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BIOAVAILABILITY OF TRACE METALS IN URBAN CONTAMINATED SOILS

A Thesis
Submitted to the Faculty of Graduate Studies and Research
of McGill University
in Partial Fulfillment of the Requirements of the Degree of
Doctor of Philosophy

by
Nicola Cook
Department of Natural Resource Sciences
McGill University, Montreal
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BIOAVAILABILITY OF TRACE METALS IN URBAN CONTAMINATED SOILS

Nicola Cook

McGill University 1997

There are two main components to the research: the theoretical and the experimental. Chapter 2 contains an analysis of the state of soil quality guidelines and the scientific methods used to determine them. A number of recommendations to improve soil quality criteria for trace metals are offered including the importance of considering bioavailability and the need to use realistic conditions, trace metal sources and organisms.

A critical review of the literature dealing with predicting the availability of trace metals to plants is presented in Chapter 3. We found little agreement among hundreds of similar studies which relate plant metal uptake to the amount of metal extracted by selective chemical dissolution procedures. An extensive summary of the data shows clearly that the extraction methods are not widely applicable. Differences between individual soils, their metal retention capacities, as well as plant factors and environmental conditions contribute to the variability of the results. Alternative ways of assessing bioavailability are suggested.

The experimental component of the thesis focuses on the availability of trace metals to plants. In Chapter 4 the uptake of Cu from different soil pools was examined and the free metal ion (Cu^{2+}) was found to be the best predictor of uptake by lettuce (*Latuca sativa* cv. Buttercrunch), ryegrass (*Lolium perenne* cv. Barmultra) and radish (*Raphanus sativus* cv. Cherry Belle).

In Chapters 5 and 6 we examined the effect of low-cost in-situ treatments on the availability of metals to plants in greenhouse and field experiments. Synthetic zeolites, P amendments, organic matter and clean soil were used and their effect on the bioavailability of Cd, Cu, Pb, Ni and Zn evaluated. The plants for the experimental work were lettuce and perennial ryegrass. Only the clean soil treatment was consistently effective in reducing the concentration of metals in the plant. We also wanted to determine whether the trace metals in the plant tissue came from the soil or from direct deposition of pollutants on the leaf surfaces. We found little evidence that metals in plants were a result of atmospheric fallout.

A method for the accurate analysis of total metal concentrations in a range of contaminated soils including those containing oil and grease was developed (Chapter 7). For this research the trace metals of concern are Cd, Cu, Ni, Pb and Zn - all commonly found in urban/industrial soils. The proposed method using $HNO_3/HClO_4$ has several advantages over the common HNO_3/H_2O_2 procedure. We were able to digest larger soil samples and hence the final

concentration of trace metals was usually in the range for analysis by inductively coupled plasma atomic absorption spectrometry or flame atomic absorption spectrometry.

BIODISPONIBILITÉ DES MÉTAUX TRACES DANS LES SOLS URBAINS CONTAMINÉS

RÉSUMÉ

La recherche se divise en deux parties principales: la théorie et l'expérimentation. Au chapître 2 se trouve une analyse de l'état actuel des critères de classification de qualité des sols et les méthodes scientifiques pour les déterminer. Plusieurs recommendations visant à améliorer les critères de qualité des sols pour les métaux traces sont offertes. L'importance de considérer la biodisponibilité et d'expérimenter sous des conditions réalistes, avec une source de métaux traces et d'organismes propres à l'environnement est soulignée.

Une revue critique de la littérature concernant la prédiction de l'absorption des métaux traces pour les plantes est présentée au chapître 3. Très peu de consensus se retrouve parmi des centaines d'études similaires mettant en relation l'absorption des métaux par les plantes en fonction des métaux extraits par diverses procédures de dissolution chimique sélective. Un résumé détaillé des données montre clairement que les méthodes d'extraction des métaux traces ne sont pas universelles. Les différences entre chaque sol, leur capacité de rétention des métaux de même que les conditions environnementales et les propriétés de la plante contribuent à expliquer la grande variabilité dans les résultats. D'autres façons d'estimer la biodisponibilité sont suggérées.

La partie expérimentale de la thèse consiste à étudier l'absorption des métaux traces par les plantes. Au chapître 4, la biodisponibilité du Cu est étudiée en fonction des différentes composantes du sol; l'ion Cu^{2+} en solution est la

meilleure espèce pour prédire l'absorption du Cu par la laitue (*Latuca sativa* cv. Buttercrunch), le ray-grass (*Lolium perenne* cv. Barmultra) et le radis (*Raphanus sativus* cv. Cherry Belle).

Au chapître 5 et 6, des traitements in-situ sont étudiés, en serre et au champ, afin d'observer leurs effets sur la disponibilité des métaux aux plantes. Des zéolites synthétiques, des amendements de phosphores, de la matière organique et un sol propre ont été ajoutés aux sols contaminés et leurs effets évalués quant à la biodisponibilité du Cd, Cu, Ni, Pb et Zn. Seul le sol propre a été constamment efficace pour réduire la concentration des métaux absorbés par la plante. En second lieu, nous avons voulu déterminer si les métaux traces mesurés dans les tissus de la plante originent du sol ou simplement du dépôt des polluants sur la surface foliaire; nous avons trouvé très peu d'évidence pour supporter cette dernière hypothèse.

Une méthode d'analyse a été élaborée afin de mesurer avec exactitude les concentrations de métaux traces contenues dans les sols contaminés, même ceux contenant des huiles et graisses (chapître 7). Les métaux d'intérêt pour cette recherche étaient Cd, Cu, Ni, Pb et Zn, trouvés régulièrement dans les sols contaminés urbains et industriels. La méthode proposée, basée sur l'utilisation de $HNO_3/HClO_4$, a plusieurs avantages sur les procédures usuelles utilisant HNO_3/H_2O_2. Il a été possible de digérer de plus grands échantillons de sols et de là, les métaux traces à mesurer se tenaient dans les écarts de concentration pouvant être mesurés par spectométrie d'absorption à plasma (ICP-AES) ou à flame (AAS).

AUTHORS STATEMENT: ROLE OF CO-AUTHORS

Dr. W. H. Hendershot's role was that of supervisor, to provide guidance through discussing my ideas and editorial assistance in the preparation of the thesis; the formation and development of the ideas contained within the thesis are wholly the work of the candidate, with the following exceptions:

Published papers

In Chapter 2 the paper 'The problem of establishing ecologically based soil quality criteria: The case of lead' by Cook, N. and Hendershot, W.H. (Canadian Journal of Soil Science 76:335-342, 1996) is presented. Dr. Hendershot and I co-authored the work. He was responsible for about fifty percent of the paper.

In Chapter 4 the paper 'Linking plant tissue concentrations and soil copper pools in urban contaminated soils' by Sauvé, S., Cook, N., Hendershot, W.H. and McBride, M.B. Environ. Pollut. 944:153-157, 1996) is presented. It was co-written with Sébastien Sauvé with Dr. McBride and Dr. Hendershot acting mainly as editors of the final manuscript. Sébastien conducted the chemical analysis of the $CaCl_2$ soil solutions with the ion selective electrode. I ran the greenhouse experiment and analysed the plant tissue. I wrote the sections on the plant study, edited the manuscript and contributed to the analysis and interpretation of the data. The soils used for the work were collected and used by a group of students working under Dr. Hendershot's direction.

Unpublished papers

Chapter 7 presents the results of a digestion method that I conceived, ran and tested. Marie-Claude Turmel, the technician in Dr. Hendershot's laboratory, helped with much of the analytical work. We also discussed the results of the various elements of the work as it progressed. Her contribution significantly speeded up the process of obtaining final results.

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TABLE OF CONTENTS

LIST OF TABLES

Chapter 1

GENERAL INTRODUCTION

Soils contaminated with trace metals have been of concern to government regulators, research scientists and the public for decades because of their impact on human health (Ernst, 1996). Industrialization has contributed to the burden of trace metals in soils in urban areas. The use of sewage sludge, pesticides, irrigation waters and fertilizers on agricultural land has made some of that land of questionable quality for production of food for humans and animals. Governments in most industrialized countries have adopted soil quality guidelines that define an acceptable total soil concentration of trace metals, see Table 1.1 (CCME, 1991a&b; Anonymous, 1994). Researchers have found very little evidence that would suggest that the total concentration of metal in soil is directly related to the threat to human health or the ecological health of a contaminated ecosystem. It has been observed that only a small fraction of the total soil concentration of metal is potentially dangerous (Delft, 1997). This fraction, known as the mobile or bioavailable fraction, is of concern due to the potential for leaching into groundwater and/or entering the food chain through plant uptake (Cook and Hendershot, 1996; Angelone et al., 1993; Davies, 1992).

The most common approach for determining what constitutes a toxic or dangerous amount of a trace metal in a soil, on which soil quality criteria are based, is to spike a clean soil with the soluble salts of a metal, for example $PbCl_2$, $CdCl_2$ or PbO, and then introduce an organism to it. Plants are most often used in this type of study. At some concentration an adverse effect on the plant will be observed. Unfortunately, using these very soluble forms does not give an accurate picture of a real soil-plant system. Contaminated soils are much more likely to contain metals bound with phosphates or carbonates which are several orders of magnitude less soluble than chlorides and oxides. Khan and Frankland (1983) observed adverse effects (chlorotic radish seedlings) when Pb was applied to soil as $PbCl_2$ at 50 mg kg^{-1} and at 500 mg kg^{-1} when PbO was used. Lead phosphate ($PbPO_4$) is about one million times less soluble than PbO (Santillan-Medrano and Jurinak, 1975). What the literature indicates then, is that relatively low concentrations have a toxic effect upon living organisms. The origin of this project stems from the problems that we found associated with establishing and justifying, generic remediation limits for Pb while preparing the background document for Environment Canada (O'Brien et al., 1994).

Another factor which is generally ignored in toxicity studies and the protocol for establishing soil quality guidelines is the possibility that some of the metal found in plant tissue may be derived from atmospheric input. Various researchers have found that metal in tissue of plants grown in the field and in greenhouses come from atmospheric fallout (Haygarth and Jones, 1992; Dalenberg and van Driel, 1990; Mosbæk et al., 1989; Hovmand et al., 1983).

If the goal in cleaning up a soil is based on the total soil concentrations and therefore, to reduce total soil concentrations (to background levels), the task is enormous, costly and probably not necessary. In this case, removal (excavation and storage) of the soil is one of the few options and costs run at about $100-200/tonne. A storage facility must also be available and the resuspension of contaminated soil particles into the atmosphere upon disturbance of the site must be considered (Huang et al., 1997).

If, on the other hand, the goal is to reduce the portion of the contaminant which is available and potentially toxic, amendments to cause precipitation or sorption may be desirable. Soil amendments including organic matter, clays, hydrous manganese oxides, $FeSO_4$, lime, zeolites and phosphorus have shown good results in laboratory (Gworek et al.,1991; Hertzenberg, 1983). Greenhouse studies and some field studies are also beginning to show promising results (Boisson, 1997; Rebedea, 1997; Chlopecka, 1997; Mench et al., 1994; Didier, 1993; Khattak and Page, 1992; Gworek, 1992; Czupyrna et al., 1989). Applicability of the laboratory results to field situations has not yet been established and work needs to be focussed in this area. Using plants in greenhouse and field studies is an effective way of guaging trace metal bioavailability with and without treatments.

The Metals

Excess concentrations of Cd, Cu, Pb and Zn in urban/industrial soils may be a result of the natural chemical weathering of rocks or, more likely, anthropogenic activity. Some industries and land uses associated with urban trace metal contamination are: chemical manufacturing and disposal, electroplating industries, land fill sites, paint and textile manufacturing, pharmaceutical production, railway yards, service stations and scrap yards (Ross, 1994; Tiller, 1992). The form of metal being added to the soil will govern its mobility and availability. Metals associated with acetates, chlorides and nitrates are readily soluble whereas metals bound with phosphates, hydroxides, carbonates and organic complexes are rather stable (Santillan-Medrano and Jurinak, 1975). Metal particles deposited on soils from atmospheric fallout are usually in the form of oxides, silicates, carbonates, sulfates and sulfides. Metals associated with sludge are often organically bound (Kabata-Pendias and Pendias, 1992). The bioavailability of these metals depends largely on the form, soil physico-chemical properties and the organism they are in contact with (Ross, 1994; Kabata-Pendias and Pendias, 1992; Jones, 1991; Bahlsberg, 1989; Tyler et al., 1989; Adriano, 1986; Koeppe, 1981).

These elements have many similarities in terms of their behaviour in soils. They are often found in their divalent form, but can also form monovalent cations and complex anions. The fate of the metals depends on soil properties which control reactions such as: dissolution, adsorption, complexation, precipitation and occlusion. The soil factors that most influence metal availability in soil are pH, organic matter content, clay content, redox potential and Fe and Mn oxide concentration (Abd-Elfattah and Wada, 1981; McBride, 1981; Lindsay, 1979; Santillan-Medrano and Jurinak, 1975; McLaren and Crawford, 1973; John, 1972). Also, the concentration of potential complexing ions, such as PO_4 and CO_3, in the soil are important (Evans, 1989; McBride, 1981; Lindsay, 1979). Competition for ligands among trace metal ions also occurs (Christensen, 1987). These metals have a strong affinity for S^- anions found under reducing conditions; metals complexed with S are virtually insoluble in water.

Zinc and Cu are considered essential for plant growth. They have been shown to aid in plant metabolism, RNA and ribosome formation, photosynthesis and respiration. Excess concentrations of these metals in plants may result in an alteration of root membrane permeability, tissue damage, depressed plant growth and chlorosis of new leaves. See Table 1.2 for concentrations considered acceptable in some plants.

Cadmium and Pb are considered non-essential for plant growth. Excess concentrations of these elements in plants have resulted in depressed nutrient uptake and the inhibition of chlorophyll formation (Kabata-Pendias and Pendias, 1992; Burton et al., 1986).

Contaminated soils in urban areas are often contaminated with organic pollutants such as PCB's (polychlorinated biphenyls), PAH's (polyaromatic hydrocarbons) and oil and grease. The soils used for this work contained mainly Cd, Cu, Ni, Pb, Zn and oil and grease. Research on these mixed systems, including methods for digesting soils contaminated with oil and grease and trace metals, is lacking. Various methods are available for the digestion of soils for trace metal analysis but none have been developed to tackle the problem of oil and grease coatings, which make soil difficult to digest. The most common reagents used are concentrated HNO_3 followed by 30% H_2O_2 (Edgell, 1988; Miller and McFee, 1983) or aqua regia (Mench et. al., 1994; Agemian and Chau, 1976). Methods using HF may recover metals that are part of the silicate structure, but are considered dangerous for daily laboratory use and require specialized equipment. Perchloric acid is also used to dissolve metals bound to soils. All of these acids are more effective at dissolving metals when boiling (Agemian and Chau, 1976). Other methods like spark source and isotope dilution mass spectroscopy as well as neutron and particle activation analysis may be more precise, but most laboratories are not equipped for them (Stoeppler, 1985).

Table 1.1 Remediation Criteria for Soil in mg kg^{-1}*

Land use	Cd	Cu	Pb	Zn
Agricultural	3	100	375	600
Parkland/ Residential	5	150	500	500
Industrial/ Commercial	20	500	1000	1500

*CCME, 1991b

Table 1.2 Plant concentrations considered acceptable in mg kg^{-1} dw*

Plant	Cd	Cu	Pb	Zn
grasses	0.05 - 1.2	1 - 15	1.2 - 3.6	15 - 30
grains	0.01 - 0.3	1 - 8	0.01 - 2.2	5 - 37
lettuce	0.12 - 0.7	6 - 8	0.7 - 3.6	44 - 73

*revised from Kabata-Pendias and Pendias, 1992

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Chapter 2

THE PROBLEM OF ESTABLISHING ECOLOGICALLY-BASED SOIL QUALITY CRITERIA: THE CASE OF LEAD

Nicola Cook and William H. Hendershot

Canadian Journal of Soil Science 1996, 76:335-342.

ABSTRACT

Soil quality guidelines are being developed to address the problem of lead in soils. They define an acceptable **total** soil concentration of lead. Recent studies indicate that only a small portion (found in the soil solution) of the total is immediately available to biota and therefore an environmental hazard. This paper focuses on the difficulty of assessing the environmental risk of lead in soils and the factors controlling the fraction of the total that is available to soil organisms. Toxicity data on plants and soil animals used to create guidelines indicates negative effects at concentrations ranging from 50 to over 40,000 mg Pb kg^{-1} soil; however, the tests, using clean soil spiked with soluble lead salts, do not adequately reflect the conditions likely to be found in the field. In soils from contaminated sites the lead can be expected to be in relatively stable, insoluble forms. The selective chemical extraction procedures used to define different 'pools' of lead in soils, and to define the amounts of bioavailable lead, have not been properly validated. The philosophy behind the derivation of soil quality guidelines is criticized and recommendations are made for the development of scientifically defensible guidelines for lead in soils.

Key Words: Bioavailability, soil contamination, toxicity, soil quality criteria

INTRODUCTION

The concern of the public, scientists and governments for lead in soils stems from its impact on human health. Another aspect is the belief that the normal functioning of ecosystems must not be adversely affected by pollutants if we are to sustain acceptable living conditions on this planet. However, levels of pollutants in soils deemed acceptable to protect human health may not be adequate for the protection of other organisms (Zach et al., 1992). Currently, many governments approach the problem by attempting to combine a human-health and an ecological-risk based protocol. They are struggling to find numerical limits for lead that will "maintain, improve, or protect environmental quality and human health at contaminated sites in general" (CCME, 1991). Generic guidelines are being created that define an acceptable **total** soil concentration of lead (O'Brien et al., 1994). In contrast, recent studies suggest that the lead found in the soil solution, a measure of the portion available to biota, is a more reliable indicator of the threat posed to the environment than total lead (Kabata-Pendias and Pendias, 1992). The focus of this paper is the problem of establishing the environmental risk of lead. We will also discuss remediation criteria based on the factors affecting the bioavailability of lead in contaminated soils. An understanding of the mechanisms that control bioavailability would facilitate the creation of scientifically defensible and realistic soil quality guidelines.

ESTABLISHING ECOLOGICALLY-BASED SOIL QUALITY CRITERIA

The main problem is how to determine a maximum amount of lead in soil that does not cause environmental damage. Environmental damage may mean an adverse effect on the most sensitive soil organism or a reduction in soil processes like decomposition of organic matter or nitrogen, phosphorus, and sulfur cycling. It may also be manifested as an accumulation of lead in the food chain resulting in widespread toxic effects. Erosion of soils by wind or water provides another important pathway by which lead contaminated soils can degrade the surrounding environment. Each of these pathways has a different potential for conveying lead to ecological receptors. This potential is dependent on many factors often making the relationship between the contaminant and the actual danger it poses ambiguous (Sheppard et al., 1992).

The standard approach of determining what constitutes a toxic or dangerous amount of a lead in a soil, on which soil quality criteria are based, is to spike a clean soil with the soluble salts of a metal, for example $PbCl_2$ or $Pb(NO_3)_2$ and then introduce an organism to it. Plants and soil invertebrates are most often used in this type of toxicity test. At some concentration an adverse effect (e.g., mortality or a decrease in reproduction rates for invertebrates or a decrease in dry weight yield or decrease in germination rates for plants) on the organism will be observed. The weakness of using these very soluble forms is that they do not simulate the behaviour of metals in a real soil system (Merry et al., 1986).

Real contaminated soils are much more stable systems and are likely to contain metals bound with phosphates or carbonates which are several orders of magnitude less soluble than acetates, chlorides, nitrates and oxides. These more insoluble compounds will be less likely to be toxic. For example, Khan and Frankland (1983) observed adverse effects (chlorotic radish seedlings) in a pot experiment when lead was applied to soil as $PbCl_2$ at 50 mg kg^{-1} and at 500 mg kg^{-1} when applied as PbO. One of the forms thought to control lead solubility in soils is $Pb_3(PO_4)_2$ a compound about one million times less soluble than PbO (Santillan-Medrano and Jurinak, 1975; Lindsay, 1979). What the literature indicates then, is that relatively low concentrations of about 50 mg Pb kg^{-1} soil, commonly found in mildly polluted soils, have a toxic effect upon living organisms and/or the potential to accumulate in organisms that would pose a threat to the food chain. These low concentrations are adopted for soil quality guidelines. However, the guidelines then use the total amount of lead in soil, not the available portion, as the criteria for identifying soils that require remediation.

Another factor which is generally ignored in toxicity studies and the protocol for establishing soil quality guidelines is the very real possibility that much of the lead found in plant tissue is derived from atmospheric input. Dalenberg et al. (1990) conducted an experiment designed to distinguish airborne lead from lead in soil as a source for plants. Spiking soil with lead labelled with the isotope Pb^{210} and growing four species of plants (grass *Lolium multiflorum*, spinach *Spinacia oleracea*, spring wheat *Triticum aestivum* and carrots *Daucus carota*) in pots in the field and in a dust free growth chamber, Dalenberg compared the amounts of Pb^{210} with non-labelled lead found in the whole mature plants. The study indicated that a significant portion (73-95%) of the lead found in the test plants was from atmospheric deposition. Similar results were obtained by Tjell and Mosbæk (1979), who concluded that airborne lead was responsible for 90-99% of whole plant tissue lead concentrations. Chaney et al. (1984) also conducted studies to separate the effect of aerially deposited lead from soil lead on a variety of plant species. They concluded that for lettuce and some other leafy vegetables the aerosol source of lead was a more influential factor than soil lead content.

