attached to the soil colloid surfaces, while CO_3^{2-} ions will react with water molecules to form HCO_3^- and OH^-. OH^- ions will neutralize H^+ and Al^{3+} ions to form water and $Al(OH)_3$ precipitates. The decrease in H^+ and Al^{3+} ions will then increase the soil pH. Dolomite (($CaMg(CO_3)_2$) is also a popular liming material, that has another benefit due to its Mg, which is also a major element in the soil environment. The chemical reactions of liming with calcite and dolomite are shown by **Eq. 6.4** and **Eq. 6.5**, respectively.

$$\mathbf{CaCO_3 \leftrightarrow Ca^{2+} + CO_3^{2-}} \quad \text{.......} \quad \textbf{Eq. 6.4}$$

$$\mathbf{CaMg(CO_3)_2 \leftrightarrow Ca^{2+} + Mg^{2+} + 2\,CO_3^{2-}} \quad \text{.......} \quad \textbf{Eq. 6.5}$$

The Ca^{2+} and Mg^{2+} released from limes may displace exchangeable H and Al from the surfaces of soil solids and neutralize them to become HCO_3- and $Al(OH)_3$ through ion exchange and precipitation processes as described in **Eq. 6.6**, **Eq. 6.7**, **Eq. 6.8**, and **Eq. 6.9**.

$$\mathbf{X\text{-}2H + Ca^{2+} \leftrightarrow X\text{-}Ca + 2\,H^+} \quad \text{.......} \quad \textbf{Eq. 6.6}$$

$$\mathbf{X\text{-}2H + Mg^{2+} \leftrightarrow X\text{-}Mg + 2\,H^+} \quad \text{.......} \quad \textbf{Eq. 6.7}$$

$$\mathbf{X\text{-}2Al + 3\,Ca^{2+} \leftrightarrow X\text{-}3Ca + 2\,Al^{3+}} \quad \text{.......} \quad \textbf{Eq. 6.8}$$

$$\mathbf{X\text{-}2Al + 3\,Mg^{2+} \leftrightarrow X\text{-}3Mg + 2\,Al^{3+}} \quad \text{.......} \quad \textbf{Eq. 6.9}$$

where X is the negatively charged surface of soil solids. Al^{3+} ions may finally be hydrolyzed and the resulted H^+ ions are neutralized by CO_3^{2-} forming bicarbonate ions (HCO_3^-) as shown in E**q. 6.10** and **Eq. 6.11**

$$\mathbf{Al^{3+} + 3\,H_2O \leftrightarrow Al(OH)_3 + 3\,H^+} \quad \text{.......} \quad \textbf{Eq. 6.10}$$

$$\mathbf{H^+ + CO_3^{2-} \leftrightarrow HCO_3^-} \quad \text{.......} \quad \textbf{Eq. 6.11}$$

Through the series of the above chemical reactions, calcite and dolomite may finally increase the soil pH. By these reactions, the active source of acidity (soluble H^+) and the potential source of acidity (Exchangeable H and Al) are neutralized and the soil pH increases.

The effect of liming on soil pH is different depending upon some soil properties. Among these factors, the soil buffering capacity and all factors affecting this chemical property such as soil texture are of great importance and must be understood. Clay soils in most cases show greater buffering capacities towards pH. Therefore, clay soils need more lime materials that do sand or sandy soils to increase the soil pH. For example, to increase soil pH 1 unit higher from 4.5 to 5.5 only 1 ton ha^{-1} lime is needed for sand soil, but as high as 3 ton ha^{-1} is needed by a sandy loam soil to satisfy the increase. Organic soils need more lime to increase 1 unit pH from 4.5 to 5.8 (**Table 6.3**). Soil organic matter is another soil factor important to consider, since it can chelate Al^{3+} to be exchangeable Al (Hargrove and Thomas, 1981).

Table 6.3. Estimated lime requirements for soils of different textures[1].

	Soil Texture	Lime (ton ha^{-1})
1	Sand	1
2	Sandy Loam	2
3	Clay Loam	4
4	Organic Soils (*Peat*)	8

1)Singer and Munns (1987), **To raise pH from 4.5 to 5.5

To set the soil pH to a desired value by lime, the amount of lime must be previously determined. There are several methods available to calculate or estimate the amount of lime to be added to raise the soil pH (Liu et al., 2004). One of the methods that may determine the lime needed to raise the soil pH is by a direct titration of particular soils (Liu et al., 2004). To conduct this, soil sample is treated with an increasing levels of a particular lime. After a thorough mixing the limed soil is moistened and incubated for a particular time span, usually 1 week. The amount of lime is determined based on the curve developed with pH as the Y axis and the level of lime in the X axis (Salam, 2000; Liu et al., 2004). In their experiment, Liu et al. (2004) found that the soil pH as a function of added base or lime was linear the pH range of 4.5 to 6.5, therefore, it was possible to determine the slope of the relationship by regression analysis using a minimum number of base additions. An example of this curve is depicted in **Fig. 6.1**.

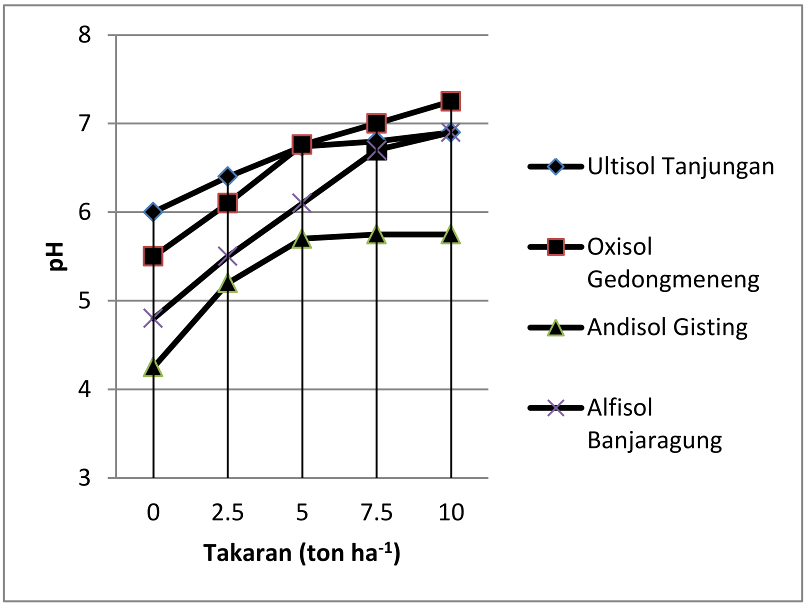


Fig. 6.1. Direct titration of several tropical soils from Lampung, Indonesia, with calcite (Salam, 2000).

The titration may show different pattern of curves depending on the soil types. As shown in **Fig. 6.1**, the initial soil pH for soil increases as follows: Andisol Gisting, Alfisol Banjaragung, Oxisol Gedongmeneng, and Ultisol Tanjungan. The amounts to raise the soil pH to a particular value are also different. For example, using the curve in **Fig. 6.1**, the prediction of lime requirement to raise the soil pH to 6.0 is about 0 ton ha^{-1} for Ultisol Tanjungan < 2.5 ton ha^{-1} for Oxisol Gedongmeneng < about 5 ton ha^{-1} for Alfisol Banjaragung. The pH value of 6.0 for Andisol Gisting is impossible to reach because the related curve is already stagnant at pH about 5.7 at lime addition or more than 5 ton ha^{-1}.

There is a great deal of limes available in the market. These lime materials may include among which are Calcite ($CaCO_3$), $Ca(OH)_2$, and dolomite ($CaMg(CO_3)_2$), that show different effectiveness in enhancing soil pH and lowering heavy metal solubility. One indicator that may show the lime effectiveness is the percent recovery of heavy metals from soils treated with lime. Salam et al. (1999g) observed the percent recovery of Cu, Cd, Zn, and Mn introduced into some tropical soils including Ultisols, Oxisols, and Alfisols. Percent recovery is calculated by **Eq. 6.12**. The data obtained are given in **Table 6.4**.

Table 6.4. The percent recovery of Cu and Cd in some tropical soils treated with Several lime materials[1)].

Soil Order	Lime[2)]	Cu	Cd
		.... %	
Ultisols	Control	49.8	147
	$CaCO_3$	27.5	131
	$Ca(OH)_2$	26.7	128
	$CaMg(CO_3)_2$	37.0	133
Oxisols	Control	24.4	60.3
	$CaCO_3$	14.5	49.0
	$Ca(OH)_2$	15.0	42.8
	$CaMg(CO_3)_2$	21.9	56.8
Alfisols	Control	19.1	48.8
	$CaCO_3$	10.8	46.9
	$Ca(OH)_2$	9.50	31.7
	$CaMg(CO_3)_2$	15.8	39.6

[1)]Adapted from Salam et al. (1997g); [2)]Lime given at rate equivalent to 5 ton $Ca(OH)_2$

$$\text{Rec (in \%)} = M_{x1} - M_{x0}/M_x\ 100 \quad \ldots\ldots \quad \text{Eq. 6.12}$$

where Rec is heavy metal recovery in percent, M_{x1} is the extracted heavy metal in soil treated with lime x and spiked with the related heavy metal, x is either $CaCO_3$, $Ca(OH)_2$, or $CaMg(CO_3)_2$, M_{x0} is the extracted heavy metal in soil treated with lime but not spiked with the related heavy metal, and M is the amount of heavy metal added into the soil, which in this experiment equals to 10 mg kg^{-1}.

The degree of heavy metal recovery in **Table 6.4** suggests that parts of the heavy metals added were strongly adsorbed by the soil solids. Based on the recovery values, the order of the soil adsorption capacities with respect to Cu, Cd, and Zn followed the order of: Alfisols > Oxisols > Ultisols and the soil preference towards the heavy metals generally followed the order of: Cu > Cd > Zn. In General, ($CaCO_3$) and $Ca(OH)_2$ are more effective than is $CaMg(CO_3)_2$ in lowering heavy metal in all soils.

6.2 Effect of Soil pH

The shifting in soil pH as affected by any of the above reactions and many other reactions will drive the changes in the the soil adsorptive capacity towards heavy metals. A great deal of experimental researches focusing on this soil-heavy metal behavior in the environment have been reported (Forbes et al., 1976; Cavallaro and McBride, 1980; Kuok and Baker, 1980; Train and Downer, 1985; Salam, 1993a; 1993b; Salam and Maswah, 1994; Salam, 1995a; 1995b; Salam et al., 1996; Salam et al., 1997a; 1997e; 1997f; 1997g; 1997h; 1997l; 1997m; Salam et al., 1998a; 1998e; 1998j; Salam, 1999; Salam et al., 1999c; 1999f; 1999i; Salam, 2000; Salam et al., 2000; Salam, 2001; Bang and Herter erg, 2004; Kukier et al., 2004; Salam et al., 2005; and Stehouwer et al., 2006). The results confirmed the predicted relationship. The labile heavy metal fractions in the soil environment are in general decrease with the increase in soil pH. He and Singh (1994), for example, observed that the DTPA and NH_4NO_3-extractable Cd decreased with the increases in soil pH. Kuo and Baker (1980) reports that the reduction in heavy metal adsorption at higher pH levels was attributed to the formation of metal-organic complexes. They revealed that soil CEC play an important role in the adsorption process of heavy metals in soils. While Ziper et al. (1988) suggests that CEC alone is not the only variable determined the Cd adsorption behavior. The strength of Cd adsorption is also dependent on the charge density. The highest charge density solids desorbed the least of Cd.

The decrease in the soil heavy metals in several tropical soils spiked with Zn, Cu, Mn, and Cd at 10, 10, 10, and 5 g kg^{-1}, respectively, by lime treatment is given in **Table 6.5**. The magnitude of the decrease indicates the soil adsorption capacity. The data shows that the adsorption capacity of the four soil decreases following the order: Soil of Banjaragung (Alfisols) > Soil of Gedongmeneng (Oxisols) > Soil of Tanjungan (Ultisols). The adsorption capacity of soil of Gisting (Inceptisols) is actually high, but is not manageable by lime.

Table 6.5. The average decrease in extracted heavy metals in some tropical soils by lime treatment[1].

Lime Treatment	Soil	Zn	Cu	Cd	Mn
ton ha^{-1}		%[2]			
0	Tanjungan	43.4	46.1	31.1	31.7
	Gedongmeneng	17.4	10.7	46.3	37.4
	Banjaragung	33.0	32.1	31.0	21.0
	Gisting	(-) 92.3	(-) 187	(-) 196	24.3
10	Tanjungan	34.0	41.0	11.6	24.8
	Gedongmeneng	1.11	24.7	18.5	32.1
	Banjaragung	17.1	34.3	19.5	18.1
	Gisting	(-) 85.2	(-) 129	1.05	(-) 49.9

[1] After Salam (2000); [2] Calculated as follows: $[\{M_0 - (SM_x/3)\}*100/M_0]$ where M_x is extracted heavy metals in soils treated with lime x; x includes $CaCO_3$, $Ca(OH)_2$, and $CaMg(CO_3)_2$ and M_0 is extracted heavy metals in unlimed soils.

Salam et al. (1997k) treated Alfisol from Banjaragung East Lampung Indonesia in a laboratory experiment with heavy metal containing waste at 0, 20, and 40 ton ha^{-1} and lime at 0 and 5 ton $CaCO_3$ ha^{-1}. Analysis of Cu shows that the soluble Cu extracted by DTPA, 1 M $CaCl_2$ as well as distilled water was in general lowered by lime treatment. The exchangeable Cu is observed to decrease the most significant. The increasing concentrations of Cu did not change the lowering effect of lime on the soluble Cu. These phenomena are shown in **Table 6.6** that clearly show that part of the water soluble Cu was shifted to the adsorption sites, part of the adsorbed Cu was shifted to stronger bonding energy. Therefore, the available Cu (DTPA extractable) was also lowered in limed soils. This suggests the importance of Option 2 in coping with the problem of heavy metal polluted soils by indirectly increase the soil adsorptive capacity to increase Cu retention.

Table 6.6. The effect of lime on the labile Cu fractions extracted by several extracting agents from soil of Banjaragung Lampung Indonesia$^{1)}$.

Waste	**Lime**	**H_2O**	**M $CaCl_2$**	**DTPA**
(ton ha^{-1})	(ton ha^{-1})	µg kg^{-1}	mg kg^{-1}	
0	0	50.2	0.57	3.00
	5	54.3	0.15	1.79
20	0	74.2	1.03	49.2
	5	50.0	0.13	36.5
40	0	98.3	0.90	82.5
	5	54.2	0.24	61.4

$^{1)}$Adapted from Salam et al. (1997k)

Salam et al. (1998a) also added organic matter in the form of cassava-leaf compost to the above experimental unit (Salam et al., 1997k) at 0, 5, 10, and 20 ton ha^{-1} and measured the changes in Cd concentrations after a one month incubation at field capacity moisture content. The effect of lime in lowering Cu concentrations was also observed, independent of the soil types and the organic matter treatment levels. The difference was that the concentrations of Cd were measured much lower at higher cassava-leaf compost treatment particularly at lower lime levels. The phenomena are shown in **Table 6.7**.

Salam et al. (1998f) also report a similar behavior of Zn in the same soils of Tanjungan, Gedongmeneng, and Banjaragung (**Table 6.8**). They observed that the soluble and exchangeable Zn as extracted by water and 2 N $CaCl_2$, respectively, decreased with liming in relation to the increase in soil pH. As shown in **Table 6.8**, the Δ (Soluble Zn) and Δ (exchangeable Zn) are generally negative, indicating the shifting of soluble and exchangeable Zn to stronger bondings with liming, probably by adsorption or precipitation processes at higher pH. A similar pattern was also observed for Cu in the same soils as reported previously by Salam et al. (1997k) The changes in labile Cu as affected by lime in some tropical soils are given in **Table 6.9**.

Table 6.7. The effect of lime and organic compost on the labile fractions of Cd in several tropical soils from Lampung Indonesia$^{1)}$.

Lime	**Compost**	**Tanjungan**	**Gedong-meneng**	**Banjar-agung**
(ton ha^{-1})	(ton ha^{-1})	mg kg^{-1}		
0	0	5.45	4.42	4.45
	5	5.22	4.15	3.80
	10	5.05	4.10	4.95
	20	4.82	3.93	3.70
2.5	0	4.78	4.11	3.80
	5	4.70	3.86	3.69
	10	4.66	3.80	3.58
	20	4.25	3.51	3.45
5	0	4.41	3.70	3.65
	5	4.46	3.52	3.55
	10	4.50	3.45	3.42
	20	4.70	3.62	3.25
10	0	4.50	3.25	2.90
	5	4.40	3.55	2.88
	10	4.35	3.50	2.90
	20	4.65	3.45	2.87

^{1})Adapted from Salam et al. (1998a); Lime as $CaCO_3$ and organic compost as cassava-leaf compost

Observation in the root zone of several weeds also showed the negative effect of lime at 4 ton ha^{-1} on the measured Pb in soil spiked with 20 mg Pb ha^{-1} (**Table 6.10**). The decrease in the measured Pb by liming were consistent in the root-zone of pigweed (*Amaranthus spinosus*), green kyllinga (*Cyperus kyllingia*), alang-alang (*Imperata cylindica*), and also amaranth (*Amaranthus tricolor*) (Salam et al., 1997i; Sriyani and Salam, 1998). However, the measured Pb in the root zone of alang-alang was the lowest, related to the highest pH in the root zone of alang-alang than in the other weed plants.

Table 6.8. The changes in the labile fraction of Zn in some limed tropical soils[1)].

Compost	Waste	Δ (Soluble Zn)	Δ (Exch. Zn)
… ton ha^{-1} …		… % …	
Soil of Gedongmeneng:			
0	0	(-) 21.2	(-) 97.8
	20	(+) 33.8	(-) 89.2
	40	(-) 2.47	(-) 80.7
5	0	(-) 23.9	(-) 98.5
	20	(+) 39.2	(-) 85.1
	40	(+) 11.6	(-) 75.8
Soil of Banjaragung:			
0	0	(-) 5.01	(-) 100
	20	(-) 25.5	(-) 87.2
	40	(-) 10.0	(-) 82.8
5	0	(-) 9.00	(-) 98.7
	20	(+) 29.1	(-) 90.1
	40	(+) 9.32	(-) 79.4
Soil of Cihea:			
0	0	(-) 21.8	(-) 100
	20	(+) 26.0	(-) 94.6
	40	(-) 2.78	(-) 85.2
5	0	(-) 19.6	(-) 100
	20	(+) 20.8	(-) 90.8
	40	(-) 3.24	(-) 81.8

[1)] Adapted from Salam et al. (1998f); Δ Zn = (Extracted Zn in lime soils – Extracted Zn in the related unlimed soils)

Table 6.9. The changes in the labile fraction of Cu by some limed tropical soils$^{1)}$.

Compost	Waste	Δ (Soluble Cu)	Δ (Exch. Cu)
… ton ha^{-1} …		… % …	
Soil of Gedongmenergy:			
0	0	(-) 46.1	(-) 53.3
	20	(-) 34.7	(-) 76.6
	40	(-) 27.1	(-) 70.9
5	0	(-) 24.6	(-) 85.0
	20	(-) 36.0	(+) 51.1
	40	(-) 23.9	(+) 83.8
Soil of Banjaragung:			
0	0	(-) 55.0	(-) 72.4
	20	(-) 26.8	(-) 86.7
	40	(-) 27.2	(-) 74.2
5	0	(-) 52.4	(+) 13.9
	20	(-) 29.7	(-) 28.4
	40	(-) 24.5	(-) 37.7
Soil of Cihea:			
0	0	(-) 11.7	(-) 27.9
	20	(-) 19.8	(-) 26.1
	40	(-) 11.6	(-) 34.9
5	0	(+) 7.09	(-) 45.9
	20	(-) 12.5	(-) 37.2
	40	(-) 13.7	(-) 34.8

$^{1)}$Adapted from Salam et al. (1998f); Δ Cu = (Extracted Cu in lime soils – Extracted Cu in the related unlimed soils)

Table 6.10. The effect of lime on the measured pH, Pb, and Cu in a Pb spiked Oxisol from Lampung Indonesia[1).

Weeds/Plant	Treatment	pH	Measured Pb (mg kg^{-1})	Measured Cu (mg kg^{-1})
Alang-Alang	Control	6.25	0.19	0.44
	+ Pb	6.16	1.27	0.68
	+ Lime	6.72	1.15	0.70
Green Kyllingia	Control	5.64	0.50	1.13
	+ Pb	5.44	7.20	1.38
	+ Lime	6.34	6.76	1.30
Pigweed	Control	5.01	0.74	0.69
	+ Pb	4.65	7.72	0.59
	+ Lime	5.09	6.25	0.57
Amaranth	Control	5.03	1.13	1.00
	+ Pb	5.19	8.13	0.99
	+ Lime	6.35	1.24	1.00

1)Adapted from Salam et al. (1997i) and Sriyani and Salam (1998)

The measured free ionic Cu^{2+}, Cd^{2+}, and Zn^{2+} also showed the effect of long term treatment of lime (Salam, 1993a). The concentrations of these free ionic elements in the limed soils were lower than those in the unlimed soils. In accordance with some other findings, the concentrations of these heavy metal cations were in good correlation with the soil pH. The concentrations of free Cu^{2+}, Cd^{2+}, and Zn^{2+} increased with the increase in soil pH with correlation coefficient (r) 0.90, 0.89, and 0.90, respectively.

The effect of lowering heavy metals by liming may induce the improvement of plant growth in heavy metal polluted soils as shown previously in **Fig. 5.6**. The plant height of corn was inhibited by the presence of high concentration of heavy metals in soil of Sri Bawono East Lampung Indonesia (Alfisols). Treatment with lime was observed to significantly improve the plant height of corn. The obvious reason is related to the decrease in heavy metal concentration by liming. Other reasons like the improvement of soil fertility related to the increase in soil pH are probable. The improvement in corn growth as seen from plant height is more significant when organic matter was also added. The organic matter may provide abundant functional groups that may increase the soil adsorptive capacity. With liming, these organic matters may increase the soil adsorptive capacity much more significantly. Thereby, the heavy metal concentration may decrease much more significantly and cause the better growth of corn. A comparison of corn height after 5 weeks is shown in **Fig. 6.2**.

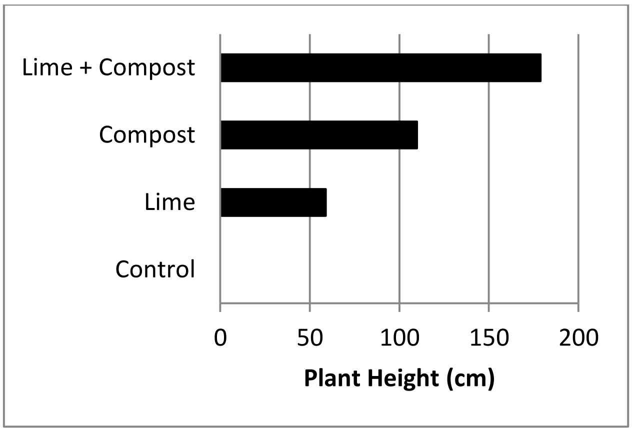


Fig. 6.2. The effect of lime and cassava-leaf compost on corn growth in heavy metal polluted soil of Sri Bawono East Lampung Indonesia (Adapted from Salam et al., 1999g)

A similar phenomenon was observed in soil of Sidosari South Lampung treated with the metal-spoon industrial waste, lime, and organic compost **(Table 6.11**). The industrial waste did not affect the plant height but increase it when the soil was also treated with lime and organic compost. However industrial waste decreases the production of corn. The corn production increased when soil was also treated with lime. This trend is related to the increase in soil pH and the decrease in Cu availability in soil.

