



Bioavailability of Arsenic - Timber Treatment Guidelines

**A report for the Ministry of Health,
Ministry for the Environment, and Industry
(interim report)**

Literature review of the Bioavailability of Arsenic

March 2000

**Jacqui Horswell, Ph.D.
Scientist
Environmental Health Effects, ESR**

**Dominique Noiton, Ph.D.
Manager, Environmental Health
Effects Programme, ESR**

**Institute of Environmental Science & Research Limited
Kenepuru Science Centre
Kenepuru Drive, PO Box 50-348, Porirua, New Zealand
Telephone: (64-4) 237-0149, Facsimile: (64-4) 237-2370**

**A CROWN RESEARCH
INSTITUTE**

**Bioavailability of Arsenic -
Timber Treatment Guidelines**

Interim Report

**A report for the Ministry of Health,
Ministry for the Environment, and Industry**

Literature review of the Bioavailability of Arsenic

by Jacqui Horswell

**Toxicology Group
Environmental Health Effects Programme
ESR: Kenepuru Science Centre
PO Box 50-348, Porirua**

March 2000

DISCLAIMER

This report or document (“the Report”) is given by the Institute of Environmental Science and Research Limited (“ESR”) solely for the benefit of the Ministry of Health, Crown Health Enterprises and other Third Party Beneficiaries as defined in the Contract between ESR and the Ministry of Health, and is strictly subject to the conditions laid out in that Contract.

Neither ESR nor any of its employees makes any warranty, express or implied, or assumes any legal liability or responsibility for use of the Report or its contents by any other person or organisation.

CONTENTS

Executive Summary	1
Introduction	2
Aim	3
Chemistry of As	3
Background Sources	4
Table 1. World-wide production and emission of As to the environment from natural and anthropogenic sources					4
Uses	5
<i>Timber treatment</i>					
Toxicity	5
Bioavailability			6
<i>Role of oxides of aluminium and iron</i>			7
<i>Phyllosilicate clay minerals</i>	8
<i>Organic matter</i>	8
<i>Micro-organisms</i>	8
<i>Redox</i>	9
<i>pH</i>	9
<i>Liming</i>	10
<i>Competing ions – phosphate</i>	10
<i>Plant species</i>	11
Table 2. Data from toxicity tests with As on terrestrial plants					14-19
Variability of metal toxicity data		20
Relationship between plant and total soil concentrations of As					21
Table 3. Data from toxicity tests with bioavailable As on terrestrial plants					22
Conclusions	23
References	23

Executive summary

Salts of copper, chromium and arsenic (CCA) have been used for many years throughout New Zealand for the preservation of wood against insect and fungal attack. The treatment sites can provide a point of entry for the preservative into the general environment by way of spills and leaks, or run-off from treated wood. One of the contaminants of primary concern is arsenic (As).

In terms of human exposure to As, food constitutes the largest source of As intake with smaller amounts coming from drinking water and air. In absolute terms, such exposure is generally low due to natural constraints on As uptake by plants. Toxicity of As to plants is often reached prior to accumulation to levels that would be toxic to wildlife, or to humans ingesting the plants; however, the inability to grow plants on contaminated sites is a far from satisfactory impact.

Inorganic As can cause a range of serious acute and chronic health effects, including skin abnormalities, heart problems, central and peripheral neurological damage. Exposure to As has also been linked to the development of several cancers (e.g. skin and lung cancer) in humans.

An understanding of the environmental behaviour of As assists in interpretation of the phytotoxicity data, and is essential in setting regulatory thresholds for As toxicity in soils. Arsenic is present as an anion in soils, and in the majority of soils will be found as the +5 state (arsenate). A large proportion of the As in soils is not directly available to plants, much being sorbed to iron and aluminium oxides in the soil. The total concentration of As in soil is a poor indicator of the fraction of As that is plant-available. Plant uptake, and hence toxicity, is dependent on the soil solution free ion concentration, i.e., the bioavailable fraction. Bioavailability of As to plants is influenced by many factors including plant species, the form and concentration of As in the soil, soil properties such as pH, and the presence of other ions. Bioavailability is one of the key areas of uncertainty in the derivation of the current Timber Treatment Guidelines. Interim soil acceptance criteria for As of 30 mg/kg for agricultural/residential uses, and soil acceptance criteria of 500 mg/kg for commercial/industrial uses have been proposed. — adopted? was

Setting the regulatory criteria is not simple. Commonly reported phytotoxicity thresholds are very close to, or overlap with, commonly reported background levels of As in soils. In addition, the bioavailability of As added experimentally to soil, often as metal salts, in pot trials, may be the “worst case”, and soil quality criteria based on such data (e.g. The Dutch Soil Quality Criteria) may have an un-quantified safety factor built into them. It may be more appropriate to establish criteria for different soil types (e.g. for clay soils and one for other soils), or by using soil solution arsenic concentrations. A full review of the assumptions made in the risk assessments in the timber treatment guidelines will be presented in the final report.

Introduction

Arsenic is a naturally occurring element, ubiquitous in our environment. It can be released to the environment from natural sources, such as erosion from mineral deposits, or from anthropogenic sources such as smelting of copper or lead ores (Smith *et al.*, 1998; McLaughlin *et al.*, 1999). Arsenic is present in the earth's crust at an average concentration of 2-5 mg/kg and is primarily associated with igneous and sedimentary rocks, and especially in ores that contain copper or lead (US DoH, 1999).

For members of the general population, possible exposure to As present in contaminated soils comes via a number of pathways: contaminated foodstuffs and water sources, dust ingestion and inhalation. The most important pathway of human exposure has been shown to be the soil-plant-human route (Mitchell and Barr, 1995; US DoH, 1999). Thus, food constitutes the largest source of As intake with smaller amounts coming from drinking water and air (Chen and Lin, 1994). In absolute terms, such exposure is generally low, due to natural constraints on As uptake by herbage, cereal crops and vegetables (Mitchell and Barr, 1995; Moore *et al.*, 1998; Carbonell Barrachina *et al.*, 1995). However, fish and seafood can accumulate considerable amounts of As from their environment (WHO, 1981). Levels in food are usually about 20-140 µg/kg, and levels in water are about 2 µg/l (US DoH, 1999). A Maximum Allowable Daily Body Load (MADL) of total As of 50 µg/kg body weight (bw)/day was set in 1967 by WHO. More recently the Joint FAO/WHO Expert Committee on Food Additives (JECFA) set a Provisional Tolerable Weekly Intake (PTWI) of 15 µg/kg bw/week for inorganic As (WHO, 1989). The average daily intake of As from food in New Zealand is 8.7 µg/kg bw/day (for the most exposed individual, taken from New Zealand Dietary Survey (1997/98 NZTDS); Vannoort *et al.*, 2000), calculated as less than 25% of the PTWI for inorganic As, with most exposure coming from seafood (85%). Thus the dietary exposures found in the 1997/98 NZTDS are unlikely to have any adverse health implications for the general New Zealand population (Vannoort *et al.*, 2000).

Inorganic As can cause a range of serious acute and chronic health effects, including skin abnormalities, heart problems, central and peripheral neurological damage (Vannoort *et al.*, 2000; Chen and Lin, 1994). Exposure to As has also been linked to the development of several cancers (e.g. skin and lung cancer) in humans, and the US Environmental Protection Agency (USEPA) has classified As as a Group A human carcinogen. However, it is considered by the US Department of Health Services that chronic adverse health effects are not likely to be caused by exposure to ambient levels of As (Report to the Air Resources Board on Inorganic Arsenic, 1990).

Arsenic has been found to be an essential element of the diet of a few mammalian species. However, there is disagreement about whether it is essential to the human diet (Report to the Air Resources Board on Inorganic Arsenic, 1990; USEPA, 1988), as neither a biochemical or physiological role, nor an As deficiency syndrome have been identified (USEPA, 1988). In plants, root growth is stimulated by small amounts of As in solution, but evidence of its essentiality for plant growth still needs to be established (Carbonell Barrachina *et al.*, 1997; Moore *et al.*, 1998). At higher concentrations,

however, As has been reported to interfere with metabolic processes and to inhibit plant growth, sometimes leading to death (Merry and Alston, 1986; Wiersma *et al.*, 1986; Smith *et al.*, 1998).