FORMS AND BEHAVIOUR OF LEAD IN SOILS

Bioavailability is the key to understanding the behaviour and fate of lead in soils. The bioavailable portion of lead is the amount that can be taken up by an organism. Many factors influence the mobility and bioavailability of lead, especially pH, organic matter content, clay content and clay type (Chaney et al., 1984; Adriano, 1986; Kabata-Pendias and Pendias, 1992).

As mentioned earlier, lead is added to soils by fallout from the atmosphere, but it is also added to soils by either accidental or deliberate dumping of lead containing wastes on soils, or from the addition of pesticides and fertilizers that contain lead. The form of the metal that is being added to the soil will effect its solubility and initial mobility. For example, lead chlorides, nitrates and acetates are readily soluble in the soil environment and will be leached into the soil. Lead oxides, often associated with smelting operations, although much less soluble than the salts, are still much more soluble than some of the lead compounds that form in soils. Unstable lead particles that reach the soil from automotive exhaust quickly transform into the more insoluble forms, for example of $Pb(CO_3)_2$ and $PbSO_4$ (Kabata-Pendias and Pendias, 1992). Metallic lead is relatively insoluble; however, in the soil environment it will oxidize to form PbO which will then be transformed into a more stable compound. In aerobic soils, weathering of soluble lead compounds results in the formation of more stable compounds such as $Pb_3(CO_3)_2(OH)_2$ (Lindsay, 1979). In anaerobic soils the reduction of SO_4^{2-} to S^{2-}, leads to the formation of PbS, a very insoluble, non-reactive lead species. Even in composted municipal solid waste, the solubility of lead decreases as the material ages and becomes more highly stabilized (Leita and DeNobili, 1991).

In soils, lead solubility seems to be controlled by relatively insoluble compounds such as $PbCO_3$, $Pb(OH)_2$, $Pb_3(PO_4)_2$, or $Pb_5(PO_4)_3OH$ (Santillan-Medrano and Jurinak, 1975). In contrast to the lead salts normally used in toxicity testing, these compounds have a pH-dependent solubility; for example, $Pb(OH)_2$ would maintain a concentration of Pb^{2+} of about 300 g L^{-1} in solution at pH 4.0 but only 0.0003 g L^{-1} at pH 7.0. If, in fact, the dissolved lead is responsible for toxicity to plants and animals, the pH of the soil environment must play a crucial role. In soils with high pH, lead will precipitate as hydroxides, phosphates and carbonates as well as form strong bonds with organic matter (Kabata-Pendias and Pendias, 1992). Since dissolved inorganic lead in soils is mainly in the ionic form (i.e., Pb^{2+}, $PbOH^{+}$) the adsorption on cation exchange sites of clay or organic matter can decrease the mobility and availability of lead in the short term.

In the soil solution, the different species of lead, including Pb^{2+} and complexes with Cl, OH, SO_4, CO_3, HCO_3 and organic ligands, can affect the bioavailability of the metal to organisms (Morrison, 1989). In general, the free ion Pb^{2+}, can react with biological membranes and have a direct toxic effect. The bioavailability of heavy metals bound to organic or inorganic anions will depend on the strength of the bonding; strongly bound metals will tend to be non-bioavailable while weakly bound metals may be readily taken up by biota. Lead bound to lipid soluble complexes may be more bioavailable than those bound to other organic compounds (Morrison, 1989). Relative availability of the various species of lead from soils is in the order: cations in the solution phase > exchangeable cations > chelated cations > compounds precipitated onto soil particles > bound in organic substances > bound inside mineral particles (Kabata-Pendias and Pendias, 1992).

There is considerable interest in finding a laboratory procedure that can be used to identify bioavailable lead in soils. One rather simplistic approach is to use a strong digestion procedure to obtain the total lead content in the soil. This is easily criticized because most of the metal is likely to be strongly held in forms that are not readily available. Another common approach is to use different selective chemical extractants to dissolve metal from different 'pools' which can be related to the solid phase that is most likely to be broken down by that treatment. These 'pools' are operationally defined as: water soluble, exchangeable, bound to carbonate, bound to Fe or Mn oxides, bound to organic matter and residual (contained within minerals not dissolved by the treatments). The effectiveness of any of these extractants to identify the bioavailable 'pool or pools' is based on the correlation between the amount extracted from the soil and either the toxic effect on, or the accumulation in, soil biota.

There seems to be no conclusive evidence as to which forms of lead are available to biota. The evidence relating soil properties, such as pH, cation exchange capacity and the presence of ligands capable of binding lead (PO_4 or organic matter), all suggest that the amount of free metal in solution is the critical fraction (Adriano, 1986; Kabata-Pendias and Pendias, 1992). Some soil scientists stress the importance of the amount of dissolved or easily exchangeable metal (0.01 $CaCl_2$ extractable) as being a better indicator of the bioavailable portion of soil lead (Jopony and Young, 1991) or other trace metals (Boekhold et al., 1992). Hardiman and Banin (1984) found that the amount of lead in the soil solution was five times the amount absorbed by beans from the transpiration stream and concluded that only a fraction of the dissolved lead was available; the rest was strongly bound in organic and inorganic macromolecules. However, numerous studies have also shown good correlations between uptake of metal by plants and animals and the amounts extracted from different 'pools'. Xian (1989) grew cabbage on polluted soils and found good correlation between the amount of lead absorbed and the amounts operationally defined as total, exchangeable and exchangeable plus carbonate. Davies (1992) found that lead uptake from garden plots in England was best predicted by total soil lead. In contrast, Zurera-Cosano et al. (1989) found no statistically significant correlation between the concentration of total lead in soils and the amount taken up by vegetables. Boon and Soltanpour (1992) showed that AB-DTPA was the best indicator of available lead to lettuce and spinach grown in contaminated Aspen, Colorado, garden soils. Khan and Khan (1983) found that DTPA extractions had good correlations with plant uptake whereas Miles and Parker (1979) and Merry et al. (1986) found that DTPA was a poor indicator of metal availability to plants. Although single reagent extractants to determine specific metal 'pools' have been criticized for a lack of specificity, the use of sequential extraction procedures appears to be even more suspect (Beckett, 1989; Nirel and Morel, 1990). According to these authors problems related to redistribution during the sequential extraction procedures cause large errors. It is obvious that more work is required to validate the methods being used so that the results can be attributed to a specific form of metal in the soil with some confidence.

A few reasons for the failure of selective chemical extraction procedures can be proposed. First, the lead will be bound to different materials depending on the type of soil. For example, in dry regions such as those found in many parts of western Canada, western U.S.A. or the Mediterranean, the soils accumulate $CaCO_3$; in contrast, the soils of more humid regions tend to collect hydrous oxides of iron and aluminum. Soils also vary enormously in the amount, kind and distribution of organic matter as well. Clearly, an extractant that is capable of efficiently extracting $CaCO_3$ might be very good at estimating bioavailability in soils in which lead is co-precipitating with, or being adsorbed on $CaCO_3$; but it would be a poor indicator of bioavailability for soils in which lead is being held by iron and aluminum hydrous oxides or organic matter. A second reason might quite simply be that different plants or soil animals create different micro-environments that cannot be simulated by a single extractant. Finally, even if the extractants provided a reasonable estimate of the amount of metal in the different 'pools', this may not be closely related to the amount that is actually capable of moving through a biological membrane.

Estimating bioavailability of a metal can be likened to the problem of estimating the 'acidity' of a soil. While soil pH is a good estimate of the 'intensity' of the acidity, exchangeable acidity is a better estimate of the 'capacity' of the system to resist change; it is known that soil organisms are more strongly influenced by the intensity of the acidity than the buffering capacity. Similarly, it might be much more useful to measure the chemical activity of the most bioavailable form of the metal in the soil solution, thought to be Pb^{2+}, - an intensity factor - than to measure the amounts in different 'pools' - a capacity factor. The fact that the lead can only get to the organism by passing through the soil solution provides additional support for this approach. The lack of consistency in the ability of different operationally defined 'pools' to explain the accumulation of metals in soil biota, or toxic effects, may simply be due to the variations in the relationship of the 'pools' to Pb^{2+} activities in the soil solutions.

BIOAVAILABILITY VERSUS UPTAKE

As has already been stated, there are many soil factors that control the portion of lead in the soil that is available to be taken up by an organism. This indicates that the derivation of a single lead concentration value as the remediation criterion for all soils may be a good starting point but problematic. Confounding the problem further is the individual nature of each organism in a soil system and its effect on uptake. The amount that will be taken up and the amount at which a toxic effect will be generated will vary greatly depending on the organism. For example, plant species, intraspecific variations, growth rate, the developmental stage of the plant and growth conditions such as temperature, light and nutrient availability are all contributing factors to the relationship between lead and plants (Koeppe, 1981; Adriano, 1986; Balsberg-Pählsson, 1989; Tyler et al., 1989; Jones, 1991).

Some vascular plants have developed mechanisms that enable them to tolerate high levels of metals, including lead. Some mechanisms discussed by Tyler et al. (1989) are avoidance (i.e., root redistribution), exclusion (i.e., selective uptake and restricted translocation to sensitive organs), immobilization at the cell wall, and excretion (i.e., guttation, foliar leakage). Seighardt (1989) found *Silene vulgaris* and *Minuartia verna* growing well on mining dump material with lead concentrations of 24 700 mg kg^{-1} soil. Leita et al. (1989) observed herbaceous plants, for example, *Helichrysum italica* with leaf concentrations of 4 036 mg kg^{-1} growing in soil with a lead level of 71 000 mg kg^{-1}.

Uptake and accumulation rates of lead vary among species and within species. Tobacco (*Nicotiana tabacum*) leaves accumulate between 24 and 49% of total soil lead concentrations (Adamu et al., 1983). Leita et al. (1989) analyzed plants growing on lead contaminated sites for lead concentrations and found fodder plants (graminae) with concentrations from 5.5 to 174% of the total soil concentration and herbaceous species (*Helichrysum italica*) and (*Scolymus hispanicus*) with 1.3 to 51% of the total soil concentration. In a study of vegetables grown on soil with a history of sludge application, Chumbley et al. (1982) found that spinach (*Spinacia oleracea*) was the greatest accumulator with concentrations at 3% of the soil concentration. In this study, only washed, edible parts of the vegetables were analyzed for lead and results showed that edible tissues of plants tested were low in lead compared to the soil: lettuce (*Lactuca sativa*) accumulated 1.5% of total soil lead, cabbage (*Brassica oleracea*) 0.26%, leeks (*Allium porrum*) 0.82%, beetroot (*Beta vulgaris*) 0.39% and sweetcorn (*Zea mays*) 0.06% of total soil lead. In a pot study using urban garden soils Chaney et al. (1984) illustrated the intraspecific differences in lead accumulation in lettuce. On the same soil there was up to a 250 percent difference between lettuce cultivars.

Similar problems are encountered when synthesizing results from toxicity and accumulation studies on mammals, birds and soil invertebrates. In mammals and birds, for example, age, general health, dietary factors and reproductive status all play a crucial role in the amount of lead that will be absorbed. There is also a high degree of differential uptake in terrestrial invertebrates. Body weight and age were the greatest determining factors for uptake (and excretion) of lead in earthworms (*Pheretima hilgendorfi*) in a study conducted by Honda et al. (1984). Activity rates (Bengtsson and Rundgren, 1992) and food preferences (Morgan and Morgan, 1991) are also considered important factors controlling lead uptake in earthworms.

ESTABLISHING GENERIC CRITERIA

Table 2.1 presents a cross section of the type of data available for the derivation of remediation criteria. These data come from toxicological tests using clean soil spiked with various amounts of soluble lead salts. The lowest adverse effects concentrations (LOAEC) range from 50 to more than 40 000 mg Pb kg^{-1} soil. The low values can be explained by the use of soluble salts or very acidic conditions. The data do not provide a good indication of what would be expected if the lead in the soils had been given the time to reach equilibrium, as we would expect at real contaminated sites.

Soil quality guidelines are intended to protect the ability of ecosystems to function properly. This means that the criteria should be set in such a way as to protect the most sensitive organism in the ecosystem. In practice there seems to be very little consideration as to whether the test organism would really be found in the soil being tested. For example, it is common to use an earthworm (*Eisenia foetida*) that lives in manure piles to test the toxicity of soils from a wide range of environments (Malecki et al., 1992). We would argue that if the purpose of the criteria is to protect the functioning of an ecosystem, then the test organisms should be either: (1) those that would be living on the site in the absence of the pollutant or (2) those living on the polluted site. The first option would protect biodiversity on the site but is very conservative - perhaps this should be our goal in terms of natural habitats and agricultural land. The second option might be a reasonable approach to the evaluation of the need for remediation on heavily polluted sites related to industry, urbanization or mining. In both cases the 'health' of the ecosystem could be judged, in part, by the ability of the organisms to successfully maintain critical ecosystem functions.

In many cases the most sensitive organism will be some species of microorganism responsible for the cycling of carbon or plant nutrients. Obviously, any rupture in nutrient cycling will lead to a rapid degradation of the site. However, having a negative effect on one microorganism may not indicate that there is a significant alteration of nutrient cycling; rather it could simply mean that one organism is being replaced by another. For example, in highly contaminated urban soils nutrient cycling seems to be taking place relatively normally: there is no exceptional build-up of organic matter and nitrogen and phosphorus are being cycled through the ecosystem.

Fundamentally we need to decide whether we are basing the criteria on the correct endpoint. Should the criteria be based on an effect on the most sensitive organism or should it be based on the ability of the ecosystem to function "normally"? Do we need to define an acceptable limit in the rates of key processes such as carbon decomposition or nitrogen and phosphorus mineralization?

One of the dangers associated with the establishment of soil quality guidelines is that they will inevitably be interpreted as acceptable limits for the amount of a pollutant that can be added to soils. On the one hand, we need to make a best estimate of the level of pollution that is unacceptable because we believe that it presents a real and immediate threat. On the other hand, we need to prevent soil pollution because we do not fully understand the long-term effects of the pollutants nor the rates at which long-distance transport by air pollution is slowly degrading all soils. One could argue that sewage sludge application to agricultural lands should only be permitted when the amounts of heavy metals being added annually are as low as would be added from the use of farmyard manure - since this is considered a normal and acceptable practice. Another way of looking at the problem would be to use a mass balance approach where the addition of heavy metal would not be allowed to exceed the amount taken up by the crop and removed from the field. This of course assumes that the levels of metals in the crop remain within acceptable limits as well. This also assumes that the manure does not contain excessive levels of pollutants due to feed additives; manure from hog operations in the Netherlands contain such high levels of copper that accumulation in the soils is a serious concern (F.A.M. de Haan, personal communication). Another approach to this problem is to establish different criteria for application of pollutants to soils than for the clean-up of already contaminated soils. According to Sheppard et al. (1992) this "reflects a demand by society for a greater margin of safety for purposeful contamination than for remediation of historic contamination".

GENERIC VERSUS SITE SPECIFIC

The cost of cleaning up lead contaminated soils poses a significant threat to the economic health of most large industrialized cities. Land surrounding most transportation corridors would also be deemed unacceptably high in lead under current guidelines. In most countries guidelines for deciding whether a soil is contaminated are based on the total concentration of all forms of the contaminant in the soil. In other words, highly soluble, reactive and toxic forms are considered to be as much a threat to the environment as insoluble, non-reactive and non-bioavailable forms. With the current state of knowledge, this is a wise and safe approach to the problem; from an economic point-of-view, it is a disaster. Clean up of severely lead contaminated sites, for most jurisdictions those containing 3 500 mg Pb kg^{-1} soil, involves the very costly procedure of removing the soil and transporting it to a landfill site. Not only is this just moving the problem but it is also a threat to the environment. Disturbing a contaminated site sends fine particles of soil (the most concentrated in the metal) into the atmosphere to be inhaled by humans and animals and spreads the dust on land and waters via aerial deposition.

Canadian Soil Quality Criteria Guidelines are based on the standard toxicity tests discussed above. Although the studies are required to contain data on soil properties such as pH, CEC, organic matter content and percent clay content, which have been shown to strongly influence metal availability, they are not taken into account when the actual numerical derivation is made. Other countries such as the Netherlands and Denmark do regard some soil properties as essential to the derivation process. Corrections are made based on the amount of organic matter and clay in the soil. Most other countries such as Germany, England and China consider only total metal concentrations in determining the need for remediation.

Table 2.1. A summary of representative data on the toxicity for lead

Species	Exposure period	Pb compound	Test substrate	Endpoint^1	Soil Pb Conc. mg kg^{-1}	Reference
Terrestrial plants						
Red Spruce *Picea Rubens*	seedings for 19 weeks	PbCl$_2$ at rates of: 0, 150, 300, 600, 1200 mg kg^{-1}	Spodosol pH 3.98	LOAEC dry root weight	160	Seiler & Paganelli 1987
				LOAEC dry shoot weight	160	
Loblolly Pine *Pinus taeda*			Aquic Hapludult fine-loamy, mixed, thermic pH 5.77	LOAEC dry root weight	1210	
				LOAEC dry shoot weight	1210	
Radish *Raphanus sativa*	from germinated seed to economic maturity (42 days)	PbCl$_2$ at rates of: 0, 100, 500, 1000, 5000 mg kg^{-1}	brown earth, loamy sand pH 5.4	LOAEC dry root weight	550	Khan & Frankland 1983
				LOAEC dry shoot weight	5050	
		PbO at rates of: 0, 1000, 5000, 10 000 mg kg^{-1}		LOAEC dry root weight	1050	
				LOAEC dry shoot weight	10 050	
Onion *Allium cepa*	germinated seedlings to maturity	Pb(NO$_3$)$_2$ at rates of: 0, 50, 100, 200, 400 mg kg^{-1}	clay loam 40% sand 24% clay pH 8.3 % O.C. 0.3	LOAEC dry matter yield	50	Dang et al. 1990
Fenugreek *Trigonella poenumgraceum*	seeds 8 weeks			LOAEC dry matter yield	400	
Tomato *Lycopersicum esculantum*	maturity	Pb(NO$_3$)$_2$ at rates of: 0, 25, 50, 100, 200, 400, 800 mg kg^{-1}	silty clay clay 40% sand 16% pH 7.45 OM 2%	LOAEC fruit dry weight yield	50	Balba et al. 1991

Table 2.1. A summary of representative data on the toxicity for lead

Species	Exposure period	Pb compound	Test substrate	Endpoint[1]	Soil Pb. Conc mg kg^{-1}	Reference
Terrestrial invertebrates						
Earthworm *Lumbricus rubellus*	12 wks	$PbCl_2$ at rates of: 0, 20, 150, 1000, 3000 mg kg^{-1}	Sandy loam soil 17% clay 8% organic matter 5.5% $CaCO_3$ pH 7.3(KCl)	LOAEC growth	3 000	Ma 1982
Earthworm *Dendrobaena rubida*	3 months	$Pb(NO_3)_2$ at rates of: 0, 100, 500 mg kg^{-1}	C horizon sand (coniferous forest soil) and cattle dung pH 4.5	LOAEC cocoon production	500	Bengtsson et al. 1986
Earthworm *Eisenia foetida*	14 day	$Pb(NO_3)_2$	EEC artificial soil 10% sphagnum peat 20% kaolinite clay 69% fine sand 1% $CaCO_3$ pH 6.0	LC_{50}	5 941	Neuhauser et al. 1985
Earthworm *Eisenia foetida*	8 wk	Pb acetate $PbCl_2$ $Pb(NO_3)_2$ $PbCO_3$ PbO $PbSO_4$	metal and horse manure mixture over screened soil	LOAEC growth	12 000 >40 000 20 000 40 000 20 000 16 000	Malecki et al. 1982
Soil microorganisms and soil processes						
Nitrification	70 day	$PbCl_2$	loamy sand pH 6.0	NOAEC EC_{50}	1000 4000	Wilke & Keuffel 1988
Denitrification	21 day	$Pb(NO_3)_2$	silty clay loam, pH 6.75	LOAEC	1000	Bollag & Barabasz 1979

1 - LOAEC= Lowest observed adverse effects concentration
NOAEC= No observed adverse effects concentration
EC_x = Effects concentration for a reduction of x%
LC_x = Lethal concentraction for x% of the population

Modified from O'Brien et al. 1994

CONCLUSION

Despite the large body of research on the toxicity of lead, the problem of establishing meaningful soil quality guidelines has not been solved. In order to develop the needed scientific data a number of recommendations can be made:

1. Studies using less soluble forms of lead that more closely mimic a real contaminated soil system are needed along with field studies on non-contaminated (benchmark) and contaminated sites.

2. Study designs that accurately represent environmental conditions (e.g., exposure period for an organism to lead - two months or one year?), toxicity studies with relevant endpoints and in situ data from organisms inhabiting areas with elevated soil lead concentrations.

3. Studies investigating toxicity and accumulation of lead that also look at the factors controlling availability such as pH, cation exchange capacity and soil organic matter content and ideally allow for the direct measurement or estimation of the activity of Pb^{2+} in the soil solution.

4. An interdisciplinary approach to the problem, integrating knowledge from biologists, soil chemists and toxicologists would allow for a more global perspective and approach.

