

Review

Kinetics of radionuclides and heavy metals behaviour in soils: Implications for plant growth

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The extent of metal and radionuclide contamination in the world is immense. In soils, metals and radionuclide can be dissolved in solution, or ion exchanged in reaction, complexed with soil organics or precipitate as pure or mixed solids. Soluble contaminants are subject to migration with soil water, uptake by plants or aquatic organisms or loss due to volatilization. Lead, chromium, zinc, arsenic and cadmium are the most frequently identified inorganic contaminants in soil and ground water. Unlike degradable organic contaminants and ever short-lived radionuclides that can become less toxic over time, metals can be considered conservative. However, many metals, especially radio-sensitive elements such as arsenic and chromium can undergo transformation or sorption reaction that alter both mobility and relative toxicity. This paper therefore, makes a review of these behaviours of radionuclides and heavy metals in soils, in connection to soil contamination and their effects on plant growth.

Key words: Kinetics, radionuclides, Heavy metals, Soil, plant growth.

INTRODUCTION

Soil is a dynamic layer in which many chemical, physical and biological activities are going on constantly. It is not a lifeless zone but an active system having inputs and outputs of energy and matter. Through time, the soil has become adjusted to prevailing conditions of climate and plant cover, and may change when the prevailing conditions change (Ademorati, 1996). Soil is made up of matter existing in three states such that the solid liquid and gaseous states are not regionalized but co-exist together. For plant growth, a proper balance of all the three states of matter is necessary. The entire soil could be segmented into the earth crust, the mantle and the core (Jackson, 1964). The crust is made up of the sial and sima. The sial is composed of solid rocks like lignite with a low density. Beneath the sial is the sima having denser rock materials and lying in the region of higher temperature. This is the substance from which the rocks

on the surface of the earth are made. The rocks in the mantle region are denser than those in the sial and sima of the crust and are hotter. Because of the heat, the material can flow and change its shape. The core region existing in the centre of the earth consists of an inner solid metallic part and an outer ring of lignite materials composed mostly of iron and nickel (Jackson, 1964; Boene, 1978).

Generally, soil, varies enormously in composition. The solid particles are both inorganic and organic. The inorganic portions consists of silicates of aluminum, iron, calcium and magnesium, etc, derived from rocks by weathering and producing characteristic soil types such as sand, silt, clay and loam. These give the soil the main part of the mass and volume. The organic portions are produced by decomposed plant and animals as a result of the activity of innumerable micro-organisms particularly bacteria. Colloidal particles are an important function in soil chemistry. The liquid portion of soil is a complex chemical solution necessary for many important activities that go on in the soil. Soil without water cannot have these chemical reactions nor can it support life. Gases in

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the open pore space of the soil form the third essential component. They are principally gases of the atmosphere together with gas liberated by biological activities due to micro-organisms and fungi and chemical activity (Tisdall, 1994).

PHYSICAL AND CHEMICAL PROPERTIES OF SOIL

Colour is one of the characteristics of soil, which tells much about how the soil was formed and what it is made up of. One colour sequence ranges from white – brown – black as a result of an increasing content of humus (Brandy, 1974), which is finely divided particularly, decomposed organic matter. Red and yellow colours are the result of small quantities of iron compounds. The reddish colour is particularly associated with the sesquioxide (the mineral hematite) Fe_2O_3 . The yellow colours may indicate the presence of limonite. Grey and bluish colours in soils of humid climate often mean the presence of reduced iron compounds, for example, FeO . Grey colour in dry climates means a meager amount of humus. A white colour may mean deposits of salts in the soil (Brandy, 1974). Soil texture generally gives the amounts of sand, silt and clay present in percentage.

