# The Accumulation of Copper, Lead and Arsenic in Orchard Soils and its Effects on Plants

A thesis submitted by

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# SUMMARY

The objectives of this work were to assess the extent and consequences of the accumulation of copper, lead and arsenic from sprays in the soils of apple and pear orchards in Australia. In field investigations, the concentrations of copper, lead and arsenic in surface soils and their re-distribution throughout the soil profile were studied, as well as the seasonal variation in their uptake by pasture plants. Glasshouse pot experiments were used to assess the effects of soil temperature, pH, waterlogging and fertilizers on the growth and content of vegetables.

The area of Australia on which apple and pear trees are grown has declined rapidly since 1970 and is now estimated to be less than half of the post-war peak of approximately 50000 ha. This decline in area was caused by declining profitability and losses of traditional markets in Europe and was accelerated by the Fruitgrowing Reconstruction Scheme (1972-6) which encouraged growers to clear or partial fell unprofitable orchards. Orchard soils have accumulated residues from copper-containing and lead arsenate sprays over many decades. The extent of accumulation of copper, lead and arsenic in soils, and their possible effects on agricultural activities following tree removal have not been investigated in Australia.

A number (98) of surface soils were sampled from orchards or former orchard areas in South Australia and Tasmania. The copper, lead and arsenic concentrations exceeded 300, 550 and 100 $\mu g\ g^{-1}$, respectively, which are 20 to 30 times the concentrations usually found in uncontaminated soils. Copper and lead extracted by DTPA and EDTA were linearly correlated with total concentrations. The ratios of lead to arsenic in the surface soils, when compared to the ratio in lead arsenate spray, suggested that losses of arsenic had occurred, especially in the Tasmanian soils. Examination of a series of soil profiles from the Huonville area confirmed that substantial leaching of arsenic occurs in coarse textured soils relative to lead and copper which were both retained in the top 25 cm of the orchard soils. Data are also presented for a representative soil profile from the Mt. Lofty Ranges near Adelaide which suggested that an additional mechanism for loss - as volatile organic arsenic compounds - may occur in these soils.

Pasture plants growing on former orchard soils were sampled from near Adelaide and Huonville and were found to have higher than normal concentrations of copper, lead and arsenic. The copper concentrations of the plants sampled near Adelaide varied with species and occasion of sampling, many being in excess of 30-40 $\mu g\ g^{-1}$. The lead concentrations of the plants were usually less than 5 $\mu g\ g^{-1}$ despite high concentrations in the soil, although *Actotheca calendula*, which grew on a soil with a lead mineralization, contained up to 75 $\mu g\ g^{-1}$. The arsenic concentrations of the plants were low (usually about 0.5 $\mu g\ g^{-1}$), but marked increases in concentration to about 2 $\mu g\ g^{-1}$ occurred in all species at the end of the growing season. The copper, lead and arsenic concentration of the tops of *Trifolium repens* and *Lolium perenne* sampled in the Huonville area differed little from what might be expected from plants grown on uncontaminated soils and showed no relationship with the total concentration of the elements in the soils.

In a pot experiment, it was shown that increasing the soil temperature of an orchard soil and a mineralized soil from 12°C to 22°C resulted in increases in yield and in the concentration of copper, lead and arsenic in the tops of subterranean clover, silver beet and radish. Small but significant increases were also observed in copper and lead concentration of radish roots grown in the orchard soil.

The pH of eight soils (four orchard soils, two dosed with lead, arsenic and copper, and two affected by mining or mineralization) was modified by treatment with sulphur, gypsum or calcium carbonate. Silver beet and radish were grown. The effects of the treatments on the copper and lead contents of the plants were largely attributable to pH and it was found that the concentrations in the plants decreased with increasing pH whereas the concentration of arsenic in the plants was usually much less sensitive to soil pH. Visual symptoms of toxic effects usually occurred only on the most acidified treatments and were more likely to be attributable to other elements such as manganese or aluminium than to the elements being studied. The results suggested that DTPA extracts for copper and lead are not suitable for use on contaminated soils in situations where pH changes occur. An additional "prior-waterlogging" treatment resulted in no consistent effects on plant growth or composition.

The response of silver beet grown on two orchard soils to fertilizer phosphorus, sulphur or nitrogen was investigated in pot experiments. The effects observed were usually small, but beneficial in decreasing the concentrations of copper, lead and arsenic in the plants. Nitrogen applications may have a more marked effect in decreasing the arsenic concentration of silver beet.

The most serious consequence of the accumulation of copper, lead and arsenic appears to be the possibility of chronic copper toxicity to sheep grazing pastures established on orchard soils. Some risk may also be presented to horses if sufficient lead is ingested as soil contamination of fodder. The arsenic concentration of silver beet and radish grown on soils containing 95-120 $\mu g\ g^{-1}$ of total arsenic may approach the current health limit for humans and it is this element which has the least margin for safety. The copper, and possibly the lead concentrations of vegetables grown on orchard soils are unlikely to exceed the established health limits.

# Statement

This thesis contains no material that has been accepted for the award of any other degree or diploma in any university, and, to the best of my knowledge and belief, it contains no material previously published or written by another person, except when due reference is made in the text.

Richard Hugh Merry.

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# 1.0 INTRODUCTION

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Increases in the occurrence of toxic metals in the environment have led to concern for human health and for production losses due to detrimental effects on animals, plants and soils. Contamination from industrial and urban sources is well known and is frequently reported. Agricultural practices, especially the spraying of crops with pesticides and fungicides, are also sources of toxic compounds, both organic and inorganic, which have a high potential to gain entry into food products.

There has been a long history of the use of fungicidal sprays containing copper on crops such as grapes and pome, stone and citrus fruit. Toxic effects associated with copper were reported from Florida (citrus) and France (grapes) mainly between 1940 and 1960. Although the toxicities observed clearly involved copper, the reports implicated soil acidity along with high soil copper accumulations as the principal cause.

Widespread use of both Bordeaux mixture and lead arsenate sprays began about 90 years ago. Reports of toxic effects of lead arsenate on apple trees, although not well documented and disputed at the time, appeared in North America after less than 20 years of use. Many further reports of toxic effects attributed to lead arsenate appeared in North America between 1930 and 1950, especially associated with difficulties in growing new crops on areas where pome fruit orchards had recently been removed. Lead was discounted as a cause quite early in the associated investigations.

Although reports of high concentrations of copper, lead and arsenic in soils resulting from agricultural activities have come from many countries, no estimates have been made of the proportion of orchard or vineyard soils which may have been detrimentally affected. This makes it difficult to gauge the full extent of the problems discussed in the literature. Although residence times of copper, lead and arsenic in surface soils may be very long, earlier reports of toxic effects have not been sustained. This is despite continued widespread use of sprays containing copper. The use of lead arsenate declined drastically over the past 20 years as a result of the use of alternative organic chemicals (such as DDT) and more recently in Australia due to export regulations.

No Australian reports of toxicity problems related to soils or plants due to sprays containing copper, lead or arsenic have appeared in the literature. This does not mean that detrimental effects do not or will not occur and suggests that the situation has not been investigated in this country.

There has been a large decrease in the area devoted to orchards in Australia over the past 15 years because many traditional markets for apples and pears have been lost. Due to the subsequent restructuring of the industry, many former orchard soils are being used for other purposes such as grazing, vegetable growing and urban development. These soils are an important resource because they are usually suitable for intensive agriculture and have often received large inputs of fertilizer. They are often located close to or within urban areas.

The aims of this work are:

(a) to review the literature on the accumulation and effects of copper, lead and arsenic in the soil-plant system,

(b) to estimate the area of soils in Australia which were formerly apple and pear orchards and are now being put to other uses,

(c) by field sampling, to investigate the accumulation of copper, lead and arsenic in surface soils and the redistribution of these elements within orchard soil profiles, and

(d) to investigate some of the effects of the soil accumulations on the agricultural activities which may follow tree removal. Specifically included are:

- studies of the uptake of the elements by pasture species in grazing situations, and
- assessment, by means of glasshouse pot experiments, of the effects of soil temperature, pH, waterlogging and fertilizers on the growth and content of copper, lead and arsenic of two vegetable species.

With respect to these latter aims, some comparison is made with soils affected by ore mineralization and mining activities.

# 2.0 LITERATURE REVIEW

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## 2.1 Introduction

In recent years, studies of toxic materials in the environment have received more attention than previously because of greater recognition of their implication in problems of human health and behaviour, and in a less emotive context, because of economic losses to the agricultural industry. Copper, lead and arsenic, where they occur in soils, waters and plants at higher than normal concentrations, are considered here in relation to their entry into food chains. Other modes of uptake exist, for example the breathing of polluted air in urban and industrial environments.

The widespread use of organic pesticides and herbicides, some of which contain arsenic and toxic metals, periodically comes into question. Population pressure and economic necessity require that agriculture be highly productive, which at present leaves little alternative to the continued use of some of these substances. Potentially undesirable effects should be minimized since a multitude of contributing sources may act to place an increasing burden on the ultimate biological recipients and it is unlikely that animals and plants can adapt at rates which would be sufficient to cope.

Huisingh (1974) reviewed the implications of toxic metals in agriculture and has made general recommendations for research in this area. These include improved understanding of the mechanisms of mobilization of metals such as lead, copper and arsenic into agricultural products, management practices for the amelioration of adverse effects, and the investigation of long-term exposure and subclinical effects on micro-organisms, plants and animals.

Since the effects of acute metal toxicity in plants and animals are usually starkly evident and counter measures can be taken rapidly, the recommendations of Huisingh (1974) have some relevance to agricultural management practices where, for example, toxic metals may accumulate and equilibrate in soils over periods of many years. Subclinical effects and interactions may be more far-reaching in consequence and correspondingly more difficult to prove. Koshal and Koshal (1973), for instance, constructed a statistical model based on levels of air pollution and other sociological factors for forty United States cities which enabled estimates to be made of their contribution to mortality rates. They concluded that the cost of a 50% reduction in air pollution would be far outweighed by the benefits such as reduced morbidity and mortality, and reduced damage to buildings. However, it seems that the investment necessary to reduce air pollution in the United States to this extent is unlikely to be made, at least in the short term.

With the multiplicity of toxic substances to which we are exposed daily, the complex interactions with socio-economic and environmental factors and the difficulties of definition and diagnosis of subclinical effects, it would seem that actions leading to better definition and reduction of exposure would be of benefit.

## 2.2 Copper, Lead and Arsenic in the Natural Environment

There is a considerable literature in geochemistry outlining the distributions of the elements in nature. These include the works of Clarke and Washington (1924), Goldschmidt (1958), Mason (1958), Hawkes and Webb (1962), and Bowen (1966). They present periodic upgrading and revision of accumulated analytical data. A more recent and comprehensive coverage has been provided by the 'Handbook of Geochemistry' (executive editor, K.H. Wedepohl, 1969-78). Much of the geochemical information presented here is from this source and, since a large number of references have been used in this compilation, for the most part only the main contributing authors will be cited.

### 2.2.1 Mineral Forms and Some Geochemical Associations

All three elements, but copper and arsenic in particular, are what are frequently called chalcophiles because of their common association with sulphur in minerals. The main mineral forms of copper are chalcopyrite ($CuFeS_2$) and, to a lesser extent, bornite ($Cu_5FeS_4$). Galena (PbS) and arsenopyrite (FeAsS) are the most common forms of lead and arsenic respectively. Copper and arsenic in particular are also associated with complex sulphosalts. These are minerals with metallic lustre occurring in about 80 known forms which are usually sulphides or arsenides of transition metals i.e. Ag-Pb-Cu-S-As-Sb complexes (Wedepohl 1974a). The complexes are possible because of similarities in properties of the elements. For example, the ionic radii of sulphur (1.04Å) and arsenic (1.15Å) are similar (Baur 1978).

There are about 200 copper minerals, 80 being sulphosalts and a further 70 containing hydroxyl with arsenate, chromate and phosphate anions (Wedepohl, 1974a). Hydroxycarbonates of copper such as azurite $[(Cu_3(CO_3)_2(OH)_2]$ and malachite $[Cu_2CO_3(OH)_2]$ are also common. About 240 minerals containing lead are known, 80 being sulphides or sulphosalts and, like copper, a further 80 contain hydroxyl with sulphate, phosphate and arsenate anions (Wedepohl, 1974b). There are about 200 arsenic containing minerals, 120 being arsenates, 40 being sulphides or sulphosalts, while the remainder are arsenides, arsenites, oxides or alloys (Baur, 1978).

Similarities of the three elements evident in the formation of sulphides and sulphosalts extends to the oxidized minerals mentioned above, though arsenic occurs as an anion and the others as cations. There are very few natural arsenite containing minerals known but there are many acidic, basic, hydrated or anhydrous arsenates of copper, lead, manganese and zinc which, like the sulphides and sulphosalts mentioned above, have low solubility. Arsenate minerals are isostructural with those of containing phosphate and vanadate.

Accordingly phosphate substitution has frequently been observed in arsenate minerals (Baur, 1978). All three elements are found in nature in the elemental form and arsenic is sometimes associated with volcanic sulphur and hot spring waters (Onishi, 1969).

While arsenic has only one natural isotope of significance ($^{75}$As) and copper has two ($^{63}$Cu and $^{65}$Cu), lead has four naturally occurring stable isotopes. Three of these ($^{206}$Pb, $^{207}$Pb and $^{208}$Pb), which account for 50 percent of the abundance of lead, have radio-active parents ($^{238}$U, $^{235}$U and $^{232}$Th, respectively) while $^{204}$Pb has no long lived radioactive parents. Lead isotope ratios are used for dating some rocks and identifying mineral ores (Doe, 1972).

### 2.2.2 Copper, Lead and Arsenic in Rocks and Rock-Forming Minerals

Chalcopyrite and other sulphides are the main forms of copper in rocks and they occur in 75 percent of basaltic and 40 percent of granitic rocks. Copper concentration is often positively correlated with sulphur in rocks and negatively with silicon (Wedepohl, 1974a). Copper is commonly associated with biotite, often in high concentration, but this is usually due to intergrowth of chalcopyrite. The dark minerals in basalt usually contain about 100 $\mu g\ g^{-1}$ of copper and plagioclase 62 $\mu g\ g^{-1}$ (Wedepohl, 1974a).

Lead is common in rock-forming minerals. It has a similar ionic radius to $K^+$, $Sr^{2+}$ and $Ba^{2+}$ and may even substitute for $Ca^{2+}$ and other cations which have smaller radii. Lead is incorporated into silicate minerals, especially potassium feldspars, where concentrations as high as 1.1% have been reported. Mean concentrations of lead in potassium feldspars from pegmatites and granites are 98 $\mu g\ g^{-1}$ and 53 $\mu g\ g^{-1}$ respectively and in mica is 21 $\mu g\ g^{-1}$. Plagioclases and amphiboles contain an average of 19.5 $\mu g\ g^{-1}$ and 15 $\mu g\ g^{-1}$ respectively while olivine and quartz have concentrations of about 1 $\mu g\ g^{-1}$ (Wedepohl, 1974b).

Arsenic is uniformly low in rock-forming minerals with concentrations usually less than 2 µg $g^{-1}$, although it has been found as high as 41 µg $g^{-1}$ in magnetite. Arsenic as $As^{3+}$ and $As^{5+}$ can probably substitute for $Si^{4+}$, $Al^{3+}$, $Fe^{3+}$ and $Ti^{4+}$ (Onishi, 1969).

The average concentrations of copper, lead and arsenic in common rock types are shown in Table 2.1. These values are, for the most part, collected from many sources although few are available for arsenic in sandstones. These values vary slightly from those of Goldschmidt (1958) for example, but are more recent and based on a larger number of samples and perhaps on better analytical techniques. Collections of data specifically from Australian sources are non-existent (Swaine, 1979, personal communication).

### 2.2.3 Copper, Lead and Arsenic Concentrations in Uncontaminated Soils

There are a number of reports containing analytical data for copper, lead and arsenic in soils not affected by contamination. It is difficult to make comparisons of mean values because the analytical method is often described as 'semi-quantitative', and different sampling and averaging procedures have been used (Shacklette *et al.*, 1971). There appear to be few recent reviews of such data from systematically sampled soils. Vinogradov (1959) provides a summary of soil analyses from many parts of the world. It is stated that the average copper, lead and arsenic concentrations in surface soils are 20, 10 and 5 µg $g^{-1}$ respectively. Bowen (1966) gives similar values and states that the usual ranges for uncontaminated soils are 2-100, 2-100 and 0.1-40 µg $g^{-1}$ for the same elements respectively. Shacklette *et al.* (1971) gave arithmetic means (and ranges) for copper and lead of 25 (< 1-300) and 20 (< 10-700) µg $g^{-1}$ respectively for soils of the United States sampled at a depth of approximately 20 cm. It should be noted that recent estimates of averages frequently quote earlier work. For example, Allaway (1968) quotes Bowen (1966) as his source.

Table 2.1 Concentrations of Cu, Pb and As in Rocks

(averages in $\mu g\ g^{-1}$)

| | Cu[1] | Pb[2] | As[3] |
|---|---|---|---|
| Basaltic rocks | 90 | 3.7 | 1.5 |
| Intermediate rocks | 50-55 | 5.8 | 2.1 |
| Granitic rocks | 9 | 23 | 1.6 |
| Sands and sandstones | 25 | 10 | 1† |
| Clays and shales | 35 | 21.6 | 13 |
| Limestones and carbonates | 6 | 5 | 1 |
| Coal | 17 | 10 | - |
| Australian coal[4] | 15 | 10 | 3 |
| Gneisses and schists | 22 | 19.6 | <2† |
| Phosphate rocks | - | - | 21 |
| Upper continental crust[5] | 55 | 12.5 | 1.8 |

Sources:

1. Wedepohl (1974a)
2. Wedepohl (1974b)
3. Onishi (1969)
4. Swaine (1977)
5. Taylor (1964)

† based on limited data

Yet both Bowen (1966) and Hawkes and Webb (1962) quote Vinogradov (1959) and Swaine (1955).

No thorough compilations of data on copper, lead and arsenic have been published for Australian soils. Table 2.2 presents some data for agricultural soils from south-eastern Australia (Merry and Tiller, unpublished). These concentrations were obtained using atomic absorption spectrophotometry following digestion of fine ground soil with nitric and perchloric acids, and the values shown should be only marginally less than total concentrations. A small contribution to these concentrations from fertilizers, copper more so than lead, is to be expected.

Table 2.2 Copper and Lead in Soils from South-Eastern Australia

(surface 0-5 cm, $\mu g\ g^{-1}$)

| | Number | Mean | Range | Number less than detection† |
|---|---|---|---|---|
| Cu | 84 | 13.1 | 3-64 | 0 |
| Pb | 85 | 14.9 | 5-55 | 15 |

† detection limits were 2 and 5 $\mu g\ g^{-1}$ for Cu and Pb respectively.

Table 2.3 presents data obtained in a similar manner to that in Table 2.2 but from an area of about 500 $km^2$ near Adelaide, South Australia. Data for soils which showed evidence of mineralization or contamination from orchard sprays were omitted, but the surface soils may have received small contributions from fertilizers and approximately one third of the samples may have a small accession of lead from motor vehicle exhausts originating in Adelaide. The means shown in Tables 2.2 and 2.3 are arithmetic means since this is the form which is usually quoted by others. It should be noted, however, that the distributions, especially in Table 2.3 are positively skewed so that the modal values are lower than the means presented.

Table 2.3 Copper and Lead in Soils from the Southern Mt. Lofty Ranges, South Australia ($\mu g\ g^{-1}$)

| | Number | Mean | Range | Number less than detection[†] |
|---|---|---|---|---|
| Surface (0-5 cm) | | | | |
| Cu | 178 | 16.0 | 2-55 | 0 |
| Pb | 178 | 20.0 | 5-100 | 1 |
| Subsoil[§] | | | | |
| Cu | 250 | 29.8 | 2-270 | 0 |
| Pb | 250 | 18.3 | 5-200 | 9 |

[†] detection limits were 2 and 5 $\mu g\ g^{-1}$ for Cu and Pb respectively.

[§] the 10 cm interval above decomposing rock or the 90-100 cm interval.

There have been no reports of arsenic concentrations in uncontaminated Australian soils. In the United States, Williams and Whetstone (1940) analysed 68 soils and found that the arsenic concentrations in the surface soils ranged from 0.1 to 38 $\mu g\ g^{-1}$ with a mean of 6.5 $\mu g\ g^{-1}$. About 30% of the samples contained less than 5 $\mu g\ g^{-1}$, 50% contained between 5 and 10 $\mu g\ g^{-1}$, and 20% contained more than 10 $\mu g\ g^{-1}$. The 121 subsoil samples ranged from 0.2 to 41 $\mu g\ g^{-1}$ arsenic with a mean of 7.8 $\mu g\ g^{-1}$. A similar range of values were reported by Swaine (1955) for uncontaminated soils.

### 2.2.4 Copper, Lead and Arsenic in Oceans, Streams and Precipitation

Data for the concentration of the three elements in natural waters have been discussed by Turekian (1969). Because many of the analytical techniques used were considered unreliable, only selected representative data were considered. Turekian (1969) selected 0.9, 0.03 and 2.6 $\mu g\ L^{-1}$ of copper, lead and arsenic respectively as typical concentrations in oceanic waters. Concentrations of about 7, 3 and 2 $\mu g\ L^{-1}$ of the same elements respectively were reported as being representative of stream waters. Few analyses of the elements were available for precipitation, but Turekian (1969) quoted Sugawara (1967, personal communication) as finding 0.8 and 1.6 $\mu g\ L^{-1}$ of copper and arsenic respectively in rainwater from Japan.

## 2.3 Sources of Copper, Lead and Arsenic Contamination in the Environment

### 2.3.1 Contamination from Mining and Smelting

Both copper and lead are metals of great economic importance. As a consequence of the close association of arsenic with these metals in ore minerals, pollution of air, soils, sediments, groundwaters, and streams by one or all of these elements is possible due to spillage, waste dumping, and losses of airborne particles during mining, ore treatment and smelting operations. There have been many recent reports of such occurrences; for example, Goodman and Roberts (1971 Buchauer (1973), Kobayashi *et al.* (1973), Beavington (1973), Porter and Peterson (1975), Temple *et al.* (1977) and Cartwright *et al.* (1977).

Because of the composition of and processes occurring in soils and sediments, they become the most important sinks for polluting metals released into the environment. Factors such as wind speed and direction, and rainfall, control the deposition of airborne pollutants onto the soil surface. Both Little and Martin (1972, 1974) at Avonmouth (United Kingdom) and Cartwright *et al.* (1977) at Port Pirie (South Australia) showed that smelter fallout followed the pattern of prevailing winds and rainfall. The former showed that the rate of deposition increased with lowered windspeeds found downwind from windbreaks, and that in wooded areas there were increased concentrations in the soil due to leaf surface accumulations with eventual incroporation into litter. Cartwright *et al.* (1977) found that concentrations of lead and other metals were increased measurably for distances up to 40 and 65 km from the smelter source. The distribution patterns of polluting elements in the surface soils were reflected by increased concentrations in pasture plants (Merry and Tiller, 1978) and wheat (Merry *et al.*, 1981). Stubbs (1972) noted that ore mining and smelting are generally subject to pollution regulations, and have been for some time, but other activities such as the burning of urban waste, coal, lead alkylated petrol, and cigarettes are either not controlled or have only recently (i.e. in 1972) become subject to regulation. Production of volatile metals, their oxides and halides is common from high temperature processes. The fact remains that, despite current and possible future regulations, large areas of soil and the waters that drain them have been or may become contaminated and present a continuing problem. For instance, Davies and Lewin (1974) described alluvial soil chronosequences resulting from mining activities which took place upstream. In this case, mining began long ago, reached peak production in 1850 and ceased in 1900. Recent alluvium ie. in (1972) still contained anomalously high copper, lead, cadmium and zinc.

### 2.3.2 Contamination from Other Industrial and Urban Sources

Elements which are toxic to humans are continuing causes for concern in urban environments, particularly when the urban areas have concentrations of industrial activity (Warren *et al.*, 1971). An often quoted source of metal pollutants in urban areas is the burning of coal, a practice which is likely to increase in the future. Although the concentration of arsenic in coal is usually low (Swaine, 1977), Goldschmidt (1958) stated that coal ash can contain up to 8000 $\mu g\ g^{-1}$ of the element. Other sources of toxic elements include plating and plumbing works.

City street dusts have been the subject of many studies. Residential and commercial street dusts averaged 1636 and 2413 $\mu g\ g^{-1}$ of lead respectively in 77 cities in the United States (National Research Council, 1972) and Warren *et al.* (1971) quote values up to 6.8% of lead for some Canadian street dusts. Solomon and Hartford (1976) made an intensive study of lead in and around homes and made comparisons with non-residential sites. Lead concentrations in house dusts and the soils adjacent to houses and roads were of the order of hundreds to thousands of micrograms per gram. Although much of the lead in and near houses is attributable to the use of lead-containing paint, which may contain up to 27% lead by weight, the most significant source was emissions from the exhausts of motor vehicles.

Purves (1972) compared the concentrations of toxic elements in urban and non-urban soils and in vegetables. He expressed concern that the general contamination of urban soil (which is largely irreversible), when coupled with increased usage of home gardens for vegetable production, may detrimentally alter the yields and chemical composition of the vegetables. Le Riche (1968) and Purves (1972) found that the use of sewerage sludge leads to higher concentrations of toxic metals in soils and plants. More recently, de Vries and Tiller (1978) reported that increases in metal uptake by vegetables grown in soils with dry sewerage sludge in the glasshouse could not be reproduced on the same neutral to alkaline soils in the field in South Australia. Although this was true for the short term, the field soils were still contaminated by the high concentrations of toxic elements contained in the sludge. This problem of soil contamination would be largely overcome if household and industrial wastes could be separated.

Concentrations of 10 to 70 $\mu g\ g^{-1}$ of arsenic in common household detergents were reported by Angino *et al.* (1970). These may have been a source of arsenic pollution in the Kansas River which received water following sewerage treatment by a process that did not effectively remove arsenic. Other sources of metal contamination in urban areas include lead and copper from the pipes of reticulated water supplies, especially in 'soft' water areas (Moore, 1973).

The accumulation of lead in roadside soils and vegetation has long been known and there is a considerable literature on the subject (for example, Warren and Delavault (1960), Cannon and Bowles (1962), Motto *et al.* (1970), Page *et al.*

(1971), Ward *et al.* (1974), Noller and Smythe (1974) and Solomon and Hartford (1976)). Page *et al.* (1971) comprehensively investigated lead alkyl compounds from motor vehicle exhausts in the air, soils, and 27 crop species in southern California. Traffic volumes of less than 5000 vehicles per day were considered insignificant whereas volumes greater than 35000 per day substantially affected the lead content of crops grown close to roads.

Although it is evident that industrial and urban areas, roadside soils and the environs of smelters are usually heavily contaminated with toxic elements, there is also evidence that low concentrations may be dispersed over much wider areas. For example, Cartwright *et al.* (1977) found that there were measurable increases in lead concentration in surface soils at distances of 40 to 65 km from a smelter and Murozumi *et al.* (1969) associated increased lead in the Greenland icecap dating from the 1930's with the increased usage of lead alkyls in petrol. Davies (1974) showed that the sediments of the continental shelf off New South Wales were contaminated with arsenic to the extent of 50 to 100 $\mu g\ g^{-1}$ in close proximity to urban and industrial areas. Since the arsenic was not related to phosphorus in the sediments, and rocks in the adjacent drainage basins were low in arsenic, he concluded that urban and/or industrial pollution was responsible.

### 2.3.3 Contamination Due to Agricultural Activities

Increased accumulations of copper, lead and arsenic in soils and plants may result from several practices which are commonly used in agriculture. The most important of these, certainly in the past, has been the use of a wide range of organic and inorganic chemicals in pesticide, fungicide and herbicide sprays.

The copper-containing sprays, for which there are many formulations, have been in use since about 1885 (Walker, 1957). In 1882 Professor Millardet, working in Bordeaux, noticed that there was a check in the development of downy mildew when the local vignerons sprayed a mixture of $CuSO_4$ and $CaCO_3$ on grapes to discourage thieves. Although $CuSO_4$ had been used on vines for about 100 years, and the effect of lime in reducing toxicity was also known, it was not until 1885 when Bordeaux mixture (approximately $[Ca(OH)_2]_3.CuSO_4$) was formulated that its use on downy mildew of grapes and numerous other fungal diseases became widespread (Walker, 1957). Bordeaux mixture, copper oxychloride (approximately $Cu(OH)_2.CuCl_2$) and other similar mixtures are still widely used in vineyards, pome fruit, stone fruit, almond, citrus and berry fruit plantings as well as on vegetables such as celery, lettuce and potatoes.

Lead arsenate ($PbHAsO_4$) is the only lead-containing compound used as an insecticide. It was first used as a classic stomach poison in 1892 and has been used to control apple maggots, codling moth, plum cuculio beetles, fruit flies and other chewing insects. According to Lagerwerff (1972), the use of lead arsenate in the United States decreased from $16 \times 10^6$ kg in 1950 to $1.5 \times 10^6$ in 1968, the decline being due to the introduction of DDT. Usage of lead arsenate in the United States was thought by Lagerwerff to be increasing again in reaction to increased awareness of the possible adverse effects of using DDT and other organic compounds. However, commercial use of lead arsenate in Australia declined in the early 1970's and has ceased completely for export crops in response to the requirements of European importers. It is not used commercially in South Australia at the present time.

Apart from lead arsenate, a wide range of arsenical compounds are, or have been used as desiccant herbicides, soil sterilants and insecticides. Paris green (copper aceto-arsenite) and calcium arsenate have been used as pesticides in North America (Walsh and Keeney, 1975; Frank *et al.*, 1976). Arsenites, which are considered more toxic than arsenates, have been used in excessive amounts as desiccant herbicides (Steevens *et al.*, 1972; Rosenfels and Crafts, 1939). The use of sodium arsenite for these purposes has now been banned in the United States (Walsh and Keeney, 1975). Organic arsenic compounds such as methanearsonates have found increasing use as selective herbicides in recent years, their rates of application usually being much lower than those of the inorganic arsenicals (Sachs and Michael, 1971; Hitbold, 1975).

There have been many reports of toxicity problems resulting from the accumulation of lead arsenate and other arsenic-containing compounds in soils. Walsh *et al.* (1977) reported ranges of arsenic concentrations in soils which were frequently of the order of hundreds of $\mu g\ g^{-1}$ and a value as high as 2550 $\mu g\ g^{-1}$ was reported for an orchard soil from Washington State in the United States. This implies a very high concentration of lead since the ratio of lead to arsenic in lead arsenate is about 2.77 : 1. Frank *et al.* (1976) found that lead and arsenic had accumulated up to about 800 and 120 $\mu g\ g^{-1}$ respectively in the top 15 cm of Canadian orchard soils. Mochikuzi *et al.* (1974) reported up to 750 and 250 $\mu g\ g^{-1}$ of lead and arsenic respectively in Japanese orchard soils. There have been no reports in the literature of the concentrations of these elements in Australian orchard soils.

As early as 1909, Headden claimed that collar rot and death of apple trees in Colorado was due to arsenic poisoning. This conclusion was contested by Ball *et al.* (1910) who suggested alternative causes. The total soil arsenic concentrations of up to 69 $\mu g\ g^{-1}$ and water soluble arsenic of 0.7 $\mu g\ g^{-1}$ reported by Headden (1910), insofar as they are correct, do not seem particularly high compared to more recent reports.

Reports of arsenic toxicity which were better substantiated appeared later (Cooper *et al.*, 1931) from South Carolina where calcium arsenate was used to counter the cotton boll weevil. The problems arose when the cotton crops were followed by rice and the soils were waterlogged for up to three months. Reed and Sturgis (1936) investigated a similar problem in Louisiana and suggested that reducing conditions may have encouraged the formation of more toxic arsenites.

After apple tree plantings reached a peak in Washington State in 1919, a decline began in the 1930s and tree removals accelerated after 1934 (Vincent, 1944). Snyder (1935) reported crop failures on recently pulled orchard areas. Vandecaveye *et al.* (1936) noted poor germination of lucerne and poor growth of barley in the field, which they reproduced in pots. They concluded that the problem was due to arsenic and not to lead. Keaton (1937) made a similar observation. Although the soils used by Vandecaveye *et al.* (1936) did not have particularly high concentrations of arsenic (extracted using concentrated nitric acid), the 'readily soluble' (ammonium acetate extractable) arsenic was greater than 4.5 $\mu g\ g^{-1}$ where toxicities were noted.

Vincent (1944) and Jones and Hatch (1945) found that shallow rooted vegetables were more susceptable to arsenic injury than deeper rooted varieties, and survival improved when surface soils were treated or mixed with subsoil to lower the effective arsenic concentration. Further problems arose when peach and apricot trees were planted on arsenic-treated soils. The symptoms were initially attributed to viruses, but Reeves and Hutchins (1940) and later, Lindner (1943) and Thompson and Batjer (1950) confirmed that the cause was arsenic injury. Symptoms, including marginal discolourations, were usually evident on older leaves which eventually developed a 'shothole' appearance. Small fruit and stunting appeared on the more affected trees. The trees usually recovered after a period of years, presumably as deeper root systems developed. Apparently peach and apricot show some sensitivity to arsenic and symptoms appeared when concentrations of arsenic in the leaves exceeded 2 $\mu g\ g^{-1}$ (Lindner, 1943).

Trappe *et al.* (1973) suggested that mycorrhizal development may be adversely affected by high soil arsenic concentrations. This interaction may be responsible for the poor growth of apples, peaches and other species which appear to require mycorrhizal root infection for adequate nutrition and growth.

There have been a number of reports of the accumulation of high concentrations of copper in soils due to fungicides (Delas, 1963). Some examples are shown in Table 2.4. Hirst *et al.* (1961) found up to 2500 $\mu g\ g^{-1}$ of copper in the surface mat of some apple orchard soils in the United Kingdom. They suggested that this high concentration may have detrimentally affected the crumb structure and lowered the worm population of the soil.

Table 2.4 High Concentration of Copper in Some Horticultural Soils Resulting From the Use of Fungicides

| $\mu g\ g^{-1}$ Cu | Use | Reference |
|---|---|---|
| 845 | Vineyard, France | Delas *et al.* (1960) |
| 1280 | Vineyard, Germany | Gärtel (1957) |
| 522 | Hop field, Germany | Rieder and Schwertmann (1972) |
| 250 | Citrus orchard, Florida | Reuther and Smith (1954) |
| 459 | Citrus orchard, South Africa | DuPlessis and Burger (1972) |
| 110 | Apple orchard, Ontario | Frank *et al.* (1976) |
| 700 | Apple orchard, Japan | Mochizuki *et al.* (1975) |

As is the case with arsenic toxicity in the field, there are few well documented reports of the occurrence of copper toxicity. Delas *et al.* (1959) reported three successive crop failures with maize, potato and vetch in a former vineyard soil which had a pH of 4.3 and 170 $\mu g\ g^{-1}$ of exchangeable copper (ammonium acetate, pH 7) in the surface 25 cm. This report followed that of Drouineau and Mazoyer (1953) who noted that copper toxicity in spinach and gladiolus (on former peach orchard soils) increased where sulphur had been used as a fungicide. This caused the soil pH to decrease to below 5. Symptoms of iron deficiency were produced although no difference was found in 'exchangeable' copper between healthy and toxic soils. Plant analyses were apparently typical of the classical copper toxicity produced in solution and pot culture, but no concentrations were quoted. Depardon and Buron (1956) suggested that the failure of cereal crops on former vineyard soils was more likely to have been due to the lowered organic matter, nitrogen and pH rather than copper toxicity.

Hirst *et al.* (1961) reported that despite finding 2500 $\mu g\ g^{-1}$ of copper in surface organic mats in some orchard soils, there was no apparent effect on the trees, although some apple varieties known to be susceptible were avoided when the orchard was replanted. The report by Gibson (1958) of copper toxicity related to a special case where pine seed beds were treated with a large amount of $Cu_2O$ to prevent fungal disease. In this case too, effects were evident only at pH values lower than about 5.0.

Reuther and Smith (1953) and others (reviewed by Reuther and Labanauskas, 1966) have reported the effects of excess copper on citrus trees in Florida which also manifested as iron deficiency. These occurrences were on very sandy soils with low pH and cation exchange capacities. They were evident at lower soil copper concentrations than those reported from France.

There are reports of toxicity due to lead arsenate or copper which may be criticized for incompleteness or lack of relevance to the field situation. Details on which field observations were based are often conspicuously absent, particularly in the early reports of arsenic toxicity and the copper toxicity reports from France. Many workers have, on the basis of high soil concentrations, set up glasshouse experiments to match field concentrations by applying soluble salts in a single dose to small volumes of soil. There was often no account taken of the long equilibration times, the wetting and drying cycles found in the field or the possible build up of pathogenic organisms in orchard soils. There have been no reports in the literature of attempts to monitor the population of plant pathogens (for example, as attempted by Sitepu and Wallace,

1974) as well as arsenic, lead or copper at the time of tree or vine removal, when problems are most evident.

Judging by the high concentrations of copper, lead and arsenic reported in some soils after only 50 to 70 years of spray usage, it would appear that excessive use may have occurred in the early years. Hirst *et al.* (1961) reported that one orchard had received in excess of 70 kg $ha^{-1}$ in one year and the Washington State orchard soil containing 2500 $\mu g\ g^{-1}$ of arsenic (Walsh *et al.*, 1977) must be considered unusual. Most other cases of toxicity arising from agriculture, such as that reported by Gibson (1958) are accidental, or as in the case of Rosenfels and Crafts (1939) result from deliberate attempts to sterilize the soil.

Apart from the cases outlined above, there have been no substantial recent reports of copper, lead or arsenic toxicity to plants due to the effects of sprays. In fact, Walsh and Keeney (1975), when discussing arsenic phytotoxicity, place more emphasis on the frequently observed stimulation at low levels of applied arsenic. The large decrease in the use of arsenic compounds to sterilize soils and the increased availability of alternative sprays probably contributed to the decreased occurrence of toxicity.

The possible effects of copper, lead and arsenic accumulations in Australian orchards, many of which have been removed recently, and the consequences of subsequent management have not been reported.

Copper, lead and arsenic may also be introduced into the agricultural environment with fertilizer applications, though the levels are low compared to sprays. Swaine (1962) summarized the available data on all three elements in fertilizers and fertilizer materials. Lisk (1971) also reported values for lead and arsenic. Superphosphate usually contains from 2 to 1200 $\mu g\ g^{-1}$ of arsenic, and less than about 90 $\mu g\ g^{-1}$ of lead. Senesi *et al.* (1979) reported from 2 to 321 $\mu g\ g^{-1}$ of arsenic in a comprehensive range of fertilizers. David *et al.* (1978) analysed Australian superphosphates and found mean concentrations (and ranges) of about 28(10-201) $\mu g\ g^{-1}$ and 19(2-71) $\mu g\ g^{-1}$ for copper and lead respectively, with values for other fertilizers in approximately the same range.

Other agricultural practices which may lead to accumulations of these elements in soils include supplements to pig and poultry feeds. The feeds may be supplemented with copper in concentrations up to 250 $\mu g\ g^{-1}$. Manure containing 750 $\mu g\ g^{-1}$ of copper has been reported and its use as a fertilizer could raise the copper concentration of the surface soil by up to 3 $\mu g\ g^{-1}$ per application (Baker, 1974). Allaway (1968) and Calvert (1975) reported that arsanilic acid and other organic arsenic compounds are added to pig and poultry feed. Sewerage sludge, as mentioned above, may also be a significant source of lead and copper in soils if contaminated sludge is used as a fertilizer.

The foregoing examination of the literature within the chosen research area indicates that there are deficiencies in knowledge, especially in connection with Australian soils and agriculture.

Specifically,

(a) there are inadequate data on the normal ranges of copper, lead and arsenic in Australian soils,

(b) there have been no assessments of the accumulation of the elements in soils from agricultural sprays,

(c) the effects of these accumulations on agricultural produce are unknown,

(d) the results of changing management practices on soils with accumulations have not been investigated.

## 2.4 Forms and Reactions of Copper, Lead and Arsenic in Soils

There have been a number of reviews of trace metals and their chemistry including those of Hodgson (1963), Mitchell (1964) and Bowen (1966). More recently, Woolson (1975) edited a review of arsenical pesticides in soils and Rickard and Nriagu (1978) reviewed the aqueous chemistry of lead. Since there is an extensive literature on the behaviour of the elements in soils, the present review will concentrate on aspects relevant to situations where they are accumulating in surface soils and highlight some of the important reactions determining their solubility and mobility.

### 2.4.1 The Soil Solution

The merits of various techniques for obtaining soil solution have been discussed by Adams (1974). He suggested that suction and displacement techniques were more reliable than others. Data on copper, lead and arsenic in the soil solution are meagre and measurements using modern analytical techniques are needed.