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Chapter 3

THE PROBLEM OF PREDICTING TRACE METAL AVAILABILITY TO PLANTS USING CHEMICAL EXTRACTION METHODS

Nicola Cook and William Hendershot

ABSTRACT

Soil quality guidelines for trace metals are currently based on total soil metal concentrations. It is becoming widely accepted that the concept of bioavailability must be incorporated into soil quality guidelines since the total metal load gives an overly conservative estimation of what is an environmental threat. Determining the relationship between the total and available soil metal concentration has proven to be difficult. This paper is a critical review and synthesis of the literature dealing with predicting the availability of trace metals to plants from contaminated soils. Traditionally, metal concentrations from chemical extractions are correlated with plant tissue metal concentrations. There is little agreement among hundreds of similar studies that span three decades. There are numerous plant and methodological factors that make it difficult to obtain relevant and widely applicable results. This review indicates clearly that the methods do not work in any consistent manner for any metal, soil and/or plant system. New methods will have to be found, standardised and adopted. Extraction methods may be useful in partitioning studies to distinguish potentially available metal (in the short or long-term) from the residual. The scope of this review is limited to extractions conducted on oxic soils, contaminated with Cd, Cu, Pb and Zn, and their relationship to uptake by plants.

Key Words: bioavailability, Pb, Zn, Cu, Cd, review, chemical analysis

INTRODUCTION

The concern about trace metals is mainly due to their effect on human health. Cadmium is associated with bone and kidney diseases (Kido et al., 1992) and Pb with neurological disorders (Bhattacharya and Sarkar, 1995). Excess Cu and Zn in the diet is associated with metabolic disorders potentially resulting in death (Davies, 1995). Ingestion of soil particles is an important pathway for trace metals, especially to children (Sheppard et al., 1995). The pathways of metals to humans that cause the greatest concern, as they may expose many people, are the food chain (Pezzarossa et al., 1990) and leaching into groundwater (Evans, 1989).

Soils are sinks for trace metals. The soil particles act as scavengers for elements like Cd, Cu, Pb and Zn. Industrialization has contributed to the burden of trace metals in soils in urban areas. Metals added from the application of sewage sludge, pesticides, lime, irrigation waters and fertilizers have threatened the quality of agricultural land. Excess concentrations of these metals in urban/industrial soils may be a result of the natural chemical weathering of rocks or, more likely, anthropogenic activity. Some industries and land uses associated with urban trace metal contamination are: textile, plastic, explosives, paint and chemical manufacturing and disposal, defense works, land fill sites, oil refineries, pharmaceutical production, railway yards, service stations and scrap yards (Ross, 1994; Tiller, 1992). Although high levels of metals can be found on these sites, aerial deposition of metals is also an important source of metals in soils at some distance from the source (Pierzynski and Schwab, 1993; Haygarth and Jones, 1992).

Governments in most industrialized countries have adopted soil quality guidelines that define an acceptable **total** soil concentration of trace metals (CCME, 1991; Anonymous, 1994). Remediating soils to 'background' or natural levels is very costly with current technology and the vast areas of land involved, and in most cases, not justified. It is well established that only a small fraction of the total soil metal concentration is mobile or bioavailable (Angelone et al., 1993; Davies, 1992; Kabata-Pendias and Pendias, 1992).

In order to have scientifically defensible soil quality guidelines the concept of bioavailability must be included. Although many researchers are conducting studies to assess the bioavailable fraction using plants and soil extraction methods, after almost 30 years there is no conclusive evidence that we can predict the availability of a metal to an organism. The objective of this review is to show the range of results coming from this research and hopefully encourage researchers to find new ways to assess availability. This review looks at the numerous types of extractions used and the conditions under which they are performed, the variety of plants the data are correlated with and the wide range of results reported. The problems associated with current research practice are discussed and suggestions are provided for approaching the problem in future research.

EXTRACTION METHODS

Soil extraction methods have been used for decades, beginning with geochemists looking for ways to identify anomalies (areas in bedrock that are high in certain valuable elements) and later by soil scientists to determine nutrient deficiencies in soils so that they could be improved for plant growth (Neilsen et al., 1987; Lindsay and Norvell, 1978; Haq and Miller, 1972). Scientists started using the extraction methods to determine toxic levels of trace metals in soils and sediments when trace metal loadings to soil by human activity became a concern (Pickering, 1986).

The most common method for identifying what portion of the total metal load is potentially hazardous or bioavailable is to grow plants on contaminated soil and compare the concentrations found in plant tissue with the concentrations from various soil extractions. These extraction procedures are performed singly or sequentially.

Sequential extractions

Soil samples are subjected to sequential extractions starting with water or a weak salt solution followed by acids, bases, oxidizing agents or chelating agents. Water soluble, exchangeable, oxide bound, carbonate bound, organically bound and residual fractions are then defined and related to bioavailability. Fractionation methods are supposed to extract one 'pool' at a time. There are a variety of problems associated with these schemes, particularly that the fractions are operationally defined and they are not as specific as intended (Ure, 1996). As well, labile metal may be transformed during the sample preparation and readsorption or precipitation may occur during the procedures (Ross, 1994). The most common sequential extraction method used (Tessier et al., 1979) has not been validated (Nirel and Morel, 1990; Martin, 1987). They are not considered by many authors to be useful for the purposes of predicting plant availability (Nirel and Morel, 1990; Beckett, 1989; Pickering, 1986).

Single extractions

The same reagents used in sequential extractions are used in single extractions and are supposed to extract the same pools, but only one extraction is performed on an individual soil sample. A large number of different extracting solutions have been used to relate soil concentrations of metals to the available portion. Like the sequential extractions, metals from the weakly to strongly held are removed with increasingly aggressive chemicals. In the water soluble phase the metals exist as free ions or are complexed with organic or inorganic ligands. Generally organically complexed metals are more strongly bound. The extraction is done by shaking soil and water. Metals may also be measured in water retrieved after centrifugation of a saturated paste. The exchangeable form of metal is described as that which is easily displaced from exchange sites by salts such as KCl, KNO_3, $CaCl_2$, $MgCl_2$. The carbonate bound pool is theoretically released by acetic acid, the oxide bound by oxalic acid, sulfide bound by HCl and $H_2O_2$and residual by strong acid digestion with $HNO_3/HClO_4/HF$. DTPA (diethylenetriaminepentaacetic acid) and EDTA (ethylenediaminetetraacetic acid) are frequently used as extractors of 'available' metal, defined as the water soluble plus the easily exchangeable fraction as well as metal held on the surfaces of soil particles by stronger forces. The biggest drawback, especially with the stronger extractants is that they are not specific. Table 3.1 provides an overview of the various extractants used and the form of metal they are supposed to remove from the soil. For a comprehensive review of extractions and their effects on metal release in soils see Beckett (1989) and Pickering (1986).

Table 3.1. Extractant and operationally defined pool of metal extracted

Extractant	Pool (fraction) extracted
H_20	water soluble, free, uncomplexed,
$MgCl_2$, $CaCl_2$, Mehlich I & III, NH_4NO_3, $Ca(NO_3)_2$, NH_4Cl, $Mg(NO_3)_2$, Na_2CO_3, NH_4OAc	exchangeable
DTPA, AB-DTPA,	water soluble plus exchangeable
CH_3COOH, CH_3COONH_4	carbonate
NaOAc, HCl, EDTA	carbonate, exchangeable plus carbonate
H_2O_2, HNO_3, HCl, EDTA, NTA	organic, sulfide
HNO_3, $HClO_4$, *aqua regia*,	total minus residual
$HF/HClO_4$	residual: bound to silicate structure

One of the most commonly used methods, 0.005 M DTPA at pH 7.3, was successful at predicting Cu, Fe, Mn and Zn deficiencies in calcareous soil (Lindsay and Norvell, 1978). The authors suggest that the inclusion of the pH term in the regression equation relating extractable metal and plant uptake will make it applicable to non-calcareous soils. King and Hajjar (1990) used DTPA and showed that it is a better predictor of available Cu and Zn, to tobacco (*Nicotiana tabacum* L.) and Cd and Zn to peanut (*Arachis hypogaea* L.) compared to a Mehlich III extraction. The R^2 values for DTPA extractable Zn explaining tobacco uptake were improved (0.75 to 0.87) and for Zn in peanut (0.64 to 0.81), by adding the pH term. They did not get significant regression results for either of the two extractants for Pb for peanuts. This highlights one of the main problems of chemical extractants; they do not work for all metals and when they work for a particular metal, they do not necessarily work for every plant. Even within a species such as corn results are highly variable.

The following factors influence the results of the extraction: sample size fraction used, length of extraction, temperature, soil:solution ratio, efficiency of the mixing stage, concentration of the extractant, treatment of sample (air or oven dried, frozen), vessel used and storage of extract i.e., speed of analysis after extraction (Ure, 1996; Pickering, 1986).

Definitions of the 'available' fraction vary. In a study of pH effects on the adsorption of Cu, Pb, Ni and Zn, Harter (1983) uses 0.01 M HCl extractable as an estimation of plant available metal. Khan and Khan (1983) say that NH_4OAc extractable is the available form of Pb and Cd and compare its value to growth and nutrient concentrations of tomato (*Lycopersicum esculentum*) and eggplant (*Solanum melongena*). Dang et al. (1990) conducted a similar study on onion (*Allium cepa*) and fenugreek (*Trigonella poenumgraceum*) growth and nutrient status but used DTPA extractable Cd, Pb and Zn to represent the available portion.

FACTORS CONTROLLING AVAILABILITY

We are looking for a theory that will explain the relationship between the solid phase, the solution phase and what is taken up by a plant or other organism. Researchers have been trying to find a relationship between the metal concentration in the soil and the 'available' metal concentration by comparing uptake in plants with extractable amounts of metals in the soils.

The fundamental questions that apply are:

- What is the available form and what factors affect it?
  How do we measure/predict it?
- What controls the release of metals from the solid phase into solution? How do we measure/predict this?
- What controls the metal activity in the solution phase? How do we measure/predict it?

SOLID ?➔ SOLUTION ?➔ PLANT

Plant Factors

Plant uptake of trace metals is dependent on environmental, genetic and toxicological factors. Correlation ratios (CR) or bioconcentration factors (BCF) are often used to describe soil to plant transfer of metals. The ratio is that of the plant dry weight tissue concentration to the soil 'total' concentration (Sheppard, 1995). The concentration of metals taken up by most plants (except hyperaccumulators) is very small compared to the total. The BCF's reported for lettuce (*Latuca sativa* cv. Buttercrunch) growing in urban contaminated soil are between 0.0005 and 0.005 for Cu, 0.0007 and 0.008 for Pb and 0.02 and 0.03 for Zn (Chapter 5).

The relationship between plant uptake and extractable metal is highly plant dependent. Variation between species (see Table 3.2) and even within a family (grasses: see Taylor et al., 1993) is enormous. This reflects the varying ability of plants to tolerate and accumulate metals in their tissue (Kabata-Pendias and Pendias, 1992). Hyperaccumulator species like *Thlaspi caerulescens* can concentrate up to 21000 mg Zn kg^{-1} and 164 mg Cd kg^{-1} compared to between 10 - 50 mg Zn kg^{-1} and 0.05 - 0.1 mg Cd kg^{-1} for most plants grown on the same soil (Baker et al., 1994).

It is generally assumed that the form of metal taken up by the plant is the uncomplexed or free metal ion (M^{2+}) (Hamon, 1995). Toxic metal ions are thought to be taken up in the same way as essential micronutrients, like Cu^{2+} and Mn^{2+} (Ross, 1994). Some researchers suggest that organically complexed and even inorganically complexed metals can cross the cell membrane. Lead introduced to plants as Pb-EDTA entered plants more easily and was more mobile within the plant compared to the unchelated, free metal ion (Huang et al., 1997; Cunningham, 1997). McLaughlin et al. (1997, 1995) and Smolders et al. (1996) observed strong correlations between Cd uptake by potato and the Cd-Cl species in the soil solution, suggesting that either $CdCl^+$ was taken up, or that Cl^- facilitates diffusion of Cd^{2+} to the root. In their studies, no relationship between Cd^{2+} activity and uptake was observed.

Assuming the plant generally prefers the free metal ion there are still a number of factors that will affect our ability to make generalizations based on a particular plant. Some species and/or cultivars have adapted exclusion mechanisms (excluders) whereas others actively take up metals into their tissue (accumulators). As well, metal concentrations may vary depending on the part of the plant analysed (root, shoot or leaf). Sauvé et al. (1996) showed that radish (*Rafanus sativa* cv. Cherry Belle) leaf concentrated significantly more Cu than the bulb. In one study relating soil extractable metal to plant uptake the R^2 values were higher for carrot leaf versus carrot root (He and Singh, 1994). Similar results were found for radish (Symeonides and MacRae, 1977) and snap beans (Latterell et al., 1978). The developmental stage, growth conditions like humidity, temperature and light are also important.

Biological activity at the soil-root interface may also mediate metal uptake. Hamon et al. (1995) observed an increase in Cd and Zn complexation in a soil planted with radish (*Raphanus sativus*) compared to an unplanted soil. Organic exudates produced by active plant roots are more concentrated in the rhizosphere compared to the bulk soil and provide binding sites for metal ions (Ross, 1994). VAM (vesicular-arbuscular mycorrhizae) may also play an important role but may be dependent on the metal concentration of the soil. Schüepp et al. (1987) found that in soils with high Zn concentrations, VAM reduced the amount of Zn taken up by lettuce (*Latuca sativa* L. cv. Capitata) and corn (*Zea mays* L. cv. Jubilee) whereas in low Zn soils, plant uptake was increased. In another study, Cd and Zn in soybean (*Glycine max* L. Merr. Essex) leaf tissue was reduced in soils with high metal concentrations and increased in soils with low and moderate metal concentrations when VAM were present (Heggo et al., 1990).

Another problem with using extractable metal to predict plant metal is the time frame involved in the two distinct systems. Plants in real soils take up metals over the whole growth period (usually months) whereas the release of metals from soils during an extraction takes less than a few hours. In a real plant/soil system the soil has a long period over which it will be replenishing the soil solution with metals as the plant takes them up. Bruemmer (1986) suggests that time of contact is one of the most important factors controlling bioavailability.

Soil Factors

Some of the soil properties that influence the behaviour of metals in soils are organic matter concentration, pH, CEC, redox status, particle size distribution and bulk density and the type and number of binding sites in the solid phase. The soil solid phases that are known to control trace metal sorption in soils, in order of affinity, are organic matter (particulate and dissolved), hydrous iron oxides, Al hydroxides, clay minerals, $CaCO_3$, PO_4^{3-}, SO_4^{2-}, OH^- and silicates. The affinity for metals to adsorb on soil surfaces is related to their electronegativity as well as the level of metal in the solution. A commonly observed order of affinity of cations to negatively charged surfaces is: $Cu^{2+} > Ni^{2+} > Pb^{2+} > Zn^{2+} > Cd^{2+} > Mn^{2+} > Mg^{2+}$ (McBride, 1994).

Adsorption is the main reaction controlling metal availability, especially in the short term. It can occur within hours/days whereas precipitation reactions may take months, or more likely, years (McBride, 1992). Christensen (1984) found that 95% of added Cd was adsorbed to two Danish soils after 10 minutes and equilibrium was reached in one hour. Also, adsorption reactions are much more likely at the low solution concentrations of metals and ligands that we find most often in contaminated soils.

Unfortunately, we cannot simply calculate the sorption capacity of a soil by adding up the number of adsorption sites associated with the different solid fractions. Oxides can coat mineral and clay particles, and organic matter may coat oxides. The type of oxide present will also determine its adsorption capacity. Amorphous oxides have a much higher surface area than crystalline oxides, and will therefore be more reactive. There is often a mixture of all of these types of surfaces in a given mineral soil. The process of adsorption is time and pH dependent and somewhat governed by ionic strength (McBride, 1994). It has been shown that the adsorption of metals onto oxides is negligible below pH 5 while organic matter has a high capacity to bind under acid conditions (pH 3-5) but diminishes above pH 8. Competition between trace metal ions and the more abundant ions, like Ca^{2+}, must also to be considered (Cavallaro and McBride, 1978). The Ca^{2+} ion will be preferentially adsorbed because of its high concentrations in the soil solution compared to, for example, Cd or Pb. Even competition between trace metals can be important; in a study of 12 Danish soils, sorption of Cd was decreased in the presence of Zn (Christensen, 1987).

The potential for metals to precipitate or complex with ligands can be estimated using chemical speciation computer programs like MINTEQ or GEOCHEM. They provide information about the speciation of the soil solution. The different ligand concentrations are first determined using atomic adsorption spectroscopy, ion chromatography or colourimetric methods and entered into the database. Each ligand has an associated stability constant that the program uses to calculate the concentration of a certain complex at equilibrium. Unfortunately, the constants for many organic ligands are not known, so these programs are not necessarily able to give an accurate picture of the whole system (Evans, 1989). Also, the programs assume equilibrium conditions which may rarely be obtained in the field.

The form of metal being added to the soil will also partially govern its mobility and availability. Metals bound with phosphates, hydroxides, carbonates and organic complexes are quite stable compared to metals associated with acetates, chlorides and nitrates which are readily soluble (Santillan-Medrano and Jurinak, 1975). Metal particles deposited on soils from atmospheric fallout are usually in the form of oxides, silicates, carbonates, sulfates and sulfides. Metals associated with sewage sludge are usually organically bound (Kabata-Pendias and Pendias, 1992). In studies where metals are added as soluble salts the proportion that is bioavailable will probably be very high compared to real contaminated soils since the metals generally have not had time to react with the soils.

Clearly, there are a number of ways that a metal can bind to a soil particle (organic or inorganic) and a variety of factors that influence that behaviour. An extractant is supposed to remove metals from a certain soil fraction. The ability of the various chemicals to release metals from the complexed state is governed by the same factors that keep the metal bound to the soil. If or how a particular chemical isolates and releases metals from one particular phase is not at all clear.

Solution Factors

There is no clearly defined relationship between total dissolved metal and the free ion activity of the metal in the soil solution. The concentration of the free metal ion in a soil solution is typically very low (parts per billion). The methods for analyzing such small concentrations are generally labour intensive (anodic stripping voltametry: ASV) or costly (inductively coupled plasma mass spectroscopy: ICP-MS). There is also a confounding problem of losing the metals to storage container walls, so samples have to be analysed immediately after being sampled. For the same reason, preparation of standard solutions must be done just before analysis. Ion selective electrodes exist and work well for Cu, but not for the other metals. Obtaining a representative soil solution sample is another problem, one soil scientists have been trying to solve for more than a century. The latest methods include high speed centrifugation of a field moist sample (Gollany et al., 1997). Other methods involve displacement (Hamon, 1995; Sanders, 1986) or extraction by water. A sample that is most like the solution condition in the field is desirable so field soil solution samplers, or lysimeters, are often preferred. Even these will not produce solutions identical to that in the soil since CO_2 partial pressure will decrease as soon as the solution is sampled.

Researchers are beginning to make attempts at predicting the free metal ion concentration, or activity, based on the total metal concentration and other factors like pH and Ca^{2+} concentration. Sauvé et al. (1996) showed that relationship between Cu^{2+} (free ion) activity measured using an ion selective electrode and plant (radish, lettuce and ryegrass) uptake was highly significant. In a later study, Sauvé et al. (1997) attempted to predict Cu^{2+} activity over a range of soils and metal concentrations as a function of total metal and pH. They found a strong relationship between total Cu and total soluble Cu with no improvement to the regression with the addition of the pH term. The free cupric ion could be predicted using total soil Cu and pH. Delft Hydraulics (1997) are trying to make the same predictions using existing data sets. They propose an equation that includes the potentially available metal concentration (extracted with 0.43 M HNO_3), pH and the Ca^{2+} concentration of the soil. The results show promise, but as the equation was based and tested on the same data set it could not be considered conclusive. More work needs to be focused in this area.

It is clear that we either need to establish the relationship between total and free metal or be able to measure it directly. ICP-MS analysis, although costly, would be the most desirable way to obtain direct measurements of trace metals in soil solutions. Attempting to predict free metal activity is likely going to lead to the same problems as predicting based on extractions; too many influential variables to control. Perhaps as we obtain more data on the metal activity in a range of soils (types and metal concentrations) we will be able to apply such a predictive equation. The fundamental research still needs to be done.

RESULTS FROM THE SURVEY

Table 3.2 shows a chronological summary of representative studies linking extractable metal with metal in the plant tissue. DTPA was used most frequently and yielded confusing results. Haq and Miller (1972) obtained poor results using DTPA to explain Cd uptake in corn whereas Street et al. (1977) and Sadiq (1985) found a good relationship ($R^2 > 0.85$). For other species, the relationship between DTPA extractable Cd and Cd concentration in Little Bluestem, Black-eyed Susan (Miles and Parker, 1979), Swiss chard (Haq et al., 1980), oat grain and straw (He and Singh, 1994) was not significant. DTPA extractable Cd was well correlated ($R^2 > 0.90$) with peanut (King and Hajjar, 1990), radish, lettuce and oats (Liang and Shoenau, 1995) and only moderately correlated ($R^2 \leq 0.60$) with wheat (Lee and Zheng, 1993), carrot and spinach (He and Singh, 1994). In this last study when the pH term was added to the equation the relationship was improved for most of the plant species used. DTPA was equally inconsistent at predicting a relationship between soil Cu and uptake. In one study (Taylor et al., 1993) sorghum, oat and wheat showed a significant negative relationship with DTPA extractable Cu, i.e., the more extracted by DTPA from the soil, less was taken up by the plant. Plant Pb was predicted only 40 % of the time with R^2 values ranging from 0.28 - 0.98. Plant Zn was well predicted by the DTPA extraction. In only three out of 22 cases was the result non-significant. In two of these cases the soil pH was low, 4.3 - 4.9 (Miles and Parker, 1979) and in the other case none of the extractions worked for that particular wheat species (Taylor et al., 1993). It should be noted that in most of the studies that compared extractants, and where DTPA was significant, it was not necessarily the best predictor of availability (Haq et al., 1980; King and Hajjar, 1990; Taylor et al., 1993; Lee and Zheng, 1993; He and Singh, 1994; Lee and Zheng, 1994; Liang and Schoenau, 1995).