The most important constituents of the soil are the colloids which may be of either inorganic matter, that is, clay minerals or organic matter that is humus. The colloids make up the active fraction because of their high surface area and chemical activity. On the other hand, the silt and sand particles are largely inert and act more or less as skeleton for the soil (Jackson, 1964). The molecular structure of clay is such that oxygen atoms, which are relatively negatively charged, are nearest the upper and lower surfaces. This means that positive ions in the soil will be attracted by the clay particle and held there by electrostatic attraction. Ions such as H^+ , Na^+ , K^+ , Ca^{2+} and Mg^{2+} are commonly present in soil solutions and all are found on clay particle surfaces. In many soil reactions these cations replace one another in the process of cation exchange.

Cation exchange is governed by a replacement order indicating which cation is capable of replacing another. The factors governing this order include the nature of exchanging cations (Brandy, 1974; Coleman and Mehlich, 1967):

1. At low aqueous concentrations and at ordinary temperatures, the extent of replacement at constant valency for univalent cations increases with decrease in sizes of hydrated ion ($\text{H}^+ > \text{Li}^+ > \text{K}^+ > \text{Rb}^+ > \text{Cs}^+$), while for divalent cations, the ionic size is an important factor but the incomplete dissociation of salts of divalent metals plays a part ($\text{Cd}^{2+} < \text{Be}^{2+} < \text{Mn}^{2+} = \text{Zn}^{2+} < \text{Cu}^{2+} = \text{Ni}^{2+} < \text{Ca}^{2+} < \text{Sr}^{2+} < \text{Pb}^{2+} < \text{Ba}^{2+}$).

2. Under similar conditions the extent of exchange increases with increasing valency of the exchanging cation ($\text{Na}^+ < \text{Ca}^{2+} < \text{Al}^{3+} < \text{Th}^{4+}$).

One application of this principle in soils is that, where acids are formed in the soil by decay of plant matter, H^+ ions are formed in abundance and will replace the common base cations, which are then carried out of the soils by surplus water during rainfall. As a result, these plant nutrients are lost and a soil of low fertility with respect to certain plant nutrients occurs. Nutrient elements such as iron, manganese and zinc that are readily available in acid soils, sometimes at toxic level, are sparingly available in many alkaline soils, leading to deficiencies of these elements in plants. Unfortunately, adding these macronutrients as residues and fertilizers is sometimes ineffective because the elements are quickly tied up in insoluble forms in high pH soils. Special protective organic complexes called chelates help the nutrient needs of plants growing on these soils (Jackson, 1964). In alkaline soils, both native and applied phosphorous are tied up in highly insoluble calcium and magnesium phosphates, rendering the added phosphorous sparingly available for plant uptake.

The cation exchange capacities of alkaline soils are commonly higher than those of acid soils with comparable soil textures. This is because of two primary factors:

- i. The high cation exchange capacity association with the constant charges on 2:1 type clays that are most common in alkaline soils.
- ii. The even higher cation exchange capacity resulting from the pH dependent charges present on the humus colloids at these high pH levels.

Soil pH, acidity and alkalinity

Whether a soil is acid, neutral or alkaline is determined by the relative concentrations of H^+ and OH^- ions. No other single characteristic is more important in determining the chemical environment of higher plants and soil microbes than the pH. There are few reactions involving any component of the soil or of its biological inhabitants that are not sensitive to soil pH. This sensitivity must be recognized in any soil management system. Soil pH is largely controlled by fine soil particles and their associated exchangeable cations. Aluminum and hydrogen enhance soil acidity, whereas calcium and other base forming cations especially sodium encourages soil alkalinity (Daniel and Edward, 1998; Ademorati, 1996). The charge complex is also a mechanism for soil buffering, which resists rapid changes in soil reaction giving stability to most plant-soil systems.

RADIONUCLIDES AND HEAVY METALS

Nuclides of any element that have atomic number greater than bismuth - 83 is unstable and therefore radioactive.