Salam et al. (1999b) showed that the concentrations of Cu and Zn from a model waste were higher in spinach shoot that that in corn shoot. The Cu content decreased with lime or cassava-leaf compost treatment. The effect of lime on the concentration of shoot Cu is shown in **Table 6.12**.

Table 6.11. The effect of industrial waste, organic compost, and lime on corn plant height and production1).

Soil Treatment	Industrial Waste (ton ha^{-1})		
	0	15	60
Plant Height (cm):			
Control	205	205	207
+ Compost	213	224	201
+ Lime	205	214	214
+ Compost + Lime	221	230	225
Plant Production (kg plot^{-1}):			
Control	10.6	9.60	7.71
+ Compost	9.50	9.00	9.52
+ Lime	9.00	11.5	11.60
+ Compost + Lime	9.03	9.50	11.52

1) Adapted from Salam et al. (Salam et al., 1998h)

Table 6.12. The effect of lime on the accumulation of Cu in corn shoots grown in Alfisol Banjaragung1).

Lime Treatment	Model Waste2)	Industrial Waste3)
ton $CaCO_3$ ha^{-1}	μg kg^{-1}	
Spinach:		
0	55.0	4.34
2.5	12.1	5.11
5	8.11	0.51
Corn:		
0	0.31	0.51
2.5	0.01	2.11
5	0.08	0.81

1) Adapted from Salam et al. (1999b), 2) containing Cu, Zn, and Pb 10 mg kg^{-1}, and Cd 5 mg kg^{-1}; 3) at 80 ton metal-spoon industrial waste ha^{-1}.

The effectiveness of lime and/or compost in ameliorating the effect of heavy metals in soils of Banjaragung and Gedongmeneng planted with corn was also reported by Salam et al. (1999g). The growth of corn was depressed by heavy metals of a model waste containing Cu, Zn, Pb, and Cd at 40, 40, 40, and 20 mg kg^{-1}, respectively. The negative effect of these metal elements was attenuated by lime and/or cassava-leaf compost at 10 and 10 ton ha^{-1}, respectively. This phenomenon is demonstrated by data on the root and shoot weight of corn as depicted in **Table 6.13**. However, a Cu and Zn containing industrial waste showed little effect on the growth of corn (**Table 6.14**)

Table 6.12. The effect of cassava-leaf compost on the accumulation of Zn in corn shoot grown in Alfisol Banjar agung$^{1)}$.

Compost Treatment	**Model Waste$^{2)}$**	**Industrial Waste$^{3)}$**
ton $CaCO_3$ ha^{-1}	μg kg^{-1}	
Amaranth:		
0	55.2	11.1
5	44.1	10.3
10	40.1	8.4
Corn:		
0	0.21	0.62
5	1.51	0.60
10	0.08	0.00

$^{1)}$Adapted from Salam et al. (1999b), $^{2)}$containing Cu, Zn, and Pb 10 mg kg^{-1}, and Cd 5 mg kg^{-1}; $^{3)}$at 80 ton metal-spoon industrial waste ha^{-1}.

Salam et al. (1999i) shows that the growth of amaranth in soil of Sidosari (Ultisol) was depressed by metal-spoon industrial waste. This observation indicates the negative effect of heavy metals contained in the waste particularly Cu and Zn. The growth of amaranth was also depressed by the same industrial waste in field experiment in soil of Sri Bawono (Alfisols). The treatment with lime ($CaCO_3$) and/or cassava-leaf compost was shown to significantly decrease the negative effect. Unlike that in soil of Sidosari, the growth of amaranth in soil of Banjaragung was significantly elevated by the presence of lime or compost and much better in the presence of both lime and compost. These phenomena are shown in **Table 6.15**.

Table 6.13. The effect of lime and cassava-leaf compost on growth of corn in a model waste heavy metal contaminated soils of Lampung Indonesia1).

Soil Treatment	Root Dry Weight	Shoot Dry Weight
	g plant^{-1}	
Soil of Banjaragung:		
Control	0.90	1.80
+ Waste	0.60	1.20
+ Waste + Compost	0.65	1.80
+ Waste + Lime	0.40	2.20
+ Waste + Compost + Lime	0.90	2.20
Soil of Gedongmeneng:		
Control	0.65	2.40
+ Waste	0.45	1.65
+ Waste + Compost	0.60	2.35
+ Waste + Lime	0.60	2.10
+ Waste + Compost + Lime	0.60	2.45

1)Adapted from Salam et al. (1999g)

Table 6.14. The effect of lime and cassava-leaf compost on the growth of corn in soil treated with a Cu and Zn containing industrial waste1).

Soil Treatment	Root Dry Weight	Shoot Dry Weight
	g plant^{-1}	
Soil of Banjaragung:		
Control	0.90	1.80
+ Waste	0.95	2.10
+ Waste + Compost	0.95	2.50
+ Waste + Lime	1.00	2.30
+ Waste + Compost + Lime	1.15	2.40
Soil Of Gedongmeneng:		
Control	0.65	2.40
+ Waste	0.50	2.15
+ Waste + Compost	0.70	2.70
+ Waste + Lime	0.75	2.15
+ Waste + Compost + Lime	0.50	1.95

1)Adapted from Salam et al. (1999g)

Table 6.15. The effect of lime and/or compost on the field growth of amaranth in heavy metal containing waste treated soils of Lampung Indonesia[1).]

Observation Time	Treatment			
	Control	Lime	Compost	Lime + Compost
… week …	……. cm …….			
Soil of Sri Bawono:				
2	0	1.5	1.4	1.6
3	0	14.8	7.5	21.9
4	0	37.3	20.5	50.0
5	0	57.1	54.2	68.3
Soil of Sidosari:				
2	1.5	1.4	1.4	1.6
3	1.9	2.5	6.0	5.0
4	5.1	3.9	15.1	10.1
5	7.8	5.1	22.1	14.2

1)Adapted from Salam et al. (1999i); waste at 15 ton ha^{-1}

The relationship between soil pH, available Pb, and absorption of Pb in an Ultisol from Gedongmeneng Bandar Lampung Indonesia treated with a Pb containing electronic industrial waste planted with corn is reported by Salam et al. (1998g), as shown in **Table 6.16**. The DTPA extracted Pb in soil was linearly enhanced by the waste addition, about 0.89 mg kg^{-1} in control treatment to about 1.65 g kg^{-1} in soil treated with waste at rate of 40 ton ha^{-1}. The presence of lime significantly decreased the extracted Pb, particularly at waste treatment rate of > 10 ton ha^{-1}, related to the increase in soil pH caused by liming. Liming also caused the decrease in Pb intake by plant. The Pb intake was, however, decreased with waste treatment. This phenomenon is caused by the increase in pH caused by waste addition.

Table 6.16. The relationship between the extracted and the uptake of Pb and pH in soil treated with Pb containing waste[1].

Waste (ton ha^{-1})	pH		Extracted Pb		Absorbed Pb	
	Ulimed	Limed	Unlimed	Limed	Unlimed	Limed
			mg kg^{-1}		ng plant^{-1}	
0	5.71	6.90	0.89	1.12	78.8	155
10	5.92	7.11	1.21	1.22	117	78.1
20	6.29	7.32	1.45	1.23	60.0	43.0
40	6.91	7.39	1.65	1.60	90.0	40.0

[1] After Salam et al. (1998g)

All the above findings support the use of Option 2 in coping with the heavy metal in the soil environment, i.e. to indirectly increase the soil adsorptive capacity towards heavy metals indirectly by increasing the soil pH. One of the methods to increase the soil pH is liming. However, this method does not apply to all soil types. One exception was reported in an andic soil for Cu and Zn by Salam et al. (1997j).

The DTPA extracted Pb and Cd from Andisol from Gisting Lampung Indonesia spiked with 10 mg kg^{-1} Cu, Zn, Pb and 5 mg kg^{-1} Cd decreased with the increase with in soil pH as those occurred in soils of Banjaragung, Cihea, and Gedongmeneng (Salam et al., 1998g; 1998h; 1999g). However, the extracted Cu and Zn were increased by lime (Salam et al., 1997j. These phenomena are depicted in **Table 6.17**.

The metastable property of allophane mineral in Andisol may have caused these phenomena. The stability of allophane is very sensitive to the changes in soil pH. Paterson et al. (1991) show that the pH ranges for the stability of this mineral is very narrow and narrower with the decrease in Al^{3+} activity. For example, at Al^{3+} activity of 10^{-8} M allophane is stable in the pH range 5.5 – 6.5. This range in narrower at Al^{3+} activity < 10^{-8} M. Therefore, it was probable that the increase in soil pH caused by liming has caused the allophane destruction and lowered the adsorption capacity of allophane towards Cu and Zn. As a result, it decreases the adsorption of Cu and Zn at higher pH.

Table 6.17. The effect of lime on the DTPA extracted Cu, Zn, Pb, and Cd in Andisol Gisting Lampung Indonesia$^{1)}$.

Lime	pH	Cu	Zn	Pb	Cd
(ton ha-1)		mg kg-1			
0.0	4.24	2.03	4.11	5.61	3.41
2.5	4.49	2.37	5.46	4.95	3.23
5.0	5.05	2.62	5.68	4.28	3.06
10.0	5.94	3.52	6.66	3.79	2.65

$^{1)}$Adapted from Salam (1997c) and Salam (1997j)

6.3 Effect of P-fertilizers

As pointed out in Salam (2014), other than the addition of organic matter and/or lime, heavy metals in the soil environment can also be attenuated by employing some other materials and processes. Phosphatic rocks and phosphatic fertilizers may be used through adsorption of heavy metals by phosphatic substances or precipitation to be phosphatic secondary minerals (Rabinowitz, 1993; Ruby et al., 1994; Ma et al., 1993; 1994; 1995; Brown et al., 2004; 2009; Moseley et al., 2008; Kilgour et al., 2008; and Richards et al., 2011). This phenomena have been reported by several soil workers. Norvell et al. (1987) observed that additions of P caused small decreases in the concentrations of Zn^{2+} and the divalent cations in soil solution of calcareous soils. He and Singh (1994) showed that unlike the high-Cd NPK fertilizer that increased the soil extractable Cd, addition of high Cd phosphatic rocks did not increase the soil Cd.

It was reported that the soil CEC is not only affected by soil pH but also by P-fertilizers. Several workers reported that phosphates may react with the soil colloids and may increase the soil adsorption capacity towards cations, including heavy metals cations (Saeed and Fox, 1979; Xie and McKenzie, 1990). Addition of 1 mmol pyrophosphate increased the soil CEC as high as 0.52 – 0.89 cmol$_c$ kg^{-1} (Xie and McKenzie, 1990). This process was related to increased Zn adsorption equivalent to 0.3 – 12% of the pyrophosphate induced increase in CEC. Therefore, plant roots were not able to absorb P and this reaction may induce deficiency symptom in plants (Friesen et al., 1980; Norvell et al., 1987). This process may result in the decrease of the availability of heavy metal micronutrients (Brown et al., 1970; Saeed and Fox, 1979; Kuo and McNeal,1984; and Xie and McKenzie, 1990).

The decrease may also be attributed to the increase in soil pH as affected by addition of P and the increase in soil CEC induced by pH increase. To a lesser extent, the use of P-fertilizer may also gradually increase the soil pH as shown in **Fig. 6.3**. The effect of P-fertilizer on soil pH can be explained by the dissolution of calcium phosphates, the minerals used to make commercial P-fertilizers. In the presence of water and H$^+$ ions, this mineral will dissolve to release Ca^{2+} ions, orthophosphates, and OH$^-$ ions as shown in the following reaction (**Eq. 6.13**).

$$Ca_3(PO_4)_2 + 2\ H_2O + 2\ H^+ \leftrightarrow 3\ Ca^{2+} + 2\ H_2PO_4^- + 2\ OH^- \quad \text{.......} \quad \textbf{Eq. 6.13}$$

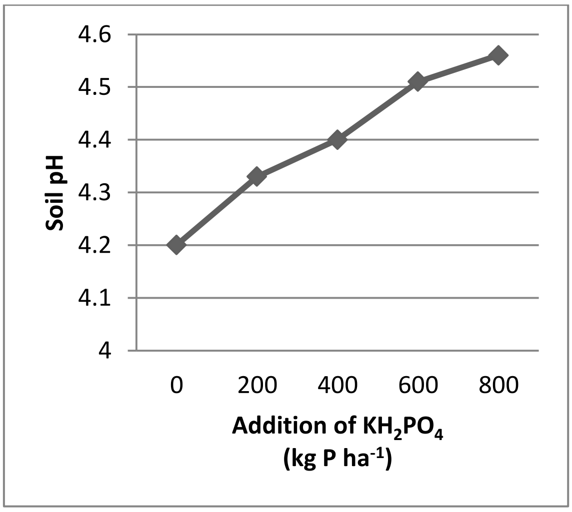


Fig. 6.3. The effect of P-fertilizer on soil pH (Adapted from Salam, 1997b).

This decomposition reaction consumes H^+ ions and produces OH^- ions; therefore, it increases the soil pH. In general, the higher the concentrations of H^+ ions or the lower the soil pH, the more intensive the decomposition of calcium phosphates, and also the higher the increase in soil pH. In some cases, it is also shown that the weathering of apatite (**Eq. 6.13**) and its related product like TSP, SP 36, and KH_2PO_4 treated into the soil environment may increase the soil pH (Salam, 1997b).

Salam (1997b) treated an Ultisol from Gunung Sugih Central Lampung Indonesia with KH_2PO_4 at rates ranging from 0 to 800 kg P ha_{-1} and/or lime at rates equivalent to 0 to 6 ton $CaCO_3$ ha^{-1} in a laboratory experiment. The DTPA extracted Cu and Mn were negatively correlated with P fertilizer additions that tended also to increase the soil pH (**Table 6.18**). The lime addition was observed to consistently decrease the extracted heavy metals. However, this pattern was most probably not due to the treatment of KH_2PO_4. Observations showed that P fertilizers reduces the extracted of metal element due to their liming effect on soil by increasing the soil pH (extracted heavy metals are highly correlated with soil pH), not to their phosphate component's reaction with soil surfaces. It was reported that the soil CEC is not the addition of P substances that may decrease the concentrations on heavy metals in the soil environment.

In fact, a great deal of reseaches reveal that phosphates decrease the solubilities of some heavy metals (Rabinowitz, 1993; Ruby et al., 1994; Ma et al., 1993; 1994; 1995; Nicholson et al., 1994; Brown et al., 2004; Kilgour et al., 2008; and Moseley et al., 2008;). McGowen et al. (2001) report that addition of phosphates of $(NH_4)_2HPO_4$ lowered the solubilities of Cd, Pb, and Zn due to metal-phosphate precipitation. For example, Pb-phosphates may form Chloropyromorphite ($Pb5_{(}PO_4)_3Cl$), Hydroxypyromorphite ($PB_5(PO_4)_3OH$), Fluoropyromorphite ($Pb_5(PO_4)_3F$), and Bromopyromorphite ($Pb_5(PO_4)_3Br$) (Ruby et al., 1994). McGowen et al. (2001) also report the retardation of Cd, Pb, and Zn in smelter-contaminated soils by diammonium phosphates. The presence of soluble phosphates increased the precipitation of these metal elements and, therefore, retarded their movement in the soils.

However, Moseley et al. (2008) states that even though the reduction in Pb bioaccessability with P amendments are technically possible, it requires large amendment masses to achieve relatively modest reductions in bioaccessability. These phenomena are sometimes also not good for plant nutrient menagement. Induced Zn deficiencies by P fertilization may limit the plant production (Bugbee and Frink, 1995).

Table 6.18. The relationship between the changes in the extracted heavy metal elements with soil pH and available P from KH_2PO_4[1].

P Treatment	pH	Avail. P	Fe	Mn	Zn	Cu
kg ha^{-1}		mg kg^{-1}		mg kg^{-1}/1000		
0	4.20	2.27	28.4	27.2	700	180
	5.44	2.53	22.7	16.7	780	180
	6.33	2.79	12.3	10.2	620	140
	7.07	2.00	11.6	9.34	460	100
		b[2]	- 6.42	- 6.49	- 8.43	- 27.9
		r^2	0.94	0.95	0.58	0.81
200	4.33	41.6	31.4	27.6	840	200
	5.32	36.3	21.0	15.5	540	160
	6.31	23.2	16.2	11.5	500	160
	7.02	23.2	9.20	7.72	540	100
		b[2]	-7.85	- 7.10	- 108	- 35.0
		r^2	0.98	0.93	0.65	0.97
400	4.40	91.1	33.0	29.9	720	200
	5.45	88.4	23.2	16.7	740	160
	6.30	59.5	14.5	11.5	680	120
	7.13	51.6	12.0	8.02	600	120
		b[2]	- 7.99	- 7.95	- 44.8	- 31.3
		r^2	0.96	0.94	0.72	0.91
600	4.51	142	38.8	29.4	680	200
	5.52	148	24.3	16.8	420	200
	6.39	137	15.3	11.7	560	120
	7.01	108	9.80	9.46	540	140
		b[2]	- 11.6	- 7.95	- 38.8	- 31.6
		r^2	0.99	0.94	0.16	0.69
800	4.56	224	40.9	28.9	820	240
	5.56	203	27.7	17.8	640	200
	6.43	161	15.9	11.3	520	160
	7.09	166	9.80	7.92	500	140
		b[2]	- 12.5	- 8.32	- 130	- 40.4
		r^2	1.00	0.98	0.95	1.00

[1] After Salam (1997b); [2] b indicate the gradient of M = a + b pH with M is the related extracted heavy metal.

Important questions

1. Explain the indirect effect of lime treatment on increasing the soil adsorption capacity towards heavy metals!
2. Explain the direct and the indirect effect of lime treatment on increasing the soil adsorption capacity towards heavy metals!
3. Explain the similarities of lime and phosphates in affecting the soil adsorption capacity towards heavy metals!
4. Explain the two master variables greatly affecting the soil chemical properties!
5. Explain the effect of pH on the soil adsorptive capacity towards heavy metals in the soil environment!
6. Explain several natural and anthropogenic reactions that lower the soil pH!
7. How do the root respiration and excretion decrease the soil pH? Explain!
8. How does the urea affect the soil pH? Explain!
9. In addition to the unintended soil acidification, there are practices that may change the soil pH. Give example(s) and explain!
10. Explain the difference between soil acidification and soil alkalization!
11. Explain the chemical reactions of lime like $CaCO_3$ and $CaMg(CO_3)_2$ in raising the soil pH!
12. Explain the method to determine the lime requirement to raise the soil pH to a particular value!
13. Explain the direct titration to determine the lime requirement of soils!
14. Explain the factors that may affect the lime requirements!
15. How does the soil texture affect the lime requirement? Explain!
16. Explain example of the effect of lime on the concentration of heavy metals in heavy metal polluted soils!
17. Explain several examples of the effect of lime and organic matter on the concentration of heavy metal in heavy metal polluted soils!
18. How are the effect of lime on the heavy metal concentration extracted by DTPA, $CaCl_2$, and Water? Explain!
19. How are the effects of lime and/or organic matter on the growth of plants in heavy metal contaminated soils? Explain!
20. Explain the two possibilities that may affect the increase heavy metal retention in P-treated soils!
21. Explain the indirect effect of phosphatic rocks in lowering the concentrations of heavy metals in the soil environment!

22. Explain the effect of P-fertilizers on the concentrations of heavy metals in the soil environment!

Chapter 7

Heavy Metal Movement and Translocation

Ulike the adsorbed and precipitated heavy metals, dissolved heavy metals that include free ions, complex ion, and chelates are relatively mobile in the soil environment. They move from one point to another point in any direction in the soil body through moistened or water saturated pore channels. The movement may cause heavy metal translocation to the soil depths and their distribution in the soil profile. When the movement is driven fast and intensive, the translocation and distribution may be fairly significant. This may happen when the movement of water through infiltration and percolation are relatively fast.

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However, when the soil water content is relatively low and no gravitational water is present, the heavy metals may move relatively slowly through mass flow and diffusion or through capillary movement from the soil depths to the surface of soils.

The rates of the water and heavy metal movement in the soil environment are directly dependent of soil physical and chemical properties and are probably indirectly on soil biological and microbiological properties. Among the important soil physical properties are soil pores, porosity, and pore-channels. Micro- and mesopores are important to retain water molecules in the soil system and, therefore, pore-distribution with high amounts of micro and mesopores may retain significant amounts of water. The presence of water may accumulate the soil water in the soil pore and improve the pore-channels containing water for heavy metal movement. High porosity and content of water like in the currently-tillaged soils may enable heavy metals to move faster through water saturated pore-channels. However, when the soil is dense, with low amounts of soil pores and pore-channels, the movement of heavy metals is probably inhibited. Therefore, in this situation the heavy metal movement and translocation is minimum.

Among the important soil chemical properties is the soil heavy metal retention capacity as expressed by the soil negative charges. The presence of high amount soil negative charges may inhibit the movement and translocation of heavy metals in the soil environment. The negative charges may attract the heavy metal cations. The attraction force is directly related to the magnitude of the soil CEC and the heavy metal charges. Higher soil CEC may cause the higher attraction of soil solids towards the heavy metal cations. Higher heavy metal oxidation number may cause stronger heavy metal attraction onto the soil solids. For example, the attraction of montmorillonite on Pb^{2+} is higher than the attraction of kaolinite with low CEC to Pb^{2+}. This fact may inhibit the movement of heavy metal cations. Therefore, the movement of Pb^{2+} is strongly inhibited by the negatively charged pore channels. The inhibition is also stronger at high pH since the soil solid negative charges may increase with the increase in soil pH (Helling et al., 1964; Trehan and Sekhon, 1977; Elliott, 1983; Tan and Dowling, 1984; McGrath et al., 1988; Alloway 1990b; Parfitt et al., 1995; Rodella et al., 1995; Medonca and Rowel, 1996; Tack et al., 1996; Suryanto and Susetyo, 1997; Choi et al., 1999; Tokunaga et al., 2003; Quaghebour et al., 2005; Schroder et al., 2008; and Gagnon et al., 2013;).

Among the important soil biological and biochemical properties is the microbial biomass and activity as well as the soil enzymatic activities. These soil biological and biochemical properties are related to the fast decomposition of soil organic matters that may provide a great amount of organic sources of negative charges important to immobilize heavy metal cations. Good soils with good microbial biomass and activities, and thus provide high activities of soil enzymes, may immobilize heavy metals cations much better. Soil with these properties may definitely retard the movement and translocation of heavy metal in soil body and may lower the potential of ground water contamination and pollution.

