International Meeting on Soil Fertility Land Management and Agroclimatology. Turkey, 2008. p: 987-996

Factors Controlling the Bioavailability of Potentially Harmful Metals in Wastewater Treated Soils

Hadi Ghorbani
Assistant Professor in Soil and Environmental Pollution
Shahrood University of Technology, shahrood, Iran
Ghorbani1969@yahoo.com

ABSTRACT

Sewage sludge contains significant proportions of nitrogen, phosphorus and organic matter. It therefore has a similar fertiliser value to animal manures and slurries. Typical applications can provide a significant contribution to the nitrogen and phosphate requirements of arable and grassland crops. In addition, sludge can contain potentially harmful substances, including pathogens, persistent organic pollutants and toxic metals. It is therefore necessary to control the use of sewage sludge in order to protect human and animal health and to maintain soil fertility and crop yields. The bioavailability of heavy metals can be affected by several factors. Some of these factors are related to soil and some others may be related to plant characteristics. Soil pH, organic mater content, redox status, carbonate content, chloride content, moisture, source and form of metals and plant genotype may be the most important. However, investigation of any factors which may reduce or enhance the availability of heavy metals in soil and uptake by plants would be crucial. Such knowledge and information on these factors could be used and would help the authorities to manage and control the environmental problems which are concerned with sludge application to agricultural land and could threaten the human health. This paper is going to review and describe the factors and circumstances of which the bioavailability of potentially harmful metals would reduce or enhance in soil.

Keywords: Heavy Metals, Bioavailability, Soil, Sewage sludge.

INTRODUCTION

Application of sewage sludge to soil can influence the chemical, physical and biological properties of the soil. After loading of sewage sludge to soils, regardless of the sources, a series of chemical and biological processes will be initiated. Some of these processes, such as those microbiologically-related and adsorption processes may be rapid, but some others such as physical properties may take some time. Nonetheless, these may be beneficial, particularly in arid and semi-arid regions where soils normally have poor physical characteristics due to low organic matter. However, application of sewage sludge in these regions would also raise the risk of increasing metal availability in soil solution because many of these soils have high salinity and chloride concentrations in the soil solution. Application of sewage sludge could also influence the chemical and biological properties of the soil. There may be changes in soil cation exchange capacity, soil pH and soil metal concentration, as well as changes in soil biological activity. Of course, change in any of these factors would result in changes in the bioavailability of potentially toxic metals and their uptake by plants.

In recent years, sewage sludge has been used as a soil fertiliser. In addition, the organic matter content of sludge can improve the water retaining capacity and structure of some soils, particularly when applied in the form of dewatered sludge cake (MAFF 1996). Although, some benefits support the sewage sludge application to soils, some other factors may limit its utilisation (Alloway and Jackson 1991). In order to reduce the hazards involved with sludge application to agricultural land, governmental agencies have set up rules which restrict the sludge application to control disadvantages. To achieve the minimum harm and the maximum benefit of sewage sludge, Sludge Regulations and Code of Practice for Agricultural Use of Sewage Sludge have been prepared to provide guidance and requirements on the application of sludge to agricultural lands (MAFF 1996)

Since potentially toxic metals are frequently found in sewage sludge and application of sewage sludge to soil and agricultural lands has significantly increased recently, the behaviour of heavy metals in soils treated with sewage sludge has received a marked attention. In the past few years, a large number of projects have been conducted on heavy metals, sewage sludge and their potentially toxic impact to environmental ecosystems. Human health risks as well as environmental pollution implications could be the main reasons for this attention.

Soil pH and Carbonate Content

One of the factors that has received the most attention is soil pH. This can markedly affect the bioavailability and consequently the plant uptake of metals. The effect of pH on the solubility and plant-availability of different metals is greater for some than others (Smith 1996). It is also found that pH has a greater influence on the extraction of heavy metals with chemical solvents than on their uptake from the soil by plants. This may be due to an increased efficiency in the process of plant uptake at higher pH values. Apparently, there are also some differences in the influence of pH on the uptake of native and applied metals. The availability of most metals decreases with increase in pH (Sillanpaa 1976, Ross 1996, Alloway and Jackson 1991) but the availability of Mo and elements with anionic species increases with increasing soil pH (Sillanpaa 1976, Smith 1996). Most researchers have found that the bioavailability of cationic forms metals to plant from sludge-treated soils decrease as the pH is increased either by liming or applying calcareous sludges (Alloway and Jackson 1991).This effect can be due to both a pH effect and / or an increase in Ca^{+2}ions (due to lime) (Alloway and Jackson 1991).