Perhaps the most reliable information currently available is that of Hodgson *et al.* (1965) and Hodgson *et al.* (1966) who used a displacement method to study copper in soil solution. Concentrations varied from about 3 to 40 $\mu g\ L^{-1}$ in a range of acid and calcareous soils. Bradford *et al.* (1971) used a suction technique and found from less than 10 to 200 $\mu g\ L^{-1}$ of copper and from less than 10 to 300 $\mu g\ L^{-1}$ of lead in solutions from 68 Californian soils. However, although they could detect copper in 67 of the soil solutions, they could detect lead in only 19. Davis (1979) reported values of 200 to 480 $\mu g\ L^{-1}$ for copper in soils with a history of sewerage sludge applications. Jackson and Levin (1979) studied arsenic transport through undisturbed soil cores and field plots. Leachates contained about 20 $\mu g\ L^{-1}$ of arsenic but this value coincided with their analytical detection limit. Applications of arsenic to the surface of field plots increased the arsenic in leachates to about 1000 µg $L^{-1}$ but concentrations returned to about 20 µg $L^{-1}$ within two months. There appears to be little information as to whether or not surface soils with accumulations of copper, lead or arsenic also contain elevated concentrations in the soil solution. Davis (1979), who used a centrifuge technique, found a significant linear increase of copper concentration in the soil solution with total soil copper in soils amended with sewerage sludge and soil:sludge mixtures containing up to 74% sludge (which seems unrealistically high).

### 2.4.2 Organic Complexes and Forms in the Soil Solution

Beckwith (1955) supported an earlier suggestion (Hasler, 1943) that the metals of the first transition series are held largely as organic complexes in organic soils, but they are not necessarily rendered unavailable to plants. Hasler (1943) found, as did Irving and Williams (1948), that copper and lead form organic complexes which are very stable. Schnitzer (1969) found that copper and lead had the highest stability of a range of elements with fulvic acid and that deviations occur from the so-called Irving-Williams series of binding strengths of metals in organic complexes .

Dawson and Nair (1940) found that sulphhydryl groups were effective in complexing copper in peat. More recently, Ramamoorthy and Manning (1974) suggested that mixed-ligand complexes such as $\mathrm{Pb}\mathit{FA}\mathrm{HPO_4}$ (where *FA* is fulvic acid) may form. These complexes are very stable (stability constant = $10^{11.3}$) and may be important at low concentrations.

Hodgson *et al.* (1965) and Hodgson *et al.* (1966) partitioned copper into organically complexed and uncomplexed components in the soil solution. Although some suppositions were made that were expected to lead to an underestimate of complexed copper, it was found that the copper was overwhelmingly (76-99%) in organic complex form. Complexation was found to account for 98-99% of the copper in the soil solution in calcareous soils. Complexing was thought to enhance copper mobility in soils and especially movement to the plant root.

Mercer and Richmond (quoted by Russell, 1966, p.651) investigated copper in soils in southern England and concluded that copper in compounds with a molecular weight of less than 1000 were available to plants, but those with a molecular weight greater than 5000 were much less available.

Geering and Hodgson (1969) attempted to further characterize the ligands responsible for the complexing of copper in soil solution following separation into dialyzable and non-dialyzable fractions of which the latter formed more stable complexes. Stability constants of the dialyzable fraction were found to be higher than that of acetic acid which was the main constituent of an ether extract. In the pH range 2.0 - 4.5, a single hydrogen ion was displaced from the acid ligand for every metal ion complexed and little displacement occurred above pH 5. Bloomfield *et al.* (1976) studied the effect of decomposing plant material on copper and lead oxides. Copper and lead were mobilized by colloidal humic substances and as complexes which had some anionic character. They showed that the dialyzable copper complex was not sorbed by clay mineral colloids nor precipitated under alkaline conditions.

Stephenson (1976) noted that the stabilities of copper and lead complexes were of the same order as those reported for metal complexes with biochemical compounds and that differences between humic acids were slight. Stephenson supported earlier proposals by Broadbent and Bradford (1952), Schnitzer (1968), van Dijk (1971) and others that the active sites of complexation involved adjacent -COOH groups or -COOH and phenolic -OH groups. The cause of proton release observed during complexation was explained as being due to displacement of a proton from the ligand at low pH and the lesser rate of release at higher pH, due to the protons dissociated from hydration water of the metal in forming a hydroxo complex. Stephenson (1976) also observed that the amino acids and hydroxycarboxylic acids secreted by plants into the rhizosphere should compete favourably with humic acids for metals.

Bloom and McBride (1979) used electron spin resonance studies to investigate the binding of metal ions to peat. Although they agreed that metal ions were associated with carboxylate sites, they maintained that there is no direct evidence for chelation and preferred to regard natural soil organic matter as a solid phase ion exchanger. They also noted that most divalent metal ions are bound as hydrated ions but that copper is involved in the exchange of one or two aquo ligands with carboxylate oxygen atoms.

It seems, in summary, that copper and lead may behave similarly in soil solution and in their relation to organic matter, though most of the literature relates to copper.

Two further processes may influence the forms and behaviour of lead and copper remaining in solution which is not associated with organic complexes. These are hydrolysis and inorganic complex formation. The solubility products (log $K_{so}$, see Table 2.5) and hydrolysis constants (log $^*K_1$) of the two elements are similar although there is some variation in the values reported. At low concentrations of lead in solution, as might be expected in soils, $Pb^{2+}$ will increase at acid pH values. As the pH approaches neutrality, $PbOH^+$ becomes more important. The equilibrium constant, ($K_1 = \frac{[PbOH^+]}{[Pb^{2+}][OH^-]}$) is $10^{-6.3}$ (Smith and Martell, 1976). Similar behaviour can be expected from copper which has a similar equilibrium constant. Bingham *et al.* (1964) explained apparent excess retention of copper in a clay system by the precipitation of $Cu(OH)_2$, but the importance of hydroxide precipitation at the much lower concentrations of copper and lead in soils has yet to be demonstrated.

The formation of inorganic complexes, especially of lead, is possible in soils. Hahne and Kroontje (1973) calculated that $PbCl^+$ and $PbCl_2$ are likely to appear at solution concentrations of chloride above 35 and 350 µg $g^{-1}$ respectively. Concentrations of chloride greater than 350 µg $g^{-1}$ are common in the soil solution. The complexes $PbCO_3^o$ and $Pb(CO_3)_2^{2-}$ are also thought to exist in solution (Rickard and Nriagu, 1978).

There appear to be no references in the literature to forms of arsenic in the soil solution. This is not altogether unexpected considering the general lack of data on the composition of soil solution. However some work has been published (Waslenchuk and Windom, 1978; Waslenchuk, 1978) concerning arsenic in rivers in the southeast United States. The river waters were found to average 0.15 - 0.45 µg $L^{-1}$ of arsenic, and arsenate, the only species found, was associated with low molecular weight, dissolved organic carbon.

Arsenate can be readily methylated by common soil microorganisms, at least in the laboratory (Woolson, 1977). These alkylated arsenic compounds are also commonly used weedicides (such as cacodylic acid), which are known to be water-soluble and are readily degraded in soils but natural levels of organoarsenicals in soils have not been reported (Woolson, 1977). Arsenite may also be present in reduced soil environments (Reed and Sturgis, 1936). Deuel and Swoboda (1972) however, attributed the observed increase in arsenic solubility in reduced environments to the reduction of iron resulting in the release of greater amounts of arsenate, but did not rule out the possibility of arsenite formation.

### 2.4.3 Adsorption Processes

Cation and anion adsorption rather than precipitation are probably the more important processes controlling the association of copper, lead and arsenic with the solid phase of soils. Although copper and lead are predominantly organically complexed in soil solutions, adsorption probably controls the equilibrium of the two elements, and also of arsenic, between solid and solution phases. Some adsorption processes occur very quickly in soils, especially the 'cation exchange' reaction involving weak electrostatic bonding, but much slower reactions are frequently observed (Delas, 1963; Barrow, 1974a). The constituents of soils which are responsible for adsorption include organic matter, clay minerals and the metal oxide-hydroxides of iron, aluminium, manganese and titanium. Clay minerals of different types behave differently as adsorbents (Tiller and Hodgson, 1962) and the behaviour may be further influenced in soils by small oxide particles (Fordham and Norrish, 1979) or organic matter adhering to the surface of larger particles. With the variable nature of soils, the importance in adsorption of the different types of soil constituents will also vary.

Early work on the adsorption of trace elements onto soils has been reviewed by Hodgson (1963) and more recently discussed by Schwertmann and Taylor (1977), Harmsen (1979) and Bruggenwert and Kamphorst (1979). The latter authors suggested the following principal interactions between cations and soil constituents:

(a) reversible cation exchange, which is largely pH independent and results from normal coulombic forces due to isomorphous substitution,

(b) highly selective or specific adsorption involving the displacement of equivalent amounts of other cations (including hydrogen ions). Sometimes the adsorption is only partly reversible, and

(c) adsorption bordering on chemical bonding which results in modification of surface charge of the adsorbent.

Bruggenwert and Kamphorst (1979) also recognised that transitions between these reactions may occur and that all probably contribute to some extent. It is recognised that chemisorption or specific adsorption is the most important mechanism for the adsorption of heavy metals such as copper and lead and also for anions such as arsenate and phosphate (Quirk and Posner, 1975; Schwertmann and Taylor, 1977). Sites responsible for specific adsorption occur in organic matter, on the edges of and at other defects in clay plates and on the surfaces of oxides of metals such as iron and manganese. An exchange of OH and/or $OH_2$ ligands occurs which results in covalent bonding of the adsorbed ions to the structural cation resulting in the release of hydrogen ions. Formation of bridging ligands (Padmanabham, quoted by Quirk and Posner, 1975) and the presence of silicic acid in solution (Tiller, 1968) may result in growth or surface extension which could help explain the lack of reversibility of some adsorption reactions.

A number of equations, such as the frequently used Freundlich and Langmuir adsorption isotherms and models such as those of James and Healy (1972) and Bowden *et al.* (1973) have been used to describe and explain adsorption processes. Forbes *et al.* (1976) used ion exchange, electrochemical and hydrolysis models to evaluate the specific adsorption of divalent copper, lead and other metals on goethite in relation to pH dependence.

Most authors recognise that hydrolysis plays an important role in cation adsorption (Hodgson *et al.* 1964; Grimme, 1968; James and Healy, 1972; Kinniburgh *et al.*, 1976). Adsorption increases markedly with pH. The ability of a cation to become adsorbed is thought to be related to its hydrolysis constant, even though, on the basis of calculations made using stability constants, $CuOH^+$ and $PbOH^+$ species are present in increasingly small amounts as the pH enters the acid range. Explanations have been proposed for the apparent involvement of hydrolysed species in the acid pH range. Since a single hydrogen is displaced for each metal ion adsorbed, Quirk and Posner (1975) proposed that there is either a strong affinity of the adsorbing surface for the hydrolysed ion causing equilibrium displacement or hydrolysis may be promoted by the surface itself.

Much of the soil chemistry of arsenic has been pursued on the basis of the close parallels between arsenate and phosphate. Work on arsenate and its relationship with hydrated ferric oxides and soils took place as early as 1904 (see Schollenberger, 1947) and exchangeability of phosphate and arsenate was noted by Antoniani (1927). Dean and Rubins (1947) found that phosphate adsorption by soils was double that of arsenate and that arsenate could not displace all of the adsorbed phosphate. However phosphate could displace all of the adsorbed arsenate. In field soils with a history of phosphate applications, arsenate was able to replace most of the 'exchangeable' phosphate (*i.e.* that exchangeable with fluoride or hydroxide) but when the soils were saturated with phosphate in the laboratory, only about half of the adsorbed phosphate could be displaced by arsenate. Schollenberger (1947) obtained similar results and also found that arsenate displaceable phosphate increased with increasing pH. Since strength of adsorption decreases with increasing coverage of the adsorption surface (see below), desorption of a proportion of the phosphate by arsenate would be expected under the circumstances of these experiments.

Hingston *et al.* (1968) studied the specific adsorption of anions into goethite. Adsorption maxima were plotted against pH and the 'adsorption envelopes' so obtained showed distinct breaks in slope, the pH values of which were highly correlated the $pK_a$ values of the acid forms of the corresponding anions. The arsenate and phosphate anions behaved very similarly and adsorption conformed to a Langmuir isotherm. These authors suggested that in cases of competition for adsorption between specifically adsorbed anions, desorption of an anion by surface hydrolysis takes place when a competing anion can occupy sites in addition to those of the anion being displaced and is able to increase the surface negative charge.

Barrow (1974a) obtained results similar to those of Dean and Rubins (1947) and Hingston *et al.* (1968) and in addition noted that slow adsorption of phosphate took place even in the presence of 0.5 M arsenate. These results emphasize the fact that phosphate will always be adsorbed preferentially to arsenate in orchard soils where large amounts of fertilizer phosphate are applied.

Adsorption isotherms are often used to estimate bonding strengths and give some indication of the adsorption mechanism. Bonding energy of anions on oxide surfaces is considered to alter with surface charge, which changes with both pH and adsorption, so that bonding strengths decrease with increasing surface coverage. As pointed out by Tiller *et al.* (1969) it is likely that most soils do not present the uniform adsorbing surfaces common to many of the isotherm studies reported in the literature and it is probable that many adsorbing sites with different, but not appreciably so, bonding energies are involved.

Although some simplification of the soil system and its components is necessary for experimental reasons, the isotherm studies mentioned above help to explain the behaviour of ions in soils. Nevertheless, some of the resultant differences between the system studied and the natural soil may adversely affect the relevance of the studies. In many investigations of adsorption isotherms of soils and soil components, abnormally high solution concentrations of the adsorbing ion are used. In addition, the common cations and anions present in the soil solution may not be taken into account. Cation concentrations in soil solutions at field capacity are usually about 0.01 N and about 0.1 N at wilting point (Bolt and Bruggenwert, 1976). The ratios of solution to adsorbing material commonly used are also usually much higher than normal in soils. While this is unavoidable for practical reasons, it should be kept in mind that, under normal circumstances in soils, films of water on particles are very thin and may affect the formation of the diffuse double layer (Harmsen, 1979) and related adsorption reactions, though this is certainly not the case in pores.

### 2.4.4 The Formation of Sparingly Soluble Inorganic Compounds

The formation and dissolution of sparingly soluble inorganic compounds have a role in the control of amounts of elements in the soil solution, but their importance is difficult to assess. Reports in the literature are often theoretically based and the values of solubility products, formation constants and hydrolysis constants chosen may vary considerably. Rarely are the more important competing reactions with soil organic constituents or adsorption processes considered. Some aspects of inorganic chemistry which are relevant to contaminated soils are discussed here.

Some values of solubility products (log $K_{so}$) are shown in Table 2.5. No solubility product is quoted for $PbHAsO_4$ which is the form of modern lead arsenate sprays, but, by analogy with phosphate, it is probably much more soluble than $Pb_3(AsO_4)_2$. Although the sulphides of copper, lead and arsenic are very insoluble, they are stable only in the presence of sulphide because they are susceptible to oxidation. Basic salts of lead and copper, for example hydroxycarbonates such as azurite (log $K_{so}$ -45.6) and pyromorphite

Table 2.5 Solubility Products (log $K_{so}$) of Some Compounds of $Cu^{2+}$ and $Pb^{2+}$

| Anion | $OH^-$ | $CO_3^{2-}$ | $PO_4^{3-}$ | $HPO_4^{2-}$ | $AsO_4^{3-}$ | $S^{2-}$ | $SO_4^{2-}$ |
|---|---|---|---|---|---|---|---|
| $Cu^{2+}$ | -19 | - 9.6 | -36.9 | - | -35.1 | -36 | - |
| $Pb^{2+}$ | -19.5 | -13.1 | -42.1 | -9.9 | -35.4 | -28 | -7.8 |

Source: Sillén and Martell (1964)

($Pb_5(PO_4)_3OH$, log $K_{so}$ -76.8) are also very insoluble (Sillén and Martell, 1964; Nriagu, 1974). The fungicidal sprays, Bordeaux mixture and copper oxychloride, which are basic salts, also have low solubility.

Rickard and Nriagu (1978) have provided a review of the chemistry of lead in aqueous environments. Santillan-Medrano and Jurinak (1975) concluded that the inorganic lead in the solution of calcareous soils was controlled by the solubility of $PbCO_3$ and in non-calcareous soils was governed by $Pb(OH)_2$, $Pb_3(PO_4)_2$, $PbO(PO_4)_2$ and $Pb_5(PO_4)_3OH$ depending on pH. Nriagu (1974) suggested that soluble lead compounds accumulating at the soil surface react with phosphate to form $Pb_3(PO_4)_2$, plumbogummite [$PbAl_3(PO_4)_2(OH)_5.H_2O$] and pyromorphites and that iron and manganese oxyhydroxides may assist their formation by becoming adsorbents which concentrate both lead and phosphate. Harter (1979) noted a significant correlation between the capacity of the soils to adsorb lead and the amount of phosphate extracted by hydrochloric acid, and, at least in soils low in adsorption capacity, there was a suggestion of the presence of stoichiometric $PbHPO_4$. The above-mentioned reports of compounds containing lead and phosphate are largely based on theoretical grounds. Although minerals containing both lead and phosphate do occur in soils as a result of weathering processes (Norrish, 1975), widespread occurrence in contaminated soils is yet to be established. An electron microprobe study of an orchard soil (Norrish and Merry, unpublished) failed to show any evidence of specific lead compounds, but suggested instead that the lead was associated with organic matter.

Hess and Blanchar (1976) concluded from work on two orchard soils that, at pH values above 4.75, either lead or manganese arsenate are stable and should control the level of arsenic in solution. Below this pH, manganese arsenate is more stable than the arsenates of iron, aluminium, lead or calcium. In this study however, no account was taken of the elevated phosphate concentrations or other elements such as copper usually found in these soils. Lead phosphate is much less soluble than lead arsenate (see Table 2.5) or manganese arsenate.

### 2.4.5 Characterization of Copper, Lead and Arsenic in Soils

Two common approaches have been adopted in attempts to characterize the main fractions of these elements in soils. These are firstly the use of reagents to extract supposedly discrete chemical forms, and secondly the use of regression analyses to relate soil components with either the total content of the elements in the soil or to adsorption maxima calculated from Langmuir isotherms.

McLaren and Crawford (1973a) undertook a comprehensive fractionation of soil copper using chemical extractants on 24 representative British soils containing 4.4 to 63.5 ppm copper. "Solution plus exchangeable" and "weakly specifically-bound" copper together accounted for less than 2 percent, "organically bound" accounted for 13 to 47 percent, "oxide occluded" accounted for 0 to 36 percent of total copper with a residue of 38 to 77 percent. Although the extractions were not mutually exclusive, the various fractions generally correlated well with respective soil components and the "residual" copper correlated with clay content. Similar information about some of these fractions may be found elsewhere in the literature e.g. Le Riche and Weir (1963), Gupta and Mackay (1965), Taylor and McKenzie (1966). and Du Plessis and Burger (1971). McLaren and Crawford (1973b) also investigated the specific adsorption of copper using Langmuir constants and multiple regression analyses with the same set of soils as mentioned above. Specific adsorption maxima at pH 5.5 ranged from 340 to 5780 $\mu g\ g^{-1}$ with organic matter and free manganese oxides being the main soil components involved. Further work (McLaren and Crawford, 1974) showed the between 2 and 21% of the total copper was isotopically exchangeable (0.19 - 12.4 $\mu g\ g^{-1}$). Equilibrium was reached within 24 hours although a secondary, slow equilibrium was associated with iron oxides and montmorillonite. Delas *et al.* (1960) had also noted this slow equilibrium. Isotopic exchange studies with copper are limited by the short half life of its isotope ($t_{\frac{1}{2}}$ = 12.9 h). McLaren and Crawford (1974) concluded that

i) copper in soil solution is in equilibrium with specifically adsorbed forms, and

ii) equilibrium between forms of copper, which is specifically adsorbed, complexed or as hydrated ions in solution, must be readily attained.

Considerably less is known of the forms of lead in soils than is known of copper. Soldatini *et al.* (1976) studied lead adsorption in 12 Italian soils. Adsorption maxima based on Langmuir isotherms were correlated with organic matter and clay, and little was attributed to iron and manganese oxides though the contents of all of these components were themselves correlated to some extent. The same authors (Riffaldi *et al.*, 1976) found essentially the same results for specific adsorption. Petruzelli *et al.* (1978) investigated experimentally the effect of organic matter on copper adsorption. Removal of organic matter decreased adsorption and cation exchange capacity but it was not clear whether the process used to remove organic matter was likely to affect other adsorbing surfaces.

Le Riche and Weir (1963) extracted 'free' iron and manganese oxides from soils and in doing so removed about 60 percent of soil lead. Norrish (1975) reviewed some of the earlier work (e.g. Taylor and McKenzie 1966) suggesting relationships between lead and manganese oxides in soils. He also presented analyses of iron and manganese oxides from three Australian surface soils. Manganese-rich nodules showed marked accumulations of lead (but not copper). Lead was also reported to be found in gorceixite and hinsdalite minerals associated with laterites. This agrees with the suggestion of Nriagu (1974) that lead phosphate minerals may control the immobilization of soluble lead in surface soils, at least in environments with high lead concentrations.

The similarities of arsenate and phosphate chemistry has prompted the use of modified Chang and Jackson (1957) procedures for partitioning soil arsenic into "water-soluble", "iron-bound", aluminium-bound" and "calcium-bound" arsenate. Jacobs *et al.* (1970) used this approach with modifications to overcome re-adsorption. Arsenic was sorbed by soils which were then extracted using this procedure. The amounts of arsenic extracted were well correlated with free iron oxides in the soils studied, and chemical removal of amorphous iron and aluminium oxides greatly decreased or eliminated the ability of the soils to adsorb arsenate. Organic matter was thought to be contributing very little to arsenic retention in the soils studied. Woolson *et al.* (1971b) used a similar approach to Jacobs *et al.* (1970) on soils (average 165 $\mu g\ g^{-1}$ arsenic) with a history of arsenic applications. "Water soluble" arsenic was rarely detected and most arsenic was associated with the "iron-bound" (0.1 N NaOH extractable) component. "Aluminium-" and "calcium-bound" arsenic appeared only in soils low in iron.

In a follow-up study in the laboratory, Woolson *et al.* (1973) found that the equilibrium between applied arsenic and the various soil forms took 4 to 6 weeks to attain depending on the concentration of arsenic applied. With increasing applications, water soluble arsenic also increased, especially in the sandier of the two soils studied. The proportion of arsenic associated with iron decreased with increasing application while the proportion associated with aluminium remained more or less constant. However, the latter decreased after 4 to 8 weeks and the former increased over a period of 36 weeks. Similar findings suggesting that iron is more important in arsenic fixation, were reported by Fassbender (1975).

Wauchope (1975) found that the sorption of arsenate and organic arsenicals was correlated with clay and iron oxide contents. Some correlation was also noted with calcium.

Fordham and Norrish (1974, 1979) made direct measurements of soil components in the clay fraction responsible for arsenic fixation using autoradiography, electron microscopy and electron probe microanalysis. Iron oxides and titanium oxides (the latter to a smaller degree) were the main components responsible for adsorption of arsenate, with gibbsite being important only where it made up the majority of the clay fraction. Very finely divided oxide particles coating the surface of other clay minerals were responsible for the adsorption rather than the clay minerals themselves.

In summary the forms of lead in soils are less well known than those of copper and arsenic. Although there has been at least one study of arsenate (Woolson *et al.*, 1971b) in soils with a long history of applications, there do not appear to be studies of the fractionation type available on soils with a long history of lead and copper applications. Most studies have used uncontaminated soils dosed or otherwise treated, often with soluble chemicals, in a manner that bears little resemblance to the field applications and the long periods of time involved in, for example, the accumulation of orchard sprays.

### 2.4.6 Leaching of Copper, Lead and Arsenic

In general, it is possible to predict from the chemistry of these elements that leaching is unlikely in most natural situations except perhaps in soils with low adsorption capacities. In many leaching experiments such as those reported by Zimdahl and Hassett (1977), and Jackson and Levin (1979), large amounts of the elements being studied and high intensities of leaching water were applied. In the natural situation, patterns of rainfall and wetting and drying of soil profiles are usually very different. It is also usual, at least in agriculture, for surface accumulations of contaminating substances to be a slow process taking place over many years. Few attempts appear to have been made to discriminate leaching in solutions from translocation associated with the downward movement of fine particles.

Zimdahl and Hassett (1977) reported studies which showed that soils could hold metals in amounts equivalent to 40 to 72 percent of their cation exchange capacity before leaching occurred. The proposition that most surface soils have sufficient capacity to adsorb metals is strengthened by numerous reports in the literature showing profile distributions (e.g. Cartwright *et al.*, 1977) with pronounced surface accumulations of elements of atmospheric origin. Some mixing or reinforcement of surface concentration can be expected due to biological action. Tso (1970) showed that limited amounts of $^{210}Pb$ were leached from soil by water, but the rates increased with agitation suggesting that physical movement of colloids with adsorbed ions may be a more probable mechanism of loss from surface soils.

Jones and Belling (1967) studied the movement of copper down soil profiles under the influence of fertilizers, $CO_2$-saturated water and a lucerne extract. Soils with high contents of organic matter or calcium carbonate (or possibly free iron oxides) and with moderate ion exchange capacity showed no movement of copper down profiles after the equivalent of several years' rainfall. However, in deep sandy soils movements of 1 to 3 centimetres or more occurred with both $CO_2$-saturated water and lucerne extracts.

The leaching rates of heavy metal ions in organic forest soils under the influence of rainfall of varying acidity was reported by Tyler (1978). Copper, chromium and lead were most resistant to leaching and the time required to reduce total concentrations of both copper and lead by 10 percent was of the order of hundreds of years with rainfall at a pH of 4.2. These times were shortened dramatically to less than 20 years for rainfall at a pH of 2.8.

The leaching of arsenic (mainly applied as organoarsenicals) has been discussed by Hitbold (1975). Organoarsenical herbicides are readily converted to arsenate, which is the usual form of arsenic in soil (Woolson, 1977). Hitbold (1975) reported that under normal circumstances, arsenic accumulates in the surface of soils and is leached to lower horizons very slowly, if at all, except in coarse textured soils with low sorption capacities. Tammes and de Lint (1969) calculated that it took about 6 to 7 years to leach half of the added arsenic from the surface of a light loam soil to which sodium arsenate had been added at rates in excess of 250 $kgha^{-1}$ of arsenic. Over a period of 10 years, considerable amounts of arsenic were leached to below 40 cm.

### 2.4.7 The Effects of Oxidation and Reduction, and Interactions With Micro-organisms

*Oxidation and Reduction*

Changes in oxidation state, which are usually biologically mediated, may significantly alter the adsorbing surfaces in soils. Hem (1972) has discussed the effects of redox potential and pH on iron and manganese in aqueous systems. Both elements have low solubility at pH levels near neutral in oxidizing systems, but small decreases in pH or reducing potential may markedly increase their solubility. These effects are reversed by a return to oxidizing conditions. As has been discussed previously, iron oxides adsorb copper, lead and arsenate ions, and manganese oxides are particularly efficient in adsorbing lead. Reducing conditions, by altering the surfaces of iron and manganese oxides in soils, may profoundly affect the solubility of copper, lead and arsenic.

Reddy and Patrick (1977) found that copper chelated by DTPA and EDTA became less stable under reducing conditions. This was attributed to chemical fixation of the copper rather than to physical adsorption or microbial decomposition of the metal-chelate complex. The processes involved seem somewhat unclear and the subject requires further investigation since similar effects may occur with lead and copper which are complexed with organic substances in the soil solution.

In addition to the effects of reducing conditions on adsorbing surfaces, oxidizing and reduction conditions greatly affect the forms of arsenic in the soil environment. This subject has been reviewed by Woolson (1977). Possibly the most important effect of reducing conditions is the production of arsenite anions from arsenate, which is the usual form of arsenic in oxidized soils. Arsenite is also considered more toxic than arsenate, but is readily re-oxidized to arsenate.

Keaton and Kardos (1940) investigated the arsenate-arsenite system in soils. They found that arsenate was adsorbed 4 to 10 times more strongly than arsenite. They also found that the addition of ferric oxides to soils was effective in increasing the oxidizing potential of the soil. This had the ameliorative action of oxidizing arsenite to arsenate. Reed and Sturgis (1936) investigated the toxicity symptoms which appeared in rice when soils on which cotton had been grown were flooded. The previous cotton crops had been sprayed with insecticides containing arsenate. They suggested that, since the Eh of the flooded soils decreased from 670 mV to 190 mV during submergence, reduction of arsenate to the more toxic arsenite had occurred. More recently, Deuel and Swoboda (1972) were able to attribute increases in water-soluble arsenic with reducing conditions to the reduction of ferric iron and the subsequent release of arsenate rather than the formation of arsenite, though the possibility of formation of arsenite in flooded soils was not discounted.

Bohn (1976) considered that arsenate is unlikely to be reduced to elemental arsenic or arsine ($AsH_3$) in soils. Deuel and Swoboda (1972) were unable to detect any gaseous arsenic compounds in their reduced soils. However, it has been known for a considerable period (since about 1900) that arsenate can be reduced and methylated by fungi, bacteria and animals (Cox, 1975; Woolson, 1977) and dimethylarsine and trimethylarsine gases have been detected in the atmosphere (Johnson and Braman, 1975).

Microorganisms may contribute significantly to detoxification and dispersal of arsenic in contaminated soils. Various organisms are able to reduce and metabolize arsenite, arsenate, monosodium methanearsonate and cacodylic acid from insecticides and herbicides forming volatile arsenic compounds (Cox, 1975; Woolson, 1977). The products of microbial action are most likely to be di- and trimethylarsine. The dissolution products, trimethylarsine oxide and cacodylic acid are readily interconverted to methanarsonic acid and arsenic acid which is sorbed by the soil colloids. Cacodylic acid herbicide is readily metabolized in soils to arsenate (Woolson and Kearney, 1973). Woolson (1977) summarized the fate of various arsenicals and estimate losses in the range of 0.02 to 0.15% per day though the conditions required for such losses are poorly defined and it was not possible to distinguish accurately the losses due to volatilization from those due to leaching or particulate removal.

The microbial alkylation of lead in soils producing volatile compounds may be possible since it is well known for arsenic and mercury. The process has not been reported for lead, but if it exists, it may be a mechanism for the dispersal of lead from contaminated soils.

### *Effects of Copper, Lead and Arsenic on Microorganisms*

The presence of toxic elements may have important effects on the balance between the bacteria, fungi and algae in soils. Selective effects on pathogens may be beneficial and may be partly responsible for beneficial responses of plants to arsenic (Walsh and Keeney, 1975) and to lead (Keaton, 1937). The basis of the action of copper-containing fungicides is believed to be due to the fact that fungal spores are able to concentrate copper to many times that of the surrounding environment (Corbett, 1974).

Greaves (1916) reported that nitrogen fixing organisms were stimulated by arsenic. Quirashi and Cornfield (1971, 1973) reported a stimulation of nitrification and nitrogen mineralization in incubation studies when high concentrations of copper were present. Tyler (1974) reported that the activity of urease and acid phosphatase enzymes in the soil, as well as respiration rates, in an organic forest soil in Sweden decreased with very high (up to 40,000 $\mu g\ g^{-1}$) copper and zinc concentrations. The mechanisms of these effects are unknown in detail and it is doubtful whether the effects are significant at lower soil concentrations of toxic elements such as are found in orchards.

## 2.5 The Uptake, Distribution and Effects of Copper, Lead and Arsenic in Plants

The general subject of the movement of nutrients (and other elements) to the vicinity of plant roots and their uptake, distribution and function within the plant has been the subject of many books and reviews (e.g. Olsen and Kemper, 1968; Epstein, 1972; Moore, 1972; Tiffin, 1972; Wilkinson, 1972; Hodges, 1973; Loneragan, 1975; Nambiar, 1975; Nye and Tinker, 1977). Detailed discussion of these topics will not be attempted here.

However, most reviews have been concerned largely with plants growing in 'normal' or nutrient deficient situations. Copper, for instance, is best known as an essential trace element. The present discussion will be directed more towards the toxic situation though material will be drawn from 'normal' situations where relevant.

One further aspect will be mentioned briefly because it is concerned with the ability of plants to cope with an excess of toxic metals. This is the development of genetic tolerance by plants, a subject which was extensively reviewed by Antonovics *et al.* (1971). The situations where genetically controlled tolerance by plant communities have been studied are usually on reclaimed mine dumps or mineral anomalies. Although twenty-one possible mechanisms are listed by Antonovics *et al.* (1971), little appears to be known of specifically how the tolerant plants manage to withstand concentrations of toxic metals which are of a very much higher order than is usual for plants growing on contaminated soils. For instance, Barry and Clark (1978) reported concentrations of 2500 $\mu g\ g^{-1}$ of lead in the tops of grass growing in metalliferous waste and Porter and Peterson (1975) reported arsenic concentrations in excess of 6000 $\mu g\ g^{-1}$ on plants growing on mine waste. These situations appear to be somewhat unusual and the development of genetic tolerance with associated high concentration of elements in plants has not apparently been reported for contaminated soils from orchards.

### 2.5.1 Copper

Critical concentrations of copper in soil above which plants may be detrimentally affected are difficult to ascertain because of the profusion of extracting media which have been used, coupled with variations of fertilizer use, soils and plant genotypes (Delas, 1963). For example, factors such as poor drainage (Mitchell *et al.*, 1957) and increasing temperature may lead to enhanced uptake of copper. Smith (1971) investigated the copper concentration of lucerne at flowering in uncontaminated soils and found an increase of about 11°C in day and night temperatures raised copper concentrations from 9 to 15 $\mu g\ g^{-1}$.

Demolon (1956) and Struckmeyer *et al.* (1969) observed toxicity of copper on plants grown in solution cultures at concentrations of about 0.1 to 0.2 $\mu g\ ml^{-1}$. Forster (1953) showed that there was a considerable decline in plant yields, with marked species differences, when copper applied to soils in pots exceeded 160 μg $g^{-1}$. Reuther and Smith (1953) found that total concentrations of copper greater than 50 to 200 μg $g^{-1}$ in soils resulted in toxicity to citrus plants. The appearance of toxicity varied with cation exchange capacity in sandy soils so that 50 to 100 μg $g^{-1}$ were toxic at exchange capacities of 1.5 to 2 meq $(100\ g)^{-1}$ and 125 to 200 μg $g^{-1}$ were toxic at 4 to 6 meq $(100\ g)^{-1}$. Reuther and Labanauskas (1966) reviewed data on copper in soils. Toxicity symptoms were often observed when total soil copper was in the range 100 to 150 μg $g^{-1}$ and soil pH was less than 5.0.

A number of workers have applied copper salts to soils in the field and found correlations between plant response and the amounts of copper extracted from the soils by various reagents. For example Walsh *et al.* (1972) applied up to 486 kg $ha^{-1}$ of copper sulphate to soils on which beans were grown. This rate of application was intended to be equivalent to 27 years of fungicidal applications. Good linear correlations of increase in extractable copper and concentration in leaves with reductions in yield were obtained. Since the copper concentration in the leaves was still declining after two years, it is probable that the copper applied to the soil, at least at the high rates, had not reached equilibrium with adsorption and complexing mechanisms. Comparison of these results with what may occur with annual applications over 27 years is probably not justified.

Reuther and Labananskas (1966) have listed plant concentrations for deficient, normal, high and toxic ranges of copper in various parts and experimental conditions. Citrus leaves with greater than 20 to 25 μg $g^{-1}$ entered the toxicity range, but roots with up to 600 μg $g^{-1}$ were not regarded as high. No other concentrations in plants which were related to toxic symptoms were reported. Delas (1963) explained that critical toxic concentrations within plants require careful interpretation since, in many cases, the most drastic effect is on the root system and toxicity is not always accompanied by increased transport of the toxic element to tops. Forster (1954) noted that mortality of plants and variation in concentration (possibly the result of root damage) increased with copper application rate to oats in pots.

Copper toxicity symptoms and effects vary with species. The more common symptoms, summarized from Smith and Specht (1953) and Delas (1963) are:

a) yield reductions and general stunting,
b) poor root growth, often with brown discolouration,
c) absence of root apical meristems,
d) strong chlorosis symptoms resembling iron deficiency, and
e) suppression of tillering in cereals.

Similar symptoms of stunting and cellular collapse were reported for tobacco by Struckmeyer *et al.* (1969) at copper concentration greater than 0.32 µg $ml^{-1}$ in solution culture. Fewer chloroplasts were observed in the cells of leaves. Brown *et al.* (1955) noted that those plants which were prone to iron deficiency, such as citrus, were also prone to copper toxicity. Symptoms are rare in many species with large, deep root systems when copper is concentrated in the surface soil, but the establishment of young, shallow-rooted plants may be difficult. This has also been noted for arsenic and can be overcome by deep ploughing or planting in small amounts of imported, uncontaminated soil.

Goodman and Linehan (1979) confirmed earlier suggestions that copper was likely to be present in plants as 1:2 copper-amino acid complexes. Tiffin (1972) showed that copper is translocated in the xylem of peanuts in anionic form probably as amino acid complexes. Goodman and Linehan (1979) also suggested that the appearance of the complex depends on the structural integrity of the roots and that uptake is metabolically mediated, a conclusion opposite from that of, for example, Cathala and Salsac (1975) who used excised roots.

The mode of action of toxic copper remains largely unknown. The lack of information on specific effects may result from considerable between and within species differences, the large number of possible sites of action within the plant from roots to leaves and an apparent host of interacting elements, e.g. manganese, iron, molybdenum, nickel, cobalt, calcium and phosphorus (Forster, 1954). Doubt exists as to whether some antagonisms take place inside or outside the plant and, since many have been demonstrated only in solution or pot culture, whether they are important under field conditions.

The symptoms of chlorosis attributed to copper toxicity in citrus, which are often evident when other elements are toxic, have been variously attributed to immobilization of iron either in the soil, root or leaves (e.g. Forster, 1954; Struckmeyer *et al.*, 1969 and others). The consensus is probably that although copper concentration increases in leaves showing chlorosis, the iron concentration remains about the same, suggesting some biochemical blocking action in the leaf. Hewitt (1948) found that iron chelates alleviated chlorosis symptoms in sugar beet, but had no effect on the root damage symptoms. A 500-fold increase in soil copper concentration resulted in only a fourfold increase in copper concentration in the root and no difference in concentration in the shoot despite yields being halved. Higher concentrations of ammonium ion appeared to increase copper translocation to tops of the plants. In the tops of these plants, iron concentrations decreased so that Hewitt concluded that the site of action was in the roots. Smith and Specht (1953), working with citrus in solution culture, obtained results similar to those of Hewitt (1948) and found that the toxic effects of copper, zinc and manganese were not additive. Nitrogen and calcium had no effect, but lowering the pH of the growing medium markedly increased toxicity. Although different mechanisms may be operating on different plant species, it is evident that excess copper primarily damages roots and visual symptoms of chlorosis are dependent on the concentration of other elements in the plants.

The biochemical action of copper is known through its role in the functioning of enzymes, electron transport and presence in some copper proteins (e.g. tyrosinase, polyphenoloxidase, cytochrome C oxidase and plastocyanin; Piesach *et al.*, 1966) and through its function as a pesticide (Corbett, 1974). Copper at high concentrations is known to denature most enzymes. The postulated action through thiol or carboxyl groups is sometimes reversed by treatment with cyanide or EDTA. Cedeno-Maldonado *et al.* (1972) investigated copper excess and the photosynthetic electron transfer system in isolated chloroplasts and found a number of effects:

(a) light of a sufficient intensity was required for inhibition,
(b) copper binds directly to chloroplasts,
(c) concentrations greater than 1 micromolar (63.5 $\mu g L^{-1}$) were toxic,
(d) components of the oxidising side of the photosynthesis pathway were sensitive and
(e) the electron donating properties of $Mn^{2+}$ were inhibited.

Specific biochemical information related to toxic copper and interactions with iron, manganese, molybdenum and zinc appears to be lacking.

### 2.5.2 Lead

There have been reports of yield increases in plants resulting from applications of lead to soils (Keaton, 1937; Lagerwerff, 1971). These may have been due to ions associated with the applied lead, such as nitrate (Keaton, 1937; Zimdahl and Foster, 1976) carbonate (Keaton, 1937) or, as was proposed by Lagerwerff (1971), due to the treatment rendering other elements, such as zinc, more available in a deficient situation.

Reports of toxicity in plants which were attributed to lead have been recorded for a considerable time. Forster (1954) quoted such a report by Glanvil in England in 1668. More recent reports on lead, though not often present in toxic amounts, resulted from investigations of mine-affected soils in Wales, accumulation of lead arsenate sprays, smelter emissions, motor vehicle exhaust emissions and sewage sludge applications. Early work relating to lead in plants has been briefly discussed by Keaton (1937) and Brewer (1966). Uptake by plants, with a bias to atmospheric sources, has been reviewed by Zimdahl and Koeppe (1977).

Much of the work on lead uptake by plants has employed sand or solution culture and frequently soils amended with large amounts of relatively soluble salts. Although the relevance of many of the experiments to the field situation may be criticized on these grounds, they do serve to show that very efficient barriers to lead uptake occur in plants, and that lead is strongly bound in the soil. Illustrative of this point are the experiments of Keaton (1937) who applied approximately 5 t $ha^{-1}$ of lead carbonate to soils on which barley was grown. It was found that the high rates of application, which resulted in an increase in concentrations in washed roots from 5 to 730 µg $g^{-1}$, but in the tops only increased from below detection (concentration not stated) to 3 µg $g^{-1}$.

