Heavy Metal Phytotoxicity in Soils

EPHC

Environment Protection & Heritage Council

This paper was presented
at the Fifth National
Workshop on the Assessment
of Site Contamination

enHEALTH

Proceedings of the Fifth National Workshop on the Assessment of Site Contamination

Editors: Langley A, Gilbey M and Kennedy B

The editors may be contacted through the NEPC Service Corporation for which contact details are provided below.

DISCLAIMER: This document has been prepared in good faith exercising due care and attention. However, no representation or warranty, express or implied, is made as to the relevance, accuracy, completeness or fitness for purpose of this document in respect of any particular user's circumstances. Users of this document should satisfy themselves concerning its application to, and where necessary seek expert advice about, their situation. The Environment Protection and Heritage Council, the National Environment Protection Council, the NEPC Service Corporation, Environment Australia or enHealth shall not be liable to the purchaser or any other person or entity with respect to liability, loss or damage caused or alleged to have been caused directly or indirectly by this publication.

Suggested policy directions and health and environment values presented in papers comprising these proceedings have not been endorsed by the Environment Protection and Heritage Council, the National Environment Protection Council, Environment Australia nor enHealth.

Further copies of these proceedings can be purchased from:

NEPC Service Corporation
Level 5, 81 Flinders Street
ADELAIDE SA 5000

Phone: (08) 8419 1200
Facsimile: (08) 8224 0912
Email: exec@ephc.gov.au

© National Environment Protection Council Service Corporation 2003

Printed version ISBN 0-642-32355-0 Electronic (web) ISBN 0-642-32371-2

This work is copyright. It has been produced by the National Environment Protection Council (NEPC). Apart from any use as permitted under the *Copyright Act 1968*, no part may be reproduced by any process without prior permission from the NEPC, available from the NEPC Service Corporation. Requests and enquiries concerning reproduction and rights should be addressed to the Executive Officer, NEPC Service Corporation, Level 5, 81 Flinders Street, ADELAIDE SA 5000.

Printed on environmentally-friendly recycled content paper.

Heavy Metal Phytotoxicity in Soils

Ravi Naidu, Danielle Oliver and Stuart McConnell
CSIRO Land and Water and EPA Victoria

1 INTRODUCTION

There are over 80,000 contaminated sites in Australia (Natusch, 1998) and many of these sites are either in the urban environment or related to former mining activities. Rehabilitation of these historically contaminated sites are regulated by both State and National guidelines on total metal(loid) concentrations. The contaminants of major concern, Cd, Cu, Zn, As and Pb arise from a number of industrial, mining and agricultural activities. Although regulatory criteria has been established with limits on environmental and human health, phytotoxic thresholds have not been listed for these metals. This may be because the reported effects of concentration vary with soil and plant type. Sheppard (1992) produced a summary of phytotoxic levels of soil As. They found that the source of As and the nature of soil type are the key factors regulating the phytotoxic effects of As in soils. Given these constraints setting the regulatory criteria for other heavy metals such as Cd, Cu, Pb and Zn may not be simple. This paper presents an overview of the current state of knowledge on heavy metal phytotoxicity to plants with particular emphasis on the Australian environment.

2 DEFINITION

The term *phytotoxicity* has normally been associated with phenomenon whereby a potentially harmful substance has accumulated in the plant tissue to a level affecting optimal growth and the development of the plant (Beckett and Davis, 1977). Such a definition is not adequate for developing the phytotoxicity standards because plants that experience varying degrees of phytotoxicity exhibit a variety of symptoms during the course of growth, and differing levels of injury can result. However, retardation of plant-growth may not be limited to accumulation of toxic substances since environmental factors associated with growing plants such as nutrient deficiencies, water, salt stress, root diseases, other chemical exposure produce similar visual symptoms and also result in yield depression (Bould *et al*., 1984). Positive confirmation of an incidence of metal toxicity requires that (Chang *et al*., 1992):

- Plants have sustained injuries;
- A potentially phytotoxic metal has accumulated in the plant tissue;
- The observed abnormalities are not due to other disorders of plant growth; and
- The biochemical mechanisms that cause metal toxicity to be harmful to plants are observed during the course of growth.