The movement of heavy metal in the soil system can be beneficial and unbeneficial. The benefit is obvious for the essential elements for plant. The heavy metals must move from the bulk soil to the surface of plant roots that may occur through heavy metal mass flow and/or heavy metal diffusion. The immobilization of heavy metals by soil solids is temporally, to avoid their leaks to the ground water through leaching processes. When the concentrations of dissolved cations decrease, part of the immobilized heavy metals may release the soil water. In contrast, when the heavy metal micronutrients in the soil water due to some reasons increase, part of the dissolved heavy metal micronutrient is temporally immobilized. By this mechanism, the micronutrients are safe for plant root absorption.

The movement and translocation of heavy metals are considered not beneficial for heavy metal elements that are considered toxic to the living things. The rule is to lower the dissolved heavy metals as low as possible to avoid their movement in the pore-channels. This means that the major part of the soluble heavy metal must be immobilized. As previously stated, among the heavy metals considered toxic are Hg, Pb, Cd, and Cr. The micronutrient elements that include Fe, Mn, Zn, Cu, and Co are also considered toxic when their concentrations in the soil environment are high. Since most of the elements must be immobilized, efforts must be conducted to increase the soil capacity of heavy metal retention so that the dissolved heavy metals are low and their movement and translocation in the soil body are highly inhibited. By this mechanism, the contamination and pollution of the soil water and ground-water may be avoided.

7.1 Mechanisms of heavy metal movement in soils

Dissolved heavy metals in the soil water that include the free ionic form of heavy metals, heavy metal complexes, and heavy metal chelates, are prone to movement by or through water. Above saturated condition, these heavy metal forms are subject to movement of the percolating water. The movement may reach the soil depth depending on several factors that affect the infiltration and percolation rates. The faster rates may cause the faster and deeper movement of heavy metals. Of course, the movement is also affected by the soil pores, soil pore-size distribution, and the soil-pore channels. Soil macropores and good soil pore channels may stimulate the heavy metal movement and translocations (Luo et al., 2010b). The movement of water and heavy metals may also reach the ground water and cause contamination and pollution.

The amount of heavy metal transported by the percolating water is simply calculated by multiplying the amount of water influx through percolation and the concentration of heavy metals in the percolating water. The transported of heavy metals may be calculated by **Eq. 7.1**.

$$\mathbf{Q = V.C} \quad \ldots\ldots. \quad \textbf{Eq. 7.1}$$

where Q is the amount of particular heavy metal transported to the ground water, V is volume of water transported, and C is the concentration of each heavy metal. The degree of Q is theoretically easy to calculate but it is practically difficult to estimate. However, this formula is very useful to understand that the environment pollution by heavy metals is speeded by the increase in concentration of heavy metal in soil water (C) and by the increase in water percolation rates. Therefore, land application of heavy metal containing waste water is potential for ground water contamination and pollution.

Under unsaturated conditions, heavy metals may move through two major mechanisms i.e. Mass Flow and Diffusion. The presence of interconnected pore water is very important as water channels than enable the heavy metal movement. The pore channels may inhibit the movement of heavy metals when an unconnected pore-water is present. In addition to this soil physical property, tortuosity is also important and determines the rate of heavy metal movement. Tourtosity is related to the length of pore channels. Higher soil tortuosity may cause longer pathway for heavy metal movement which means longer time of heavy metal movement.

Mass flow is a process of heavy metal movement with the movement of water mass. Mass flow is therefore controlled by the water pressure gradient. Water may move from high pressure to lower pressure regions. In the case of plant rooting zones, mass-flow may occur from the bulk soil to the surface of plant roots. In this case, the rates of mass flow is determined by several factors: (a) Concentration of Heavy metal in soil water, (b) the need of plants with respect to the related heavy metals, (c) the rate of water absorption by plant roots, and (d) the rate of water transpiration. The rates of heavy metal movement is higher when: (a) the concentration of heavy metals in soil water is relatively high, (b) plant need of the element is relatively high, (c) the uptake rate of water by plant roots is relatively high, and (4) the transpiration rate is relatively high and may stimulate the higher water absorption by plant roots. The mass flow of heavy metal element is shown in **Fig. 7.1**.

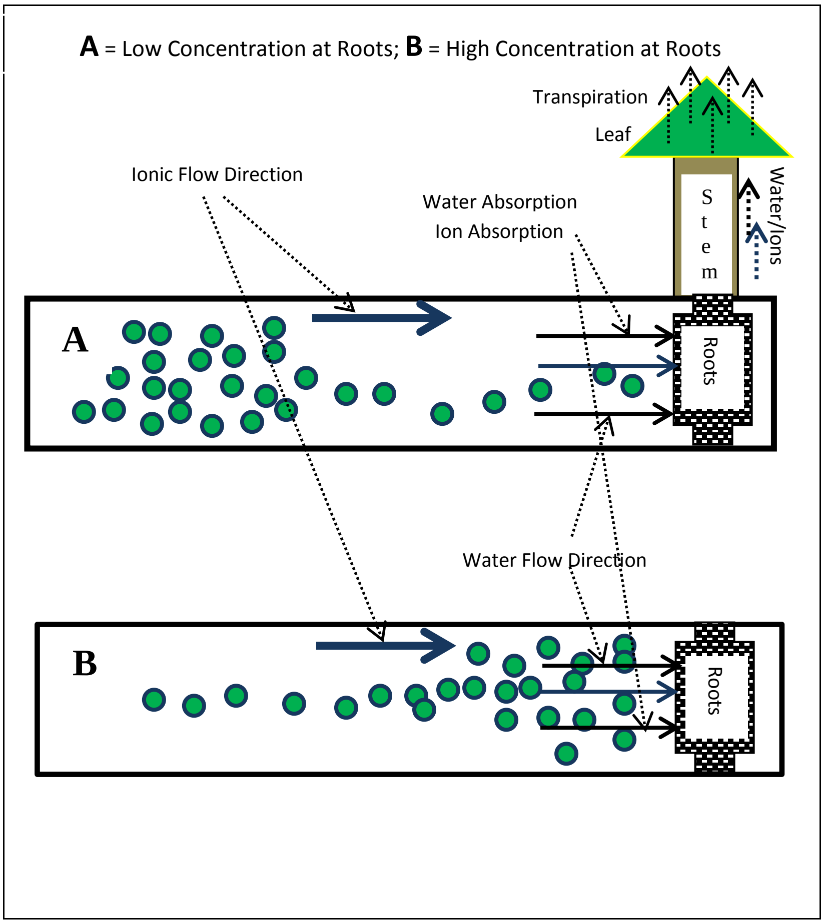

Fig. 7.1. Heavy metal movement by mass flow (Salam, 2012).

Unlike that in Mass Flow, the heavy metal movement of heavy metals does not necessarily in the same direction with the water movement like that occurs with diffusion. Diffusion of heavy metals is controlled by the concentration difference between two points. This phenomenon is shown in **Fig. 7.2**. The heavy movement may occur from points with high concentration to points with low concentrations. The bigger the difference between two points, the faster the rates of heavy metal diffusion. Therefore, heavy metals may move in the direction or in the opposite direction to plant roots; the principle is to move towards the lower concentrations. When the concentrations of a particular heavy metal around plant root surfaces are low, for example due to plant absorption, the element moves towards the surface of plant roots. Conversely, when the concentrations of particular heavy metals in the rhizosphere are high due to the presence of heavy metal sources, the element may preferentially moves avoiding the rhizosphere.

There are some factors affecting the diffusion of heavy metal in the soil environment. These factors are usually summarized in **Eq. 7.2**.

$$\frac{\Delta Q}{\Delta t} = \mathrm{D_e}\frac{\mathrm{C_2 - C_1}}{\mathrm{L}} \quad \ldots\ldots\ \textbf{Eq. 7.2}$$

where $\frac{\Delta Q}{\Delta t}$ is the rate of diffusion, D_e is the diffusion coefficient of a particular ion in soil water, C_1 is the heavy metal ion concentration at the surface of plant root, C_2 is the heavy metal concentration at a distance L from C_1,. and L is the distance between C_1 and C_2.

Based on **Fig. 2**. several factors that may affect the rates of heavy metal diffusion are: (a) diffusion coefficients, D, (b) heavy metal concentration at a particular point in the soil body far from the plant root surface, C_2, (c) heavy metal concentration of heavy metal element at plant root surface, C_1, and (d) the soil buffering capacity. Diffusion coefficient is heavy metal dependent. In addition, diffusion is also controlled by soil moisture content and tortuosity of the soil pore channels.

The dependence of diffusion rates on the above factors is summarized in **Eq. 7.3** (Fick's Equation).

$$\boldsymbol{D_e = D_w \theta f \frac{1}{b}} \quad \ldots\ldots\ \textbf{Eq. 7.3}$$

where $\boldsymbol{D_e}$ is the diffusion coefficient of a particular heavy metal element in soil water, $\boldsymbol{D_w}$ is the diffusion coefficient of a particular heavy metal element in water, $\boldsymbol{\theta}$ is soil volumetric water content, **f** is the soil tortuosity factor which is the reciprocal value of length of continuous pore channels, and **b** is the soil buffering capacity (Barber, 1981). This equation describes how these factors affect the rate of heavy metal diffusion. In general, the rate of diffusion increases with the increase in soil water content, tortuosity factor, and the soil buffering capacity.

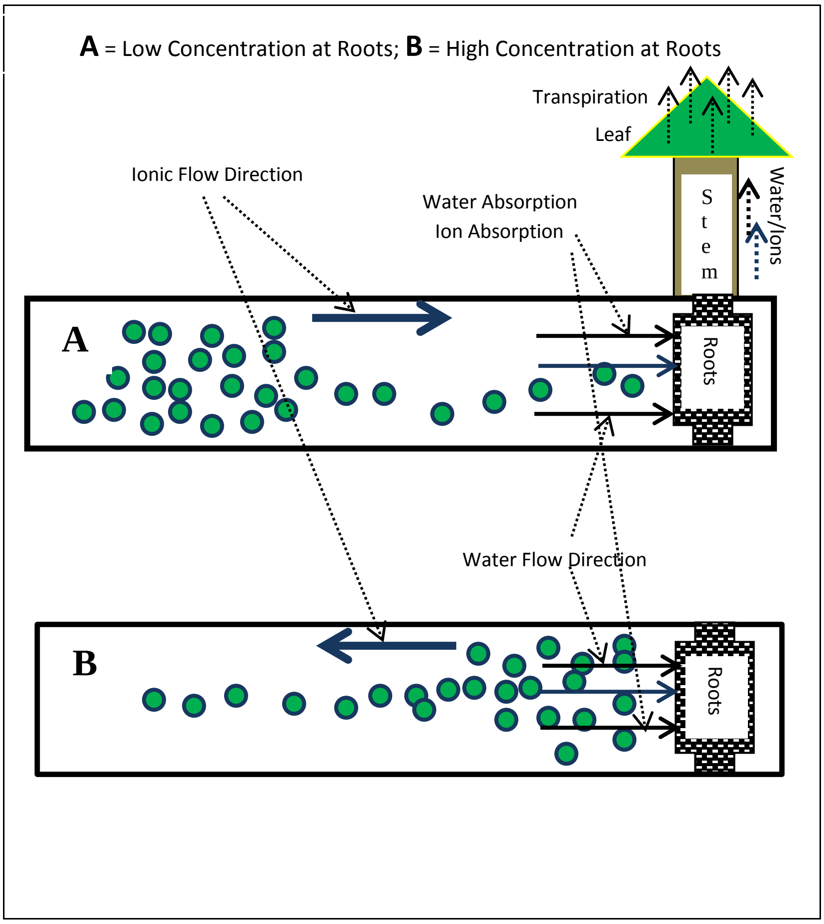

Fig. 7.2. Heavy metal movement by diffusion (Salam, 2012).

The heavy metals in soils may move to any direction, dependent of the movement mechanism, water content, and heavy metal concentrations. The principle is that heavy metals may move from wet areas to dry areas through mass flow or from high concentration to low concentration through diffusion. The first is dependent on water content (mass flow) and the second is controlled by two factors i.e. the availability of water as the heavy metals highways and the concentration difference. In any case, the presence of water and heavy metals are prerequisite for heavy metal movement in the soil environment. As an example, the capillary movement of heavy metals is related to the transport of heavy metal by capillary force, in which the heavy metals move from the soil depths to the soil surface stimulated by the difference in water pressure. In this case, the water content in the topsoils may probably lower while that in the soil depths is higher. This movement direction is the opposite of heavy metal movement with the percolating water.

The movement of heavy metals may not only occur with percolating water in the soil body but also through the surface runoff. He et al. (2004) monitored the movement of some heavy metal through water runoff over a 2 year-period in vegetable farm and citrus groves of Florida the United States of America. They found that the concentrations of heavy metals including Cd, Co, Cr, Cu, Fe, Ni, Pb, Zn, Mn, and Mo in the surface runoff were associated with the accumulation of the metals in the soils. This is suggested by the fact that the 0.01 M $CaCl_2$ extractable Cu, Fe, Zn, and Mn in soils were found to be significantly correlated with Cu, Fe, Zn, and Mn concentrations in the surface runoff.

7.2 Translocation of heavy metals in soils

The easiest way to observe the heavy metal translocation and distribution is to observe their vertical translocation and distribution. This phenomenon is easier to observe in the tropical regions with heavy rain like in Lampung Indonesia. This vertical distribution of heavy metals is assumed to be caused by high rates of water infiltration and percolation in which the heavy metals move together with the mass of the moving water. The heavy metals are moved to the depths and, depending on soil properties, rainfall and the rates of water infiltration and percolation, the heavy metals may be distributed along the vertical dimension with the highest concentrations in the topsoils and decreases with the soil depth and may probably reach the ground water causing ground-water contamination and pollution.

There are some important factors that significantly affect the rates of heavy metal translocation. As explained previously, the presence of connected soil pore-channel is very significant. The amount of water from rainfall is also detemining because the moving water in the pore channels is the vehicle for heavy metals to move downwards in the soil body. The presence of competing cations such as the soil major cations Ca^{2+}, Mg^{2+}, Na^{+}, and K^{+} may increase the heavy metal movement in the pore channels, because these competing cations may hinder the heavy metal adsorption by soil solids. The soil temperature may also affect the rates of heavy metal movement. In general, higher temperature may speed up the movement of heavy metals. However, not all factors stimulate the translocation of heavy metal in soil body. The higher soil CEC may give negative effect on the movement of heavy metals. The presence of negative charges along the pore channels may inhibit the movement of the positively charges heavy metal cations. Following the coloumbic law, the interaction of the soil negative charges and the heavy metal positive charges may stimulate the adsorption of heavy metals and this may inhibit the heavy metal movement. Similarly, the presence of precipitation agents may inhibit the heavy metal movement. The interaction of positively charged heavy metals and the negatively charged precipitation agents may form complexes and precipitates and, thereby, the heavy metals may not move.

The vertical distribution of heavy metals in tropical soils has been reported by Salam et al. (1998b; 1998e; 2005). Salam et al. (1998e) every 2 days washed soils treated with heavy metal containing waste, lime, and/or compost in a column experiment (**Fig. 7.3**.). Soil samples were taken along the depth of column (every 1/3 of the column depth) and analyzed for heavy metals. A 30 day observation showed that the translocation of Cu and Cd was in general miniscule. The extracted heavy metals in soils increased after soil column washing for 30 days. However, the effects of lime and/or cassava-leaf compost in lowering the extracted Cu and Cd was observed both in soil of Tanjungan (Ultisol) and soil of Banjaragung (Alfisols).

From another column experiment, Salam et al. (1998b) report that most of Pb, Cd, and Cu added into soil columns were immobilized in topsoils. In general, these metal elements (Pb, Cd, Cu, and Zn) moved in the soil columns driven by water leaching for 30 and 60 days; the translocation was clearly shown by Zn. Lime effectively decreased the heavy metal solubility and retarded their movement due to lime role in enhancing topsoil pH and soil adsorptiom capacity. The presence of zeolite reduced the extracted Pb and Zn but did not affect the solubility of Cu. The extracted Cd from topsoil and subsoil of Banjaragung Central Lampung Indonesia is given in **Table 7.1**.

Salam et al. (1995) report an investigation on the movement of Cu and Zn in cultivated field-plots 3 years after treatment with an industrial waste containing considerable Cu and Zn, lime, and organic compost. Three levels of industrial waste (0, 15, and 60 ton ha^{-1}) were mixed with field topsoils of 0-15 cm one week after treatment with lime and organic compost.

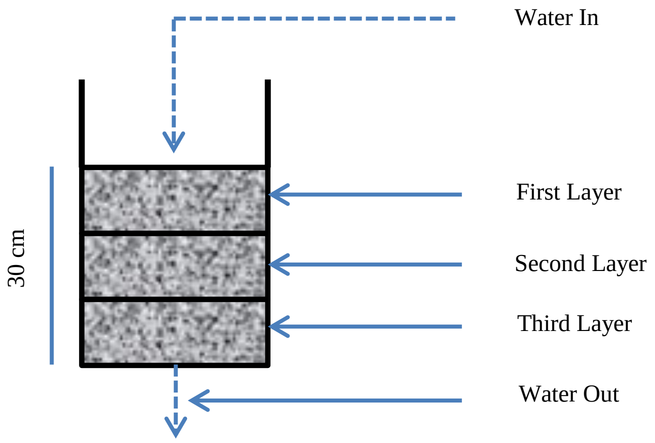

Fig. 7.3. Soil sampling in an experimental column to observe heavy metal movement in soils (After Salam et al., 1998e).

Field experimental plots were set up in Sidosari, Natar, South Lampung, in July 1998. Some initial soil characteristics were sand 41.2%, silt 26%, clay 32.8%, organic C 12.8 g kg^{-1}, total N 0.94 g kg^{-1}, C/N 13.6, pH 5.11, Cu 1.6 mg kg^{-1} and Zn 0.13 mg kg^{-1}. The experimental field consisted of 12 plots for one block, each measuring 4 m x 4.5 m with distances 50 cm between plots and 100 cm between blocks. Treatments were arranged in a completely randomized block design with 3 treatment factors, i.e. industrial waste, lime, and cassava-leaf compost. Industrial waste (with Cu 754 mg kg^{-1}, Zn 44.6 mg kg^{-1}, and pH 7.3) was given at 0, 15, and 60 ton ha^{-1}; lime ($CaCO_3$) at 0 and 5 ton ha^{-1}; and cassava-leaf compost (C/N 6.85) at 0 and 5 ton ha^{-1}. A complete report on the preparation of industrial waste, cassava-leaf compost, and experimental field plots were reported previously (Salam, 2000). All plots were planted with one time corn and one time upland paddy and were left bared until the time of soil sampling.

Table 7.1. The extracted Cd from soil column of Banjargung treated with lime and zeolite after a 30-day leaching(1).

Soil Layer	Control	+ Cd	+ Cd + Lime(2)	+ Cd + Zeolite(3)	+ Cd + Lime + Zeolite
	……. mg kg^{-1} …….				
Topsoil					
Layer 1	0.27	2.25	1.87	2.63	1.67
Layer 2	0.11	0.11	0.11	0.11	0.11
Subsoil					
Layer 3	0.10	0.10	0.10	0.10	0.10
Layer 4	0.10	0.10	0.10	0.10	0.10

(1)After Salam et al. (1998b), (2)lime as $CaCO_3$ at 8 ton ha^{-1} and (3)zeolite at 1%

Soil sampling was conducted in July 2001. Soil samples were taken depth-wise: 0 – 15, 15 –30, 30 – 45, 45 – 60, and 60 – 75 cm in the exact middle of plots of two blocks. Sampling from the exact middle of the plots was considered very important to ensure representative soil samples because all sides of plots were prone to contamination from outside of plots (Liang, 1991). Soil samples were all ground, screened to pass a 2 mm sieve, and thoroughly mixed before chemical analysis.

Extracted Cu and Zn were measured in soil samples collected depth-wise from 0 to 75 cm in field-plots 3 years after treatments. Copper and Zn only from high-level waste-treatments were observed to have significantly moved from topsoils to subsoils of 30 – 75 cm (**Table 7.2** and **Table 7.3**). Unlike that of Zn, the movement of Cu was also shown to be significantly lowered by topsoil treatment with lime and/or compost, suggesting that the increase in soil adsorption capacity inhibited the movement of Cu cations. Most Cu and Zn were retained in topsoils.

Salam and Ginanjar (2017) evaluated the soil labile fractions of Cu ±10 years after soil treatments with Cu-containing industrial waste, lime, and cassava-leaf compost. Soil samples were taken from topsoils and subsoils of ±10 years old experimental the above plots set in 1998 (Salam et al., 2005). The measured Cu labile fractions were compared to those in soils sampled at ±1.5 years and ±3 years after treatments. The results showed that the soil Cu labile fractions in waste treated soil were higher than those in the control treatments even though their concentration decreased with the years of sampling.

Table 7.2. The effects of industrial waste, lime, and cassava-leaf compost on the depth-wise plant availability of Cu in soil of Sidosari three years after treatment[1).]

Soil Depth (cm)	W_0				W_1				W_2			
	L_0		L_1		L_0		L_1		L_0		L_1	
	C_0	C_1	C_0	C_1	C_0	C_1	C_0	C_1	C_0	C_1	C_0	C_1
0 – 15	0.67	1.06	0.63	0.81	1.67	2.24	2.21	2.13	9.66	8.57	8.10	8.81
15 – 30	0.55	0.85	0.49	0.71	1.36	1.62	1.67	1.29	6.98	4.32	5.74	5.87
30 – 45	0.63	0.81	0.44	0.75	0.75	0.81	0.84	0.67	2.03	1.14	1.14	1.09
45 – 60	0.63	0.75	0.30	0.75	0.67	0.78	0.74	0.67	0.88	0.84	0.99	0.93

[1)]Adapted from Salam et al. (2005); all values are in square root; W = waste, W_1 = 0, W_2 = 15, and W_3 = 60 ton ha-1; L = lime, L_0= 0 and L_1 = 5 ton ha^{-1}; and C = compost, C_0 = 0 and C_1 = 5 ton ha^{-1}; effect of W, L, and C was significant.

The concentration of Cu of industrial waste at 60 ton ha^{-1} decreased after 10 years (**Table 7.4**) as seen from the relative concentrations of Cu. For example at Treatment Unit 1 (No Compost and No Lime), the relative Cu concentration decreased from 1.00 to 0.77, and to 0.19 after 1.5, 3, and 10 years. The missing labile fraction of Cu for the last ±10 years (about 81%) was due to several possibilities: (1) enhanced retainment by soil adsorptive surfaces or by precipitation, (2) absorbed by plant roots, and (3) leached by percolating water to subsoil or ground water, as described in **Fig. 7.4**. It is probable that most of the missing Cu is caused by the translocation through the pore channels to the soil depths and ground water as proven by observation after 3 years (Salam et al., 2005). As shown in **Table 7.2** and **Table 7.3**, Cu and Zn from high-level waste-treatments (60 ton ha^{-1}) were observed to have significantly moved from topsoils to subsoils of 30 – 75 cm.