Like DTPA, EDTA is supposed to be a good predictor of plant available metal in soils. The studies reviewed were hard to compare because many different extractants (0.01 M, 0.05 M, pH 8.6 or 7.0 and NH_4EDTA) and plant species were used. Generally, the relationship with Cu was significant for all forms and plants (R^2 = 0.3 -0.86) with the exception of corn (Haq and Miller, 1972; Davis et al., 1979; Haq et al., 1980; Tiwari and Kumar, 1982; Sanders et al., 1986; Davies, 1991). Zinc had an average R^2 of 0.687 over all plant species tested. Too few results were available for Pb and Cd, although significant relationships were obtained for Cd in Swiss chard (Haq et al., 1980) and radish leaf and bulb (Davies, 1992).

Results for the other extractions are difficult to compare, because of the range of extractants used. Table 3.2 illustrates the problem and shows clearly that not one extractant will consistently predict any metal/plant relationship. In several studies weak salt or water extractants gave the same results as strong acids (Haq et al., 1980; Taylor et al., 1993; Lee and Zheng, 1994) putting into question the theory that the 'available' form is in the solution or on exchange sites, that can be represented by a single static extraction. It shows that plant uptake of metals is more dynamic than any single extractant can imitate.

Some researchers, also disillusioned with traditional extraction methods, are using ion exchange resins (membranes, Chelex) that may more closely mimic an active plant root and its relationship to metals in the soil. The membrane is buried in the soil near the plant root and takes up metal over the same period of time as the plant root. It also takes up a variety of metals simultaneously. The membranes are relatively inexpensive, reusable and convenient to use. Based on so few studies, it is too soon to say they work better than selective chemical extractants, but the results do look promising. Lee and Zheng (1994) found that collective plant available metal (Cd, Cu and Pb) was more strongly correlated with the resin membrane (Chelex) relative to other extractions. In an earlier study, Lee and Zheng (1993) showed that this method was better at predicting Cd availability to wheat seedlings than any of the other extractants used. Liang and Schoenau (1995) obtained good results with the membrane but not significantly better than DTPA for predicting radish, lettuce and oat metal concentrations. Their feeling is that given the relative simplicity of the method, the membrane is a better tool.

Table 3.2. Representative data relating extractable metal with plant uptake

Extractant	Plant metal relationship with extractant (R^2) $p \geq 0.05$	Plant Species	Soil pH/%OM	Metal source	Reference
2 N $MgCl_2$ 0.1 N HCl Na_2CO_3	Zn = 0.93 Zn = 0.73 Zn = 0.27	millet *Echinochloa frumentacea*	5.5 - 7.5/30-150 lb/acre	background	Stewart and Berger, 1965
0.05 M DTPA pH 7.3	Zn = 0.603 Cu = n.s.	corn shoots *Zea mays* L.	6.8/3.965	background	Haq and Miller, 1972
0.01 M EDTA pH 8.6	Zn = 0.607 Cu = n.s.				
1 N NH_4NO_3 pH 7	Cd = 0.97	radish tops *Raphanus sativus* *cv. French Breakfast*	7.95/22.8	added salts	Symeonides and McRae, 1977
	Cd = 0.75	radish roots			
DTPA	Cd = 0.96	corn seedlings *Zea mays* L.	5.7-8.25/0.3-3.7	spiked or sludged	Street et al., 1977
DTPA	Zn = 0.97 Cu = 0.28	snap beans leaf *Phaseolus vulgaris* L.cv. Tendergreen	5.3/n.a.	sludge	Latterell et al., 1978
	Zn = 0.90 Cu = 0.72 Cd = 0.52	snap beans edible			
0.05 M NH_4EDTA	Cu = 0.86	barley *Hordeum vulgare* L *cv. Julia*	5.5 - 6.5 OM=40-50 g kg-1	sludge	Davis, 1979
0.5 acetic acid	Zn = 0.71				
HNO_3	Cu = 0.88 Zn = 0.44				
0.05 M NH_4EDTA	Cu = 0.77	ryegrass *Lolium perenne* L *cv.S23*			
0.5 acetic acid	Zn = 0.67				
HNO_3	Cu = 0.79 Zn = 0.67				

*n.s.=not significant, n.a.= information not available
DTPA is 0.005 M at pH 7.3 unless otherwise specified

Extractant	R^2	Plant	pH/%OM	Metal source	Reference
DTPA	Cd = n.s. Cu = n.s. Pb = n.s. Zn = n.s.	Little Bluestem *Andropogon scoparius*	4.3-4.9	rural and urban spiked and unspiked soil	Miles and Parker, 1979
	Cd = n.s. Cu = n.s. Pb = n.s. Zn = n.s.	Balck-eyed Susan *Rudbeckia hirta*			
aquaregia	Zn = 0.31	Swiss Chard *Beta vulgaris* L. cv. Fordhook Giant	5.2-7.9/1.4-17 mean pH on 46 soil = 7.0 SD=0.9 mean OM on 46 soil = 4.8 SD=3.7	sludged/ pesticide/ dumps/smelter sites (aerial deposition also)	Haq et al., 1980
0.01M EDTA	Zn = 0.63				
0.005 M DTPA	Zn = 0.65				
0.2 M NTA	Zn = 0.64				
0.5 N CH_3COOH_4	Zn = 0.60				
1 N CH_3COONH_4	Zn = 0.81				
0.6 N $HCl+AlCl_3$	Zn = 0.53				
$(COOH)_2+(COONH_4)_2$	Zn = 0.01				
H_2O	Zn = 0.35				
aquaregia	Cd = 0.23				
0.01M EDTA	Cd = 0.34				
0.005 M DTPA	Cd = 0.34				
0.2 M NTA	Cd = 0.30				
0.5 N CH_3COOH_4	Cd = 0.29				
1 N CH_3COONH_4	Cd = 0.23				
0.6 N $HCl+AlCl_3$	Cd = n/a				
$(COOH)_2+(COONH_4)_2$	Cd = 0.56				
H_2O					
aquaregia	Cu = 0.22				
0.01M EDTA	Cu = 0.34				
0.005 M DTPA	Cu = 0.35				
0.2 M NTA	Cu = 0.35				
0.5 N CH_3COOH_4	Cu = 0.36				
1 N CH_3COONH_4	Cu = 0.29				
0.6 N $HCl+AlCl_3$	Cu = 0.34				
$(COOH)_2+(COONH_4)_2$	Cu = 0.31				
H_2O	Cu = 0.25				
25 mM NTA	Zn = 0.81 Cd = 0.80 Pb = n.s. Cu = n.s.	corn stover *Zea mays* L.			Soon et al., 1980
0.1 N HCl	Cu = 0.94	rice seedlings cv. IR-8	3.3 - 5.5/0.9-7	background	Tiwari and Kumar, 1982
0.05 M EDTA	Cu = 0.78				
0.01 M EDTA	Cu = 0.44				
NH_4OAc	Cu = 0.29				
0.1 M $NaNO_3$	Zn = 0.96 Cu = 0.74	red clover	5.7-7/n.a.	added salts	Hani and Gupta, 1985

Extractant	R^2	Plant	pH/%OM	Metal source	Reference
0.001 M DTPA	Cu = 0.58 Zn = 0.66 Cd = 0.87 Pb = 0.28	corn *Zea mays*	7.3-8.1/n.a.	added salts	Sadiq, M., 1985
DTPA	Zn = 0.77	corn earleaf *Zea mays* L.		sludge	Rappaport, 1988♦
0.25 M $MgCl_2$	Zn = 0.89	navy beans *phaseolus vulgaris*	6.42/3.3	background	Neilsen et al., 1987
EDTA pH 7.0	Zn = 0.80*(0.87) Cu = 0.61 (0.62)	ryegrass *Lolium perenne* L. cv. S24	4.6-7.8/n.a.	sewage sludge	Sanders et al., 1986
DTPA	Zn = 0.87 (0.93) Cu = 0.67 (0.67)				
0.1 M $CaCl_2$	Zn = 0.75 (0.91) Cu = 0.66 (0.75)				
♦1.0 M $MgCl_2$ 1.0 M NaOAc HNO_3+$HClO_4$ +HCl	Cd = 0.999 Cd = 0.991 Cd = 0.906	cabbage	4.3-7.0/2.76 g kg^{-1}	zinc smelter	Xian, X., 1989
1.0 M $MgCl_2$ 1.0 M NaOAc HNO_3+$HClO_4$ +HCl	Zn = 0.965 Zn = 0.974 Zn = 0.910				
1.0 M $MgCl_2$ 1.0 M NaOAc HNO_3+$HClO_4$ +HCl	Pb = 0.637 Pb = 0.702 Pb = 0.836				
DTPA	Cd = n.s. Cu = 0.59 Pb = n.s. Zn = 0.75 (0.87)	Tobacco *Nicotiana tabacum* L.	n.a./4.9-12.2 g kg^{-1}	sewage sludge	King and Hajjar, 1990
Mehlich III	Cd = n.s. Cu = n.s. Pb = n.s. Zn = n.s.				
DTPA	Cd = n.s. (0.90) Cu = n.s. Zn = 0.64 (0.81) Pb = n.s.	Peanut *Arachis hypogaea* L.			
Mehlich III	Cd = 0.84 Cu = n.s. Zn = 0.82 Pb = n.s.				

*R^2 in parentheses includes pH in the regression ♦ this is a sequential extraction

Extractant	R^2	Plant	pH/%OM	Metal source	Reference
1 M HNO3	Pb = 0.803	radish bulb *Raphanus sativus* L. CV. Webb's French Breakfast	6.0/10	garden plots - some associated with lead mining	Davies, B.E., 1991
0.05 EDTA pH 7	Pb = 0.767				
CH$_3$COOH	Pb = 0.837				
1 M NH$_4$NO$_3$	Pb = n.s.				
1 M HNO3	Zn = 0.581				
0.05 EDTA pH 7	Zn = 0.624				
CH$_3$COOH	Zn = 0.637				
1 M NH$_4$NO$_3$	Zn = 0.749				
1 M HNO3	Cu = -0.223				
0.05 EDTA pH 7	Cu = -0.116				
CH$_3$COOH	Cu = -0.184				
1 M NH$_4$NO$_3$	Cu = n.s.				
1 M HNO3	Cd = 0.703				
0.05 EDTA pH 7	Cd = 0.757				
CH$_3$COOH	Cd = 0.771				
1 M NH$_4$NO$_3$	Cd = n.s.				
1 M HNO3	Pb = 0.904	radish leaf			
0.05 EDTA pH 7	Pb = 0.879				
CH$_3$COOH	Pb = 0.856				
1 M NH$_4$NO$_3$	Pb = n.s.				
1 M HNO3	Zn = 0.623				
0.05 EDTA pH 7	Zn = 0.592				
CH$_3$COOH	Zn = 0.619				
1 M NH$_4$NO$_3$	Zn = 0.783				
1 M HNO3	Cu= 0.365				
0.05 EDTA pH 7	Cu = 0.338				
CH$_3$COOH	Cu = 0.265				
1 M NH$_4$NO$_3$	Cu = n.s.				
1 M HNO3	Cd = 0.841				
0.05 EDTA pH 7	Cd = 0.860				
CH$_3$COOH	Cd = 0.869				
1 M NH$_4$NO$_3$	Cd = n.s.				
Mehlich I	Zn = 0.92	Bermudagrass *Cynodon dactylon*	3.86-4.92/n.a.	acid mine spoil	Taylor et al., 1993
DTPA	Zn = 0.92				
0.1 N HCl	Zn = 0.91				
Mehlich I	Cu = n.s.				
DTPA	Cu = n.s.				
0.1 NHCl	Cu = n.s.				
DTPA	Pb = n.s.				
0.1 N HCl	Pb = n.s.				

Extractant	R^2	Plant	pH/%OM	Metal source	Reference
Mehlich I DTPA 0.1 N HCl	Zn = 0.96 Zn = 0.96 Zn = 0.85	Sorghum *Sorghum bicolor*	3.86-4.92/n.a.	acid mine spoil	Taylor et al., 1993 continued
Mehlich I DTPA 0.1 N HCl	Cu = -0.73 Cu = -0.74 Cu = -0.81				
Mehlich I DTPA 0.1 N HCl	Zn = 0.93 Zn = 0.97 Zn = 0.97	Oat *Avena sativa*			
Mehlich I DTPA 0.1 N HCl	Cu = -0.60 Cu = -0.62 Cu = n.s.				
DTPA 0.1 N HCl	Pb = n.s. Pb = n.s.				
Mehlich I DTPA 0.1 N HCl	Zn = 0.75 Zn = 0.79 Zn = 0.85	P. ryegrass *Lolium perenne*			
Mehlich I DTPA 0.1 N HCl	Cu = n.s. Cu = n.s. Cu = n.s.				
DTPA 0.1 N HCl	Pb = n.s. Pb = -0.58				
Mehlich I DTPA 0.1 N HCl	Zn = 0.96 Zn = 0.95 Zn = 0.96	K-13 tall fescue *Festuca arundinacea*			
Mehlich I DTPA 0.1 N HCl	Cu = n.s. Cu = n.s. Cu = n.s.				
DTPA 0.1 N HCl	Pb = n.s. Pb =0.96				
Mehlich I DTPA 0.1 N HCl	Zn = 0.90 Zn = 0.91 Zn = 0.88	triticale *X. triticosecale Wittmack*			
Mehlich I DTPA 0.1 N HCl	Cu = 0.84 Cu = 0.70 Cu = 0.79				
DTPA 0.1 N HCl	Pb = n.s. Pb = 0.65				

Extractant	R^2	Plant	pH/%OM	Metal source	Reference
Mehlich I	Zn = n.s.	W. wheat *Triticum aestivum*	3.86-4.92/n.a.	acid mine spoil	Taylor et al., 1993 continued
DTPA	Zn = n.s.				
0.1 N HCl	Zn = -0.62				
Mehlich I	Cu = -0.86				
DTPA	Cu = -0.78				
0.1 N HCl	Cu = -0.63				
DTPA	Pb = n.s.				
0.1 N HCl	Pb = n.s				
Mehlich I	Zn = 0.89	Orchardgrass *Dactylis glomerata*			
DTPA	Zn = 0.83				
0.1 N HCl	Zn = n.s.				
Mehlich I	Cu = n.s.				
DTPA	Cu = n.s.				
0.1 N HCl	Cu = n.s.				
DTPA	Pb = 0.72				
0.1 N HCl	Pb = 0.89				
0.1 M HCl	Cd = 0.59	wheat seedlings cv. Taichumg select No.2	4.3-8/1.6-5.4	industrial wastewater	Lee and Zheng, 1993
0.01 M $CaCl_2$	Cd = 0.84				
DTPA (pH 7.3)	Cd = 0.59				
DTPA (pH 5.3)	Cd = 0.61				
CHELEX	Cd = 0.97				
DTPA	Cd = 0.64 (0.81)*	carrot leaf *Daucus carota*	4.97-6.8/n.a. loamy soil	super-phosphate fertilizer	He and Singh, 1994
NH_4NO_3	Cd = 0.70 (0.70)				
DTPA	Cd = 0.48 (0.50)	carrot root			
NH_4NO_3	Cd = 0.37 (0.49)				
DTPA	Cd = 0.50 (0.89)	spinach *spinacea oleracae*			
NH_4NO_3	Cd = 0.72 (0.88)				
DTPA	Cd = n.s. (0.78)	ryegrass *Lolium multiflorum*			
NH_4NO_3	Cd = 0.77 (0.77)				
DTPA	Cd = n.s.	oat grain *Avena sativa*			
NH_4NO_3	Cd = n.s.				
DTPA	Cd = n.s. (0.42)	oat straw			
NH_4NO_3	Cd = n.s.				

*R^2 in parentheses icludes pH in the regression equation

Extractant	R^2	Plant	pH/%OM	Metal source	Reference
DTPA	Cd = 0.80 (0.90)	ryegrass *Lolium multiflorum*	4.97-6.8/n.a. sandy soil	super-phosphate fertilizer	He and Singh, 1994 continued
NH_4NO_3	Cd = 0.73 (0.82)				
DTPA	Cd = 0.66 (0.66)	oat grain *Avena sativa*			
NH_4NO_3	Cd = 0.80 (0.82)				
DTPA	Cd = 0.53 (0.53)	oat straw			
NH_4NO_3	Cd = 0.59 (0.59)				
0.1 M HCl	Cd = 0.61	wheat seedlings *Triticum vulgare* cv. Taichumg select No.2	4.3-8/1.6-5.4	industrial wastewater	Lee and Zheng, 1994
0.01 M $CaCl_2$	Cd = 0.93				
DTPA (pH 7.3)	Cd = 0.64				
DTPA (pH 5.3)	Cd = 0.63				
CHELEX	Cd = 0.86				
0.1 M HCl	Cu = 0.60				
0.01 M $CaCl_2$	Cu = 0.69				
DTPA (pH 7.3)	Cu = 0.71				
DTPA (pH 5.3)	Cu = 0.52				
CHELEX	Cu = 0.82				
0.1 M HCl	Pb = 0.98				
0.01 M $CaCl_2$	Pb = n.s.				
DTPA (pH 7.3)	Pb = 0.98				
DTPA (pH 5.3)	Pb = 0.99				
CHELEX	Pb = 0.80				
H_2O	Cd = 0.64	ryegrass *Lolium multiflorum* cv. Augusta	7.8/31 g kg^{-1}	industrial: non-ferrous metal fallout	Mench et al., 1994
0.1 N $Ca(NO_3)_2$	Cd = 0.94				
0.05 M EDTA pH 7	Cd = n.s.				
H_2O	Pb = n.s.				
0.1 N $Ca(NO_3)_2$	Pb = 0.96				
0.05 M EDTA pH 7	Pb = 0.82				
H_2O	Zn = n.s.				
0.1 N $Ca(NO_3)_2$	Zn = 0.64				
0.05 M EDTA pH 7	Zn = n.s.				
H_2O	Cd = 0.79	tobacco *Nicotiana tabacum* L. cv. PBD6			
0.1 N $Ca(NO_3)_2$	Cd = 0.95				
0.05 M EDTA pH 7	Cd = n.s.				
H_2O	Pb = n.s.				
0.1 N $Ca(NO_3)_2$	Pb = n.s.				
0.05 M EDTA pH 7	Pb = n.s.				
H_2O	Zn = n.s.				
0.1 N $Ca(NO_3)_2$	Zn = n.s.				
0.05 M EDTA pH 7	Zn =0.95				

*R^2 in parentheses icludes pH in the regression equation

Extractant	R^2	Plant	pH/%OM	Metal source	Reference
DTPA	Cd = 0.986	radish cv. Cherry Belle	8.3/3.0	background	Liang and Schoenau, 1995
MEMBRANE	Cd = 0.989				
DTPA	Pb = 0.656				
MEMBRANE	Pb = 0.670				
DTPA	Cd = 0.986	lettuce cv. Slobolt			
MEMBRANE	Cd = 0.980				
DTPA	Pb = 0.973				
MEMBRANE	Pb = 0.984				
DTPA	Cd = 0.989	oat cv. Cascade			
MEMBRANE	Cd = 0.994				
AB-DTPA	Cd = 0.771	durum wheat *Triticum turgidum* cv. durum L.	6.0-7.8/ 7-40 g kg^{-1}	sewage sludge or spiked	Krishnamurti et al., 1995
0.05 $CaCl_2$	Cd = 0.919				
1 M NH_4NO_3	Cd = 0.566				
1 M NH_4OAc	Cd = 0.827				
1 M NH_4Cl	Cd = 0.940				
1 M $MgCl_2$	Cd = 0.924				
1 M $Mg(NO_3)_2$	Cd = 0.443				

CONCLUSION

Given all the factors influencing the ability of an extractant to predict plant availability of metals, the discrepancies among results are not surprising. The metals are bound in a variety of ways to different soil components. With varying amounts of these discrete components it is seemingly impossible to create an extraction system that will isolate a particular soil fraction that would also mimic all plant roots under all possible soil conditions. Plants have their own distinct set of parameters that must be considered. Some plants have developed strategies for sequestering toxic metals rendering them harmless whereas others may be susceptible to the metal's toxic effects. The variations in uptake among plants is diverse. The choice of extraction technique and the way it is employed is also a critical factor when attempting to come up with a standard method for predicting metal availability. Sample preparation, storage of extracts and the time between extracting and analyzing the extract is also important. This said, the problems with extractions seem to be fundamental and not a matter of slight variations in technique. Resin membrane techniques may provide a better estimate of available metal as they may be better at mimicking plant root behaviour in soil. Research should be focused in this area and also in creating a data base relating free metal activity to plant uptake. Identifying complexes that are plant available is also an important step in clarifying the source of metal in soils and the mechanisms by which the metals move to and through the root .

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Linking Paragraph

The proceeding two Chapters provide the theoretical framework on which the experimental work is based. Chapters 4 through 7 consist of the experimental work.