No reliable critical concentrations of lead in soils, above which toxicity may be expected, are available in the literature. This is probably a result of the scarcity of reports on toxicity in plants which can be attributed to lead alone. Those that have appeared commonly present results of deliberate lead applications. Baumhardt and Welch (1972) found that the addition of 1000 µg $g^{-1}$ of lead (as acetate) had no effect on maize grown in soil apart from increased concentrations of lead in the plants, but growth was retarded in sand culture when concentrations were as low as 240 µg $g^{-1}$ (Miller and Koeppe, 1971). Significant linear correlations have been reported between lead removed from the soil by various extractants and lead concentrations in plants (e.g. John, 1972; Merry and Tiller, 1978). Symptoms of lead toxicity are apparently of a non-specific kind since no detailed description, apart from yield reductions, have appeared in the literature.

A number of interactions of lead with other elements have been reported. In some cases it is not clear whether these effects are due to mechanisms taking place in the soil, at the root surface or within the plant. McLean *et al.* (1969) and John and van Laerhoven (1971) found that lead concentrations in plants decreased with application of lime to the soil. McLean *et al.* (1969) reported that phosphate applications decreased the uptake of lead by plants. McKenzie (1978) found that, when manganese oxides were applied to pots containing soil with high lead concentrations (including an orchard soil), the concentration of DTPA-extractable lead concentration decreased in the soil and also the uptake of lead by subterranean clover decreased. Interactions between lead and sulphur were investigated by both Jones *et al.* (1973) and Karamanos *et al.* (1976). The former found marked increases in the lead concentration in the tops of sulphur deficient ryegrass although there were no differences in total uptake when yield was taken into account. Karamanos *et al.* (1976) obtained significant yield increases with applied sulphur, but lead concentrations in the tops of lucerne and ryegrass did not alter significantly. A number of experiments using treated soils have resulted in the observation of interactions of lead with cadmium in various plant species (Hassett *et al.*, 1976; Koeppe, 1977; Miller *et al.*, 1977; Carlson and Bazzaz, 1977). Synergisms, some of which were beneficial, were evident when the two metals were applied together. Whether or not beneficial effects could be expected from other metals, such as iron and zinc, has not been demonstrated.

Lead may accumulate on the surfaces of leaves from sprays, motor vehicle exhaust emissions or other atmospheric sources. According to Brewer (1966), lead sulphate sprayed onto plants had no effects until eventually the stomates became clogged. Evidence provided by Lagerwerff (1971), Little (1973) and Arvik and Zimdahl (1974a) suggested that foliar absorption of lead by plants is either insignificant or non-existant because of the effective barrier provided by the waxy cuticle of leaves.

The distribution of lead within plants is quite well known. Jones and Hatch (1945) compared the lead concentrations of a range of vegetable and forage plants. They were grown on orchard soils which had accumulated lead arsenate equivalent to 375 $\mu g\ g^{-1}$ of lead and the lead concentrations compared with plants grown on adjacent soils with no lead arsenate. The average increase in lead concentration of the tops of the plants was from 12.1 to 15.1 $\mu g\ g^{-1}$, of washed roots was from 4.0 to 12.3 $\mu g\ g^{-1}$ and of edible parts was from 0.9 to 1.4 $\mu g\ g^{-1}$. Jones and Hatch (1945) differ from the majority of more recent literature (e.g. Karamanos *et al.*, 1976; Baumhardt and Welch, 1972) in finding lower concentrations of lead in the roots than were found in tops. Although species differences are to be expected, this raises the question of the possibility of atmospheric contamination, but it was also true that many of the roots in the study of Jones and Hatch (1945) were edible and may naturally have lower lead concentrations. These roots are also much more easily cleaned.

It is usual to find the highest lead concentrations in, or on, the roots of plants. Precipitation of lead phosphate on root surfaces or in the root free space was proposed by McLean *et al.* (1969) and Miller and Koeppe (1971). Broyer *et al.* (1972) found that lead in excised barley roots was readily removed by extractants and reached similar conclusions about the site of residence of lead, but observed no relationship to phosphate or any other element. The same authors also studied effects of temperature on the uptake of lead. Initial uptakes were independent of temperatures and described as passive but thereafter markedly different rates were noted and ascribed to metabolically controlled processes. In contrast, Arvik and Zimdahl (1974b) interpreted results which they obtained as being due to completely non-metabolic processes. As noted above for copper, care should be taken in interpreting results of experiments in which the integrity of the plant is not maintained (Epstein, 1972).

The localization of lead in plants has been studied by a number of people. Glater and Hernandez (1972) found that lead was concentrated around the xylem of contaminated plants. Tanton and Crowdy (1971), by converting lead in plants to the sulphide, demonstrated movement of lead in chelated form in solution into the root via the apoplast, through the cytoplasm of endodermal cells and into the xylem. In maize, Malone *et al.* (1974) showed, using light and electron microscopy, that lead absorbed from solution culture precipitated on the root surface (but not when an EDTA chelate was the source) and slowly accumulated in crystal form on cell walls. The lead actually taken up by cells was concentrated in dictyosome vesicles which then fused to encase the lead deposit. After being surrounded by a membrane, the encased deposit fused with the plasmalemma and eventually with the cell wall. Similar deposits were evident in stems and leaves. They found no association of lead with mitochondria in maize despite the reports of Miller and Koeppe (1971). It must be noted that many of the above effects were observed in experiments using very high concentrations of lead in solution which are unlikely to be encountered in soils.

Foster (CSIRO Division of Soils, personal communication) has studied lead in the roots of pine seedlings grown in orchard soils. Like the majority of crop plants, these roots were infected with mycorrhizal fungi and, in these circumstances, lead was found to be deposited within the fungal cells with no obvious accumulation within the host plant cells.

Biochemically, lead could be expected to denature enzymes and other proteins, but unless some localized concentration increase or genetic intolerance to high concentration occurs, it is unlikely that many of the effects mentioned above will occur. Miller and Koeppe (1971) reported effects of lead on mitochondria, succinate oxidation and NADH but it would appear from the evidence that most of the lead in plants is extracellular.

Changes in the concentration and distribution of lead in plants with the physiological changes occurring with seasons have been observed. Mitchell and Reith (1960) reported that lead was apparently mobilized in senescent pasture plants and the concentration in the tops increased during winter. They did not consider the possibility that freezing conditions may have damaged the roots of the plants. These plants were perennials and their conclusions differed from those of Rains (1971) who used wild oats (*Avena fatua*). He concluded that, following an initial dilution due to plant growth, the continuing accumulation of lead observed through summer and the following winter were due initially to dry mass losses and later to strongly bound surface lead from atmospheric sources, in this case, a smelter. Karamanos *et al*. (1976) grew lucerne and brome grass, both perennials, and simulated autumn conditions in a growth chamber by decreasing temperature and photoperiod. This had an effect of increasing lead concentrations only in pots receiving 100 ppm lead. The small increase observed could be accounted for by diminished dry matter production and paralleled similar effects noted for phosphorus and potassium.

### 2.5.3 Arsenic

Although the toxicity of arsenic to animals has been known for a considerable time, it is only since agricultural usage of arsenic-containing compounds became widespread over the last century or so that toxic effects to plants have become evident. The more recent literature on arsenic in soils and plants has been reviewed by Liebig (1966), Woolson (1975) and National Research Council Canada (1978).

It has been suggested (Nielsen *et al*., 1975) that arsenic may be essential in the diet of rats, but its essentiality to plants has yet to be established. Liebig *et al*. (1959) and others have noted a stimulation of root growth by arsenic in solution cultures. Other workers, such as Woolson *et al*. (1971a) have reported growth stimulation from arsenic contaminated soils compared to control soils. No certain explanation has been put forward, but it is possible that interactions of arsenate with phosphate in soils and plants or even stimulation of a'hormonal' kind at low concentration may partly explain these results (Woolson *et al.* 1971a).

Critical concentrations of soil arsenic above which toxic effects may be encountered cannot be stated absolutely because of variation in the soil factors responsible for fixation and because of differences in response by different plant species. Bishop and Chisholm (1962) found 50 to 120 µg $g^{-1}$ of total arsenic to be detrimental to plants in glasshouse trials. McPhee *et al.* (1960) observed decreased yields of peas and beans grown on a sandy loam soil to which arsenic had been added over five years to attain a soil concentration of 120 to 150 µg $g^{-1}$. Many of the soil extractants used for 'available' phosphorus have also been used for arsenic (Walsh *et al.*, 1977). Vandecavaye *et al.* (1936) extracted arsenic with a range of reagents (including distilled water and concentrated $HNO_3$) and found no correlation with the appearance of toxic effects. Woolson *et al.* (1971a and 1971b) found logarithmic relationships between growth reductions in four week old maize and various extractants commonly used for phosphorus. Growth reductions began when total soil arsenic reached 50 to 100 µg $g^{-1}$ and 50% reductions occurred at about 250 µg $g^{-1}$. (Few of the soils had arsenic concentrations higher than this). Similarly, growth reductions appeared when bicarbonate extractable arsenic exceeded about 10 µg $g^{-1}$ and 50% growth reductions occurred at 30 to 40 µg $g^{-1}$. As discussed by Woolson *et al.* (1971b), arsenic soluble in water has been used frequently to define toxic concentrations for plants with varying success and often conflicting results. In summary, it would seem that problems related to high arsenic concentrations in soils appear when total concentrations exceed 50 to 100 µg $g^{-1}$, but may occur at lower concentrations in sandy soils and in 'dosed' soils with sensitive crops. In soils which are able to adsorb arsenic strongly, toxicity may not occur until much higher concentrations are reached.

Liebig (1966) has summarized reports from many sources indicating the range of arsenic found in plants and plant parts. The vast majority of plants grown in field conditions contain arsenic at concentrations less (and usually very much less) than 1 $\mu g\ g^{-1}$. Higher concentrations were found in roots (up to about 30 $\mu g\ g^{-1}$) and also in plants grown in solution culture. Although much data were summarized, only four cases of injury and one of plants showing toxicity symptoms were reported. Vincent (1944), Liebig (1966) and other authors provide lists of plants considered to have low, moderate or high tolerance to arsenic. For example, legumes are considered to have low tolerance and potatoes, tomatoes and rye to have high tolerance.

The variation in arsenic concentration in plants usually follows the pattern found for many other elements (Liebig, 1966) i.e.

roots > stems > leaves > reproductive parts

Edible parts of plants usually have low concentrations. The peeling of beet roots lowered their average arsenic concentration from 20 to 1 $\mu g\ g^{-1}$ (Jones and Hatch, 1945).

Critical concentrations of arsenic in plants are rarely quoted, probably because of the non-specific nature of toxicity symptoms. Most appear to manifest as growth reductions, though more specific symptoms of marginal and interveinal discolourations on peach leaves, which later become interveinal and necrotic, have been reported (Batjer and Benson, 1958). Arsenic toxicity symptoms of root plasmolysis and discolouration with leaf wilting and necrosis of margins and tips were described by Machlis (1941). These symptoms suggested limitations to the efficient uptake of water by plants. Different forms of arsenic have different toxicities to plants. Clements and Munson (1947) showed in solution culture that trivalent arsenic was up to ten times more toxic than the pentavalent form which predominates in soils under most circumstances. Little appears to be known of the chemical forms of arsenic in plants, though it is possible that inorganic arsenic may form arsenylated compounds in plants (National Research Council Canada, 1978).

Hurd-Karrer (1936) and Clements and Munson (1947) observed that increased phosphate in solution cultures had the effect of preventing arsenic injury. Jacobs and Keeney (1970) found no interaction of arsenic with phosphorus in maize grown in pots except that phosphorus added to a sandy soil enhanced arsenic uptake and toxicity. Some conflict arises in results obtained when investigating arsenic and phosphorus interaction. When plants are grown in soil, the interactions are often interpreted in relation to what might be expected from soil chemistry, but the solution culture work mentioned above also suggests that there may be some further interaction within the plant.

If phosphorus is able to modify the effects of arsenic injury in plants, it is possible that other, similar, anions such as sulphate and molybdate may also be effective, though the possibility does not appear to have been explored. It was suggested by Walsh *et al.* (1977) that high arsenic concentrations in some fruit trees induces zinc deficiency which is then overcome by the use of zinc-containing sprays. However, evidence was not provided to show that the zinc deficiency was actually induced by arsenic.

The biochemical function of arsenic in producing toxicity is not clear. Perhaps most important is the action of arsenate in the uncoupling of oxidative phosphorylation (Mahler and Cordes, 1966). In the presence of some enzymes it may cause rapid hydrolysis of both sucrose and glucose-1-phosphate. Interference to reactions of energy transfer to ATP has been suggested as an explanation of loss of turgor in plants, injury and death (Dixon and Webb, 1964). Trivalent arsenic reacts readily and reversibly with sulphhydryl and irreversibly with dithiol groups. The herbicidal action of organoarsenical herbicides is beyond the scope of this review, but has been well covered by Woolson (1976).

## 2.6 Copper, Lead and Arsenic in Relation to Animal and Human Health

There has been little published until comparatively recently on the effects of accumulation of copper, lead and arsenic on the macrofauna that inhabit orchard areas. Hirst *et al.* (1961) noted that earthworm populations appeared to be adversely affected by high concentrations of copper. Mochizuki *et al.* (1975) also reported detrimental effects on earthworms and insect larvae of residual copper, lead and arsenic in orchard soils, especially when accompanied by low soil pH and exchangeable calcium. Elfving *et al.* (1979) studied the body burden of arsenic in rodents inhabiting the surface of orchard soils. A correlation between body burden and soil concentration was obtained, but pathological effects, if any, were unknown, as were the possible effects on predatory animals.

Specific pathological effects resulting from the chronic exposure of domestic animals to pasture and soils contaminated by copper, lead, or arsenic from sprays do not appear to have been reported although situations where stock have grazed freshly sprayed orchards or 'accidental' poisonings of an acute nature have occurred. The effects of copper on domestic animals and humans has been extensively reviewed by Underwood (1971). Deficiency and toxicity effects depend not only on copper intake, but also on the intake of zinc, iron, calcium and cadmium (Underwood, 1971; Mills and Dalgarno, 1972) which are generally antagonistic to copper. Ruminant animals such as sheep and cattle may be protected to some extent from excess copper provided that the molybdenum and sulphur status is adequate. Excess copper is accumulated in the liver of most animals and, since the ability to store copper varies, there are considerable species differences in tolerance. Haemolytic jaundice as a result of liver failure due to excess copper has not been recorded for rats, rabbits or birds but has been reported for sheep.

The diets of pigs are frequently supplemented with copper to increase rates of weight gain and feed efficiency (Baker, 1974). Supplementation is as high as 250 $\mu g\ g^{-1}$ in the feed, at which level the effects of toxicity may be evident. Higher amounts can be tolerated with zinc or iron additions. Sheep and cattle are more sensitive to copper, and diets containing copper concentrations as low as 80 $\mu g\ g^{-1}$ may result in toxicity. Losses of animals have been reported as a result of the grazing in orchards and vineyards. On subterranean clover based pastures in Australia, chronic copper toxicity in sheep has been observed when the plants contained as little as 10 to 15 $\mu g\ g^{-1}$ copper, but only 0.1 to 0.2 $\mu g\ g^{-1}$ molybdenum (Dick and Bull, 1945). Molybdenum supplements can effectively redress this situation.

In humans, copper toxicity is uncommon except in cases of Wilson's disease which results from a genetic disorder of the metabolism. Other cases relate to deliberate ingestion of copper salts or accidental poisoning, one of the main effects of which is to induce vomiting (Hill 1977).

Lead poisoning, on the other hand, has been known in humans for some considerable time. The common sources of lead of fifty to one hundred years ago, such as water pipes, food containers, paint and insecticides have been supplanted by others which include cigarette smoking, cosmetics and motor vehicle exhaust emissions (Underwood 1971). Apart from accidental poisoning due to the consumption of paint or insecticide, the main cause of poisoning in animals has probably been due to contamination of pastures by smelter emissions (Hammond and Aronson, 1964; Rains, 1971) and more recently there have been reports of poisoning of animals grazing pastures contaminated by motor vehicle exhaust emissions (Graham and Kalman, 1974). Horses are more sensitive to lead than cattle, with poisonings occurring on the former at forage concentrations of 80 $\mu g\ g^{-1}$ and in the latter at 200 to 300 $\mu g\ g^{-1}$. In these cases, the lead had been deposited directly onto leaf surfaces. Poisonings are unlikely where the source of lead in forage is solely by root uptake, although the potential exists for toxicity to occur due to the ingestion of highly contaminated soil in areas with low rainfall where growing seasons are short and droughts frequent (Merry and Tiller, 1978).

A more emotive and contentious issue is the subclinical effects of lead exposure on children (Bryce-Smith *et al.*, 1978) and adults (Waldron and Stöffen, 1974). The effects of lead on humans have been reviewed many times recently (Underwood, 1971; Waldron and Stöffen, 1974; Goyer and Mushak, 1977; Mehaffey, 1977 and others).

Arsenic is perhaps best known in its role as a poison, although it has had use in medicine as a tonic, and it has recently been shown that it is possibly essential in the diet of rats (Nielsen *et al.*, 1975). The poisoning of animals is usually acute and related to contamination of food supplies with herbicides or insecticides (Selby *et al.*, 1977). Occurrences are apparently related to the fact that some animals such as young dogs and calves often seek out and eat unusual materials so that poisonings for this reason are rare in older animals. Chronic effects are rare and poorly documented.

The situation with humans is similar in that chronic toxicity is unusual (Fowler, 1977). Acute toxicities commonly are the result of industrial exposure in smelters or from arsenical sprays. A number of epidemiological studies (see Sunderman, 1977) have shown that increased exposure to arsenic, either taken orally or by the respiratory tract, is correlated with increased incidence of cancer of the skin and lungs, but there has not been much supporting evidence for arsenicals causing cancers in laboratory animals.

The toxic effects of copper, lead and arsenic in both animals and humans have been extensively studied. Despite this, many aspects are still the subject of debate. Further discussion of the topic is beyond the scope of the present review.

# 3.0 EXPERIMENTAL METHODS

# 3.0 EXPERIMENTAL METHODS

## 3.1 Estimation of Area of Apple and Pear Orchards in Australia

Estimates of the area under apple and pear trees were made by the Australian Bureau of Statistics until 1971 when their system of reporting was changed. Prior to 1971, tree census information was provided by individual farmers and estimates for both the number of bearing trees and total trees were established, as well as the average number of trees per unit area for each statistical subdivision. On this basis the area producing apples and pears was calculated. With recent changes in orchard management, such as the more common use of close planting and espalier culture, calculations of area became inappropriate and, since 1971, only estimates of tree numbers have been provided. Using the average number of apple and pear trees per hectare (269 and 261 per hectare, respectively) an estimate of the maximum area for 1971 onwards was calculated.

## 3.2 Field Sampling of Soils

### 3.2.1 Surface Bulk Samples

Surface soil samples were collected from orchards and sites which were formerly orchards in South Australia and Tasmania for chemical analysis to investigate the extent of accumulation of copper, lead and arsenic. The samples were collected on a number of occasions between 1974 and 1979 from the Adelaide region and the adjacent hills in South Australia. They were also collected from fruit growing areas around Huonville, the Derwent, Tamar and Mersey Valleys, and Tasman Peninsula in February 1975, December 1977 and November 1978. A further small number of samples were obtained from other situations such as vineyards, almond and citrus orchards, hopfields and currant plantations where sprays containing copper were known to have been used.

These samples were taken from the 0-10 cm interval except for a few instances where 0-5 cm samples were collected. The 0-5 cm sample was used only when a 5-10 cm sample gave similar values for copper, lead and arsenic analyses. This is frequently the case in soils which are regularly cultivated. In former orchard soils, now in pasture, 10 cylindrical cores of 5 cm diameter were taken at random from an area of about 25 $m^2$ based on the sampling experience of Tiller *et al.* (1975). In existing orchards, a different pattern was used to take account of possible variations in drip patterns from the foliage of the trees (Miles 1968; Frank *et al.*, 1976). In this case, 10 cores were taken at approximately equal intervals in a straight line covering two inter-tree spaces *i.e.* between the trunks of three trees. In some orchards, particularly in southern Tasmania, a depression of 30-45 cm had developed between rows of trees because of repeated cultivation which was restricted to one direction. In some cases topsoil had been deliberately thrown up along the line of the rows of trees. Where cultivation effects were evident, soils were always sampled between trees along the line which appeared to have a minimum of disturbance.

### 3.2.2 Soil Profiles

Soil profiles were sampled in South Australia and Tasmania to investigate the distribution of copper, lead and arsenic within the profile and obtain evidence, if any, for translocation of the elements.

The South Australian soils were sampled from the upper Torrens River catchment near Adelaide. Soils used for apple and pear growing in this area are predominantly of the yellow and red podzolic types and have loamy surface textures. They were collected as 5 cm diameter cores to a depth of about 1 metre in the manner described by Billing (1975). The cores were divided into 10 cm sections, or lesser intervals if horizon changes were evident.

In Tasmania, soil profiles were sampled only in or close to the Huonville area surveyed by Taylor and Stephens (1935). Of the profiles described in some detail in section 4.2.4, four were sampled as close as possible to profiles sampled by Taylor and Stephens (1935). Profiles (a), (b), (d) and (e) correspond to Profiles 187, 208, 170 and 211 respectively of Taylor and Stephens (1935). These soils are described, with some analytical data, by Stephens (1935) and are typical of most of the apple and pear growing soils in Tasmania. The soils sampled in detail were either yellow podzolic soils or podzols and they possess a number of features which distinguished them from those sampled in South Australia. They frequently possessed very sandy and/or very organic surface horizons and often had impenetrable siliceous hardpans, up to 40 cm thick, developed at the bottom of the $A_2$ horizon. The Tasmanian profiles were sampled by horizon from a hand-dug pit or with the aid of a hand auger.

## 3.3 Field Sampling of Plants

### 3.3.1 Seasonal Variation in the Copper, Lead and Arsenic Concentration of Pasture Plants

After removal of orchard trees, many areas in both South Australia and Tasmania were maintained as pastures. Pasture plants were sampled at 5 locations to the northeast and east of Adelaide to assess seasonal variations in the concentrations of copper, lead and arsenic and thus their possible contribution to the diet of grazing animals.

Three sites, EH 12, E 460 and E 462, were formerly orchards. The remaining two sites were not orchard sites. Site EH 13 was adjacent to the abandoned Preamimma copper mine, the ore from which had a considerable arsenic content. Soil at the site was contaminated by both copper and arsenic without obvious accession of ore or tailing materials. Site EH 24 was a grazed pasture in a mineralized area which had resulted in increased concentrations of lead and arsenic in the soil. These five sites were selected for the range of copper, lead and arsenic concentrations in the soil which they provided (Table 3.1) and also to allow some comparison of orchard with mineralized and mine-affected soils. In the present study, site numbers are used interchangeably with soil numbers since the selection and subsequent use of a site depended initially on a soil sample.

Table 3.1 Cu, Pb and As concentrations[†] of surface soils (0-10 cm) at sites sampled for pasture plant species

| Site No. | Cu | Pb | As |
|---|---|---|---|
| E 460 | 154 | 422 | 80 |
| E 462 | 47 | 167 | 20 |
| EH 12 | 43 | 180 | 45 |
| EH 13 | 189 | 21 | 260 |
| EH 24 | 9 | 780 | 115 |

[†] $\mu g\ g^{-1}$, total concentration (aqua regia digest)

The plant species collected at each site are listed in Table 3.2. A uniform set of species could not be sampled although it was known that both *Trifolium subterraneum* and *Arctotheca calendula* grew at most of the sites. The species actually collected reflect the poor quality and weediness of pastures on former orchard soils. Only four of the species collected were perennials. These were *Holcus lanatus*, *Lolium perenne*, *Plantago lanceolata* and *Phalaris aquatica*.

Because of below average rainfall and resulting high grazing pressure, growth at three sites (EH 12, EH 13 and EH 24) was meagre. There was insufficient plant material to sample at EH 12 on one occasion and EH 13 on two occasions. The irregularity of rain resulted in the germination and growth of *Trifolium subterraneum* being very erratic. It failed to grow at EH 24, and could be sampled only once at site E 462.

Table 3.2 Plant species sampled at five sites for seasonal variation in Cu, Pb and As concentration

| Site No. | Species | Common Name |
|---|---|---|
| E 460 | *Trifolium subterraneum L.* | Subterranean clover, subclover |
| | *Holcus lanatus L.* | Yorkshire fog grass |
| | *Plantago lanceolata L.* | Plantain, ribgrass |
| | *Lolium perenne L.* | Perennial ryegrass |
| | *Arctotheca calendula (L.)* Levyns | Capeweed |
| E 462 | *T. subterraneum* | Subterranean clover, subclover |
| | *Bromus mollis L.* | Soft brome grass |
| | *A. calendula* | as above |
| | *Erodium botrys* (cav.) Bertol. | Wild geranium |
| EH 12 | *L. perenne L.* | as above |
| | *Echium plantigineum L.* | Salvation Jane |
| | *T. subterraneum* | as above |
| EH 13 | *T. subterraneum* | as above |
| | *Erodium moschatum (L.)* Ait. | Wild geranium |
| EH 24 | *A. calendula* | as above |
| | *Phalaris aquatica L.* | Phalaris |

Mean annual rainfall at the sites ranges between 675 and 850 mm except for EH 13 where it is estimated to be near 400 mm. The mean district rainfall and departures from average recorded for the area as a whole are shown in Table 3.3.

Table 3.3 Rainfall in the Mt. Lofty Ranges District[†] During 1975

| Month | April | May | June | July | Aug. | Sep. | Oct. | Nov. |
|---|---|---|---|---|---|---|---|---|
| Mean district rainfall (mm) | 36 | 126 | 33 | 117 | 82 | 68 | 128 | 24 |
| Departure from longterm mean (%) | -38 | +41 | -68 | +15 | -15 | -13 | +110 | -40 |

[†] Source: Bureau of Meterology Monthly Weather Reviews, South Australia, 1975.

Bulk samples of each species were collected on up to 4 occasions from June until November 1975. The plant material was obtained by cutting close to ground level. The samples were thoroughly rinsed with distilled water to remove possible contamination by soil and dried at 70°C. They were then ground in a stainless steel mill prior to analysis.

### 3.3.2 Concentrations of Copper, Lead and Arsenic in Soils and Pasture Plants

In order to assess possible relationships of soil concentrations of copper, lead and arsenic with that taken up by plants, plant and soil samples were collected from 13 sites in the Huonville area. The weedy and variable nature of pastures on old orchard soils near Adelaide made collection in that area difficult. The smaller Huonville district however provided uniform pastures on a range of soils with different copper, lead and arsenic concentrations.

A total of 19 pasture plant samples were collected, dried and ground as described in section 3.3.1. The plants were either *Lolium perenne* L. or *Trifolium* *repens* L. They were collected on the 2nd and 3rd of November, 1978 when they were making good growth despite late frosts.

## 3.4 Glasshouse Pot Experiments

### 3.4.1 Pot Experiment 1: The Effects of Soil Temperature on Copper, Lead and Arsenic Uptake by Three Plant Species

The aim of this experiment was to investigate the effects of different soil temperatures on the growth and copper, lead and arsenic uptake of three species, a pasture plant, a leafy vegetable and a root vegetable.

A split plot design was used with 48 plots made up of four replications of two temperatures (main plots), two soils and three species.

The three species used were:

(a) *Trifolium subterraneum L. cv.* Mt. Barker - subterranean clover,

(b) *Beta vulgaris L. cv.* Fordhook Giant - silver beet and

(c) *Raphanus sativus L. cv.* Long Scarlet - radish.

Subterranean clover is a pasture plant frequently grown on former orchard soils in South Australia. The silver beet and radish are easily grown vegetables commonly found in home gardens.

The two soils used were E 505, from an orchard, and EH 24, a mineralized soil. Further details of the soils and their chemical analysis are shown in Tables 3.4 and 3.5. The 0-10 cm surface soil was used in the pot experiments.

Table 3.4 Soils Used in Glasshouse Pot Experiments

| Soil Number | P.P.F.[†] | Great Soil Group[§] | Location | Soil Name | Reference |
|---|---|---|---|---|---|
| EH 12 | Dr 2.22 | Non-calcic brown soil | Coromandel Valley | Eden Hills Association | Ward (1966) |
| E 460 | Dr 3.41 | Red podzolic soil | Paracombe | Inglewood Association | Jackson (1957) |
| EH 21 | | | Verdun | Unmapped, yellow duplex | - |
| E 505 | Dr 2.11 | Non-calcic brown soil | Gumeracha | Cudlee Ck. Association | Jackson (1957) |
| EH 1 | Ug 5.16 | Black Earth | Reynella | Claremont Clay Loam | Ward (1966) |
| EH 23 | Uc 2.21 | Podzol | Mt. Crawford | Unmapped, alluvial sand | - |
| EH 13 | Um 1.43 | Lithosol | Monarto | Monarto Unit, Skeletal Phase | Chittleborough *et al.* (1976) |
| EH 24 | Dr 2.12 | Non-calcic brown soil | Mt. Torrens | Birdwood Association | Jackson (1957) |

[†] Principal Profile Form, Northcote (1971)

[§] Great Soil Group, Stace *et al.* (1968)

Table 3.5 Analysis of Soils Used in Glasshouse Pot Experiments

| | $\mu g\ g^{-1}$ | | | | | % | | | | meq (100 g)$^{-1}$ |
|---|---|---|---|---|---|---|---|---|---|---|
| Soil | Cu[1] | Pb[1] | As[1] | P[2] | Mn[3] | Fe[3] | Clay[4] | 0.6X WHC[5] | pH[6] | CEC[7] |
| EH 12 | 43 | 180 | 26 | 38 | 800 | 2.8 | 13 | 36 | 6.0 | 15 |
| E 460 | 155 | 455 | 120 | 120 | 215 | 8.3 | 12 | 34 | 6.4 | 17 |
| EH 21 | 295 | 340 | 85 | 250 | 70 | 1.2 | 9 | 35 | 6.7 | 17 |
| E 505 | 195 | 290 | 95 | 140 | 355 | 3.5 | 17 | 36 | 6.3 | 19 |
| EH 1† | 30 | 23 | 16 | 67 | 220 | 1.5 | 20 | 32 | 8.3 | 22 |
| EH 23† | 1.1 | 5.5 | 2 | 92 | 10 | 0.2 | 3 | 21 | 5.7 | 5.6 |
| EH 13 | 190 | 21 | 260 | 21 | 200 | 1.3 | 3 | 20 | 6.7 | 6.2 |
| EH 24 | 8.5 | 780 | 140 | 44 | 125 | 1.6 | 13 | 26 | 5.6 | 12 |

† Soils to which 250, 350 and 125 $\mu g\ g^{-1}$ of copper, lead and arsenic respectively were added

[1] Determined from analysis of an aqua regia digest.

[2] Extracted with 0.5M $NaHCO_3$ by the method of Colwell (1965).

[3] Determined from analysis of a nitric acid and perchloric acid digest.

[4] Determined by the method of Smith and Tiller (1977).

[5] Water holding capacity at a suction of ∿ 10 kPa by the method of Piper (1950).

[6] Determined on a 1:5 soil to water suspension.

[7] Cation exchange capacity by the method of Tucker (1974).

Two soil temperatures were obtained by:

(a) maintaining pots (the sides of which were shaded) at about ambient glasshouse temperature. The air temperatures were maintained at near 20°C by thermostatically controlled heaters and evaporative coolers.

(b) placing pots in an insulated, water-filled tank in which refrigerated water was circulated under thermostatic control at about 10°C.

Soil temperatures were monitored initially by thermometers placed at 7.5 cm depth at the centre of all pots. Temperatures were found to be uniform within each temperature treatment during the first week of the experiment and thereafter only two pots in each treatment were monitored. The air and soil temperatures were maintained at or near the set level for most of each 24 hour period, but the temperature controls on both the glasshouse and the tank were unable to cope fully with temperature increases on warm to hot days. Air temperatures usually reached a maximum at about 1500 hours on warm days and soil temperatures at about 1600 hours.

Measured soil and air temperatures are shown in Table 3.6. For the purposes of this experiment, the low and high temperature soil treatments will be referred to as the 12°C and 22°C treatments.

Table 3.6 Mean Daily Temperatures in Low and High Soil Temperature Pots, and Circulating Air in the Glasshouse[†]

| | Pots | | Air |
|---|---|---|---|
| | Low Temperature | High Temperature | |
| mean minimum | 11.9 ± 0.7 | 22.3 ± 0.5 | 19.2 ± 0.7 |
| mean maximum | 14.8 ± 1.4 | 26.0 ± 2.5 | 29.5 ± 4.0 |

[†] °C ± Standard Deviation

For comparison, mean daily soil and air temperatures at Glen Osmond, South Australia, are shown in Table 3.7.

Table 3.7 Mean Daily Temperatures ($^{o}C$) at Glen Osmond, South Australia

| Depth | Soil Temperatures 2.5 cm Max. | Soil Temperatures 2.5 cm Min. | Soil Temperatures 15.2 cm Max. | Soil Temperatures 15.2 cm Min. | Air Temperatures Max. | Air Temperatures Min. |
|---|---|---|---|---|---|---|
| January | 43.1 | 18.1 | 29.9 | 22.1 | 27.8 | 16.3 |
| February | 41.9 | 18.0 | 29.5 | 22.0 | 27.5 | 16.4 |
| March | 38.0 | 16.3 | 26.8 | 20.2 | 25.6 | 15.4 |
| April | 28.5 | 13.0 | 21.1 | 16.2 | 21.4 | 12.9 |
| May | 21.2 | 10.1 | 16.2 | 12.8 | 17.8 | 10.6 |
| June | 17.6 | 8.2 | 13.3 | 10.5 | 15.1 | 8.6 |
| July | 16.5 | 7.5 | 12.3 | 9.5 | 14.2 | 7.8 |
| August | 18.6 | 8.0 | 13.6 | 10.3 | 15.1 | 8.0 |
| September | 23.3 | 9.7 | 16.8 | 12.3 | 17.6 | 9.3 |
| October | 29.1 | 12.2 | 20.8 | 15.1 | 20.2 | 10.9 |
| November | 35.2 | 14.7 | 25.0 | 18.0 | 23.3 | 12.6 |
| December | 40.1 | 16.9 | 28.1 | 20.6 | 25.7 | 14.6 |
| Year | 29.4 | 12.7 | 21.1 | 15.8 | 20.9 | 11.9 |

Source: Biennial Report of the Waite Agricultural Research Institute 1976-77.

*Procedure*

Plastic pots measuring 165 mm in diameter and 150 mm deep with a polythene liner were used in this experiment. Each pot contained 2.5 kg of air-dried and sieved (< 6 mm) soil. Basal fertilizers were applied as outlined in Appendix 1. Pots were watered with distilled, deionized water to 60% of the water holding capacity of the soil as determined by the Keen-Raczkowski method described by Piper (1950). This determination has been shown by Fergus and Stirk (1961) to correspond to a water potential of about -10 kPa. The pots were watered every 2-3 days during early growth, and daily as water demand increased.

Seeds, sieved for uniformity of size (although this was difficult for silver beet which has an irregular biconvex shaped seed) were sown on 30th July, 1974. No *Rhizobium* inoculum was applied to pots growing subterranean clover as the soils had previously grown clover which was well nodulated. Subsequent examination of the plants in the pot experiment showed that they were effectively nodulated. Most plants emerged within 3-4 days. At this stage, a mulch of white polythene beads was applied to the surface of the soil in each pot. Acid extraction of the beads revealed no detectable copper or lead. The plants were thinned to 6 per pot within 14 days except for silver beet growing at low soil temperature on soil EH 24 which were thinned a few days later. The second application of basal nutrients was made after 40 days. On 18th October, the plants were photographed, harvested and soil samples taken. After harvest, weights of the fresh plant tops and also radish roots were determined. The tops of the plants were rinsed with distilled water. The roots of radish were first washed with tap water to remove adhering soil, then with distilled water to a state suitable for human consumption. These plant samples were then dried at 70°C, weighed and then ground in a stainless steel mill prior to chemical analysis for copper, lead, arsenic and, where sufficient material was available, for manganese, zinc and iron.

### 3.4.2 Pot Experiment 2. The Effect of Varying Soil pH and Prior Waterlogging on Two Plant Species Grown on Eight Soils

The aim of this experiment was to simulate in pots some effects which may result from intensive agriculture or home garden usage of former orchard soils. Such effects could include pH changes brought about by liming the soil, or acidification due to the addition of large amounts of acidifying fertilizer. These effects were investigated, along with the effect of waterlogging which frequently occurs naturally in many of the soils in the Adelaide region for short periods in winter or may result from over-irrigation.

The experiment was set up in a randomized block design with 3 replications (one replicate per block), 8 soils and 2 plant species. The species were radish (a root vegetable) and silver beet (a leafy vegetable). For radish, the soils were subjected to 4 treatments and for silver beet, there were 5 treatments. This resulted in a total of 216 pots. The pots were re-randomized within each of the 3 blocks every fortnight in an effort to reduce within block variation which may have resulted from the large size of the experiment.

The 8 soils chosen for this experiment included two former orchard soils (EH 12 and E 460), two soils from existing orchards (EH 21 and E 505), two soils of contrasting texture, pH and organic matter contents (EH 1 and EH 23) but with low copper, lead and arsenic contents, and two soils (EH 13 and EH 24) affected by mining or mineralization. The two soils low in copper, lead and arsenic (EH 1 and EH 23) were treated with copper sulphate and commercial lead arsenate (98% $PbHAsO_4$) at rates equivalent to 250, 350 and 125 $\mu g\ g^{-1}$ of copper, lead and arsenic respectively.

Information on the 8 soils is provided in Table 3.4 with some chemical and physical data in Table 3.5. Additional information on soils EH 13 and EH 24 is provided in Section 3.3.1. The soil EH 24 was the same soil as the 'Mt. Torrens' soil investigated by Norrish (1975). Norrish (1975) reported the presence of the lead mineral hinsdalite and that it also contained a higher than normal concentration of arsenic. Two soils, EH 24 (Mt. Torrens) and E 505 (Gumeracha) were also used by McKenzie (1978) in experiments with the application of manganese oxides to soils with high lead contents.

In Table 3.5, it should be noted that soil EH 13 has a low lead concentration and soil EH 24 has a low copper concentration. The contrast in pH, clay content and cation exchange capacity of soils EH 23 and EH 1 is also shown.

The treatments used to alter the pH of the soils are summarized in Table 3.8. Apart from the untreated control, each soil was treated with sulphur to lower the pH, and with calcium carbonate to raise pH. The exception was soil EH 1 which, because of its naturally high pH, was instead treated with sulphur at two rates. A treatment of gypsum was applied to provide an additional, acidic adjustment of pH and a different source of sulphate which could assist in interpreting the sulphur treatment.

The method used to lower the pH of the soil was to add finely powdered sulphur to each pot and mix it thoroughly through the soil in a rotating paint mixer. Each pot was then inoculated with 100 ml of a solution prepared in the following manner. One gram of sulphur was added to 100 g of each soil and was moistened to a water potential of about -10 kPa. The pH of these mixtures were then observed to decrease as the natural soil population of sulphur oxidizing microorganisms began to produce acid. After about three weeks, distilled water was added to the cultures until there was sufficient inoculant to use 100 ml per pot. Soil EH 1 received a substantially greater amount of sulphur because of its high pH and $CaCO_3$ content (1.5%). Theoretically 12 g of sulphur, if completely converted to $H_2SO_4$, is required to neutralize the natural $CaCO_3$ in, each pot containing this soil.

Table 3.8 Treatments Used to Alter Soil pH in Pot Experiment 2[†]

| Treatment: Soil | Sulphur | Sulphur | Control | Calcium Carbonate | Gypsum |
|---|---|---|---|---|---|
| EH 12 | | 2 | 0 | 5.0 | 10.8 (2)[§] |
| E 460 | | 2 | 0 | 2.5 | 10.8 (2) |
| EH 21 | | 2 | 0 | 3.75 | 10.8 (2) |
| E 505 | | 2 | 0 | 3.75 | 10.8 (2) |
| EH 1 | 16 | 8 | 0 | | 43 (16) |
| EH 23 | | 1 | 0 | 2.5 | 5.4 (1) |
| EH 13 | | 1 | 0 | 2.5 | 5.4 (1) |
| EH 24 | | 2 | 0 | 3.75 | 10.8 (2) |

[†] figures indicate application rate in g per pot

[§] figures in brackets indicate sulphur equivalent of the gypsum treatment

The gypsum treatment was applied as a fine powder which was mixed through the soil in the same way as the sulphur. The amount applied matched the sulphur-treated soils in sulphur content and was only applied to pots in which silver beet was grown.

The 'prior waterlogging' treatment simply involved flooding the soils with distilled water for a period of 31 days. At the end of this period, the soils were allowed to dry. The treatment had some obvious effects. There was conspicuous growth of algae on the surface of the waterlogged soils and the growth of fungal hyphae was evident on soils EH 1, E 460 and E 505 as they dried out. Mobilized iron oxides were deposited on the plastic pot liners of all soils except EH 1.