Table 7.3. The effects of industrial waste, lime, and cassava-leaf compost on the depth-wise plant availability of Zn in soil three years after treatment[1).

Soil Depth (cm)	W_0				W_1				W_2			
	L_0		L_1		L_0		L_1		L_0		L_1	
	C_0	C_1	C_0	C_1	C_0	C_1	C_0	C_1	C_0	C_1	C_0	C_1
0 – 15	1.33	1.19	1.75	1.20	3.10	6.60	5.56	4.30	9.51	9.03	7.89	7.22
15 – 30	0.58	0.98	0.79	0.68	1.77	2.01	2.04	2.37	5.28	5.70	5.28	5.70
30 – 45	0.62	0.87	0.65	0.40	0.65	0.98	0.62	0.41	1.41	1.58	1.20	1.42
45 – 60	0.40	0.71	0.58	0.28	0.50	0.54	0.40	0.40	0.96	1.06	1.01	1.02
60 – 75	0.29	0.29	0.35	0.06	0.44	0.50	0.40	0.35	0.94	0.73	0.74	0.91

1)Adapted from Salam et al. (2005); all values are in square root; W = waste, W_1 = 0, W_2 = 15, and W_3 = 60 ton ha^{-1}; L = lime, L_0= 0 and L_1 = 5 ton ha^{-1}; and C = compost, C_0 = 0 and C_1 = 5 ton ha^{-1}.

Table 7.4. The relative concentrations of Cu (Cu/Cu_0-1.5) at waste level of 60 ton ha^{-1} 1).

No.	Treatment Unit	± 1.5 years	± 3 years	± 10 years
1	No C, No L	1.00	0.77	0.19
2	No C, With L	0.67	0.54	0.39
3	With C, No L	0.80	0.60	0.21
4	With C, With L	0.55	0.64	0.17

1) Adapted from Salam et al. (2005); Cu = the extracted Cu, Cu_0-1.5 = the extracted Cu with Treatment No C and No CL after 1.5 years; C = Compost, and L = Lime

Heavy metals in the soil environment may also move under unsaturated conditions, where the soil pore is not completely filled with water. As long there is interconnected water present on the wall of pore channels, heavy metals may move from one point to another point, particularly through heavy metal diffusion , where heavy metals move from the more concentrated to the more dilute heavy metals. The movement may go in any direction provided that the interconnected water ways in pore channels is available. In addition, there must be a gradient concentration as the driving force of heavy metal diffusion. This movement may translocate and distribute heavy metals in the soil body.

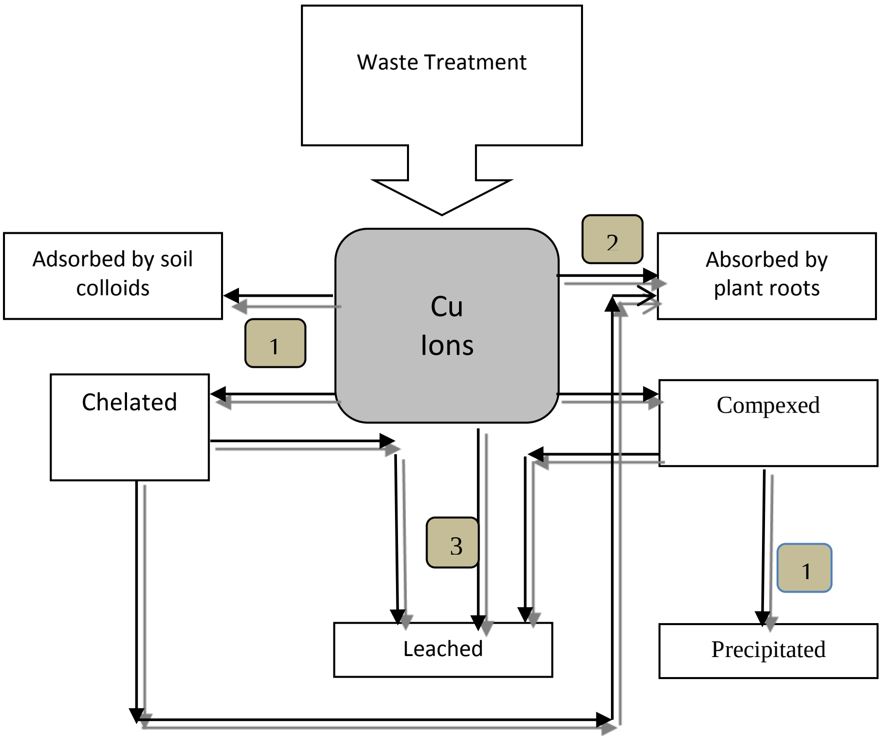

Fig. 7.4. The possibility of the waste-origin Cu removal from soil labile fractions ±10 years after waste treatment (1 – Adsorption or precipitation, 2 – Absorption by plant roots, 3 – leaching).

Heavy metals may also move through mass folw in the condition of unsaturated condition. Heavy metals may move with mass of water flow moving from wetter to dryer points. Capillary movement may be the example of this movement. This movement, by no means, may translocate and distribute heavy metals in the soil body. Unlike in wet region where heavy metals are accumulated in the soil depth, in dry region heavy metal may be accumulated in the topsoils.

A soil column experiment to study the movement of Zn was also conducted by Welch and Lund (1989) under saturated and unsaturated conditions. The Zn movement in unsaturated column ranged from 3 to 30 cm with a mean of 10 cm. Most of the Zn applied into the unsaturated columns remained in the sludge amended soil layer (98.1%). The major portion of Zn leached from the sludge amended soil accumulated in the 0-to 3 cm depth.

7.3 Retardation of heavy metal movement in soils

As repeatedly mentioned in the previous chapters, heavy metals must be contained so that those that in contact with the living things are minimum. In relation to this topic, it means that the heavy metal movement and translocation into soil depths and ground water must be avoided or at least retarded. There are several methods to retard the movement of heavy metals in the soil body, among which is by increasing the soil or soil pore-channels adsorptive capacity. The increase in the soil adsorptive capacity towards heavy metals can be accomplished by direct or indirect amendment. Among the direct amendment (Option 1) are the addition of high CEC materials like 2:1 silicate clay minerals, organic matter compost, biochars, and zeolites (Salam et al., 1998b; Setyawan, 2002; 2003; Penn et al., 2010; Gupta and Nayak, 2012; and Hua and Li, 2014), that can significantly increase the soil adsorptive capacity trough saturation with negative charges. Among the indirect method (Option 2) is by using the soil amendment that may finally increase the soil adsorptive capacity. Among the soil amendment are lime and P-fertilizers (Wang et al., 2012).

Heavy metal retardation is shown previously in **Table 7.2** and **Table 7.3**. The effect of lime on the retardation of Cu and Zn movement in the soil body treated with 60 ton ha^{-1} electronic industrial waste 3 years after treatment is also shown in **Fig. 7.5** and **Fig. 7.6**. These data show that both Cu and Zn are shifted to the higher energy bonding in limed soil due to the increase in the soil adsorptive charges caused by liming processes. Under limed condition, the heavy metals Cu and Zn are leached in smaller amount than those of under control conditions. He et al. (2006) shows that the leached Zn from sandy soils decreased linearly as the solution pH was raised from 3.0 to 9.0. Later, Elbana and Selim (2010) also report that Cd was nearly immobile in a column of calcareous soils but 20 – 30% of the applied Cd was mobile in acid soils.

The shifting to higher bonding energy by liming is of course temporary. With time the bonding energy may get lower, Cu and Zn may release into the soil water and may finally move through the soil body. However, the lime effect is reported to be long-term (Salam and Ginanjar, 2017). As shown in **Table 7.4**, the effect of lime is still observed 10 years after treatment, particularly if lime treatment is combined with organic compost treatment. This phenomenon is shown by the relative concentration of Cu is lower in limed soils than that in unlimed soils. For example, 3 years after treatment the relative concentrations of Cu in Control was 0.77, in limed soils was 0.54, and in limed soils treated with organic matter 0.64.

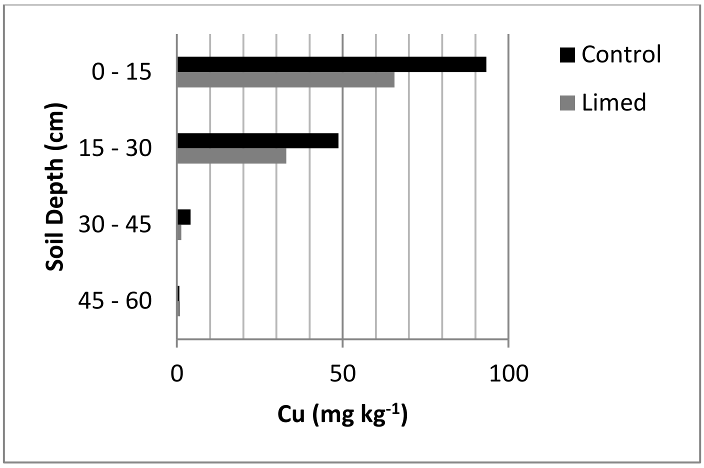

Fig. 7.5. The effect of lime on the depth-wise distribution of Cu of industrial origin in soil of Sidosari South Lampung.

The retardation may also occur when the organic matter is added. This phenomenon is shown by the relative Cu concentration in **Table 7.4**; all are lower than when organic composts are added. The relative Cu concentration is even lower when lime is also added. The increase in soil pH by lime may increase the amount of the organic functional groups that dissociate and produce negative charges. The presence of more negative charges by organic compost may shift Cu to higher a bonding energy and hence it is difficult to detach and leach. This may retard, decrease, or even stop the translocation of Cu in the soil body.

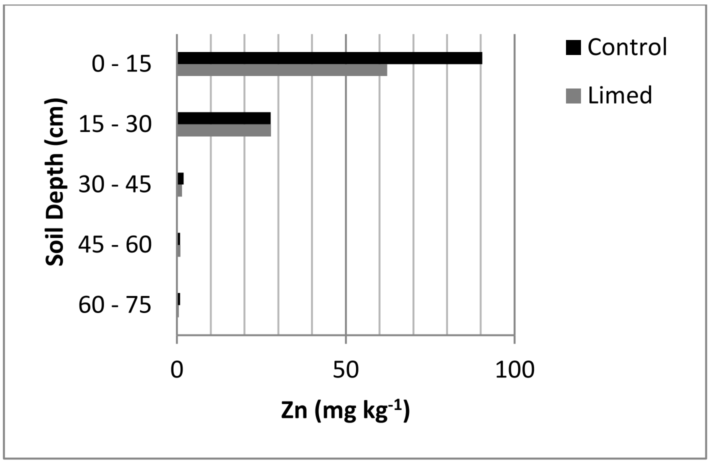

Fig. 7.6. The effect of lime on the depth wise distribution of Zn of industrial origin in soil of Sidosari South Lampung.

The organic compost is however prone to decomposition processes. When the structural organic compost is destroyed by decomposition, the effectiveness of organic matter may decrease and the adsorbed Cu may shift to lower binding energy or release to the soil water, and may encounter water leaching to the soil depths. To cope with this problem, some other more resistant materials are used, for example biochars (Buss et al., 2012; Ippolito et al., 2012). These materials are relatively long-lasting. Buss et al. (2012) suggest that biochars may adsorb several substances ranging from herbicides to allelochemicals. They also show that plants without biochar treatment were observed to show severe stress symptom after Cu application at 50 μg g^{-1} and died at 200 μg Cu g^{-1}. Application of biochar significantly increased the plant performance and eliminated Cu toxicity. Ippolito et al. (2012) show that biochars can be used for sorbing excess Cu from water system and potential to reduce the negative effect of Cu in the soil and water environment.

Some reports show the effects of the changes in soil properties by addition of soil amendment. From a column experiment, Welch and Lund (1989) observed that the movement of Zn in soil column was retarded by higher pH. The total Zn leached from sludge amended soil layer was negatively correlated with soil pH. Multiple linear regression analysis showed that the soil pH accounted for 72% of the variation in the total amounts of Zn leached from the sludge amended soil layer and accounted for 82% of the variation in the depth of Zn movement in unsaturated soil columns. Previously, Tyler and McBride (1982) report that Cu moved readily through soil columns. The least mobility of metals was observed in a mineral soil with a relatively high pH, CEC, and exchangeable base content. Liming of an acid mineral soil reduced metal mobility. The order of mobility of metals in soils was: Cu << Zn < Ni < Cd. Sharma and Yadav (1986) revealed a large amounts of Fe and Mn through drainage water when a highly alkali soil was leached without amendment addition. Increasing level of gypsum and/or farmyard manure treatment was observed to drastically decrease the losses. The interaction of gypsum and farmyard manure caused the lowest losses. Wang et al. (2012) also reports that the transport of Cu in a saturated packed column decreased with the increase in soil pH due to the increase in Cu adsorption and precipitation.

McGowen et al. (2001) also report the retardation of Cd, Pb, and Zn in smelter-contaminated soils by diammonium phosphates. The presence of soluble phosphates increased the precipitation of these metal elements and, therefore, retarded their movement in the soils.

Concersely, some metal solvents may increase the movement and translocation of heavy metals in soils. Solvent may dissolve heavy metals and prevent their adsorption by soil solids and thus increase the vulnerability of heavy metals in soil water to move in soils. Sheets and Fuller (1986) observed that soils adsorbed less Cd from ethylene glycol than did from water. Movement of Cd was therefore faster when Cd was dissolved in soil treated with ethylene glycol that was in water. Zhu and Alva (1993) also found that the rate of Cu and Zn movement in sandy soils was well correlated with the content of dissolved organic matter (DOC). As also suggested by Wang et al. (2009) the speeded rates of Cu and Zn movement were suggested to be caused by higher DOC and organic acids. The reason is that Cu and Zn may form complexes with DOC. A similar phenomenon was reported by Abumaizar (1999) and other soil workers (Lombi et al., 2000; Wu et al., 2004; Hashim et al., 2011) who found that heavy metal removal from contaminated soils was enhanced by the presence of organic ligand EDTA. Wu et al. (2004) also report that the presence of EDTA speeded up the phytoextraction of heavy metals by an indian mustard (*Brassica juncea*) and also their potential leaching because the EDTA chelated heavy metals were dissolved in soil solution. They observed that the Cu and Pb losses from soils were well-correlated with the added EDTA. Hashim et al. (2011) also suggest that EDTA lowered the adsorption of Cr(VI) in soils.

Important questions

1. Explain the translocation of heavy metals in the soil environment! What forms of heavy metals are prone to water leaching? Explain!
2. What is the effect of heavy metal leaching to all other forms of heavy metals in the soil environment? Explain!
3. Explain all the factors that affect the translocation of heavy metals in the soil body! Is there any of soil physical, chemical, or microbiological properties? Explain!
4. Is the heavy metal movement in the soil body beneficial? Explain in relation to the heavy metal as plant nutrient elements versus toxic elements!
5. How to calculate the transported heavy metals in the soil system by leaching?
6. Explain the mechanisms of heavy metal transport under unsaturated conditions!
7. Explain heavy metal movement by mass flow! What factors affect the rates of heavy metal mass flow?
8. Explain heavy metal movement by diffusion! What factors affect the rates of heavy metal diffusion?
9. Explain the effect of water content, buffering capacity, diffusion coefficient, and tortuosity on the rates of heavy metal mass flow and diffusion in the soil environment!
10. Explain the factors that may accelerate and inhibit the translocation of heavy metals in the soil body!
11. Explain the retardation of Cu and Zn movement by lime and organic matter! Give data to support your opinion!
12. Heavy metals in the soil environment may decrease with time. Explain the probability about the mechanisms of heavy metal leaks!

Chapter 8

Heavy Metal Extraction by Bioaccumulators

To cope with the problem of heavy metal toxicity in the soil environment, at least two approaches are currently available. The first approach is to let the heavy metals stay in the soil environment by elevating their retention by soil solids. This approach has been thoroughly discussed in the previous chapters dealing with how the heavy metals cations in the soil environment are immobilized through adsorption and/or precipitation reactions using direct (Option 1)or indirect (Option 2) enhancement of soil solid adsorption capacity. Therefore, the existence of the soil negative charges emerging on the surfaces of various types of solids and the precipitating agents is very important. The higher the amount of the soil negative charges and/or the precipitation agents the better the soil to be a heavy metal adsorber. Soils with particular solids such as organic matters and 2:1 silicate clay minerals or contain high amounts of OH^- ions or CO_3^{2-} ions are preferred to immobilize high amounts of heavy metals, while those with oxides/hydroxides or sesquioxides and 1:1 silicate clay minerals or low precipitating agents are not preferred. With this approach, some soil manipulations that increase the amounts of soil negative charges or precipitating agents are preferred. For example, addition of soil amendment that may directly increase the soil negative charges like zeolite, phosphates, and organic matter compost as well as biochars (Erdem et al., 2004; Penn et al., 2010; Buss et al., 2012; Ippolito et al., 2012; and Hua and Li, 2014) and also that indirectly increase the soil negative charges or precipitating agents like liming and phosphate addition that might increase the soil pH and then the soil negative charges (Helling et al., 1964; Trehan and Sekhon, 1977; Elliott, 1983; Tan and Dowling, 1984; McGrath et al., 1988; Alloway 1990b; Parfitt et al., 1995; Rodella et al., 1995; Medonca and Rowel, 1996; Tack et al., 1996; Suryanto and Susetyo, 1997; Choi et al., 1999; Tokunaga et al., 2003; Quaghebour et al., 2005; Schroder et al., 2008; and Gagnon et al., 2013). These practices are common in agricultural soils and can be applied to cope with the heavy metal problems in the soil environment.

The second approach is the other way around. The heavy metals are extracted out of the soil system. By this way, the soils are free from high levels of heavy metals and give no harm to the contacting living things. The method to do this is by using particular microorganism and/or plants that are able absorb high amounts of heavy metals (Jing et al., 2007). This approach is useful when the soil adsorptive capacity is relatively low and is difficult to enhance by chemical mechanism and causes soil pollution that may disturb the living things. This approach is also useful if the emission of heavy metals into the soil environment is so high that they may endanger the living things.

The use of this method may accumulate heavy metals in microorganisms and/or plant tissues that need solution. One of the solutions is not using the plant tissues for consumption. The plant tissues can be disposed safely so that the absorbed heavy metals may not release back the environment. The plant tissues can also be processed to use the heavy metal for some purposes. The clean plant tissue can then be used for other purposes or disposed safely into the environment.

8.1. Absorption of heavy metals by plants

As discussed in the previous chapters, free metal ions are the most important metal species in the soil environment. Free ions are related to several physical, chemical, and biological mechanisms controlling their concentrations in soil water. Therefore, free ions may encounter different fates in the soil environment (**Fig. 3.1**). Chemically, the free ions are directly related and in equilibrium with complexes and chelates through the so-called complexation/decomplexation and chelation/dechelation reactions. Free ions are also chemically related and in equilibrium with the adsorbed cations and precipitates through adsorption/desorption and precipitation/dissolution reactions. Through all these chemical mechanisms, the concentration of free ions in the soil liquid may increase or decrease controlled by the related equilibrium constants. High concentrations of free ions may drive the occurrence of complexation, chelation, adsorption, and precipitation reactions to lower the free ion concentrations in soil water. Conversely, low concentrations of free ions may stimulate the occurrence of decomplexation, dechelation, desorption, and dissolution to satisfy the related equilibrium constants. Through this mechanism, the concentration of free ions in the soil liquid are maintained.

In addition to by the above chemical reactions, the free ionic metal concentration in the soil environment is also controlled by physical mechanisms i.e. heavy metal transport including the mass flow and diffusion. The heavy metal may move from one point to another in the soil body following the water movement (mass flow) and/or concentration gradient from higher concentration to lower concentration (diffusion). Heavy metal transport is important as to avail heavy metal nutrients such as Fe, Mn, Zn, Cu, and Co in the root zone. The environmentally significant heavy metal movement in the soil body is heavy metal leaching, which may contaminate ground-water as well as rivers as and seas. The impact of this mechanism is very significant when the free heavy metal concentration is high and percolating water in pore channels is relatively fast.

In addition to the above chemical and physical mechanisms, free metal ions in the soil environment are also biologically (physiologically) controlled by plant through plant root absorption. The free metal ions in the vicinity of root surfaces can be absorbed by plant roots. In the outer sphere of plant roots, this process is controlled by chemical and physical processes, however in the inner sphere, this process is physiologically controlled. Not all heavy metal reaching the plant root surfaces is finally absorbed by plants because heavy metal absorption is plant specific. Therefore, the amount of heavy metal absorbed by plant roots is not merely the result of the chemical processes that supply heavy metal cations released from immobilized forms and the physical processes that transport the released free cations to the surfaces of plant roots but also the result of plant root performance. However, the plant root absorption of free heavy metals that may lower the free ion concentration may stimulate the chemical processes (desorption and dissolution) and the physical processes (mass flow and diffusion) to occur more intensively supplying free heavy metal ions.

8.2. Phyto (and bio)-remediation

The above discussion shows that there are two major routes of environmental pollution by heavy metals endangering the living things. The first is plant route and the second is soil route. Plant route may emits the heavy metals to the living thing through plant products including fruits, leaves, stems, and roots. Several plants may accumulate heavy metals in one of the plant parts and may eventually increase the heavy metal intake by animals and humans. Soil route may emit the heavy metal through drinking water or irrigation water like ground-water, rivers, lakes, and seas. The use of this water may also cause the increase heavy metal intakes by the living things. Some studies revealed significant emission of heavy metal through plant routes (Otte et al., 1995). Selected data on the amounts of heavy metals accumulated from heavy metal contaminated soils are listed in the previous chapters. Some studies also report the pollution of water system. Some selected heavy metal pollution data are also presented in the previous chapters. These observations show that both major routes of environmental heavy metal contamination are relatively dangerous and must be attenuated.

The attenuation of heavy metal pollution can be conducted by closing one or both of the pollution routes. As mentioned previously, the most favorable method is by closing the soil route. Heavy metals are allowed to stay longer or forever in the soil system by increasing the amount of immobilized heavy metal pools. As discussed in the previous chapters, this can be conducted by increasing the amount of heavy metals immobilized in soils by some chemical reactions such as adsorption and precipitation. This suggests the importance of soil adsorption capacity and precipitating agents, that can be modified directly by addition of some soil amendments such as high CEC clays, organic matters, zeolites, and biochars and indirectly by modifying soil soil properties such as pH by addition of pH-increasing soil-amendment such as limes and P-fertilizers. These soil amendments are shown to finally increase the soil stable heavy metals pools and decrease those of labile pools. By this reason, the heavy metals may not pollute the soil water and environment because their transports through pore channels are hindered or retarded. This method is shown in **Fig. 8.1**

In some cases, blocking the soil route is not possible. The other method is by blocking the plant route (**Fig. 8.1**). Heavy metals are allowed to dissolve in soil water and are allowed to move towards plant roots to increase their absorption by plant roots. The problem is that not every plant and vegetation may significantly absorb and accumulate heavy metals. For this purposes, plants and vegetation that significantly absorb and accumulate heavy metals are preferred. Plant factors are then very dominant in determining their effectiveness in absorbing the heavy metals from soil liquids. Some plants have been reported to show high affinities towards heavy metals (Salam and Sriyani, 1994; Sriyani and Salam, 1998; Siregar and Siregar, 2010; Jing et al., 2007; Laidlaw et al., 2012). However, as pointed out in the previous chapters, some soil factors such as pH and adsorption capacity, also determine the effectiveness of heavy metal absorption by plants.