Table 4. Soils used for the research

SOIL	LOCATION	HISTORY OF SITE	CONTAMINANT OFCONCERN	CURRENT LAND USE
1	rue Pinel - east end	agriculture then (high tension lines)	Cd, Pb, Zn	dump for snow Hydro site
2	St. Henri, rue Angers	industrial area (no point source)	Pb, Zn	dump for sale
3 & 4	Mile-End, rue Casgrain and Van Horne	dump industrial	Cu, Pb, Zn oil and grease	'réseau vert' (bike path)
5 & 6	rue Peel and Notre Dame	old repair yard	Cd, Cu, Pb, Zn and (minor oil and grease)	parking lot for sale
7	St. Henri rue Argenson	close to rail and major traffic corridors and industry (no point source)	Pb, Zn	recreation
8	St. Henri Atwater Market area	wood works industrial area	Pb, Cu	not in use
9	Morgan Arboretum	protected land	none	research recreation

Information obtained from Ville de Montréal files

Chapter 4

LINKING PLANT TISSUE CONCENTRATIONS AND SOIL COPPER POOLS IN URBAN CONTAMINATED SOILS

Sauvé, S., N. Cook, W. H. Hendershot and M. B. McBride*
Department of Natural Resource Sciences
McGill University - Macdonald Campus
Ste-Anne-de-Bellevue, QC H9X 3V9, Canada.

*Department of Soil, Crop and Atmospheric Sciences,
Cornell University, Bradfield Hall 910 Ithaca, NY, 14853

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ABSTRACT

Copper tissue concentrations of radish (*Raphanus sativa* cv. Cherry Belle), lettuce (*Lactuca sativa* cv. Buttercrunch) and ryegrass (*Lolium perenne* cv. Barmultra) grown in a greenhouse in urban contaminated soils are compared to total, soluble and free ion copper pools. The tissue concentrations of copper vary between 8.1 and 82.6 mg Cu kg^{-1} dry tissue and the total soil copper content varies between 32 and 6 406 mg Cu kg^{-1} dry soil. The linear regressions with cupric ion activity and total soil copper are both significant ($p<0.01$), but cupric ion activity yields a higher level of statistical significance in every case. The results support the hypothesis that free metal in the soil solution is a better indicator of plant metal bioavailability than either total or soluble metal.

Keywords: Bioavailability, contaminated soils, copper, ion-selective electrode, plant uptake, speciation

INTRODUCTION

Currently, soil quality criteria for trace metals are based on the total amount in the soil. This approach is excessively conservative as it does not take into account the complex interactions between metals and soils and, while it is environmentally safe it actually addresses a worst-case scenario. Most soil quality guidelines do not distinguish between the various forms of metals in the soil; insoluble, non-reactive and non-bioavailable forms are deemed as dangerous as highly soluble, reactive and toxic forms. To ensure adequate environmental protection at the most economical cost, ecotoxicological guidelines should be based on the soil metal pool that is actually posing a threat to organisms: the bioavailable portion.

Over the past 20 years, researchers have attempted to predict this "bioavailable" portion by correlating data on organism accumulation or toxicity with amounts found in various soil pools (i.e., soluble, salt exchangeable, organic-bound, oxide bound) as determined by a wide variety of extraction methods. Most of these methods, such as EDTA and DTPA extractions, grossly over estimate the available metal fraction. Also, the data derived from these studies tend to be inconsistent, making interpretations difficult (Davies, 1992). The wide variability in results suggests that some other factor(s) may be controlling the availability of the metals from the soil.

It can also be hypothesized that metal bioavailability is a function of the amount of free metal (i.e., Cu^{2+}). The speciation of soluble copper into the Cu^{2+}species can be done using various methods such as: anodic stripping voltammetry (Florence, 1986), ion-exchange resin methods (Figura and McDuffie, 1979; Holm et al., 1995) or competitive chelation (Workman and Lindsay, 1990; Sachdev et al., 1992). For copper, the cupric ion-selective electrode is specific to the free ions. It is very sensitive and is not subject to excessive interference from other metals (Gulens, 1987; Sauvé et al., 1995). Studies in aquatic from other metals (Gulens, 1987; Sauvé et al., 1995). Studies in aquatic systems have demonstrated that copper toxicity depends on the free Cu^{2+} species (Verweij et al., 1992). Since cupric ion activity controls toxicity in water, its impact in soil systems needs to be assessed.

We hypothesize that copper bioavailability in soils is controlled by the free Cu^{2+} activity in the soil solution and the soil's capacity to maintain or buffer that Cu^{2+} activity. The objective of this study is to identify the relationship between plant tissue concentration of copper vis-à-vis the soil copper pools: soil total copper content (determined by hot HNO_3 digestion), the soluble copper pool (0.01 M $CaCl_2$ extractions) and the free Cu^{2+} pool (pCu^{2+} as determined using an ion-selective electrode).

MATERIALS AND METHODS

Soil Characteristics

Soil samples were collected from the surface horizon (0.0 - 0.2 m) of eight metal contaminated sites in the city of Montréal, Québec. Historical records show no point source of contamination, although some of the sites are in close proximity to railways. Five of the eight soils have greater than 100 mg Cu kg^{-1} total copper concentrations which exceeds the acceptable amount for residential sites in Québec and Canada (CCME Subcommittee on Environmental Quality criteria for Contaminated Sites, 1991).

The soils were air dried and the fraction passing through a nylon sieve (2 mm) was then homogenised. Total metal content of the soils was determined using HNO_3 acid microwave digestion in Parr® bombs (Parr, 1989; Zehr and Fedorchak, 1991; Zehr, 1992). An inter-laboratory audit sample reported to at 23.1±0.26 mg Cu kg^{-1} dry soil. The acid digests and calcium chloride extracts were analyzed for copper on a 2380 Perkin Elmer® atomic absorption spectrophotometer with a HGA-2100 Perkin Elmer® graphite furnace. The average recovery for 3 incremental spikes was 102.7% in the HNO_3 acid digests and 99.6% in the calcium chloride extracts. The pH was measured in 0.01 M $CaCl_2$ using an Orion® 601 pH meter. The organic matter content was measured using titrimetric dichromate wet oxidation (Nelson and Sommers, 1982).

Determination of $CaCl_2$ extractable Cu and pCu^{2+}

The soils were extracted by measuring 5.00 g of soil and 10.00 mL of 0.01 M $CaCl_2$, (Aldrich® calcium chloride hydrate 99.99+%) made with reverse osmosis treated water, distilled and deionized (DD-water), into 30 mL polyethylene centrifuge tubes and mixing for 20 min on a reciprocal shaker at 250 rpm. The tubes were then centrifuged at 5000 rpm for 10 min and part of the supernatant was transferred into 20-mL polystyrene sample cups for pCu^{2+} determination. The rest was saved and analyzed for dissolved Cu. The $CaCl_2$ extractable Cu is defined as the soluble copper fraction.

The pCu^{2+} was determined using an Orion® 701 pH meter, an Orion® 94-29 cupric ion-selective electrode and an Orion® 90-02 double-junction reference electrode. The electrode is easy to use and the methodology is similar to that of pH measurements. The calibration curve was obtained using copper calibration solutions buffered with IDA (Sauvé et al., 1995).

Plant growth and tissue analysis

The experimental plants used were radish, lettuce, and perennial ryegrass. Five hundred gram sub-samples of soil were rehydrated up to field capacity and placed in 125-mm pots and then fertilized with an NPK solution (prepared with reagent grade salts) according to each plant's requirements.

Three radish seeds were planted per pot; seedlings were thinned to two after 10 days then one after 20 days. Radish bulbs were harvested after 42 days of growth (maturity). Five lettuce seeds were planted per pot and thinned to one seedling over a 4-week period. Lettuce plants were harvested after 10 weeks of growth (maturity). One quarter gram of ryegrass seed was planted in each pot. Ryegrass was harvested after 6 weeks of growth (second cutting). Soils were maintained at 25% water content throughout the experiment.

The experiment took place from June to August 1994 in a greenhouse compartment at the McGill University Phytotron (Montréal). Greenhouse temperature was maintained at approximately 20°C, relative humidity at approximately 75% and only natural light was used.

Data treatment

When needed, the concentrations in solution were transformed into activities using the extended Debye-Hückel equation (McBride, 1994). Chemical equilibrium calculations were made with MINEQL+ (Schecher and McAvoy, 1991). Statistical analyses and graphics were done using the SYSTAT software (Wilkinson, 1992a, b). The level of statistical significance is represented by * for 0.1, ** for 0.01 and *** for 0.001.

RESULTS AND DISCUSSION

The pH of the soils measured in 0.01 M $CaCl_2$ is near neutral, ranging from 6.99 to 7.62. Many of the soils contained calcareous gravel and this could explain the high pH values. The organic matter content varies according to the amount of vegetation at the sites: from 13.2 to 107.7 mg of C g^{-1}. The total copper content varies from background levels at 32 mg Cu kg^{-1} of dry soil up to contaminated levels at 640 mg Cu kg^{-1} of dry soil. The corresponding soluble Cu concentrations range from 7 to 129 μg L^{-1} and the pCu^{2+} varies from 12.22 to 7.70 (The pCu^{2+} is defined as the negative log(10) of the active molar quantity of Cu^{2+} ions, i.e., the concentration of free cupric ions corrected with the Debye-Hückel theory activity coefficient. Activities and therefore pCu^{2+} are unitless.). For comparison, Lindsay (1979) predicts an activity around 11 in a neutral-pH batch equilibrated soil. Selected soil chemical characteristics can be found in Table 4.1. The soil numbers correspond to those published earlier in Sauvé et al. (1995).

Table 4.1. Selected soil chemical characteristics

Soil	pH	Organic matter (mg of C g^{-1})	HNO_3 digestion (mg Cu kg^{-1})	$CaCl_2$ extractable (μg Cu L^{-1})	Cupric ion Activity (pCu^{2+})
1	6.99	107.7	32	7	10.63
2	7.29	21.1	58	18	10.69
3	7.41	53.4	640	74	7.70
4	7.21	53.2	488	87	8.99
5	7.57	28.4	529	100	9.14
6	7.62	31.1	424	129	9.27
7	7.59	13.2	84	27	10.73
8	7.40	27.1	60	20	10.26
Mean	7.38	41.9	289	58	10.05

The results of the plant tissue analysis are given in Table 4.2. The plant tissues can be classified in order of decreasing mean tissue copper concentrations: radish leaves > ryegrass > radish bulbs > lettuce. The higher values in radish leaves over radish bulbs are not surprising as other researchers have found that radish tends to keep toxic metals away from storage organs, translocating them to the leaf tissue (Il'in 1992). Kabata-Pendias and Pendias (1992) also discuss the ability of plants to selectively transport ions to plants tops. In most studies lettuce accumulates relatively larger amounts of metals than radish or ryegrass, which are considered less sensitive species (Davis, 1979). The results of this study differ in that the concentration of copper is lowest in the lettuce tissues. This may be due to different experimental conditions such as soil pH, plant variety or other soil/plant factors.

The copper uptake is examined using regression analysis of the tissue concentrations of copper and various soil copper pools; total (HNO_3 digestion), soluble (0.01 M $CaCl_2$ extractable) and the free copper activity (pCu^{2+}, determined by ion-selective electrode).

Table 4.2. Plant Bioaccumulation Data (mg Cu kg^{-1} of dry tissue)*

Soil	Lettuce	Radish leaf	Radish bulb	Ryegrass
1	8.1 ± 3.1	15.3 ± 1.2	18.1 ± 7.8	17.0 ± 2.8
2	9.2 ± 2.2	18.6 ± 3.0	16.1 ± 3.8	25.7 ± 6.3
3	17.9 ± 4.5	82.6 ± 17.1	27.9 ± 1.3	59.8 ± 5.2
4	12.1 ± 3.3	37.2 ± 21.9	21.1 ± 6.2	31.1 ± 13.5
5	10.9 ± 2.4	32.3 ± 8.1	25.2 ± 6.6	32.3 ± 9.4
6	12.6 ± 2.2	40.0 ± 11.1	22.8 ± 5.1	23.0 ± 9.9
7	10.2 ± 2.1	34.4 ± 9.1	19.4 ± 7.0	25.8 ± 7.7
8	10.1 ± 1.0	20.5 ± 4.9	20.1 ± 11.9	24.1± 1.7

*The mean and standard deviation of six replicate measurements are reported.

A simple regression of the tissue concentration of copper is calculated using the following equation:

$$\text{Tissue Cu Concentration} = \text{plant} + \text{Cu Pool} + \text{Cu Pool} * \text{Plant} \quad (1)$$

The copper concentration in the plant tissues is fitted to a model allowing for different mean concentrations for the different plant tissues (plant term), the effect of the Cu-pool (total, soluble or pCu^{2+}), along with the Cu-Pool*Plant interaction term. The plant term considers plant species as a class of data and allows for variations due to the different tissues. The interaction term takes into account the variations in the metal accumulated by the different plant tissues under different soil Cu concentrations. Plant species will react differently to metals in soils and therefore accumulate variable amounts of metals when submitted to similar soil metal levels.

Table 4.3 shows the statistical significance of equation 1 applied to the pCu^{2+}, the soluble Cu and the total Cu pools. It shows that the pCu^{2+}, and the total Cu regressions are significant at the 0.01 level, but the regression is not statistically significant for the soluble Cu pool. Table 4.3 also shows the statistical significance of the individual terms of equation 1. It can be seen that for the regression using total soil Cu, only the Cu-pool term is significant. In the case of pCu^{2+}, all three components of the equations are significant at the 0.001 level. The plant term illustrate the differential ability of the various tissues to accumulate copper. The Cu-pool*plant interaction term represents the difference in Cu uptake response of various plant tissues with respect to changes in the Cu pool, for example, how different plants will take up a variable proportion of a Cu-pool increase.

Not only does pCu^{2+}, give a better explanation of the variation, but the contribution of each component of the model in this case is highly significant ($p<0.001$). The pCu^{2+}, copper pool model yields a higher R^2 and, in contrast to the total Cu model, allows for different average Cu concentrations for the different plant tissues and also variations in the amount of metal taken up by the plant tissues according to the soil Cu-pool content (Cu-pool*Plant). The regressions showed that comparing the different Cu pools using the various plant tissues, the single best predictor of plant tissue concentration of copper was the free activity (pCu^{2+}), in the soil solution.

Since the model with pCu^{2+}, shows significant plant and plant*Cu-pool effects, a similar regression model (eq.2) can be applied to the tissue of each individual plant.

$$\text{Tissue Cu Concentration} = \text{Constant} + \text{Cu Pool} \qquad \textbf{(2)}$$

The resulting data are reported in Tables 4.4 and 4.5. The data for the soluble pool are not reported, since none of the regressions was significant. The R^2 for the overall regression using the total copper pool is significant in all cases ($p<0.1$ except radish bulbs $p<0.01$). The soil total Cu content term gives the same levels of significance as the overall regression. The model for the pCu^{2+} pool yields better R^2 for the regressions (higher significance) and higher levels of significance for the Cu-pool component of the model.

The regressions show that for the four kinds of plant tissues analyzed, the pCu^{2+} - pool is a better predictor of plant tissue concentration than the total Cu-pool; for each tissue type, the R^2 values have higher levels of significance and the regressions have smaller standard errors of estimate. This is even more interesting considering that the soil characteristics cover a limited span of pH and organic matter content (pH 6.99 to 7.59 and soil O.M. 13.2 to 107.7 mg C g^{-1}). Greater variations in soil pH and soil organic matter would be expected to increase the relative significance of pCu^{2+}over total Cu since, pCu^{2+} integrates the impact of pH, O.M and other soil characteristics on the fractionation and the speciation of total copper.

During the growth period of this experiment, the plant tissues accumulated an average of about 40 000 times the amount of metal present as the free Cu^{2+} species in the soil solution at any one moment. Similarly, the plant tissues accumulated an average of 2 000 times the amount of total Cu dissolved in solution. This is only possible if the free activity of Cu^{2+} ions and the soluble Cu pool in the soil solution are buffered by desorption/dissolution mechanisms. In this context the intensity/capacity concept provides a possible explanation, suggesting that while the intensity of toxicity is controlled by pCu^{2+}, the toxicity also depends on the factors controlling the buffering of that pCu^{2+}. A similar concept was observed for Fe deficiency by Bell et al. (1991) and some of the implications are also discussed in Parker et al. (1995). To test the intensity/capacity hypothesis, a capacity factor was added to the regressions in the form of a secondary Cu pool. The secondary Cu pool used was either total Cu or soluble Cu. The addition of a capacity factor did not improve the regressions for the tissue concentrations (data not reported). It is not well understood how the pCu^{2+}- pool and the soil processes controlling the buffering of Cu^{2+} ions in solution are interacting to control bioavailability. It is also possible that the pCu^{2+} in the soil solution is controlled by rapid re-equilibrium reactions which need not be considered in terms of plant uptake. Alternatively it is possible that Cu^{2+} is not the only copper species available to plants.

Table 4.3. Probability (*p*) values for individual components of the model:
tissue concentration = plant + Cu-pool + Cu-pool * Plant[a]

Cu-pool	Plant	Cu-pool	Cu-pool*plant	R2 (n=32)
pCu^{2+}	< 0.001	<0.001	<0.001	0.839^{**}
Soluble	0.476	0.053	0.553	0.496^{ns}
Total	0.451	<0.001	0.224	0.739^{**}

The level of statistical significance is represented by * for 0.1, ** for 0.01 and ns when not significant

Table 4.4. Analysis of variance for tissue concentration model:
tissue concentration = constant + total copper^{a}

Tissue Concentration (mg Cu kg^{-1})	Constant	Soil total copper concentration (mg Cu kg^{-1})	R^2 (n =8)	Standard error of estimate
Lettuce	$8.58 \pm 1.04^{***}$	$0.010 \pm 0.003^{*}$	0.613^{*}	1.87
Radish leaves	16.28 ± 8.04^{ns}	$0.065 \pm 0.021^{*}$	0.539^{*}	14.44
Radish bulbs	$17.44 \pm 1.04^{***}$	$0.013 \pm 0.003^{**}$	0.763^{**}	1.86
Ryegrass	$19.10 \pm 5.37^{*}$	$0.037 \pm 0.014^{*}$	0.449^{*}	9.63

The level of statistical significance is represented by * for 0.1, ** for 0.01 and *** for 0.001 and ns when not significant

Table 4.5. Analysis of variance for tissue concentration model:
tissue concentration = constant + cupric copper^{a}

Tissue concentration (mg Cu kg^{-1})	Constant	Cupric ion activity (pCu^{2+})	R^2(n =8)	Standard error of estimate
Lettuce	$36.01 \pm 4.30^{***}$	$-2.55 \pm 0.44^{***}$	0.847^{***}	1.27
Radish leaves	$200.6 \pm 38.2^{**}$	$-17.1 \pm 3.9^{**}$	0.759^{**}	11.3
Radish bulbs	$52.59 \pm 5.70^{***}$	$-3.23 \pm 0.59^{***}$	0.853^{***}	1.68
Ryegrass	$126.9 \pm 26.0^{**}$	$-10.0 \pm 2.67^{**}$	0.701^{**}	7.66

The level of statistical significance is represented by * for 0.1, ** for 0.01 and *** for 0.001 and ns when not significant

CONCLUSION

This study shows that the cupric ion species is a better predictor of metal accumulation by plants than either total soil content or soluble/exchangeable copper. It emphasizes the importance of chemical species in the soil solution for the evaluation of the plant uptake of metals in contaminated soils. Most current soil quality guidelines ignore the influence of chemical species in the soil solution. More research is needed to evaluate if the soil bioavailability of other metals is similar.

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Chapter 5

BIOAVAILABILITY OF TRACE METALS TO LETTUCE AND RYEGRASS FROM URBAN CONTAMINATED SOILS BEFORE AND AFTER TREATMENT: A GREENHOUSE TRIAL

Nicola Cook and William H. Hendershot

ABSTRACT

Decreasing the solubility of trace metals in soils by adding low-cost amendments is an effective way of stabilizing the metals in the soils, rendering them less bioavailable. Five contaminated soils from downtown Montreal, Quebec, Canada were used to grow lettuce and ryegrass. Low-cost treatments were added to the soil to reduce the availability of Cd, Cu, Pb and Zn to plants. The treatments used were organic matter (composted sheep manure), synthetic zeolites, phosphonic acid, phosphorous fertilizer and steel shot. Contrary to what has been shown in other studies, using the same treatments, the treatments were not effective at reducing the amount of bioavailable metal. Treatments worked only in isolated cases and sometimes increased the amount of available metal. Plant species was an important factor in terms of metal uptake. Ryegrass took up significantly more Cu and Zn than lettuce. Lettuce leaves contained about two times more Pb in its tissue than ryegrass. Lettuce also took up slightly more Cd than ryegrass. Plant Mn concentrations were significantly lower in all of the contaminated soils compared to the clean (control) soil.

Key words: Cd, Cu, Pb, Ni, Mn, Zn, P, zeolites, organic matter

INTRODUCTION

Soils contaminated with trace metals have been of concern to government regulators, research scientists and the public for decades. Industrialization has contributed to the burden of trace metals in soils in urban areas. Governments in most industrialized countries have adopted soil quality guidelines that define an acceptable total soil concentration of trace metals (CCME, 1991). Researchers have found very little evidence that would suggest that the total concentration of metal in soil is directly related to the threat to human health or the ecological health of a contaminated ecosystem. It has been observed that only a small fraction of the total soil concentration of metal is potentially dangerous. This fraction, known as the mobile or bioavailable fraction, is of concern due to the potential for leaching into groundwater and/or entering the food chain through plant uptake (Ernst, 1996; Cook and Hendershot, 1996). The bioavailability of these metals depends largely on the form, soil physico-chemical properties and the organism they are in contact with (Jones, 1991; Bahlsberg, 1989; Tyler et al., 1989; Adriano, 1986; Koeppe, 1981). Studies have also shown that trace metals found in plant tissue may be derived from atmospheric fallout (Dalenberg and Van Driel, 1990; Mosbæk et al., 1989).