The levels of soil As reported to be toxic to plants span a broad range and overlap with levels reported as background, no-effect and beneficial (Sheppard, 1991; Smith *et al.*, 1998). Bioavailability of As to plants is influenced by many factors including: plant species (Merry and Alston, 1986; Wiersma *et al.*, 1986); the form and concentration of As in the soil (Carbonell Barrachina *et al.*, 1998; Jiang and Singh, 1993); soil properties such as pH (Merry *et al.*, 1986; Jones *et al.*, 1997), soil type (Lund and Fobain, 1991; Merry *et al.*, 1986; Jiang and Singh, 1994) and the presence of other ions (Onken and Hossner, 1995; Asher and Reay, 1979). Bioavailability is one of the key areas of uncertainty in the derivation of the current Timber Treatment Guidelines. Interim soil acceptance criteria for As of 30 mg/kg for agricultural and residential uses, and soil acceptance criteria of 500 mg/kg for a commercial/industrial has been proposed.

Aim

The aim of this report is to provide a comprehensive review of the available literature on the bioavailability of As to plants in soil, to enable an assessment of the current soil acceptance criteria with regard to plant and human health impacts.

Chemistry of As

Arsenic is a metalloid element, that can form alloys with various metals, and covalent bonds with carbon, hydrogen, oxygen and sulphur (Tamaki and Frankenberger, 1992). It can occur in the environment in +5 (arsenate, or As (V)), +3 (arsenite, or As(III)), 0 (free-element) and -3 (arsenide) oxidation states (Scott-Fordsmand and Pederson, 1995). However, the negatively charged H_2AsO_4^- and HAsO_4^{2-} (arsenate) are the main forms of As found in soil and soil solution (Jiang and Singh, 1994; Smith *et al.*, 1999). The conversion of As from one oxidation state to another in soils is dependent on several soil parameters, including pH, redox potential and microbial activity (Onken and Hossner, 1995). The normal oxidising conditions at the earth's surface under which weathering takes place lead to the formation of oxyanions based on the +5 oxidation state (O'Neill, 1990). Thus, arsenate is the predominant form of As in aerated soil (oxidizing conditions of $>+100\text{mV}$) (Onken and Hossner, 1995). However, under reducing conditions (redox potential of $<+100\text{mV}$), for example in water-logged soils or in swamps, arsenite dominates (Onken and Hossner, 1995). Arsenic and phosphorus belong to the same group of elements and they both commonly form oxyanions in the +5 oxidation state. Both synergistic (Onken and Hossner, 1995) and antagonistic (Carbonell Barrachina *et al.*, 1997; Jiang and Singh, 1994) interactions between arsenate and phosphate have been reported.

- **Arsenate is the predominant form of As in soil**

Background sources

The main source of As in soils is the parent material from which the soil is derived. The native soil As content may vary considerably. Average background concentrations, world-wide, are in the region of 6 mg/kg (Tamaki and Frankenberger, 1992), although concentrations ranging from 2-30 mg/kg have been reported in New Zealand (MoH, 1997). The principal causes of anthropogenically elevated soil As are the historically widespread use of As compounds as insecticides, herbicides, and defoliants for agricultural production (McLaughlin *et al.*, 1999; Jiang and Singh, 1994). Other sources of soil As contamination include mining and smelting of non-ferrous metals, feed additives for poultry, phosphate fertiliser, fossil fuel combustion and municipal sewage sludges (Mitchell and Barr, 1995; Smith *et al.*, 1998).

Table 1 illustrates some of the important environmental inputs of As.

Table 1. World-wide production and emission of As to the environment from natural and anthropogenic sources

Source	Global production (tonnes/year)	Total As emission (tonnes/year)
Anthropogenic		
Copper smelting	8.05 x 10 ⁶	12,080
Lead smelting	3.58 x 10 ⁶	1,430
Zinc smelting	1.20 x 10 ⁶	780
Steel smelting	645 x 10 ⁶	60
Coal production	3,696 x 10 ⁶	6,240
Wood fuel	850 x 10 ⁶	425
Clearance of tropical forests	3,200 x 10 ⁶	1,600
Clearance of woodland and savannah	640 x 10 ⁶	320
Burning of pasture land	2,000 x 10 ⁶	1,000
Herbicides	8,000	3,440
Wood preservatives	16,000	150
Glass manufacture	4,000	467
Waste incineration	150 x 10 ⁶	78
Natural		
Sea-salt spray	500 x 10 ⁶	26.5
Wind erosion	330 x 10 ⁶	1,980
Forest fires	250 x 10 ⁶	125
Volcanoes	25 x 10 ⁶	17,150

(Adapted from Chilvers and Peterson, 1987)

- **Average background concentrations of As range from 2-30 mg/kg in New Zealand**

Uses

As compounds have been widely used as pesticides for over a hundred years, maximum production has been estimated at 70,000 tonnes per year (Scott-Fordsmand and Pedersen, 1995). However, most agricultural uses of As have been banned due to concerns about human health risks during production, application or accidental spillage (Loebenstein, 1994). In addition, at high concentrations, As has been reported to be toxic to plants, or may accumulate in plants and potentially impact human health by entering the food chain (Carbonell-Barrachina *et al.*, 1997).

Timber Treatment

From as early as the 1940s, the use of As as a wood preservative began to grow, and after 1980, wood preservative uses were more important than agricultural application in many countries (US DoH, 1999; Arsenault, 1975). Salts of copper, chromium and As (CCA) are used together in water-soluble formulations for the preservation of wood against insect and fungal attack. The treatment site, however, can provide a point of entry for the preservative into the general environment by way of spills and leaks, or run-off from treated wood (Grant and Dobbs, 1977). In addition, during the vacuum/pressure process of treating timber with solutions of CCA, waste sludges are formed. These sludges contain high levels of Cr, As and Cu which may leach into the environment causing contamination (Thom, 1975).

The As in treated wood, is in the form of chromium arsenate and copper arsenate, and in CCA, as sodium arsenate and copper arsenate (Arsenault, 1975; Thom, 1975). Thus soil contaminated with timber treatment preserving liquor will contain As in the form of arsenate, the least toxic and mobile of the two forms (arsenate and arsenite) commonly found in soil (Jiang and Singh, 1994; Smith *et al.*, 1999; Scott-Fordsmand and Pederson, 1995; Onken and Hossner, 1995).

- **Most agricultural uses of As have been banned**
- **Soil contaminated with timber treatment preserving liquor will contain As in the form of arsenate**

Toxicity

The toxicity of As residues is primarily a function of the chemical form and oxidation state of the element. In contrast to mercury, it is important to note that exposure to organic forms of As is not considered to result in significant health risks (Smith *et al.*, 1998; Moore *et al.*, 1998). Consequently, this discussion will focus on the inorganic forms of As, specifically arsenate and arsenite.

Arsenite reacts with dithiol groups on proteins and thus inhibits enzyme reactions requiring free sulfhydryl groups, leading to membrane degradation and cell death (Jiang and Singh, 1994; Scott-Fordsmand and Pederson, 1995). Arsenate competes with phosphate due to its chemical similarity, and acts as an uncoupler of oxidative

phosphorylation, resulting in an inadequate supply of energy (Scott-Fordsmand and Pederson, 1995). Arsenite is more toxic to plants than arsenate, and this may in part be due to its increased mobility and solubility (Jiang and Singh, 1994; Onken and Hossner, 1995; Scott-Fordsmand and Pederson, 1995). Phytotoxicity symptoms caused by arsenate and arsenite include leaf wilting, violet coloration, root discoloration, cell plasmolysis, and a growth reduction which may result in death (Carbonell Barrachina *et al.*, 1995; Carbonell Barrachina *et al.*, 1997). The root is the primary site of injury when As reaches phytotoxic levels (McLaughlin *et al.*, 1999), and symptoms suggest a restriction in the movement of water into the plants. For arsenite, this is probably due to high toxicity to radicular membranes (Carbonell Barrachina *et al.*, 1995; Carbonell Barrachina *et al.*, 1997). For arsenate, it is probable that toxicity in root systems is the result of effects on phosphorylation, however this has not been fully investigated. This may also be a reason for there being limited As accumulation in plants, because disruptions in root function would restrict adsorption and movement of As to the upper part of the plant (Carbonell Barrachina, *et al.* 1995). In general, the highest quantities of As residues are found in roots (Smith *et al.*, 1998), moderate levels in the vegetative parts (leaves and stem), and the smallest quantities in the fruit and seeds (Carbonell Barrachina *et al.*, 1995; Weaver *et al.*, 1984). Therefore As accumulation may be of particular significance to root (e.g., carrot, beet) or tuber (e.g. potato) crops (Smith *et al.*, 1998; Weaver *et al.*, 1984; Steevens *et al.*, 1972).