The soils in all pots, except for 'prior waterlogging' were maintained at a water potential of about -10 kPa for one month to equilibrate. After eleven days, subsamples were taken for pH determination on the moist sample to ensure that changes in pH were occurring. The soils were then allowed to dry, and removed from the pots. The soil from each treatment was bulked, thoroughly mixed and repotted. They were resampled prior to sowing the seeds and again at harvest.

The procedures for sowing, applying basal nutrient and watering in this experiment were as for Pot Experiment 1. Silver beet and radish were sown on the 11th of September 1974. Most pots were thinned to 5 silver beet plants and 6 radish plants within 14 days. By this time however, it was obvious that some plants were not going to survive, particularly those growing on soil EH 23. Selected pots were photographed at this time. Tops of the plants were harvested on 22nd November, 1975 and roots three days later. The roots were sampled from only one block of silver beet. The remaining two blocks were used to obtain soil samples for pH determinations (moist and dry) and the analysis of moist samples for copper and lead extractable with DTPA and arsenic extractable with 0.5 M $NaHCO_3$.

### 3.4.3 Pot Experiment 3. The Effects of Fertilizer Applications on the Uptake of Copper, Lead and Arsenic by Silver Beet Grown on Orchard Soils

The aim of this experiment was to assess the effects of the major nutrients, phosphorus, sulphur and nitrogen, on the uptake of copper, lead and arsenic by silver beet.

Applications of fertilizers containing nitrogen, phosphorus, potassium and sulphur at rates up to 1000 kg $ha^{-1}$ are not unusual in horticulture and frequently this amount is exceeded in vegetable growing. Fruit trees and vines in South Australia received an average of nearly 700 kg ha$^{-1}$ of fertilizer in 1977 (South Australian Year Book, 1979) and fruit trees in Tasmania received an average of 930 kg ha$^{-1}$ (Tasmanian Year Book, 1979). There have also been reports in the literature (e.g. Zimdahl and Foster, 1976) that phosphate lowers the uptake of lead by maize. Both phosphate (e.g. Hurd-Karrer, 1936; Jacobs and Keeney, 1970; Woolson *et al.*, 1973) and sulphate may, because of their anionic form, be expected to have some effect on arsenate uptake. The results of Thompson and Batjer (1950) with peach trees suggested that nitrogen applications may have some effect on arsenic uptake. John and van Laerhoven (1972) obtained conflicting results when they investigated the effects of nitrogen applications on the uptake of lead by lettuce and oats. The response depended on whether the lead was freshly applied and if so, what form of lead. Potassium was expected to have little or no effect on the uptake of any of the elements.

The experiment had three parts. The main part of the experiment (Pot Experiment 3a) was to assess the effects of P and S. In addition, a commercial mixed fertilizer (containing N, P, K and S) was compared with the equivalent applied as laboratory chemicals (Pot Experiment 3b), and in one soil only several rates of nitrogen were applied (Pot Experiment 3c).

## Pot Experiment 3a: The Effects of Phosphate and Sulphate on Silver Beet Grown in Orchard Soils

This experiment had a randomized block design, and three replications. The treatments, which were arranged in a factorial combination, comprised two soils, and 4 rates of phosphorus and 3 rates of sulphur application.

The two soils used were E 460, a former orchard soil, and E 505 which was from an existing orchard. (See also Tables 3.4 and 3.5.) The rates and form of phosphorus and sulphur as well as basal nitrogen and potassium are shown in Table 3.9. These rates were equivalent to those supplied by 1000 kg ha$^{-1}$ of a mixed fertilizer which is commonly used in South Australia. The elements were applied in a manner similar to that described for the previous experiments. A basal fertilizer application of nitrogen and potassium was added to all pots in two equal applications, one before sowing and the second four weeks later.

Table 3.9 Pot Experiment 3a: Rates of Phosphorus, Sulphur and Basal Nutrients Applied to the Pots

| | | | | | |
|---|---|---|---|---|---|
| P | : | 0; 17.5; 35$^{\dagger}$; 52.5 | kg ha$^{-1}$ | as | $NaH_2PO_4.H_2O$ |
| S | : | 0; 85 ; 170$^{\dagger}$ | kg ha$^{-1}$ | as | $CaSO_4.2H_2O$ |
| N | : | 80$^{\dagger}$ as two applications of 40 kg ha$^{-1}$ | kg ha$^{-1}$ | as | $NH_4NO_3$,$KNO_3$ |
| K | : | 80$^{\dagger}$ | kg ha$^{-1}$ | as | $KNO_3$ |

† nutrients at the rate equivalent to 1000 kg ha$^{-1}$ of a commercial mixed fertilizer

### Pot Experiment 3b: A Comparison of Commercial Fertilizer with the Equivalent in Pure Chemicals

This experiment compared the effects of equivalent rates of pure (analytical grade) chemical forms of nitrogen, phosphorus, potassium and sulphur with a commercial mixed fertilizer applied at 1000 kg ha$^{-1}$. There were 3 replications of each treatment (i.e. chemicals and commercial fertilizer) applied to two soils (E 460 and E 505) making a total of 12 pots. The experiment was run concurrently with Experiment 3a, and 6 pots were common to both experiments.

### Pot Experiment 3c: The Effects of Nitrogen on Silver Beet Grown on an Orchard Soil

This experiment consisted of three replicates of three nitrogen treatments (equivalent to 0, 80 and 160 kg ha$^{-1}$) applied in two equal applications to soil E 460. Three pots were common to Experiment 3a. A basal fertilizer application equivalent to 35 kg ha$^{-1}$ phosphorus, 170 kg ha$^{-1}$ sulphur and 80 kg ha$^{-1}$ potassium (equal in phosphorus, sulphur and potassium content to 1000 kg ha$^{-1}$ of commercial fertilizer) was applied to all pots. Fertilizer was applied as in Table 3.9, except that potassium was added to the control (no nitrogen) pots as KCl. The additional nitrogen added to the high nitrogen treatment was supplied as $NH_4NO_3$ in solution.

Silver beet was sown in all pots of Experiments 3a, 3b and 3c on 10th October, 1975. After 14 days all pots had been thinned to 5 plants. On day 25, the second application of nitrogen and/or potassium was made. The plants were harvested on day 53 and both tops and roots were retained for weighing, drying, determination of dry weight and grinding. These procedures, along with watering the plants during growth, were as described for previous experiments.

## 3.5 Analytical Techniques

### 3.5.1 Soil Digestions, Extractions and Other Measurements

The following methods were used:-

Aqua regia digest: the method of Merry and Zarcinas (1980) but without the addition of hydroxylamine hydrochloride.

EDTA extraction: the method of Clayton and Tiller (1979). Soils EH 24 and E 505 were included in their study.

DTPA extraction: the method of Lindsay and Norvell (1978).

$NaHCO_3$ extractable P: the method of Colwell (1965). Arsenate was found not to interfere with this method.

$NaHCO_3$ extractable As: the method was as for $NaHCO_3$ extractable P except that a 1:20 ratio of soil to solution was used instead of 1:100. Arsenic was measured spectrophotometrically on the acidified extract using the method described by Merry and Zarcinas (1980).

pH: was measured in 1:5 soil to water suspensions.

Standard soils samples and blanks were carried through all batches of analyses.

### 3.5.2 Plant Digestion Procedures

Two digestion procedures were used for plant materials. This was necessary for two reasons. Lead cannot be determined satisfactorily in digestion procedures using sulphuric acid. For arsenic however, nitric and perchloric acids are unsuitable because residual oxidizing acids interfere in the reducing step of the arsenic determination (Duncan and Parker, 1970 and confirmed by our own experience).

Nitric and perchloric acid digests were used for analysis of both lead and copper following the method of de Vries *et al.* (1975). Arsenic, copper, manganese, zinc and iron were determined on perchloric, nitric and sulphuric acid digests following the procedure described by Merry *et al.* (1980). Considerable experience in the use of both of these procedures has been gained in the laboratories of the Division of Soils, CSIRO, Glen Osmond, South Australia. The procedures have been found to perform well when analysing standard reference materials (see below for arsenic) and in international inter-laboratory comparisons.

### 3.5.3 Methods of Determination of the Elements

All of the elements except arsenic were determined by atomic absorption spectroscopy using Varian Techtron Model 1200 and Perkin-Elmer Model 400 instruments. Direct flaming was used in all cases except where lead concentrations were below about 15 μg $g^{-1}$ in the plant material. In this case a solvent extraction of the ammonium pyrrolidine dithiocarbamate complex into methyl isobutyl ketone was used following the method of de Vries *et al.* (1975). Air/acetylene flames were used except for iron, when $N_2O$/acetylene was employed.

Considerable difficulties were experienced in obtaining a suitable method for the determination of arsenic. A modified spectrophotometric procedure based originally on that of Vasak and Sedivec (1952) was eventually adopted. The modified procedure is presented in detail by Merry and Zarcinas (1980) and has been included as Appendix 6. The method involves the use of sodium tetrahydroborate (III) to generate $AsH_3$. With silver diethyldithiocarbamate in pyridine, the $AsH_3$ forms a red complex which can be measured spectrophotometrically at 540 nm.

Systematic checking of the method for arsenic showed that none of the other elements pertinent to this study interfered with either the $AsH_3$ generation or colour development. However, antimony and tin interfere. Antimony was not present in measurable quantities in the samples studied, but tin was present sporadically in soil EH 13 which came from the close vicinity of a copper mine.

As reported by Merry and Zarcinas (1980), the digestion procedures and method for arsenic produced results which agreed well with analyses of Standard Reference Material 1571 (orchard leaves) of the U.S. National Bureau of Standards. Aliquots of digested orchard leaves, other reference samples and, in some cases, standard additions were used to check the method at concentrations below 1 $\mu g\ g^{-1}$. The method was also compared with analyses by x-ray fluorescence spectrophotometry (XRF) of 12 soil samples. The relationship of XRF analyses with spectrophotometry (following digestions with aqua regia) was as follows:-

$$As_{(XRF)} = 1.05\ As_{(SPECT)} - 3.5 \qquad r = 0.99,\ n = 12$$

The concentration of arsenic in the 12 soil samples ranged from 25 to 370 $\mu g\ g^{-1}$. This range, coupled with the poorer precision of the XRF method, accounts for the value of the intercept.

# 4.0 RESULTS AND DISCUSSION

# 4.0 RESULTS AND DISCUSSION

## 4.1 Brief History of the Apple and Pear Growing Industry in Australia

Estimates of the area or number of apple and pear trees in Australia give some idea of the history of the industry. It probably reached its peak during the 1920's and 1930's. Tasmania, for instance reached a peak of $3.8 \times 10^6$ apple trees in 1925 (Stephens, 1935) compared with $1.24 \times 10^6$ in 1978. Stephens (1935) estimated that some orchards were 60 years old in 1935. The estimated total area of land planted to apples and pears in Australia at various times are shown in Table 4.1. The methods of calculation of area are discussed in Section 3.1.

After reaching an initial peak, it is evident that the industry declined generally between 1939 and 1949. After this period it rose to a new peak at about 1965 then remained stable until about 1970 (Table 4.1). In 1971, a rapid decline began when traditional markets in the United Kingdom and Europe were no longer available because of the entry of the United Kingdom into the European Economic Community.

The indicated decrease in area of about 25000 ha is certainly an under-estimate for two reasons:

(a) closer planting of trees in recent years has led to the area being overestimated because the estimate of the number of trees per hectare is too low (see Section 3.1).

(b) not all new plantings have been made on former orchard areas. Because of this, new orchard land continually replaces a proportion of land taken out of production. No accounting of this is possible from the statistics which are available. At any time, however, approximately 20% of total trees are non-bearing. This percentage gives some idea of the replacement trees and new trees being planted at any particular time.

Table 4.1 Estimated Total Area of Apple and Pear Orchards in Australia (hectares)

| | 1934-39 | 1945-50 | 1965 | 1970 | 1975 | 1978 |
|---|---|---|---|---|---|---|
| Apples | 40947 | 30459 | 38392 | 37081 | 21914 | 18863 |
| Pears | 8574 | 7862 | 10554 | 10315 | 7684 | 5808 |
| Total | 49521 | 38321 | 48946 | 47396 | 29598 | 24771 |

Source: Australian Bureau of Statistics
Crop and Fruit Statistics Publications

It is apparent that the area formerly devoted to apples and pears and now used for other purposes cannot be estimated accurately but can be conservatively placed in the vicinity of 27500 to 30000 ha. This area is approximately equivalent to the total area used for apple and pear orchards in 1978.

The total number of Australian apple and pear trees in 1978 was 68% of the number in 1973. A similar decline (62%) occurred in the stone fruit industry (apricots, peach and cherry). On the other hand, the citrus industry maintained its size over the same period and the area growing grapevines increased by 16000 ha to 73000 ha in the ten years to 1978. The stone fruit industry in particular but also the citrus and grape industries, frequently use copper-containing sprays. Lead arsenate is occasionally used on some varieties of grape.

The estimated 27500 to 30000 ha decrease in land used for growing apples and pears represents the minimum area of soils affected by copper, lead and arsenic from sprays. Within this area, the soils will have varying levels of spray contamination.

Several important land use categories are now associated with former orchard areas, but a detailed assessment of current land use is not possible in this study. The main uses are:

a) *Pasture production and small 'hobby' farms.* This is probably the main activity and is prominent in the hills adjacent to Adelaide (South Australia) and in the Huon, Tamar and Derwent River valleys (Tasmania).

b) *Urban development.* This is evident in the area east of Melbourne (Victoria), around Hobart (Tasmania), Orange (New South Wales) and in the hills to the east of Adelaide (South Australia).

c) *Vegetable production.* This occurs in the hills to the east of Adelaide and also at Huonville (Tasmania).

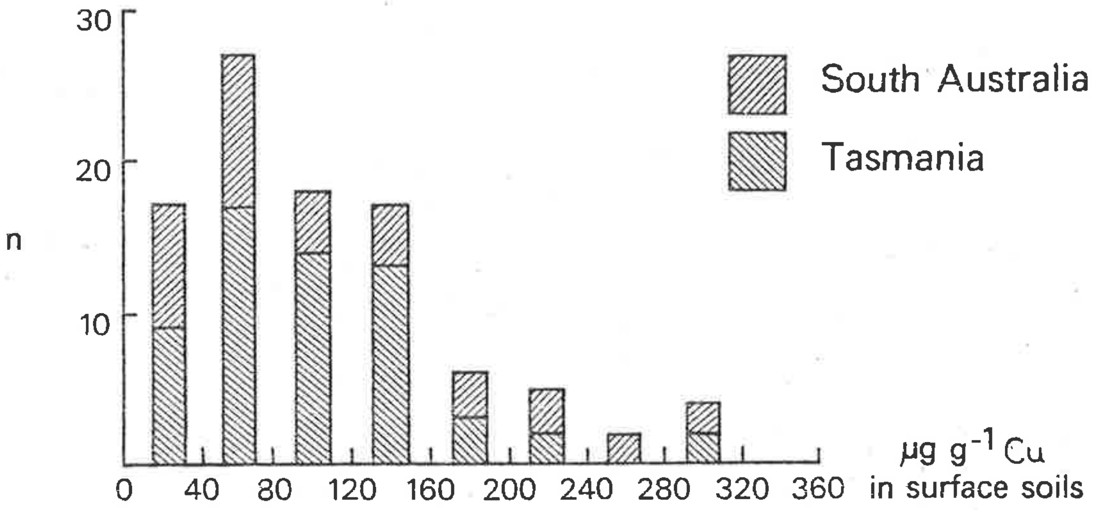
## 4.2 Copper, Lead and Arsenic in Orchard Soils

### 4.2.1 Copper, Lead and Arsenic in Surface Soils

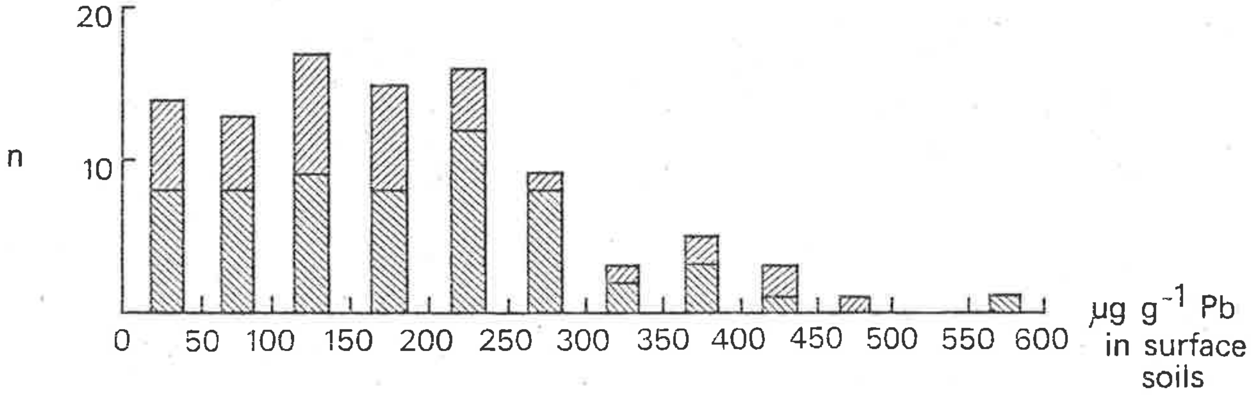
#### *Frequency Distributions of Copper, Lead and Arsenic (in Apple and Pear Orchard Soils)*

The frequency distributions of copper, lead and arsenic concentrations in the surface (0-10 cm) of 98 apple and pear orchard soils and former orchard soils from South Australia and Tasmania are shown in Figure 4.1. These concentrations were obtained by the analysis of aqua regia digests and should closely match the total concentrations of the elements in the soils.

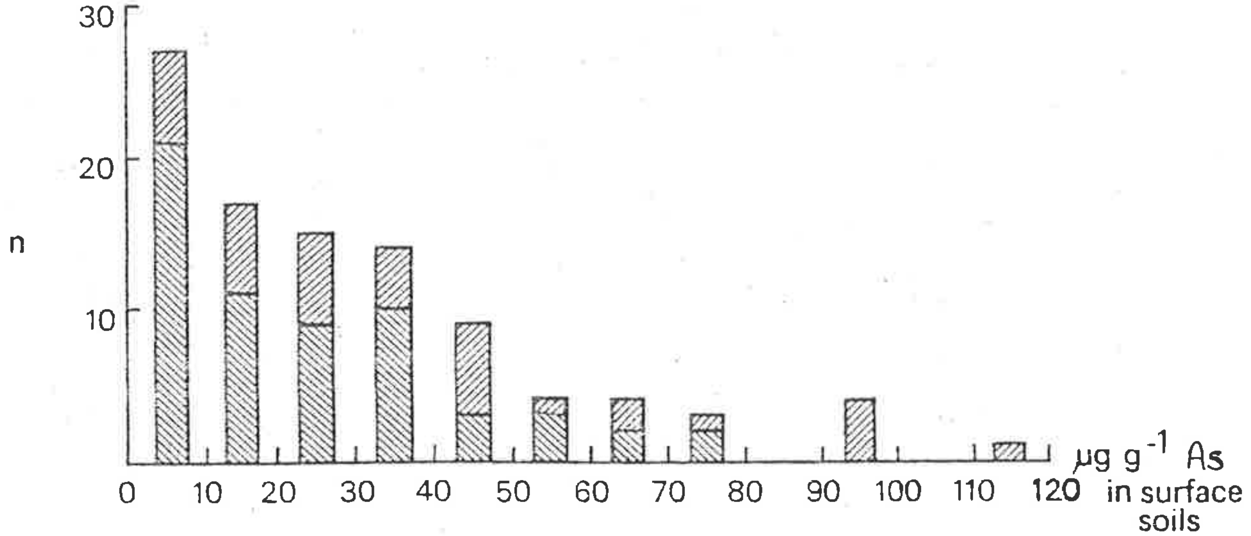
As shown earlier in Table 2.2, the mean copper and lead concentrations of uncontaminated surface soils from southeastern Australia are about 13 and 15 µg $g^{-1}$ respectively. Mean concentrations for arsenic in Australian soils are not available, but 15 soils (0-10 cm) from South Australia and 6 from Tasmania which are unlikely to have been affected by lead arsenate were found to have mean (± standard deviation) arsenic concentrations of 3.93 (± 2.02) and 0.60 (± 0.55) µg $g^{-1}$ respectively. A mean arsenic concentration of 5 µg $g^{-1}$ has been suggested for uncontaminated soils (Section 2.2.3). The concentrations presented in Figure 4.1 for orchard soils show that copper, lead and arsenic are present in surface soils in amounts which are, respectively, up to about 25, 35 and 25 times the mean concentrations for uncontaminated soils.



a) Copper in surface soils



b) Lead in surface soils



c) Arsenic in surface soils

Figure 4:1 Total Copper, Lead and Arsenic in Orchard Soils.

### *Copper, Lead and Arsenic in Vineyards and other Orchard Soils*

The copper, lead and arsenic concentrations of a further 15 horticultural soils are shown in Table 4.2. Many of these soils have received copper from agricultural sprays but apparently very little lead or arsenic. Further investigation of copper in soils growing peach, almond and citrus trees is probably desirable since copper sprays are still frequently used. Although copper sprays are periodically used in vineyards, the amounts appear to be quite small. Several of the vineyard soils sampled were old by Australian standards (established about 1840) but the copper concentrations of the soils are low compared, for example, to the concentration of 850 μg g$^{-1}$ reported by Gärtel (1957).

Table 4.2 Total Copper, Lead and Arsenic (μg g$^{-1}$) in Some Horticultural Soils From South Australia and Tasmania (0-10 cm)

| Crop and Location | Cu | Pb | As |
|---|---|---|---|
| Grapevines (S.A.)[†] | 20.1 (9.9) | 20.9 (10.1) | 4.95 (1.37) |
| Almonds (S.A.) | 22 | 15 | 4.0 |
| | 66 | 19 | 4.8 |
| Citrus (S.A.) | 40 | 23 | <0.5 |
| Peach (S.A.) | 212 | 24 | <0.5 |
| Currant (Tas.) | 29 | 26 | 0.5 |
| | 53 | 16 | <0.5 |
| Hops (Tas.) | 24[§] | 34 | 5.5 |
| | 30[§] | 28 | 0.7 |
| | 19 | 19 | 2.3 |

[†] The value for grapevines is the mean (S.D.) of 6 sites. The other values reported are for individual sites.

[§] Formerly apple orchards.

### *Relationships Between Total Copper, Lead and Arsenic*

Linear regressions between total copper, lead and arsenic concentrations in the apple and pear orchard soils with concentrations extractable by EDTA and DTPA are shown in Table 4.3. The South Australian and Tasmanian data have been separated to allow comparison.

Table 4.3 Correlations Between the Total and Extractable Copper, Lead and Arsenic Concentrations in the Surface Soils of South Australian and Tasmanian Orchards[†]

| Regression | $R^2$ | n |
|---|---|---|
| South Australia | | |
| $As_T = 0.214\ Pb_T + 13.2$ | .75[§] | 37 |
| $Pb_T = 0.947\ Cu_T + 68.4$ | .41 | 37 |
| $Cu_T = 1.73\ As_T + 44.9$ | .40 | 37 |
| $Pb_{EDTA} = 0.840\ Pb_T - 3.39$ | .94 | 25 |
| $Cu_{EDTA} = 0.835\ Cu_T - 8.37$ | .90 | 25 |
| $Pb_{DTPA} = 0.247\ Pb_T - 9.96$ | .77 | 27 |
| $Cu_{DTPA} = 0.368\ Cu_T - 7.76$ | .92 | 27 |
| Tasmania | | |
| $As_T = 0.095\ Pb_T + 6.02$ | .31 | 60 |
| $Pb_T = 1.45\ Cu_T + 36.9$ | .65 | 59 |
| $Cu_T = 1.80\ As_T + 57.4$ | .31 | 60 |
| $Pb_{EDTA} = 0.830\ Pb_T - 0.11$ | .95 | 19 |
| $Cu_{EDTA} = 0.845\ Cu_T - 1.94$ | .95 | 19 |
| $Pb_{DTPA} = 0.600\ Pb_T - 44.9$ | .73 | 24 |
| $Cu_{DTPA} = 0.373\ Cu_T - 9.96$ | .87 | 24 |

[†] The subscripts *T*, *EDTA* and *DTPA* refer to Total, EDTA and DTPA extractable concentrations, respectively.

[§] All $R^2$ values are significant at $P < 0.001$.

Although the detailed history of supply of lead arsenate in Australia appears to be unknown, commercial lead arsenate (98% $PbHAsO_4$) has been supplied from a single source for some decades (F.A. Blair, personal communication). If the main contribution of lead and arsenic to these soils is from lead arsenate, and neither element is lost from the soil, the slopes of the regression lines between lead and arsenic could be expected to approach 0.36 since this is the mass ratio of lead to arsenic in lead arsenate ($PbHAsO_4$). It can be seen from Table 4.3 that the slopes of the regressions of total arsenic concentration with total lead concentration are lower than 0.36 and that the slope of the regression for the Tasmanian data is much lower than that of the South Australian data. Inspection of the data in Figure 4.1 shows that there is a disproportionately large number of Tasmanian soils with low arsenic concentrations (less than 10 $\mu g\ g^{-1}$). This suggests that arsenic has been lost, relative to lead, from many of the surface soils.

The regressions of total lead concentrations with total copper concentrations for the two regions were also different (Table 4.3). This may merely reflect the difference between Tasmania and South Australia in disease and pest incidence and therefore spray usage. As will be shown later, it is unlikely that the differences between the regressions of total lead with total copper are due to soil factors or processes such as leaching.

### *Relationships of EDTA and DTPA Extractable Copper and Lead with Total Concentrations*

Copper and lead extracted by EDTA were highly correlated with their respective total concentrations (Table 4.3). The regression equations for copper and lead are almost identical and there is also little difference between the regressions for the South Australian and Tasmanian data.

Regressions of copper and lead extractable by DTPA with respective total concentrations of the soils are also shown in Table 4.3. The regression equation for copper extracted from the South Australian soils is similar to that for the Tasmanian soils. The regressions with lead however are different and they also differ from the copper regression equations. Inspection of the data (presented in Appendix 2) shows that above about 300 μg $g^{-1}$ of total soil lead, the proportion of lead extracted by DTPA becomes higher and very variable. The reason for this was not investigated but was probably associated with the lower affinity of lead at high concentration in some sandy soils. The much greater extraction of copper and lead achieved by EDTA compared to DTPA is probably a result of the concentrations used (0.1 M and 0.005 M respectively).

### 4.2.2 Critical Concentrations of Copper, Lead and Arsenic in Orchard Soils

As discussed in Section 2.5, there are no generally accepted 'critical concentrations' of copper, lead or arsenic above which toxicity problems might be expected to occur in plants. However, the concentrations which have been found by various workers to be harmful can, with some caution, be compared with the data in Section 4.2.1. This may indicate how many of the orchard soils could present problems to the plants growing on them.

With respect to copper, Reuther and Smith (1953) observed that toxic effects appeared in citrus at total soil concentrations greater than 125 to 200 μg $g^{-1}$ at cation exchange capacities of 4 to 6 meq $(100\ g)^{-1}$ soil. The majority of the Tasmanian (Stephens, 1935) and of the South Australian orchard soils have cation exchange capacities greater than 10 meq $(100\ g)^{-1}$. If 200 μg $g^{-1}$ of total copper is regarded as a reasonable critical value, about 10% of the orchard soils exceed this value. Walsh *et al.* (1972) found in field experiments with beans that significant yield reductions occurred when DTPA extractable copper exceeded 40 μg $g^{-1}$. Based on the equations in Table 4.3, this value is equivalent to approximately 140 μg $g^{-1}$ of total copper and 100 μg $g^{-1}$ of copper extractable by EDTA. Approximately 30% of the orchard soils shown in

Figure 4.1 have total copper concentrations exceeding 140 μg $g^{-1}$. However, it should be pointed out that the results of Walsh *et al.* (1972) were obtained from trials where large amounts of copper were freshly applied. Concentrations in the plants continued to decline over the two years for which their results were obtained. It was likely, as stated by the authors, that equilibrium of applied copper with the soil had not been reached, even after two years. Hence, the critical soil concentrations of Walsh *et al.* (1972) may be inappropriate for orchard soils where equilibration times for elements added as sprays are much longer.

A commercial soil testing service in Australia has advised clients that soils containing in excess of 20 μg $g^{-1}$ of copper extracted by DTPA are likely to be toxic (G.M. Harris, Grove, Tasmania, personal communication) although the basis for the advice was not disclosed. It is likely that this value is too low. In fact, none of the pastures now growing on former orchard soils showed any visual symptoms of toxic effects and had a normal legume component even though the total concentrations of copper in the soil frequently exceeded 150 μg $g^{-1}$. However, it is possible that yield could be affected without visual symptoms being evident.

No critical concentrations for soil lead have been suggested (as discussed in Section 2.5.2) so that it is not possible to estimate the proportion of orchard soils which may have accumulated lead to an extent where plant growth could be decreased. Pastures growing on soils containing in excess of 400 μg $g^{-1}$ total lead do not appear to be adversely affected.

Critical concentrations for total arsenic in soils are more clearly defined for a range of soils and crops (see Section 2.5.3). Growth reductions have been observed when concentrations of arsenic in orchard soils exceeded 50 to 100 μg $g^{-1}$ or higher depending on the ability of the soil to bind arsenic strongly and on the susceptibility of the plant to toxicity. Growth of maize was reduced by 50% when the concentration of arsenic in the soil reached 250 μg $g^{-1}$ (Woolson *et al.*, 1971a). Approximately 20% of the soils shown in Figure 4.1 had arsenic concentrations greater than 50 μg $g^{-1}$ but only one exceeded 100 μg $g^{-1}$. The coarse textured orchard soils from Tasmania, where the effects of excess arsenic are likely to be more severe, in fact have low arsenic concentrations because the element is easily lost from the surface layers of such soils.

### 4.2.3 Accumulation of Copper, Lead and Arsenic with Time

It was not possible to correlate the age of orchards with the accumulation of elements in the surface soils. Usually the current owner did not know the age of the orchard, but approximate and, in a few cases, accurate ages were obtained for 23 orchards, with minimum ages for a further 10. The extreme variation in management practices is illustrated by the finding that soils under orchards older than 100 years, all of which were in southern Tasmania, varied in lead concentration from 50 to 320 μg $g^{-1}$.

It was possible however to estimate that lead has accumulated in the soil at a mean annual rate of about 5 μg $g^{-1}$, copper at about 4 μg $g^{-1}$ and arsenic at about 1.25 μg $g^{-1}$ in the ten orchards showing the highest rates of accumulation. This compares with annual accumulation rates of approximately 11 μg $g^{-1}$ and 0.7 μg $g^{-1}$ for lead and copper respectively, reported by Frank *et al.* (1976) in Canada. The use of lead arsenate in Australia has declined since about 1950, when it was to some extent supplanted by DDT and other organic chemicals, and ceased in the early 1970's. It is probable that the annual accumulation rates during the period prior to 1950 were higher than those reported above for Australian orchard soils.

An approximation of the amounts of copper, lead and arsenic accumulating in the top 10 cm of orchard soils with each spray application can be calculated using currently recommended rates. This assumes that the composition of the different sprays have been uniform. Lead arsenate would add approximately 1.7 and 0.6 μg $g^{-1}$ of lead and arsenic respectively, and copper oxychloride approximately 1.5 μg $g^{-1}$ of copper per spray application. Bordeaux mixture may add up to double this amount of copper, depending on formulation. These figures suggest that orchards which have accumulated copper, lead and arsenic at the fastest rate may have received on average up to three applications of lead arsenate or copper-containing spray each year.

### 4.2.4 Element Distributions in Soil Profiles

The distributions of copper, lead and arsenic in six soil profiles are presented in Figure 4.2. Photographs of three of the profiles (Profiles *b*, *c* and *d*) and of a soil similar to Profile (*e*) are shown in Figure 4.3. In the descriptions of the soils provided below, Munsell colours are for the moist soil except where indicated. Principal profile forms (P.P.F.) and Great Soil Groups (G.S.G.) are after Northcote (1971) and Stace *et al.* (1968) respectively. Soil names are after Stephens (1935) except for Profile (*f*) which follows Jackson (1957).

*Description of Profile (a)*

| | | | |
|---|---|---|---|
| Location: | Ranelagh, Tasmania | Soil Name: | Alluvial |
| P.P.F.: | Um 1.43 | G.S.G.: | Alluvial Soil |

| Depth (cm) | |
|---|---|
| 0-22 | very dark brown (10 YR 2/2) silt loam; friable at surface: |
| 22-33 | transitional to: |
| 33-47+ | dark yellowish brown (10 YR 3/4) sandy clay loam with clayey sand in patches; friable structure |

The clay content of this soil was uniformly about 22% to at least 65 cm with no evidence of horizon development (Taylor and Stephens, 1935). Figure 4.2(a) shows that there has been very little movement of copper, lead or arsenic in Profile (a) below 25 cm. Furthermore, the arsenic distribution in the profile corresponds closely to that of lead and is in a proportion which closely resembles that of commercial lead arsenate. The As:Pb ratio in the soil is 0.30 compared to 0.36 in commercial lead arsenate ($PbHAsO_4$) which has been in use for several decades. The detailed composition of early lead arsenate sprays is not known.

### *Description of Profile (b)*

| | | | |
|---|---|---|---|
| Location: | Ranelagh, Tasmania | Soil Name: | Huon Sand |
| P.P.F.: | Dy 4.81 | G.S.G.: | Yellow Podzolic Soil |

| Depth (cm) | |
|---|---|
| 0-28 | dark yellowish brown (10 YR 4/2; 10 YR 6/2 when dry) sand with some organic accumulation near the surface; sharp, even boundary to: |
| 28-30 | light brownish grey (10 YR 6/2) sand with small amounts of siliceous gravel; conspicuously bleached; sharp, even boundary to: |
| 30-45 | greyish brown (10 YR 5/2) sand, with small amounts of gravel and some mottling (7.5 YR 5/6); sharp, wavy boundary to: |
| 45- | yellowish brown (10 YR 5/4) medium clay; massive structure. |

The clay content of this soil rises from about 8% in the surface 20 cm to about 60% in the B horizon (Taylor and Stephens, 1935). Figure 4.2(b) shows that there has been no accumulation of copper, lead or arsenic (or of phosphorus extracted by $NaHCO_3$) below 25 cm. The proportion of arsenic to lead increases with depth in the sandy surface horizons with the As:Pb ratio rising from 0.13 in the top 5 cm to 0.30 at 23-28 cm. Furthermore, when the relative amounts of these two elements in the top 25 cm are considered, it is apparent that a considerable amount of arsenic has been lost from the upper part of the profile.

At least some of this arsenic may have been leached downslope across the top of the clayey B horizon. There was no accumulation of any of the elements at the surface of the B horizon.

### *Description of Profile (c)*

| | | | |
|---|---|---|---|
| Location: | Ranelagh, Tasmania | Soil Name: | Huon Sandy Loam |
| P.P.F.: | Dy 3.31 | G.S.G.: | Yellow Podzolic Soil |

| Depth (cm) | |
|---|---|
| 0-20 | very dark grey (10 YR 2/1; 10 YR 4/1 when dry) organic sandy loam, very organic at surface; sharp, irregular boundary to: |
| 20-35 | dark grey (10 YR 4/1; 10 YR 6/1 when dry) sandy loam to loamy sand; some siliceous gravel (< 5 mm) at 30 to 35 cm; sharp irregular boundary to: |
| 35-40 | grey (10 YR 5/1; 10 YR 6/1 when dry) sandy clay loam; sporadically bleached, sharp irregular boundary to: |
| 40- | greyish brown (10 YR 5/2) medium clay with mottles (10 YR 5/8) increasing with depth; large peds in upper part with conspicuous organic (5 YR 3/4) surface coating. |

The surface horizons of this profile have a considerable accumulation of organic matter which is typical of the Huon Sandy Loam (Figure 4.3c). The $A_1$ and B horizons of this soil have 12-15% and 35-45% of clay, respectively (Taylor and Stephens, 1935). The distributions of copper and lead in this profile are similar (Figure 4.2c) with high concentrations in the surface and very low concentrations below 25 cm. It appears that significant amounts of arsenic have moved from the surface horizons (the As:Pb ratio in the top 10 cm is less than 0.03) and some has accumulated at the top of the B horizon. A recently established orchard on a similar soil nearby which had received very few spray applications had only 3 $\mu g\ g^{-1}$ of arsenic in the B and C horizons.

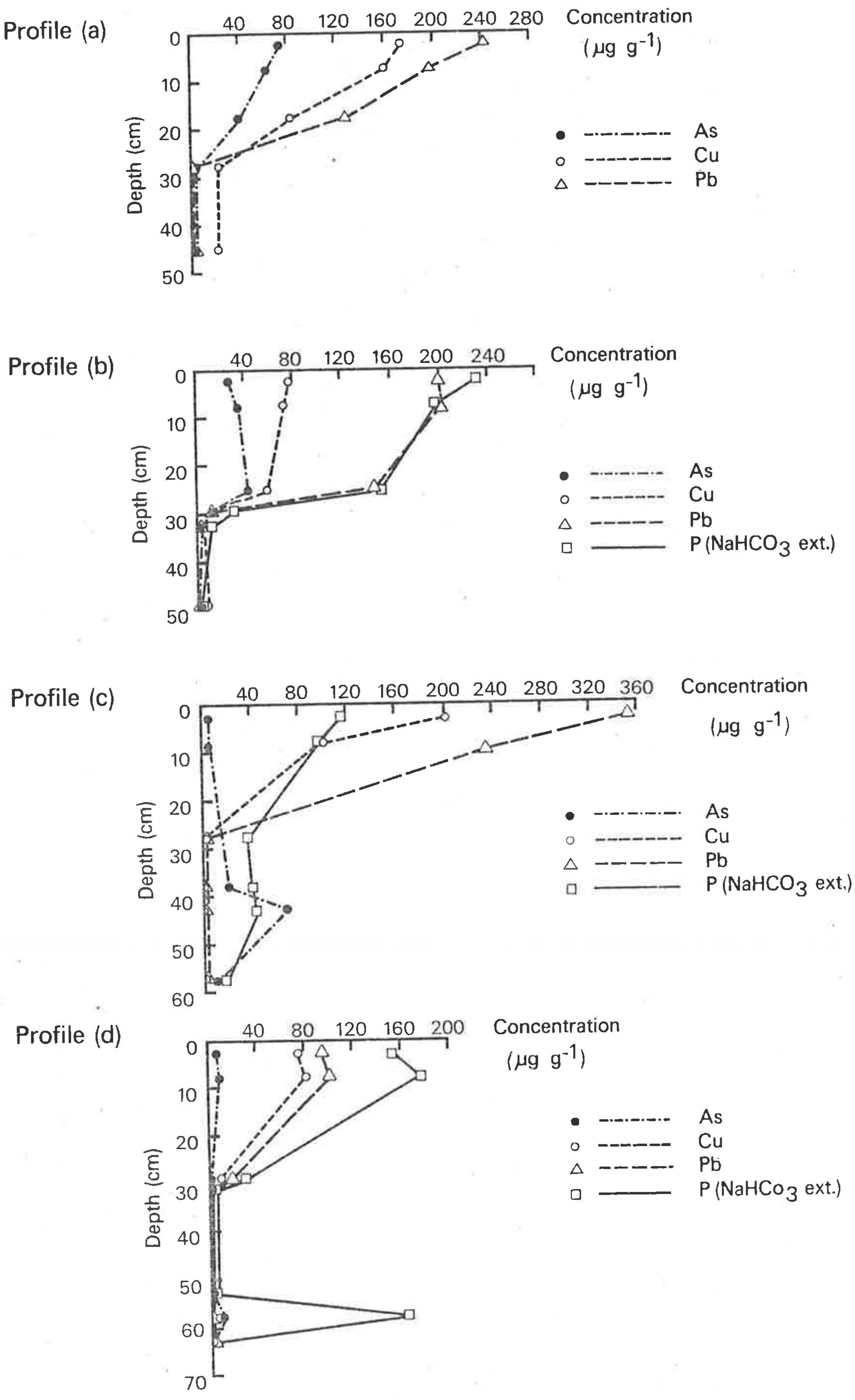
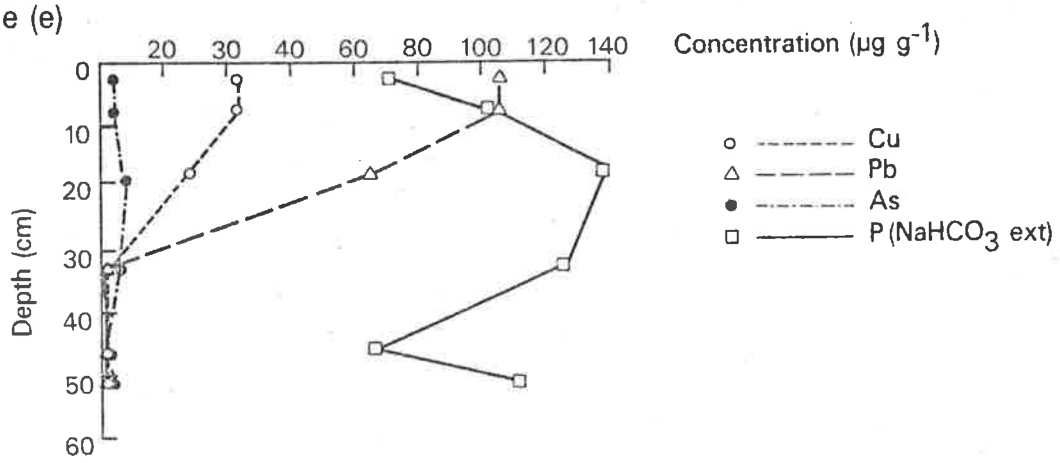


Figure 4:2 Total Concentrations of Copper, Lead and Arsenic in the Profiles of Orchard Soils.