If the goal in cleaning up a soil is based on total soil concentrations and therefore to reduce total soil concentrations (to background levels), the task is enormous, costly and probably not necessary. If, on the other hand, the goal is to reduce the portion of the contaminant which is available and potentially toxic, amendments to cause precipitation or sorption may be used. Soil amendments including organic matter, clays, hydrous oxides, $FeSO_4$, lime, zeolites and phosphorus have shown promising results in laboratory and some field studies (Chlopecka and Adriano, 1997; Rebedea et al., 1995; Davies et al., 1993; Mench et al., 1994; Geiger et al.,1993; Didier et al., 1993; Khattak and Page, 1992; Gworek et al., 1991; Czupyrna et al., 1989; Hertzenberg, 1983). Applicability of the laboratory results to field situations has not yet been established and work needs to be focused in this area. Using plants in greenhouse and field studies is an effective way of gauging trace metal bioavailability before and after treatments have been applied.

Many studies have been conducted that test treatments to immobilize metals in contaminated soils. Laboratory experiments that show the capacity of certain ligands to take trace metals out of solution are common. Using thermodynamic data Lindsay (1979) has shown that the presence of phosphates significantly reduces the solubility of Cd, Cu, Pb and Zn. Evans (1989) also emphasizes the importance of the phosphate ligand in precipitation reactions with trace metal cations. In particular, Cd and Pb have strong affinities for phosphate ions (McBride, 1994a). Phosphate in the form of apatite was shown to reduce the amount of bioavailable Pb to sudax (Laperche et al., 1997).

Chlopecka and Adriano (1997) reduced the concentration of Pb in maize by between 11 and 55% with lime, 16 and 60% with zeolite, 15 and 60% with apatite and between 26 and 60% with Fe-oxide. In the same study Pb was reduced by between 10 and 30% with lime, 16 and 46% with zeolite, 12 and 40% with apatite and between 14 and 50% with Fe-oxide in barley. The higher reductions are associated with higher doses of the treatments.

Zeolites, natural or synthetic alumino-silicate clay minerals, have also been studied in simple aqueous solutions and found to effectively remove Cu , Cd , Pb and Zn (Hertzenberg, 1983; Czupyrna et al., 1989). In a laboratory study, Gworek et al., (1991) showed that zeolites caused a reduction in soluble Pb, Cu, Zn and Cd of 70%, 57%, 67.5% and 61% respectively in contaminated sewage sludge. In a later pot study using soil from a contaminated site in Poland, Gworek (1992) observed a reduction in plant uptake of Pb. Reductions of up to 77% in grasses, 68% in oats, 62% in beet leaves and 83% in beet root were observed. Organic matter is known to reduce the solubility of Cd, Cu, Pb and Zn (Vangronsveld and Clijsters, 1991; Adriano, 1986) especially in the short term (McBride, 1994b). Piccolo (1989) showed that extractable Cd, Cu, Pb and Zn were reduced for several months after the addition of humic substances to an organic and a mineral soil. Residues from sheet metal polishing, known as steel shot, have been used to reduce the availability of Cd and Ni by providing an oxidized surface on which the metal can adsorb (Boisson et al., 1997; Mench et al., 1994).

The objective of the experiment was to test the ability of treatments to reduce the availability of Cd, Cu, Ni, Pb and Zn to lettuce and ryegrass grown on contaminated urban soils. The treatments were composted sheep manure, triple-super-phosphate fertilizer, synthetic zeolites (Valfor 100™), phosphonic acid (Dequest™), steel shot (supplied by M.Mench at INRA, Bordeaux, France) and a control (untreated). Plants were also grown on a clean soil so that aerial deposition of metals could be assessed.

MATERIALS AND METHODS

Soils

Soils were collected from the surface horizon (0 - 0.20 m) of five contaminated sites in Montreal, Quebec, Canada. The metals in the soils are associated with transportation corridors and decades of fallout and dumping of scrap from local industry. A clean soil from the Morgan Arboretum was also collected to use as a control. Soils were stored in polyethylene bags (to maintain field soil moisture) and, after being passed through a 2-mm nylon sieve and homogenised, were placed in the plant pots. Two kilogram sub-samples of each soil were air-dried to constant weight to determine moisture content and to use for physical and chemical analyses. Soils were analysed for available NH_4, NO_3, P and K to determine their fertility (Tran and Simard, 1993). Organic matter content (Nelson and Sommers, 1982), pH in H_2O and $CaCl_2$ (Hendershot et al., 1993a), CEC (Hendershot et al., 1993b), particle size distribution (McKeague, 1976), extractable oxides (McKeague and Day, 1993) and total carbonates (Bundy and Bremner, 1972) were determined on air-dried sub-samples. Sub-samples of soils and treatment materials were ground to 500 µm in a mullite mortar and pestle were homogenised again and then wet digested using a hot $HNO_3/HClO_4$

digestion method (Cook and Hendershot, Chapter 7) to estimate their total metal concentration. Total P, K, Mg, Ca and Zn was measured by ICP-AES (inductively coupled plasma mass spectrometry). Pb, Cd, and Cu were analysed on FAAS (flame atomic adsorption spectrometry. Standard reference samples for plant tissue (V8 and V5) (Koteles et al., 1992) and soils (NIST 2710 and ECSS 7) (NIST, 1993; Sheldrick and Wang, 1995) were run for quality control; results are presented in Tables 5.1 and 5.2.

Table 5.1. Quality control report for standard reference material (mg kg^{-1}): PLANT

	P	Mn	Zn	Pb	Cd	Ni	Cu
V8							
Mean*	1333	647	25.7	2.89	1.06	4.21	9.33
Median	1290	645	22.2	2.24	0.54	1.90	9.38
SD	130	4.64	8.39	2.97	1.01	4.41	1.42
CRV	1490	714	23.6	2.52	0.25	2.50	10.5
V5							
Mean*	1437	1860	27.4	1.56	0.63	0.00	10.2
Median	1441	1880	25.6	0.00	0.25	0.00	9.91
SD	37	62	3.66	0.31	0.07	0.00	0.92
CRV	1520	2010	27.6	2.55	0.6	2	11

*SD=standard deviation

**CRV=certified reference value

Table 5.2. Quality control report for standard reference material (mg kg^{-1}): SOIL

	Mn	Zn	Pb	Cd	Ni	Cu
ECSS 7						
Mean	886	95.1	17.8	1.30	25.3	20.6
Median	870	94.5	17.8	1.50	25.7	20.5
SD*	35	2.92	0.84	0.80	1.58	0.75
CRV**	892±33	100±6	15±2	n.a.	30±1	28±0.4
NIST 2710						
Mean	8566	6462	5444	21.2	14.6	2792
Median	8574	6449	5444	21	14.9	2757
SD	156	120	58	0.49	0.94	82
CRV RANGE	6200-9000	5200-6900	4300-7000	13-26	8.8-15	2400-3400
CRV/MED•	7700	5900	5100	20	10	2700

*SD=standard deviation, n/a = data not availabile

**CRV=certified reference value and •CRV/MED=median of the CRV

Plants and Set up

Six hundred grams (dry weight) of each soil were mixed with one of the treatments and placed in five inch pots and allowed to equilibrate for four weeks before planting. The treatments included an organic matter amendment (composted sheep manure) added at 5% by weight, synthetic zeolites (0.75 %), steel shots (1%), P fertilizer (1%) and phosphonic acid (Dequest™) (1%). All treatments were digested (Cook and Hendershot, Chapter 7) and analysed for trace metal concentrations (data not presented). Experimental plants used were lettuce (*Latuca Sativa* cv. Buttercrunch) and perennial ryegrass (*Lolium perenne* cv. Barmultra). Upon planting, the soils were fertilized with N at 47 mg kg^{-1} and K at 83 mg kg^{-1} for lettuce and N at 40 mg kg^{-1} and K at 55 mg kg^{-1} for ryegrass. Phosphorus fertilizer was not included in the dressing so that we could distinguish the effect of P as a metal binding ligand. Five lettuce seeds were planted in each pot; the plants were thinned to one over the first three weeks of the trial. Lettuce was harvested after ten weeks of growth (maturity). One gram of ryegrass seed was planted in each pot and the grass was harvested after six weeks of growth. Soils were maintained at approximately 15% water content (by weight) throughout the experiment. The experiment took place in a greenhouse compartment at the McGill University Phytotron. Greenhouse temperature was maintained at approximately 20°C, relative humidity at approximately 75% and only natural light was used.

Above ground parts of lettuce were collected and rinsed with distilled water. Ryegrass was rinsed and then cut 5 cm from the soil surface. Roots were discarded as we found no method that would satisfactorily remove fine soil particles from their surface. Plant tissue was dried to constant weight at 65°C and was then crushed by hand and homogenised. Aliquots of the plant tissue (1 g) were wet digested using hot HNO_3 and H_2O_2 (Mench et al., 1994). Twenty percent of all plant tissue samples were digested in duplicate. Solutions were analysed by ICP-AES for all elements except Cd, Cu and Pb which were analysed on GFAAS (graphite furnace atomic adsorption spectroscopy). Twenty percent of all solutions were analysed in duplicate.

Experimental Design

A fully factorial design was used for soils, plants and treatments. Six replicates of each soil/plant/treatment combination were set up in a completely randomized design (n=360) . Data from replicates of the plant tissue samples were averaged for the statistical analyses since only bulk soil data was collected (i.e., not from every pot). The data was analysed statistically using Systat software (Wilkinson, 1992). As the soils were all significantly different from each other, one-way Anovas on each soil were run for treatment effects. Bonferroni tests were used to determine significant differences among treatments and between plants.

RESULTS AND DISCUSSION

Table 5.3 (a,b and c) shows the results of soil analyses. Bioconcentration factors (BCF's) are a common way to indicate the proportion of the total soil metal concentration that is bioavailable (Sheppard, 1992). BCF's are the ratio between the plant tissue metal concentration and the soil total concentration. Table 5.4 presents BCF's that show the relative availability of metals among soils and between plant species. A greater proportion of Cd, Pb and Zn was available from the clean (9) and weakly contaminated soil (7). This may be explained by the lower pH of soil 9 and that the concentrations available were not close to what would be considered toxic; therefore exclusion or avoidance mechanisms may not have been triggered. Cadmium was the most soluble metal followed by Zn, Cu, Ni and Pb. This agrees with other findings (Ross, 1994; Sauerbeck and Rietz, 1982).

Table 5.3a. Soil properties

Soil	pH in H_2O 1:1	pH in $CaCl_2$ 1:2	CEC cmol(+)/kg	Extractable Oxides (g kg^{-1}) Mn	Fe	Al	% OC	% $CaCO_3$
3	7.77	7.44	6.97	0.27	26.5	1.51	6.67	5
4	7.91	7.53	15.2	0.32	21.2	2.03	4.85	7
5	7.79	7.43	11.5	0.21	14.4	1.91	2.27	28
6	8.06	7.67	10.5	0.11	8.67	1.05	1.66	45
7	8.02	7.62	6.59	0.11	4.36	1.01	0.72	11
9	6.1	5.82	23.1	1.08	9.41	3.18	4.65	6

Table 5.3b. Concentrations of macroelements (mg kg^{-1})*

Soil	Ca	K	Mg	Na	P
3	11900	1020	2170	855	543
4	14400	1570	3100	779	804
5	118000	2980	7940	684	1500
6	162000	4620	10500	927	1050
7	29900	1980	4760	389	650
9	7340	4450	7550	22	1670

*Texture: all soils are classified as sandy loams (SL)

Table 5.3c. Concentrations of microelements (mg kg^{-1})

Soil	Cd	Cu	Mn	Ni	Pb	Zn
3	2	2890	420	41	7110	1450
4	3	652	523	54	2840	1010
5	20	1030	529	55	1830	14500
6	4	167	462	43	424	377
7	1	28	318	21	181	101
9	1	21	706	51	31	98

Table 5.4. Bioconcentration factors* for untreated soils

Soil	Cd	Cu	Mn	Ni	Pb	Zn
Lettuce						
3	0.445	0.0005	0.035	0.026	0.0007	0.031
4	0.453	0.0049	0.026	0.022	0.0026	0.057
5	0.224	0.0054	0.036	0.032	0.0092	0.021
6	0.110	0.0122	0.033	0.017	0.0129	0.127
7	0.420	0.0440	0.058	0.047	0.0244	0.337
9	0.840	0.0320	0.168	0.015	0.0640	0.347
Ryegrass						
3	0.260	0.006	0.076	0.139	0.0002	0.053
4	0.073	0.032	0.038	0.084	0.0015	0.095
5	0.026	0.022	0.046	0.070	0.0023	0.026
6	0.030	0.089	0.062	0.080	0.0037	0.024
7	0.530	0.425	0.110	0.100	0.0082	0.658
9	0.450	0.319	0.141	0.045	0.0306	0.603

*BCF=plant tissue concentration/soil concentration

The concentrations of metals in lettuce and ryegrass are presented in Tables 5.5 and 5.6. Metal concentrations in plants grown on soil 9, the control soil, are at background levels which rules out aerial deposition as a possible source of metals in plant tissue. Plant species was an important factor in terms of metal uptake regardless of treatment. Ryegrass took up significantly more Cu (5 - 10 times more) and Zn (2 times more) than lettuce, except in soil 5 where concentrations of Zn were only slightly higher in ryegrass. Lettuce leaves contained about two times more Pb than ryegrass. Lettuce also took up slightly more Cd than ryegrass. Davis (1979) and others report that lettuce usually takes up more trace metals than ryegrass. The apparent discrepancy may be due to the following factors: different experimental conditions such as the form of the metal in the soil or the pH of the soil, the concentration of competing ions in the soil solution, the presence of mycorrhizae. Copper and Pb from anthropogenic sources have been shown to be more available than the forms occurring from the weathering of rock. Mycorrhizae has been shown to mediate trace metal availability (Heggo et al., 1990; Schüepp, 1987). Our soils were analysed for the presence of mycorrhizae, but none was observed.

Treatment Effects

For ryegrass, the few significant treatment effects observed were an increase in the metal concentration compared to the control or a reduction compared to another treatment. Treatment effects were seen for Pb and Zn in lettuce although few clear trends could be distinguished. Phosphorus fertilizer reduced Pb uptake in lettuce on soils 5 and 6 compared to the control. Lettuce Pb concentrations were reduced by all treatments for soil 5. This soil had the highest bioavailable Pb, which suggests that treatments may only be effective when in contact with the most labile species of metals. The zeolite treatment increased Zn uptake in lettuce grown on soils 6 and 7.

Soil was a more influential factor than treatments. Lettuce dry weight yield was significantly greater on the clean soil compared to all the contaminated soils. Ryegrass and lettuce Mn concentrations were significantly lower from the contaminated soils. High concentrations of Zn in soils has been associated with depressed Mn uptake, due to a Zn/Mn antagonism (McBride, 1997 unpublished data; Trocme et al., 1950).

The data for the untreated soils shows that although soil 3 has much higher concentrations of Cu and Pb than soil 5, plants grown on soil 5 took up significantly more metal than those grown on soil 3. Clearly, the availability of these metals is greater in soil 5 compared to soil 3. These results may be explained by looking at the soil properties that are known to control trace metal availability. Iron oxide concentration and organic matter content seem to be controlling the availability of metals in soil 3, whereas $CaCO_3$ may be controlling the solubility of metals in soil 5. This data suggests, that since $CaCO_3$ will only dissolve below pH 7, the plants may be acidifying the rhizosphere, causing the

$CaCO_3$ and the metals associated with it to dissolve and become more available for plant uptake.

Except for Pb in soil 5 , where all the treatments worked in reducing lettuce metal compared to the control, none of the metals in the other soils (for both plants) were made consistently less available. This may be explained by conditions of low metal availability for all soils (except 5), probably due to their high pH. If, as previously mentioned, metal uptake in lettuce is associated with dissolving $CaCO_3$-metal complexes at the root/soil interface then the ability of a treatment to reduce metal availability may be dependent upon the level of metal maintained in solution. This in turn is being controlled by many soil and plant factors including a possible rhizosphere effect. Other than lettuce grown on soil 5, which has higher than normal (Table 1.2) Cd, Pb and Zn concentrations and ryegrass which has Cu and Zn concentrations that exceed what is considered normal, the high soil concentrations are not reflected in the plant tissue data.

Although steel shot has been shown to be effective at reducing mobile Cd and Ni (Boisson et al., 1997) the use of this material in natural soils is questionable. Our results (from an acid digestion with three replicates) show that the steel shot had Cu concentrations greater than 900 mg kg^{-1} and Ni in excess of 700 mg kg^{-1}. In the short-term the oxidizing Fe should control most of the metal going into solution; in the long-term we may be adding a material that will eventually release Cu and Ni into the soil. Either way we would be increasing the total concentration of these metals.

Table 5.5. Effects of treatments on growth and metal concentration (mg kg^{-1} - dw): LETTUCE

Soil	Treatment	Mass (g)	Cd	Cu	Mn	Ni	Pb	Zn
3	None	2.73 ab	0.89 a	1.53 a	14.8 a	1.08 a	5.42 ab	45.0 a
3	Zeolite	2.38 a	0.55 a	1.75 ab	22.2 b	0.41 a	6.09 ab	61.2 a
3	O.M.	2.92 ab	0.38 a	1.97 ab	12.9 a	1.35 a	4.77 a	39.9 a
3	Steel Shot	2.31 a	0.83 a	2.65 b	21.8 b	1.36 a	7.40 b	54.3 a
3	DeQuest	2.87 ab	0.44 a	1.57 a	19.0 ab	0.56 a	5.49 ab	45.0 a
3	P fertilizer	3.27 b	0.48 a	2.59 b	14.6 a	1.52 a	4.47 a	41.9 a
4	None	2.51 a	1.36 a	3.22 a	13.9 a	1.20 a	7.47 a	57.8 abc
4	Zeolite	2.70 a	0.45 a	4.75 a	27.0 b	0.74 a	7.58 a	73.4 bc
4	O.M.	2.75 a	0.83 a	3.71 a	18.0 a	0.00 a	7.35 a	67.4 bc
4	Steel Shot	2.89 a	0.54 a	3.37 a	12.5 a	0.49 a	5.83 a	41.6 a
4	DeQuest	2.95 a	1.04 a	4.32 a	16.7 a	2.46 a	7.05 a	61.8 c
4	P fertilizer	3.08 a	0.44 a	4.49 a	15.3 a	1.38 a	5.49 a	49.5 ac
5	None	2.98 a	4.57 a	5.57 b	19.4 b	1.76 a	16.8 b	303 ab
5	Zeolite	3.62 a	4.26 a	4.60 ab	17.2 ab	1.24 a	9.36 a	331 b
5	O.M.	3.33 a	4.13 a	3.93 ab	8.2 a	0.15 a	7.55 a	268 ab
5	Steel Shot	2.82 a	3.37 a	5.28 ab	10.2 ab	0.94 a	9.05 a	252 a
5	DeQuest	3.33 a	3.03 a	2.75 a	8.5 a	1.38 a	6.94 a	267 ab
5	P fertilizer	2.99 a	3.30 a	3.22 ab	9.0 ab	1.43 a	6.82 a	253 a
6	None	2.95 a	0.44 a	2.04 a	15.7 ab	0.71 a	5.48 b	48.0 a
6	Zeolite	2.54 a	0.32 a	1.99 a	20.2 ab	0.00 a	6.49 b	61.1 b
6	O.M.	2.95 a	0.55 a	1.85 a	14.5 a	0.64 a	7.03 b	69.7 b
6	Steel Shot	3.10 a	0.27 a	1.72 a	20.2 ab	0.34 a	4.81 b	42.9 a
6	DeQuest	2.97 a	0.55 a	1.85 a	22.9 b	0.62 a	4.48 ab	44.8 a
6	P fertilizer	3.89 a	0.28 a	1.86 a	18.2 ab	0.53 a	3.70 a	40.9 a
7	None	2.69 ab	0.42 a	1.22 a	18.5 a	0.98 a	4.41 ac	33.9 a
7	Zeolite	1.70 a	0.46 a	1.44 a	27.2 bc	0.23 a	6.07 bc	48.5 b
7	O.M.	2.73 b	0.57 a	1.34 a	17.0 a	0.10 a	4.52 ac	29.5 a
7	Steel Shot	2.15 ab	0.34 a	1.11 a	19.1 ac	0.63 a	4.39 ac	29.0 a
7	DeQuest	2.38 ab	0.70 a	1.70 a	28.7 b	0.03 a	4.04 a	35.4 a
7	P fertilizer	2.88 b	0.64 a	1.52 a	17.9 a	0.00 a	4.18 a	31.7 a
9	None	4.50 bc	0.84 a	0.67 a	119 ab	0.79 a	1.97 ab	34.8 a
9	Zeolite	3.64 ab	0.79 a	1.21 bc	96.7 a	0.77 a	2.69 ab	37.0 a
9	O.M.	4.06 ab	0.96 a	0.83 ac	113 ab	0.62 a	2.18 ab	37.9 a
9	Steel Shot	2.99 a	0.48 a	0.69 a	89.2 a	0.32 a	2.76 b	34.2 a
9	DeQuest	4.67 bc	0.58 a	0.47 a	159 b	1.02 a	1.57 a	35.3 a
9	P fertilizer	5.23 c	0.84 a	0.70 a	159 b	0.80 a	1.70 ab	29.6 a

*Data is based on the mean of 6 replicates: different letters indicate significant differences at p= 0.05 level

Table 5.6.Effects of treatments on growth and metal concentration (mg kg^{-1} - dw): RYEGRASS