They are called heavy nucleons. Over sixty radionuclides can be found in nature and they can be placed in three general categories; the primordial, cosmogenic and anthropogenic (Brandy, 1974). Americium - 241, caesium - 137, cobalt - 60, iodine - 129 and - 131, plutonium, radium, radon, strontium - 90, technetium - 99, tritium, thorium and uranium, are the twelve radionuclides that occur naturally; caesium for example, is an alkali metal like potassium and resemble it metabolically. Whereas potassium is an essential element for man, there is no evidence that caesium is also an essential trace element. Stable caesium - 133 is fairly rare in the biosphere and in geological occurrence (Brandy, 1974). The radioactive isotope caesium - 137 is produced in nuclear fission and is one of the most significant products. The fission yield is relatively high, about 6 atoms per 100 fissions, independent of the type of fission in uranium or plutonium. It has a radioactive half-life of 30.17 years and its beta decay is accompanied by a gamma ray of moderate energy (Brandy, 1974; Mster, 1996).

Heavy metals are defined as metals having density greater than 5 g/cm³. This classification includes transition metals and higher atomic weight metals of groups III to V of the periodic table. These include aluminum, arsenic, beryllium, bismuth, cadmium, chromium, cobalt, copper, lead, mercury, nickel, selenium, strontium, titanium and zinc (Brandy and Weil, 1999). These metals and their compounds may be discharged from industries, farmlands, municipal urban runoffs, etc, into surface waters to cause pollution. The pollution of the ecosystem by toxic metals during man's activities poses serious concern because. Firstly, metals are non-degradable and are persistent in the ecosystem. Secondly, physical, chemical and biological processes may combine under certain circumstances to concentrate metals rather than dilute them. Lastly, the societal impact of a contaminated system is substantial.

Advancement in technology has led to high levels of industrialization leading to the discharge of effluent bearing heavy metals into our environment. The various activities by man in recent years have increased the quantity and distribution of these heavy metals in the atmosphere, land and water bodies (Guster, 1974). The extent of this wide spread but generally diffused contamination has caused concern about its possible hazards on plants, animals and human beings.

SOURCES OF RADIONUCLIDES AND HEAVY METALS CONTAMINATION IN SOIL

Nuclear fission in connection with atomic weapons testing and nuclear power generation provides some of the sources of soil contamination. To the naturally occurring radionuclides in soil such as ⁴⁰K, ⁸⁷Rb and ¹⁴C, a number of fission products have been added. However, only two of these are sufficiently long-lived to be of significance in

soils: strontium -90 with half life of 29.1 years and caesium - 137 with the half life of 30 years (Nyle and Ray, 1996). The average levels of these nuclides in soil in the United States are about 388 mc/km² for ⁹⁰Sr and 620 mc/km² for ¹³⁷Cs (Holmgren et al., 1993). A comparable figure for the naturally occurring ⁴⁰K is 51,800 mc/km². These normal soil levels of the fission radionuclides are not high enough to be hazardous. Even during the peak periods of weapons testing, soils did not contribute significantly to the level of these nuclides in plants (Holmgren et al., 1993). Atmospheric fallout on the vegetation was the primary source of radionuclides in the food chain (Holmgren et al, 1993; Meiwether et al., 1988). Consequently, only in the event of a catastrophic supply of fission products could toxic soil levels of ⁹⁰Sr and ¹³⁷Cs be expected. Fortunately, considerable research has been accomplished on the behaviour of these two nuclides in the soil - plant system (Meiwether et al., 1988).