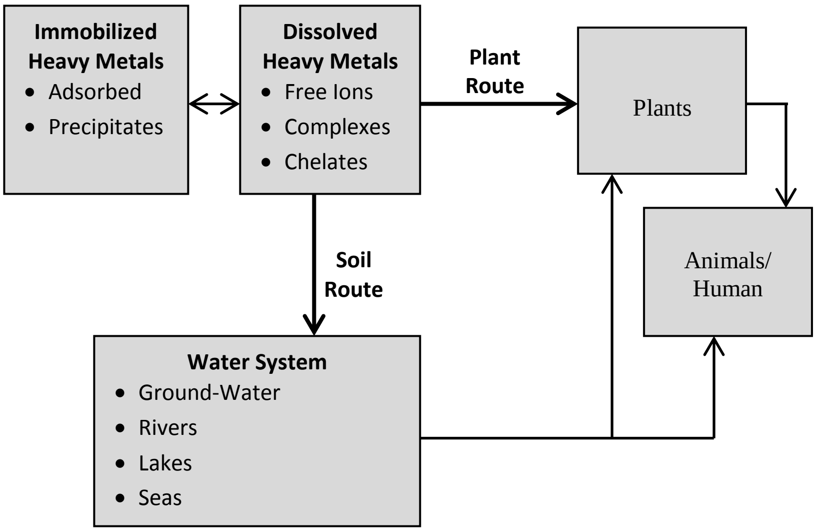

Fig. 8.1. The soil route and plant route of heavy metals emission in the soil environment.

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The existence of heavy metal accumulating plants or vegetations shows that heavy metal contaminated soils can be cleaned up by plants (Phytoremediation). By employing heavy metal accumulating plants, heavy metals in heavy metal contaminated soils and water are possible to remove. Heavy metals are finally accumulated in plant tissues, which of course need further processes safe for the environment and the living things. One of the methods is by separating the heavy metals for other purposes and returns the organic matters into the soil environment after removing the accumulated heavy metals.

Phytoremediation for heavy metals contaminated soils may include several methods i.e. phytoextraction (Baker et al., 1994; Kumar et al., 1995; Errst, 1996; Chen et al., 2000; Khan et al., 2000; Lombi et al., 2000; Hammers et al., 2003; Gaur and Adholeya, 2004; Zhang et al., 2007; and Hashim et al., 2011), phytofiltration, and phytovolatilization. Phytoextraction involves the use of plants to remove heavy metals from soils. The plant shoots containing heavy metals can be disposed or processed to use safely for other purposes. Phytofiltration involves the use of plant roots to remove heavy metals from water system. By this methods, heavy metals are adsorbed and accumulated in the plant roots, which also need further processes to make the plant roots are safer for other uses. Phytovolatilization involves the uses of plants to absorb particular heavy metals and volatilize them through plant leaves. Heavy metals to be removed with this method may include Se and Hg.

Some microorganisms are also reported to have the ability to remove heavy metals from contaminated soils. This fact also shows that remediation can be conducted by heavy metal bioaccumulating plants (phytoremediation), but also by employing heavy metal accumulating microorganism (bioremediation). This method is a potential alternative for cleaning soils and water contaminated by heavy metals. One of such microorganisms is Cyanobacteria, which is known potential to remove heavy metals including Hg, Cd, and Pb.

8.3. Heavy metal bioaccumulating plants

Heavy metal accumulating plants work without modifying the solubility of heavy metals that employs chemical reactions through increasing the process of adsorption and precipitation and their modifications. These plants work by extracting the heavy metals out of the soil system contaminated with heavy metals.

The heavy metals in the soil system are collected and disposed in safer forms or are used for other purposes after purification. There are several prerequisites for these plants: must be heavy-metal tolerant, must have high biomass, must have roots fitted to spatial distribution of heavy metal pollution, must have high root-to-shoot ratios, and must be able to absorb significant amounts of heavy metals relatively fast (Khan et al., 2000; Hammers et al., 2003).

Several plants and vegetations were indicated to be able to efficiently absorb heavy metals and, therefore, can be used as heavy metal bioaccumulating plants with the technique of phytoremediation (Kumar et al., 1995; Errst, 1996; Sriyani and Salam, 1998; Khan et al., 2000; Hammers et al., 2003; Gaur and Adholeya, 2004; Jing et al., 2007; Siregar and Siregar, 2010; Hashim et al., 2011; and Laidlaw et al., 2012). Some of these vegetations are amaranth, sunflowers, and cabbage, that can be used in the phytoextraction technique to extract heavy metal contaminants in contaminated soils, sediments, and muds. Kambhampati and Vu (2012) suggest that chickpea (*Cicer arietinum* L.) seems to be a cost-effective and environmentally friendly hyperaccumulator for Cu at 100 ppm Cu and 10 mM EDTA. Laidlaw et al. (2012) report that willows are potential phytoextractors for some metal elements in the environment such as Cd, Ni, Zn, Cr, and Cu. Gothberg et al. (2004) report that plants exposed to metals retained a major portion of metals in the roots, which had a higher tolerance than shoots for high internal metal concentrations.

The are several other vegetations indicated to be good heavy metal accumulators. Salam et al. (1999b) report that Cu intake from Alfisol Banjaragung treated with heavy metals containing waste by amaranth was higher than that by corn. This observation is given in **Table 8.1**. Previously, Sriyani and Salam (1998) report that the accumulation of Pb and Cu in several weed plants including pigweed, green kyllinga, and alang-alang were not different from that in amaranth, indicating that the plant weeds are as effective in accumulating heavy metals. It was also reported that a metalophyte plant from Belgium *Thlaspi caerulescens* was a heavy-metal hyperaccumulator, that can grow well in a medium with concentrations of up to 25,000 mg Zn kg^{-1} and 1,000 mg Cd kg^{-1}. This plant was tolerant to heavy metals and may absorb extremely high Cd without yield decrease and could be used in the phytoextraction of soils contaminated by Cu, Zn, Ni, and Cd (Brown et al., 1995; Pence et al., 2000; Hammers et al., 2003; and Deniau et al., 2006). Several varieties of Indica were also potential as contaminant Cd phytoextractors in paddy fields because this paddy variety may have accumulated Cu in its tissue and possesed high biomass. In their research, it was indicated that after planting this variety for two years, the concentration of Cd in contaminated paddy soils decreased by 18%, therefore, the soil was then safer for planting non-phytoextractor paddy. Guo et al. (2013) also report that the bioavailability of heavy metals could still be high after washing the heavy metal contaminated soils. Liming the washed soils may release the adsorbed metal-chelates. The phytoextraction by *Sedum alfredii* after soil washing was an effective to deplete the mobile Cd activated by soil washing.

Table 8.1. The accumulation of Cu and Zn in plant shoot grown in Alfisol Banjaragung Lampung Indonesia[1].

Lime Treatment	Model Waste[2]	Industrial Waste[3]
ton $CaCO_3$ ha^{-1}	μg kg^{-1}	
Amaranth:		
Cu	55.0	4.34
Zn	55.2	11.1
Corn:		
Cu	0.31	0.51
Zn	0.21	0.62

[1]Adapted from Salam et al. (1999b), [2]containing Cu, Zn, and Pub 10 mg kg^{-1}, and Cd 5 mg kg^{-1}; [3]at 80 ton metal-spoon industrial waste ha^{-1}.

Analysis of contaminated Aspen garden soils by Boon and Soltanpour (1992) showed that in general leafy portions of plants contained the highest concentrations of Pb and Cd followed by roots and fruits. Cabbage and brocolli leaves contained Pb of less than 5 mg kg^{-1} while lettuce and spinach contained 41 to 45 mg kg^{-1} of Pb. The plants (lettuce or spinach) Pb showed a linear relationship with Pb-DTPA soil extracts Pb conncentration ($Y = 2.36 + 0.05x$, $r = 0.95$) and so did Cd concentration ($y = 2.07 + 0.95x$, $r = 0.86$). These findings demonstrate that lettuce and spinach may accumulate Pb much better and may be used to accumulate the Pb in contaminated soils. Cabbage and brocolli are, therefore, recommended for vegetable consumption from contaminated soils. Lead uptake into vegetabls grown on a high-level Pb-contaminated soil (461 mg kg^{-1}) is shown in **Fig 8.2**. However, Gothberg et al. (2004) reported that water spinach exposed to metals retained most of the metals in the roots, that have a higher tolerance than shoots with respect to high internal metal concentrations. Buss et al. (2012) also reported that the accumulation of Cu in plant tissues followed the order of roots, shoot, and leaves.

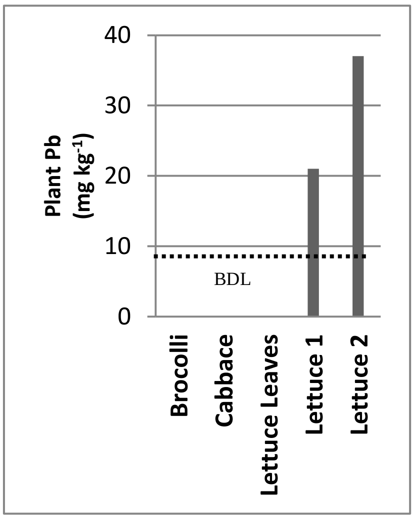

Fig. 8.2. Lead uptake by some vegetables in a high-level Pb-contaminated soil (BDL Below Detection Limit; Redrawn from Boon and Soltanpour, 1992) (After Salam, 2014).

Laidlaw et al. (2012) used several *Salix* (willows) species/cultivars to extract heavy metals from contaminated soils. Except *S. chilensis*, all other cultivars produced 10 ro 20 ton ha^{-1} biomass, while most cultivars growing in biosolids produced less biomass (< 6 ton ha^{-1}). *Salix matsudana* (20 t ha^{-1}) and *S. reichardtii* A. Kerner (18 t ha^{-1}) produced similar aboveground biomass production in both soil and biosolids. These cultivars, driven by the superior biomass production, were the most effective cultivars in extracting metals from biosolids. The willows were effective in extracting the most soluble/exchangeable metals (Cd, 0.18; Ni, 0.40; and Zn, 11.66 kg ha^{-1}).

Since plant roots are the important interfaces between soil solid and plants, the gate of heavy metals to drain out of the soil system, the effectiveness of plant roots in absorbing heavy metals are possible to enhance. One method of the enhancement is by employing rhizocabteria which has been observed to increase heavy metal absorption by plants (Jing et al., 2007). Gaur and Adholeya (2004) also report the possibility of using arbuscular mycorrhizal fungi (AMF) to increase the effectiveness of plant roots in absorbing heavy metals. Modification using nanoparticles were also experimented to increase the effectiveness of phytoremediations (Hu et al., 2005; Peng et al., 2010; Rosenfeldt et al., 2014).

Important questions

1. Explain the dynamics of various heavy metal forms in the soil system and identify the roles of plants in the system!
2. Explain two major methods to cope with the problems of polluting heavy metals in the soil environment: To Stay or To go!
3. Explain the reason for “To Stay” method! What reactions involve in this method? Explain how to manage the reactions!
4. Explain the reason for “To Go’ method!
5. Explain the physical, chemical, and biological factors involved in the “To Go’ method!
6. What is bioremediation related to heavy metals in polluted soils? How does it work?
7. What is phytoremediation related to heavy metals in polluted soils? How does it work?
8. What is the difference between phytoextraction, phytofiltration, and phytovolatilization? Give heavy metal involved in each method!
9. Explain with examples the heavy metals bioaccumulating microorganisms!
10. Explain with examples the heavy metal bioaccumulating plants or vegetations!

Chapter 9

Heavy Metal Analysis

There are a least eight forms of heavy metals existing in the soil environment. Their sequence according to their easiness to move or detach is free ionic cations, complexes, chelates, adsorbed cations, precipitates (secondary minerals), structural elements (secondary minerals), structural elements (organic matters), and structural elements (primary minerals). Most of the readily soluble heavy metal cations are generally related to the processes of complexation/chelation-decomplexation/dechelation, adsorption-desorption, and precipitation-dissolution, while those less readily soluble heavy metal cations are related to the processes of organic matter decomposition and mineral weathering. Their relationships along with the related chemical processes have been shown previously in **Fig. 3.1**. The sequence of their easiness to free along with the controlling processes is depicted in **Table 9.1**.

Table 9.1. The easiness of heavy metal forms to free cations in the soil environment.

No.	Metal Forms	Easiness to Detach Free Ions	Chemical Reactions Involved
1	Free Ions	-	-
2	Complexes	Most Readily	Complexation-Decomplexation
3	Chelates	Most Readily	Chelation-Dechelation
4	Adsorbed Cations	Most Readily	Adsorption-Desorption
5	Precipitates	Moderate	Precipitation - Dissolution
6	Structural Elements (Secondary Minerals)	Moderate	Mineral Weathering
7	Structural Elements (Organic Matters)	Moderate	Organic Matter Decomposition
8	Structural Mineral (Primary Minerals)	Less Readily	Mineral Weathering

As previously discussed in **Chapter 3**, the toxicity and availability of heavy metals in the environment are directly related to the concentrations of free ionic forms (Allen et al., 1980; Checkai et al., 1987a; 1987b; and Hernandez-Soriano et al., 2012). High concentrations of free ionic heavy metal forms are, therefore, not expected and are by any methods must be lowered. However, the total elements available to the living things, particularly to plants, are not only determined by the concentration of free ionic forms but also by all soil labile pools in the soil environment. The available heavy metals are in fact supplied by free ions, complexes and chelates, adsorbed cations, and parts of precipitates and structural elements. Therefore, the amount of various soil heavy metal cations in the soil environment must be known. The methods of the measurement of the various forms of heavy metals must be developed.

The values of each of these heavy metal forms vary from one soil to another and are also controlled by several soil properties such as pH and soil adsorption capacities. The soluble heavy metals that include free ionic forms, complexes, and chelates, are generally low compared to those in and/or on the soil solids. The concentration of free ionic heavy metals is also lower than the concentrations of metal complexes and/or chelates, ranging from 10 - 90% . These values are different for different heavy metals and different soils. Most of heavy metals in soils are present as precipitates and as the structural elements in the soil solids. All these heavy metal forms are in a dynamic equilibrium, controlled by some chemical mechanisms. The concentrations of each form may vary from time to time. Knowledge of these values is very important not only in relation to their toxicity to the living things but also to the supplies of heavy metals for plants, particularly for the elements essential for plant growth and development.

Therefore, soil heavy metal analysis must be able to differentiate the respective forms of heavy metals in the soil environment. The analysis of total soluble forms of heavy metals is usually conducted by using water as extractant. The adsorbed heavy metal cations is usually extracted by using particular salts containing a displacing cation like $Sr(NO_3)_2$, NH_4OAc, and $CaCl_2$. To differentiate from other dissolved forms of heavy metals, free ions can be measured by ion selective electrode (Oliver et al., 2005) and more accurately by donnan analysis (Blaedel dan Haupert, 1966; Salam and Helmke, 1995; 1998), or by computerized prediction (Jaiswal and Elliott, 2011). It is difficult to measure the structural heavy metal elements, except in order to measure their total content in all soil solids.

Since the plant availability of heavy metals is determined by all forms of soil heavy metals, to determine this value is more tedious. The first step is determining the kinds of extractant that are able to simulate the work of plant roots in dissolving and absorbing particular heavy metal elements from different forms i.e. dissolved heavy metal free ionic cations, dissolved heavy metal complexes and chelates, exchangeable heavy metals cations, and structural elements in precipitates, secondary minerals, organic matters, and primary minerals. The second step is to make a correlation study of each extractant between the absorbed heavy metals by plants and the content of heavy metals measured in soils, usually conducted with a greenhouse experiment. The final step is a calibration study, usually conducted in several fields with different conditions.

9.1 Dissolved heavy metals

To analyze heavy metals in the soil environment, it is mandatory to understand the relationship between the various forms of heavy metals including free heavy metal cations, heavy metal complexes, heavy metal chelates, exchangeable heavy metals (adsorbed heavy metals), heavy metal precipitates, structural organic heavy metals, and structural mineral heavy metals. The relationship of these various forms of heavy metals is depicted in **Fig. 9.1**. **Fig. 9.1**. shows that metal forms can be analytically classified at least as: (1) Dissolved Heavy Metals, (2) Free Ionic Heavy Metals, (3) Exchangeable Heavy Metals, (4) Plant Available Heavy Metals, and (5) Total Elemental Heavy Metals. Each of this analytical classification covers different forms of heavy metals in the soil environment as listed in **Table 9.2**.

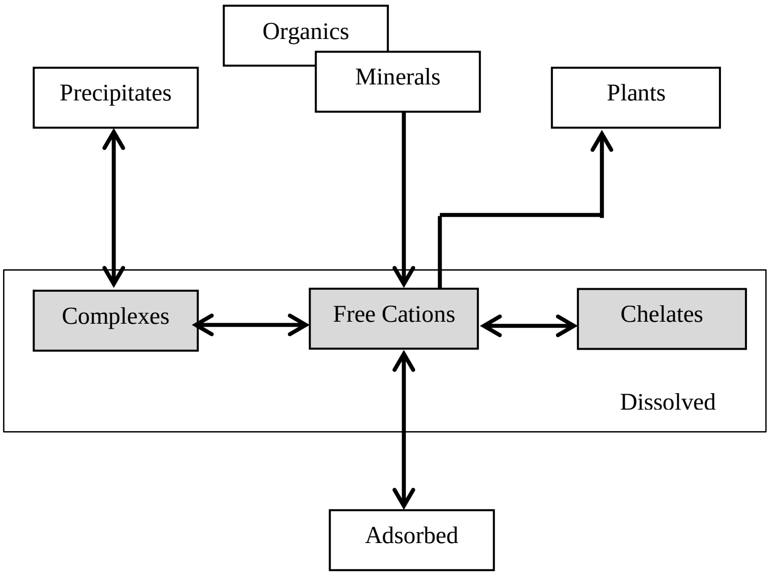

Fig. 9.1. Relationship between various forms of heavy metals in the soil environment.

Dissolved heavy metals include those soluble in soil water i.e. free heavy metal cations, heavy metal complexes, and heavy metal chelates (**Fig. 9.1**). Because their existence is in soil water, these heavy metals are mobile and, therefore, easily transported in the soil body and absorbed by plant roots. Total dissolved heavy metals in soils are excellent measures not only for heavy metal availability to plants but also of their impact and toxicity in the soil environment. Therefore, this variable is worth to measure to make better interpretation on heavy metal impact on the environment. A method to extract and measure the total dissolved heavy metals is therefore of utmost importance.

Table 9.2. Analytical classification of heavy metals in the soil environment.

No.	Analytical Classification	Included Heavy Metal Forms
1	Dissolved Heavy Metals	Free Cations, Complexes, Chelates
2	Free Heavy Metals Cations	Free Cations
3	Exchangeable Heavy Metal Cations	Exchangeable Cation
4	Plant Available Heavy Metals	Free Cations, Complexes, Chelates, Precipitates, Part of Organic Matters and Minerals
5	Total Elemental Heavy Metals	All form of Heavy Metals

Since containing the forms that dissolved in soil water, the method to extract the dissolved heavy metals is as simple as extracting the soil water filling all soil pores. To accomplish this measurement, a particular amount of known moisture content soil sample is weighed into a centrifugation bottle and then put in a centrifugator at high speed of 20,000 RPM. The soil water separated from its solid is then analyzed for heavy metals. The measured heavy metals are considered as the total dissolved heavy metals in soils water. Because the amount of soil water obtained by this method is relatively miniscule, particularly if the moisture content is below the soil field capacity, the soil sample must be previously moistened with a particular amount of water. The soil-to-water ratio of 1:1 is usually preferred. The soil and water is initially put in a shaker for a particular time to reach equilibrium, after which the water phase is filtered. The water phase or supernatant obtained is then more convenient for analysis. For some purposes, the soil-to-water ratio of 1: 10 is also used. Using this ratio, a centrifugation is no longer needed. After shaking for a particular time, the water phase can then be filtered using a whatman paper before analysis.

The total dissolved heavy metals in soil water actually contain three different forms of dissolved heavy metals, i.e. free heavy metal cation, heavy metal complexes, and heavy metal chelates. The amount of each of this dissolved heavy metals is various, but, unlike those of major cations like Na^+, K^+, Ca^{2+}, and Mg^{2+}, free heavy metal cations in general comprise smaller parts of total dissolved heavy metals. The amount of Zn^{2+} is reported to be about 40% of its total, while that of Cu^{2+} comprises about 2% of its total (Ellis and Knezek, 1982). The relative concentration of free cations and total dissolved heavy metals in Typic Argiudoll Elkhorn Wisconsin USA treated annually with 6.7 ton ha^{-1} of Milwaukee sewage sludge for more than 20 years are also reported by Salam and Helmke (1998). Their finding is given in **Table 9.3**. The total dissolved Cu and Cd were measured in the order of mM while that of free cations of Cu and Cd were measured much lower in the order of nM.

Table 9.3. Comparison of the concentration of total dissolved and free ionic heavy metals$^{1)}$.

No.	Heavy Metals	pH	Total Dissolved (mM)	Free Cations (nM)
1	log Cu	4	- 6.21	- 7.50
		5	- 6.34	- 7.75
		6	- 6.27	- 8.00
		7	- 6.00	- 8.21
2	log Cd	4	- 6.47	- 7.42
		5	- 6.91	- 7.78
		6	- 7.42	- 8.29
		7	- 8.12	- 8.72

$^{1)}$After Salam (1993) and Salam and Helmke (1998)

A routine method to determine the total dissolved concentration of heavy metals can be accomplished by weighing 2 gram of 105^0C oven-dry equivalent soil sample into an extracting bottle. To the soil sample, a 20 ml distilled water is added, after which the soil-water mixture is put in an end-to-end shaker. After a 30 minute shaking, the soil water mixture is filtered through a whatman paper. The concentration of heavy metals in the supernatant is then determined by using an Atomic Absorption Spectrophotometer (AAS). The supernatant can be diluted to obtain the concentration fitted to the standard curve developed previously. The measured absorbance is then used to determine the concentration of heavy metals using a well-prepared standard solution. The concentration of total dissolved heavy metal is then calculated using **Eq. 9.1**.

$$M_T = df.c \quad .... \quad \text{Eq. 9.1.}$$

where M_T is the total dissolved concentration of a particular heavy metal, df is the dilution factor, and c is the concentration of heavy metal in diluted supernatant. The total concentration is expressed in mg L^{-1} or in mM and can be converted into mg kg^{-1}.

Based on his batch and column experiments with water elluent, Abumaizar (1999) report that the weakly bound heavy metals are various. The weakly bound or total dissolved of some heavy metals were Cd about 70%, Zn 25 – 30%, Cr 20 – 25%, and Pb 10%. This data indicate that Cd is the most weakly bound by soil solids. The presence of EDTA was observed to increase the concentrations of heavy metals in in water leachates.