Phytotoxicity of As to plants is often reached prior to accumulation to levels that would be toxic to wildlife, or to humans ingesting the plants (Smith *et al.*, 1998; Carbonell Barrachina *et al.*, 1997; O'Neill, 1990). However, the inability to grow plants on contaminated sites is a far from satisfactory impact.

- **Arsenite is more mobile and phytotoxic than arsenate, but normally would be a minor component in soils**
- **The pattern of As uptake in plants is: highest quantities found in roots, moderate levels in the vegetative parts (leaves and stem), and the smallest quantities in the fruit and seeds**
- **Consequently, As accumulation may be of particular significance to root or tuber crops**
- **Plant toxicity of As is usually reached prior to accumulation to levels that would be toxic to wildlife, or to humans ingesting the plants**

Bioavailability

Plants take up As from the soil solution in the form of the oxyanions, arsenite or arsenate (Carbonell Barrachina *et al.*, 1997; Smith *et al.*, 1998; McLaughlin *et al.*, 1999). Concentrations of As in the soil solution are generally quite low because most of the As is adsorbed to the soil solid-phase. Arsenic availability to plants, therefore, depends on the ability of As associated with the solid-phase of the soil to move into soil solution. Although a large volume of literature exists on metal adsorption by pure

silica and oxidic soil minerals, little information is available on the adsorption of As in soil systems. Some investigations have shown that both the amount of clay and the nature of constituent clay minerals strongly influence As adsorption in soils (Sakata, 1986; Merry *et al.*, 1983; Lund and Fobain, 1991).

Role of oxides of aluminium and iron

Within soils, As oxyanions have been shown to be adsorbed on the surface of several types of minerals, the most important of which are thought to be the hydrous oxides of iron (major components of clays), for example goethite and ferrihydrite, and the short-range order aluminosilicate minerals, imogolite and allophane. Sakata (1986) carried out a study into the adsorption of arsenite by 15 soils from Japan, with different chemical and physical characteristics. It was found that adsorption of arsenite was mainly controlled by amorphous iron oxides and hydroxides, and allophane. Merry *et al.* (1983) carried out a survey of total arsenic distribution in six soil profiles from historically contaminated orchards in South Australia. It was found that the soils with relatively high iron oxides and hydroxides retained arsenate, whereas most of the arsenate had disappeared from the sandy soils. Lund and Fobain (1991) found that, in the B and C horizons of two soils, As was associated with oxides of iron, aluminium and manganese. In another study, Jiang and Singh reported a reduced toxicity of arsenite and arsenate, and lower concentration of both As oxyanions in plant tissues (rye-grass and barley) in a loam soil compared to a sandy soil. The loam soil contained much higher contents of both clay and Fe oxides and therefore adsorbed more of the applied As, rendering it unavailable for plant uptake.

Arsenic oxyanions can be held at positively charged solid-phase sites by simple anion exchange, but remain in equilibrium with the pore water, and are therefore more labile and plant available. Although few researchers have investigated the mechanisms of As adsorption in soils, it appears that adsorption by hydrous oxides is considered to take place predominantly by specific adsorption mechanisms, such as exchange of arsenate oxyanions with surface Fe-OH, Al-OH, FeOH₂⁺ and Al-OH₂⁺ groups through ligand exchange (Waychunas *et al.*, 1993; Waychunas *et al.*, 1996). This type of soil adsorbed As is thought to be less available for plant uptake.

In a study by Smith *et al.* (1999), the sorption of arsenite and arsenate in ten soils with widely varying chemistry and mineralogy was analysed. Sorption was described by the distribution coefficient, K_d , taken from the Freundlich equation: $As_{\text{sorb}} = k(As_{\text{soln}})^n$, where As_{sorb} = amount of As sorbed (mmol kg⁻¹); As_{soln} = solution concentration (mmol L⁻¹), and k and n are constants. Simple linear regression of K_d against measured soil variables indicated a strongly significant relationship between K_d and the iron oxide content of the soil. Eighty percent of the variation in As adsorption between the 10 different soils could be attributed to metal oxides. In addition it was found that the sorption of arsenate by both Fe and Al hydroxides was greater than that of arsenite (Smith *et al.*, 1999). This has also been found in other studies (Bhumbla and Keefer, 1994; O'Neill, 1990;). Other soil properties, such as organic matter content, also played a role in As adsorption.

Arsenic ions can also react with soluble iron and aluminium to form extremely insoluble precipitates, which become unavailable for plant uptake (Woolson, 1973). However, such soluble forms of iron and aluminium are generally found only in strongly acidic mineral soils (Brady, 1974).

Phyllosilicate clay minerals

Arsenic can be adsorbed by these clay minerals, with kaolinite sorbing more As from solution than vermiculite, which sorbs more than montmorillonite (Dickens and Hiltbold, 1967). However, the total amounts of As sorbed are generally far smaller than by the hydrous oxides and short-range order aluminosilicates. Clays may often be coated with Fe and Al oxides, which may modify the As-clay interactions (Naidu *et al.*, 1994).

Organic matter

Jiang and Singh (1994), investigated the availability of arsenite and arsenate to ryegrass and barley in two different soil types, a sandy and a loam soil. Reduced plant uptake and toxicity in the loam soils was reported to be due not only to a higher concentration of clay and Fe oxide, but also to its higher organic carbon content.

Clearly, as a conclusion from the above discussion, the amount of As in soil solution, i.e., "bioavailable" for plant uptake, will depend primarily on the soil type. This is why it is often difficult to correlate total soil As concentrations to plant concentrations. Much research has been carried out trying to predict plant uptake using total soil concentrations, but it has been found that this relationship is not a simple linear one. Drel and Swoboda (1972), demonstrated that the total As content of the soil did not determine toxicity, and that plant-available As depended on the particular soil. Woolson *et al.*, (1971) reported that there was a better correlation between plant growth and available As than between plant growth and total As. Even in nutrient solution, the As concentration in the roots of bean plants was not proportional to the As present in the medium (in the form of arsenite), probably due to the detrimental effect of As on the root system restricting uptake (Carbonell Barrachina, 1995). Further work needs to be carried out to determine if plant As uptake can be predicted from soil solution As concentration.

Micro-organisms

Biological transformations can be important in redistributing As in the soil (Smith *et al.*, 1998). For example, soil microbes have been shown to produce volatile arsenicals by reductive, or reductive and demethylative pathway from inorganic and methylated forms of As (Cheng and Focht, 1979). Biomethylation and bioreduction are probably the most important microbial transformations, since they can produce As species that are sufficiently stable to be mobile in air and water (Jonnalagadda and Prasad Rao, 1993). Bacterial oxidation can be carried out by many heterotrophic bacteria, such as *Bacillus* and *Pseudomonas* spp. (Smith *et al.*, 1998). Various fungi and bacteria are also able to oxidise and reduce As species; for example, the reduction of arsenate to arsenite by *Pseudomonas fluorescens* has been reported under anaerobic conditions (Cullen and Reimer, 1989). However the extent to which microbial activity is involved in the transformation and movement of As in soil is difficult to quantify.

Microbial influences on As sorption and desorption may only be important in long term studies or where the soil microflora have been pre-exposed to As. However, the long-term effects of microbial transformations have remained largely unstudied.