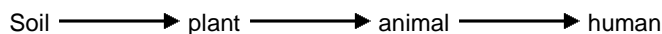
In addition to radionuclides added to soil as a result of weapons testing and accidents such as that which occurred at Chernobyl, Ukraine (Knox et al., 2000), soil may interact with low level radioactive waste materials that have been buried for disposal (Knox et al., 2000; Iskauder, 1992). Even though the materials may be in solid form when placed in shallow land burial pits, some dissolution and subsequent movement in the soil are possible (Brandy and Weil., 1999). Plutonium, uranium, americium, neptunium, curium and caesium are among the elements whose nuclides occur in radioactive wastes (Meiwether et al., 1988). Nuclides in wastes vary greatly in water solubility, uranium compounds being quite soluble, compounds of plutonium and americium being relatively insoluble and caesium compounds intermediate in solubility. Caesium, a positively charged ion, is adsorbed by soil colloids. Uranium is thought to occur as a UO²⁺ ion that is also adsorbed by soil (Nyle and Ray., 1996). The charge on plutonium and americium appears to vary, depending on the soil. There is considerable variability in the actual uptake by plants of these nuclides from soils, depending on such properties as pH and organic matter content. Uptake from soils by plants is generally lowest for plutonium, highest for neptunium and intermediate for americium and curium (Nyle and Ray., 1996; Wiler 1965). Fruits and seeds have generally much lower of these nuclides than are leaves, suggesting that grains may be less contaminated by nuclides than forage crops and leafy vegetables (Knox et al., 2000).

There are many sources of the inorganic chemical contaminants that can accumulate in soils. The burning of fossil fuels, smelting and other processing techniques release into the atmosphere tons of these elements, which can be carried for miles and later deposited on the vegetation and soil. Lead, nickel and boron are gasoline additives that are released into the atmosphere and carried to the soil through rain and snow. Borax is used in detergents, fertilizers and forest fire retardants, all of

which commonly reach the soil. Super phosphate and limestone, two widely used amendments, usually contain small quantities of cadmium, copper, metals and in the manufacture of batteries. Arsenic was for many years used as an insecticide on cotton, tobacco, fruit crops, lawns and as a vine killer (Holmgren et al., 1993).

In municipal sewage, the metallic contents are often absorbed on the sewage solids or sewage sludge. When the sludge is disposed off to farm land, the metallic contents are taken up by plants in some amounts. These may have unpleasant effect on the fruits they produce as they may be rendered unsuitable for human consumption. In some cases, they may have adverse effects on plants produced on the farm lands. Such plants can be readily consumed by grazing animals. The grazing animals as well as fruits of plants serve as food for man. In effect, the heavy metals are passed on to man through the food chain and the cumulative effects of these metals, most of which are toxic, are adverse generally.

Actually, some of the toxic metals are being released to the environment in increasing amounts, while others, most notably, lead, because of change in gasoline formulation, are decreasing. All are daily ingested by humans either through air, food, water and soil. Irrespective of their sources, toxic elements can and do reach the soil where they became part of the food chain thus:



Unfortunately, once the elements become part of this cycle, they may accumulate in animal and human body tissue to toxic levels (Daniel and Edward., 1998). This situation is especially critical for fish and other wildlife and for humans at the top of the food pyramid.

REACTIONS OF RADIONUCLIDES AND HEAVY METALS IN SOIL

Most published information on behaviour and movement of radionuclides in soils reflects pattern observed after initial deposition to soil surface, either in field conditions from sites surrounding nuclear installations or affected by fallout from weapons testing or from laboratory experiments, reflect the physico-chemical characteristics of the radionuclide, the properties of the soil including changes with depth from the surface, the types of vegetation, hydrology and underlying geology (Giddings., 1973). Residence times for turnover of radionuclides in a defined soil layer are derived generally on the basis of the total contents of radionuclides rather than on the basis of specific fractions extractable with defined extracting agents. As a result, models for radionuclides movement in soils can generally be simplified as shown

in Figure 1.

The simplest equation to describe migration is the mass conservation equation:

$$ds/dr + dC/dt = Dd^2C/dx^2 - VdC/dx + S$$

Where C is the concentration in solution, S is the concentration in solid phase, T is time, V is the interstitial solution velocity and D is apparent diffusion coefficient (Meiwether et al., 1988; Jawhney and Brown, 1989). Radionuclides present as original deposited particles irreversibly sorbed to soil particles or present in ion-exchange sites on soil particles are subject to processes involved in particle migration. Radionuclides present in soil solution or as organic complexes are subject to processes involved in solution transport.