Profile (e)



Profile (f)

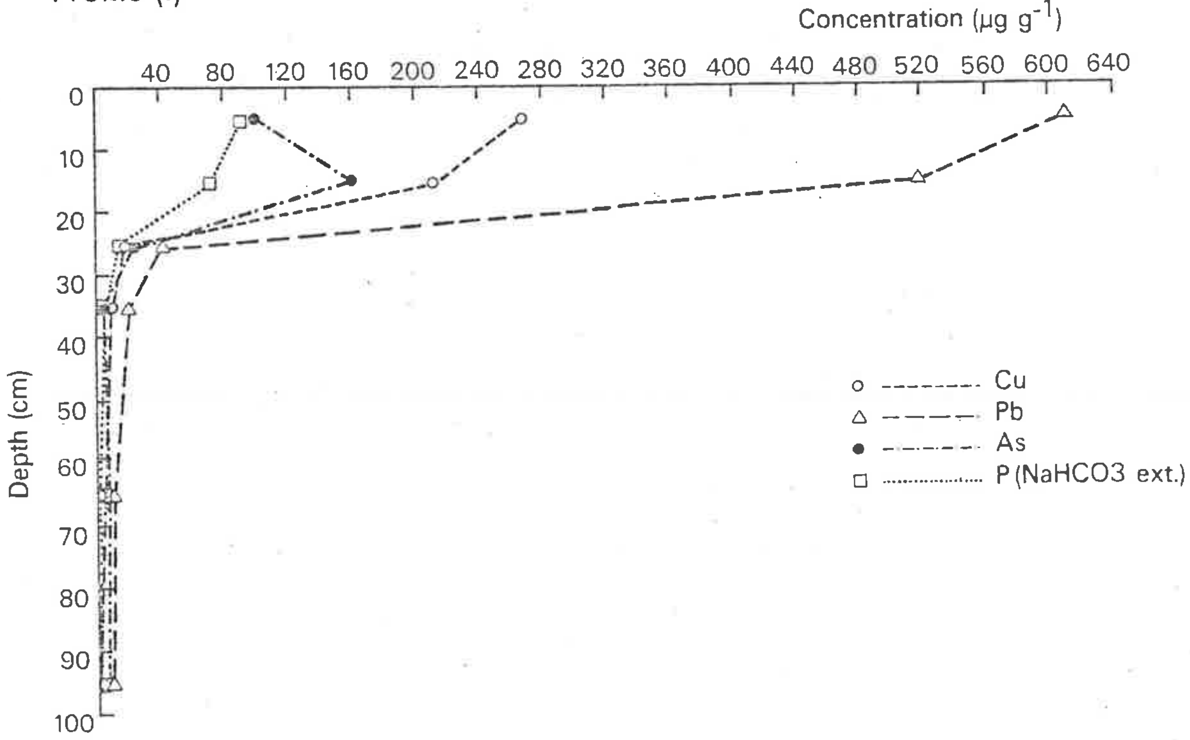


Figure 4.2 Cont'd.

Figure 4.3 Photographs of Some of the Soil Profiles Described in Section 4.2.4. (The tape is marked in 10 cm intervals).

Profile (b) Huon Sand

Profile (c) Huon Sandy Loam

Figure 4.3 (cont'd)

Profile (d) Grove Sand

Profile (e) The Lucaston Sand photographed in a road cutting approx. 3 km from Profile (e). This is one of the few places where the siliceous hardpan (60 cm thick) has been penetrated. There has been some disturbance of the surface 20 cm of this profile.

*Description of Profile (d)*

| | | | |
|---|---|---|---|
| Location: | Grove, Tasmania | Soil Name: | Grove Sand |
| P.P.F.: | Uc 2.36 | G.S.G.: | Humus Podzol |

| Depth (cm) | |
|---|---|
| 0-30 | black (10 YR 5/1; 10 YR 4/1 when dry) loose organic sand; sharp even boundary to: |
| 30-55 | light grey (10 YR 6/2; 10 YR 7/1 when dry) loose sand; grading (50-55 cm) to: |
| 55-60 | dark greyish brown (10 YR 4/2) sand; more cohesive than above; sharp, even boundary to: |
| 60-65 | strong brown (7.5 YR 5/8) cemented sand, difficult to penetrate; grading to: |
| 65- | yellowish brown (10 YR 5/6) loose sand. |

This profile (Figure 4.3d) is sandy throughout with not more than 7% clay in any horizon (Taylor and Stephens, 1935). The horizon at 55-60 cm was stained with brown organic matter and some iron oxides. The 60-63 cm horizon was strongly cemented with iron oxides. Copper and lead have accumulated at the top of the organic-rich surface horizon but there is no evidence of any accumulations in lower horizons (Figure 4.2d). Arsenic has largely disappeared from the surface horizons, where the As:Pb ratio is no higher than 0.04, but has accumulated to a small extent at 55-60 cm, *i.e.* just above the strongly cemented horizon. Phosphorus extracted by $NaHCO_3$ has accumulated to a very marked extent in the same horizon. Neither phosphorus nor arsenic have accumulated in the cemented horizon (60-65 cm). It is unlikely that either element could penetrate below this iron-oxide cemented hardpan without being adsorbed. Despite this, a considerable amount of arsenic appears to have been removed from this profile.

### *Description of Profile (e)*

Location: Ranelagh, Tasmania　　Soil Name: Lucaston Sand

P.P.F.: Uc 2.34†　　G.S.G.: Podzol†

(† applies to profile above the siliceous hardpan)

| Depth (cm) | |
|---|---|
| 0-22 | very dark grey (10 YR 3/1; 10 YR 5.6/1 when dry) loose organic sand; clear even boundary to: |
| 22-45 | light grey (10 YR 4/1; 10 YR 6/1 when dry) loose sand; grading to: |
| 45-48 | light brownish grey (10 YR 6/2; 10 YR 7/2 when dry) loose sand with small amounts of siliceous gravel (< 10 mm): |
| 48-53 | as above but with some organic colouring and a thin (< 1 cm) layer of organic matter (5 YR 3/4) just above: |
| 53- | cemented siliceous hardpan (not penetrated). |

Above the siliceous hardpan this profile is also sandy throughout and contains no more than 5% clay (Taylor and Stephens, 1935). It was not possible to penetrate the siliceous hardpan which is known from a few road cuttings and other excavations to be 20 to 60 cm thick and is certainly impervious to roots. A photograph of a similar profile of the Lucaston Sand from a road cutting is shown in Figure 4.3(e). There has been some disturbance of the top 20 cm of this profile. The copper, lead and arsenic distribution in the Lucaston Sand profile described above is shown in Figure 4.2(e). As in the previously described profiles, copper and lead have accumulated in the surface 20 to 30 cm. The arsenic distribution again differs from that of lead (As:Pb ratio of the surface 10 cm is 0.04) and much of the arsenic appears to have gone from the profile. The distribution of phosphorus extracted by $NaHCO_3$ in this profile is unusual and possibly indicates that some leaching is taking place with an accumulation occurring just above the siliceous hardpan. Total arsenic, although at a much lower concentration than phosphorus has a very similar profile distribution.

### *Description of Profile (f)*

| | | | |
|---|---|---|---|
| Location: | Paracombe, South Australia | Soil Name: | Inglewood Association |
| P.P.F.: | Dr 3.41 | G.S.G.: | Red Podzolic Soil |

| Depth (cm) | |
|---|---|
| 0-20 | dark brown (7.5 YR 3/3, dry) loam; massive; grading to: |
| 20-50 | brown to dark brown (7.5 YR 4/3, dry) fine sandy clay loam to sandy clay loam, medium blocky structure; gradient to: |
| 50-60 | brown (7.5 YR 5/4, dry) sandy clay loam; sharp boundary to: |
| 60-70 | dark red (2.5 YR 3.5/6, dry) sandy clay; large blocky peds; grading to: |
| 70-90 | dark red (10 R 3/6, dry) mottled (mainly 10 YR 4/3) sandy clay; large blocky structure; grading to: |
| 90-100 | red (2.5 YR 4/6, dry) mottled (mainly 10 YR 4/3) sandy clay with massive structure. |

The clay content of this soil is about 12% at the surface rising to 30% at 30 cm and about 40% at 60 cm. The surface 10 cm has a high iron content. The profile was sampled adjacent to the site E 460 where a bulk soil sample was taken for pot experiments.

The distribution of copper, lead, arsenic and phosphorus in this profile is shown in Figure 4.2(f). Because the soil is likely to have a high affinity for all of these elements, it was expected that the distributions of the elements in the profile would resemble those in Profile (a). Copper, lead and phosphorus were distributed as expected, but arsenic differed considerably, at least in the top 10 cm. In the 10-30 cm interval, arsenic was present in proportion to lead and in amounts which would be expected if $PbHAsO_4$ was the main source and no losses occurred (As:Pb ratio was 0.31 to 0.35). However, in the 0-10 cm only about half of the expected arsenic was present (As:Pb ratio was 0.16).

This feature occurred in four of the five soils sampled in this area of the Mt. Lofty Ranges. Leaching losses from the surface of this soil (Profile f) are unlikely because of the high clay and organic matter content of the soil and there is no evidence of accumulation of either arsenic or phosphorus lower in the profile. The low arsenic concentration of the surface soil relative to lead and phosphorus cannot be accounted for by removal in hay or by mixing due to cultivation. Losses of surface materials by wind or water could not be expected to remove arsenic selectively.

The Profiles (a) to (f) show a number of similarities with respect to their copper and lead distributions. The highest concentrations occur at the surface, diminish with depth and show no evidence of accumulation below 25 to 30 cm. The distribution of the elements may have been affected by cultivation, but this is now an infrequent practice in most orchards. Profile (d) however was cultivated on the day before it was sampled and the effects are evident in the distribution of the elements in the surface soil.

It is possible that both lead and copper may be translocated within the soil profile adsorbed on colloidal material. If this does happen, the elements must be completely removed laterally from the profile since there has been no accumulation in the soils lower than about 25 cm. It seems that the soils have sufficient complexing ability in the organic accumulations near the surface and/or adsorbing capacity by clay minerals and iron oxides that little leaching of copper or lead is likely. These findings are consistent with the conclusions of Tyler (1978) that both of these elements are resistant to leaching and have extremely long residence times in soils.

Although the composition of lead arsenate used in Australian orchards over the last 80 years is not known, the ratio of arsenic to lead in many soils where both elements appear to have been retained (e.g. Profile a) approaches 0.36

which is the ratio of the elements in the lead arsenate used over the past few decades. If no loss of arsenic relative to lead has occurred in orchard soils, profile distributions of the elements should resemble Profile (a). However this is clearly not the case and considerable amounts of arsenic have moved relative to lead. In some sites (Profiles c and d) there is evidence of leaching and retention lower down the profile, though these accumulations do not account for all of the arsenic lost from above.

Some of the profiles which have lost arsenic appear to have lost phosphorus (as suggested by the $NaHCO_3$ extracts) in the same way. The probable mechanisms are by leaching in solution or translocation on colloids in suspension. Both mechanisms may result in accumulation lower in the profile or in loss from the profile by sideways movement across less permeable subsurface horizons (e.g. Profiles, b,d and e). The evidence presented for leaching in the light-textured Tasmanian soils is supported by the findings of Tammes and de Lint (1969). These authors applied considerable amounts of arsenic to sandy soils in the field and calculated that it was possible to lose about half of the applied arsenic from the surface soil in 6.5 years.

The practice of applying large quantities of phosphatic fertilizers (up to 40-80 kg $ha^{-1}$ *per annum* of phosphorus) to orchard soils could result in enhanced leaching of arsenic. The work of Dean and Rubins (1947), Barrow (1974a) and others has shown that phosphate is adsorbed in preference to arsenate in soils. This may contribute to displacement of arsenic to sites of lower affinity and thus to increased mobility of arsenate if phosphate is competing for the same adsorption sites.

The data of Profile (f) suggests that other mechanisms of loss of arsenic from soils are also possible. In this profile, total copper and lead, and phosphorus extracted by $NaHCO_3$ all have similar profile trends. There is no clear evidence that either phosphorus or arsenic have been translocated down the profile. Yet arsenic appears to have been lost from the top 10 cm of this soil, and, as explained above was lost in a similar manner from several other similar profiles in the same region. This suggests a mechanism for the loss of arsenic which is unique to that element or happens in preference to phosphorus, copper or lead. Under conditions of intermittent waterlogging and the likely development of reducing conditions, it is possible that arsenic may be desorbed preferentially to phosphorus, reduced to the more soluble arsenite and removed by lateral leaching. A further possibility involves microbially-mediated reduction and methylation processes which have been outlined by Cox (1975) and Woolson (1977). The production by microorganisms of methylated compounds which are volatile is also known for other elements such as antimony and mercury, but not for phosphorus. Although direct measurements of such losses of arsenic have not been made in the field, appreciable losses by this mechanism have been inferred (Woolson, 1977).

In summary, the above profiles suggest the following:

(a) copper and lead are relatively immobile in orchard soils,

(b) soils with a sufficient capacity to adsorb arsenic as well as lead may retain both of these elements in a ratio similar to that of lead arsenate,

(c) arsenic may be lost from the profiles of sandy orchard soils, even if highly organic, but may accumulate in lower soil horizons if there are suitable adsorbing surfaces and

(d) a further mechanism of arsenic loss, which could apply to all of the profiles under appropriate conditions in the soil environment, is the formation of volatile organic compounds.

## 4.3 Copper, Lead and Arsenic in Pasture Species Sampled in the Field

### 4.3.1 Seasonal Changes in Copper, Lead and Arsenic Concentrations

A number of species of pasture plants was collected from five sites in the ranges east of Adelaide (see Section 3.3.1). Chemical analyses of the samples for copper, lead and arsenic are presented in Table 4.4 and in Figure 4.4 for plants sampled from site E 460, a former orchard soil where the greatest range of species was collected. Generic and common names are listed in Table 3.2.

It can be seen from Table 4.4 that there is considerable variation in concentration of the elements both between species and between sites. Most of the species showed an early season (June to July) decline in copper concentration, the exceptions being samples from site EH 24 where copper fertilizers had been applied and in *Arctotheca calendula* at site E 462. There were increases in copper concentrations at the September sampling and further increases in November, except for *Lolium perenne* and *Holcus lanatus* at site E 460. It is possible that the high copper concentrations in the soils in combination with increasing soil temperatures and transpiration rates may have contributed to higher concentrations in the tops of the plants as the growing season progressed.

Comparison of copper concentrations presented in Table 4.4 with those presented in Table 4.5 for *Trifolium subterraneum* and *A. calendula*, which were sampled from uncontaminated sites, suggests that plants growing on the contaminated soils have higher copper concentrations. The data for *T. subterraneum* in Table 4.5 also suggest that there may be considerable variation between seasons.

The within-season variations in copper concentrations found in this study differ from those of Beeson and McDonald (1951), Gladstones *et al.* (1967) and Fleming and Murphy (1968), and also from the unpublished work discussed by Temple-Smith and Munday (1976). The general conclusion of these workers was that the copper

Table 4.4 Seasonal Changes in Concentration (µg g$^{-1}$) of Copper, Lead and Arsenic in Pasture Species

| | Sampling date: | 10/6/75 | | | 23/7/75 | | | 3/9/75 | | | 25/11/75 | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Site No.[†] | Species | Cu | Pb | As | Cu | Pb | As | Cu | Pb | As | Cu | Pb | As |
| E 460<br>(O) | *A. calendula* | 35 | 10.1 | 1.9 | 26 | 10.0 | 0.8 | 39 | 21.2 | 0.9 | n | n | n |
| | *T. subterraneum* | n[§] | n | n | 21 | 4.0 | 0.4 | 24 | 5.0 | 0.6 | 30 | 6.7 | 2.3 |
| | *H. lanatus* | 39 | 6.3 | 0.2 | 25 | 7.1 | 0.6 | 34 | 6.4 | 0.2 | 34 | 6.4 | 2.3 |
| | *L. perenne* | 42 | 7.6 | 0.6 | 26 | 8.0 | 0.6 | 41 | 8.0 | 0.4 | 10 | 3.9 | 1.6 |
| | *P. lanceolata* | 22 | 4.9 | ≤.2 | 21 | 5.5 | 0.2 | 33 | 9.6 | 0.4 | 10 | 2.5 | 1.3 |
| E 462<br>(O) | *A. calendula* | 21 | 4.1 | 0.8 | 29 | 3.8 | 0.4 | 25 | 5.7 | 0.8 | 39 | 5.2 | 2.9 |
| | *E. botrys* | 35 | 3.0 | 3.8 | 17 | 3.2 | 0.8 | 20 | 3.1 | 2.0 | 30 | 4.4 | 1.9 |
| | *B. mollis* | 28 | 3.1 | 0.5 | 19 | 2.2 | 0.4 | 32 | 4.1 | 0.7 | 42 | 2.5 | 5.8 |
| EH 12<br>(O) | *T. subterraneum* | 29 | 3.4 | 0.4 | 20 | 5.0 | 0.5 | n | n | n | 29 | 3.7 | 2.2 |
| | *E. plantigineum* | 31 | 2.7 | 0.2 | 27 | 3.7 | 0.2 | n | n | n | 54 | 2.2 | 1.2 |
| EH 24<br>(M) | *A. calendula* | 24 | 8.4 | 0.8 | 31 | 14.0 | 1.2 | 24 | 18.0 | 0.6 | 63 | 75.0 | 2.1 |
| | *P. aquatica* | 22 | 5.1 | 0.5 | 37 | 7.1 | 0.2 | 42 | 8.1 | 0.4 | 52 | 6.4 | 2.4 |
| EH 13<br>(M) | *T. subterraneum* | 42 | 0.9 | 1.7 | n | n | n | 30 | 1.1 | 3.2 | n | n | n |
| | *E. moschatum* | 37 | 0.8 | 0.6 | n | n | n | 37 | 0.8 | 1.7 | n | n | n |

[†] (O): former orchard soil. (M): mineralized or mine affected soil

[§] n: insufficient material to sample

Table 4.5 Concentration ($\mu g\ g^{-1}$) of Copper and Lead in Pasture Species Sampled in the Mt. Lofty Ranges, South Australia

*Trifolium subterraneum*

| Sampled September, 1972 | Element | Mean | (S.D.) | n | Range |
|---|---|---|---|---|---|
| | Cu | 13.4 | (4.8) | 56 | 3.1-31.4 |
| | Pb | 1.4 | (0.7) | 59 | 0.3- 3.5 |
| Sampled October, 1972 | | | | | |
| | Cu | 9.1 | (2.3) | 61 | 3.2-15.1 |
| | Pb | 1.0 | (0.9) | 60 | 0.3- 5.7 |
| Sampled September, 1973 | | | | | |
| | Cu | 21.1 | (10.2) | 51 | 5.0-55.8 |
| | Pb | 1.3 | (0.8) | 51 | 0.4- 4.3 |

*Actotheca calendula*

| | | | | | |
|---|---|---|---|---|---|
| Sampled October, 1974 | Cu | 12.7 | (4.5) | 58 | 5.4-24.4 |
| | Pb | 2.2 | (0.9) | 60 | 0.8- 6.1 |

(Source: Tiller, Merry *et al.*, unpublished data)

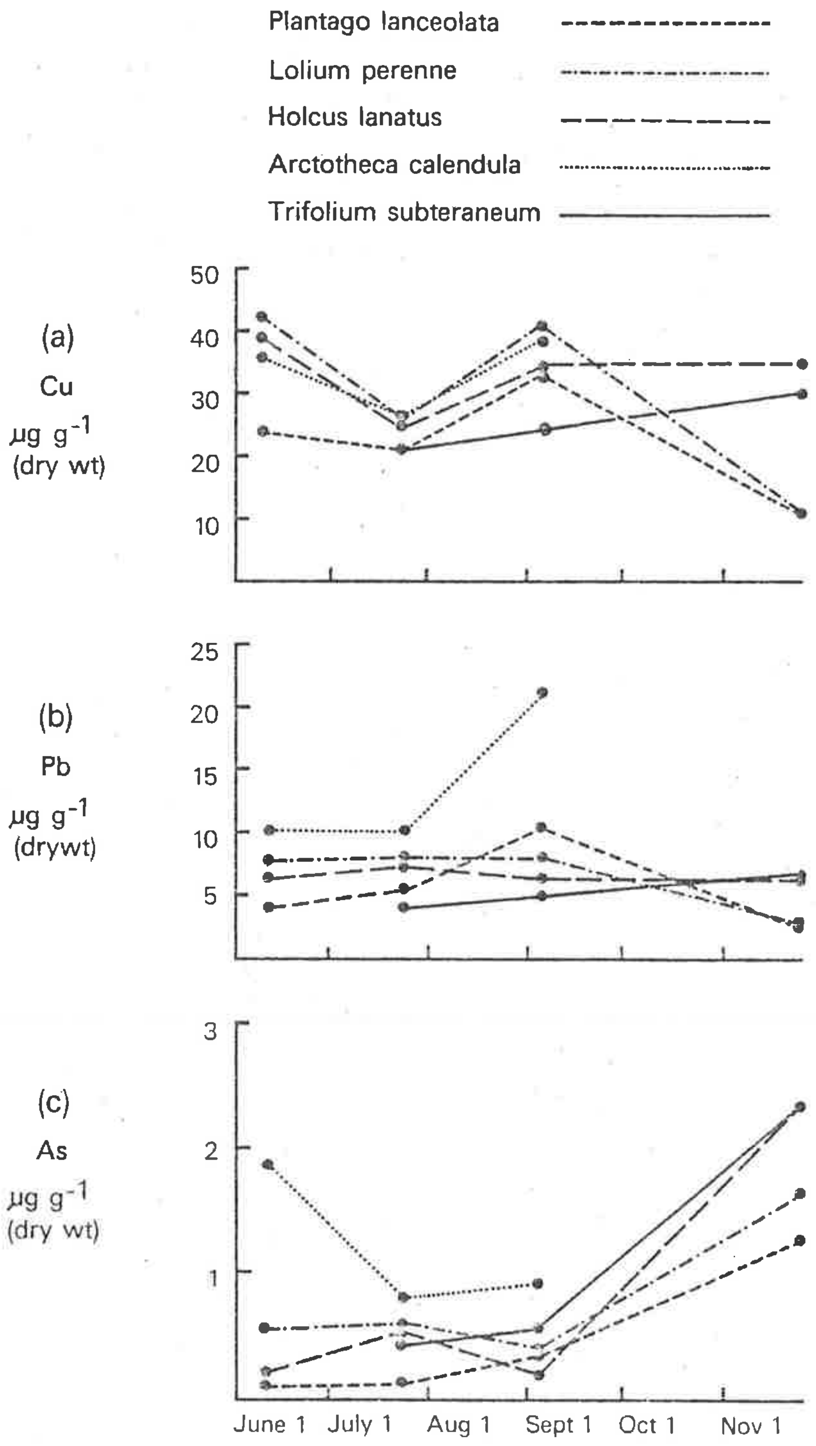


Figure 4.4

Seasonal Changes in the Copper, Lead and Arsenic Concentration in Pasture Species at Site E 460.

concentration of plants declines with advancing maturity or, in the case of pasture legumes (Piper and Beckwith, 1951; Beeson and McDonald, 1951) a mid-season peak may be followed by decline with senescence.

It has been reported (Dick *et al.*, 1953; Gladstones *et al.*, 1967) that weeds or herbaceous species have higher copper concentrations than pasture species growing at the same site. It can be seen from Table 4.4 that the weed species (*Plantago lanceolata, Echium plantigineum, Erodium* spp. and *A. calendula*) in this study generally have copper concentrations which are not markedly different from those of the other plants.

The concentrations of lead in the tops of plants sampled in the field show some interesting features (Table 4.4 and Figure 4.4b). The concentrations are generally low compared to copper, with small seasonal fluctuations. The concentrations are largely within the range shown for plants grown on uncontaminated soils in Table 4.5 and also those reported by Jones and Hatch (1945). The exception in this study is *A. calendula*. At the three sites where it was sampled it had the highest lead concentration and at two of these (E 460 and EH 24) the concentrations were considerably higher than the other species. Another feature of these two sites was the large increase in lead concentration as the *A. calendula* plants senesced (earlier at E 460 than the other sites).

Little comparable information is available in the literature on the seasonal changes of lead concentration of pasture plants. Rains (1971) observed seasonal effects which he was able to attribute to atmospheric accession. This process is thought to be of small consequence in the present study. The findings of Mitchell and Reith (1966) were also not comparable because of species and climatic differences. Plants do not senesce to the same extent in the milder conditions experienced during winters in the Adelaide region.

The arsenic concentrations of the plants were generally lower than those of lead and were uniform through much of the growing season. However, almost without exception, the concentrations of arsenic increased dramatically in both annual and perennial species at the final sampling when most of the plants were senescing (Figure 4.3c).

No comparable data for arsenic were found in the literature. The results show no similarity to those for molybdenum or phosphorus (Piper and Beckwith, 1951; Fleming, 1973) which have comparable anionic forms and might be expected to behave in a similar manner.

Some of the fluctuations in the concentration of the elements in plants may be explained in terms of growth dilution and desiccation with senescence. Other factors could be the increased availability of the elements to the plants as the soil and air temperatures and light intensities increase as well as differences in translocation from roots to tops. While it may be possible to explain many of the effects in these terms, the situation is further complicated by the fact that the pastures were grazed.

### 4.3.2 Relationship Between Concentrations of Copper, Lead and Arsenic in Soils and Plants

The relationship of total soil concentrations of copper, lead and arsenic to the concentration of the elements in the pasture species *Trifolium repens* and *Lolium perenne* sampled from former orchard soils in the Huonville area was investigated. Details of the sampling procedure were presented in Section 3.3.2. No relationships between plant concentration (on a dry weight basis) and total soil concentration were evident for any of the elements or for either species. For this reason only mean concentrations and ranges are presented in Table 4.6. Plant concentrations for all elements do not differ from what might be expected in plants grown on uncontaminated soils although the lead concentrations are marginally higher than the concentrations presented for other species in Table 4.5. Copper concentrations in the plants in Table 4.6 are lower than those found in plants growing in South Australian orchard soils which were discussed in Section 4.3.1.

Simple linear relationships between soil concentrations of lead, copper and other elements using various extractants have been reported many times with vegetable, pasture and crop plants grown on contaminated soil in the field and the glasshouse (Merry and Tiller, 1978; Davis, 1979; Merry *et al.*, 1981 and others). The reason for absence of correlation in this investigation was not obvious. Analysis of a larger number of samples coupled with other soil measurements, such as pH, may be required to improve the predictive value of soil analysis data for plant tissue concentrations.

Table 4.6 Concentrations of Copper, Lead and Arsenic in Tops of Pasture Plants and in Soils from Tasmania

| | | Concentration in Plants | | | | Concentration in Soil (Total) |
|---|---|---|---|---|---|---|
| Element | Species | $\mu g\ g^{-1}$ | (S.D.) | Range | n | Range ($\mu g\ g^{-1}$) |
| Cu | *Trifolium repens* | 9.33 | (2.57) | 6.4-13.5 | 10 | 44 - 174 |
| | *Lolium perenne* | 6.26 | (2.05) | 3.6-10.1 | 9 | |
| Pb | *Trifolium repens* | 4.53 | (2.03) | 2.99-10.0 | 10 | 99 - 425 |
| | *Lolium perenne* | 3.58 | (1.04) | 1.80-5.65 | 9 | |
| As | *Trifolium repens* | 1.00 | (0.71) | <0.20-2.44 | 8† | 4.9 - 64 |
| | *Lolium perenne* | 0.95 | (0.55) | 0.40-1.96 | 9 | |

† 2 samples were below detection limit (0.2 $\mu g\ g^{-1}$)

## 4.4 Pot Experiments

### 4.4.1 Pot Experiment 1. The Effects of Soil Temperature on Copper, Lead and Arsenic Uptake by Three Plant Species

The dry weights, and the copper, lead and arsenic concentrations found in the tops of subterranean clover, silver beet and radish plants are shown in Table 4.7 and those found in the roots of radish are shown in Table 4.8. Photographs of representative pots taken just prior to harvest are shown in Figure 4.5.

Increasing soil temperature from 12°C to 22°C significantly increased the yields and the concentrations of copper, lead and arsenic in the tops of all plants (Table 4.7) except for copper in the tops of radish grown on the mineralized soil (EH 24). Roots were sampled only for radishes (Table 4.8). Their yields did not increase significantly with increased soil temperature and in fact were less at the higher soil temperatures on the mineralized soil. This decreased yield of radish roots may have been due to the lead concentration, 110 $\mu g\ g^{-1}$, which was the highest recorded for radish in any of the experiments in this study. The concentrations of copper in roots grown in the orchard soil and of lead in roots grown in both soils increased in small, but significant, amounts with increased soil temperature. Increasing soil temperature had no significant effect on the concentration of arsenic in radish roots.

The orchard soil (E 505) yielded more than the mineralized soil (EH 24). The copper concentrations of the plants grown on the orchard soil were higher than in plants grown on the mineralized soil but the reverse was true for lead. These results were to be expected considering the copper and lead concentrations, and fertility of the soils (Table 3.5). The arsenic concentrations of the two soils were similar and, with the exception of subterranean clover grown on the orchard soil at the higher temperature, the arsenic concentrations of the plants reflect this similarity.

Table 4.7 The Effect of Soil Temperature on the Dry Weight (g per pot) and Copper, Lead and Arsenic Concentrations ($\mu g\ g^{-1}$) in the Tops of Three Plant Species. The values are geometric means of four replicates with $\log_{10}$ transformed data in italics.

| Soil Temperatures | | 12°C | | | 22°C | | | |
|---|---|---|---|---|---|---|---|---|
| Species | | Subclover | Silverbeet | Radish | Subclover | Silverbeet | Radish | $LSD_{0.05}$ |
| E 505<br>(orchard soil) | Dry Wt. | 14.4 | 4.8 | 5.2 | 25.5 | 11.1 | 7.7 | |
| | | *1.16* | *0.69* | *0.72* | *1.41* | *1.05* | *0.88* | *0.05* |
| | Cu | 21 | 77 | 19 | 30 | 134 | 26 | |
| | | *1.32* | *1.89* | *1.28* | *1.48* | *2.13* | *1.41* | *0.09* |
| | Pb | 4.8 | 3.3 | 3.2 | 11.9 | 9.6 | 5.0 | |
| | | *0.68* | *0.52* | *0.50* | *1.07* | *0.98* | *0.69* | *0.11* |
| | As | 3.9 | 1.4 | 2.5 | 19.8 | 2.4 | 3.9 | |
| | | *0.59* | *0.13* | *0.39* | *1.30* | *0.37* | *0.58* | *0.18* |
| EH 24<br>(mineralized soil) | Dry Wt. | 6.9 | 2.8 | 3.6 | 15.5 | 5.4 | 5.3 | |
| | | *0.84* | *0.46* | *0.56* | *1.19* | *0.73* | *0.72* | *0.05* |
| | Cu | 9.5 | 6.9 | 6.5 | 13.7 | 9.2 | 6.8 | |
| | | *0.97* | *0.82* | *0.81* | *1.14* | *0.95* | *0.83* | *0.09* |
| | Pb | 31 | 48 | 20 | 54 | 83 | 32 | |
| | | *1.49* | *1.68* | *1.28* | *1.73* | *1.91* | *1.49* | *0.11* |
| | As | 2.4 | 1.7 | 2.1 | 5.6 | 3.3 | 3.4 | |
| | | *0.37* | *0.22* | *0.31* | *0.75* | *0.44* | *0.53* | *0.18* |

Table 4.8 The Effect of Soil Temperature on Yield (g per pot) and the Copper, Lead and Arsenic Concentrations ($\mu g\ g^{-1}$) of Radish Roots. The data are geometric means of four replicates with $\log_{10}$ transformed values in italics.

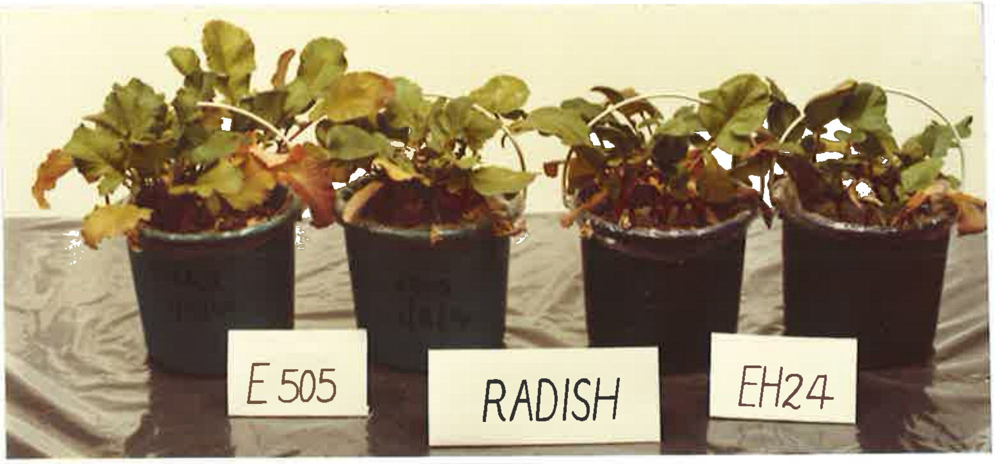
| Soil | | Temperature 12°C | Temperature 22°C | $LSD_{0.05}$ |
|---|---|---|---|---|
| E 505 (orchard) | Dry Wt. | 9.5 | 9.9 | |
| | | *0.97* | *0.99* | *n.s.* |
| | Cu | 10.5 | 15.9 | |
| | | *1.02* | *1.19* | *0.16* |
| | Pb | 8.4 | 13.2 | |
| | | *0.90* | *1.10* | *0.19* |
| | As | 2.5 | 2.1 | |
| | | *0.37* | *0.28* | *n.s.* |
| EH 24 (mineralized) | Dry Wt. | 6.3 | 5.0 | |
| | | *0.80* | *0.70* | *0.09* |
| | Cu | 5.4 | 6.6 | |
| | | *0.73* | *0.82* | *n.s.* |
| | Pb | 40 | 110 | |
| | | *1.59* | *2.03* | *0.19* |
| | As | 1.5 | 1.9 | |
| | | *0.14* | *0.26* | *n.s.* |

As would be expected with plants of differing physiologies and root morphologies there were relative differences between the plant species in the concentrations of the elements in the plant tops the extent of which depended on soil and temperature. Subterranean clover and silver beet accumulated higher concentrations of lead than radish tops. Silver beet had substantially higher concentrations of copper than the other species when grown in the orchard soil. Subterranean clover had the highest concentration of arsenic and silver beet the lowest, significantly so in most cases. The effect of soil temperature on increasing the concentration of arsenic in subterranean clover (3.9 to 19.8 $\mu g\ g^{-1}$) was the largest relative increase observed. In the natural environment, this plant usually grows at soil temperatures much lower than 22$^{o}$C for much of its life cycle so that this large increase in arsenic concentration may have less practical importance than increases observed in silver beet or radish which are usually grown at times of the year when higher soil temperatures prevail.

By the end of this experiment, all of the silver beet plants growing on the mineralized soil (EH 24) had small necrotic patches on the leaves. In addition, some of the radish plants growing on the same soil but only at the higher temperature showed symptoms of marginal necrosis. On the basis of chemical analyses of these plants and similar observations made in Pot Experiment 2, the symptoms were attributed to the accumulation of excess manganese. The manganese concentrations of affected leaves of silver beet exceeded 1500 $\mu g\ g^{-1}$.

Little information has been published on the effects of increasing soil temperatures on the uptake of copper, lead and arsenic from contaminated soils. Benson (1953) grew barley in sand cultures to which lead arsenate had been added. The experiment was carried out in a glasshouse at temperatures near 0$^{o}$C in

Figure 4.5 The effects of soil temperature on plant growth at time of harvest. For each soil, the left-hand pot was maintained at 22°C and the right-hand pot at 12°C.



winter and was repeated in the open air in summer. A much greater retardation of growth was noted at the higher application rates of lead arsenate in the experiment carried out in summer when temperatures, and presumably light intensities, were higher.

Specific reasons cannot be given for the increases in concentrations with increasing temperature observed in this experiment since a number of contributing factors are probably operating. Although root:shoot ratios and the numbers of lateral roots vary with species and soil temperature, root extension rates normally increase with temperature up to 25-30°C (Cooper, 1973). The size and morphology of root systems are strongly affected by temperature (Nye and Tinker, 1977). Increasing temperature lowers the resistance of roots to water uptake (Cooper, 1973) and affects the permeability of root membranes to cations and anions (Zsoldos, 1972). Increasing soil temperatures over the range tested also increases the rate of breakdown of organic matter and the activities of microorganisms and thus affect availability of elements. The rates of diffusion of ions to roots and the concentration of ion species in the soil solution may also increase with increasing soil temperature.

In the present experiment, the air temperatures experienced by all pots were the same. However, the greater growth of tops of the plants at the higher soil temperature would result in a much higher throughput of transpiration water and hence increase potential for transport of the elements to the roots and from the roots to the tops. Although the conditions imposed on the plants in this experiment (e.g. temperature, non-limiting water supply, root systems confined to pots, etc.) may differ from what is experienced in the natural situation, the results have clearly shown that soil temperature is an important factor in controlling the copper, lead and arsenic uptake by plants. The concentrations of the elements in the tops of the plants grown in soil at 22°C usually increased to be nearly double the concentrations of the plants grown at 12°C. The increases were not so great in radish roots. These findings imply that higher levels of contamination are likely to be encountered in summer crops such as vegetables grown with irrigation.

### 4.4.2 Pot Experiment 2. The Effects of Varying Soil pH and Prior Waterlogging on Two Plant Species Grown on Eight Soils

In this experiment, soil pH was adjusted by adding sulphur, gypsum or calcium carbonate, and in a further treatment, soils were waterlogged for one month prior to sowing radish and silver beet. All data in this experiment, except pH, were $\log_{10}$ transformed for statistical analysis to stabilise the variance associated with widely varying concentrations. Details of the soils used and experimental methods were presented in Section 3.4.2.

*Effects of Treatments on Soil pH*

The pH of air dry soil samples collected at harvest are presented in Table 4.9. These results show that sulphur treatment decreased and calcium carbonate treatment increased soil pH. Application of gypsum containing sulphur equal in amount to that added in the sulphur treatment also decreased pH, but to a lesser extent. Prior waterlogging resulted either in no change in pH or in increases of up to 0.35 units compared to the control. There were differences in pH due to species, but they were not consistent. The differences may have resulted, at least in part, from differences between the root systems of the radish and silver beet plants, their exudates and associated microflora. In addition, most of the small fibrous roots of silver beet were not removed from the soil samples.

Except where otherwise indicated, the pH of the air dry soil as presented in Table 4.9, which was determined on a uniform subsample, will be used in further discussion of the results.