Redox

Since the reduced (+3) form of As (arsenite) is more soluble and phytotoxic than the oxidised (+5) form (arsenate), the redox potential of the soil can affect the availability, and toxicity of As (Scott-Fordsmand and Pederson, 1995). Evidence indicates that in moderately reducing conditions, such as flooded soils, arsenate readily converts to arsenite (Scott-Fordsmand and Pederson, 1995; Marin *et al.*, 1993; Onken and Hossner, 1995; Merry *et al.*, 1986). Onken and Hossner (1995), determined that the dominant As species in soil solution under flooded conditions was arsenite. A redox value of +100mV was considered to be the point below which arsenate readily converts to arsenite. In a study by Marin *et al.* (1993), at a redox potential of 0 and 200mV, arsenite was the major dissolved species in the soil solution. It was also found that As plant tissue concentrations (rice) increased with decreasing redox. Thus, changes in redox potential from aerobic to anaerobic conditions alter the bioavailability of As, and may potentially impact wetland cropping systems. However, in general, the most abundant form of As present in soil solution is arsenate (O'Neill, 1990).

pH

The effect of pH on As sorption has been widely studied using both pure mineral systems and soils (Marin *et al.*, 1993; Onken and Adriano, 1997; Onken and Hossner, 1995; Merry *et al.*, 1986). In general a decrease in availability is expected for heavy metals in soils when pH increases (Scott-Fordsmand and Pederson, 1995; O'Neill, 1990). However, the role of pH with respect to As bioavailability and plant uptake is not clearly understood (Jiang and Singh, 1994; Scott-Fordsmand and Pederson, 1995).

Goldberg and Glaubig (1988) found that the sorption of arsenate by the clays montmorillonite and kaolinite was highest near pH 5, and dropped significantly between pH 7 and 9. In an investigation of the mobilisation of As residues in mine tailings (As most probably in the form of arsenate), Jones *et al.* (1997) found that increases in pH corresponded to increases in As concentration in soil solution. They suggested that this was consistent with pH dependence of As sorption reactions on iron oxide minerals and silicates in soils (Goldberg, 1986; Goldberg and Glaubig, 1988). The development of surface charge on a variable charge material, such as iron or alumina sesquioxides, is pH-dependent, and anion adsorption (e.g. As) is favoured with decreasing soil pH (Smith *et al.*, 1999). Here, variable charge refers to the fact that the amount of charge varies with pH. As soil pH, and therefore OH⁻ ion concentration, increases, H⁺ ions are removed from soil surfaces, thereby increasing the amount of negative charge on the colloid surface (McLaren and Cameron, 1996). This change in net charge would cause a desorption of As anions. Conversely, however, there is some evidence for an increase in As toxicity to plants as soils become more acidic, particularly at pHs below 5. Marin *et al.* (1993) studied the effect of redox potential and pH on arsenite and arsenate uptake by rice. They found that water-soluble As concentrations were inversely related to redox and pH. At the lowest redox potential studied (-200mV), 7.3, 2.2 and 1.4% of the total As in the soil became soluble at pH 5.5, 6.5 and 7.5 respectively. Due to the low redox potential, arsenite

was the dominant As chemical form. Irrespective of soil redox potential, most water-soluble As was found at pH 5.5, and As concentrations were highest in rice plant at pH 5.5. Increased As availability at low pH may be because Fe and Al oxy-compounds become more soluble, thus, releasing As (Brady 1974; O'Neill, 1990). However, the dominant mechanism controlling As availability is probably sorption/desorption reactions rather than precipitation/dissolution reactions (Livesey and Huang, 1981; Marin *et al.*, 1993). It is probable that soil type will have major impact on which mechanism is most important in terms of As sorption-desorption. Increased mobility and solubility, and therefore greater toxicity of arsenite in relation to arsenate, may in part be due to the greater sorption of arsenate onto soil. Greater electrostatic interactions would exist between the soil surface and the negatively charged arsenate than between the uncharged H_3AsO_3 (arsenite), at normal soil pHs (Smith *et al.*, 1999).

Soil pH also has a major effect on adsorption of As by organic matter. Thunabalasingam and Pickering (1986) found arsenite and arsenate adsorption by humic materials to be dependent on pH. Maximum sorption of arsenate occurred at pH 5.5, with the arsenite maximum being found at higher pHs. In addition, it was found that arsenite was sorbed to a greater extent than arsenate. The humic acids acted like anion exchangers, containing amino functional groups which, if strongly basic, interacted with acids or exchangeable anions. With increasing pH, sorption declines due to enhanced protonation of weak acids and competition from the hydroxyl ion for anion exchange sites (Thunabalasingam and Pickering, 1986). Additionally, as the pH becomes more alkaline the humics themselves became more soluble and their ability to adsorb As is reduced. However, Thunabalasingam and Pickering (1986) also postulated that dissolution of humic acids and associated counter ions such as iron hydrous oxides might form complexes with As. Released cations such as Ca^{2+} may also form insoluble complexes, thus affecting As bioavailability.

Liming

The practice of liming to remediate contaminated soils and acidic mine tailings with low pH, has the potential to mobilise As (US DoH, 1999). The addition of Ca^{2+} may cause a shift from As bound to iron and aluminium oxide minerals ($\text{Fe}_x(\text{AsO}_4)_x$ and $\text{Al}_x(\text{AsO}_4)_x$) to calcium bound As, increasing As availability because of the greater solubility of the calcium complexes. Experiments performed by Jones *et al.* (1997), on mine tailings heavily contaminated with As, indicated increased mobility of As with the addition of lime to soils. They reported that, in addition to the formation of soluble calcium bound As, the increased availability was consistent with the pH dependence of sorption reactions of As on iron oxide minerals. In these experiments, As in soil solution was not speciated, however, historically contaminated sites were used and it is probable that most As would be in the form of arsenate (Jiang and Singh, 1994; Smith *et al.*, 1999).

Competing ions - Phosphate

Due to their chemical similarities, phosphate and arsenate may interact and, therefore, each affects the bioavailability of the other by competing for adsorption sites on soil particles and root surfaces (Scott-Fordsmand and Pederson, 1995). In general, the

effect of phosphate on the toxicological impacts of As is to decrease toxicity (Asher and Reay, 1979; Onken and Hossner, 1995; Smith *et al.*, 1998). However, effects can be unpredictable and dependent on plant species, growth medium and chemical speciation of As (Asher and Reay, 1979; Onken and Hossner, 1995; Otte and Ernst, 1994). Because arsenate is adsorbed by plant roots via the high-affinity transport system for phosphate, its uptake is competitively inhibited by phosphate (Meharg and Macnair, 1991). Solution culture experiments of Asher and Reay (1979) showed that phosphate was a powerful inhibitor of arsenate uptake in barely seedlings. In another study, Onken and Hossner (1995) found a significant increase in dry matter production in rice plants grown in a clay soil treated with low concentrations of both arsenite and arsenate (5 mg/kg). They postulated that this was due to the displacement of sorbed phosphate from the soil by the added As, rather than competition with phosphate for uptake by the plant. Indeed, the total phosphate uptake by the plants was higher than in control plants. Attempts to control As toxicity in soil-grown plants by addition of phosphate have yielded variable results. Reactivity of the adsorptive surfaces will vary considerably depending on pH, charge density, and soil solution composition (Smith *et al.*, 1998). Anions, when present, especially phosphate, can effectively compete with As for adsorption sites, particularly aluminium and iron oxide surfaces (Scott-Fordsmand and Pederson, 1995). Further research is needed to establish the cause behind the divergent results, but displacement of sorbed arsenate by phosphate in soil could be an important factor.

Plant species

A considerable variation of sensitivity to As exists among plant species (Jiang and Singh, 1994; Duel and Swoboda, 1972; Woolson, 1973; Merry and Alston, 1986; Carbonell-Barrachina, *et al.*, 1995; Carbonell-Barrachina, *et al.*, 1997). Vegetable crops grown in three soils treated with CCA (As present in the form of arsenate), exhibited a range of sensitivities in the order of bean>tomato>carrot (Grant and Dobbs, 1977). Woolson (1973) grew six vegetable crops in three soil types (two clay-loams and one loamy sand) and found differences in sensitivities, and uptake of arsenate. Plant sensitivities followed the order of green beans>lima beans=spinach>radish>tomato>cabbage. The range of soil-As concentrations, and chemical form, that may be phytotoxic to plants is summarised in Table 2. Although the data are not extensive, they highlight both the broad range of concentrations of soil As over which toxicity symptoms may occur, and the narrow margin that exists between background concentrations (<40 mg/kg in most soils) and phytotoxic concentrations (Smith *et al.*, 1998; Sheppard, 1991). In most studies beans are classified as having low or no tolerance, while carrot and tomato are regarded as very tolerant (Grant and Dobbs, 1977; Carbonell-Barrachina *et al.*, 1995; Carbonell-Barrachina *et al.*, 1997; Sheppard, 1991).