The solubility of most radionuclides, which are formed in nuclear reactors or other nuclear devices, is low. Consequently, the major part of radionuclides released into the environment will finally accumulate in either the upper layer of soils or interstitial system of sediments in aquatic systems. In general, Pu and Am hardly migrate in soil. Neptunium and strontium migrate over short distance that is about 1 cm in a few years (Jawhney and Brown, 1989). The migration of Cs depends very much on soil characteristics; usually it is very strongly adsorbed and migrates less than Sr. Migration can be described by chromatography. The soil is divided into a number of layers and radionuclides are assumed to be present in the top layer and partly in solution flow from the upper layer to the second layer. Parts of the radionuclides are adsorbed in the second layer, depending on Kd values (Table 1) (Knox et al., 2000; Iskauder, 1992). Despite limitations, Kd is one of the best variables to indicate differences in leaching behaviour in soils of the temperate region. The mass conservation equation, over a period of 20 years was used to indicate the vertical migration velocities for Sr, Cs, Pu and Am to be 0.3 to 0.5 cm per year (Knox et al., 2000).

A very simple approach in describing the availability of radionuclides is the apparent half life concept. The assumption is that after a certain period, half of the radionuclides disappear from a certain layer. A refinement of this concept is that of the residence time. The soil is assumed to be distributed into different layers. The radionuclides move through subsequent layers, staying in each layer with a certain residence time. The advantage of the approach is that the processes, which cause migration, do not have to be considered. The disadvantage is that diffusion, dispersion and vertical transport cannot be distinguished.

For heavy metals, the concern over their possible build-up in soils resulting from large application of sewage sludge and other sources has prompted research on the fate of these chemicals in soil. Attention has been given mostly to zinc, copper, nickel, cadmium and lead, which are commonly present in significant levels in these

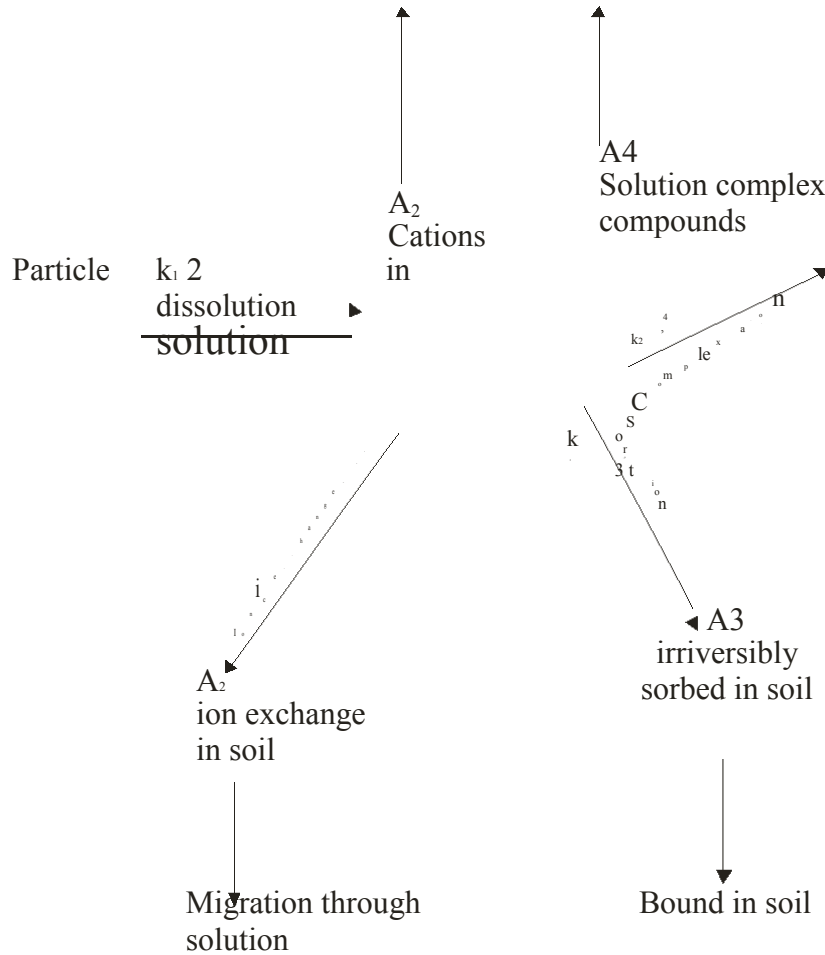


Figure 1. Radionuclide transformation processes in soil.