9.2 Free ionic heavy metals

Free ionic heavy metals in the soil solution play a central role in the chemistry of heavy metal in the soil environment. As pointed out previously, free ionic heavy metal is related to heavy metal reactivity and toxicity to the living things (Checkai et al., 1987a; 1987b). Checkai et al. (1987b) report that the accumulation of Cu, Cd, Mn, and Zn in the shoots of tomato plants appear to be related to their respective ionic activities rather than to their total concentrations. All chemical environmental reactions are directly related to the concentration of free ionic heavy metals (Allen et al., 1980; Checkai et al., 1987a; 1987b; and Hernandez-Soriano et al., 2012). These include the complexation/decomplexation, chelation/dechelation, precipitation/dissolution, adsorption/dissolution and oxidation/reduction. Plant root absorption on heavy metals is also related to their free ionic form concentration in soil water. Therefore, the analysis of free ionic heavy metal concentration is very important. However, the analysis of this species is under research and development. The available technique is either tedious or shows some drawbacks.

The easiest way is using some available computerized models to predict their concentrations based of the measurement of controlling soil properties that are easier to measure like soil pH, soil clay, and soil organic matter content (Kamewada and Nakayana, 2009). The models developed by Lindsay and his coworkers for calcareous soils assuming that the free ionic heavy metals are controlled by precipitation-dissolution reactions are good examples. For example, the concentration of Cu, Cd, and Zn in calcareous soil with pH of 7.0 is $10^{-11.2}$, $10^{-7.50}$, and $10^{-8.20}$ M, respectively. When pH is raised to 8.5, the concentration of Cu, Cd, and Zn is lowered to be $10^{-14.20}$, $10^{-10.50}$, and $10^{-11.20}$ M, respectively. These phenomena are listed in **Table 9.4**.

Table 9.4.. The prediction of free ionic heavy metal concentration by Lindsay models1).

Heavy Metals	Equation Model1)	Concentration (M) at pH	
		7.0	8.5
Cu	$\log(\mathrm{Cu}^{2+}) = 2.80 - 2\ \mathrm{pH}$	$10^{-11.2}$	$10-^{14.20}$
Cd	$\log(\mathrm{Cd}^{2+}) = 6.50 - 2\ \mathrm{pH}$	$10^{-7.50}$	$10^{-10.50}$
Zn	$\log(\mathrm{Zn}^{2+}) = 5.80 - 2\ \mathrm{pH}$	$10^{-8.20}$	$10^{-11.20}$

1)Taken from Lindsay (1979), Workman and Lindsay (1990), Ma and Lindsay (1990), El-Falaky et al. (1991)

Kamewada and Nakayana (2009) also developed an empirical mathematical equation to predict the activity of free Cd^{2+} in soil solution. The equation is shown in **Eq. 9.2**.

$$\mathrm{Log}\,(\mathrm{Cd}^{2+}) = \mathrm{Log}\,K_{mon} + \mathrm{Log}\,Q_{Cd} - \mathrm{pH} - \log C_{Cd} \quad .... \quad \text{Eq. 9.2}$$

where K_{mon} is the equilibrium constant for Cd adsorption, (Cd^{2+}) is the activity of Cd^{2+}, Q_{Cd} is the amount of adsorbed Cd, and C_{Cd} is the soil Cd adsorption capacity.

Computerized programs to predict the concentrations free ionic heavy metals such as MINTEQ (Jaiswal and Elliott, 2011) can be developed by employing some soil properties. These properties must suffice some important requirements. First, the soil properties must control or be related to the concentration of free ionic heavy metals. In other words, changing these soil properties may cause the changes in free ionic heavy metal concentrations. These may include, for example, soil E and soil pH, soil clay content, soil organic matter content, soil P, soil CEC, and soil moisture content. These soil properties are all well-correlated with the concentrations of free ionic heavy metals. Second, the soil properties are easy to measure to obtain accurate results. The inclusion of all these soil properties with accurate values may enable the developed computer program to predict the concentration of free ionic heavy metals easier and more accurately.

The measurement of total dissolved heavy metals in soil water does not provide the information on the concentration of free ionic heavy metal since soil water contain various forms of dissolved heavy metals including free heavy metal cations, heavy metal complexes, and heavy metal chelates. To directly obtain the free ionic concentrations, several methods are actually available. Anodic stripping Voltammetry (ASV) is one of the methods that may accurately measure the concentration of free ionic heavy metals in soil water at ppb and sub-ppb levels. However, as pointed out by Figura and McDuffle (1980), this method is prone to interference for natural water system. Ion Selective Electrode may also measure the concentration of free ionic heavy metals (Oliver et al., 2005). However, the detection limit of this method is too high for natural water system (Jackson and Bondietti, 1977; Minnich and McBride, 1987). On the other side, ion exchange chromatography (HPLC) may suffice the needed detection limit for free ionic heavy metal concentration of natural water system. However, the natural heavy metal complexes are often not stable in the appropriate chromatography (Ge and Wallace, 1988).

Cantwell et al. (1982) and Treit et al. (1983) suggest that Ion Exchange Resin can be employed to equilibrate the sample solution in a batch or column experiment. The equilibrium can be reached by passing the sample solution through the cation-exchange resin until a complete breakthrough of heavy metals. After water leaching, the adsorbed cations can be extracted from resin and measured. This method shows a good detection limit, but may disturb the equilibrium of soil water under study (Treit et al., 1983). Schneider (2006) also used ion exchange resin for the determination of free ionic fraction of Cd in soil solution.

Free ions can also be separated and accurately measured using ion exchanger as a selective membrane (Lampert, 1982; Fitch and Helmke, 1989; Helmke et al., 1995; and Salam and Helmke, 1995; 1998). This method is the best to selectively separate and accurately measures the free ionic heavy metals from soil water by donnan equilibrium (Blaedel dan Haupert, 1966; Salam and Helmke, 1995; 1998). This method is relative sensitive, free from interference, and does not disturb the soil water equilibrium. However, this method is relatively tedious.

Example of analysis using this method for free ionic heavy metals in soil are previously shown (**Table 9.3**).

9.3 Exchangeable heavy metals

Exchangeable heavy metals cations are not in soil water but on soil solids. Even though not included as dissolved form, this heavy metal form is readily dissolved releasing the cation from solid surface into the soil water (**Fig. 9.1**). The release of free heavy metal cations from the solid phase is controlled by ion exchange as depicted in **Eq. 9.3** for the case of exchangeable Cd.

$$\textbf{X-Cd} + \textbf{Ca}^{2+} \leftrightarrow \textbf{X-Ca} + \textbf{Cd}^{2+} \quad \ldots\ldots\ \textbf{Eq. 9.3}$$

where **X-Cd** and **X-Ca** are adsorbed Cd and adsorbed Ca, respectively, $\mathbf{Cd}^{2+}$ and $\mathbf{Ca}^{2+}$ are dissolved Cd and Ca, respectively. Because the adsorbed Cd and adsorbed Ca are exchangeable, adsorbed Cd and adsorbed Ca are also called exchangeable Cd and exchangeable Ca.

The amount of the exchangeable cation is controled by the concentration of dissolved heavy metals in soil water. When the concentration of heavy metal cation in the soil environment is high then the concentration of adsorbed heavy metal is high because parts of dissolved heavy metals are adsorbed by the soil solid as exchangeable heavy metals. Conversely, when the dissolved heavy metals in soil water are lower, the exchangeable heavy metals may release into the soil solution to reach the constant equilibrium. This shows that the amount of exchangeable cations is very important in the management of heavy metals in the soil environment. The amount of exchangeable heavy metals is then very important to measure accurately.

To measure the exchangeable heavy metals, the principle of cation exchange is employed. An excessive amount of salt solution containing particular displacing cation is added to a known amount of soil sample. Some common displacing cation are NH_4^+, Na^+, Ca^{2+}, and Ba^{2+} contained as various salts like NH_4OAc, $NaNO_3$, $Ca(NO_3)_2$, and $BaCl_2$. After equilibration through shaking for a particular time span, the soil water is filtered and the supernatant is then analyzed for the heavy metals. The amount of heavy metals in the extracted soil water is considered the soil exchangeable heavy metals. Maiz et al. (2000) used 0.01 M $CaCl_2$ to measure the soil exchangeable heavy metals which in their term is referred to as mobile Cu, Cd, Zn, and Pb. They observed that these concentrations were related to the total metal concentration in grass.

The amount of exchangeable heavy metal cations is higher than those in the dissolved heavy metal cations. This relationship is shown by Cu and Zn measured in soils treated with heavy metal containing industrial waste as given in **Table 9.5** for Cu and **Table 9.6** for Zn. For example, the amount of exchangeable Cu in unlimed Ultisol Gedongmeneng is 0.64 mg kg^{-1} compared to the dissolved Cu 58 μg kg^{-1}, or about 11 times higher. Liming these soils at 5 ton $CaCO_3$ per hectare shifts the exchangeable and dissolved Cu to lower values. Some of the dissolved Cu is probably adsorbed onto the soil exchange site and part of the exchangeable Cu is shifted to a stronger adsorption site or precipitated due to the increase in soil pH. However, the exchangeable Cu is still higher than of the dissolved Cu (**Table 9.5**). Similar phenomenon is also observed with Zn (**Table 9.6**).

Table 9.5. Comparison of dissolved, exchangeable, and plant available Cu in limed Indonesian soils treated with heavy metal containing waste$^{1)}$.

Soil	Lime (ton ha^{-1})	Forms of Cu		
		Dissolved (Water) (μg kg^{-1})	Exchangeable ($CaCl_2$) (mg kg^{-1})	Plant Available (DTPA) (mg kg^{-1})
Ultisol Gedong Meneng (Bandar Lampung)	0	58	0.64	60
	5	52	0.13	41
Alfisol Banjar Agung (East Lampung)	0	75	0.98	49
	5	54	0.14	35
Vertisol Cihea (Cianjur, West Java)	0	31	0.45	53
	5	88	0.34	35

$^{1)}$Adapted from Salam et al. (1997k)

In a routine analysis, analysis for exchangeable heavy metals can be conducted by weighing a 2 g oven-dry (105 0^{o}C, 24 hours) soil sample into an extracting bottle and was then added a 20 ml extracting solution of 1 M $CaCl_2$ or other salts like $Sr(NO_3)_2$, $NaNO_3$, and NH_4OAc. The mixture is put in an end-to-end shaker for about 30 minutes. After filtration, the supernatant is then analyzed for heavy metal concentrations using Flame Atomic Absorption Spectrophotometer (AAS) for ppm level or graphite furnace AAS for heavy metals with low concentration at ppb or sub-ppb levels. The absorbance is compared to the standard curve for the related heavy metals. The standard curves must be developed very carefully as to cover the concentration range but fulfilling the requirement of a straight line with high correlation coefficient. Sometime, dilution of sample solution must be conducted to fit the absorbance into the absorbance of the standard curve.

Table 9.6. . Comparison of dissolved, exchangeable, and plant available Zn in limed Indonesian soils treated with heavy metal containing waste[1).

Soil	Lime (ton ha^{-1})	Forms of Zn		
		Dissolved (Water) (µg kg^{-1})	Exchangeable ($CaCl_2$) (mg kg^{-1})	Plant Available (DTPA) (mg kg^{-1})
Ultisol Gedong-meneng (Bandar Lampung)	0	107	11.5	8
	5	16	1.3	11
Alfisol Banjaragung (East Lampung)	0	104	10.2	9.4
	5	35	1.3	11.5
Vertisol Cihea (Cianjur, West Java)	0	37	6.7	10.4
	5	24	0.4	12.4

1)Adapted from Salam et al. (1998f)

The concentration of the exchangeable heavy metals can be calculated by **Eq. 9.4**.

$$\text{Exch. M} = \text{df}\,\frac{1000}{w}\,\frac{v}{1000}\,\text{c} \quad \ldots\ldots \quad \textbf{Eq. 9.4}$$

where Exch. M is the soil exchangeable heavy metal M in mg kg^{-1}, df is dilution factor, w is the soil sample weight in gram, v is the volume of the extracting solution used, and c is the concentration of heavy metal in sample solution. Simplifying **Eq. 9.4** may result in **Eq. 9.5**.

$$\textbf{Exch. M} = \textbf{df}\,\frac{v}{w}\,\textbf{c} \quad \ldots\ldots\ \textbf{Eq. 9.5}$$

When the soil weight is 2 g and the volume of the extracting solution used is 20 ml, then the Exchangeable M equals to 10 times df times c. This equation is convenient to use in calculating the exchangeable heavy metals based on the measurement data.

Soil exchangeable heavy metals are various, depending on soil pH and organic matter contents. Gerritse and van Driel (1984) report that the soil exchangeable fractions of soils were found to lie in the range of 1 to 5% of the soil total metals for Pb and about 10 to 50% for Cd, Zn, and Cu.

9.4 Plant available heavy metals

Plant roots possess extraordinary ability to extract and absorb plant nutrients from the soil environment. Plant roots absorb not only the readily available plant nutrients and heavy metals from the soil water and the surfaces of soil solids but also parts of the structural elements in the solid minerals and solid organics by first detaching them through dissolution (weathering) processes. The root excretion of H^+ ions and organic acids may lower the soil pH adjacent to the plant rooting system, that eventually intensify the detachment of the structural elements including heavy metals from secondary and primary minerals. The excretion of soil enzymes like phosphatase and arylsulphatase by plant roots may also intensify organic matter decomposition that may contain heavy metals. All these reactions raise the amount of heavy metals thatl can be absorbed by plant roots.

The above explanations suggest that plant roots absorb a wide range of heavy metal forms in the soil environment. These may include the readily available forms such as free heavy metals cations, heavy metal complexes, heavy metal chelates, and exchangeable heavy metals as well as that moderately and slowly available heavy metal in precipitates (secondary minerals), primary minerals, and organic matters (**Fig. 9.1**). These fact causes the higher content of absorbed heavy metals compared to the sum of free ionic heavy metals, heavy metal complexes, heavy metal chelates, and exchangeable heavy metal cations. The difference is originated from the organic and inorganic solids which are actually slowly available to plant root absorption.

Therefore, the analysis of plant available heavy metals must use an extractant that successfully imitate the ability of the plant roots in extracting the various forms of heavy metal in the soil environment. To accomplish this, the best extractant must be developed through several steps that need several experimental researches. A good plant available extractant must go through three steps before being used successfully for routine analysis. The steps are: (1) extractant development, (2) correlation study, and (3) calibration test. The first step in purely conducted in laboratory using soil samples collected from different fields. The second step is usually conducted in a greenhouse using several selected soil samples collected from one or several field. The third step in purely conducted in the fields under field conditions; fields with different soil types and microclimates are preferred.

To devise a method to test the plant available heavy metals in the soil environment, the first thing to do is to determine a number chemical solution that is potential to employ. The chemical solution may include those that can extract all dissolved heavy metals and exchangeable heavy metal cations as well as parts of the insoluble heavy metals in primary and secondary minerals and release heavy metal bounded in the structure of organic matters. These chemical substances can be salts like $Sr(NO_3)_2$, NH_4NO_3, $BaCl_2$, etc. or chelating agents like Ethylene Diamine Tetraacetic Acid (EDTA) and Diethylene Triamine Pentaacetic Acid (DTPA). These chemical substances may extract different amounts of heavy metals from any different heavy metal forms. However, the amount of heavy metals extracted by any extractant does not matter. The most important is that in a correlation study the amounts of the heavy metals extracted by the extractant is well correlated with the amounts of the heavy metals absorbed by plants. When the correlation coefficient is high approaching 1, the extractant is a good predictor for plant heavy metal availability, the total absorption of heavy metal can be accurately predicted by the analytical results (**Fig. 9.2**). Conversely, the correlation coefficient approaching 0 indicates that the chemical substance is not a good predictor for plant heavy metal availability. It is also important to notice that the exctractant C is better that Extractant A and B because of the higher b value.

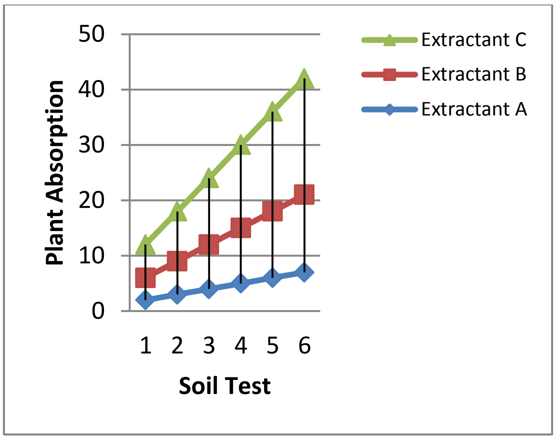

Fig. 9.2. A linear relationship between plant absorption and soil test result.

The relationship between the analytical result and the absorption of heavy metal can be expressed in a regression equation in **Eq. 9.6**, where **Y** = the absorbed heavy metals by plants, **X** is the result of soil heavy metal analysis, **a** is an intercept on Y axis or the value of heavy metal absorbed when the heavy metal analysis result is 0, while **b** is the equation gradient or the increase in plant heavy metal absorption by plants per unit increase in soil heavy metal analysis.

$$Y = a + bX \quad \ldots\ldots \quad \textbf{Eq. 9.6.}$$

The value of **b** may vary depending on the soil types. For example, the b values in clay soil may reach 3 times of that in sand soil. This means that the absorption in the clay soils is 3 times higher than that in sand soils.

He and Singh (1994) used DTPA and NH_4NO_3 as extractants to observe the soil availability of Cd to oat (*Avena sativa* L.), ryegrass (*Lolium multiflorum* L.), carrot (*Daucus carota* L.), and a spinach (*Spinacia oleracea* L.). They found that the Cd concentrations determined by using these extractants were significantly correlated with the total Cd uptake by plants. Maiz et al. (2000) used 0.005 M DTPA to measure the soil plant available heavy metals which in their term is referred to as mobilizable Cu, Cd, Zn, and Pb. They observed that these concentrations were related to the total metal concentration in grass.

There are number factors important to conduct a good correlation study to evaluate the effectiveness of a number of chemical extractants (Corey, 1964). The correlation coefficient is more accurate if greater number of soil samples is used. The correlation coefficient is also better when heavy metal concentrations in soil samples vary with a greater range. The correlation coefficient is also better when the variables normally distributed with no outlier (outlier are eliminated). A better correlation coefficient may show the effectiveness of each extractant in predicting the plant heavy metal availability. The effectiveness of each chemical extractant can be compared by comparing the values of correlation coefficients. For a number of soil clusters, the comparison between several chemical extractants can be conducted by evaluating the standard deviation. In comparing different method, the scattered diagrams must be shown.

A good extractant as a result of a correlation study must be tested in a calibration study under field condition to develop calibration curves shown in **Fig. 9.3**. Calibration study actually evaluate the relationship between the result of soil heavy metal test in laboratory and the response of plants, for example plant height or plant yields. As suggested by Corey (1964), the plant response is curvilinear (**Fig. 9.8**). The curve is higher or better when no other limiting factors other than the heavy metal under study (Curve A). In any case, the soil test must be able to predict the plant yield or responses. The calibration curve must be able also toshow the optimum and maximum yields as well as the deficient areas. A good soil heavy metal test must be tested in different fields with different status of heavy metal nutrients, soil types, microclimates, and seasons. Studies in different seasons may also improve the accuracy of calibration study.

Calibration test is conducted in the fields, therefore this test may encounter more problems than does the correlation test that is conducted in green houses. Among the problems are the uncertainty of climate related to water supply, temperature, and pest and disease control. Corey (1964) suggests that to minimize the effect of field problems of climate and pest and disease, calibration test must be conducted in different locations and seasons for several years. The number of location is more important than the number of replication, particularly in order to obtain a wide range of soil test results. The size of experimental plots must be enough to obtain an appropriate production. The soil sampling must also be conducted with an appropriate method.

Correlation and calibration tests may produce a good soil heavy metal test that is appropriate for the analysis of plant available heavy metals in the soil environment. The values obtained by the chemical test may provide the amount of heavy metals absorbed by plants as well as the plant production. However, the soil heavy metal test is generally plant species specific. The plant heavy metal absorption and the plant production greatly depend on plant species. Different plant species may need different amounts of heavy metals, thereby, may give different responses of the availability of heavy metals in the soil environment

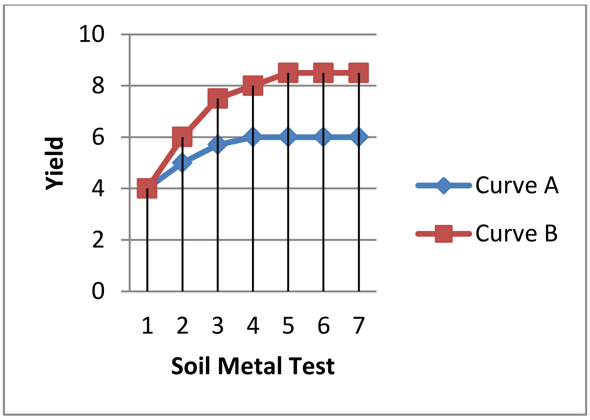

Fig 9.3. The calibration curve of soil heavy metal test (Curve A = when no other limiting factor other than the related heavy metal, Curve B = when other limiting factors exist).

The calibration curve may provide the amount of heavy metal nutrients to be added through soil fertilization. However, the fertilizer recommendation must consider several other factors, not only on the calibration curve (Corey, 1964). Some of the factors to consider in recommending fertilization are: (1) the yield increase to reach, (2) the price of plant products, (3) the price of fertilizers, (4) additional cost as affected by the increase in production to reach, (5) residual effect, (6) the availability of fund and credit, (7) alternatives of fund usage if capitals are limited, (8) the time span of field rent, (9) the size of agricultural land, and (10) the capability of farmers to manage lands.

The analysis of plant available heavy metals may also involve the chelation of heavy metals in the soil system, The chelation is usually conducted using Ethylene Diamine Di-(o-hydroxyphulacetic) Acid (EDDHA), Ethylene Diamine Tetraacetic Acid (EDTA), and Diethylene Triamine Pentaacetic Acid (DTPA). The common method available in literature used for the analysis of plant available heavy metals is the DTPA method (Baker and Amacher, 1982). This extractant extracts the heavy metals not only from the dissolved forms like free ions, complexes, and chelates, but also parts of the adsorbed and structural heavy metals in organic matters and minerals. The detachment is caused by the chelation of free ion heavy metals that may detach all other heavy metal cations bonded on the soil solid surfaces and also the structurally bonded in the soil solids of organic matters as well as primary and ssecondary minerals. The result is that the extracted heavy metals is higher than those of free ions, complexes, chelates, and exchangeable cations. Example of plant available heavy metals are previously given in **Table 9.5** and **Table 9.6**, showing the concentrations of free ions, exchangeable cations, and plant available heavy metals in limed soils treated with heavy metal containing industrial waste.