Jackson and Alloway (1991) showed that liming soils (to pH 7) which had been heavily amended with sewage sludge reduced the Cd concentration in crops. Similar results were found by Hooda and Alloway (1996). They found that liming the soils to pH 7 prior to sowing significantly reduced metal concentrations in carrot and spinach. This reduction was greater for Cd, Ni and Zn than Cu and Pb. The effect of sewage sludge on crops when used alone or in combination with mineral fertilizers or lime was studied by Merzlaya (1995). He reported that sewage sludge had a greater effect on yield whereas sewage sludge + lime were ineffective and N and P fertilizers had practically no effect. The effect of lime on crops and bioavailability of heavy metals have been studied by many other researchers. Metal mobility decreases with increasing soil pH due to precipitation as insoluble hydroxides, carbonates and as organic complex adsorption on to clay minerals and organic matter is also raised by increasing soil pH value (Smith 1996). Some metals such as Zn, Ni and Cd tend to be influenced strongly by soil pH whereas Cu, Pb and Cr are little affected by changes in soil pH (Smith 1996). Hooda et al (1997) showed that the surest way to control the accumulation of metals in food plants is by controlling their concentrations in the soil. They found that soils with a non-acidic pH and clayey texture tended to achieve better control of metal accumulation in food plants compared to those with an acidic reaction and a course texture.

The Effect of Organic Amendments

Any change in the amount of organic matter may result in a noticeable change in soil cation exchange capacity. In soils with greater CEC, lower concentration of metals may be expected in an extracted solution. In particular, DTPA extractable metals have been found to be lower in soils with a higher CEC compared to lower CEC (Korcak and Fanning 1985). In sludge-treated soils or soils with high organic matter content (e.g. organic soils), increasing organic matter would increase not only the soil CEC but also it would act as a specific absorbent. In these conditions, the effect of CEC, itself, may become unclear due to domination of adsorption and complexation reactions introduced by organic matter. The effect of organic matter on the availability of metals will be discussed separately.

Soil Organic Matter

Organic matter is a very important adsorptive source of metals in soils. Organic matter has a high cation exchange capacity and can adsorb a high concentration of heavy metals. Sludges contain a lot of organic products so they adsorb metals. In addition to the organic matter, sludges contain Fe and Mn oxides that can adsorb other metals (Alloway and Jackson 1991). In some cases, adsorption of metals by organic matter may be great enough to cause deficiency (Sillanpaa 1976). Many metals form insoluble complexes with the soil organic matter and can be efficiently sorbed in relatively unavailable form (e.g. Pb and Cu) (Alloway 1997). Increasing the complexing capacity of soil and the formation of stable organo-metallic complexes by applying sewage sludge, reduces the mobility of metals in soil and thus lowers their availability to plants (Smith 1996). However, in addition to the solid-state organic matter acting as a sink for metals in sludge-treated soils, soluble low molecular weight organic molecules produced during the microbial decomposition of sludge in the soil form soluble complexes with metals. These complexes are more mobile, less readily adsorbed and possibly more readily taken up by plants than free metal ions (Alloway 1997, Antoniadis 1998).

There are some differences between the reactions of various metals with different organic compounds. Humus holds di- and tri-valent metallic cations more firmly than alkaline metal cations. Some researchers showed that Cu forms rather strong complexes with organic compounds and is more likely than Mn to be fixed in humus (De Mumbrum and Jackson 1956). Sometimes plants seem to be able to adsorb organically complexed heavy metals and it appears that many of the metal deficiency cases found in peat soils are not due to the low degree of bioavailability but to the inadequate total metal sources in these soils (Sillanpaa 1976).