For plants, the potential uptake of an element is enhanced when it is an essential trace element such as zinc, and depressed when it is not. Consequently, it is assumed that the movement of As into plant tissues is not favoured (Mitchell and Barr, 1995). However, due to the chemical similarity of arsenate and phosphate, it has been suggested that the uptake mechanism is the same, but greatly favours phosphate (Mitchell and Barr, 1995; Meharg and Macnair, 1991). A study by Meharg and

Macnair (1990) of the uptake of arsenate by a tolerant and by a non-tolerant genotype of *Holcus lanatus* L. showed that the non-tolerant genotype accumulated arsenate to a much greater extent than the tolerant genotype. In contrast, however, the tolerant plants transported a far greater proportion of the arsenate to the shoots compared with the non-tolerant plants (Meharg and Macnair, 1991). However, the data presented in Table 2 suggest that there is no simple relationship between plant sensitivity and uptake.

Avoidance of uptake of As by many plants may possibly due to selective anionic membrane transport which allows the passage of nitrate and phosphate but not arsenite and arsenate (Harper and Haswell, 1988). Additional mechanism of metal tolerance in higher plants may be:

Avoidance mechanisms

- Alteration of membrane permeability
- Changes in metal binding capacity of the cell wall
- Increased exudation of metal chelating substances

Tolerance mechanisms

- Production of intracellular metal binding compounds
- Alterations of metal compartmentation patterns
- Alteration of cellular metabolism and alterations of membrane structure (Mitchell and Barr, 1995; Verkleij and Schat, 1990)

Research into As accumulation by plants indicates, in most instances, that concentrations of As in edible plant portions (fruit and grain) are low and do not exceed recognised health-based food standards (2 mg/kg; New Zealand Ministry of Health, 1984) (Carbonell-Barrachina *et al.*, 1997; Carbonell-Barrachina *et al.*, 1995). Further, the onset of plant toxicity is noted before the accumulation of levels of As harmful to human-health (Smith *et al.*, 1998; Carbonell Barrachina *et al.*, 1997; O'Neill, 1990). In addition, levels of As in terrestrial plants remain well below the level in soil. Roots generally contain higher levels than stems, leaves or fruit (Carbonell Barrachina, *et al.* 1995; Smith *et al.*, 1998; Weaver *et al.*, 1984); thus there is some concern that As concentration in root tissue may pose a potential risk in root-vegetable crops, or in close-grazing situations where animals would be consuming some roots, or to root-feeding wild animals. For example, Steevens *et al.* (1972) found up to 53.7 mg/kg As in potato peelings in soil treated with 720 mg/kg arsenite, but, regardless of treatment, As concentrations in the potato flesh never exceeded 1 mg/kg (Steevens *et al.*, 1972). In this study it should be noted that arsenite was added to the soil and would therefore be more bioavailable to the potato (Steevens *et al.*, 1972). In studies where plants were grown on highly contaminated sites, such as derelict and contaminated mine sites, levels of between 0.26-9.60 mg/kg As have been found in herbage, with soil levels of between 28-1,200 mg/kg As (Mitchell and Barr, 1995). Weaver *et al.* (1984) found that tropical grass (bermuda-grass) grown on soil containing 45 mg/kg arsenite, accumulated concentrations in leaves, stems and roots of 15, 25 and 200 mg/kg respectively. In general, however, many plants do not

take up high concentrations of arsenic, possibly due to selective anionic membrane transport (Harper and Haswell, 1988). Since exceptions to this are generally found only on highly contaminated sites, it follows that plants colonising heavily contaminated areas have evolved tolerance to the high As concentrations and in the process take up quantities of arsenic that may be toxic to livestock (Mitchell and Barr, 1995). In addition, the form of As added to soils in the above experiments was arsenite, known to be more bioavailable and phytotoxic than arsenate (Smith *et al.*, 1999; Bhumbra and Keefer, 1994; O'Neill, 1990;). In most cases of soil contamination arsenate would be the dominant form of As in soil solutions (Jiang and Singh, 1994; Smith *et al.*, 1999).

- **The amount of As in soil solution, i.e., “bioavailable” for plant uptake, will depend primarily on the soil type, and chemical form of As**
- **Concentrations of As in the soil solution are generally quite low because most of the As is adsorbed to the soil solid-phase**
- **Adsorption of As is mainly controlled by amorphous iron oxides and hydroxides, and allophane (major components of clays)**
- **Other soil properties such as organic matter also play a role in As adsorption**
- **Biological transformations can be important in redistributing As in the soil**
- **Changes in redox potential from aerobic to anaerobic conditions alter the bioavailability of As**
- **In general an increase in availability of As is seen in soils when pH increases**
- **The practice of liming has the potential to mobilise As**
- **Phosphate and As may interact antagonistically, in general, the effect of phosphate on the toxicological impacts of As is to decrease toxicity**
- **A considerable variation in plant sensitivity to As exists among plant species, in most studies beans are classified as having low or no tolerance, while carrot and tomato are regarded as very tolerant**

Table 2 contains reports of the soil concentration of As causing deleterious effects (usually yield reduction) on plant species, and plant uptake (concentrations in edible part of plant). Research on this subject was most active prior to the 1980s. Each soil and crop combination is listed, along with soil type, plant concentration and type of experiment. However it should be noted that few literature papers provide all of these ancillary data. Comparisons between data sets is therefore difficult.

Table 2. Data from toxicity tests with As on terrestrial plants

Reference	Soil type	Compound	Time	Experiment type	Parameter	Species	Concentration in soil (mg/kg)	Corresponding concentration in plant (mg/kg)							
Jiang and Singh 1994	Sandy	Arsenate	1 year / 3 year	Pot trial	Growth	Rye-grass	2	1/1							
							10	2/2							
							50	7/4							
							250	24/16							
							2	1/1							
							10	2/2							
							50	5/5							
							250	15/16							
							Duel and Swoboda 1972*	Loam	Arsenate	1 year / 3 year	Pot trial	Growth	Rye-grass	2	1/1
														10	2/1
50	5/2														
250	6/7														
2	1/1														
10	1/1														
50	2/1														
250	5/2														
Duel and Swoboda 1972*	Fine, Sandy	Arsenite	6 weeks	Pot trial	Growth	Soybean								0	0.5
														14	2.5
							28	6.5							
							42	-							
							56	-							
							70	-							
							84	-							
							98	-							
							112	-							
							126	-							
140	-														

*concentration in edible part of plant only or herbage

continued ...

Table 2 / 2. Data from toxicity tests with As on terrestrial plants

Reference	Soil type	Compound	Time	Experiment type	Parameter	Species	Concentration in soil (mg/kg)	Corresponding concentration in plant (mg/kg)							
Duel and Swoboda 1972	Fine, Sandy	Arsenite	6 weeks	Pot trial	Growth	Cotton	0	0.5							
							14	4							
							28	8							
							42	9							
							56	-							
							70	-							
							84	-							
							98	-							
							112	-							
							126	-							
							140	-							
								Black Clay	Arsenite	6 weeks	Pot trial	Growth	Soybean	0	0.5
														28	1
56	1.5														
84	3														
112	5														
140	14														
168	-														
196	-														
224	-														
252	-														
280	-														

Continued ...

Table 2 / 3 Data from toxicity tests with As on terrestrial plants

Reference	Soil type	Compound	Time	Experiment type	Parameter	Species	Concentration in soil (mg/kg)	Corresponding concentration in plant (mg/kg)
						Cotton	0 28 56 84 112 140 168 196 224 252 280	0.5 2 3 4 6 12
Weaver <i>et al.</i> , 1984*	Silt, loam	Arsenite	6 weeks	Pot trial	Growth	Bermuda-grass	0 10 45	0 2 6
	Fine, Sandy	Arsenite	arsenite	Pot trial	Growth	Bermuda-grass	0 10 45	2 6 20
	Black Clay	Arsenite	6 weeks	Pot trial	Growth	Bermuda-grass	0 10 45	2 6 20
Yeates <i>et al.</i> , 1994	Silt, Loam	Historically contaminated with CCA	35 days	Field trial	Growth	Rye-grass	12 161 469 790 4.9 64	1 3.5 5.7 11.1 0.2 2.45
Marin <i>et al.</i> , 1993	Silt, Loam			Plant microcosm	Growth	Rice		
Merry and Alston, 1986		Historically contaminated orchard soil – loam soil	10 weeks	Pot experiment	Growth	Radish – tops Radish – roots Silver beet	26	1.5 1 0

*concentration in edible part of plant only or herbage

Continued ...