The DTPA method is conducted using DTPA extracting solution made by dissolving 0.005M DTPA, 0.01 M $CaCl_2$, and 0.01 M triethanolamine (TEA) in a pH adjusted to 7.30. To conduct the analysis, a 10 g of air-dried soil sample is shaken with 20 mL of the DTPA extracting solution for 2 hours and centrifuged and/or filtered to obtain the solution phase. The concentration of heavy metals is then measured using flame AAS. The method is found in Baker and Amacher (1982). Like those extracted by $CaCl_2$ and Mehlich-1, the heavy metal concentrations extracted from soil by DTPA were well-correlated with the concentrations of heavy metals in plants (Sukkariyah et al., 2005).

Plant available heavy metals can also be predicted by their concentrations in soil solution using empirical mathematical equation. Kamewada and Nakayana (2009) predict the uptake of Cd by garland chrysanthemum using the value of Cd concentration in soil solution using **Eq. 9.7**.

$$\mathbf{U_{Cd} = Vp[Cd]_T + \{V_{max}[Cd_T]/Km + [Cd_T]\} \quad .... \quad Eq.\ 9.7.}$$

where U_{cd} is plant Cd uptake, Cd_T is the total concentration of Cd in the soil solution, and V_p, V_{max}, and K_m are constants. Adams et al. (2004) also developed a mathematical model to predict Cd concentration in wheat and barley grain as seen in **Eq. 9.8**.

$$\mathbf{\log (Grain\ Cd) - a + b \log (Soil\ Cd) - c\ (Soil\ pH) \quad .... \quad Eq.\ 9.8}$$

where Grain Cd is the concentration of Cd in grain, Soil Cd is the concentration of Cd in soils , soil pH is the soil pH, and a, b, and c are constants.

9.5 Total elemental heavy metals

Plant available indices of heavy metals comprise the heavy metals relatively weakly hold in the soil environment and, thereby, they are easily released and absorbed by plant roots. As mentioned previously, this include: free ions, complexes and chelates, exchangeable cations, and the part of structural elements hold with a relatively weak bonding energy. The rest of the structural elements in the soil solids may release the heavy metals through mineral weathering and organic matter decomposition, and thus are considered to potentially contribute heavy metals in the soil environment in the future. Therefore, though plant available heavy metals are considered the most important, in the long run the insoluble soil solids may supply some heavy metals. Hence, it is important also to understand the total analysis of heavy metals.

Total analysis may include all forms of heavy metals in the soil system. Therefore, the analysis must involve the chemical substances that dissolve all heavy metals elements in soil water and soil solids into the soluble forms. This can be conducted by acid digestion of fusion as reported by Lim and Jackson (1982). The total elemental concentration is then measured using flame AAS.

One of the methods to analyze the total metal contents in soils is by digestion with HNO_3-HF, after which their elemental contents are analyzed using inductively coupled plasma-optical emission spectroscopy (ICP-OES). The value of total concentration of Cu, Cd, and Zn in a Typic Argiudoll of Wisconsin USA treated with municipal sewage sludge and lime as reported by Helmke et al. (1995) is given in **Table 9.7.**

Table 9.7. Total concentrations of heavy metals elements and pH in soil treated with municipal sewage sludge and lime [1].

Sludge	Lime	pH	Cu	Cd	Zn
(ton ha^{-1})			mg kg^{-1}		
0	Yes	6.3	41	1.1	98
	No	5.8	36	1.1	98
46	Yes	6.1	34	3.2	100
	No	5.6	39	3.9	109
93	Yes	5.9	38	4.2	103
	No	5.0	37	6.2	117

[1] After Helmke et al. (1995)

Important questions

1. Explain the relationship between all heavy metal forms in the soil environment!
2. Explain the dissolved forms of heavy metals in soil water that include free ions, complexes, and chelates! What are the difference?
3. Explain the structural forms of heavy metals in soil solids that include precipitates, secondary minerals, primary minerals, and organic matters!
4. Differentiate the relationships between the chemical forms controlled by equilibrium constants and those not controlled by equilibrium constants!
5. Explain the analytical methods to measure the concentrations of the total dissolved heavy metals!
6. Explain the analytical method to measure the exchangeable heavy metal cations!
7. Explain the methods to measure or to predict the concentrations of free ionic heavy metal in the soil water!
8. What are plant available heavy metals? What is the relationship of these forms with other forms of heavy metals in the soil environment?
9. Explain the method to measure the plant available heavy metals in the soil environment!
10. Explain the strategy to develop a good extractant to measure the plant available heavy metals in the soil environment!
11. Explain how to conduct a good correlation study! What factors must be considered to obtain a reliable correlation coefficient?
12. Explain how to conduct a calibration study! What factors must be considered in obtaining a reliable calibration curve?
13. How to use the result of calibration study to make a fertilizing recommendation? What factors must be considered to make a good fertilizing recommendation?

Chapter 10

Conclusions

Heavy metals in the environment is now of great concern due to the fact that these elements have been silently accumulating in the environment and endangering the living things. Their concentrations in the environment are high and their emissions significantly increase related to the growth of world population and industries. The accumulation of heavy metals is higher in urban areas and begins to affect rural environment. Together with this pattern, the impact on the living things also increases because most heavy metals are carcinogenic and may cause cancer and several other diseases. Some monumental emerging diseases have been reported in the literature, among which are Minamata, Itai-itai, and Wilson diseases caused by polluted environment by Hg, Cd, and Cu, respectively (Lagerwerff, 1982; Bohn et al., 1985; Tiller, 1989; Alloway, 1990d; Baker, 1990; Steinnes, 1990; Kabata-Pendias and Pendias, 1992; Daoust et al., 2006; Oporto, 2007; and Widowati et al., 2008). Some other cases related to heavy metal pollution have also been reported from several parts of the world (Lagerwerff, 1982; Kardoz et al., 1986; Leung, 1988; Hegstrom and West, 1989; Alloway, 1990c; Davies, 1990; Kiekens, 1990; Rivai, 1990; Dowdy et al., 1991; Boon and Soltanpour, 1992; Jing and Logan, 1992; Wang et al., 1992; Herrero and Martin, 1993; Sweet et al., 1993; Cabrera et al., 1994; Nicholson et al., 1994; Schuhmacher et al., 1994; Tsoumbaris and Tsoukali-Papadopoulou, 1994; Bilski and Alva, 1995; Flegal and Smith, 1995; Vile et al., 1995; Gimeno-Garcia et al., 1996; Salam et al., 1996; Yeh et al., 1996; Salam et al., 1997a; Juracek and Ziegler, 2006; Biasioli et al., 2007; Benke et al., 2008; Berenguer et al., 2008; Lin et al., 2008; Hobara et al., 2009; Benn et al., 2010; Cakmak et al., 2010; Kien et al., 2010; Wang et al., 2010; and Tu et al., 2012).

Heavy metal elements are not necessarily toxic to the living things. Some heavy metal elements such as Fe, Mn, Zn, Cu, and Co are essentially needed by plants (Salam, 2012). These elements are needed but at low concentrations. Some other heavy metal elements are not needed by plants and animals or at least their functions in plants and animals are not yet known. Even though not needed, these elements are not harmful to the living things as long as their concentrations are below the allowable levels. Their presence becomes problem when their concentrations are higher that their allowable levels, particularly at concentration too high for the soil environment. All micronutrient heavy metal elements may also cause problem when their concentrations are above the allowable levels. Therefore, both kinds of heavy metal elements are safe at low concentration (below the allowable levels) and toxic at high concentrations. The differences between micronutrient heavy metal elements and non-nutrient heavy metal elements are depicted in **Fig. 10.1** (Alloway, 1990c).

Fig. 10.1 clearly shows that heavy metals, both micronutrients or non—micronutrients, are toxic and may cause health problem for the living things. This means that at low concentrations, heavy metals are good; micronutrient heavy metal elements may stimulate plant growth and development while those of non-nutrients may not give negative effects on the plant growth and developments. However, at high concentrations of both nutrient and non-nutrient elements are toxic and may give negative effect on the plant growth and development or cause phytotoxicity. The phytotoxicity may include the causal mechanisms as listed in **Table 10.1** (Kabata-Pendias and Pendias (1992).

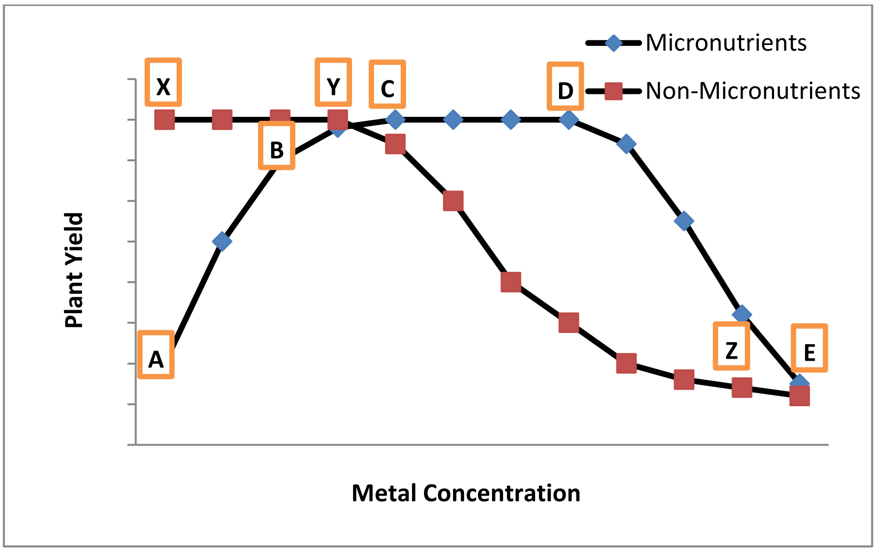

Fig. 10.1. The differences between nutrient- and non-nutrient heavy metal elements. (A-B Severe Deficiency, B-C Mild Deficiency, C-D Optimum, and D-E Toxicity; X-Y No Effects, Y-Z Toxicity; Adapted from Alloway, 1990c)

Table 10.1. Some causal mechanisms of heavy metal phytotoxicities[1).]

No.	Causal Mechanisms	Metal Elements
1	Changes in cell membrane permeability	Ag, Au, Cd, Cu, Hg, Pb
2	Reaction with Sulfhydryl (-SH)	Ag, Hg, Pb
3	Competition with essential metabolites for sites	As, W
4	Affinity for reaction with phosphates and active groups od ADP and ATP	Al, Be, Zr
5	Replacement of essential ions (mainly major cations)	Cs, Li, Rb, Se
6	Site occupation for essential groups like phosphates and nitrates	As, Se

1)Adapted for Kabata-Pendias and Pendias (1992)

As discussed above, high concentrations of heavy metals in the environment are dangerous. If these concentrations are not controlled, they may cause negative effects on the living things. Some of the negative effects of high heavy metals have been discussed previously. Therefore, efforts must be conducted to control the heavy metal concentrations in the environment.

10.1 Uncontrolled heavy metals concentrations in soils

As pointed out in the previous chapters, heavy metals are emitted from various sources and are accumulated in the environment. Their existence is not only in the soil system, but also in water system and air system, and therefore, endangering the living things in contact with the respective system. Their accumulation is alarming in some urban areas and also in rural areas in the vicinity of heavy metal emitting activities such as minings and factories. If the accumulating concentrations are not controlled, their potential dangers may come in effect. Of course, the heavy metals in the air system are more difficult to control due to their great mobilities. In some degree, this fact is also similar for those in the water system. Among the three, those in soil system are more easily managed.

In general, as long as their concentrations in soils are below the allowable levels, the emission of heavy metals into the soil system will actually not endanger the living things. Ross (1994) shows that the toxic levels of total Cu concentration in soils is 60 mg kg^{-1}, of total Zn concentration is below 70 mg kg^{-1}, of total Cd is < 9 and that for Pb is < 100 mg kg^{-1}. In fact, some of the metal elements such as Cu, Fe, Mn, and Zn may be used as micronutrients for plants if managed at lower concentrations. Particular industrial wastes with heavy metal concentrations relatively low are possible to be used as fertilizers precursor to enhance soil fertility (Salam et al., 2000). Pereira et al. (2012) reported that the irrigation with reclaimed waste water increased the availabilities and total concentrations of nutrients and non-essential elements in soils, and also soil salinity and sodicity by two to three times compared to that with irrigated well water. The major parts of nutrients in reclaimed waste water were free ionic species readily available for plant absorption such as: NH_4^+, NO_3^-, K^+, Ca^{2+}, Mg^{2+}, SO_4^{2-}, H_3BO_3, Cl^-, Fe^{2+}, Mn^{2+}, Zn^{2+}, Co^{2+}, and Ni^{2+}. More than 80% of Cu, Cr, Pb, and Al were complexed with CO_3^-, OH^-, and/or organic matters.

However, if the concentrations are highly uncontrolled, they will cause some problem and potential disasters. Some health disasters are pointed out in the literature related to the uncontrolled and probably at that time unrealized excessive concentration of heavy metals in the environment. Oporto (2007) reports an estimation of Cd intake from potato consumption by local population in soil irrigated with contaminated river water in Potosi Bolivia was about 100 mg d^{-1}, exceeding the WHO recommended total daily intake. Health disaster caused by Cd accumulation in human tissue also occurred as a result of contamination of river and paddy field water in Jintsu Valley, Toyama, Japan, in 1940 is included in current literatures (Alloway, 1990d). This phenomenon caused a disease called *Itai-Itai*. In 1950s a similar case also occurred in Minamata Bay, Japan, caused by methyl mercury accumulation which caused Minamata Desease. The accumulation was first observed in fishes consumed by Minamata community (Steinnes, 1990). Baker (1990) also showed that Cu accumulation may cause a heredity desease called Wilson desease. In 2010, a similar tragedy also occurred in Buyat Bay, Minahasa, North Celebes, Indonesia.

To avoid such disasters, the silent accumulating heavy metals must be controlled. Regulations pertaining to the heavy metal emission and disposal must be employed and laws related to heavy metal in the environment must be consistently enforced. Environment technology may also be developed so that heavy metals in the environment can be set at very safe levels. Environment technology related to the metal retention in the soils system can be employed. Soil system is more useful because it has more solids that have adsorbing potential towards heavy metals through adsorption and precipitation processes. The retention capability of soil solids is manageable. Some soil and environmental properties can be employed to increase soil ability in metal retention.

10.2 Mechanisms for controlling of heavy metal concentrations

Heavy metal retention in the soil environment is probably the safest way to control heavy metals in the environment, particularly compared to those in the water system and air system. Heavy metal retention also occur on the solid phase of water system and air system, but these solids are mobile, may move easily from one point to another and may endanger the living things in contact. The soil solid phase is, however, more immobile. Furthermore, the soil solids comprise most of the soil system, normally about 50% of the soil volume and may be more when soils are dry. Therefore, the soil solids may immobilize a great amounts of heavy metals. The purpose is to maintain the concentrations of heavy metal cations in soil water below the allowable levels, which are safe for the living things. This means that heavy metals must be collected from water and air system into the soil system. Once they come into the soil system, heavy metals are easier to manage.

The heavy metal retention in the soil system can be conducted using three approaches. The first approach is to widen the soil adsorption capacity towards heavy metals cations, by assuming that the major controlling mechanism for heavy metal is the adsorption-desorption process. This approach is increasing the amount of the sources of the negative charges in the soil system through addition of one or more negative source materials. As discussed previously, some of the usual materials employed are organic matter compost and zeolites, and currently biosolids called biochars is also used to increase the soil solid adsorption capacity. Upon addition to soil system, these materials may increase the capacity of soil solids to immobilize the dissolved heavy metals. Biochar is reported better than composts due to its durability in the soil system. Its decay process is relatively slower compared to organic matter compost. It is suggested that biochar is long-lasting.

Included in the first approach is the use of some soil amendments to stimulate the precipitation process. Some authors suggest that heavy metal concentrations in the soil system is controlled by the precipitation-dissolution processes. Among the soil amendments are lime and P-fertilizers. The presence of more OH^- by lime treatment may stimulate the precipitation of some heavy metal hydroxides such as $Fe(OH)_3$ and $Pb(OH)_2$. These solid secondary minerals may hold the heavy metals as long as the soil water is saturated with respect to the heavy metal cations and OH^- ions. The dissolution may occur only and only when the concentrations of heavy metal cations and the OH^- ion are lower so that their products are lower than the related solubility constants. When this situation happens, the precipitates may readily dissolve releasing its constituents. Compared to compost and zeolites, Castaldi et al. (2005) report that $Ca(OH)_2$ was more effective at increasing heavy metal retention in soils and decreasing heavy metal uptakes by white lupin. The residual fractions of Pb, Cd, and Zn were also found greater in soils amended with $Ca(OH)_2$.

A similar process may occur when the soils are treated with phosphates. Phosphates like primary and secondary orthophosphates $H_2PO_4^-$ and HPO_4^{2-} may combine with heavy metals and form metal phosphate precipitates like $Fe(H_2PO_4)_3$ and $Fe_2(H_2PO_4)_3$. Some of the metal-phosphates formed by the precipitation reaction are discussed in the previous chapters. The precipitation may occur when the soil water is saturated with respect to the concentration of heavy metal cations and phosphate ions. The precipitates are not stabile, depending on the concentrations of these ions. When the soil water is not saturated or the concentrations of heavy metal cations in the soil water are lower, these soil secondary minerals may dissolve releasing the heavy metals cations and phosphate ions. This reaction is not expected for the toxic heavy metals.

The second approach is by indirectly increasing the soil adsorption capacity by managing some soil and environmental properties like soil pH and soluble P. This approach may enlarge the soil negative charges and, thereby, the soil may immobilize more heavy metal cations. Increasing the soil pH has been reported to increase the amount of the soil negative charges, particularly in soils dominated by non-silicate clay minerals, 1:1 silicate minerals, and organic matters, which are pH-dependent. The enlargement of the soil negative charges may eventually increase the heavy metal retention. The increase in soil pH is generally attained by the addition of lime, which is added at particular levels. The lime level is carefully determined through laboratory experiments.

In addition to by increasing the soil pH, the enlargement of the soil negative charges can also be conducted by phosphate addition, through addition of P-fertilizers or addition of phosphatic mineral like apatite. Addition of phosphates has been reported to be able to increase the soil negative charges. The phosphate addition is also reported to increase the soil pH. Even though the pH increase is relatively slight, this may also indirectly increases the soil negative charges. Altogether, phosphate addition may increase the soil negative charges through both a direct and indirect effect, which may eventually increase the heavy metal retention. This phenomenon has been experimented by some soil chemists to immobilize heavy metals in the soil environment.

The third approach is to extract the heavy metals out of the soil environmental systems, particularly from the soil system and the water system. One of the methods to do this is by employing the heavy metal hyperaccumulators. Some soil workers show that some soil and water microorganisms and plants are potential to extract heavy metals from soil system and water system. These methods are called bioremediation in which microorganisms or plants are employed or phyotoremediation in which heavy-metal hyperaccumulating plants are employed. Phytoremediation may include phytoextraction for removing heavy metal from soil system, phytofiltration for removing heavy metals from water system, phytovolatilization for removing heavy metals from soil system or water system by vilaltilization through plant leaves, particularly for Hg, and phytostabilization for removing heavy metal from soil system and water system and retain them in plant root system (Dary et al., 2010). The plant parts accumulating heavy metals must be carefully handled so that the accumulated heavy metals do not cause further environmental contamination and pollution. All these approaches and methods are listed in **Table 10.2**.

Table 10.2. The methods for controlling heavy metals concentration in the soil environment.

No.	Approach	Methods	Notes
1	Direct Soil Solid Immobilization	Directly increasing Soil Adsorption Capacity by addition of negative Sources	- Nano Particles like Oxides Kaolinite, and Montmorillonite - Zeolites - Biosolids like Compost and Biochars
		Directly increasing precipitating agents	- Lime - P-Fertilizers
2	Indirect Soil Solid Immobilization	Indirectly increasing Soil Adsorption Capacity by increasing soil pH and/or soluble P	- Lime - P-Fertilizers
3	Soil Extraction	Extracting heavy metals out of the soil system	- Heavy Metal Accumulating Microorganisms - Heavy Metal Accumulating Plants (Hyperaccumulators) -

10.3 Important factors for heavy metal management

The success of heavy metal management through heavy metal retention in the soil environment is determined by numerous factors that are in general of two groups, soil factors and heavy metal factors. Soil factors include those of solids/minerals, chemistry, physics, and biology, while those of heavy metals among which includes oxidation numbers, ionic radii, and diffusivity. These factors are summarized in **Table 10.3**.

Table 10.3. The soil and heavy metal factors controlling the heavy metal retention in the soil environment.

No.	Soil Factors	Heavy Metal Factors
1	Soil Solids/Minerals: Clay Types and Contents, Organic Matter Types, Contents, and Properties like C/N Ratios, Mineral Weathering and Organic Matter Decomposition, Adsorption Capacity	Oxidation Numbers
2	Soil Chemistry: Cation Exchange Capacity, pH, E, Common Cations and Anions, Ligands	Ionic Radii
3	Soil Physics: Soil Pores, Soil Porosity, and Soil Pore-Channels, Soil Water Content, Soil Temperature, Rain Drop – Infiltration – Pecolation – Leaching, Water Table, Ground-Water	Water and Soil Diffusivity
4	Biology: Microbial Types, Population, and Activities, Plant Roots, Acid and Enzyme Production, and Plant Need of Heavy Metals	

The soil solids/minerals include the clay types and contents, organic matter types, properties, and contents, mineral weathering and organic matter decomposition. Soil with high content of 2:1 silicate clay minerals and/or organic matters may have greater capacity for heavy metal retention due to the high emerging negative charges from these soil solids. The weathering of soil minerals and decomposition of organic matter may also enlarge the amounts of the negative charges of soils. These may increase the capacity of soil solids in adsorbing the heavy metal cations in the soil environment.

The soil negative charges of CEC are of importance in heavy metal retention in the soil environment particularly through adsorption reaction. Several types of the soil negative charges i.e. of oxides/hydroxides, 1:1 silicate clay minerals, and organic matters are significantly affected by soil pH, generally increase with the increase in soil pH. The higher content of OH^- with the increase in soil pH may hydrolyze H^+ ion in the solid surfaces and leave negative sites. Proper management of these behaviors enables us to control the concentrations of heavy metals in the soil environment.

There are some other soil chemical factors determining the heavy metal retention in the soil environment. The soil redox potential (E) may determine the oxidation number of some heavy metal elements. Oxidized condition causes some elements to have higher oxidation number and, thereby, increases their affinity towards the soil exchange sites. For example, Fe^{3+} may have higher affinity towards the soil surface than does Fe^{2+}. However, the heavy metal affinity is also determined by common ion. For example, the presence of Fe^{3+} in soil solution is probably higher when Ca^{2+} and Mg^{2+} are also present in the soil system because these common ions may hinder the Fe^{3+} adsorption by the soil negative charges. In contrast to the common ions, anions and ligands may complex or chelate the heavy metals in the soil water. The difference is that complexes and ligands may stay in soil water, and the similarity is that these ions also hinder the heavy metal adsorption by soil solids. However, complexes may increase the heavy metal retention because they can precipitate if the soil water is saturated.