The major limitation of the use of the above 4 criterion is the lack of reliable information in the literature on metal phytotoxicity. The most limiting of the current set of data is the short duration of growth studies where metal treatments are not equilibrated sufficiently to reflect long-term contaminated sites. Moreover, many data sets currently available are based on solution culture studies, which at best give a very crude estimate of metal phytotoxicity.

3 CURRENT GUIDELINES ARE BASED ON TOTAL METAL CONCENTRATIONS AND ARE INADEQUATE

The National Environment Protection (Assessment of Site Contamination) Measure 1999 establishes interim urban ecological investigation levels. These are total metal concentrations derived using professional judgement to interpret and apply information from a range of sources including published data on background metal concentrations and provisional phytotoxicity-based levels published by the NSW EPA (NSW EPA, 1998).

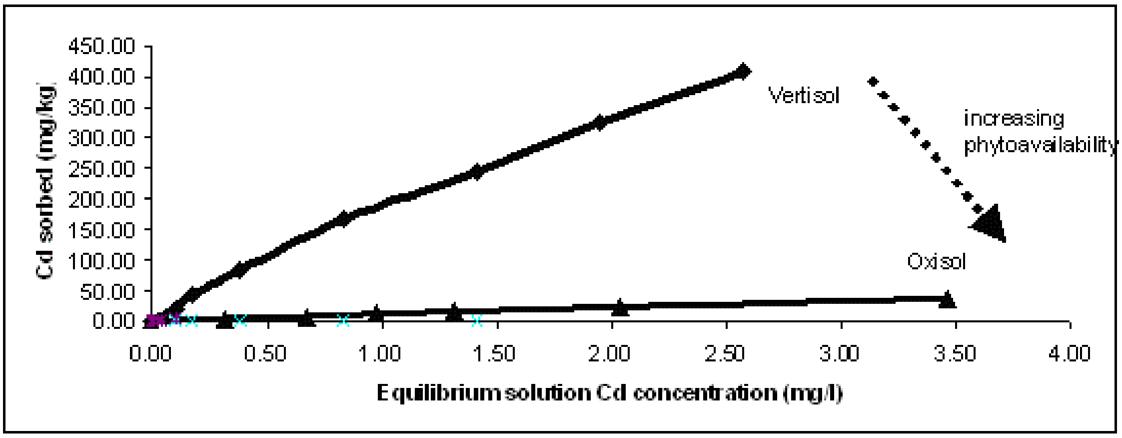
The provisional phytotoxicity-based levels published by NSW EPA are the only published guideline values for soils in Australia that are based explicitly on the protection of plant-life. These values were based on a review of published phytotoxicity information for a range of metals. However, the levels are, as with other guideline values, specified in terms of total metal concentrations. The values are also presented only for sandy loam and similar soil types with pH in the range 6 to 8.

It is therefore possible that, depending on the specific conditions, soil type etc., significantly higher metal concentrations can be tolerated in some cases without appreciable risk of detriment to plant life. This is consistent with other approaches for the derivation and application of investigation levels.

4 MANY SOIL AND ENVIRONMENTAL FACTORS INFLUENCE METAL PHYTOAVAILABILITY

Metal interactions in soils vary considerably with the nature of soil types. The phytoavailability of metals is determined by the nature of the metal species, their interaction with soil colloids, the soil characteristics and duration of contact with the surface binding these metals. Soil characteristics (eg. soil pH, clay, organic matter content and type, and moisture content) also determine availability to plants by controlling the speciation of the elements, temporary binding by particle surfaces (adsorption-desorption processes), precipitation reactions and availability in soil solution. Both the concentration of trace metals and their speciation vary significantly with the composition of soil solution and the amount of moisture present in the soils (Fotovat *et al.*, 1997). As shown in Figure 1, the amount of Cd retained by Oxisols commonly found in northern Australia at natural soil pH values (5 to 6) is significantly less than that retained by Vertisol (pH 6 to 7) a soil type common to southern Australia. At any given total metal concentration the phytoavailable metal fraction is higher in Oxisols relative to Vertisols unless the pH of the Oxisols are increased (to >6) to enhance their binding capacity. This indicates that plants growing in different soils with the same total metal concentration may vary in their phytotoxic response due to the differences between soils in their sorptive capacity. The different amount of metals retained by different soil types may be attributed to the different clay content and mineral composition of the soils, their pH, organic matter content and soil solution composition which is the medium of reaction in soils.