*The Time Course of Changes in pH*

The changes in pH of the moist soil during equilibration and growth of the plants are illustrated in Figure 4.6 for two soils, E 505 which is representative of most of the soils, and soil EH 1 which, because of its naturally

Table 4.9 The Mean pH of Soils (Air Dry) at the Completion of Pot Experiment 2

| Plant: | Radish | | | | Silver Beet | | | | |
|---|---|---|---|---|---|---|---|---|---|
| Treatment†: | S(*2*) | Control | $CaCO_3$ (*5*) | W'Log | S(*2*) | Gypsum (*2*) | Control | $CaCO_3$ (*5*) | W'Log |
| Soil: EH 12 | 4.27 | 5.43 | 6.40 | 5.57 | 4.70 | 4.90 | 5.34 | 6.35 | 5.60 |
| | S(*2*) | Control | $CaCO_3$ (*2.5*) | W'Log | S(*2*) | Gypsum (*2*) | Control | $CaCO_3$ (*2.5*) | W'Log |
| E 460 | 4.13 | 5.80 | 6.27 | 5.83 | 4.00 | 4.70 | 5.40 | 5.80 | 5.55 |
| | S(*2*) | Control | $CaCO_3$ (*3.75*) | W'Log | S(*2*) | Gypsum (*2*) | Control | $CaCO_3$ (*3.75*) | W'Log |
| EH 21 | 4.73 | 6.07 | 6.70 | 6.13 | 4.60 | 5.35 | 6.05 | 6.65 | 6.00 |
| | S(*2*) | Control | $CaCO_3$ (*3.75*) | W'Log | S(*2*) | Gypsum (*2*) | Control | $CaCO_3$ (*3.75*) | W'Log |
| E 505 | 4.50 | 6.00 | 6.53 | 6.00 | 4.65 | 5.50 | 5.75 | 6.40 | 5.90 |
| | S(*16*) | S(*8*) | Control | W'Log | S(*16*) | S(*8*) | Gypsum (*16*) | Control | W'Log |
| EH 1 | 4.73 | 6.93 | 7.87 | 7.87 | 4.85 | 7.00 | 7.40 | 7.80 | 7.85 |
| | S(*1*) | Control | $CaCO_3$ (*2.5*) | W'Log | S(*1*) | Gypsum (*1*) | Control | $CaCO_3$ (*2.5*) | W'Log |
| EH 23 | 3.60 | 4.77 | 5.60 | 4.90 | 3.60 | 4.50 | 4.80 | 5.35 | 4.80 |
| | S(*1*) | Control | $CaCO_3$ (*2.5*) | W'Log | S(*1*) | Gypsum (*1*) | Control | $CaCO_3$ (*2.5*) | W'Log |
| EH 13 | 4.83 | 6.57 | 8.00 | 6.90 | 5.05 | 5.95 | 6.75 | 7.75 | 6.65 |
| | S(*2*) | Control | $CaCO_3$ (*3.75*) | W'Log | S(*2*) | Gypsum (*2*) | Control | $CaCO_3$ (*3.75*) | W'Log |
| EH 24 | 3.73 | 5.00 | 5.83 | 5.20 | 3.70 | 4.30 | 4.80 | 5.70 | 5.00 |

† Figures in brackets indicate rate (g per pot) of elemental sulphur (S) and calcium carbonate applied to each pot. For gypsum, they also indicate the rate of sulphur, but applied as $CaSO_4.2H_2O$. 'Control' and 'W'log' denote untreated and prior waterlogged soils, respectively. LSD = 0.12 ($P < 0.05$).

high pH, was treated differently. The pH values shown in Figure 4.6 are for moist soils. Difficulties in obtaining a representative subsample of moist soil meant that the results of the measurements were likely to be more variable than those presented for air dry samples in Table 4.9. Nevertheless the data for moist soils in Figure 4.6 show that the equilibration time allowed (about 40 days) appeared to have been sufficient for the microbial oxidation of sulphur to achieve a fairly stable pH in all soils. The 'moist' pH values for the various treatments maintained relativity and changed by less than half a unit when the pH at harvest was compared with the value at sowing.

The pH of five of the waterlogged soils (EH 12, E 460, EH 23, EH 13 and EH 24) increased by 0.4 to 0.8 units when compared to the control at the end of the period of submergence. At this time the pH of the remaining three soils (EH 21, E 505 and EH 1) did not differ from the control treatment. During the period of growth of the plants, the pH of the previously waterlogged soils tended to revert to that of the control. At harvest, the differences between the two treatments, although often statistically significant, were small, except for soil EH 13 growing radish where a larger difference with control was maintained (see Table 4.13 for pH of moist soils at harvest).

### *Effects of Treatments on Yield, and Copper, Lead and Arsenic Concentrations of Radish and Silver Beet*

A summary of treatment effects is presented in Table 4.10. The mean values are for five of the eight soils used in Pot Experiment 2. Statistical analyses were carried out on $\log_{10}$ transformed data. The results for soil EH 1, which was treated differently from the others, and for soils EH 23 and EH 24, where some plants failed to survive, were excluded from this table. In soil EH 23 (an acid, sandy soil which was dosed with copper, lead and arsenic) no plants survived to harvest except for radish on the soil treated with calcium carbonate and in soil EH 24, no plants survived the sulphur treatment. The summary

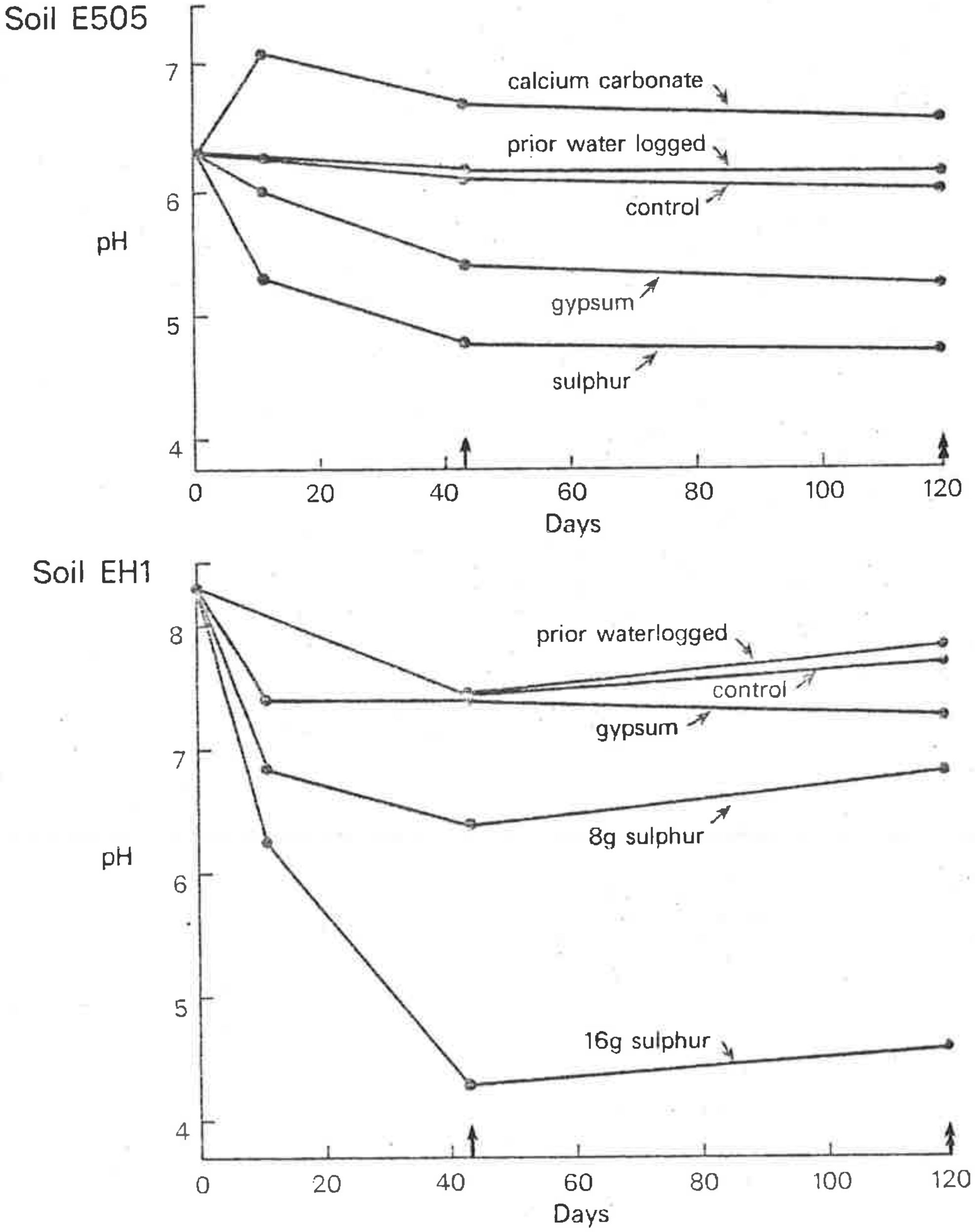


Figure 4.6

The Change of Soil pH (moist) with Time in Pot Experiment 2.
(↑ and ↟ indicate sowing and harvest respectively).

in Table 4.10 provides an indication of the overall effects of the treatments, although the rates of sulphur (S), gypsum and calcium carbonate applied to each soil were not uniform.

The mean effect of sulphur applications, compared to the control treatment, was to decrease yields, increase copper concentrations in radish, increase lead concentrations in radish and silver beet and increase arsenic concentrations in the roots of radish and tops of silver beet. Sulphur increased the concentration of copper in silver beet on some soils but decreased it in others, the net effect being a mean concentration which was not significantly different from the control. Applying gypsum to the soils on which silver beet plants were grown resulted in increased yields and small increases in copper concentration. There were small decreases in the lead and arsenic concentrations though uptake was little affected when yield is taken into account. Calcium carbonate applications increased yields and decreased the concentrations of copper, lead and arsenic in both plants. The prior waterlogging treatment increased the yield of radish roots, increased the copper concentration in the tops of radish and silver beet, had little effect on lead and increased the arsenic concentrations in both plants. The treatment effects on individual soils will be discussed more fully later.

The mean yields and concentrations of copper, lead and arsenic for each treatment and individual soils are presented in detail in Appendix 3. It is from the data presented in Appendix 3 that the summary in Table 4.10, and Figures 4.7 to 4.10 were constructed.

### *The Relation of Element Concentration and Yields of the Plants to pH*

Covariance analysis was used to remove soil pH as a linear covariate with log transformed plant parameters. Based on analysis of variance, independent estimates of 'between treatment' and 'between soil' effects which are attribut-

Table 4.10 Mean Effects of Treatments on Yield (g per pot) and Concentration ($\mu g\ g^{-1}$) of Copper, Lead and Arsenic in Radish and Silver Beet

| Treatment[†] | | S | Gypsum | Control | $CaCO_3$ | W'Log |
|---|---|---|---|---|---|---|
| Radish Tops | Dry wt. | 4.4 a[§] | - | 5.0 b | 5.8 c | 5.2 b |
| | Cu | 39 d | - | 16 b | 13 a | 20 c |
| | Pb | 2.5 c | - | 1.9 b | 1.1 a | 2.0 b |
| | As | 3.0 a | - | 4.6 c | 3.7 b | 6.2 d |
| Radish Roots | Dry wt. | 5.4 a | - | 5.9 a | 7.6 b | 7.4 b |
| | Cu | 21 c | - | 13 b | 11 a | 14 b |
| | Pb | 10.2 c | - | 4.5 b | 1.9 a | 4.2 b |
| | As | 5.9 b | - | 4.8 a | 4.2 a | 6.2 b |
| Silver Beet Tops | Dry wt. | 5.1 a | 8.3 c | 6.8 b | 8.5 c | 6.9 b |
| | Cu | 63 b | 68 c | 63 b | 35 a | 74 d |
| | Pb | 5.8 d | 2.1 b | 2.8 c | 1.6 a | 2.3 bc |
| | As | 4.2 d | 2.6 ab | 3.0 bc | 2.2 a | 3.7 cd |

[†] Treatments are as indicated in Table 4.9

[§] In each row, numbers followed by the same letter are not significantly different at $P \leqslant 0.05$.

Table 4.11 Contribution of pH to the Main Effects of Treatment and Soil on Element Concentration and Yield of Plants: Percentage Changes in the Sums of Squares when pH is Removed as a Linear Co-variate.

| Main Effects: | Treatments | Soils |
|---|---|---|
| Radish Tops | | |
| Yield | -95 | -95 |
| Cu | -94 | -36 |
| Pb | -85 | -13 |
| As | -28 | -87 |
| Radish Roots | | |
| Yield | -56 | -97 |
| Cu | -95 | -22 |
| Pb | -95 | -16 |
| As | +9 | -96 |
| Silverbeet Tops | | |
| Yield | -63 | -67 |
| Cu | -40 | -55 |
| Pb | -79 | -18 |
| As | -79 | -64 |

able to pH can be obtained as a percentage reduction in the sums of squares. The results are shown in Table 4.11.

High percentage reductions in the sums of squares (for example, for lead in radish) indicate that the observed effects correlate highly with pH. Low percentages may mean that pH is not an important factor or that the relationship with pH is not linear. Evidence of this is obtained by referring to Figure 4.10 which indicates for example that the low percentage reduction for arsenic 'between treatments' is due to lack of a pH effect within soils but the low percentage reduction for copper in silver beet is probably due to the existence of a non-linear relationship in some soils.

Table 4.11 shows that pH contributed substantially to the observed treatment effects except for arsenic in radish. It also contributed to 'between soil' differences, notably arsenic concentration and yield.

The mean concentrations of copper, lead and arsenic in the plants (Appendix 3) and their relation to pH of the dry soil (Table 4.9) are shown in Figures 4.7 to 4.10. The data for the prior waterlogged treatments are not plotted and will be discussed later.

Increases in soil pH were associated with significant decreases in the copper concentration of radish tops and roots (Figure 4.7). Concentrations were higher in the tops. Lead concentrations (Figure 4.8) in radish responded similarly except that a more marked decrease as a function of pH occurred in the roots. These results for lead reflect the poor translocation (*c.f.* copper) of lead from the roots to the tops of plants which has been observed many times before (Keaton, 1937 and others). Compared to copper and lead, the arsenic concentration in radish is, for the most part, insensitive to soil pH (Figure 4.9). The soils with the highest arsenic concentration (EH 13) and

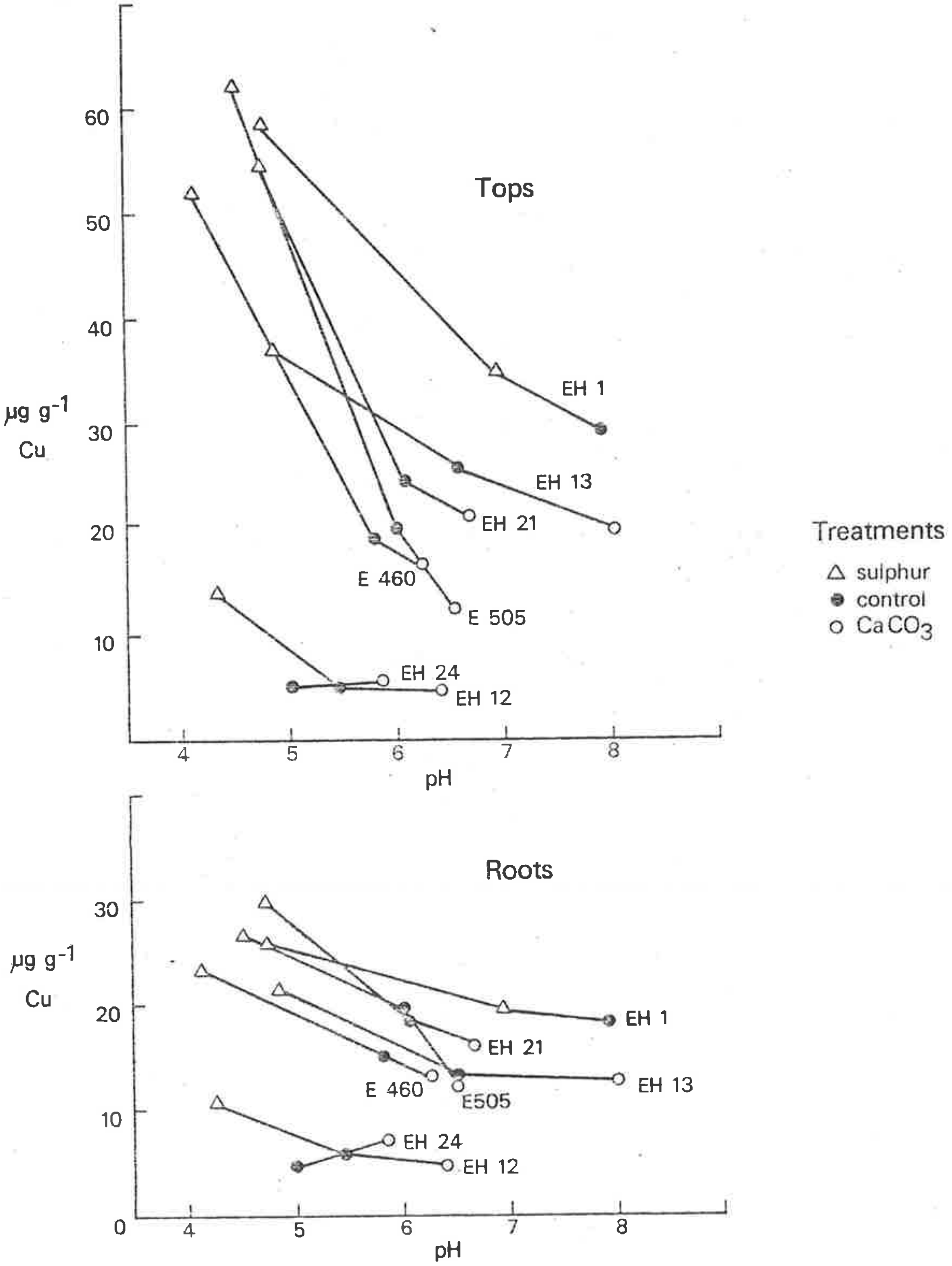


Figure 4.7
The Effects of Soil pH on Copper Concentration in Radish.

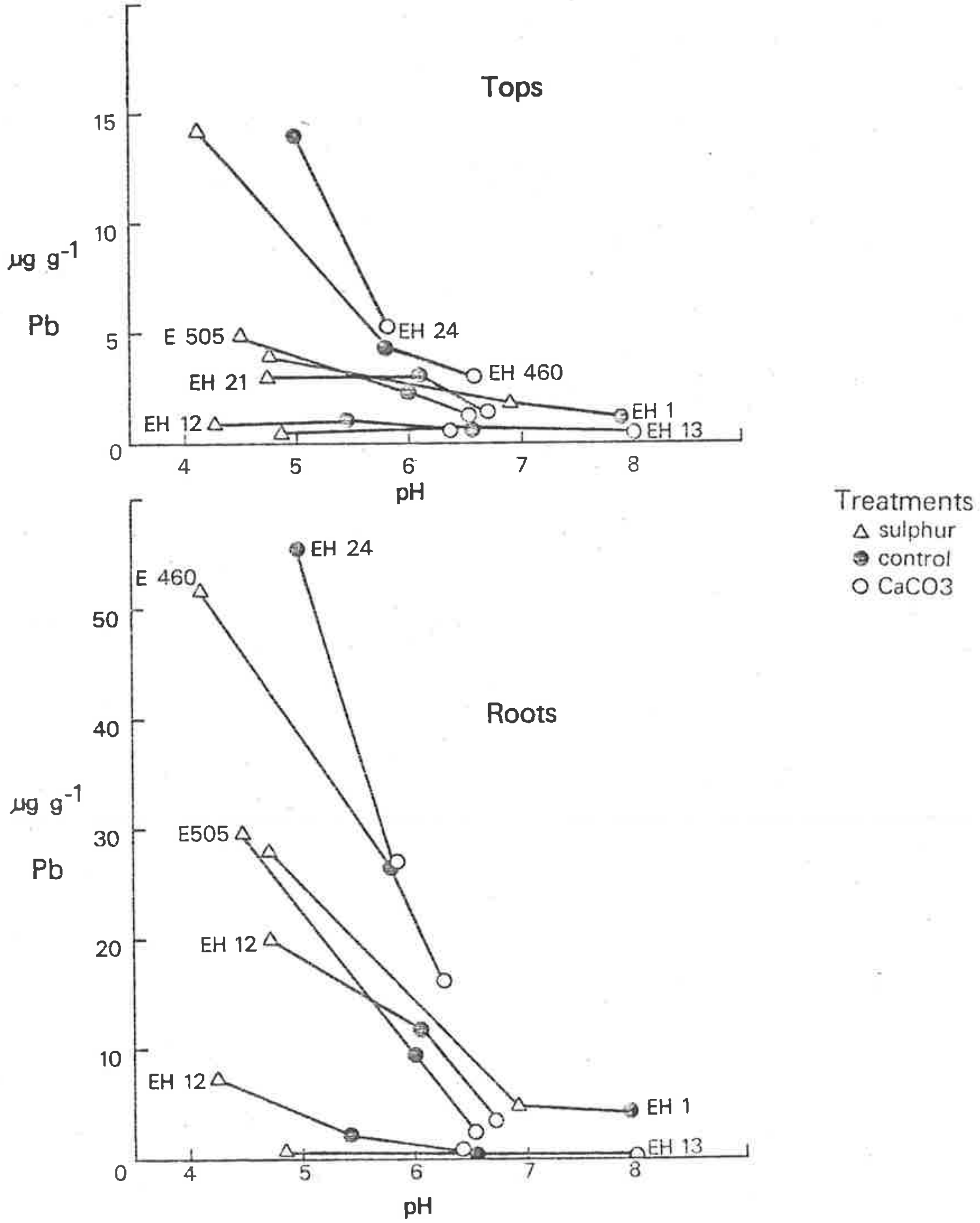


Figure 4.8

The Effect of Soil pH on the Lead Concentration in Radish.

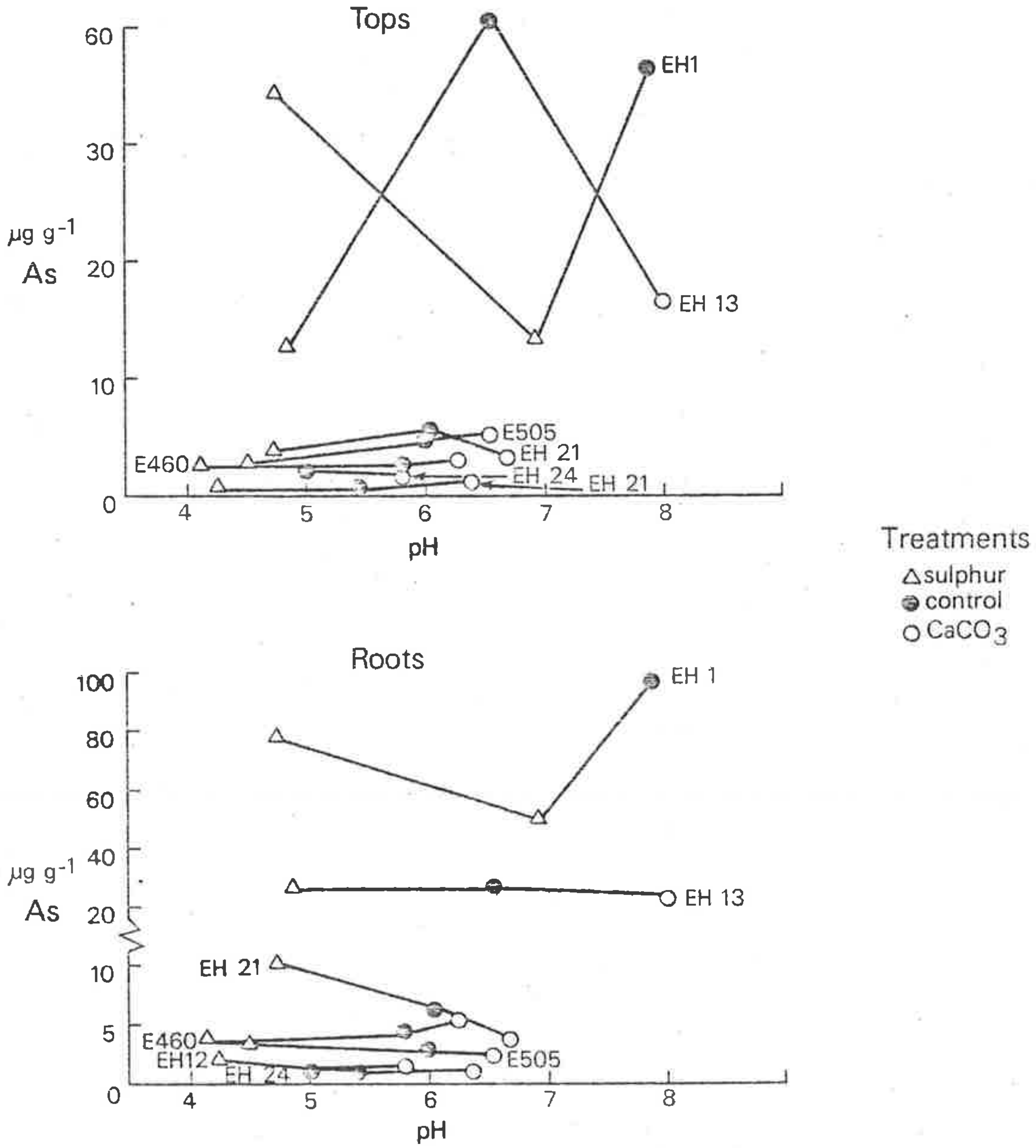


Figure 4.9

The Effect of Soil pH on the Arsenic Concentration in Radish.

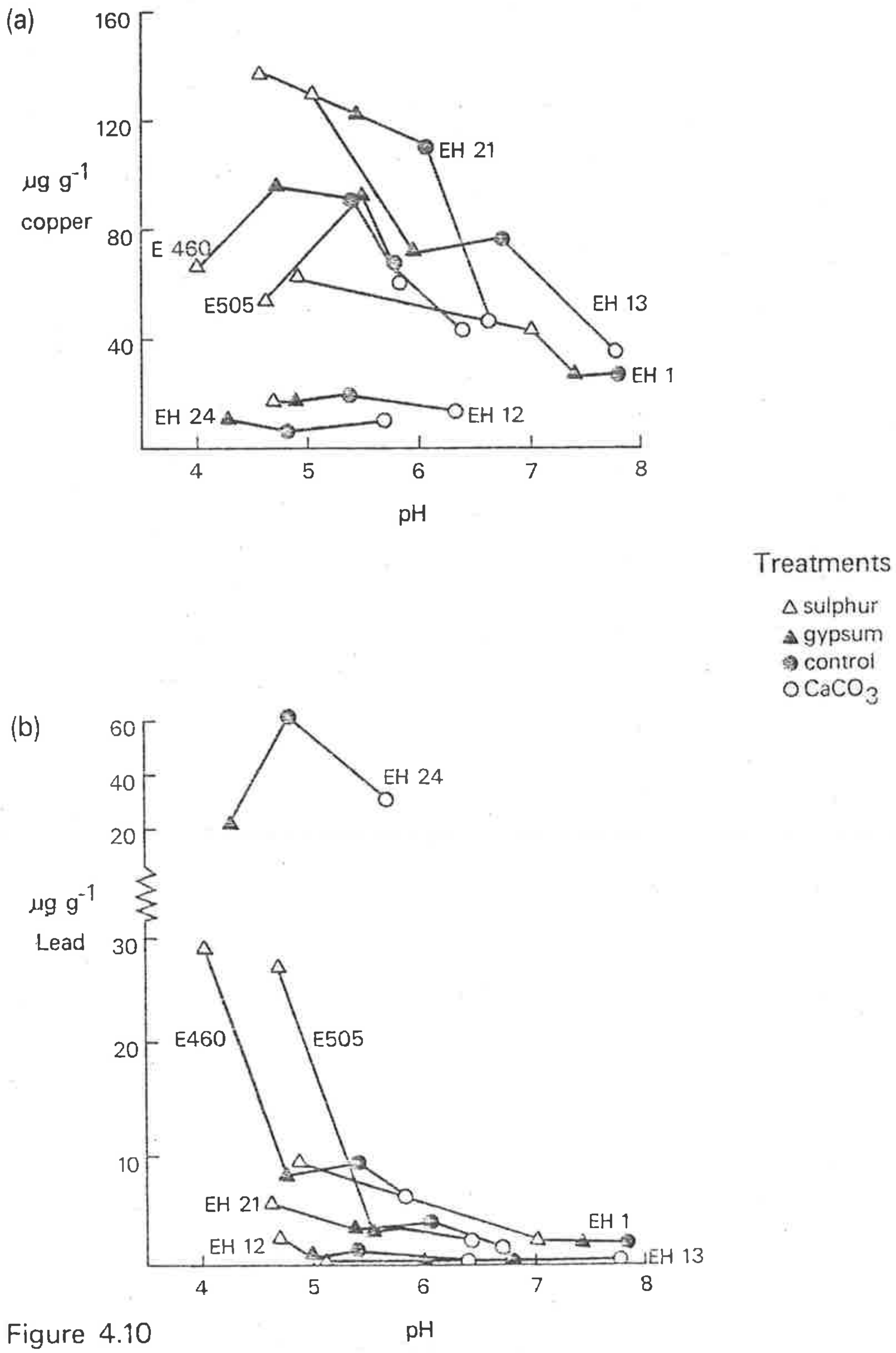
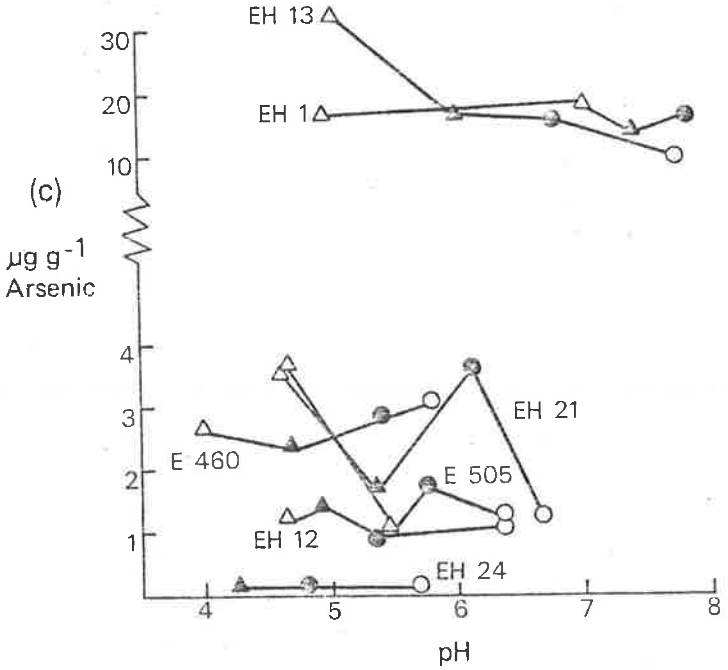


Figure 4.10

The Effect of Soil pH on the Copper, Lead and Arsenic Concentration of Silver Beet Tops.

Figure 4.10 continued



the dosed soil (EH 1) produced plants with very much higher and more variable arsenic concentrations than the other soils. The arsenic concentrations in the radish roots were usually higher than, or similar to, those of the tops. Comparison of the results for radish tops with those of silver beet (Figure 4.9) underlines the differences which may be expected between plant species. The copper concentrations of silver beet tops (Figures 4.10a) are higher than the concentrations in the tops of radish and varying soil pH has resulted in markedly different responses. In the soils with the lowest copper concentrations (EH 12 and EH 24) the concentration of copper in silver beet showed little variation with pH. A decline in copper concentration with increasing pH was observed with plants grown on soils EH 1, EH 13 and EH 21. The plants grown on two soils, E 460 and E 505 also had copper concentrations which declined as pH increased, but decreased markedly in the most acidic treatment as well. Although no certain explanation can be put forward for the behaviour of copper in the plants grown on the acidified soils, it is possible that interactions with manganese and/or aluminium may have been responsible. Blevins and Massey (1959) reported that copper uptake by plants decreased as aluminium concentration increased in solution culture and also as aluminium extracted by 0.1 N $CaCl_2$ increased when plants were grown in soil. Aluminium concentrations in the silver beet plants were not measured, but data for manganese are presented in Appendix 4. In all cases where the soils were acidified with sulphur, the manganese concentrations of the silver beet tops exceeded 1500 $\mu g\ g^{-1}$, and in at least one case, manganese toxicity symptoms were present. Although only one replicate of the silver beet roots were retained for chemical analysis, the results (Appendix 5) suggested a similar pattern of copper concentration as was found in the tops but concentrations were much higher.

The relationship of pH of the dry soil to lead concentration in the tops of silver beet plants (Figure 4.10b) were similar to those found for radish tops except that the concentrations in radish tops were lower. Analyses of the single replicate of silver beet roots showed a similar trend in lead concentration to the tops, but concentrations were higher (Appendix 5).

The arsenic concentrations of silver beet tops (Figure 4.10c) were, like radish, much less sensitive to pH change though there was fluctuations in some soils. The arsenic concentrations of the single replicate of roots were usually much higher (20 to 50 times) than concentrations in the tops (Appendix 5).

Element concentrations in the silver beet plants grown on the gypsum-treated soils are shown as closed triangles in Figure 4.10. These plots suggest that the concentrations, although not always significantly different from concentrations in the plants grown in the untreated, control soils, are often lower than would be expected from the decrease in pH which resulted from gypsum application. In some, but not all, cases the lower concentrations can be accounted for by growth dilution due to the increased yields of silver beet on the gypsum-treated soils. A similar effect of gypsum on arsenic concentration was noted in Pot Experiment 3a although the rates of application were only one fifth or less than the amounts used in this experiment and resulted in no significant change in soil pH. It is not obvious why gypsum applications should affect copper and lead concentrations in the silver beet. If sulphate anions are responsible, it is likely that the soils acidified with elemental sulphur are also affected. Since some of the sulphur in this treatment may not have been completely oxidized and some would have been incorporated into the microbial biomass, any decrease in concentrations of the elements due to sulphate is likely to have been smaller than that produced by the sulphate in gypsum. The concentrations of arsenic, copper and lead in the plants grown on some of the acidified soils might well have been higher in the absence of the 'sulphate effect'.

Decreased pH of the soils was associated with decreased yields of radish and silver beet in soils EH 1, EH 12 and EH 24 (where no plants grew), of radish roots in soil E 460 and of silver beet tops in soil E 505 (Appendix 3). The decreased yields in soils EH 12 and EH 24 may have been due in part to the effects of high manganese concentrations (Appendix 4). The application of calcium carbonate to the soils increased yields of radish tops and roots in soil EH 21, radish roots in soil E 505 and silver beet tops in soil EH 13.

In summary, treatments produced copper and lead concentrations in radish and silver beet which were clearly associated with changes in pH. Acidification generally increased and calcium carbonate generally decreased the concentrations of copper and lead in the plants, although the effects of calcium carbonate were not always significant. The arsenic concentrations and yields appear to be much less affected by the treatments. The gypsum, and possibly to a lesser extent the sulphur treatment, produced conditions in which factors other than pH (e.g. sulphate) may have made an appreciable contribution to the results obtained.

Little published data appears to be available on the effects of varying soil pH on the concentrations of copper, lead and arsenic in plants, especially in contaminated soils. Piper and Beckwith (1951) found that copper concentrations in plants grown on uncontaminated soil increased under acid soil conditions although there were differences between species and soils. Applications of lime were found by John and van Laerhoven (1972) and Cox and Rains (1972) to decrease lead uptake by a number of species, though the analytical methods used by the latter authors cast some doubt on the high lead concentrations that they reported. No information is available on the effects of pH on the arsenic concentration of plants. By analogy with molybdenum and phosphorus (e.g. Piper and Beckwith, 1951; Truog, 1946) it might be expected that the arsenic concentration in plants would increase with increasing soil pH, at least in the acid range. Pot Experiment 2 suggests that this does not happen.

*Factors Influencing Element Concentrations and Yields of the Plants*

Multiple regression analyses were used to relate the yield and concentration of elements in the plants to factors such as pH of the air-dry soil and the concentrations of the elements in the soils. This analysis combines both the 'treatment' and 'soil' effects discussed earlier as part of the covariance analysis. Data from soils EH 23 and EH 24 were excluded. The soil parameters tested were selected from those listed in Table 3.5 and also included arsenic extracted by $NaHCO_3$ from soil in the control pots (Table 4.13). The choice of parameters from Table 3.5 was simplified by knowledge of highly correlated factors such as DTPA-extractable copper with total copper, and cation exchange capacity with clay content.

Multiple regression equations relating concentrations of copper, lead and arsenic in the plant with various soil factors are shown in Table 4.12. A maximum of three factors, apart from pH of air-dry soil and interactions, were required to account for most of the variation. Addition of more factors did not contribute appreciably to the regressions.

As expected, pH was important in most cases, usually in combination with total concentrations in the soil of the element under examination. In two cases, significant contributions to the regressions were made by other elements: there were negative correlations between total soil manganese and the lead concentration in plants, and between total soil iron and the arsenic concentration in radish roots. The implication of manganese is in agreement with the findings of McKenzie (1978) who applied manganese oxides to soils (two of which were the soils EH 24 and E 505 used in this study) and observed a decrease in the lead concentration of subterranean clover grown in pots. Iron oxides would be expected to have some effect on the concentration of arsenic in plants because of the relationships of the elements discussed earlier in Section 2.5.3. Other factors such as clay contents and phosphorus extractable by $NaHCO_3$ were not

Table 4.12 Multiple Regressions Relating Concentrations of Copper, Lead and Arsenic in Plants to Soil Factors[†] in Pot Experiment 2

| | $R^2$ |
|---|---|
| Radish Tops | |
| $\text{Log Cu} = 2.07^{***} - 0.88^{***}\text{pH} + 0.06^{***}\text{pH}^2 + 1.02^{***}\log \text{Cu}_T$ | .86[§] |
| $\text{Log Pb} = -2.00^{**} + 0.31^{**}\text{pH} + 1.19^{***}\text{Log Pb}_T - 0.02^{***}\text{pH Log Pb}_T - 0.41^{***}\text{Log Mn}_T$ | .74 |
| $\text{Log As} = -2.94^{**} + 0.08^{**}\text{pH} + 1.40^{***}\text{Log As}_T + 0.49^{***}\text{Log NaHCO}_3\text{-As}$ | .84 |
| Radish Roots | |
| $\text{Log Cu} = 1.03^{***} - 0.40^{***}\text{pH} + 0.03^{***}\text{pH}^2 + 0.72^{***}\text{Log Cu}_T$ | .89 |
| $\text{Log Pb} = -1.10 + 0.01\text{ pH} + 1.59^{***}\text{Log Pb}_T - 0.01^{*}\text{pH Log Pb}_T - 0.48^{***}\text{Log Mn}_T$ | .89 |
| $\text{Log As} = -0.45 - 0.69^{*}\text{pH} + 0.05^{*}\text{pH}^2 + 1.21^{**}\text{Log As}_T + 0.68^{***}\text{Log NaHCO}_3\text{-As}$ | .82 |
| $= 0.60 - 0.99^{**}\text{pH} + 0.09^{**}\text{pH}^2 + 1.60^{***}\text{Log As}_T - 0.59^{***}\text{Log Fe}_T$ | .72 |
| Silver Beet Tops | |
| $\text{Log Cu} = -2.57^{***} + 0.88^{***}\text{pH} - 0.09^{***}\text{pH}^2 + 1.01^{***}\text{Log Cu}_T$ | .78 |
| $\text{Log Pb} = -4.13^{***} + 0.57^{**}\text{pH} + 2.77^{***}\text{Log Pb}_T - 0.33^{***}\text{pH Log Pb}_T - 0.34^{***}\text{Mn}_T$ | .76 |
| $\text{Log As} = -2.77^{***} + 1.57^{***}\text{Log As}_T + 0.25^{**}\text{Log NaHCO}_3\text{-As}$ | .70 |

[†] Cu, Pb, As denote plant concentrations in $\mu g\ g^{-1}$: pH denotes pH of air dry soil after harvest: subscript 'T' denotes total concentration in soil as presented in Table 3.5: $NaHCO_3$-As denotes 0.5 M $NaHCO_3$-extractable As from the untreated soil, Table 4.13.

[§] All regressions were significant at $P < 0.001$: *, **, *** denote significance at $P \leqslant 0.05$, 0.01, 0.001 respectively.

significantly correlated with the copper, lead and arsenic concentration in the plants.

An attempt was made to determine which of the elements in the soils had a significant effect on yield of the plants. Total soil copper and arsenic, which were themselves correlated, were also correlated with small, but statistically significant, decreases in yield and total lead with small yield increases. Soil pH alone, or in combination with total soil copper, lead or arsenic was found to be unimportant in determining plant yields. Covariance analysis (Table 4.11) suggested that pH should be important only in determining 'between' soil differences. The 'within' soil effects of pH on yields, according to Table 4.11 are of little significance. Since the multiple regression analysis incorporates both 'within' and 'between' soil effects, and the majority of degree of freedom are associated with 'the insignificant 'within' soil effects on yield, it appears that the 'between' soil effect suggested in Table 4.11 has been masked. No satisfactory regressions were found which indicated the factors which determined yields.

*Effects of Treatments on Copper and Lead Extracted by DTPA, and on Arsenic Extracted by $NaHCO_3$ from Moist Soil*

At harvest, subsamples of soil were extracted while still in a moist state with 0.005 M DTPA and with 0.5 M $NaHCO_3$. The data for copper, lead and arsenic, as well as for the pH of the moist soil, are presented in Table 4.13. The results show that, apart from the 'prior waterlogging' treatment, which will be discussed later, the effects of the treatments on the amounts of copper and lead extracted by DTPA were not consistent. The extraction of arsenic by 0.5 M $NaHCO_3$ appears to be relatively insensitive to the soil treatments.

The relationships between pH of the moist soil (and soil treatments) and the concentrations of the elements are illustrated in Figure 4.11 for four of the soils (EH 12, EH 21, EH 1 and EH 13) on which silver beet was grown. The results for soils on which radish was grown were similar. Figure 4.11(a) indicates that copper extracted by DTPA showed consistent trends for each soil although the trends varied from soil to soil. Lead extracted by DTPA behaved similarly (Figure 4.11b).

The DTPA extraction was devised for testing deficiency situations for copper and zinc in calcareous soils (Lindsay and Norvell, 1978) and has been widely applied, often successfully, to other elements and also to contaminated soils (e.g. Walsh *et al.*, 1972; Korcak and Fanning, 1978). However, the results presented here suggest that the DTPA extract is inappropriate as an indicator of plant availability where treatments of the soil greatly affect soil pH. As soil pH increased, the concentrations of copper and lead in plants grown on contaminated soils usually declined (Figures 4.7, 4.8, and 4.10) yet for many of the soils, the copper and lead extractable with DTPA increased with increasing soil pH (Figure 4.11a and b). In this experiment, the equilibrium pH of the soil extracts were not measured and it is possible that the results obtained are a result of the extraction procedure being insufficiently buffered to cope with wide variations in pH.