Table 1. Kd values for some radionuclides for agricultural soil.

Radionuclides	Sand	Loam	Clay	Organic
Sr	1.4×10^1	2.0×10^1	1.1×10^2	1.15×10^2
Cs	2.7×10^2	4.5×10^3	1.8×10^3	2.7×10^2
Np	4.1×10^0	2.5×10^1	5.5×10^1	1.2×10^3
Pu	5.5×10^2	12×10^3	4.9×10^3	1.8×10^3
Am	2.0×10^3	9.9×10^3	8.1×10^3	1.1×10^5

Source: Knox et al. (2000), Iskauder (1992).

sludges. Studies have shown that if the soil is not very acidic, these elements are generally bound by soil constituents such that they do not then easily leach from the soil, and they are not even readily available to plants. Only in moderately to strongly acid soil is there significant movement down the profile from the larger application of the sludge.

By using chemical extractants, researchers (Iskauder, 1992; Kabata-Peudias and Pendias, 1992), have found that heavy metals are associated with soil solids in four major ways:

- i. A very small proportion is held in adsorbed or exchangeable forms which are available for plant uptake.
- ii. The elements are bound by the soil organic matter and by the organic materials in the sludge. A high proportion of copper is commonly found in this form, while lead is not so highly attracted. Organically bound elements are not readily available to plants, but can be released over a period of time.
- iii. The association of heavy metals in soil is with carbonates and with oxides of iron and manganese. These forms are less available to plants than either the exchangeable or organically bound forms, especially if the soils are not allowed to become too acidic.
- iv. The fourth association is commonly known as the residual form, which consists of sulfides and very insoluble compounds that are less available to plants than any of the other forms.

Soil plants do not readily adsorb applied heavy metals but, the heavy metals are also not easily leached from the soil. Thus, the immobility of the metals means that they will accumulate in soils if repeated sludge

applications are made, which is not good for the healthy growth of the plants.

IMPLICATIONS ON THE ENVIRONMENT

The toxicity of inorganic contaminants released into the environment over the years is now estimated to exceed that from organic and radioactive sources combined (Ademorati, 1996). A fair share of these inorganic substances end up contaminating the soil. The greatest problems involve mercury, cadmium, lead, arsenic, nickel, copper, zinc, chromium, molybdenum, manganese, selenium, fluorine and boron. To a greater or lesser degree, all these elements are toxic to humans and other animal. Cadmium and arsenic is extremely poisonous; mercury, lead, nickel and fluorine are moderately lower in mammalian toxicity (Wiley 1965). Mercury contamination of lake beds and of swamp areas has resulted in toxic levels among certain species of fish. Insoluble forms of mercury in soils, not normally available to plants or in turn to animals, are converted by microorganisms to an organic form, methyl mercury, in which it is more soluble and available for plant and animal absorption (Wiley 1965). The methyl mercury is concentrated in fatty tissue as it moves up the food chain, until it accumulates in some fish to levels that may be toxic to humans (Iskauder, 1992). Arsenic has accumulated in orchard soils following years of application of arsenic containing pesticides. Being present in an anionic form, for example, H_2AsO_4 , it is absorbed by hydrous iron and aluminum oxides especially in acid soils. In spite of the capacity of most soils to tie up arsenates, long- term additions of arsenical sprays can lead to toxicities for sensitive plants and earthworms (Tisdall, 1994). All these contamination and accumulation of heavy metal and radionuclides in soil have adverse effects on the plants:

- They cause nutrient depletion in the soil.
- The availability of nutrients in the soil for plant uptake is reduced.
- Those that mimic some nutrients tend to take up their place during plant up-take.
- The solubility of these nutrients becomes affected as some of the contaminants are soluble.
- The plants suffer from deficiency of these nutrients.
- The plants become stunted in growth, showing yellowish leaves, perforated leaves and contaminated fruits.
- This is then passed on to man through the food chain.