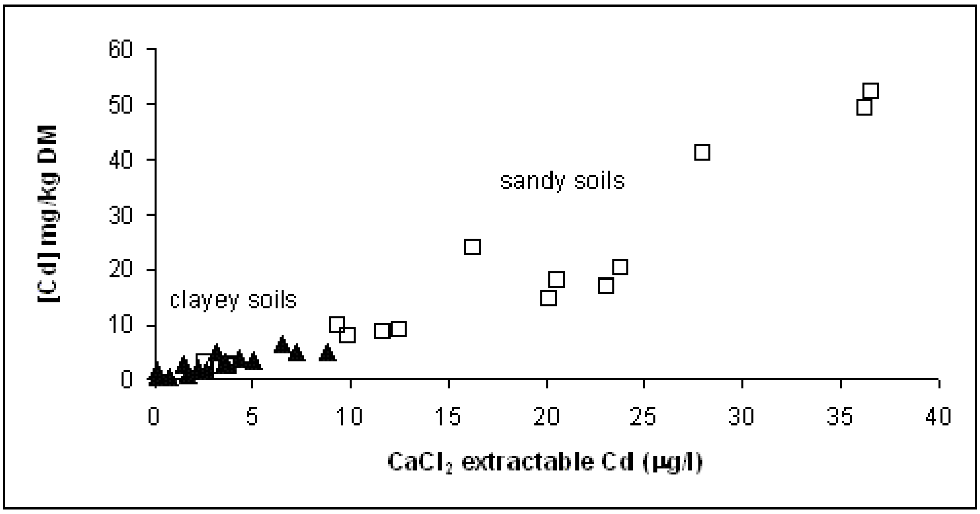
Figure 1. Metal binding capacity varies with soil type (R Naidu, unpublished)



5 REPLENISHMENT CAPACITY OF SOIL INTERSTITIAL WATER

Chemicals present in the interstitial water are defined as the most readily available fraction in the terrestrial ecosystem. As chemicals from this pool are utilised by living organisms or leached by physical gravitational forces, the capacity of soils to replenish this pool dictates chemical bioavailability. Our study shows that the replenishment factor is controlled by clay content, mineral and organic matter composition, partition coefficient and the chemical saturation index. In soils with high reaction capacity (high clay content soils) but low saturation index (ie binding sites are unsaturated with respect to metals), the phytoavailable fraction is low. Limited studies using spinach, which has the capacity for significant metal uptake, shows metal uptake is much higher in low sorbing sandy soils compared to high sorbing clayey soils, although both soils had similar total metal content (Figure 2). A similar growth study conducted by Verloo *et al*. (1996) showed that the phytotoxicity of Zn and Cd to maize varied with soil type. They observed that the availability of these metals was very low in clay soils relative to sandy soils and that clayey soils had a higher critical metal level compared to sandy soil. However, caution must be exercised with such conclusions as metal phytoavailability may vary with soil pH where decreasing pH decreases the binding capacity of metals and also with plant type. Further studies on metal uptake by plants with varying soil and plant type is in progress in our laboratory.