Soil	Treatment	Mass (g)	Cd	Cu	Mn	Ni	Pb	Zn
3	None	0.658 a	0.52 a	17.2 a	32.1 a	5.73 a	1.59 a	76.8 a
3	Zeolite	0.602 a	0.18 a	16.2 a	51.1 b	5.00 a	3.02 a	74.8 a
3	O.M.	0.637 a	0.43 a	14.2 a	33.4 a	3.84 a	1.99 a	76.6 a
3	Steel Shot	0.565 a	0.35 a	14.3 a	37.9 a	3.88 a	1.57 a	73.9 a
3	DeQuest	0.524 a	0.72 a	18.2 a	37.6 a	6.00 a	2.00 a	80.3 a
3	P fertilizer	0.584 a	0.59 a	15.7 a	34.9 a	4.76 a	1.65 a	71.0 a
4	None	0.652 a	0.22 a	21.3 b	20.0 a	4.58 a	4.50 a	96.3 a
4	Zeolite	0.837 a	0.27 a	19.0 ab	30.3 b	3.02 a	3.17 a	96.6 a
4	O.M.	0.762 a	0.23 a	14.6 a	20.0 a	2.54 a	1.98 a	76.7 a
4	Steel Shot	0.627 a	0.41 a	18.3 ab	25.3 ab	2.34 a	3.24 a	90.7 a
4	DeQuest	0.581 a	0.39 a	18.2 ab	28.5 ab	2.36 a	2.63 a	86.0 a
4	P fertilizer	0.681 a	0.18 a	18.7 ab	19.8 a	2.66 a	3.29 a	86.3 a
5	None	0.660 a	0.53 a	23.1 a	24.4 a	3.88 a	4.34 a	377 a
5	Zeolite	0.678 a	0.38 a	24.1 a	25.0 a	2.79 a	4.13 a	369 a
5	O.M.	0.601 a	0.56 a	23.1 a	17.1 a	2.22 a	3.48 a	342 a
5	Steel Shot	0.502 a	0.65 a	27.1 a	20.6 a	2.84 a	4.07 a	335 a
5	DeQuest	0.759 a	0.54 a	24.5 a	19.8 a	4.23 a	3.35 a	369 a
5	P fertilizer	0.645 a	0.60 a	23.9 a	18.9 a	3.25 a	3.71 a	371 a
6	None	0.681 a	0.12 a	15.0 a	28.9 a	3.44 a	1.61 a	90.8 a
6	Zeolite	0.587 a	0.38 ab	15.4 a	42.3 a	0.93 a	1.78 a	83.0 a
6	O.M.	0.669 a	0.15 a	13.7 a	31.2 a	1.59 a	1.44 a	78.7 a
6	Steel Shot	0.632 a	0.96 b	15.9 a	34.0 a	2.92 a	1.85 a	80.9 a
6	DeQuest	0.656 a	0.25 ab	16.1 a	43.0 a	1.75 a	3.19 a	84.6 a
6	P fertilizer	0.619 a	0.43 ab	15.4 a	30.4 a	1.63 a	1.83 a	90.5 a
7	None	0.545 a	0.53 a	11.9 a	35.2 a	2.10 a	1.49 a	66.5 a
7	Zeolite	0.325 a	0.45 a	12.8 a	35.4 a	0.68 a	1.75 a	58.6 a
7	O.M.	0.514 a	0.32 a	10.3 a	35.6 a	2.00 a	1.50 a	66.2 a
7	Steel Shot	0.471 a	0.40 a	12.6 a	39.0 ab	1.76 a	1.22 a	66.6 a
7	DeQuest	0.543 a	0.24 a	13.2 a	47.2 b	0.81 a	1.26 a	70.7 a
7	P fertilizer	0.449 a	0.15 a	13.7 a	31.3 a	2.27 a	0.91 a	70.1 a
9	None	0.619 a	0.45 a	6.7 a	99.5 b	2.32 a	0.95 a	59.1 a
9	Zeolite	0.724 a	0.17 a	5.5 a	39.3 a	1.93 a	0.78 a	44.8 a
9	O.M.	0.858 a	0.23 a	6.9 a	80.3 b	1.46 a	0.75 a	56.1 a
9	Steel Shot	0.479 a	0.36 a	5.5 a	99.8 b	2.72 a	0.44 a	51.0 a
9	DeQuest	0.531 a	0.38 a	7.5 a	142 c	2.22 a	0.84 a	52.8 a
9	P fertilizer	0.656 a	0.29 a	6.6 a	103 b	2.66 a	1.00 a	54.0 a

CONCLUSION

This work demonstrates that the total metal concentration is not controlling bioavailability and that soil and plant factors must be considered when assessing the potential threat of a contaminated soil. This study also shows that treatments that have the potential to reduce metal availability to plants do not work in the same way on all soils. Their efficiency may be related to the concentration of metal in the soil solution and other soil and plant factors. It is also clear that plant species plays an important role when trying to quantify the available or 'dangerous' portion of metals in soils.

This work also shows that although other researchers have found the same treatments to significantly reduce metal uptake in ryegrass (and other species) for example, Gworek (1991) using zeolites and Boisson et al. (1997) using steel shot, they can not be expected to work on all soil types and with all plant species. We need a better understanding of what is controlling the availability of the metals so that we may be able to choose appropriate amendments for specific soil types.

This work illustrates the need for a more fundamental understanding of the mechanisms that are controlling the solubility of trace metals in soils. It also points to an investigation of rhizosphere effects.

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Chapter 6

REDUCING THE AVAILABILITY OF CD, CU, PB, NI AND ZN IN URBAN CONTAMINATED SOILS USING LOW-COST IN-SITU TREATMENTS: A FIELD TRIAL

Nicola Cook and William Hendershot

ABSTRACT

Reducing the bioavailability of trace metal in-situ is an economical way of reducing the risk associated with urban/industrial contaminated soils. The effects of additions of zeolites, P fertilizer and organic matter amendments to reduce the availability of Cd, Cu, Pb, Ni and Zn to ryegrass (*Lolium perenne* cv. Barmultra) growing on contaminated sites in Montreal, Quebec are presented. A layer (20 cm thick) of clean soil was also used as a treatment. Only plants grown on clean soil were low in metals although elevated Cu in plant tissue was found under this treatment. Soil Cu concentrations do not explain these results which suggests that either Cu solubility is very high or Cu is being provided to the plant via aerial deposition. Over all soils, no treatments were effective at reducing bioavailability. P fertilizer was associated with an increase in uptake of Cu and Ni and a decrease in Pb uptake. Ryegrass production on the P amended plots was significantly higher than all other treatments, including the clean soil. The zeolite treatment was associated with no growth on one of the plots (5) and low growth on another plot (6). The results of this study are compared to an earlier greenhouse study where the same soil/treatment combinations were used.

Key Words: treatment, zeolites, P fertilizer, organic matter, ryegrass

INTRODUCTION

Soils contaminated with trace metals have been of concern to government regulators, research scientists and the public for decades because of their impact on human health and the environment. Industrialization has contributed to the burden of trace metals in soils in urban areas. Some industries and land uses associated with urban trace metal contamination are: airports, chemical manufacturing and disposal, electroplating and explosives industries, land fill sites, paint manufacturing, pharmaceutical production, railway yards, service stations and scrap yards (Tiller, 1992).

Governments in most industrialized countries have adopted soil quality guidelines that define an acceptable total soil concentration of trace metals (Anonymous, 1994; CCME, 1991). Researchers have found very little evidence that would suggest that the total concentration of metal in soil is directly related to the threat to human health or the ecological health of a contaminated ecosystem (Delft, 1997; Ernst, 1996). It has been observed that only a small fraction of the total soil concentration of metal is potentially dangerous. This fraction, known as the mobile or bioavailable fraction, is of concern due to the potential for leaching into groundwater and/or entering the food chain through plant uptake (Ernst, 1996; Cook and Hendershot, 1996; Pezzarossa, 1990; Evans, 1989).

Assessing bioavailability is the key to determining what portion of the total trace metal load of a soil is dangerous. It has been shown clearly that only a very small portion of the total soil metal concentration is mobile and therefore a threat (Angelone, 1993; Davies, 1992). Reducing this mobile portion by adding nontoxic, low-cost amendments is the goal of many researchers and managers of contaminated soil. Others are looking at ways of removing the metal from the soil. So far, engineering-based methods are very expensive and are therefore not viable for municipalities with vast areas of land that exceed the remediation criteria (Huang et al., 1997; Cunningham, 1997). Reducing the amount of unvegetated soil at contaminated sites to prevent wind and water erosion is another important goal. Urban/industrial soils tend to be fairly infertile (Vangrosveld et al., 1995) and do require fertilization and careful species selection to establish dense vegetation.

Clean soil placed on top of contaminated soil may seem like a clear cut and obvious solution, but studies have not yet been conducted to gauge long-term mixing effects of roots and soil fauna. To protect food crops from Cd, Cu and Zn, Van Driel et al. (1995), showed that a layer of no less than 1.6 m of clean clay soil is required. This was based on one growing season. This is also a costly solution, economically and environmentally.

In a previous experiment (Chapter 5) we applied treatments to contaminated soils from downtown Montreal, to render trace metals less available to ryegrass and lettuce. The study took place in a greenhouse compartment of the McGill University Phytotron. This study was designed to test the treatments used in the greenhouse study under field conditions, this time using only ryegrass.

There have been numerous experiments conducted under controlled greenhouse conditions that test the efficacy of soil amendments to reduce the availability of trace metals to plants (Chlopecka and Adriano, 1997; Jones et al., 1997; Rebedea et al., 1995; Mench et al., 1994; Gworek, 1992 and 1991). In a study testing synthetic zeolites and apatite, Chlopecka (1997) found that both these treatments significantly reduced the availability of Cd. Pb and Zn. The treatments also caused a pH reduction in the system, which may partially explain the lower metal solubility. Mench et al. (1994) observed a 40% reduction in Zn bioavailability to ryegrass using steel shot. Jones et al. (1997) added various forms of P to contaminated soil and observed a 40% reduction in bioavailability using H_3PO_4. However, few studies show how these experiments can be related to field situations where the system is more complex and less predictable.

Also, no long-term studies of this sort exist, although some are underway (Boisson et al., 1997; Rebedea et al., 1997). In a short-term field trial, Boisson et al. (1997) found beringite, an aluminosilicate clay, to successfully reduce the availability of Cd and Ni to corn. Rebedea et al. (1997) showed that zeolite treatments reduced the level of water soluble Cu by 60%, Pb by about 50% and Zn by 45%. They could not measure plant tissue concentrations because of fallout from a nearby copper-rod-rolling plant that was in production. We know of no studies of this type that have been conducted on urban soils. Vangrosveld et al. (1995) did rehabilitate a soil in an industrial area of Belgium. In that study the goal was to revegetate, so that suspension of metal rich soil particles was reduced. To achieve this, they applied beringite to reduce toxic metal availability. Geiger et al. (1993) showed that out of several treatments (dilution, organic matter amendment, exchanger resin and clean soil) used to reduce availability of Cd, Cu and Zn to lettuce (*Latuca sativa* L. Apollo) and cress (*Lepidium sativum* L.) , and improve germination and growth, only the replacement of the highly contaminated soil with clean soil was effective.

One objective of our study was to determine whether metals found in plants originated from the soil or air. Some researchers have found that metal in plants grown in the field or greenhouse may be a result of aerial deposition (Dalenberg and van Driel,1990; Mosbæk et al., 1989) or a combined effect of soil and atmospherically derived metal (Haygarth and Jones, 1992). The main objective of the trial was to find low-cost in-situ treatments that could be used to significantly decrease the phytoavailability of Cd, Cu, Pb, Ni and Zn in contaminated soils from downtown Montreal, Quebec. Some comparisons to the greenhouse study are made.

MATERIALS AND METHODS

Three sites were selected on which to conduct the final field trial, after the completion of a preliminary trial on five sites the previous fall. The site numbers correspond with the soil identification numbers for Chapters 4 and 5. In the preliminary trial (fall 1995) ryegrass was grown on 6 m x 6 m plots and fertilized with N and K. The plots were divided into 36, 1 m x 1 m subplots, of which the centre 40 cm x 40 cm square was harvested after six weeks of growth. Plant tissue was analysed for trace elements and it was determined that there were excess bioavailable trace metals.

In the spring of 1996 experimental sites (3, 5 and 6) that had been set up the previous fall were divided by 20 cm high, hard plastic barriers into 1 m x 1 m subplots. The barriers were installed to prevent movement of soil and treatments from adjacent subplots. Six treatments were applied to the soils to a depth of 15 cm (except the clean soil treatment which was 20 cm in depth) and allowed to equilibrate for four weeks before planting 100 g of seed per subplot. Just before planting, N was added as NH_4SO_4 at 21 mg kg^{-1} and K as KSO_4 at 50 mg kg^{-1} soil. The fertilizer was in granular form. The plots were fertilized every two weeks after that at the same rate.

The treatments used were: composted sheep manure (5% by weight), wheat shorts (residue from flour production) (5%), P fertilizer (1%), synthetic zeolites (Valfor 100™) (0.75%), clean soil (McGill Arboretum) and nothing (control). The clean soil used in this study was not the same as the clean soil used in the greenhouse study. Both came from the Morgan Arboretum, but from different sites.

Ryegrass was grown on the plots and harvested after six weeks; only the centre 40 cm x 40 cm square from each subplot was collected. The soil was kept moist as much as possible during the equilibration and growth periods.

Rainfall was sporadic at the beginning of the experiment and watering was done by hand for the first two weeks after planting. After six weeks of growth the centre 40 cm x 40 cm square was harvested.

Plant tissue was dried to constant weight at 65°F, ground by hand and digested with hot HNO_3 and H_2O_2 (Mench et al., 1994) and analysed for total Cd, Cu, Pb, Mn, Ni and Zn on FAAS or on GFAAS when concentrations of Cd and Pb were too low for the FAAS. Total P was determined colourimetrically. In all of the above analyses, 20% of the measurements were replicated. Standard reference material (SRM) V8 (Koteles et al., 1992) reported to contain 2.52 mg Cd kg^{-1}, 10.5 mg Cu kg^{-1}, 2.5 mg Ni kg^{-1}, 2.55 mg Pb kg^{-1} and 23.6 mg Zn kg^{-1} was measured at 1.1± 0.35 mg Cd kg^{-1}, 9.0± 0.66 mg Cu kg^{-1}, 2.0± 0.75 mg Ni kg^{-1}, 3.0± 0.72 mg Pb kg^{-1} and 20.0±1.56 mg Zn kg^{-1}.

Soil samples (500 g) were collected from each subplot before planting. They were air dried, ground and sieved (nylon sieve) first to 2 mm and then to the size fractions required for the various analyses. Sub-samples of treatment materials and soils were ground to 500 μm in a mullite mortar and pestle, were homogenized again and then wet digested using a hot $HNO_3/HClO_4$ digestion method (Chapter 7) to estimate their total metal concentration (data not presented). Total soil Cd, Cu, Pb, Ni and Zn were analysed on FAAS. Organic matter content (Nelson and Sommers, 1982), pH in H_2O and $CaCl_2$ (Hendershot et al. 1993a), CEC (Hendershot et al. 1993b), extractable oxides (McKeague and Day, 1993) and total carbonates (Bundy and Bremner, 1972) were determined. Soil SRM 2710 (NIST, 1993) reported to contain 21.8 mg Cd kg^{-1}, 2950 mg Cu kg^{-1}, 14.3 mg Ni kg^{-1}, 5530 mg Pb kg^{-1} and 6950 mg Zn kg^{-1} was measured at 21.5± 0.90 mg Cd kg^{-1}, 2770± 113 mg Cu kg^{-1}, 16.27±1.56 mg Ni kg^{-1}, 5090±195 mg Pb kg^{-1} and 5790±188 mg Zn kg^{-1}.

Experimental design and data treatment

Soil/treatment combinations were replicated six times in a completely randomized design. Treatment effects were determined using ANOVA tests and Bonferroni tests for significant differences on Systat software (Wilkinson, 1992).

RESULTS AND DISCUSSION

The results of selected soil characteristics are shown in Table 6.1. The effects of the treatments on dry weight yield and on metal uptake are presented in Table 6.2. The zeolite treatment was associated with no growth on soil 5 and very low growth on soil 6. The no/low growth is probably a result of Na toxicity (osmotic effect) or high pH. The zeolites are a Na based synthetic silicate mineral with a pH of 10. Reduced growth was not observed for zeolites used in the greenhouse study. The difference may be due to less water infiltration in the field, resulting in less leaching of Na from the root zone. High pH conditions would also exist, possibly making essential nutrients less available. The pH of soil is known to be one of the most influential property governing metal mobility in soils (Ross, 1994; McBride, 1994). As pH increases in the soil, metal (and cation nutrient) concentrations in the soil solution decrease.

Trace metals measured in the plants grown on clean soils were significantly lower than those grown on contaminated soils, except for Cu on soil 6. These numbers were also compared to metal levels in plants grown on clean soil in the greenhouse study to assess aerial deposition. Only Cu in the plant tissue was noticeably higher in the field study; 13 mg kg-^{1} compared to 7 mg kg^{-1} in the greenhouse. The Cu concentration of the clean soil (9) used in the greenhouse study was 20 mg kg^{-1} compared to 4 mg Cu kg^{-1} in the clean soil (C) used for the field study. The pH of the two soils is similar and would not account for the difference in Cu availability. This suggests that either the form of Cu is very mobile (soluble) in soil C or that Cu is being provided to the plant via atmospheric fallout. Sites 5 and 6 are close together whereas site 3 is on the other side of the city, several miles away. It seems unlikely that there is a Montreal wide source of aerial Cu. The data shows clearly that Cd, Pb, Ni and Zn in plants are not the result of atmospheric fallout.

Table 6.1. Soil Properties (metal concentrations in mg kg^{-1})

Soil*	pH H_2O	% OC	Cd	Cu	Pb	Ni	Zn
3	7.77	0.78	2.0	278	740	41	536
5	7.79	2.88	20	744	835	55	4070
6	8.06	3.35	4.0	119	274	43	354
C**	7.20	0.20	0.5	11.1	20.0	26	55.8

*Soils are all classified as sandy loams (SL), metal analysis based on 36 replicates
**C=Treatment 5=clean soil

No treatment effects were observed for Cd in any of the soils. Cadmium in the plant tissue from the untreated plots are within the range of what is considered acceptable for grasses (Table 1.2). Plant Cu concentrations from all the soils and Pb and Zn concentrations from soils 3 and 5 exceeded the acceptable range. Nickel in ryegrass grown on soil 6 was at the outer limit of what is considered normal.

In terms of treatments effects, no clear trends were observed except for a significantly higher dry weight yield under the P fertilizer amendment. This treatment was also associated with higher plant tissue concentrations of Cu and Ni compared to the control. Ryegrass Pb, on the other hand was significantly reduced by P on soils 3 and 5. The added P may cause precipitation of Pb in the soil and at the root resulting in better root development which may cause an increased ability to take up Cu and Ni. Also, Pb may out-compete Cu and Ni for metal uptake sites at the root, suppressing Cu and Ni uptake until P is added to complex the Pb (McBride, personal communication). Cu in the plant tissue may be a combined result of a high amount of bioavailable soil Cu and Cu from atmospheric fallout.

Table 6.2. Effect of treatments on plant mass (g) and metal concentration (mg kg^{-1})

Soil	Treatment	Mass		Cd		Cu		Ni		Pb		Zn	
3	clean soil	12.5	c	0.42	a	13.5	a	3.26	a	4.73	a	55.2	a
3	none	5.32	ab	0.38	a	25.8	b	5.15	ab	13.0	b	92.8	b
3	zeolite	2.02	a	1.38	a	25.9	b	3.35	a	15.2	b	83.7	b
3	compost	7.39	b	0.50	a	26.3	b	5.42	ab	13.5	b	108	b
3	wheat	7.99	b	0.53	a	29.7	bc	7.05	b	7.57	a	108	b
3	P fertilizer	13.5	c	0.57	a	35.2	c	10.5	c	7.06	a	97.8	b
5	clean soil	9.14	b	0.21	a	13.7	a	2.94	a	2.17	a	58.4	a
5	none	2.26	a	0.72	a	24.9	b	2.78	a	8.64	c	261	c
5	zeolite	0.00		-		-		-		-		-	
5	compost	3.31	a	0.83	a	23.8	b	2.56	a	5.55	bc	253	c
5	wheat	2.96	a	0.60	a	27.8	b	2.84	a	6.26	bc	285	c
5	P fertilizer	16.4	c	1.13	a	35.6	c	15.0	b	4.13	ab	148	b
6	clean soil	10.4	b	0.39	a	12.2	a	4.29	a	2.91	a	55.1	a
6	none	2.33	a	0.48	a	15.2	ab	2.54	a	5.32	a	59.2	ab
6	zeolite	0.54	a	0.55	a	15.4	ab	1.90	a	4.65	a	67.2	ab
6	compost	4.24	a	0.36	a	14.8	ab	2.18	a	4.98	a	64.6	ab
6	wheat	2.24	a	0.39	a	18.8	bc	3.04	a	4.09	a	75.8	b
6	P fertilizer	17.6	c	0.30	a	25.2	c	7.90	b	2.99	a	63.3	ab

Different letters indicate significant differences between treatments ($p \le 0.05$)
All data is based on 6 replicates.