Table 2 / 4 Data from toxicity tests with As on terrestrial plants

Reference	Soil type	Compound	Time	Experiment type	Parameter	Species	Concentration in soil (mg/kg)	Corresponding concentration in plant (mg/kg)
		Historically contaminated orchard soil – loam soil				Radish – tops Radish – roots Silver beet	120	3 4 4
		Soil from existing orchard – sandy soil				Radish – tops Radish - roots Silver beet	85	5 6 4
		Soil from existing orchard – loam soil				Radish – tops Radish – roots Silver beet	95	4 3 2
		Spiked with 125 mg/kg As – loam soil				Radish – tops Radish – roots Silver beet	125	No growth
		Spiked with 125 mg/kg As – sandy soil				Radish – tops Radish – roots Silver beet	125	40 80 16
		anthropogenically contaminated soil (mining) – sandy soil				Radish – tops Radish - roots Silver beet	260	40 25 13

Continued ...

Table 2 / 5. Data from toxicity tests with As on terrestrial plants

Reference	Soil type	Compound	Time	Experiment type	Parameter	Species	Concentration in soil (mg/kg)	Corresponding concentration in plant (mg/kg)	
Grant and Dobbs, 1977		Naturally contaminated soil – loam soil				Radish – tops	140	2	
						Radish - roots		2	
						Silver beet		0.6	
	Potting compost			Until seeding	Pot experiment	Growth	Dwarf French	14	0.02
								10	0.02
								24	0.29
								200	-
								1700	-
							Carrots	14	0.05
								10	0.04
	24	0.11							
	200	1.94							
	1700	-							
Woolson, 1973	Loamy, sand	Sodium arsenate	Grown until ripe	Pot experiment	Growth	Tomatoes	14	0.08	
							10	0.06	
							24	0.14	
							200	0.20	
							1700	-	
	Silty, clay, loam	Sodium arsenate	Grown until ripe	Pot experiment	growth	Green bean	50	Not measured	
						Lima bean	100	Not measured	
						Spinach	50		
						Cabbage	500		
						Tomato	500		
						Radish	50		

Continued ...

Table 2 / 6. Data from toxicity tests with As on terrestrial plants

Reference	Soil type	Compound	Time	Experiment type	Parameter	Species	Concentration in soil (mg/kg)		Corresponding concentration in plant (mg/kg)
Covey <i>et al.</i> , 1981	Clay, loam	Sodium arsenate	Grown until ripe	Pot experiment	Growth	Green bean	0-10		Not measured
						Lima bean	0-10		
						Spinach	0-10		
						Cabbage	0-10		
						Tomato	50		
						Radish	0-10		
Woolson <i>et al.</i> , 1973	Volcanic soil	Arsenate	55 days	Pot experiment	Growth	Corn	0-50		
						Oats			
Sheppard <i>et al.</i> , 1982	Silty, clay, loam	Sodium arsenate	4 weeks	Pot experiment	Growth	Corn	10-100		
						Oats	0-10		
						Corn	10-100		
						Oats	0-10		
Sheppard <i>et al.</i> , 1982	Loamy, sand	Sodium arsenate	4 weeks	Pot experiment	Growth	Pine	0		0.43
							15		-
							30		-
							60		0.6
							120		4.4
							250		98.6
							500		1770
							1000		9730
							0		3.4
							15		8.0
							30		16.0
							60		31.0
							120		62.0
							250		62.0
	500		1110						
	1000		3240						
Sheppard <i>et al.</i> , 1982	Sand	Sodium arsenate	29 days (tomato) 1 year (pine seedlings)	Pot experiment	Growth	Radish	0		0.53
							15		8.5
							30		8.5
							60		14.0
							120		58.0
							250		-
	500		-						
	1000		-						

Variability of metal toxicity data

The levels of soil As reported to be toxic to plants reported in Table 2, are highly variable, span a broad range, and overlap with levels reported to be background, no-effect and beneficial (Sheppard, 1991). In principle there are two factors which may contribute to the variability between studies: (1) factors which affect the toxicity of As, (or As bioavailability) and (2) differences in sensitivity of the plant species (Giller *et al.*, 1998).

Factors that control the bioavailability of As are largely determined by the following factors:

- Soil pH

- Soluble iron, aluminium, and manganese

- Presence of iron-, aluminium-, and manganese-containing minerals

- Available calcium and calcium minerals

- Amount of organic matter

- Activities of micro-organisms

- Presence of competing ions

The outcome of toxicity tests with As are highly dependent on the way the test plants are exposed. In many studies a “worst case scenario” has been applied in which a sensitive plant species, such as bean, are used, and the As is added to soil in the form of a metal salts. This approach is simplistic in that it bears little resemblance to most real-life contamination of soils, where metal concentrations are gradually built up over a large number of years, and where the metals are well-equilibrated with the surrounding soil (Giller *et al.*, 1998). When the chemical is added as a salt immediately before the test is started (in many cases in the form of the more phytotoxic arsenite), toxic effects will almost certainly be higher than in contaminated field sites or experiments where As is allowed to adsorb to the soil particles before the start of the experiment (Scott-Fordsmand and Pederson, 1995). This was demonstrated in the extensive risk assessment carried out by the US EPA (1995) Guidelines for Heavy Metals in Biosolids. The EPA found that when pure metals were added to soils, a linear response of plant uptake occurred (i.e. as the concentration of metals salts increased in the soil, the concentration of metals increased in the plants). However, in contrast, a plateau response in plant uptake occurred when plants were grown in soil-biosolids mixtures, because the adsorptive materials in the biosolids decreased metal bioavailability to plants. There is some evidence to suggest that As residues become less bioavailable to plants with time in soil, as the As becomes bound to soil particles. Jiang and Singh (1994) found that As concentrations in rye-grass and barley were significantly correlated with As application rates in soil, when the As was applied in the form of soluble salts. However, by the second and third year of the experiment this correlation did not hold true. This suggested that As availability to crops decreased over the years due to its fixation in soils (adsorption and other reactions discussed above) with time. Merry *et al.* (1986), looked at As uptake in radish and silver beet in the following As contaminated soils: two former orchard soils, two current orchard soils, two dosed soils (lead arsenate), one mine-site soil, and one soil with naturally

high As content. As uptake (in the form of arsenate) and toxicity was highest in the dosed soils, and indeed in one of these, no plant growth was seen at all. The lowest As uptake was in the former orchard soils and in the soil with naturally high As concentrations. These results would again suggest that 'aged' As residues are less available for plant uptake. In addition, many studies use pot trials, and there is some concern that pot trials also accentuate phytotoxic effects of As. This is because the conditions prevailing in pots, e.g., plant root confinement, elevated soil temperatures, a rapidly changing water environment due to evaporation and transpiration, tend to increase the uptake of pollutants by plants compared to what occurs under field conditions (US EPA, 1995). Thus care must be taken when using experimental data from pot experiments where metals have been added as salts, because results may not reflect the TRUE As availability to plants.

- **Levels of soil As reported to be toxic to plants, are highly variable, span a broad range and overlap with levels reported to be background, no-effect and beneficial**
- **Outcome of toxicity tests with As are highly dependent on the way the test plants are exposed**
- **When metal salts and pot trials are used the bioavailability of As may have an un-quantified safety factor built into it.**

Relationship between plant and total soil concentrations of As

It is evident from Table 2 that there is no simple relationship between total soil concentrations of As, and plant uptake. Sheppard (1991) carried out an extensive comparison of phytotoxic levels of soil As from 44 studies. It was found that there was no significant correlation between soil-As level and either the degree of effect or the plant-As concentration. However, this is the measure normally used to establish Soil Quality Criteria. A full assessment of assumptions made in the risk assessments in the timber treatment guidelines will be presented in the final report.

Perhaps a more realistic measure of the bioavailability of arsenic to plants would be measure soil solution arsenic concentrations. Table 3 contains reports of the soil solution concentration of As causing deleterious effects (usually yield reduction) on plant species, and plant uptake (concentrations in edible part of plant).