RECOMMENDATION

Compost is considered to be a good amendment agent for bioremediating heavy metal polluted soil (Knox et al.,

2000). Unfortunately, very little information has been published about the effects of compost amendments on the stabilization of heavy metal-contaminated soil. A mixture of compost and lime or modified aluminum silicate or wood chips was mixed with soil that was heavily polluted with Zn, Cd and Cu (Holmgren et al., 1993). Addition of mature compost to soil is known to enhance soil fertility by modifying the chemical, physical and biological properties of the soil (Knox et al., 2000; Iskauder, 1992). Compost increases the water -holding capacity of the soil, pH and microbial activity. The organic matter in compost also complexes metals into less bioavailable forms. Copper especially is known to form stable complexes with organic matter. Compost also introduce new active microbiota and provides a nutrient source for the microorganisms; woodchips is added to the compost in order to increase the amount of slow released carbon. Mulching a polluted forest floor with a layer of organic material has several advantages in the remediation of heavy metal polluted soil, since it prevents drying and erosion of the soil and thus promotes revegetation.

Sorption of cationic surfactant on negatively charged clay minerals and zeolites has been studied extensively in the past decade (Nyle and Ray, 1996; Lyon and Buckman, 1952). However, the main focal points were mechanisms of sorption and the potential for using surfactant modified clays and zeolites to retard movement of organic contaminants. Infact, the strong affinity of cationic surfactants for soil particles arises due to electrostatic attraction and hydrophobic bonding making them ideally suitable for removal of sorbed metal cation, including caesium and lead. The ultimate goal is to explore the feasibility and applicability of using cationic surfactant as a soil flushing agent to desorb and extract heavy metals and radionuclides from soil. It is expected that the surfactant flushing will significantly increase the recovery of heavy metals and radionuclides from soil compared to conventional extracting agents. In addition, the cost for the surfactant enhanced soil flushing will compare favourably to cost for traditional soil flushing.

The arsenic toxicity can be reduced by applications of sulfates of zinc, iron and aluminum, which tie up the arsenic to insoluble forms. Care must be taken not to add such large quantities of sludge that the capacity of the soil to react with a given element is exceeded. It is for these reactions that regulations set maximum cumulative loading limits for each metal. It has also become necessary to curtail the release of these toxic elements in the form of industrial wastes (Mster, 1996). Again, monitoring soil activity and using judicious applications of lime can prevent leaching into ground waters and can minimize uptake by plants (Giddings, 1973).

Currently research is underway to take advantage of plant uptake of radionuclides in phytoremediation exercises. Plants such as sunflowers are being used to remove ^{137}Cs and ^{90}Sr from a pond area near the

Chernobyl, Ukraine nuclear disaster. Sunflowers and other plants such as maize and coconut fiber have been used in the bioremediation of heavy metals (Igwe and Abia, 2003; Igwe and Abia, 2005; Igwe et al., 2005). Indian mustard is also being used to remove such nucleotide contaminants.

Thus we conclude that heavy metals and radionuclides contamination in soil is immense. Solubility of these contaminants play a vital role in their availability to plants; hence toxicity is also affected by solubility. The many effects of these metals have been outlined. Such factors as pH, acidity and alkalinity, organic matter content and microorganisms also contribute to heavy metal and radionuclide contamination. These factors also affect solubility. Remedies for these heavy metal and radionuclides were also recommended.

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