The soil physical factors are in general related to the movement of heavy metals in the soil environment. Soil pore, soil porosity, and soil pore channels are important in determining the movement and translocation of heavy metals in the soil body. The movement and translocation are better when the soils are porous with good porosity and pore channels. Therefore, soil tillage is very important to stimulate the movement of substances in the environment. In this case, the presence of water is mandatory since the pore and pore channels must be partially filled with water to avail continuous pore channels that facilitate the water and substance movement. Since heavy metal elements need vibration to move, the soil temperature may have a significant influence on the heavy metal element movement. Generally, higher temperature is needed to accommodate heavy metal element movement.

Since the heavy metal element movement is water dependent, some soil factors related to water presence in soils are important. This includes the rainfalls and also the process of infiltration, percolation, and water leaching. The heavier the rain, the higher the rates of infiltration, rates of percolation, and the rates of leaching, the higher the gravitational heavy metal movement in the soil body. Unlike the heavy metal retention, this condition may increase the water leaching and groundwater contamination or pollution. To hinder such processes, heavy metals are better to immobilize in the soil body. This process may of course lower the heavy metals leached through the soil and contaminated the ground water.

The soil biological aspects may also give indirect impacts on heavy metal retention. The organic matter decomposition, which is important in producing the soil negative charges, is dependent on microorganisms. Therefore, the microbial types, population, and activities and all controlling factors, are of great importance. Soil enzymes, produced by soil microorganism, mesoorganisms (earthworms), and plant roots, involved in the decomposistion processes are of course very important because they determine the rates of organic matter decomposition. The production of acids and CO_2 by organisms and plant roots may change the soil pH, which may in turn indirectly affect the heavy metal retention. The plant needs for heavy metals also determine the amount of heavy metal absorption and accumulation by plants.

There are numerous factors related to heavy metals must be considered. In addition to the oxidation numbers, which determine the coloumbic forces of attraction to the soil negative charges, some other factors are also important. Ionic radii may determine the strength of heavy metal retention, particularly by adsorption process. It is shown that higher ionic radii may weaken the attraction forces of any cation on the surface of soil solids. As pointed out previously that Ca^{2+} and Mg^{2+} are both divalent cations, but the soil preference is higher for Ca^{2+} than for Mg^{2+}. Some reports show that Mg^{2+} possess higher ionic radii than does Ca^{2+}. Another heavy metal factor affecting the heavy metal retention is their diffusivity. Heavy metals with high diffusivity may move faster in the soil body, and thereby, may contaminate ground water more easily than those with low diffusivity.

Important questions

1. Explain the trend of heavy metal accumulation in the soil environment of urban and rural areas!
2. What are the effects of heavy metal pollution on the living things! Explain the diseases occurred in the last few decades!
3. Are all heavy metals toxic to the living thing? What about heavy metal micronutrients like Fe, Mn, Zn, Cu, and Co?
4. Explain the causal mechanisms for heavy metal toxicity to the living things!
5. Explain why heavy metal retention in soil solids is safer than in the air solids or water solids!
6. Explain the two chemical approaches to immobilize heavy metal in the soil environment!
7. Explain the chemical mechanisms to directly widen the soil solid adsorption capacity! Give examples! What chemical reactions are involved?
8. Explain the chemical mechanisms to indirectly widen the soil solid adsorption capacity! Give examples!
9. What are the differences between biosolids: compost and biochars both in characteristics, durability, and effects in the soil environment? Explain!
10. Explain the approach of bioremediation and phytoremediation to solve heavy metal pollution in the soil environment!
11. What are the differences between phytoextraction, phytofiltration, phytovolatilization, and phytostabilization?
12. What soil factors affecting the effectiveness to manage heavy metals in the soil environment?
13. What heavy metal factors affecting the effectiveness to manage heavy metals in the soil environment?
14. What soil physical factors involved in the management of heavy metals in the soil environment? Explain!
15. What soil chemical factors involved in the management of heavy metals in the soil environment? Explain!
16. What soil biological factors involved in the management of heavy metals in the soil environment? Explain!

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Glossary

(Salam, 2014)

Acidification is to make a reaction medium to have a lower pH. For example, soil acidification is to make the soil pH lower by using S powder or naturally by root excretion of organic acids or by producing CO_2 during root respiration.

Adsorption is the attachment of any substances or elements onto the surfaces of any adsorbent. For example the electrostatic attachment of any positively charged ion such as Cd^{2+} on the negatively charged soil solids containing clay minerals.

Adsorption Capacity is the maximum amount of any substance or element that can be adsorbed onto any adsorbent.

Air Phase is a unique part of a system containing gas substances. For example, air phase of soil system contains several gas substances such as O_2, N_2, CO_2, etc.

Air System is a system mostly containing air phase complemented with liquid and solid phases. The air is an air system containing solid, liquid, and gas substances in which gas substances are the major part complemented with small parts of solid and liquid substances.

Alkalization is to make a medium to have a higher pH. For example, soil alkalization is to make the soil pH higher by liming materials such as calcite or dolomite. In general it is referred to as liming.

Alfisol is one of the eleven soil orders in the Soil Taxonomy characterized among which by high exchangeable bases.

Analysis is the determination of the amount of any substance or element contained in a particular quantity of a particular matter.

Andisol is one of the eleven soil orders in the Soil Taxonomy characterized among which by andic property due to high content of allophanes.

Arylsulphatase is an organic substance produced by microorganisms, earthworms, and/or plant roots acting as a biocatalyst functioning to accelerate the detachment of S from organic S to form inorganic SO_4^{2-} available for plant root absorption.

Available Elemental Analysis is a chemical analysis to measure the nutrient elements in soils that can be absorbed readily by plant roots.

Available Soil Water is the amount of water content in soils lying between the soil field water capacity (FC) and the soil permanent wilting point (PWP).

Bioaccumulator is a vegetation that can easily grow and absorb heavy metals and is used to extract the heavy metals from contaminated soil, water, and muds. Examples of this vegetation are spinach and lettuce.

Bulk Density of soil is a soil physical property calculated by the equation $\boldsymbol{\rho_b = \frac{M_s}{V_t}}$; where ρ_b is soil bulk density, M_s is soil mass, V_t is soil total volume.

Calibration Test is a field test on the accuracy of a chemical extractant in predicting the plant response in particular plant production. The result is usually presented as a curvilinear curve describing the relationship between the plant yield and soil test result.

Carbon Cycle or C-Cycle is the chain of all the processes of C transformation from CO_2 in the atmosphere to CH_2O (sugars, proteins, and fats) as structural and functional substances in plant tissues and microorganisms, and then their ultimate decomposition back to form inorganic C as CO_2 available to plants.

Catalyst is a substance that may accelerate the rate of a reaction to a magnitude of several orders without itself participates in the reaction. Examples of catalysts are phosphatase and urease.

Cation Exchange Capacity is the maximum quantity of all free ionic metals that can be adsorbed by the surface of a quantity of soil solids, expressed in $\mathrm{cmol_c\ kg^{-1}}$.

Chelate is a chemical species of any element formed between any cation with organic multi-functional groups. One example of chelates is Fe-EDTA in which a divalent cation Fe^{2+} is associated with organic multi-ligand EDTA.

Chelation is a chemical process by which a cation is hold by multidentate organic agent forming a soluble complexes.

Clay Mineral is a secondary mineral, the result of extensive weathering of silicate minerals occurring in tropical regions with high temperature and rainfall that enable extensive weathering of primary minerals and leaching the weathering products.

1:1 Clay Mineral is a secondary mineral, the result of extensive weathering of primary silicate minerals occurring in tropical regions with high temperature and rainfall that enable extensive weathering and leaching the weathering products.

2:1 Clay Mineral a secondary mineral, the result of mild weathering of primary silicate minerals occurring in temperate regions with low temperature and rainfall that may not enable extensive weathering and leaching the weathering products.

Coloumbic Force is an attracting or repelling force existing between two charged species. For example, there is an attracting force between a divalent metal cation and the negatively charged soil surface. The force is expressed $\boldsymbol{F} = \mathbf{k}\,\frac{\mathbf{q_1 q_2}}{\mathbf{r^2}}$, where F the force of adsorption of heavy metal on the negatively charged soil exchange site, k is a constant, q_1 is the amount of soil negative charges represented by soil CEC, q_2 is the quantity of cationic charges adsorbed on the soil exchange sites, and r is the distance between the negative charges of soil mineral surfaces and the metal ion.

Compaction is a physical process by which the porosity of soils is significantly decreased.

Complexation is the association on one elemental species with another elemental species with different charges such as $Cu(OH)^+$, $Pb(H_2PO_4)^+$, or $Al(OH)_4^-$.

Complex Ion is an ionic species formed by the association on one elemental species with another elemental species with different charges such as $Cu(OH)^+$, $Pb(H_2PO_4)^+$, or $Al(OH)_4^-$.

Compost is a more stable organic matter as a result of fresh organic matter decomposition under conditions: organic matters must be prepared in small chunks, microorganisms must be present in the mixture, inorganic N must be enough to sustain the development of microorganisms, reaction (pH) must be maintained by lime, the mixture must be moistened during the decomposition process, and oxygen must be available for oxidation, and CO_2 must be pumped out from the stacks of organic residues. The C/N ratios of compost are about 12.

Correlations Test is a green-house test on the accuracy of a chemical extractant in predicting the plant absorption of any element. The result is usually presented as a linear curve describing the relationship between plant absorption and the result of soil test.

Decomplexation is a chemical process in which a complex ion release its cations driven by low concentration of the participating species. For example, $Zn(OH)^+$ becomes Zn^{2+} and OH^-.

Decomposition is a chemical process by which the organic and structurally bound elements not available to plants are detached to be inorganic elements available to plants. For example, the decomposition of organic P to form inorganic P (orthophosphates) available for plant root absorption.

Desorption is a chemical process by which an attached ion onto a charged solid is detached. For example, the detachment of exchangeable Ca on soil solids to form Ca^{2+} in soil solution.

Diffusion is the movement of any element in soil body through pore channels governed by the element concentration gradient.

Dissolution is a chemical process in which precipitates or minerals dissolve forming all related species at concentrations lower than those needed to compensate the related solubility constant.

Enzymes are biocatalysts produced by soil microorganisms, earthworms, and/or plant roots that accelerate the changes of organic elements not available to plants into inorganic elements available to plants.

E – pH Diagram a graph presenting the stability of any chemical species in the soil-water environment with different redox potential (E) and pH as the y and x axis, respectively.

Equilibrium Constants are constant values indicating the relationship between the activities of products relative to the activities of reactants of the related steady state chemical reactions.

Erosion is destruction of topsoils by water runoff at relatively high rates on the tilted soil surfaces.

Exchangeable Elemental Analysis is a chemical method to measure the soil exchangeable elements.

Extraction is a chemical method intended to force the detachment of particular classification of elements from soil system for quantity measurement.

Field Water Capacity or FC is the water hold by soil matrix at water potential of 10 – 35 kPa.

Free Ion is an elemental species does not associate with any other elemental species such as Pb^{2+}, Fe^{3+}, Cl^-, NO_3^-, or $H_2PO_4^-$.

Free ionic Analysis is a chemical method to measure the concentration of free ions in soil solution or water system.

Freundlich Equation is a mathematical expression of element or substance adsorption expressed by the equation of $\mathbf{x = kc^n}$ where x is the amount of adsorbed heavy metal cation per unit adsorbent at concentration c of adsorbate while k and n are constants

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Fulvic Acid is a humic substance soluble or do not precipitate in dilute acids after being separated from Humic Acids

Functional Group is the edge of organic substance structure which shows unique properties including its reactivity and reaction with elements..

Gravitation Water is the water drained by gravitation after all soil pores are being saturated.

Humic Acid is a humic substance not soluble in dilute acids.

Humic Substance is plant residue that has been decomposed, consisting of three fractions, each of which is a mixture of several undescribed organic compounds: Humin, Humic Acids, and Fulvic Acids (Tan, 1986; 1993).

Humin is a humic substance not soluble in alkaline solution.

Infiltration is the entrance of water through the soil pores on the soil surface.

Infiltration Rate is the rate of water infiltration.

Isomorphic Substitution is the replacement of the central elements in the Al-octahedral of 2:1 silicate clay minerals by lower oxidation-number elements causing the emergence of clay negative charges.

Labile Fraction is all elements in soils that are easily detached by a particular extractant.

Langmuir Equation is a mathematical expression of element or substance adsorption expressed by the equation of $\frac{M}{x/m} = \frac{1}{Kb} + \frac{M}{b}$ where M is the activity of the heavy metal cation, x/m is the amount of heavy metal cation per unit adsobate, K is a constant related to the bonding energy, and b is the maximum heavy metal cation that can be adsorbed by a given adsorbate

Leaching is an excessive wash out of elements or substances from topsoils by high rate percolating water.

Liquid Phase is a unique part of a system containing liquid substances. For example, the liquid phase of soil system contains several dissolved elements and organic matters.

Mass Flow is the movement of elements or substances in soils governed by water gradient, any element may move in any direction of water movement.

Microorganisms are soil micro-inhabitants containing among which are fungi and bacteria, which play important roles in the soil environment.

Mollisol is one among the eleven soil orders in the Soil Taxonomy characterized among which by high amount organic matters.

Non-Available Water is the soil water that is not able to be extracted by plants, the moisture of which is below the soil Permanent Wilting Point.

Non-Humic Substance is plant residue that has not been decomposed; is easy to identify and consists of polysaccharides, lignin, and polypeptides.

Non-Silicate Clays is clay minerals not containing silicates in their composition, usually formed in soils under high rainfall and high temperature. Examples on these are oxides and hydroxides.

Nutrient Elements are the elements that are needed by plants for their growth and development.

Oxidation is a chemical process in which the oxidation number of an element in one substance increases due to the loss of one or more electrons released and accepted by any other substance

Oxidator is any substance that may accept one or more electrons and cause any other substance to release the electron and to oxidize.

Oxisol is one of the eleven soil orders in the Soil Taxonomy characterized among which by high contents of oxide mineral with low CEC.

Particle Density is the relative mass of soil solid with respect to the volume of only soil solid. It can be calculated as $\boldsymbol{\rho_s} = \frac{\mathbf{M_t}}{\mathbf{V_s}}$ where ρ_s is the soil particle density, M_t is the total soil mass, and V_s is the volume of soil solid.

Permanent Wilting Point or PWP is the water hold by soil matrix at water potential of about 1,520 kPa.

pH-Dependent Charge is a soil solid charge the magnitude of which is dependent on the degree of soil acidity.

pH-Independent Charge is a soil solid charge the magnitude of which is not dependent on the degree of soil acidity

Phosphatase is an organic substance produced by microorganisms, earthworms, or plant roots acting as a biocatalyst functioning to accelerate the detachment of P from organic P to form inorganic orthophosphates ($H_2PO_4^-$ and HPO_4^{2-}) available for plan root absorption.

Phosphatic Fertilizers are all fertilizers containing any phosphate component.

Phytoextraction is a heavy metal removal technique employing a particular plant to remove heavy metals from soil system.

Phytofiltration is a heavy metal removal technique employing particular plant roots to remove heavy metals from water system.

Phytoremediation is a heavy metal removal technique from environment by employing particular plants.

Phytovolatilization is a heavy metal removal technique employing particular plants to absorb particular heavy metals and volatilize them through plant leaves.

Point of Zero Charge is a soil pH value at which the net soil solid charges equals to zero.

Pores are spaces between soil particles that build soil structure or spaces between soil aggregates that includes macropores, mesopores, and micropores depending on the pore sizes.

Pore Channel is an interconnected soil pores filled with water which is very important as heavy metal transport route through mass flow and/or diffusion.

Porosity is a soil physical property that indicates the part of soil volume not occupied by soil solids. Total porosity of soils can be calculated by the following equation: $f = \frac{V_p}{V_t}$ or $f = \frac{V_a + V_w}{V_s + V_a + V_w}$, where f is Total Porosity, V_p volume of pores, V_t total volume of soil, V_a volume of soil air, and V_s volume of soil solid. Total porosity of soils can also be calculated by the following equation: $f = 1 - \rho v/\rho s$, where f is the total porosty of soils, ρ_v is the soil bulk density, and ρ_s is the soil particle density.

Precipitate is a chemical compound resulted by precipitation process that occur at saturated concentrations of all the related species controlled by the reaction solubility constant.

Precipitation is a chemical process resulting in precipitates that occur at saturated concentrations of all the related species controlled by the reaction solubility constant.

Primary Minerals are naturally inorganic crystallic compounds mostly composed of Si, Al, and O with small amount of other complementary elements formed through volcanic activities.

Pyrite is an acid mineral found in acid sulphate soils which may significantly acidify soils upon oxidation when exposed to the atmosphere.

Recovery is percent quantity of extractable elements or substances of a particular amount introduced into soil system.

Reduction is a chemical process in which the oxidation number of an element in one substance decreases due to the acceptance of one or more electrons released by any other substance.

Reductor is any substance that may release one or more electron and causes any other substance to accept the electron and being reduced.

Redox Reaction is a pair reactions containing a simultaneous oxidation and reduction reactions in which electrons are transferred from the oxidized substances to the reduced substances.

Retention is immobilization of a substance or element by adsorption and precipitation processes.

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Secondary Minerals is natural inorganic crystallic compounds mostly composed of Si, Al, and O with small amount of other complementary elements formed through dissolution of primary minerals under extensive leaching and recombination of the results.

Sesquioxides are soil secondary minerals containing oxides and hydroxides of Fe, Mn, and Al; found abundant in old soils like Oxisols.

Soil Color is the color of soil as affected by soil organic matter and oxide contents and water regimes, usually determined using Munsell Soil Color Chart.

Soil Enzyme is a catalyst that accelerates the transformation of elements in organic matter not available for plant root absorption to inorganic elements easily absorbed by plant roots.

Soil Minerals are naturally formed inorganic crystallic compounds mostly composed of Si, Al, and O with small amount of other complementary elements.

Soil Structure is a microtridimensional building of soil silts and sands cemented by clay, organic matter, and/or sesquioxides.

Soil Texture is the relative composition of soil particle sizes which includes clay, silt, and sand fractions.

Retardation is the decrease in movement rate of any substance due to one or more natural or artificial hindrance.

Runoff is water movement on the soil surface as a result of the lower infiltration rates compared to water influx on the soil surface caused by soil pore saturation with water.

Soil System is a system mostly containing solid substances completed with liquid and gas substances. The soil system contains solid, liquid, and gas substances in which solid substances are the major part completed with small parts of air and liquid substances.

Solid Phase is a unique part of a system containing solid substances. For example, the solid phase of soil system contains several minerals and organic matters.

Total Dissolved Analysis is a chemical analysis of soil contents on all chemical species dissolved in soil water which is in the case of heavy metals includes free ions, complexes, and chelates.

Tillage is a physical process to increase the porosity of soils. This may include conventional tillage and conservation tillage (No tillage and minimum tillage).

Total Elemental Analysis is a chemical analysis of soil contents on all chemical species contained in a matter.

Toxic Element is an element that may cause significant disturbance on the living things if its concentrations in the environment exceed its allowable or toxic level.

Toxicity is the degree of disturbance of any element on the living things. For example, the toxicity of heavy metals on fungi follow the following order of Ag > Hg > Cu > Cd > Cr > Ni > Pb > Co > Zn > Fe.

Toxic level is an allowable level of any element above which may cause a significant disturbance to the living things. For example, the toxic levels of for Cd and Pb are < 9 and < 100 mg kg^{-1}, respectively

Translocation is the movement of any substance from one point to another. For example, heavy metal translocation in soils.

Transport is a physical process to move quantities of any substance from one point to another point. For example, heavy metal transport in soils.

Ultisol is one of the eleven soil orders in the Soil Taxonomy characterized among which by high contents of clay minerals with low CEC.

Urease is an organic substance produced by microorganisms, earthworms, or plant roots acting as a biocatalyst functioning to accelerate the detachment of N from Urea to form NH_3.

Water Content is the amount of water contained in soils expressed as percent weight.

Water System is a system mostly containing liquid substances completed with gas and solid substances. The water is system contains solid, liquid, and gas substances in which liquid substances are the major part completed with small parts of solid and lair substances.

Weathering is a physical or chemical or biological destruction of soil mineral structure resulting in new and simpler minerals. In chemical weathering, some inorganic elements are freed and are available to plants. For example, during the chemical weathering of feldspars in the presence of H^+ ions and H_2O molecule, K^+ ions are freed to be available for plants.

Subject Index

Biography of The Author

Abdul Kadir Salam was born in Bandung, West Java, Indonesia, on the first of November 1960. He finished elementary school (1972), junior high school (1976), and senior high school (1980) in Cirebon West Java, Indonesia. He got his bachelor's degree in Soil Science from Bogor Agricultural University in Bogor, Indonesia (1984). He earned his master's and Ph.D.'s degrees from the University of Wisconsin-Madison, the United States of America in 1989 and 1993, respectively, in the fields of Soil Chemistry-Fertility and Water Chemistry. He participated in a *Postdoctoral Program* in the field of Soil Biochemistry (Soil Enzymes) in *Nagoya University*, Japan, in 1995 – 1996.

As a faculty staff since 1984 in the Faculty of Agriculture the University of Lampung, he taught several courses for bachelor's, master's program, and doctor's: Basic Chemistry, Fundamentals of Soil Science, Soil Chemistry, Soil Fertility, Fertilizers and Fertilizing, Soil and Plant Analysis, Research Methodology, Scientific Writing Techniques, and Environmental Chemistry and Pollution. He also conducted research projects on various soil problems, particularly related to nutrient and non-nutrient elements (heavy metals) and soil enzyme management funded by the University of Lampung, the Ministry of Culture and Education, Japan Society for the

Promotion of Science, Indonesia Toray Science Foundation, and the Ministry of Research and Technology. He published more than 60 technical papers in national and international journals. He was also a trainer in several research methodology trainings and scientific paper trainings.

In addition to write *Enzymes in Tropical Soils* (2014) he also published *Ilmu Tanah Fundamental* or *Fundamental of Soil Science* (2012) and currently *Management of Heavy Metals in Tropical Soil Environment* (2017), which is a summary of his research results for the last 30 years (1987–2017) and *Manajemen Hara Tanaman or Management of Plant Nutrients* to be published in 2018. He also published *Melatih Guru Muda Menyusun Karya Tulis* or *Training Young Teachers to Compose Articles* as The Editor (2014) and *Tujuh Tahun Sekolah Global Madani* or *Seven Years of School of Global Madani* (2018) as one of the Editor.

In the University of Lampung, he had been assigned to the following posts: Chair of the Laboratory of Soil Chemistry and Fertility (1985-1986, 1997-1999), Chair of the Soil Science Department (1998-2001), Expert Staff of the Vice Rector of Academic Affairs (1999-2004), The Director of the Sub-Project Management Unit Technological and Professional Skills Development Project TPSDP (2001-2008), and the Director of the Graduate School (2006–2011). He was also the Executive Director of Al-Kautsar Education Foundation Lampung (2002-2010), that managed pre-elementary school, elementary school, junior high school, and senior high school. Since 2010 he was assigned as the Director of Education Foundation of Global Madani Lampung, that managed elementary school, junior high school, and senior high school with enriched curriculum, and the University of Al-Madani.

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