Arsenic extracted by $NaHCO_3$ gave a better indication of the general level of plant uptake (Figures 4.9 and 4.10c) and was also relatively less sensitive to changes in soil pH (Figure 4.11c). Arsenic extracted from the untreated soil was found to be a useful adjunct to total soil arsenic in the multiple regression analyses for arsenic shown in Table 4.12. The use of 0.5 M $NaHCO_3$ has been based on the use of similar extractants for phosphate (Section 2.5.3).

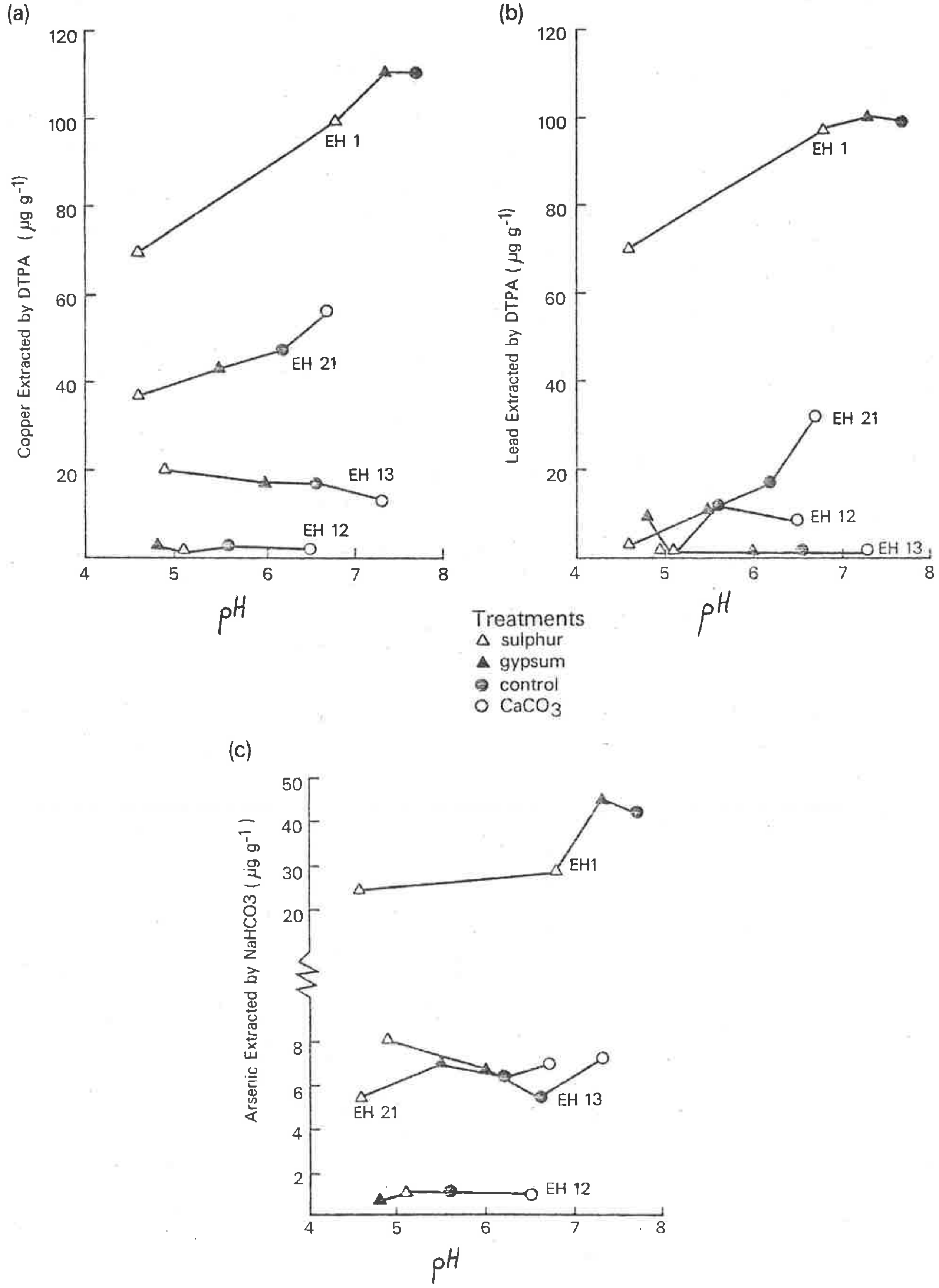


Figure 4.11 The Relationship of Extractable Copper, Lead and Arsenic with Soil pH. (Pooled Standard Deviations are Presented in Table 4.13).

### *The Effects of the Prior Waterlogging Treatment*

The data showing the effects of prior waterlogging on soil pH, plant yields and concentrations, and soil analysis have been presented, respectively, in Table 4.9, Appendix 3 and Table 4.13.

Prior waterlogging had no significant effect on yields of radish tops or silver beet tops except for a yield decrease in silver beet grown on soil EH 24. The treatment did result in increased yields of radish roots on three orchard soils, E 460, EH 21 and E 505 (Appendix 3). The effects of the treatment on copper, lead and arsenic concentrations of the plants were sporadic and inconsistent in that they were difficult to reconcile with changes in soil pH or extractable copper and lead (Table 4.13). For example, the copper concentrations increased in the tops of radish grown on soils E 460 and EH 21, and also in the tops of silver beet grown on soils E 460, E 505 and EH 24 yet in none of these cases was a corresponding increase observed in copper extractable with DTPA. Generally, copper extracted by DTPA decreased due to the treatment (Table 4.13) except for the soils EH 13 and EH 24. Lead extracted by DTPA decreased in five soils, EH 12, E 460, EH 21, E 505 and EH 24 yet plant concentrations did not change. The decreased extraction of copper and lead by DTPA may have resulted from the greater saturation with iron released by the waterlogging treatment. Apart from soil EH 1 where a decrease was observed, waterlogging generally resulted in increases in arsenic extractable with $NaHCO_3$ (Table 4.13). Significant changes in the concentration of arsenic in plants which corresponded to changes in the amount extracted from the soil were observed in radish grown on soil E 460 (increase), radish and silver beet grown on soil EH 1 (decrease) and silver beet grown on soil EH 13 (increase).

The prior waterlogging treatment of the soils in this experiment produced few effects which were consistent with the observed changes in pH or soil analysis. The alterations to the surfaces of iron and manganese oxide minerals in soils under reducing conditions (Hem, 1972) and to the availability of arsenic to

Table 4.13 Copper and Lead Extracted with DTPA (µg $g^{-1}$), Arsenic Extracted with $NaHCO_3$ (µg $g^{-1}$) and pH Determined on the Moist Soil at Harvest, Pot Experiment 2. (Treatments are as for Table 4.9).

| Plant: | | | Radish | | | | Silver Beet | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Treatment: | | | S (2) | Control | $CaCO_3$ (5) | W'Log | S (2) | Gypsum (2) | Control | $CaCO_3$ (5) | W'Log | S.D.[†] |
| Soil: EH 12 | | pH | 4.3 | 5.8 | 6.5 | 6.0 | 5.1 | 4.8 | 5.6 | 6.5 | 5.9 | 0.08 |
| | DTPA | Cu | 2.2 | 2.9 | 2.3 | 2.4 | 1.3 | 2.5 | 2.8 | 1.9 | 2.5 | 0.24 |
| | DTPA | Pb | 3.8 | 10 | 9.1 | 1.6 | 1.3 | 9.3 | 12 | 8.5 | 3.4 | 0.73 |
| | $NaHCO_3$ | As | 0.8 | 1.2 | 1.2 | 1.0 | 1.1 | 0.8 | 1.1 | 1.0 | 1.2 | 0.3 |
| | | | S (2) | Control | $CaCO_3$ (2.5) | W'Log | S (2) | Gypsum (2) | Control | $CaCO_3$ (2.5) | W'Log | SD |
| Soil: E 460 | | pH | 4.2 | 6.1 | 6.5 | 6.2 | 4.0 | 4.7 | 5.7 | 6.1 | 6.1 | 0.10 |
| | DTPA | Cu | 22 | 23 | 25 | 20 | 24 | 22 | 23 | 25 | 23 | 0.6 |
| | DTPA | Pb | 5 | 19 | 39 | 5 | 6 | 16 | 20 | 38 | 8 | 1.8 |
| | $NaHCO_3$ | As | 5.7 | 6.4 | 6.3 | 9.8 | 6.7 | 7.1 | 5.5 | 6.6 | 9.0 | 2.0 |
| | | | S (2) | Control | $CaCO_3$ (3.75) | W'Log | S (2) | Gypsum (2) | Control | $CaCO_3$ (3.75) | W'Log | SD |
| Soil: EH 21 | | pH | 4.8 | 6.3 | 6.8 | 6.5 | 4.6 | 5.5 | 6.2 | 6.7 | 6.5 | 0.09 |
| | DTPA | Cu | 39 | 47 | 52 | 46 | 37 | 43 | 47 | 56 | 49 | 3.4 |
| | DTPA | Pb | 4.3 | 15 | 18 | 8.6 | 3.1 | 11 | 17 | 32 | 12 | 1.6 |
| | $NaHCO_3$ | As | 7.1 | 5.9 | 6.0 | 7.4 | 5.5 | 7.1 | 6.4 | 7.0 | 10 | 1.1 |
| | | | S (2) | Control | $CaCO_3$ (3.75) | W'Log | S (2) | Gypsum (2) | Control | $CaCO_3$ (3.75) | W'Log | SD |
| Soil: E 505 | | pH | 4.6 | 6.2 | 6.7 | 6.3 | 4.9 | 5.3 | 5.8 | 6.5 | 6.0 | 0.07 |
| | DTPA | Cu | 30 | 39 | 32 | 31 | 30 | 38 | 38 | 36 | 32 | 2.5 |
| | DTPA | Pb | 8 | 39 | 59 | 8 | 9 | 48 | 43 | 46 | 8 | 3.2 |
| | $NaHCO_3$ | As | 4.4 | 5.8 | 5.6 | 6.0 | 5.6 | 4.1 | 4.6 | 5.1 | 7.1 | 1.1 |

[†] Pooled standard deviation of duplicate determinations

Table 4.13 (cont'd)

| Plant: | | | Radish | | | | Silver Beet | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Treatment: | | | S (16) | S (8) | Control | W'Log | S (16) | S (8) | Gypsum (16) | Control | W'Log | SD[†] |
| Soil: EH 1 | | pH | 4.7 | 6.9 | 7.8 | 7.9 | 4.6 | 6.8 | 7.3 | 7.7 | 7.8 | 0.13 |
| | DTPA | Cu | 74 | 93 | 111 | 86 | 69 | 99 | 110 | 110 | 100 | 8.8 |
| | DTPA | Pb | 78 | 91 | 92 | 76 | 70 | 97 | 100 | 99 | 85 | 5.4 |
| | $NaHCO_3$ | As | 35 | 36 | 40 | 28 | 25 | 29 | 45 | 42 | 34 | 7.8 |
| | | | S (1) | Control | $CaCO_3$ (2.5) | W'Log | S (1) | Gypsum (1) | Control | $CaCO_3$ (2.5) | W'Log | SD |
| Soil: EH 23 | | pH | 3.7 | 4.9 | 5.9 | 5.1 | 3.8 | 4.60 | 4.9 | 5.4 | 5.0 | 0.09 |
| | DTPA | Cu | 13.0 | 130 | 120 | 120 | 130 | 125 | 130 | 125 | 125 | 3.6 |
| | DTPA | Pb | 20 | 18 | 27 | 29 | 22 | 20 | 19 | 23 | 20 | 1.9 |
| | $NaHCO_3$ | As | 50 | 64 | 81 | 73 | 52 | 55 | 57 | 79 | 79 | 20. |
| | | | S (1) | Control | $CaCO_3$ (2.5) | W'Log | S (1) | Gypsum (1) | control | $CaCO_3$ (2.5) | W'Log | SD |
| Soil: EH 13 | | pH | 4.9 | 6.5 | 7.2 | 7.2 | 4.9 | 6.0 | 6.6 | 7.3 | 6.8 | 0.23 |
| | DTPA | Cu | 23 | 17 | 14 | 23 | 20 | 17 | 17 | 13 | 22 | 1.0 |
| | DTPA | Pb | 1.4 | 0.8 | 0.8 | 0.7 | 1.4 | 1.0 | 0.9 | 0.7 | 0.9 | 0.08 |
| | $NaHCO_3$ | As | 9.9 | 4.1 | 7.5 | 23 | 8.1 | 6.8 | 5.4 | 7.2 | 27 | 2.0 |
| | | | S (2) | Control | $CaCO_3$ (3.75) | W'Log | S (2) | Gypsum (2) | Control | $CaCO_3$ (3.75) | W'Log | SD |
| Soil: EH 24 | | pH | 3.9 | 5.2 | 6.1 | 5.6 | 3.8 | 4.3 | 4.9 | 5.8 | 5.2 | 0.06 |
| | DTPA | Cu | 0.5 | 0.4 | 0.6 | 1.7 | 0.2 | 0.3 | 0.3 | 0.2 | 0.3 | 0.7 |
| | DTPA | Pb | 85 | 81 | 77 | 25 | 85 | 81 | 84 | 79 | 31 | 3.8 |
| | $NaHCO_3$ | As | 0.9 | 1.0 | 0.8 | 1.8 | 0.8 | 0.8 | 0.8 | 0.6 | 2.2 | 0.4 |

[†] Pooled standard deviation of duplicate determinations

plants (Keaton and Kardos, 1940; Deuel and Swoboda, 1972) were probably reversed with the return to oxidizing conditions during growth of the plants. Plants actually experiencing reducing conditions during the growth period may react quite differently.

### *Comparison of the Behaviour of Soils with Differing Sources of Contamination*

The soils used in this experiment can be placed into four groups depending on the source of contamination. These are:

1) former orchard soils (EH 12) and E 460),
2) soils from existing orchards (EH 21 and E 505),
3) soils dosed with copper, lead and arsenic (EH 1 and EH 23) and
4) soils affected by mining or mineralization (EH 13 and EH 24).

The former orchard soils usually behaved in a similar manner to the soils from existing orchards even though they had received no copper, lead or arsenic for about 20 years.

The soils which were freshly dosed with the three elements showed that, at least in some respects, it is not appropriate to compare them with orchard soils. It is not possible to state with certainty which element or elements were responsible for the death of plants grown on soil EH 23 but analysis of plants from the treatment which did survive (Appendix 3) suggests that copper alone or copper and arsenic were responsible. Making comparisons in terms of anticipated dosage rather than residual contamination of this coarse textured soil with, for example, the sandy orchard soils from Tasmania is not valid because it has been clearly shown in a previous section that arsenic is readily leached or otherwise removed from such soils. Consequently, the concentration of arsenic to which soil EH 23 was dosed (125 $\mu g\ g^{-1}$) is not likely to be attained in coarse-textured orchard soils. The other dosed soil, EH 1, which was fine textured, calcareous and contained more organic material, behaved in a manner comparable to the orchard soils with respect to both copper and lead taken up by plants, but not arsenic since it was absorbed by plants in greater amounts (Figures 4.9 and 4.10c). The much shorter equilibration time may have resulted in higher availability of arsenic to plants. The high affinity reactions of anions similar to arsenate, such as phosphate and molybdate, may require considerably longer periods of equilibration before concentrations in the soil solution are substantially decreased (Barrow, 1974b; Barrow and Shaw, 1975).

Soil EH 13 had the highest arsenic (280 $\mu g\ g^{-1}$) and EH 24 had the highest lead (730 $\mu g\ g^{-1}$) concentrations of the soils studied. The concentrations of the elements in plants grown on these latter soils were correspondingly higher than in plants grown on the orchard soils, as might be expected. Although soil EH 24 had the second highest arsenic concentration (140 $\mu g\ g^{-1}$), the concentrations in the plants were very low. It is probable that the arsenic in this soil was present in the mineral hinsdalite (Norrish, 1975) and not readily available to plants. It is likely that either high concentrations of lead (Appendix 3) and/or high manganese (Appendix 4) in the plants proved toxic on the acidified treatment. On the basis of these results, soils affected by mining or mineralization may be no more toxic to plants than contaminated orchard soils at comparable pH and concentration of the element. There may, in fact, be less danger from mineralized and mine affected soils if the element is in a form which is not readily available to plants.

### *Toxicity Symptoms*

During this experiment, symptoms of toxicity or nutrient imbalance appeared only on plants grown on the soils acidified with elemental sulphur, except for soil EH 23. All plants on the latter soil were affected with the exception of radish grown on pots where $CaCO_3$ was applied: these were the only plants to survive until harvest in that soil. However in only one situation could symptom be confidently attributed to a specific element, *viz* manganese. Figure 4.12 (a) and (b) show radish and silver beet plants grown on acidified soil EH 12. The symptoms of small necrotic patches concentrated near the leaf margins are similar to those described in a number of other species by Labanauskas (1966) for manganese toxicity. The radish and silver beet plants contained, respectively, 4100 and 5400 µg $g^{-1}$ of manganese, while the copper, lead and arsenic concentrations were comparatively low. Similar symptoms appeared on silver beet grown on soil EH 24 in Pot Experiment 1.

Figure 4.12 (c) shows leaves of silver beet grown on soil E 505 at pH 4.65. The cause of the symptoms is not clear but it is possible that this reflects a more advanced stage of manganese toxicity since the manganese concentration of the leaves were 7100 µg $g^{-1}$.

The leaves of young radish plants grown in soil E 460 at pH 4.1 are shown in Figure 4.12 (d) and in Figure 4.12 (e) the same plants are shown at harvest when the leaves contained 1000, 52, 14 and 2.6 µg $g^{-1}$ of manganese, copper, lead and arsenic respectively. The symptoms do not resemble those observed in plants grown on soil EH 12 and attributed to manganese.

The plants which grew briefly, but failed to survive on the dosed soil, EH 23, were stunted and showed symptoms only of a general chlorosis which could not be related to any specific element.

It is possible that some of the visual effects noted on plants grown on acidified soils were due to aluminium toxicity. Pratt (1966) described aluminium toxicity as causing decreased growth particularly of roots, which can be severely affected before there are any obvious effect on the tops. No specific symptoms were observed at harvest on the roots of the plants in acidified soils except for stunted growth. Where symptoms were apparently

Figure 4.12 Toxicity Symptoms in Plants

(a) Radish plants grown on soil EH 12 (pH 4.3)

(b) Silver Beet plants grown on soil EH 12 (pH 4.7)

Fig. 4.12 (continued)

(c) Silver Beet grown on soil E 505 (pH 4.65)

(d) Young radish plants grown on soil E 460 (pH 4.1)

Figure 4.12 (continued)

(e) Radish plants grown on soil E 460 (pH 4.1) just prior to harvest not due to manganese toxicity, the cause was not evident from the chemical analyses carried out in this experiment. Iron and zinc concentrations were checked in the plants and should have been adequate although high concentrations of other elements may decrease their effectiveness. Deficiencies of other elements may have been induced but no analyses were carried out to confirm this or to investigate the possibility of aluminium toxicity in the acidified soils.

### 4.4.3 Pot Experiment 3a: The Effects of Phosphorus and Sulphur on Silver Beet Grown on Orchard Soils

This experiment was designed to measure the extent to which two major constituents of fertilizers (phosphorus and sulphur) affect the growth and composition of plants grown in orchard soils contaminated with copper, lead and arsenic. Phosphorus and sulphur which were applied to the pots are shown in Table 3.9. Applications of 25 kg $ha^{-1}$ phosphorus and 170 kg $ha^{-1}$ sulphur are frequently applied in commercial vegetable growing. For convenience, the phosphorus and sulphur treatments will be referred to in the tables of results as $P_0$, $P_{17.5}$, $P_{35}$ and $P_{52.5}$, and $S_0$, $S_{85}$ and $S_{170}$ respectively, where the subscripts indicate the equivalent rate of application of the element in kg $ha^{-1}$.

The mean yields and concentrations of the elements in silver beet grown on the two soils (E 460 and E 505) are shown in Table 4.14. The yields and concentrations of lead and arsenic in plants grown on soil E 460 were significantly higher than those grown on soil E 505. The differences in concentrations of lead and arsenic in the silver beet reflect the total concentrations of the elements in the soils (Table 4.15). Despite the higher copper concentrations of soil E 505, there was no significant differences in the concentrations of copper in plants grown on the two soils. Variability between replicates of concentration of copper in the roots was quite high (coefficients of variation

Table 4.14 Mean Yields (g per pot) and Concentrations (μg $g^{-1}$) of Elements in Silver Beet Grown in Pot Experiment 3a

| | Soil | E 460 | E 505 | |
|---|---|---|---|---|
| Tops | Dry Wt. | 12.1 | 10.7 | ***† |
| | Cu | 80. | 79 | n.s. |
| | Pb | 10.4 | 4.7 | *** |
| | As | 3.0 | 1.2 | *** |
| Roots | Dry Wt. | 4.2 | 2.5 | *** |
| | Cu | 285 | 275 | n.s. |
| | Pb | 185 | 85 | *** |
| | As | 112 | 58 | *** |

† soils significantly different ($P < 0.001$)

Table 4.15 Total Concentrations (μg $g^{-1}$) of Copper, Lead and Arsenic in the Soils Used in Pot Experiment 3a

| Soil | Cu | Pb | As |
|---|---|---|---|
| E 460 | 155 | 455 | 120 |
| E 505 | 195 | 290 | 95 |

were about 40% compared with 15 to 10% or less for the other yield and concentration data).

Statistically significant effects due to phosphorus were fewer than those due to sulphur and are presented in Table 4.16. Phosphorus had no effect on yield but decreased copper in the roots of plants grown on soil E 505. The lead concentration in the roots of plants grown on soil E 505 decreased with increasing phosphorus up to the 35 kg ha$^{-1}$ application rate, but the concentration at the highest rate of application (52.5 kg ha$^{-1}$ phosphorus) was no different from the control. Phosphorus also had a significant effect on the arsenic concentration of roots grown in soil E 460 but the trend was not consistent. The trend for arsenic in roots grown in soil E 460 was affected by an interaction with sulphur, the only significant interaction observed in this experiment (Table 4.17).

Sulphur applications significantly affected the growth and concentrations of elements in the plants (Table 4.18). The effects due to sulphur were predominantly in the roots and were accompanied by significant effects on the tops in only two cases, *viz.* a marginal decrease in lead concentration of plants grown on soil E 505, and a decrease in arsenic in the tops of plants grown on soil E 460. Usually sulphur applications were small but beneficial in that they decreased the concentrations of the elements, and the greater part of the decrease occurred at the lower rate of application (equivalent to 85 kg ha$^{-1}$ sulphur). In some cases, however, such as for lead in roots grown in soil E 460, concentrations increased again at the highest rate of application of sulphur to concentrations not significantly different from that of the control. The small changes in pH which resulted from the addition of salts to the soil did not account for the observed effects.

Table 4.16 The Effects of Phosphorus on Yield (g per pot) and Concentrations ($\mu g\ g^{-1}$) of Copper, Lead and Arsenic in Silver Beet

| | | | Treatment | | | | |
|---|---|---|---|---|---|---|---|
| Soil | | Plant Part | $P_0$ | $P_{17.5}$ | $P_{35}$ | $P_{52.5}$ | LSD ($P < 0.05$) |
| E 460 | Yield | Tops | 12.1 | 12.2 | 12.3 | 12.1 | n.s. |
| | | Roots | 4.5 | 4.1 | 4.1 | 4.2 | n.s. |
| | Cu | Tops | 82 | 77 | 78 | 83 | n.s. |
| | | Roots | 335 | 310 | 275 | 230 | n.s. |
| | Pb | Tops | 10.7 | 9.8 | 10.4 | 10.5 | n.s. |
| | | Roots | 190 | 200 | 170 | 175 | n.s. |
| | As | Tops | 2.6 | 3.2 | 3.1 | 3.2 | n.s. |
| | | Roots | 102 | 116 | 106 | 122 | 12 |
| E 505 | Yield | Tops | 10.5 | 11.1 | 10.5 | 10.9 | n.s. |
| | | Roots | 2.4 | 2.3 | 2.3 | 2.7 | n.s. |
| | Cu | Tops | 83 | 76 | 76 | 82 | n.s. |
| | | Roots | 395 | 250 | 220 | 235 | 112 |
| | Pb | Tops | 4.9 | 4.5 | 4.1 | 5.1 | 0.85 |
| | | Roots | 91 | 85 | 78 | 88 | 9 |
| | As | Tops | 1.5 | 0.9 | 1.4 | 1.1 | 0.4 |
| | | Roots | 57 | 59 | 58 | 58 | n.s. |

Table 4.17 The Effect of Phosphorus and Sulphur on Arsenic Concentration ($\mu g\ g^{-1}$) in the Roots of Silver Beet Grown in Soil E 460

| Treatment | $P_0$ | $P_{17.5}$ | $P_{35}$ | $P_{52.5}$ |
|---|---|---|---|---|
| So | 118 | 132 | 118 | 116 |
| $S_{85}$ | 100 | 101 | 78 | 126 |
| $S_{170}$ | 102 | 116 | 123 | 126 |

$LSD_{0.05}=22$

Table 4.18 The Effects of Sulphur on the Yields (g per pot) and Concentrations of Copper, Lead and Arsenic in Silver Beet

| Soil | | Plant Part | Treatments<br>$S_0$ | $S_{85}$ | $S_{170}$ | LSD ($P < 0.05$) |
|---|---|---|---|---|---|---|
| E 460 | Yield | Tops | 12.2 | 12.3 | 12.0 | n.s. |
| | | Roots | 4.8 | 3.9 | 4.1 | 0.5 |
| | Cu | Tops | 75 | 81 | 84 | 5 |
| | | Roots | 365 | 273 | 223 | n.s. |
| | Pb | Tops | 10.1 | 10.3 | 10.7 | n.s. |
| | | Roots | 205 | 155 | 190 | 20 |
| | As | Tops | 3.6 | 2.9 | 2.6 | 0.4 |
| | | Roots | 120 | 100 | 113 | 11 |
| E 505 | Yield | Tops | 10.6 | 11.2 | 10.4 | n.s. |
| | | Roots | 2.6 | 2.4 | 2.3 | n.s. |
| | Cu | Tops | 80 | 76 | 80 | n.s. |
| | | Roots | 365 | 250 | 215 | 80 |
| | Pb | Tops | 4.9 | 4.2 | 4.9 | 0.5 |
| | | Roots | 92 | 84 | 81 | 8 |
| | As | Tops | 1.1 | 1.3 | 1.2 | n.s. |
| | | Roots | 68 | 55 | 51 | 10 |

There is a possibility that some of the results obtained for plants and roots in this experiment (as well as the other experiments where roots were sampled) were influenced by other factors. It was difficult to remove soil entirely from the roots and the treatments themselves could conceivably influence the configuration of the root system and the efficiency of washing. Nevertheless contamination was not considered a sufficiently serious problem to influence the conclusions drawn from the experiment. Effects of gypsum on concentration of the elements in silver beet plants in this experiment were also observed in the tops of the silver beet plants in Pot Experiment 2.

McLean *et al.* (1969) and Zimdahl and Foster (1976) found that applications of phosphate decreased the lead concentration in the roots and tops of plants. Both of these results were produced on soils dosed with lead and incubated for two or four weeks prior to growing plants. A similar result was obtained in Pot Experiment 3a on soil E 505 at rates up to 35 kg ha$^{-1}$, but effects were small, and lead concentrations in plants grown on soil E 460 were unaffected by phosphate application. That phosphorus had a small or no effect on lead in the present study may be related to the long history of lead accumulation and the concurrent applications of phosphate fertilizers to these soils.

Hurd-Karrer (1936) and Rumberg *et al.* (1960) showed that increasing phosphate in nutrient solution could decrease the arsenic uptake by plants. However, the effects are less clear with plants grown in soil. Carrow *et al.* (1975) found no effect of phosphate on arsenic uptake, but Jacobs and Keeney (1970) and Woolson *et al.* (1973) observed increased arsenic toxicity to plants when phosphate was applied to soils. This they attributed to increased arsenic uptake due to the displacement by phosphorus of arsenate from adsorption sites in the soil. The same mechanism may apply to the results obtained for arsenic in soil E 460.

Attempts to alleviate arsenic toxicity using chemicals containing sulphate have been reported. Thompson and Batjer (1950) successfully used zinc sulphate (with nitrogen, sometimes as ammonium sulphate) to alleviate the symptoms of arsenic injury to peach trees. However, Walsh *et al.* (1977) attributed this result to the correction of zinc deficiency induced by high concentrations of arsenic in the soil, a cause and effect which was not substantiated. Steevens *et al.* (1972) found that neither ferric nor aluminium sulphate was effective in countering toxicity due to applications of arsenite to soil. They expected that these compounds might be effective through the formation of adsorbing surfaces by precipitation with iron and aluminium oxides. Sulphate applied in the present experiment may have decreased the arsenic concentration in the plants as a result of competition between similar ions such as was reported by Epstein (1962) for sulphate and selenate. Similar results to those obtained in the present study were presented by Reddy (1976) who found that sulphate application to soil decreased the molybdenum concentration in clover plants. It is not clear why sulphate applications should affect the uptake of lead or copper by the roots of silver beet plants but it is possible that the associated cation (calcium) may be involved.

In summary, sulphur and to a lesser extent phosphorus (applied respectively as sulphate and phosphate) were beneficial in that they frequently decreased the concentration of copper, lead and arsenic in plants growing on contaminated soils, but the effects were not large.

### 4.4.4 Pot Experiment 3b: Comparison of Commercial Fertilizer with the Equivalent in Pure Chemicals

A rate equivalent to 1000 kg $ha^{-1}$ of a mixed fertilizer which is used commercially in South Australia and contains 3.5% phosphorus, 17% sulphur, 8% nitrogen and 8% potassium was compared with the same nutrients supplied as pure chemicals. The results are shown in Table 4.19. Copper concentrations in the roots of the plants were found to be variable, a feature also observed in Pot Experiment 3a.

Table 4.19 A Comparison of Yields (g per pot) and Concentrations ($\mu g\ g^{-1}$) of Copper, Lead and Arsenic in Silver Beet Grown with Nutrients Supplied as Commercial Fertilizer and as Pure Chemicals[†]

| Soil | | E460 | | | | E505 | | | |
|---|---|---|---|---|---|---|---|---|---|
| Fertilizer | | Commercial | | Pure Chemical | | Commercial | | Pure Chemical | |
| Yield | Tops | 12.1 | b | 13.2 | b | 10.2 | a | 10.8 | a |
| | Roots | 4.1 | b | 4.0 | b | 2.1 | a | 2.0 | a |
| Cu | Tops | 80 | a | 77 | a | 83 | a | 91 | a |
| | Roots | 180 | a | 280 | a | 210 | a | 205 | a |
| Pb | Tops | 10.8 | b | 9.2 | b | 4.3 | a | 5.1 | a |
| | Roots | 190 | b | 190 | b | 78 | a | 54 | a |
| As | Tops | 2.0 | a | 1.9 | a | 1.4 | a | 1.5 | a |
| | Roots | 120 | b | 120 | b | 47 | a | 51 | a |

[†] Means of three replicates. Numbers followed by the same letter are not significantly different.

Although only compared at one rate of application, no significant differences in yield or copper, lead and arsenic concentrations were observed in plants grown on either of the soils used, E 460 and E 505. Differences may be observed at different rates of application. These results suggest that the results obtained in Pot Experiment 3a, where pure chemicals were used, may also be obtained when commercial fertilizers are used.

### 4.4.5 Pot Experiment 3c: The Effects of Nitrogen Applications on Silver Beet Grown on an Orchard Soil

In this experiment, three rates of nitrogen equivalent to 0, 80 and 160 kg ha$^{-1}$ ($N_0$, $N_{80}$ and $N_{160}$ respectively) were applied to pots containing soil E 460 and silver beet was grown. Yields of tops and roots were measured as well as their copper, lead and arsenic concentrations. The results are presented in Table 4.20. Because three of the root samples were undoubtedly contaminated with copper, probably during grinding, no data for the concentrations of copper in the roots are shown. Such contamination is very unusual under our laboratory conditions and no explanation can be offered.

Table 4.20 The Effect of Nitrogen on the Growth of Silver Beet in an Orchard Soil[†]

| | Treatment | $N_0$ | $N_{80}$ | $N_{160}$ | LSD ($P<0.05$) |
|---|---|---|---|---|---|
| Tops | Yield | 8.5 | 12.1 | 15.5 | 1.3 |
| | Cu | 70 | 80 | 76 | n.s. |
| | Pb | 10.4 | 10.8 | 10.4 | n.s. |
| | As | 6.1 | 2.0 | 1.7 | 0.7 |
| Roots | Yield | 3.8 | 4.1 | 4.0 | n.s. |
| | Pb | 315 | 190 | 190 | n.s. |
| | As | 110 | 125 | 120 | n.s. |

[†] Yields are in g per pot (dry weight) and concentrations are in µg g$^{-1}$

Increasing the rate of application of nitrogen resulted in a significant increase in the yield and a significant decrease in the arsenic concentration in the tops of the plants. No significant effects were observed on the copper and lead concentrations of the tops or yields of the roots.

The decrease in arsenic concentration with increasing nitrogen application is an interesting and unexpected result. Uptake values (yield X concentration) indicate that the decrease in concentration is much greater than would be expected from growth dilution alone. Little information appears to have been published on the effects of nitrogen on the arsenic concentrations in plants. Thompson and Batjer (1950) found that treatments which included nitrogen helped alleviate the symptoms of arsenic toxicity in peach trees but the role of nitrogen was not specifically commented on. These results suggest that the effects of nitrogen on arsenic uptake by plants should be further investigated on a wider selection of soils and plants. Nitrogen could be more effective in decreasing the arsenic concentration in plants than treatment of soils with phosphate or sulphate. Since applications of nitrogen were made to all pot experiments in this study (equivalent to 24 kg $ha^{-1}$ in Pot Experiments 1 and 2), the concentrations of arsenic in silver beet may be lower than would have been obtained if no nitrogen was applied. In practice, substantial amounts of nitrogen are usually applied to commercial vegetable and fruit crops.

# 5.0 GENERAL DISCUSSION AND CONCLUSIONS

## 5.0 GENERAL DISCUSSION AND CONCLUSIONS

It has been conservatively estimated that over the last 40 years there has been a decrease of at least 30 000 ha in the area of land on which apples and pears are grown in Australia (Section 4.1). Frequently, pastures have been established on areas that were formerly orchards but other major uses include urban development and vegetable growing.

The accumulations of copper, lead and arsenic found in orchard and former orchard soils in South Australia and Tasmania can be placed into perspective by comparing the concentrations with values reported in orchard soils elsewhere. Copper, lead and arsenic from orchard sprays have accumulated in the Australian soils to concentrations greater than 300, 550 and 100 $\mu g\ g^{-1}$ respectively. These copper concentrations were as high as or higher than those reported from Florida (Reuther and Smith, 1952) and Canada (Frank *et al.*, 1976) but are much lower than the concentrations reported in some soils in European vineyards (Delas, 1963). Lead and arsenic concentrations in the Australian orchard soils appear to be comparable to those in Canadian orchards (Frank *et al.*, 1976), but the highest arsenic concentrations are much lower than those reported for orchard soils in the United States (Walsh and Keeney, 1975).

The concentrations of copper, lead and arsenic were also measured in a limited number of soils on which other crops such as grapes, hops, stonefruits and citrus were grown. This preliminary investigation suggested that the copper concentration of soils growing stonefruit and citrus may require further investigation.

Total concentrations of lead and arsenic (determined from aqua regia digests) in the 0-10 cm layer of 98 South Australian and Tasmanian orchard soils suggested that there have been losses of arsenic relative to lead, especially from the coarse textured soils from Tasmania (Section 4.2.1). The copper and lead concentrations in EDTA and DTPA extracts of the orchard soils were found to be highly correlated with total concentrations (Table 4.3). Furthermore, the regressions relating EDTA extractable copper and lead with total concentration were similar. Similar regressions for EDTA extractable copper and lead, and DTPA extractable copper were obtained for the South Australian and the Tasmanian soils. At high concentrations of lead in the soils, the proportion of total lead extracted by DTPA becomes variable, possibly because of reagent saturation (Clayton and Tiller, 1979). DTPA may have some limitations as an extractant for lead in highly contaminated soils. Furthermore, for contaminated soils in which the pH had been altered, the extraction of copper and lead by DTPA was shown (Pot Experiment 2, Section 4.4.2) to frequently increase with increasing pH whereas the concentrations within the plants decreased with increasing pH.

Critical values for the total concentration of the elements in soils in which problems in growing plants may be expected, can be stated only in general terms. If a critical concentration of 200 $\mu g\ g^{-1}$ is used for total copper (Section 4.2.2) and this value is applied to the data presented in Figure 4.1, problems could be expected to occur in susceptible crops on about 10% of orchard soils. If this percentage applies to the total area involved, at least 3 000 ha of former orchard soils may be affected. This area could become much larger because copper sprays are still being used in orchards and are widely used on other fruit crops such as stone fruit and citrus.

It would appear from the literature and from the concentrations found in the soils and plants in this study (Sections 2.5.2 and 4.2.2), that accumulations of lead in Australian orchard soils are unlikely to cause toxicity problems in plants, even if lead arsenate again finds favour as a pesticide.

Arsenic is in a similar situation to lead in that its future use in pesticides appears to be limited. From literature reports (Sections 2.5.3 and 4.2.2) arsenic toxicity may occur in susceptible plants when the total soil concentration exceeds 50 $\mu g\ g^{-1}$ in sandy soils and 100 $\mu g\ g^{-1}$ in fine textured soils. None of the sandy soils from Tasmania contained more than 50 $\mu g\ g^{-1}$ because of losses from the soil profiles, and only one of the finer textured soils had an arsenic concentration exceeding 100 $\mu g\ g^{-1}$. This suggests that few problems in plants due to arsenic may be expected on Australian orchard soils. However, as will be discussed later, the situation with vegetables in relation to human health may give some cause for concern.

The findings of this study (Section 4.2.4) support those reported elsewhere (e.g. Tyler, 1978) that both copper and lead are relatively immobile in soils and accumulations of these elements are likely to remain at or near the surface of the soils for considerable periods. On the other hand, this study clearly shows that arsenic can be readily leached from the surface horizons of sandy soils and either retained on adsorbing surfaces deeper in the profile or be removed completely. The formation of volatile organic compounds in some South Australia soil profiles is a possible mechanism of loss from these soils. The loss of arsenic by leaching and/or volatilization from orchard soils may effectively disperse the element in the soil environment and prevent its accumulation in concentrations which are toxic to plants. Arsenic which has been leached from the coarse textured soils in Tasmania may contribute to the contamination of streams and related parts of the environment thereby affecting aquatic flora and fauna. Such a possibility should be investigated.

The greater proportion of former orchard soils in Australia now supports pastures. Many existing orchards with high concentrations of copper, lead and arsenic in the soil supported good stands of grasses, frequently with legumes, as ground cover. No visible symptoms of toxic effects were encountered in plants in any of the pastures which were sampled. Nevertheless the accumulations in the soils could cause decreased yields of pastures or other crops compared to uncontaminated soils. No evidence was sought for this possibility in the present study. If yields are shown to be less on former orchard soils, lead would be an unlikely culprit. Problems of animal health may arise from pastures growing on orchard soils. Acute poisoning of stock is not an uncommon occurrence (e.g. Selby *et al.*, 1977) and is frequently accidental in nature. For example, several sheep died when allowed to graze an area where trees were only recently removed and which had been used to clean out spray equipment over a period of many years (D. James, Balhannah, South Australia, 1980, personal communication).

The main danger to animals on former orchard soils may result from the increased copper concentrations in pasture plants which frequently contain 30 to 40 $\mu g\ g^{-1}$ of copper (Section 4.3.1) and thus two to three times the concentration usually found in plants grown on uncontaminated soils. Sheep appear to be particularly susceptible to excess copper. Bull (1951) reported that chronic copper poisoning (causing jaundice and haemoglobinuria) can result when sheep graze mixed pastures on soils with high copper concentrations and can also occur on pastures dominated by subterranean clover with 'normal' concentrations of copper but with low molybdenum. In both of these situations, the problem results from a high intake of copper by the animal relative to molybdenum and sulphur. It is not known whether the accumulation of arsenic in orchard soils has an effect on molybdenum uptake by the pasture plants, but a decrease in the molybdenum concentrations in the presence of high concentrations of copper would enhance the problems associated with high copper intake by sheep. Furthermore, high application rates of sulphate in the fertilizers applied to orchards may decrease the molybdenum uptake if the sulphate is retained by the soil (Reddy, 1976). Cattle are much less sensitive than sheep to copper toxicity. Chronic toxicity was not observed in calves until their diets contained in excess of 500 $\mu g\ g^{-1}$ of copper, which is about ten times the amount required to affect sheep (Todd and Thompson, 1965). Other animals including horses and pigs, and humans in most cases, are able to tolerate relatively high concentrations (300 to 600 µg $g^{-1}$) in the diet (Hill, 1977).