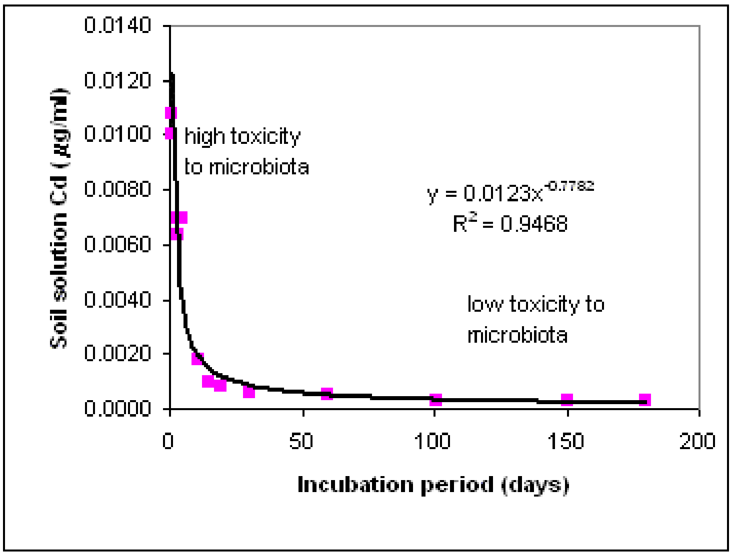
Figure 2. Metal Cd uptake by spinach in soils with varying clay content (R Naidu, unpublished)



6 METAL PHYTOAVAILABILITY MAY ALSO VARY WITH THE DURATION OF CONTAMINATION.

Long-term incubations of contaminant spiked soils, simulating field conditions, showed an exponential decline in contaminant bioavailability with aging (figure 3). The partition coefficient of contaminants increased with aging and this seemed to have a direct impact on chemical toxicity to plants, microorganisms and earthworms. The reduced toxicity of contaminants (As, Cr) to earthworms was attributed to increased binding of chemicals to soil colloids with ageing and consequent decrease in the bioavailable fraction in soil interstitial water. These results demonstrate the critical role that metal bioavailability may play in dictating the effectiveness of strategies devised for rehabilitating contaminated sites both in the short and long term.

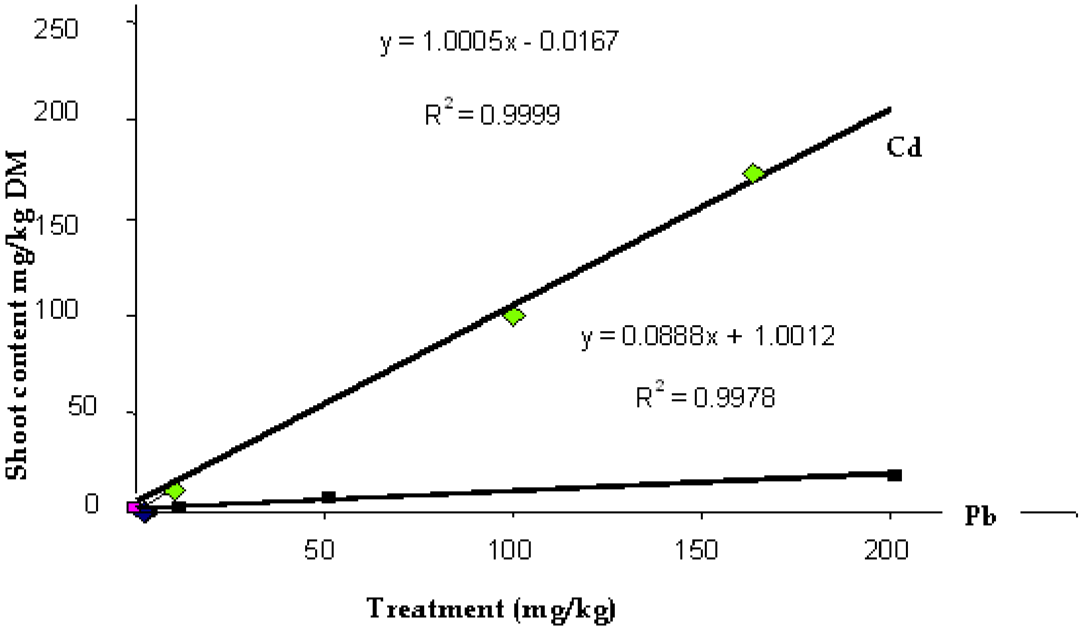
Figure 3: Effect of aging on soil solution Cd in a Xeralf from South Australia (R. Naidu, unpublished)