Organic matter differs widely in composition and degree of humification and consequently there are different decomposition rates which can affect availability of metals and uptake by plants. Pascual et al (1998) examined the changes in organic matter mineralization when six amendment rates of municipal solid waste, sewage sludge and compost were added to an arid soil. They found that potentially mineralizable C in municipal solid waste-amended soil was significantly higher than in the soil amended by sewage sludge and compost and it increased as the amendment rate of compost and sewage sludge increased. The results also showed that the CO_2 loss:TOC (total organic carbon) ratio differed with amendment rate between fresh and composted wastes. Other results showed that sewage sludge increased the Zn, Cu, Pb, Cd, Ni and Cr content of soil and plants. They indicated that differences in metal content of various composts are generally related to differences in their composition and soil-climate management system in which they are used (Pinamonti 1998, Pinamonti et al 1997).

The effect of temperature on organic matter decomposition and availability of metals and nutrients have also been studied.The behaviour and bioavailability of Cd and Pb from two soils mixed with sewage sludge was studied at two temperatures (15 and 25 ^{o}C) by Hooda and Alloway (1993). They found that Cd and Pb concentration in ryegrass was significantly higher in the warmer temperature compared to lower temperature. Similar results were found by Antoniadis and Alloway (2001).

Hydrous Oxides

Al, Fe and Mn hydrous oxides can adsorb metals (Alloway and Jackson 1991, Alloway 1997). Kuo et al (1985) found that the hydrous Fe oxide content of soils was an important factor in the prediction of metal uptake by Swiss chard. Hue et al (1988) reported that soils contain volcanic ash had the greatest adsorptive capacity for heavy metals and P.

Source and Form of Metals

The form of metals from different sources has an important effect on their availability. It has been found that metals originating from sewage sludge applied to soil tend to be less available than those from many inorganic sources. Tills and Alloway (1983) using liquid chromatographic fractionations found that Cd^{+2} predominated in the solutions of Cd-polluted soils. Around 13% of the total Cd in the soil solution from a sludged soil was found in organic compounds. Ghorbani (2003) found that the addition of the metals to soils as either sewage sludge or metal salts resulted in increased concentrations of these metals in ryegrass tissue but accumulation was greatest from the metal-spiked soils. Similar results were also reported by Hooda (1992) and Antoniadis (1998).

Redox Status

Redox conditions can affect the behaviour of metals. In the reducing environment hydrous oxides of Fe and Mn dissolve and release any metals which were adsorbed or co-precipitated with them thus increasing the availability of several metals (Alloway 1997). Obviously the availability of Mn and Fe is more affected by oxidation and reduction than other metals. Reduction caused by high moisture content or flooding can increase the availability of S, Cu, Mo, Ni, Zn, Pb and Co . The low availability of Mn and Fe in oxidized conditions is usually explained in terms of the lower solubility of the tri-valent as compared with the reduced di-valent form (Sillanpaa 1976). However, oxidation - reduction processes are usually accompanied by changes in soil pH, which may complicate the picture as well as interactions between Fe and Mn and other elements.

Some metals such as Cd tend to form insoluble sulphides with reduced sulphate ions in saturated soils (Alloway 1997). Change in soil conditions such as a fluctuating water table or seasonal changes causes a change in the redox status, and this has been linked to the availability of many metals (Sillanpaa 1976, Alloway 1997). Soil with a fluctuating water table will often have a lower adsorptive capacity for metals such as Cd and As which are strongly sorbed by hydrous oxides of Fe and Mn . The availability of Cd in rice grown-soils can be affected by oxidation-reduction conditions. In flooded conditions, CdS will be formed which is insoluble but in oxidising conditions the Cd^{+2} and SO_4^{-2} will be the main ions. The SO_4^{-2} will cause the soil pH to decrease and consequently Cd will be more available (Alloway 1997).

Antagonistic Effects of Other Metals

Several elements can have antagonistic effects on the availability of metal to plants. Some researchers have found that excessive phosphorus fertilisation has reduced the availability of Cu and Zn (Bingham 1963, Bingham and Garber 1960). Several possible explanations for P-induced Zn or Cu deficiency have been given, including the immobilisation of the metals within the plant by abnormal amounts of P being present, precipitation by P-Zn antagonism within the roots and reactions occurring outside the physiologically active roots, so reducing the uptake of Cu and Zn . Some other antagonistic effects between metals have been reported by some other researchers. Antagonistic effect of Zn/Cu, Zn/Cd, Ca/Cd, Ca/Pb and Mo/Cu are some of them (Alloway 1997).