CONCLUSIONS

Treatments were not effective at reducing metal availability in these soils. Differences between our results and those of other researchers using the same treatments at the same rates of application on soils of similar pH may be explained by differing experimental conditions. Speciation of metals in soils, plant cultivar or developmental stage may be important factors controlling available metal. The metals in our soils may be controlled by a less soluble phase or phases than metals in other studies. Plant factors (species) may also make the comparison of results difficult. Taylor et al. (1993) showed that even among grasses metal uptake varies considerably. For example, oat (*Avena sativa*), wheat (*Triticum aestivem*) and ryegrass (*Lolium perenne*) grown on the same contaminated soil had Pb tissue concentrations of 11.8 mg kg^{-1}, 226 mg kg^{-1} and 165 mg kg^{-1} respectively. Equilibration time may also be a factor. We allowed four weeks of equilibration of treatments with soils before planting. Other studies (Rebedea et al., 1997) used longer periods of time. Field conditions (temperature, moisture) during this period may also affect equilibration. No studies are available that have looked at the problem of choosing an appropriate equilibration time.

Phosphorus fertilizer was associated with an increase in Cu and Ni plant tissue concentrations and decrease in Pb uptake. Aerial deposition of Cu may be a factor in this study although we know of no widespread Cu source in the Montreal area. Cd, Pb, Ni and Zn in plant tissue was not a result of atmospheric fallout. It is clear from this study and the greenhouse study that the effectiveness of a treatment may depend on a variety soil, plant and environmental factors. Extrapolating results from controlled laboratory or greenhouse conditions to the field or to other soils must be done with caution. Understanding the mechanisms that control availability and exactly how treatments function in the soil is critical before any amendment can be considered a solution to the problem.

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Chapter 7

A DIGESTION METHOD FOR THE RECOVERY OF TRACE METALS IN A RANGE OF SOIL TYPES INCLUDING THOSE CONTAMINATED WITH OIL AND GREASE

Nicola Cook, Marie-Claude Turmel and William H. Hendershot

ABSTRACT

Oil and grease contaminated soils are difficult to digest using the common HNO_3/H_2O_2 digestion method. We developed a modified procedure using $HNO_3/HClO_4$ for the analysis of 'total' trace metals that can be used on all types of soils including those with oil and grease. Recovery rates of 102% 94%, 114%, 92% and 83% for Cd, Cu, Ni, Pb and Zn respectively, were obtained for standard reference material (SRM) NIST 2710 (Montana Soil). Soils with approximately 1000 mg kg^{-1} oil and grease were successfully digested and gave extract concentrations suitable for analysis by flame atomic absorption spectrometry or inductively coupled plasma - atomic emission spectrometry. Compared to the common HNO_3/H_2O_2 soil digestion method, the proposed method was as effective in removing trace metals from the soil. Variability of results using the proposed method was reduced in some cases. Particle sizes of < 100 µm did not yield significantly higher concentrations of metals in solution than those < 500 µm. The same results were obtained using 100 mL digestion tubes as 250 mL Erlenmeyer flasks.

Key Words: urban soils, extraction, total metal, inorganic, organic

INTRODUCTION

Determining the total trace element concentration of a soil is the first step in evaluating its potential health or ecological hazard. The literature dealing with contaminated soils is divided neatly into issues of organic or inorganic pollutants. This may be appropriate for contamination problems like oil spills (organic) or mine tailings (inorganic). In other situations, especially in urban soils, a mixture of contaminants at a site is likely to be found. Metals from the dumping of ash, scrap metal and leaded paint are often found with organics like oil and grease from railway activity, automotive and industrial scrap disposal. The presence of oil and grease in soils complicates the use of standard soil digestion methods to measure the 'total' soil metal concentrations, especially when metal concentrations are low. The trace metals of concern here are Cd, Cu, Pb, Ni and Zn although other metals like Al, Fe, Mn, Ca, Mg and K can be analyzed on the digests.

A standard, relatively safe, method that allows for the recovery of most of the metal (>90%) bound to the soil is required in most laboratories working with trace metal contaminated soil. The most common methods used to digest trace metal contaminated soils and sediments are concentrated HNO_3 followed by 30% H_2O_2 (Edgell, 1988; Miller and McFee, 1983) or aqua regia (Mench et. al., 1994; Agemian and Chau, 1976). Nitric acid acts as a strong oxidizer and the H_2O_2 destroys the organic matter and releases the metals bound to it. Methods using HF may recover metals that are part of the silicate structure, but are relatively dangerous for daily laboratory use and require specialized equipment (i.e., Teflon digestion vessels). Soils spiked with trace metals and digested with HF are reported to yield recoveries between 92 and 104% of the added metal (Gupta and Chen, 1975). Perchloric acid is also used to dissolve metals bound to soils. It is a strong oxidizer, dehydrator and leaching agent. All of these acids are more effective at dissolving metals when boiling (Agemian and Chau, 1976).

Other methods like spark source and isotope dilution mass spectroscopy as well as neutron and particle activation analysis may be more precise, but most laboratories are not equipped for them (Stoeppler, 1985).

A search of the literature yielded no information on how to digest soils contaminated with oil and grease to measure the trace metal concentrations. Due to the problems encountered using a modified (longer extraction time) commonly used soil digestion method (Edgell, 1988) on soils coated with oil and grease, a new method was needed. The introduction of H_2O_2 to soil partially digested by hot HNO_3 caused a violent reaction resulting in the loss of the sample from some tubes and contamination of other samples being digested. The less soil used the less of a problem this was, but then the metal concentrations in the digests were below the limit of detection by flame atomic absorption spectrometry (FAAS) or inductively coupled plasma - atomic emission spectrometry (ICP-AES). Solution concentrations higher than the detection limit of the FAAS of 0.02 mg Cd L^{-1}, 0.08 mg Cu L^{-1}, 0.19 mg Pb L^{-1}, 0.07 mg Ni L^{-1} and 0.01 mg Zn L^{-1} are required. Pretreatment with solvents may be used to break down the oil and grease in soils (Martin et al, 1990) but we fear they may remove some of the metals.

The objective of this study was to develop a standardized digestion method that can be used on a range of soil types including those contaminated with oil and grease that will yield digests that can be analyzed on FAAS or ICP-AES. Factors such as the particle size, digestion vessel, reagents, temperatures and length of extraction time were also investigated. Methods described in the literature show a variety of ways to carry out soil digestions and these factors are considered influential (Beckett, 1989; Oliver, 1973).

Homogeneity of the soil sample is the first factor to consider when doing soil digestions. Urban/industrial soils are notoriously heterogeneous due to the presence of, for example, metal fragments, Pb rich paint, chunks of pure Pb or Cu from construction materials and batteries containing Pb, Cd and Zn. Consequently, relatively large soil samples need to be ground to pass at least a 500 µm sieve.

MATERIALS AND METHODS

The soils

Soils were collected from the surface horizon (0 - 0.20 m) of five contaminated sites in Montreal, Quebec, Canada. The metals in the soils are associated with transportation corridors and decades of fallout and dumping of scrap from local industry. A clean soil from the Morgan Arboretum, Ste. Anne de Bellevue, Quebec, was also used. Two kilogram sub-samples of each soil were air-dried to constant weight, homogenized, ground using a mullite mortar and pestle to pass a 500 µm sieve, and a 100 g subsample was further ground to pass a 100 µm sieve. Sub-samples were homogenized again prior to digestion. Standard reference materials (SRM) were run for quality control (NIST, 1993; Sheldrick and Wang, 1995). Oil and grease concentrations were previously determined by the Ville de Montréal and found to contain up to approximately 1000 mg kg^{-1} (Anonymous, 1992).

The Procedure

The standard method was adapted from (Mench et al., 1994). We used 0.2 g samples of <500 µm soil and 100 mL Tecator digestion tubes. Fifteen milliliters of trace metal grade HNO_3 was added and the tubes allowed to stand overnight. The tubes were then placed in a block digestor and heated to 150 °C for 3-6 h (or until brown vapours stopped). The tubes were then removed from the block and allowed to cool before the addition of 5 mL of 30% H_2O_2. The tubes were then heated at 120 °C. Additions of 1 mL H_2O_2 were continued until the reaction (bubbling) stopped. The total digestion time was approximately 8 h.

The proposed method was adapted from several studies including Miller and McFee (1983) and Agemian and Chau (1976). We used 1.0 g samples of <500 µm or < 100 µm soil and 100 mL Tecator digestion tubes. Fifteen milliliters of trace metal grade HNO_3 was added and the tubes allowed to stand overnight. The tubes were then placed in a block digestor and heated to 120 °C; the heat was then gradually raised to 150 °C until there were no more brown fumes (3 to 6 h). If the tubes ran dry, HNO_3 was added to maintain the volume between 10-15 mL. The tubes were then removed from the block and allowed to cool before the addition of 5 mL of trace metal grade $HClO_4$. The tubes were then placed back on the block, the temperature raised gradually (over 2 hours) to 160°C. The digestion was complete when the white smoke stopped and the soil looked white with small black specks (3-6 h). The solution, especially for soils with oil and grease, was not always clear. The tubes were removed from the block, allowed to cool, and brought to volume with deionised H_2O. After 16 h the top 70 - 80 mL of solution was decanted without filtering and used for metal analysis.

To determine the effect of using different digestion vessels the proposed method was also carried out in 250 mL Erlenmeyer flasks on a hot-plate.

Since the amount of HNO_3 used in the digestion varied as a function of the length of time it took to digest the sample, and the position in the block digestor, we undertook a study of the effect of the final concentration of acid on the amount of metal measured in the digests. Standards were prepared with 5, 10, 15 and 20% HNO_3 with and without $HClO_4$. No matrix effects were observed (data not presented).

RESULTS AND DISCUSSION

Table 7.1 shows the results of the recovery tests using two different particle sizes of sample SRM-ECSS 7 (Sheldrick and Wang, 1995). There is no significant difference between the amount of metal in the extracts when using the < 500 µm or < 100 µm size sample. What is important in obtaining a representative measurement is the degree of homogeneity of the bulk sample and the sub-sample. The NIST 2710 sample is available only in the < 74 µm size, so could not be used for the particle size test. There was no significant difference in metal recovery between samples (ECSS 7) digested in the 100 mL tubes compared to the 250 mL flask; the results are shown in Table 7.2. If a block digestor is available, 40 samples can be digested simultaneously and the samples are easily brought up to volume whereas it is much more labor intensive to transfer the solutions quantitatively from the Erlenmeyer flasks to volumetric cylinders when using flasks and a hot-plate. With the latter, the amount of space available on the hotplate limits the number of samples that can be digested at one time.

Table 7.1. Concentrations in particle size fraction (values in mg kg^{-1})

Size Fraction	Cu	Ni	Pb	Zn
< 500 µm				
Mean*	21.0	26.0	17.1	98.1
SD	0.84	0.84	0.02	1.81
% Recovery	75	88	113	98
< 100 µm				
Mean	20.0	26.1	18.2	94.3
SD	0.02	0.65	0.57	0.27
% Recovery	71	87	121	94

*Based on 6 replicates

Table 7.2. Concentrations recovered using different vessels (values in mg kg^{-1})

Vessel	Cu	Ni	Pb	Zn
100 mL tube	18.0±0.83	22.0±0.85	15.0±0.44	87.2±0.90
250 mL flask	16.3±0.56	24.0±0.08	18.9±.0.64	87.9±1.09
CRV	28±0.4	30±1.0	15±2.0	100±6

*Our measured values are the mean of at least 4 replicates of ECSS #7 SRM.

The efficiency of the method on a typical, highly contaminated soil (SRM NIST 2710) is presented in Table 7.3. This soil does not contain oil or grease; no such SRM was available. These results show that the method is effective at removing Cd, Cu, Pb and Ni. We obtained better results for Zn on the ECSS 7 sample compared to the NIST sample. Differences in recovery rates may be explained by the geochemistry of the sample. The data we are comparing our results with comes from samples digested with $HNO_3/HClO_4/HF$, which is capable of destroying the silicate structure of some soil minerals that our technique would not be able to attack. Therefore we did not expect to obtain 100% recovery if the samples contained trace metals in silicate minerals.

Table 7.3. Quality Control: SRM NIST 2710 - Montana Soil (values in mg kg^{-1})

	Cd	Cu	Ni	Pb	Zn
Mean*	21.6	2790	16.3	5090	5790
SD	0.91	113	1.6	195	188
% Recovery	99	94	114	92	83
CRV**	21.8	2950	14.3	5530	6950

*Based on 10 replicates.
**CRV= certified reference value

Table 7.4 shows the results obtained using two different digestion methods on the contaminated soils from Montreal (3-7) and the clean soil (9). Soils 3-6 contain oil and grease with 3 and 4 having concentrations approximately 1000 mg kg^{-1} soil. The two methods are comparable in terms of recovery when metals are not associated with oil and grease and are not in low concentrations e.g., Cd. In many of the cases the variability was reduced using the proposed method (2), in part because 1 g of soil was used in the proposed method instead of 0.2 g.

Table 7.4. Comparison of HNO_3/H_2O_2 (1) and $HNO_3/HClO_4$ (2) methods (values in mg kg^{-1})*

Soil	Cd	Cu	Ni	Pb	Zn	Method
3	< l.d.**	2760 ± 131	29 ± 1.0	5170 ± 630	1657 ± 13	1
3	2.52 ± 0.07	3240 ± 74	37 ± 3.5	7550 ± 343	1530 ± 30	2
4	< l.d.	527 ± 37	40 ± 3.0	1650 ± 198	1030 ± 44	1
4	3.30 ± 0.03	586 ± 101	57 ± 1.8	2310 ± 61	892 ± 17	2
5	14.5 ± 0.50	1430 ± 245	33 ± 1.0	968 ± 81	11600 ± 1400	1
5	17.2 ± 0.40	1470 ± 79	53 ± 1.7	1280 ± 80	11400 ± 135	2
6	< l.d.	112 ± 8.0	20 ± 3.0	263 ± 22	387 ± 16	1
6	3.49 ± 0.01	157 ± 14.2	43 ± 2.6	395 ± 29	322 ± 8.7	2
7	< l.d.	16 ± 1.8	13 ± 2.2	73 ± 0.49	145 ± 8.1	1
7	0.50 ± 0.01	22 ± 0.01	21 ± 1.3	140 ± 4.0	155 ± 10	2
9	< l.d.	16 ± 0.67	43 ± 1.6	< l.d.	79 ± 2.5	1
9	0.5 ± 0.01	13.6 ± 0.87	47 ± 2.4	17.6 ± 0.4	84 ± 1.2	2

*Based on at least 4 replicates.
**l.d.=lower than the detection limit of ICP-AES and FAAS

CONCLUSIONS

The proposed method allows the digestion of soils contaminated with oil and grease. It is practical for routine laboratory analysis as 40 samples can be run at one time if a block digestor is available, if not the method can be carried out equally well using Erlenmeyer flasks and a hot-plate. High temperatures and long extraction times ensure complete digestion. It permits the use of 1 g of soil and so yields extract concentrations in the range required for FAAS or ICP-AES analysis. It works well on a range of soil types and metal concentrations.

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CONCLUSION

Chapter 2 is a critical evaluation of how soil quality criteria are established, using Pb as an example. Soil quality guidelines that define an acceptable total soil concentration of trace metal are overly conservative and do not reflect the real hazard of most contaminated soils. Recent studies suggest that only a small portion of the total trace metal content is bioavailable and therefore a threat to the environment. This work establishes the difficulty of assessing the environmental risk of lead in soils and the factors that control the available fraction. Toxicity data on plants and soil animals used to create guidelines indicates negative effects at concentrations ranging from 50 to over 40,000 mg Pb kg^{-1} soil. However, many of this studies used clean soil spiked with soluble lead salts and do not adequately reflect the conditions likely to be found in the field. In soils from most contaminated sites the lead can be expected to be in relatively stable, insoluble forms. Recommendations are made for the development of scientifically defensible guidelines taking into account the bioavailable pool and the representativeness of organisms used. The concepts may be applied to other metals such as Cd, Cu and Zn.

In Chapter 3 we present a comprehensive review of the literature on how the bioavailable fraction of metal in soils is being measured. Identifying the relationship between the solid and solution phase while determining which metal species is bioavailable is critical. This requires some fundamental rethinking of the methods currently used. Methods that relate extractable metal (from selective chemical extraction procedures) with plant tissue metal concentrations do not work in any consistent manner. There are many plant and methodological factors that make it impossible to obtain pertinent and widely applicable results. Using direct measurements of the free metal ion in solution or resin membranes that more closely simulate plant root-soil interactions may be more suitable to help us understand this very complex system.

The experimental work focuses on the availability of trace metals to plants. We found that Cu tissue concentrations of radish, lettuce, and ryegrass grown in urban contaminated soils are more closely related to the free ion copper pools compared to the total or $CaCl_2$ extractable fractions (Chapter 4). The results support the hypothesis that free metal in the soil solution is a better indicator of plant metal availability than either total or soluble metal and that direct measurement of the free metal ion may be a good way to estimate plant available metal. This study showed that plant species and plant parts vary in metal concentrations when grown under the same conditions on the same soil. Radish leaves took up the most Cu, even compared to radish bulbs, and that ryegrass concentrated more Cu than lettuce.

Decreasing the plant available fraction by stabilizing with low-cost amendments is an effective way of reducing the threat of trace metals in some soils. In a greenhouse study using contaminated soils from Montreal, Quebec, lettuce and ryegrass metal concentrations were measured with and without treatments (Chapter 5). The amendments, organic matter, synthetic zeolites, phosphonic acid, phosphorous fertilizer and steel shot did not reduce bioavailability of Cd, Cu, Ni, Pb and Zn. Treatments worked only in isolated cases and sometimes increased the amount of available metal. Ryegrass took up significantly more Cu and Zn than lettuce whereas lettuce contained more Pb in its tissue than ryegrass. Lettuce concentrations of Cd were slightly higher than Cd in ryegrass. This indicates clearly that plant factors are important to consider when trying to assess metal availability.

Following the experiments in the greenhouse, we applied the same approach in a field experiment (Chapter 6). Applying treatments in-situ is an economical way of reducing the risk associated with urban/industrial contaminated soils. The effects of additions of zeolites, P fertilizer and organic matter amendments to reduce the availability of Cd, Cu, Pb, Ni and Zn to ryegrass growing on contaminated sites in Montreal, Quebec, do not confirm the results of other researchers using the same amendments. Only plants grown on a 20 cm layer of clean soil were low in metals although elevated Cu in plant tissue was observed under this treatment. The form of the Cu in the clean soil may be very soluble or Cu may be provided to the plant via aerial deposition. No evidence of aerial deposition of the other metals was seen. Over all soils, no treatments were effective at reducing bioavailability. Phosphorous fertilizer was associated with an increase in uptake of Cu and Ni and a decrease in Pb uptake and a general increase in dry weight production of ryegrass.

The common (HNO_3/H_2O_2) soil digestion method was found to be very difficult to use on soils that contained oil and grease. A modified procedure for the analysis of 'total' trace metals that can be used on all types of soils including those with oil and grease was developed. Recovery rates of 102% 94%, 114%, 92% and 83% for Cd, Cu, Ni, Pb and Zn respectively, were obtained for standard reference material (NIST 2710). Soils with approximately 1000 mg kg^{-1} oil and grease were successfully digested and yielded extract concentrations suitable for analysis by FAAS or ICP-AES. Variability of results using the proposed method was reduced in some cases. Particle sizes of < 100 µm did not yield significantly higher concentrations of metals in solution than those < 500 µm nor did the solutions obtained using 100 mL digestion tubes differ from those obtained with 250 mL Erlenmeyer flasks.

FUTURE RESEARCH

A unifying theory that will explain the relationship between soil trace metal concentration and bioavailability is required in order to ascertain the true threat of trace metal contaminated soils. Research needs to focus on the identification of the species of metals that are available to plants and the factors that control uptake among different species. Much more data of direct measurements of free metal ion activity in the soil solutions must be made as part of research on plant uptake so that a better predictive model can be formulated. We also need to identify the mechanisms by which metals are released from the solid phase (sorption/desorption) and find a way of predicting that behavior. Much of this work in the past has focused on single metal systems; the interactions of several metals also needs to be understood since real contaminated soils are rarely simple systems.

ORIGINAL CONTRIBUTIONS TO KNOWLEDGE

Research into the factors controlling, and means of estimating, the bioavailability of trace metals is soils has been the focus of numerous papers during the past several decades. Despite the large effort that has been put into these studies, there does not seem to be a consensus on what is controlling bioavailability or how it can be measured. This thesis attempts to clarify the issues and provide some concrete data that can be used to test some of the hypotheses that have been put forward.

One of the significant contributions to knowledge is the examination of how soil quality guidelines are currently being formulated, and how the scientific data being used is flawed. The thesis also makes recommendations for their improvement.

A literature study elucidates the relationship between metal uptake and different forms of metal found in the soil as identified by various chemical extractants. The review shows conclusively that extraction methods do not work in predicting the availability of trace metals in any consistent manner. Two alternative approaches to the problem, based on the estimation of Me^{2+} in solution in one case, and the use of exchange resins or membranes in the other case, are suggested as being more scientifically defensible.

The greenhouse and field research projects presented here are among the first to look at the bioavailability of metals, using different plant species, from urban/industrial contaminated soils. In addition, the study compares the results of a greenhouse study and a field study where the same soil/treatment/plant combinations were used. To our knowledge this has not been done previously and clearly demonstrates that the results of greenhouse research should not be assumed to be repeated under field conditions.

Due to the problems with currently available digestion methods a new technique was developed to digest soils that are coated in oil and grease. The method will work on a wide range of soil types. The digests will have metal concentrations that can be easily analyzed on a flame atomic absorption spectrometry.