7 METAL PHYTOAVAILABILITY MAY VARY WITH PLANT SPECIES

The ability of plants to bioaccumulate metals and possibly other contaminants varies with both the nature of plant species and the nature of metal contaminants. Laboratory studies consistently demonstrate that the capacity of plants to bioaccumulate metals varies extensively with the nature of metals as well as with plant types. Figure 4 illustrates the marked differences in the uptake of Cd and Pb by peas (*Pisum sativum).* These differences in metal uptake may be attributed to both the markedly different binding capacity of soils for these metals and also to plant-root-metal interactions, which vary with metal types. Whilst variances in metal uptake capacity of plants may have limited significance to metal phytotoxicity guidelines, the marked differences in the capacity of plants to bioaccumulate metals will have major implications to guidelines which are neither soil type specific nor plant type specific.

Figure 4. The capacity of plants (pisum sativum) to bioaccumulate metals varies considerably (Megharaj, Krishnamurti and Naidu, unpublished).



Although much data is available in the literature on variable uptake and subsequent phytotoxicity to plants, the following summarises data on Cu which is the only metal for which relevant information was found for Australian conditions. These studies were conducted under glasshouse conditions and were of short-term duration. Mitchell *et al.* (1988) investigated the effects of environmental hazardous chemicals on the emergence and early growth of selected native Australian plants (*Banksia ericifolia, Casuarina distyla and Eucalyptus eximia)* using soils treated with the chemicals. Seeds were grown in pots (100 mm-diameter) in a glasshouse study in a sandy loam soil at Cu concentrations of 0, 10, 100, 1000 and 2000 mg kg^{-1} depending on plant type. They found that the EC_{50} values for the plants ranged from 205 to 610 while the LC-50 values ranged from 580 to 1845 mg kg^{-1} soil. The most sensitive plant species was *Cassurina distyla.* These values are markedly different from those reported in the provisional NSW phytotoxicity guidelines (for Cu this value is 100 mg/kg). Given the markedly different Cu toxicity recorded with different plant types, simple generalisation of single metal phytotoxicity levels in any fixed regulatory guidelines might restrict rehabilitation of contaminated sites with Cu concentrations exceeding the guideline limits although there may be plants tolerant of high metal concentrations. While screening or investigation levels may play an important part in determining the potential for phytotoxic effects, there is also a need to make provision to consider variations in response with soil type and plant type at a site level.

8 METAL PHYTOAVAILABILITY MAY DICTATE TOXICITY GUIDELINES

Although Will and Suter (1995) derived a benchmark Cu concentration of 100 mg kg^{-1} for the protection of terrestrial plants, incidence of Cu phytotoxicity has not been recorded at concentrations in the order of 100 mg/kg in the Australian environment. This is evident from numerous but limited studies in Australia (Olszowy *et al.*, 1993; Merry *et al.*, 1983). Olszowy *et al.* (1993) observed maximum Cu concentrations of 466 mg kg^{-1} soil with the 95th percentile of 122 mg kg^{-1} in Australian urban soils but found no incidence of phytotoxicity at these sites. Similarly, Merry *et al.* (1983), report Cu concentrations in

Australian orchard soils of 11 - 320 with an average value exceeding 100 mg kg $^{-1}$ (orchard soil mean Cu of 101 mg kg^{-1}). These investigators recorded no incidence of Cu toxicity either. There are however, many solution and pot culture studies that show toxicity at concentrations lower than that recorded by Will and Suter (1995). For instance studies using grass and herbaceous species as the test species show toxicity at comparatively low levels of Cu in the growth medium. Wainwright and Woolhouse (1977) reported growth retardations of 50 to 60% compared to control when a non-tolerant genotype of Agrostis capillaris was treated with 64 µg Cu L^{-1} solution. Metal toxicity to plants at relatively lower solution culture Cu concentrations is not surprising given that unlike soils these solutions are not buffered and almost all Cu is present in bioavailable form. In soils, depending on the total metal concentration and pH, between 50 to 99% of total metal could be present in bound form and this would negate adverse effects of metals unless present in highly bioavailable form. Given that it is the bioavailable metal fraction that dictates plant availability and potential toxicity problems, there is a need for revisiting phytotoxicity guidelines with a view to developing values based on metal bioavailability.