Salinity

Many factors influence Cd uptake by plants, but the identification of salinity as an important determinant of Cd concentrations in field crops (Li et al 1994, McLaughlin et al 1994) has encouraged further investigation of the effects of Cl on Cd uptake by plants (Smolders and McLaughlin 1996a, Smolders and McLaughlin 1996b).

In an experiment (Smolders and McLaughlin 1996b) the ability of Cd-Cl complexes to be taken up by plants was investigated using Swiss chard in resin-buffered nutrient solutions. The results showed that as solution Cl concentration increased, Cd concentrations in plant shoots also increased from 6.5 to 17.3 mg/kg and in roots from 47 to 106 mg/kg. Since the activity of Cd^{+2} in solution was well buffered during the plant growth using the resin system, complexation of Cd with Cl, increased soluble Cd in culture solution while no significant changes were found in Cd^{+2} activity with increased Cl concentration. Based on these findings, it was concluded that enhancement of Cd uptake by Cl need not to be related only to enhanced diffusion of Cd^{+2} through soil to the roots, but that (i) Cd-Cl complexes species would be available (in addition to Cd^{+2} species) and / or (ii) Cl enhances diffusion of Cd^{+2} through the unstirred liquid layer adjacent to the root surfaces or through the apoplast to sites of Cd uptake within the root itself. It was also mentioned that mechanism (i) is more likely to be the main explanation for increased Cd plant uptake with increased Cl concentration in the solutions.

Cabrera et al (1988) have also reported that Cd uptake by barley was enhanced in NaCl solutions compared to $NaNO_3$ in the presence of humic acid. However they reported more Cd uptake in $NaNO_3$ in the absence of humic acid in the solutions. Although they finally concluded that Cd^{+2} was the preferred species to be taken up by roots over the Cd-Cl species, the effect of Cl in enhancing the Cd uptake in the presence of humic acid could not be ignored. In fact, humic acid may act as a buffer to control Cd^{+2} activities in the presence of Cl in the solution.

Ghorbani (2003) also showed that increased Cl concentration in the soil solution can significantly increase the concentration of Cd in ryegrass as well as spinach. Cadmium speciation in the solutions using $MINEQL^+$ computer model programme, showed that the plants have strong affinity to uptake Cd-Cl complexes as well as Cd^{+2} free ions. Other experiments (Ghorbani 2003) also showed that ionic strength, inorganic complexation, index cation as well as pH are the most factors affecting the adsorption of Cd in both soil and sludge-treated soil. He finally concluded that Cd uptake could be affected by Cd complexation in soil and in the solutions through change in Cd^{+2} activity as well as plant absorption of Cd-Cl complexes.

Bingham et al (1984) evaluated the effect of salinity on the availability of Cd by Swiss chard. They found that there was an important relationship between the calculated chemical speciation of Cd in the soil solution and Cd availability to Swiss chard as judged by leaf Cd concentration. Bingham et al (1986) also studied the effect of sulphate salinity on availability of Cd in soil. They reported that the absence of a statistically significant effect of SO_4 on leaf Cd may be associated with the general lack of the effect of SO_4 treatment on total free Cd ions (Cd^{+2}) in the soil solution. This behaviour contrasts with that reported by Bingham et al (1984) for the effect of Cl treatment which tended to increase total Cd in soil solution and was highly significant in affecting leaf Cd in Swiss chard. The authors concluded that these differences are due to differences in speciation of SO_4 and Cl with Cd in solution. In contrast with the above results, some other workers reported the significant effect of SO_4 on Cd uptake by Swiss chard. They found that increasing SO_4 concentration in nutrient solution and soil solution causes increased Cd uptake. They concluded that the $CdSO_4$ complex is clearly as available to plant as Cd free ions (McLaughlin et al 1998a and McLaughlin et al 1998b). Increasing Cd uptake with increase in Cl concentration in soil solution in Potato tubers, Swiss chard and Sunflower kernels have also been reported by others (McLaughlin et al 1994, Bingham et al 1983 and Yin-Ming Li et al 1994).