Table 3. Data from toxicity tests with bioavailable As on terrestrial plants

Reference	Soil type	Compound	Time	Experiment type	Parameter	Species	Toxic concentration soil (mg/kg)	Toxic concentration in soil solution (mg/L)	Corresponding concentration in plant (mg/kg)
Grant and Dobbs, 1970	Potting compost		Until seeding	Pot experiment	Growth	Dwarf French Beans Carrots Tomatoes	24 24 1700	10 10 270	0.29 0.11 no growth
Jacobs and Keeney, 1970	Sand	Sodium arsenate	40 days	Pot experiment	Growth	Corn	80	35	7.9
	Silt, loam		40 days	Pot experiment	Growth	Corn	80	4.5	2.2
Lee <i>et al.</i> , 1982	Sediment – flooded environment	Historically contaminated		Pot experiment	Growth	Marsh grass	320	11	131
	Sediment – upland environment	Historically contaminated		Pot experiment	Growth	Marsh grass	320	1.5	37.2
Davis <i>et al.</i> , 1978	Sand culture	Sodium arsenate	5 leaf stage	Pot experiment	Growth	barley		20	4
Carbonell-Barrachina <i>et al.</i> , 1997	Nutrient solution	Sodium arsenite	44 days	Pot experiment	Growth	Bean (fruit)		5	3
Carbonell-Barrachina <i>et al.</i> , 1995	Nutrient solution	Sodium arsenite	Fruit ripening	Pot experiment	Growth	Tomato (fruit)		2	0.14

Conclusions

Salts of copper, chromium and As (CCA) have been used in New Zealand for the preservation of wood. The treatment sites can become highly contaminated with these metals, especially arsenate.

The toxicity of As compounds depends on a number of factors, including the chemical form present. In well-aerated soils at "equilibrium", inorganic **arsenate** is expected to predominate, and its chemistry is very similar to that of phosphate.

One of the most important factors affecting the bioavailability of arsenate to plants is soil type. Both the amount of clay and the nature of clay minerals control arsenate adsorption in soils. Iron, Al and to a lesser extent Mn oxides are important soil constituents in controlling soil solution concentrations of As.

Arsenate is adsorbed by plant roots via the high-affinity transport system for phosphate, and phosphate competitively inhibits As uptake. Unlike phosphate, translocation of As to shoots is generally low, however, and the root is the primary site of injury when As reaches phytotoxic levels. Consequently aerial parts are typically low in As and crop damage and even failure is usually expected before tissue As levels are a concern for human health.

References

- Arsenault, R.D. 1975. CCA-treated wood foundations a study of permanence, effectiveness, durability and environmental considerations. *American Wood Preservatives Association*. 126-149.
- Asher, C.J. and Reay, P.F. 1979. Arsenic uptake by barley seedlings. *Australian Journal of Plant Physiology*. **6**, 459-466.
- Bhumbla, D.K. and Keefert, R.F. 1994. Arsenic mobilisation and bioavailability in soils. *In Arsenic in the Environment: Part 1. Cycling and Characterisation*. Edited by Nriagu, J.O. John Wiley and Sons, Canada, pp 51-118.
- Brady, N.C. 1974. *The Nature and Properties of Soils*. Macmillan Publishing Co., Inc, New York.
- Carbonell Barrachina, A.A.; Burlo-Carbonell, F. and Mataix-Beneyto, J. 1997. Arsenic uptake, distribution, and accumulation in bean plants: Effect of arsenite and salinity on plant growth and yield. *Journal of Plant Nutrition*. **20**, 1419-1430.
- Carbonell Barrachina, A.; Burlo Carbonell, F. and Mataix Beneyto, M. 1995. Arsenic uptake, distribution and accumulation in tomato plants: Effect of arsenite on plant growth and yield. *Journal of Plant Nutrition*, **18**: 1237-1250.
- Chen, C-J and Lin, L-J. 1994. Human carcinogenicity and antherogenicity induced by chronic exposure to inorganic arsenic. *In Arsenic in the Environment. Part II: Human Health and Ecosystem Effects*, Edited by O'Nriagu, J.O. John Wiley and Sons, Inc. New York, pp 109-131.

- Cheng, C.N., and Focht, D.D. 1975. Production of arsine and methylarsines in soil and in culture. *Applied and Environmental Microbiology*. **38**, 494-498.
- Chilvers, D.C. and Peterson, P.J. 1987. Global cycling of arsenic. *In* Lead, Mercury and Arsenic in the Environment. Edited by Hutchinson, T.C. and Meema, K.M. John Wiley and Sons Ltd, Great Britian. pp 280-301.
- Covey, R.P.; Koch, B.L. and Larsen, H.L. 1981. Influence of vesicular arbuscular mycorrhizae on the growth of apple and corn in low-phosphorous soil. *Ecology and Epidemiology*. **71**, 713-715.
- Cullen, W.R. and Reimer, K.J. 1989. Arsenic speciation in the environment. *Chemical Reviews*. **89**, 713-764.
- Davis, R.D.; Beckett, P.H.T. and Wollan, E. 1978. Critical levels of twenty potentially toxic elements in young spring barley. *Plant and Soil*. **49**, 395-408.
- Deul, L.E. and Swoboda, A.R. 1972. Arsenic toxicity to cotton and soybeans. *Journal of Environmental Quality*. **1**, 317-320.
- Dickens, R. and Hiltbold, A.E. 1967. Movement and persistence of methanearsonate in soil. *Weed Science*, **15**, 299-304.
- Giller, K.E.; Witter, E. and McGrath, S.P. 1998. Toxicity of heavy metals to micro-organism and microbial processes in agricultural soils: A review. *Soil Biology and Biochemistry*. **30**, 1389-1414.
- Goldberg, S. 1986. Chemical modelling of arsenate adsorption on aluminium and iron oxide minerals. *Soil Science Society*. **50**, 1154-1157.
- Goldberg, S. and Glaubig, R.A. 1988. Anion sorption on a calcareous, montmorillonitic soil-arsenic. *Soil Science Society*. **52**, 1297-1300.
- Grant, C. and Dobbs, A.J. 1977. The growth and metal content of plants grown in soil contaminated by a copper/chrome/arsenic wood preservative. *Environmental Pollution*. **14**, 213-226.
- Harper, M. and Haswell, S.J. 1988. A comparison of copper, lead and arsenic extraction from polluted and unpolluted soils. *Environmental Technology Letters*. **9**, 1217-1280.
- Jacobs, L.W. and Keeney, D.R. 1970. Arsenic – Phosphorous interactions in corn. *Soil Science and Plant Analysis*. **1**, 85-93.
- Jiang, Q.Q. and Singh, B.R. 1994. Effect of different forms and sources of arsenic on crop yield and arsenic concentration. *Water, Air and Soil Pollution*. **74**, 321-343.
- Jones, C.A.; Inskeep, W.P. and Neuman, D.R. 1997. Arsenic transport in contaminated mine tailings following liming. *Journal of Environmental Quality*. **26**, 433-439.
- Jonnalagadda, S.B. and Prasada Rao, P.V.V. 1993. Toxicity, bioavailability and metal speciation. *Comparative Biochemistry and physiology*. **106C**, 585-595.
- Lee, C.R.; Folsom, B.L. and Engler, R.M. 1982. Availability and plant uptake of heavy metals from contaminated dredged material placed in flooded and upland disposal environments. *Environment International*. **7**, 65-71.
- Livesey, N.T. and Huang, P.M. 1981. Adsorption of arsenate by soils and its relation to selected chemical properties and anions. *Soil Science Society*, **131**. 88-94.