9 IMPLICATIONS TO REGULATORY GUIDELINES

It is evident from the above brief overview that metals concentrations at which plants show phytotoxicity is dependent on a number of factors that include soil type, plant type, soil properties and the bioavailable metal concentrations. Different soils may have the same total metal concentrations but remarkably different effect on plant metal uptake and potential for metal phytotoxicity. Generally highly weathered soils such as Oxisols common to Northern Australia will exhibit high metal bioavailability at their natural pH (5 to 6) while less weathered soils such as Vertisols, commonly found in Southern Australia will exhibit low bioavailability at pH's 5.5 to 6. This variability in metal bioavailability suggests that total metal concentration may not be appropriate and sensitive indicator for phytotoxicity. An appropriate strategy for the guideline may be a two-tiered system that in the first instance requires an assessment of total metal concentration followed by phyto or bioavailability assessment using a chemical extraction technique.

DISCLAIMER

The views presented in this paper are those of the authors and do not necessarily represent the views of EPA Victoria or CSIRO.

REFERENCES

1. Beckett, PHT and Davis, RD (1988) Upper critical levels of toxic elements in plants. New Phytologist 79: 95-106.

2. Chang, AC., Granato, TC and Page, AL (1992) A methodology for establishing phytotoxicity Criteria for chromium, copper, nickel and zinc in agricultural land application of municipal sewage sludges. J Environ. Qual. 21 : 521-536.

3. Fotovat, A, Naidu, R and Sumner, ME. (1997) Water: Soil ratio influences aqueous phase chemistry of indigenous copper and zinc in soils. *Aust. J Soil Res.* 35:687-710

4. Heale, EL and Ormrod, DP (1982) Effects of nickel and copper on *Acer rubrum, Cornus stolonifers, Lonicera tatarica, and Pinus resinosa.* Can. J Botany, 60: 2674-2681

5. Merry, RH., Tiller, KG and Alston, AM (1983) Accumulation of copper, lead and arsenic in some Australian orchard soils. Aust J Soil Res. 21 : 549-561.

6. Mitchell, RL., Burchett, MD., Pulkownik, A and McCluskey (1988) Effects of environmentally hazardous chemicals on the emergence and early growth of selected Australian plants. Plant and Soil 112: 195-199.

7. Nastusch, J (1997) Application and development of contaminated site remediation technologies in Australia. ANZAC Fellowship Report to Department of Internal Affairs, Wellington, New Zealand and Department of Foreign Affairs and Trade, Canberra, Australia.

8. NSW EPA (1998) Guidelines for the NSW Site Auditor Scheme

9. Olszowy H, Torr P, Imray P, Smith P, Hegarty J and Hastie G 1993 Report on Studies of Levels of Trace Elements in Soils from Rural and Urban Areas of Australia. Contaminated Sites Monograph No. 4, Department of Human Services and Health, Environmental Protection Agency and South Australian Health Commission.

10. Rehab, FE and Wallace, A (1978) Excess trace metal effects on cotton: 2. Copper, zinc, cobalt and manganese in Yolo Loam soil. Communications in Soil Science and Plant Analysis. 9: 519-527.

11. Sheppard, SC (1992) Summary of phytotoxic levels of soil arsenic. Water, Air and Soil pollution 64: 539-550, Will, ME and Suter II, GW (1995) Toxicological Benchmarks for screening potential contaminants of concern for effects on terrestial plants: 1995 Revision, Environmental Restoration Risk Assessment Program, Oak Ridge National Laboratory.