Plant Species and Genotype

It is recognised that metal concentrations in plants grown on the same soil can vary up to 100-fold between different species but mostly between 4 and 20-fold. However, inter-varietal differences within plants of the some species may vary between 1 and 4 fold (Alloway 1997).

Some researchers have worked on the effect of plant species on metal uptake. Alloway and Morgan (1986) found that there are some differences between species in metals uptake. They reported the following order for Cd and Ni accumulation by lettuce, cabbage, carrots and radish (Alloway 1997):

Cd : lettuce > cabbage > carrots > radish

Ni : radish > lettuce > cabbage > carrots

Jackson and Alloway (1991) reported that the component of the diet which made a major contribution to the overall exposure to the metal and which were also sensitive to changes in soil Cd concentration were : cereal grain, potatoes, root vegetables and leafy vegetables (Alloway 1997). Some differences between cultivars have also been reported. McLaughlin et al (1994) found that 15 cultivars of potato varied widely in Cd concentrations on the same soil with ranges of 9-39 µg/kg on one site and 29-56 µg /kg at others (Alloway 1997).

Genotype variations in metal uptake by plants may be partly due to differences in root morphology and biochemistry. The rhizosphere which is the zone surrounding plant roots at the interface with the soil seems to have an important role in this. The zone contains a very active and diverse population of micro organisms and organic materials from roots. Some metals and micronutrients can become more available in the rhizosphere. As the composition of the rhizosphere may differ in plant species, it has been reported that some species may be able to take up different amounts of metals by roots (Alloway 1997). The differences between plant genotypes in term of Cd uptake have also been reported (Hocking and McLaughlin 2000).

Other Factors

The main factors affecting availability of metals in soils have already been discussed. There are some other factors such as soil texture, soil moisture, soil temperature and soil aeration which may contribute to metal availability. The effect of theses factors is likely to be indirect. Clay content can directly influence the soil CEC and contribute to the adsorption of metals in soils. The effect of other factors such as temperature and soil moisture may be through their effect on the soil microbial activity or qualifying the chemical reactions in solution. The availability of all metals seems to be greater in the presence of adequate moisture (e.g. near to field capacity) due to existence of better mass flow and diffusion of metals and their complexes (Alloway 1997). Soil aeration is also important for biological activity and decomposition processes in soils.

Plant Uptake and Accumulation of Metals

The amount of metals taken up by plants may be significantly influenced by their ability to be absorbed and accumulate in a particular plant part. For example, spinach, lettuce, celery and cabbage are known as high accumulators of Cd while potato and maize are low Cd accumulators (Pais and Jr 1997). Such characteristics are useful for selecting those crop plants best situated for soils that have a particular metal content, thereby avoiding the potential of introducing the metal concerned into the food chain (Chaney 1983). Also, some plant parts tend to accumulate more metal than others. For instance, it is widely accepted that for most plants, cadmium is accumulated much more in roots than in leaves.

When the soil substrate is ready to be assimilated by plant roots, and the mineral salts, including metals, are mobile, it could be expected that the proportion of the metals absorbed by plants would be the same as their proportion in the soil solution, but this is not normally so. In fact, plants selectively absorb certain metals in definite proportions (Ermolenko 1972). The entry of mineral substrates into the plants is determined by electrolyte concentration in the soil solution, ion exchange, permeability of membranes, Donnan equilibrium, membrane potential, etc. As a result minerals and water are supplied to the cells, while the decomposition products are eliminated from the cells. While diffusion is possible into and out of the cells, such a cell is not in equilibrium with the surrounding medium; the cell is controlling the biological migration of different ions. It has been established by work using radioactive isotopes that when ions are absorbed by roots from the surrounding medium, both diffusion and active migration of specific ions take place (Ermolenko 1972).

Thus, the selective sorption of specific ions by plants is due to the metabolic activity of the cells. The theory of active migration of ions in the organism by way of carriers was found to be applicable to most of the cations and anions, even though the selective absorption of some ions can be explained in other ways. The transfer of oxygen by haem to the cells of living organism is an excellent example of an element being transported on a carrier and not by diffusion. It is also noticeable that haemoglobin selectively absorbs oxygen rather than nitrogen from the air, even though the amount of available nitrogen in the atmosphere is more than three times larger than that of oxygen. Similar selectivity is shown in plant uptake mechanisms.

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