- Loebenstein, J.R. 1994. The materials flow of arsenic in the united states <note> information circular/1994 (final). Bureau Of Mines, Washington, Dc. Div. Of Mineral Commodities, United States Department of the Interior. BUMINES-IC-9382.
- Lund, U. and Fobain, A. 1991. Pollution of two soils by arsenic, chromium and copper, Denmark. *Geoderma*. **49**, 83-103.
- Marin, A.R.; Masscheleyn, P.H. and Patrick, Jr. 1993. Soil redox-pH stability of arsenic species and its influence on arsenic uptake by rice. *Plant and Soil*, **154**, 245-253.
- McLaren, R.G. and Cameron, K.C. 1996. Soil Science. Sustainable Production and Environmental Protection. Oxford University Press, Auckland.
- McLaughlin, M.J.; Parker, D.R. and Clarke, J.M. 1999. Metals and micronutrients – food safety issues. *Field Crops Research*. **60**, 143-163.
- Meharg, A.A. and Macnair, M.R. 1990. An altered phosphate uptake system in arsenate tolerant *Holcus lanatis* L. *New Phytology*, **116**, 29-35.
- Meharg, A.A. and Macnair, M.R. 1991. Uptake, accumulation and translocation of arsenate in arsenate-tolerant and non-tolerant *Holcus lanatus* L. *New Phytology*. **117**, 225-231.
- Merry, R.H.; and Alston, A.M. 1986. The effects of soil contamination with copper, lead and arsenic on the growth and composition of plants. *Plant and Soil*. **95**, 255-269.
- Merry, R.H.; Tiller, K.G. and Alston, A.M. 1983. Accumulation of copper, lead and arsenic in some Australian orchard soils. *Australian Journal of Soil Research*. **21**, 549-561.
- Ministry of Health. (1997). Food and nutrition guidelines for healthy children aged 2-12 years. A background paper. Wellington: Ministry of Health.
- Mitchell, P. and Barr, D. 1995. The nature and significance of public exposure to arsenic: a review of its relevance to South West England. *Environmental Chemistry and Health*. **17**, 57-82.
- Moore, M.R.; Ng, J.C. and Lewis, R.J. 1998. Environmental Poisoning: Presentation and Management. *Therapeutic Drug Monitoring*. **20**, 502-509.
- Naidu, R.; Bolan, N.S.; Kookana, R.S. and Tiller, K.G. 1994. Ionic-strength and pH effects on the sorption of cadmium and the surface charge of soils. *European Journal of Soil Science*, **45**, 419-429.
- O'Neill, O. 1990. Arsenic. In *Heavy Metals in Soils*. Edited by Alloway, B.J. John Wiley and Sons, New York. Pp. 83-89.
- Onken, B.M. and Adriano, D.C. 1997. Arsenic availability in soil with time under saturated and subsaturated conditions. *Soil Science Society of America Journal*. **61**, 746-752.
- Onken, B.M. and Hossner, L.R. 1995. Plant uptake and determination of arsenic species in soil solution under flooded conditions. *Journal of Environmental Quality*. **24**, 373-381.
- Otte, M.L. and Ernst, W.H. 1994. Arsenic in vegetation of wetlands. In *Arsenic in the Environment. Part I: Cycling and Characterisation*, Edited by O'Nriagu, J.O. John Wiley and Sons, Inc. New York, pp 365-380.
- Regulation 257 of the Consolidated Food Regulations 1984. New Zealand Ministry of Health.
- Report to the Air Resources Board on Inorganic Arsenic. Part B Health Effects of Inorganic Arsenic Compounds. 1990. Prepared by the staff of the Air Toxicology and Epidemiology Section Hazard Identification and Risk Assessment Branch Department of Health Services.

- Sakata, M. 1986. Adsorption of arsenic (III) and boron by soils. Criepe report for Central Research Institute of Electric Power Industry.
- Scott-Fordsmand, J.J. and Pederson, M.B. 1995. Soil Quality Criteria for selected inorganic compounds. Report for Ministry of Environment and Energy, Denmark.
- Scott-Fronsmand, J.J. and Bruus Pederson, M.B. 1995. Soil quality criteria for selected inorganic compounds. Working Report No. 48, for The Ministry of Environment and Energy, Denmark. Danish Environment Protection Agency.
- Sheppard, M.I.; Sheppard, S.C. and Thibault, D.H. 1982. Identification of the problem phytotoxicant in soil from a radioactive waste disposal area. Atomic Energy of Canada Limited, Pinawa, Mantioba, Report WNRE-461.
- Sheppard, S.C. 1992. Summary of phytotoxic levels of soil arsenic. *Water, Air and Soil Pollution*. **64**, 539-550.
- Smith, E.; Naidu, R. and Alston, A.M. 1998. Arsenic in the soil environment: A Review. *Advances in Agronomy*, **64**: 149-195.
- Smith, E.; Naidu, R. and Alston, A.M. 1998. Arsenic in the soil environment: A review. *Advances in Agronomy*. **64**, 149-195.
- Smith, E.; Naidu, R. and Alston, A.M. 1999. Chemistry of arsenic in soils: I. Sorption of arsenate and arsenite by four Australian soils. *Journal of Environmental Quality*. **28**, 1719-1726.
- Steevens, D.R.; Walsh, L.M. and Keeney, D.R. 1972. Arsenic phytotoxicity on a plainfield sand as affected by ferric sulfate or aluminium sulfate. *Journal of Environmental Quality*. **1**, 301-303.
- Tamaki, S. and Frankernberger, W.T. 1992. Environmental biochemistry of arsenic. *Reviews of Environmental Contamination and Toxicology*. **124**, 79-110.
- Thom, N.G. 1975. Recommended treatment method for arsenic timber treatment wastes prior to disposal by landfilling. National Environmental Chemistry and Acoustics laboratory, Department of health.
- Thunabalasingam, P. and Pickering, W.F. 1986. *Environmental Pollution Series B*, **12**, 233-246.
- United States Environmental Protection Agency, 1995. A Guide to the Biosolids Risk Assessment for the EPA Part 503 Rule.
- United States Environmental Protection Agency. 1988. Risk assessment forum, special report on ingested arsenic: skin cancer; nutritional essentiality. EPA/3-87/013.
- United States Environmental Protection Agency. 1999. Toxicological Profile for Arsenic. Draft for Public Comment.
- Vannoort, R.; Cressey, P. and Silvers, K. 2000. 1997/98 New Zealand, Total Diet Survey. Part 2 : ELEMENTS - Selected Contaminants & Nutrients. Prepared as part of a Ministry of Health.
- Vannoort, R.; Cressey, P. and Silvers, K. 2000. 1997/98 New Zealand Total Diet Survey Part 2 : ELEMENTS - Selected Contaminants & Nutrients. Prepared as part of a Ministry of Health contract for scientific services.

- Verkleij, J.A.C. and Schat, H. 1990. Mechanisms of metal tolerance in higher plants. *In* Heavy Metal Tolerance in Plants: Evolutionary Aspects. Edited by Shaw, A.J. CRC Press.
- Waychunas, G.A.; Rea, B.A.; Fuller, C.C. and Davis, J.A. 1993. Surface chemistry of ferrihydrite: Part I. EXAFS studies of the geometry of co-precipitated and absorbed arsenate. *Geochem. et Cosmochim Acta*, **57**, 2251-2269.
- Waychunas, G.A.; Fuller, C.C.; Rea, B.A. and Davis, J.A. 1996. Wide-angle X-ray scattering (WAXS) study of "two-line" ferrihydrite structure: Effect of arsenate sorption and counter ion variation and comparison with EXAFS results. *Geochem. et Cosmochim Acta*, **60**, 1765-1781.
- Weaver, R.W.; Melton, J.R.; Wang, D. and Doble, R.L. 1984. Uptake of arsenic and mercury from soil by Bermudagrass *Cynodon dactylon*. *Environmental Pollution*. **33**, 133-142.
- WHO. (1981). Arsenic. Environmental Health Criteria No. 18. Geneva: World Health Organization.
- Wiersma, D.; Van Goor, B.J. and Van der Veen, N.G. 1986. Cadmium, lead, mercury, and arsenic concentrations in crops and corresponding soils in the Netherlands. *Journal of Agriculture and Food Chemistry*. **34**, 1067-1074.
- Woolson, E.A. 1973. Arsenic phytotoxicity and uptake in six vegetable crops. *Weed Science*. **21**, 524-527.
- Woolson, E.A.; Axley, J.H. and Kearney, P.C. 1973. The chemistry and phytotoxicity of arsenic in soils: II. Effects of time and phosphorous. *Soil Science Society of America Proceedings*. **37**, 254-259.
- Yeates, G.W.; Orchard, V.A.; Speir, T.W.; Hunt, J.L. and Hermans, M.C.C. 1994. Impact of pasture contamination by copper, chromium, and arsenic timber preservative on soil biological activity. *Biology and Fertility of Soils*. **18**, 200-208.