Deaths due to lead toxicity of animals grazing former orchard soils are unlikely. Where grazing of lead-contaminated pastures has caused the death of animals, atmospheric inputs from sprays, smelters (Hammond and Aronson, 1964; Rains, 1971) or motor vehicle exhaust emissions (Graham and Kalman, 1974) resulting in the deposition of lead directly onto leaves have been implicated. Translocation of lead to plant tops is restricted and the lead concentration of pasture plants grown on former orchard soils were shown in the present study to be not substantially greater than would be expected from plants grown on un-contaminated soils (*viz.* usually less than 5 µg $g^{-1}$), even when the concentration of lead in the soils was high. The concentration of lead in the plants growing on soils which were formerly orchards rarely exceeded 10 µg $g^{-1}$. The lead concentrations in fodder which may result in toxicity to horses and cattle have been estimated to be about 80 and 2-300 µg $g^{-1}$ respectively (Hammond and Aronson, 1964).

Feeding trials with rats and dogs over a period of two years showed that there were no toxic effects until the concentration of arsenic (as arsenate) in the diet exceeded about 125 µg $g^{-1}$ (Byron *et al.*, 1967). The increase in arsenic concentration observed in the pasture plants grown on former orchard soils towards the end of the growing season (Section 4.3.1) may result in dry, standing fodder or hay which has a higher than normal arsenic content. By themselves, these increases are inconsequential to animal health (Fowler, 1977) but contributions from other sources, such as ingested soil, could complicate this assessment.

It has been estimated that sheep can consume up to 100 g or more and cattle up to 1000 to 2000 g of soil material each day though the actual amount depends on fodder availability, soil type and stocking rate (Healy, 1973). This soil may provide an additional source of copper, lead and arsenic of some significance during prolonged dry periods which are more characteristic of the climate of the orchard-growing areas of South Australia than of Tasmania. If contamination of herbage by soils is about 20% on a dry weight basis (it is usually less, but can be up to about 35%; Healy, 1973), the contribution of the elements in soil to the diet of grazing animals may be substantial. In pasture plants growing on land formerly in orchard, the concentration of lead and arsenic are usually low and effectively dilute the concentration from soil contamination. However, contamination of fodder by soil may be sufficient to present a risk to horses which have a lower level of tolerance to lead (Graham and Kalman, 1974). The additional amounts of copper from soil may be sufficient to exacerbate the effects of the already high concentrations of copper in the pasture plants when copper concentrations in the soil and levels of contamination of herbage are high. These conclusions assume that the availability to animals of the elements in the soil is equivalent to that of the inorganic salts which were used in the feeding trials mentioned above where critical concentrations for copper and arsenic were established. In fact this is unlikely to be true (Healy *et al.*, 1970; Healy, 1972) though it appears that high concentrations of none of the three elements have been tested in feeding trials using contaminated soil as the source.

The acceptable limits set by government health authorities for copper, lead and arsenic in vegetables for human consumption are 30, 4 and 1.1 $\mu g\ g^{-1}$ respectively on a fresh weight basis (South Australia, 1964). These health limits are conventionally presented on a fresh weight basis but in Table 5.1 have been converted to the equivalent concentration in dried material. The conversion is based on radish roots and silver beet tops having, respectively 10% and 18% dry weight.

Table 5.1 The Health Limits for Copper, Lead and Arsenic in Radish and Silver Beet on a Dry Basis ($\mu g\ g^{-1}$)

| Element | Cu | Pb | As |
|---|---|---|---|
| Radish roots (10% d.w.) | 300 | 40 | 11.4 |
| Silver beet tops (18% d.w.) | 170 | 22 | 6.3 |

In the pot experiments, the acceptable concentrations of lead and arsenic, but not of copper, were exceeded on several occasions. The highest copper concentrations (about 135 $\mu g\ g^{-1}$) recorded was in silver beet grown at a soil temperature of 22°C on the orchard soil E505 in Pot Experiment 1 (Section 4.4.1) and acidity (Section 4.4.2) increased the copper concentration in plants which may then exceed the health limit, however it is possible that toxicity to the plant will be evident before the limit is reached. Few of the radish roots grown in these experiments exceeded 30 $\mu g\ g^{-1}$ of copper, one tenth of the health limit.

The acceptable concentration of lead in vegetables was exceeded in both radish and silver beet grown on soil EH 24. However this soil was affected by lead mineralization, and should be considered unusual. In the orchard soils, the health limit for lead was exceeded only in silver beet grown on the acidified E 460 (Pot Experiment 2), but in this situation toxicity symptoms (almost certainly due to excess manganese) were evident.

The edible parts of silver beet and radish had arsenic concentrations which exceeded the health limit when grown on the two dosed soils, EH 1 and EH 23, and on the mine affected soil, EH 13 (Pot Experiment 2). None of the vegetables grown on any of the orchard soils exceeded the health limit for arsenic. However, many of the plants had concentrations approaching the limit and it was this element which had the least margin for safety. Vegetables grown in the field would probably have lower plant concentrations if the roots are not confined to surface soils as they are in pots, and if conditions of temperature, light and water relations during growth do not favour increased uptake. The root systems of vegetable such as radish are confined to the top 10 to 15 cm of soil and are thus exposed to the highest concentration of the elements throughout the growth period.

The pot experiments have shown that management practices which lead to short term acidification of former orchard soils may result in increased concentrations of copper and lead in plants, but only at low values of soil pH (less than about 5) do toxic effects appear. In orchard soils studied these toxic effects are probably not related to increases in the copper, lead or arsenic concentrations in the plants but more likely to the effects of excesses of manganese or aluminium. Acidic fertilizers and the use of lime sulphur as a fungicide may contribute to soil acidity. Lime sulphur can produce elemental sulphur on exposure to the atmosphere (Martin, 1969). The pot experiments carried out in this study have clearly shown that liming the soil and to a marginal extent applications of fertilizers containing sulphate and phosphate may decrease plant concentrations of the elements. The arsenic concentration of silver beet was found to decrease substantially as a result of the application of nitrogen but this effect should be tested on a wider range of soils and plants.

In some cases high concentrations of arsenic in vegetables may give cause for concern. In practice, vegetables are likely to be mixed with produce grown in non-contaminated areas. Consequently, it is people who produce their own vegetables on former orchard soils with high accumulations of copper, lead and arsenic who face the most risk, however slight.

In the future, it is probable that lead and arsenic may present a decreased risk because commercial usage of lead arsenate has largely ceased. However the use of copper-containing sprays will continue and some monitoring of concentrations may be required. Identifying the soils which have been seriously affected will be the greater part of the problem because chronic toxicity is difficult to establish. In practice it is likely that it will only be after a catastrophic event, such as the death of animals, that the relevant chemical analyses of soils and plants will be performed. However this work shows that soil and plant analysis for copper, lead and arsenic as well as soil pH may give adequate indication of likely hazards to animal health and contamination of food products.

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# APPENDICES

## Appendix 1. Basal Nutrient Applied to Each Pot in Experiments 1 and 2

Only the major nutrients nitrogen, phosphorus, potassium and sulphur were supplied in the basal fertilizer. Soil EH 23 in particular would be considered to have a low P content (as determined by extraction with 0.5 M $NaHCO_3$) for the production of vegetables. Five of the soils (EH 12, EH 21, EH 23, EH 24 and E 460) had a deficient to marginal potassium status based on contents of exchangeable potassium. Zinc extracted by EDTA (Clayton and Tiller, 1979) was adequate in all soils and no history of manganese deficiency was known for any. Soils EH 23 and EH 24 had received copper-fortified superphosphate as part of their normal agricultural management. Pastures at the site from which EH 23 was collected have a history of copper insufficiency for grazing cattle.

Nutrients were applied in pot experiments 1 and 2 as an initial application of 7.5 ml prior to planting. The solution was allowed to dry on the dry soil surface, then thoroughly mixed throughout the soil in a rotating paint mixer. The second application of nutrients (10 ml) was made partway through each experiment. This was also as a solution and was watered into the pot as part of the normal watering procedure.

The nutrients supplied (mg per pot) and their chemical form are shown below.

### Initial Application

| | | | |
|---|---|---|---|
| N | 16.8 mg | as | $NH_4H_2PO_4$ |
| P | 37.2 mg | as | $NH_4H_2PO_4$ |
| K | 73.4 mg | as | $K_2SO_4$ |
| S | 30.0 mg | as | $K_2SO_4$ |

Second Application

| | | | |
|---|---|---|---|
| N | 34 mg | as | $NH_4NO_3$, $NH_4H_2PO_4$ |
| P | 20 mg | as | $NH_4H_2PO_4$ |
| K | 98 mg | as | $K_2SO_4$ |
| S | 40 mg | as | $K_2SO_4$ |

Applications of 2.14 mg to the soil surface area of a pot were equivalent to 1 kg $ha^{-1}$.

## Appendix 2 A Comparison of the Amounts of Copper and Lead Extracted From Orchard Soils Using Three Extractants - Aqua Regia, EDTA and DTPA.

### Table 1. Copper and Lead Extracted With Aqua Regia (Total) and with EDTA from South Australian and Tasmanian Orchard Soils

These data ($\mu g\ g^{-1}$) are the basis of regressions presented in Table 4.3

| South Australia | Total | | EDTA | | Tasmania | Total | | EDTA | |
|---|---|---|---|---|---|---|---|---|---|
| Soil No. | Cu | Pb | Cu | Pb | Soil No. | Cu | Pb | Cu | Pb |
| EH 7 | 35 | 25 | 27 | 10 | EH 25 | 56 | 70 | 40 | 53 |
| 8 | 6 | 22 | 3 | 13 | 26 | 46 | 53 | 34 | 43 |
| 9 | 96 | 91 | 35 | 57 | 27 | 103 | 300 | 74 | 238 |
| 10 | 235 | 375 | 109 | 327 | 28 | 53 | 96 | 48 | 105 |
| 11 | 141 | 91 | 54 | 71 | 29 | 23 | 11 | 20 | 9 |
| 12 | 43 | 180 | 22 | 43 | 30 | 56 | 110 | 51 | 109 |
| 19 | 20 | 79 | 6 | 56 | 31 | 105 | 197 | 100 | 179 |
| 20 | 25 | 47 | 16 | 40 | 32 | 48 | 126 | 41 | 115 |
| 21 | 300 | 340 | 273 | 305 | 33 | 152 | 266 | 135 | 218 |
| 81 | 167 | 210 | 159 | 192 | 34 | 77 | 97 | 65 | 36 |
| 90 | 45 | 46 | 37 | 35 | 35 | 125 | 207 | 103 | 161 |
| 95 | 230 | 127 | 210 | 122 | 36 | 43 | 152 | 42 | 149 |
| E 60 | 60 | 174 | 60 | 165 | 37 | - | 11 | - | 8 |
| 67 | 40 | 23 | 21 | 24 | 38 | 6 | - | 6 | - |
| 73 | 130 | 147 | 117 | 136 | 39 | 31 | 127 | 17 | 58 |
| 92 | 39 | 115 | 33 | 108 | 40 | 86 | 280 | 53 | 239 |
| 115 | 31 | 161 | 24 | 152 | 41 | 9 | 14 | 10 | 7 |
| 118 | 174 | 152 | 124 | 122 | 43 | 66 | 106 | 49 | 74 |
| 458 | 28 | 86 | 26 | 68 | 44 | 39 | 92 | 31 | 70 |
| 459 | 282 | 430 | 251 | 386 | 45 | 61 | 161 | 44 | 133 |
| 460 | 154 | 420 | 134 | 362 | | | | | |
| 461 | 79 | 178 | 53 | 146 | | | | | |
| 462 | 48 | 167 | 30 | 114 | | | | | |
| 505 | 265 | 490 | 210 | 357 | | | | | |
| 510 | 110 | 145 | 74 | 133 | | | | | |

Appendix 2 (cont'd)

Table 2. Copper and Lead Extracted with Aqua Regia (Total) and with DTPA from South Australian and Tasmanian Orchard Soils

These data (μg $g^{-1}$) are the basis of regressions presented in Table 4.3

| South Australia | Total | | DTPA | | Tasmania | Total | | DTPA | |
|---|---|---|---|---|---|---|---|---|---|
| Soil No. | Cu | Pb | Cu | Pb | Soil No. | Cu | Pb | Cu | Pb |
| EH 7 | 35 | 25 | 9 | 4 | EH 25 | 56 | 70 | 12 | 13 |
| 9 | 96 | 91 | 22 | 19 | 26 | 46 | 53 | 10 | 15 |
| 10 | 235 | 375 | 85 | 103 | 27 | 103 | 300 | 25 | 65 |
| 11 | 141 | 91 | 36 | 25 | 29 | 23 | 11 | 7 | 3 |
| 12 | 43 | 180 | 7 | 52 | 31 | 105 | 197 | 27 | 46 |
| 19 | 20 | 79 | 1 | 17 | 33 | 152 | 266 | 39 | 56 |
| 20 | 25 | 47 | 5 | 9 | 34 | 77 | 97 | 18 | 15 |
| 21 | 300 | 340 | 113 | 75 | 35 | 125 | 207 | 30 | 33 |
| 81 | 167 | 210 | 52 | 52 | 39 | 31 | 127 | 3 | 13 |
| 90 | 45 | 46 | 12 | 12 | 43 | 66 | 106 | 14 | 23 |
| 95 | 230 | 127 | 78 | 15 | 44 | 39 | 92 | 10 | 18 |
| 134 | 255 | 180 | 108 | 73 | 45 | 61 | 161 | 12 | 33 |
| 135 | 205 | 235 | 66 | 49 | 114 | 29 | 26 | 4 | 3 |
| 136 | 132 | 112 | 47 | 36 | 115 | 53 | 16 | 7 | 1 |
| 138 | 51 | 140 | 16 | 39 | 116 | 122 | 172 | 39 | 42 |
| 139 | 110 | 74 | 29 | 19 | 119 | 138 | 124 | 36 | 27 |
| 141 | 74 | 365 | 19 | 131 | 120 | 319 | 382 | 96 | 58 |
| 144 | 65 | 295 | 22 | 120 | 121 | 228 | 202 | 47 | 42 |
| 146 | 165 | 205 | 50 | 65 | 127 | 147 | 276 | 55 | 276 |
| E 60 | 60 | 174 | 12 | 66 | HV 1 | 202 | 350 | 69 | 181 |
| 73 | 130 | 147 | 44 | 38 | 4 | 304 | 550 | 144 | 440 |
| 118 | 174 | 152 | 52 | 33 | 13 | 162 | 220 | 50 | 66 |
| 460 | 154 | 420 | 21 | 65 | 20 | 172 | 250 | 43 | 50 |
| 505 | 265 | 490 | 60 | 99 | 25 | 156 | 425 | 55 | 209 |
| 510 | 110 | 145 | 36 | 38 | | | | | |
| Orchard Std. 1 | 155 | 455 | 50 | 136 | | | | | |
| 2 | 297 | 340 | 86 | 73 | | | | | |

## Appendix 3. Yields, and Copper, Lead and Arsenic Concentrations of Radish and Silver Beet Plants Grown in Pot Experiment 2.

Treatments are indicated by the column headings in the tables and correspond to the treatments presented in Tables 3.8 and 4.9. The amounts of elemental sulphur, calcium carbonate and gypsum applied varied from soil to soil. Only soil EH 1, a naturally calcareous soil, was treated with two rates of elemental sulphur (indicated by $S_2$ and $S_1$). This soil did not receive the calcium carbonate treatment.

Columns in the tables have been arranged so that soil pH, measured at harvest increases from left to right, apart from the prior waterlogging treatment. In this order they also correspond to the pH data presented in Table 4.9.

A dash (-) indicates that the plants did not survive until harvest. This occurred on soils EH 23, where only the plants growing in the calcium carbonate treated pots survived, and soil EH 24, where no plants survived the sulphur treatment.

The mean values for three replicate pots are presented in the tables with the corresponding $\log_{10}$ transformed value in italics. Statistical analyses were performed on $\log_{10}$ transformed data. Consequently the least significant differences (LSD, $P < 0.05$) refer to the transformed data. Data for soil EH 23 have been excluded from the statistical analysis. A separate analysis taking into account the missing data for soil EH 24 showed that LSD values were almost identical to the ones presented and do not substantially affect the interpretation of the results.

Appendix 3 (Cont'd) Yield (g per pot, dry weight) of Radish

| Treatment: | Tops | | | | | Roots | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | $S_2$ | $S_1$ | Control | $CaCO_3$ | W'Log | $S_2$ | $S_1$ | Control | $CaCO_3$ | W'Log |
| Soil: EH 12 | | 5.3 | 7.2 | 8.6 | 7.3 | | 6.0 | 9.5 | 11.0 | 12.4 |
| | | *0.72* | *0.86* | *0.94* | *0.86* | | *0.78* | *0.98* | *1.04* | *1.09* |
| E 460 | | 4.9 | 5.8 | 5.6 | 6.3 | | 4.7 | 7.7 | 8.8 | 11.4 |
| | | *0.69* | *0.76* | *0.75* | *0.82* | | *0.68* | *0.89* | *0.90* | *1.06* |
| EH 21 | | 4.1 | 4.9 | 6.4 | 4.0 | | 5.9 | 4.2 | 7.7 | 6.3 |
| | | *0.61* | *0.69* | *0.81* | *0.60* | | *0.77* | *0.63* | *0.89* | *0.80* |
| E 505 | | 4.3 | 4.9 | 4.9 | 5.8 | | 7.4 | 4.9 | 8.8 | 8.7 |
| | | *0.64* | *0.69* | *0.69* | *0.76* | | *0.87* | *0.69* | *0.94* | *0.94* |
| EH 1 | 1.9 | 3.1 | 3.3 | | 3.9 | 2.0 | 3.2 | 4.8 | | 3.8 |
| | *0.28* | *0.49* | *0.51* | | *0.59* | *0.29* | *0.51* | *0.69* | | *0.58* |
| EH 23 | | - | - | 2.2 | - | | - | - | 1.5 | - |
| | | - | - | *0.35* | - | | - | - | *0.18* | - |
| EH 13 | | 3.4 | 3.2 | 4.0 | 3.3 | | 3.8 | 4.2 | 4.2 | 2.9 |
| | | *0.54* | *0.51* | *0.60* | *0.52* | | *0.57* | *0.63* | *0.62* | *0.47* |
| EH 24 | | - | 3.0 | 3.9 | 3.1 | | - | 3.5 | 4.3 | 4.8 |
| | | - | *0.48* | *0.60* | *0.50* | | - | *0.55* | *0.63* | *0.68* |

$LSD_{0.05}$ = *0.11*

$LSD_{0.05}$ = *0.16*

## Appendix 3 (cont'd) Copper Concentration (µg $g^{-1}$) in Radish

| | | | Tops | | | | | Roots | | |
|---|---|---|---|---|---|---|---|---|---|---|
| Treatment: | $S_2$ | $S_1$ | Control | $CaCO_3$ | W'Log | $S_2$ | $S_1$ | Control | $CaCO_3$ | W'Log |
| Soil: EH 12 | | 14.3 | 5.1 | 4.9 | 6.0 | | 11 | 5.9 | 5.0 | 6.2 |
| | | *1.16* | *0.70* | *0.69* | *0.78* | | *1.03* | *0.77* | *0.70* | *0.79* |
| E 460 | | 52 | 19 | 17 | 33 | | 24 | 15 | 13 | 19 |
| | | *1.72* | *1.28* | *1.22* | *1.52* | | *1.37* | *1.18* | *1.12* | *1.27* |
| EH 21 | | 54 | 25 | 21 | 35 | | 30 | 19 | 16 | 22 |
| | | *1.73* | *1.39* | *1.33* | *1.55* | | *1.47* | *1.27* | *1.21* | *1.33* |
| E 505 | | 62 | 20 | 12 | 22 | | 27 | 20 | 12 | 16 |
| | | *1.79* | *1.30* | *1.09* | *1.34* | | *1.43* | *1.29* | *1.09* | *1.21* |
| EH 1 | 58 | 35 | 29 | | 34 | 26 | 19 | 18 | | 20 |
| | *1.77* | *1.54* | *1.47* | | *1.53* | *1.41* | *1.28* | *1.26* | | *1.30* |
| EH 23 | | - | - | 75 | - | | - | - | 41 | - |
| | | - | - | *1.87* | - | | - | - | *1.61* | - |
| EH 13 | | 37 | 26 | 20 | 25 | | 21 | 13 | 13 | 15 |
| | | *1.57* | *1.41* | *1.30* | *1.40* | | *1.33* | *1.12* | *1.11* | *1.19* |
| EH 24 | | - | 5.1 | 5.6 | 5.4 | | - | 4.9 | 7.2 | 4.8 |
| | | - | *0.71* | *0.75* | *0.73* | | - | *0.69* | *0.86* | *0.68* |

Tops: $LSD_{0.05}$ = *0.12*

Roots: $LSD_{0.05}$ = *0.10*

## Appendix 3 (cont'd) Lead Concentration ($\mu g\ g^{-1}$) in Radish

| | Tops | | | | | Roots | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| Treatment: | $S_2$ | $S_1$ | Control | $CaCO_3$ | W'Log | $S_2$ | $S_1$ | Control | $CaCO_3$ | W'Log |
| Soil: EH 12 | | 0.95 | 1.05 | 0.64 | 0.77 | | 7.1 | 2.2 | 0.59 | 2.1 |
| | | *-0.02* | *0.02* | *-0.20* | *-0.12* | | *0.85* | *0.35* | *-0.23* | *0.33* |
| E 460 | | 14 | 4.4 | 3.3 | 4.8 | | 52 | 27 | 16 | 25 |
| | | *1.15* | *0.64* | *0.51* | *0.68* | | *1.71* | *1.42* | *1.20* | *1.40* |
| EH 21 | | 3.1 | 3.1 | 1.4 | 4.3 | | 20 | 12 | 3.4 | 13 |
| | | *0.49* | *0.49* | *0.14* | *0.63* | | *1.30* | *1.09* | *0.53* | *1.11* |
| E 505 | | 4.8 | 2.3 | 1.0 | 3.0 | | 29 | 9.5 | 2.2 | 9.0 |
| | | *0.68* | *0.36* | *0.01* | *0.48* | | *1.47* | *0.98* | *0.35* | *0.96* |
| EH 1 | 4.0 | 1.8 | 1.3 | | 1.0 | 28 | 4.7 | 4.2 | | 4.4 |
| | *0.60* | *0.26* | *0.11* | | *0.02* | *1.44* | *0.68* | *0.63* | | *0.64* |
| EH 23 | | - | - | 3.8 | - | | - | - | 15 | - |
| | | - | - | *0.58* | - | | - | - | *1.18* | - |
| EH 13 | | 0.44 | 0.80 | 0.56 | 1.41 | | 0.54 | 0.28 | 0.32 | 0.20 |
| | | *-0.35* | *-0.10* | *-0.25* | *-0.15* | | *-0.27* | *-0.55* | *-0.50* | *-0.70* |
| EH 24 | | - | 14 | 5.2 | 22 | | - | 56 | 27 | 76 |
| | | - | *1.15* | *0.72* | *1.35* | | - | *1.75* | *1.42* | *1.88* |

$LSD_{0.05}$ = *0.22*

$LSD_{0.05}$ = *0.18*

Appendix 3 (cont'd) Arsenic Concentration ($\mu g\ g^{-1}$) in Radish

| | Tops | | | | | Roots | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| Treatment: | $S_2$ | $S_1$ | Control | $CaCO_3$ | W'Log | $S_2$ | $S_1$ | Control | $CaCO_3$ | W'Log |
| Soil: EH 12 | | 0.62 | 0.81 | 1.16 | 0.86 | | 2.0 | 1.2 | 1.1 | 1.2 |
| | | *-0.21* | *-0.09* | *0.07* | *-0.07* | | *0.30* | *0.07* | *0.06* | *0.09* |
| E 460 | | 2.6 | 2.8 | 3.1 | 14 | | 3.9 | 4.2 | 5.4 | 7.9 |
| | | *0.41* | *0.45* | *0.49* | *1.14* | | *0.59* | *0.63* | *0.74* | *0.90* |
| EH 21 | | 3.8 | 5.6 | 3.2 | 5.6 | | 10 | 6.5 | 3.7 | 7.8 |
| | | *0.58* | *0.75* | *0.51* | *0.75* | | *1.00* | *0.81* | *0.57* | *0.89* |
| E 505 | | 2.8 | 4.0 | 4.1 | 4.1 | | 3.4 | 2.8 | 2.5 | 2.8 |
| | | *0.45* | *0.60* | *0.61* | *0.61* | | *0.53* | *0.45* | *0.39* | *0.44* |
| EH 1 | 34 | 13 | 37 | | 32 | 77 | 50 | 95 | | 55 |
| | *1.54* | *1.13* | *1.56* | | *1.51* | *1.89* | *1.70* | *1.98* | | *1.74* |
| EH 23 | | - | - | 27 | - | | - | - | 94 | - |
| | | - | - | *1.44* | - | | - | - | *1.97* | - |
| EH 13 | | 13 | 41 | 17 | 34 | | 27 | 28 | 23 | 41 |
| | | *1.10* | *1.61* | *1.22* | *1.53* | | *1.43* | *1.44* | *1.37* | *1.61* |
| EH 24 | | - | 2.3 | 1.8 | 1.5 | | - | 1.5 | 1.3 | 1.3 |
| | | - | *0.36* | *0.25* | *0.18* | | - | *0.17* | *0.13* | *0.12* |

$LSD_{0.05}$ = *0.23* $LSD_{0.05}$ = *0.22*

Appendix 3 (cont'd)

Plant: Silver Beet Tops

| Treatment: | $S_2$ | $S_1$ | Gypsum | Control | $CaCO_3$ | W'Log |
|---|---|---|---|---|---|---|
| | | YIELD (g per pot, dry weight) | | | | |
| Soil: EH 12 | | 7.2 | 12.0 | 10.7 | 11.0 | 9.4 |
| | | *0.86* | *1.08* | *1.03* | *1.04* | *0.97* |
| E 460 | | 8.2 | 10.8 | 7.9 | 9.0 | 8.8 |
| | | *0.91* | *1.03* | *0.90* | *0.95* | *0.94* |
| EH 21 | | 7.6 | 7.4 | 6.3 | 8.2 | 5.7 |
| | | *0.88* | *0.87* | *0.80* | *0.91* | *0.75* |
| E 505 | | 2.2 | 8.8 | 8.5 | 10.4 | 9.8 |
| | | *0.34* | *0.94* | *0.93* | *1.02* | *0.99* |
| EH 1 | 3.4 | 5.1 | 5.5 | 5.6 | | 8.1 |
| | *0.54* | *0.71* | *0.74* | *0.75* | | *0.75* |
| EH 23 | | - | - | - | - | - |
| | | - | - | - | - | - |
| EH 13 | | 3.8 | 5.0 | 3.5 | 5.4 | 3.5 |
| | | *0.56* | *0.70* | *0.55* | *0.73* | *0.54* |
| EH 24 | | - | 4.8 | 4.9 | 5.5 | 3.9 |
| | | - | *0.68* | *0.69* | *0.74* | *0.59* |

$LSD_{0.05}$ = *0.13*

Appendix 3 (cont'd)

COPPER CONCENTRATION ($\mu g\ g^{-1}$)

| | $S_2$ | $S_1$ | Gypsum | Control | $CaCO_3$ | W'Log |
|---|---|---|---|---|---|---|
| EH 12 | | 17 | 17 | 20 | 12 | 21 |
| | | *1.22* | *1.23* | *1.30* | *1.09* | *1.32* |
| E 460 | | 66 | 96 | 90 | 60 | 127 |
| | | *1.82* | *1.98* | *1.95* | *1.78* | *2.10* |
| EH 21 | | 137 | 121 | 110 | 47 | 112 |
| | | *2.14* | *2.08* | *2.04* | *1.67* | *2.05* |
| E 505 | | 54 | 92 | 66 | 43 | 93 |
| | | *1.74* | *1.97* | *1.82* | *1.64* | *1.97* |
| EH 1 | 62 | 43 | 26 | 27 | | 28 |
| | *1.80* | *1.64* | *1.42* | *1.43* | | *1.44* |
| EH 23 | | - | - | - | - | - |
| | | - | - | - | - | - |
| EH 13 | | 130 | 71 | 77 | 36 | 79 |
| | | *2.12* | *1.85* | *1.88* | *1.55* | *1.90* |
| EH 24 | | - | 10 | 6.3 | 10 | 8.2 |
| | | - | *1.01* | *0.80* | *1.02* | *0.91* |

$LSD_{0.05}$ = *0.09*

Appendix 3 (cont'd)

Plant: Silver Beet Tops

| Treatment: | $S_2$ | $S_1$ | Gypsum | Control | $CaCO_3$ | W'Log |
|---|---|---|---|---|---|---|
| | | LEAD CONCENTRATION ($\mu g\ g^{-1}$) | | | | |
| Soil: EH 12 | | 2.3 | 0.78 | 1.5 | 0.44 | 1.3 |
| | | *0.36* | *-0.11* | *0.17* | *-0.35* | *0.10* |
| E 460 | | 29 | 8.3 | 9.5 | 6.6 | 9.0 |
| | | *1.46* | *0.92* | *0.98* | *0.82* | *0.96* |
| EH 21 | | 5.8 | 3.1 | 4.0 | 2.0 | 4.1 |
| | | *0.76* | *0.49* | *0.60* | *0.29* | *0.61* |
| E 505 | | 27 | 3.7 | 3.7 | 2.5 | 4.0 |
| | | *1.43* | *0.57* | *0.57* | *0.39* | *0.60* |
| EH 1 | 9.5 | 2.4 | 1.9 | 2.1 | | 1.4 |
| | *0.98* | *0.28* | *0.38* | *0.32* | | *0.15* |
| EH 23 | | - | - | - | - | - |
| | | - | - | - | - | - |
| EH 13 | | 0.57 | 0.57 | 0.76 | 0.72 | 0.35 |
| | | *-0.24* | *-0.24* | *-0.12* | *-0.15* | *-0.45* |
| EH 24 | | - | 32 | 61 | 21 | 68 |
| | | - | *1.50* | *1.79* | *1.33* | *1.82* |

$LSD_{0.05}$ = *0.21*

Appendix 3 (cont'd)

ARSENIC CONCENTRATION (µg $g^{-1}$)

| Treatment: | $S_2$ | $S_1$ | Gypsum | Control | $CaCO_3$ | W'Log |
|---|---|---|---|---|---|---|
| EH 12 | | 1.2 | 1.4 | 0.96 | 1.1 | 1.0 |
| | | *0.09* | *0.16* | *-0.02* | *0.04* | *0.00* |
| E 460 | | 2.6 | 2.3 | 2.8 | 3.1 | 4.9 |
| | | *0.42* | *0.37* | *0.45* | *0.49* | *0.69* |
| EH 21 | | 3.3 | 1.7 | 3.3 | 1.3 | 3.6 |
| | | *0.52* | *0.23* | *0.52* | *0.11* | *0.56* |
| E 505 | | 3.7 | 1.0 | 1.7 | 1.2 | 1.2 |
| | | *0.57* | *0.01* | *0.24* | *0.08* | *0.08* |
| EH 1 | 17 | 19 | 14 | 16 | | 5.9 |
| | *1.22* | *1.28* | *1.13* | *1.20* | | *0.77* |
| EH 23 | | - | - | - | - | - |
| | | - | - | - | - | - |
| EH 13 | | 32 | 17 | 15 | 9.6 | 30 |
| | | *1.51* | *1.23* | *1.18* | *0.98* | *1.47* |
| EH 24 | | - | 0.68 | 0.62 | 0.71 | 0.50 |
| | | - | *-0.17* | *-0.21* | *-0.15* | *-0.31* |

$LSD_{0.05}$ = *0.25*

## Appendix 4 Manganese Concentration ($\mu g\ g^{-1}$) of Radish and Silver Beet Plants Grown in Pot Experiment 2

(Figures in italics are $\log_{10}$ transformed. Treatments are as indicated in Table 4.9)

| Plant: | | Radish Tops | | | | Radish Roots | | | |
|---|---|---|---|---|---|---|---|---|---|
| Treatment: | | S(2) | Control | $CaCO_3$ (5.0) | W'Log | S(2) | Control | $CaCO_3$ (5.0) | W'Log |
| Soil: EH 12 | Mn | 4100 | 180 | 60 | 200 | 980 | 51 | 15 | 57 |
| | | *3.61* | *2.25* | *1.78* | *2.31* | *2.99* | *1.71* | *1.18* | *1.76* |
| | | S(2) | Control | $CaCO_3$ (2.5) | W'Log | S(2) | Control | $CaCO_3$ (2.5) | W'Log |
| E 460 | Mn | 1000 | 102 | 70 | 94 | 250 | 30 | 15 | 23 |
| | | *2.45* | *1.59* | *1.32* | *1.51* | *2.39* | *1.48* | *1.17* | *1.36* |
| | | S(2) | Control | $CaCO_3$ (3.75) | W'Log | S(2) | Control | $CaCO_3$ (3.75) | W'Log |
| EH 21 | Mn | 280 | 39 | 21 | 32 | 71 | 15 | 7.4 | 14 |
| | | *2.45* | *1.59* | *1.32* | *1.51* | *1.85* | *1.17* | *0.87* | *1.15* |
| | | S(2) | Control | $CaCO_3$ (3.75) | W'Log | S(2) | Control | $CaCO_3$ (3.75) | W'Log |
| E 505 | Mn | 2990 | 130 | 55 | 100 | 600 | 26 | 11 | 26 |
| | | *3.48* | *2.10* | *1.74* | *2.01* | *2.78* | *1.41* | *1.04* | *1.41* |
| | | S(16) | S(8) | Control | W'Log | S(16) | S(8) | Control | W'Log |
| EH 1 | Mn | 260 | 31 | 57 | 28 | 80 | 5.1 | 7.9 | 3.5 |
| | | *2.42* | *1.50* | *1.75* | *1.45* | *1.91* | *0.71* | *0.90* | *0.55* |
| | | S(1) | Control | $CaCO_3$ (2.5) | W'Log | S(1) | Control | $CaCO_3$ (2.5) | W'Log |
| EH 23 | Mn | - | - | 81 | - | - | - | 23 | - |
| | | - | - | *1.91* | - | - | - | *1.36* | - |
| | | S(1) | Control | $CaCO_3$ (2.5) | W'Log | S(1) | Control | $CaCO_3$ (2.5) | W'Log |
| EH 13 | Mn | 320 | 75 | 40 | 72 | 90 | 19 | 12 | 24 |
| | | *2.50* | *1.88* | *1.60* | *1.86* | *1.95* | *1.28* | *1.08* | *1.38* |
| | | S(2) | Control | $CaCO_3$ (3.75) | W'Log | S(2) | Control | $CaCO_3$ (3.75) | W'Log |
| EH 24 | Mn | - | 330 | 110 | 400 | - | 76 | 36 | 77 |
| | | - | *2.52* | *2.04* | *2.60* | - | *1.88* | *1.56* | *1.89* |

$LSD_{0.05}$ ($\log_{10}$ transformed data) = *0.14*　　$LSD_{0.05}$ ($\log_{10}$ transformed data) = *0.14*

## Appendix 4 (cont'd)

Plant: **Silver Beet Tops**

| Treatment: | | S(2) | Gypsum (2) | Control | $CaCO_3$ (5) | W'Log |
|---|---|---|---|---|---|---|
| Soil: EH 12 | Mn | 5350 | 2210 | 1290 | 600 | 1810 |
| | | *3.73* | *3.35* | *3.11* | *2.77* | *3.26* |
| | | S(2) | Gypsum (2) | Control | $CaCO_3$ (2.5) | W'Log |
| Soil: E 460 | Mn | 1530 | 1200 | 880 | 500 | 480 |
| | | *3.19* | *3.08* | *2.95* | *2.69* | *2.68* |
| | | S(2) | Gypsum (2) | Control | $CaCO_3$ (3.75) | W'Log |
| Soil: EH 21 | Mn | 2280 | 410 | 270 | 72 | 210 |
| | | *3.36* | *2.61* | *2.43* | *1.86* | *2.32* |
| | | S(2) | Gypsum (2) | Control | $CaCO_3$ (3.75) | W'Log |
| Soil: E 505 | Mn | 7140 | 1730 | 1050 | 500 | 1150 |
| | | *3.85* | *3.24* | *3.02* | *2.70* | *3.06* |
| | | S(16) | S(8) | Gypsum (16) | Control | W'Log |
| Soil: EH 1 | Mn | 1660 | 205 | 80 | 140 | 120 |
| | | *3.22* | *2.32* | *1.89* | *2.13* | *2.07* |
| | | S(1) | Gypsum (1) | Control | $CaCO_3$ (2.5) | W'Log |
| Soil: EH 23 | Mn | - | - | - | - | - |
| | | - | - | - | - | - |
| | | S(1) | Gypsum (1) | Control | $CaCO_3$ (2.5) | W'Log |
| Soil: EH 13 | Mn | 3160 | 800 | 450 | 210 | 670 |
| | | *3.50* | *2.90* | *2.65* | *2.33* | *2.82* |
| | | S(2) | Gypsum (2) | Control | $CaCO_3$ (3.75) | W'Log |
| Soil: EH 24 | Mn | - | 4130 | 2200 | 960 | 3710 |
| | | - | *3.62* | *3.34* | *2.98* | *3.57* |

$LSD_{0.05}$ ($Log_{10}$ transformed data) = *0.13*

Appendix 5. The Yields (g per pot) and Concentration (μg $g^{-1}$) of Copper, Lead Arsenic and Manganese in the Roots of Silver Beet Plants, Pot Experiment 2. Data are unreplicated. (Treatments are as presented in Table 4.9. n : no data).

| Soil | Treatment | S(2) | Gypsum (2) | Control | $CaCO_3$ (5) | W'Log |
|---|---|---|---|---|---|---|
| EH 12 | Dry wt. | 2.1 | 6.5 | 4.8 | 7.3 | 4.3 |
| | Cu | 41 | 27 | 32 | 29 | 38 |
| | Pb | 49 | 18 | 28 | 12 | 20 |
| | As | 32 | 11 | 19 | 17 | 19 |
| | Mn | 4440 | 2630 | 1570 | 650 | 1610 |
| | | S(2) | Gypsum (2) | Control | $CaCO_3$ (2.5) | W'Log |
| E 460 | Dry wt. | 3.6 | 6.6 | 4.6 | 5.8 | 5.8 |
| | Cu | 140 | 190 | 160 | 150 | 180 |
| | Pb | 220 | 200 | 175 | 185 | 175 |
| | As | 130 | 75 | 85 | 100 | 180 |
| | Mn | 2750 | 360 | 1630 | 520 | 200 |
| | | S(2) | Gypsum (2) | Control | $CaCO_3$ (3.75) | W'Log |
| EH 21 | Dry wt. | 5.0 | 3.7 | 4.6 | 5.1 | 4.1 |
| | Cu | 275 | 255 | 350 | 160 | 320 |
| | Pb | 115 | 70 | 165 | 55 | 130 |
| | As | 220 | 130 | 155 | 85 | 160 |
| | Mn | 4880 | 240 | 220 | 70 | 120 |
| | | S(2) | Gypsum (2) | Control | $CaCO_3$ (3.75) | W'Log |
| E 505 | Dry wt. | 0.9 | 3.6 | 3.1 | 5.5 | 4.0 |
| | Cu | 190 | 215 | 90 | 95 | 170 |
| | Pb | 125 | 87 | 49 | 58 | 63 |
| | As | 125 | 68 | 37 | 61 | 67 |
| | Mn | n. | n. | 1240 | 560 | n. |

Appendix 5 (cont'd)

| Soil | Treatment | S(16) | S(8) | Gypsum (16) | Control | W'Log |
|---|---|---|---|---|---|---|
| EH 1 | Dry wt. | 0.8 | 3.1 | 3.6 | 4.4 | 5.1 |
| | Cu | - | 115 | 70 | 103 | 94 |
| | Pb | - | 54 | 36 | 51 | 43 |
| | As | - | 390 | 360 | 340 | 140 |
| | Mn | - | 79 | 57 | 72 | 86 |
| | | S(1) | Gypsum (1) | Control | $CaCO_3$ (2.5) | W'Log |
| EH 23 | Dry wt. | - | - | - | - | - |
| | Cu | - | - | - | - | - |
| | Pb | - | - | - | - | - |
| | As | - | - | - | - | - |
| | Mn | - | - | - | - | - |
| | | S(1) | Gypsum (1) | Control | $CaCO_3$ (2.5) | W'Log |
| EH 13 | Dry wt. | 2.4 | 3.2 | 2.5 | 3.5 | 2.0 |
| | Cu | 275 | 112 | 175 | 105 | 220 |
| | Pb | 8.4 | 4.3 | 5.8 | 2.9 | 3.9 |
| | As | 920 | 285 | 340 | 170 | 940 |
| | Mn | 475 | 480 | 320 | 255 | 330 |
| | | S(2) | Gypsum (2) | Control | $CaCO_3$ (3.75) | W'Log |
| EH 24 | Dry wt. | - | 3.0 | 2.4 | 4.1 | 1.7 |
| | Cu | - | 24 | 12 | 18 | 20 |
| | Pb | - | 255 | 235 | 285 | 300 |
| | As | - | 66 | 45 | 69 | 44 |
| | Mn | - | 3750 | 1070 | 760 | 2100 |

Merry, R. H., & Zarcinas, B. A. (1980). Spectrophotometric determination of arsenic and antimony by the silver diethyldithiocarbamate method. *Analyst*, *105*(1251), 558-563.