A Study Of Novel Methods For The *In Situ* Remediation Of Arsenic Contaminated Soils.

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ABSTRACT

The aim of the work described in this thesis was to evaluate the effectiveness of a number of iron-bearing additives in order to attenuate the toxic trace element arsenic in contaminated soil. These were selected for their known or potential ability to adsorb arsenic anions, thus changing the speciation of As in a soil system. Three arsenic contaminated soils were chosen: canal dregings, coal fly ash deposits, and low-level alkali waste. The selected amendments were goethite (αFeOOH), iron grit, iron II and III sulphates (plus lime), and lime. A series of investigations were conducted to evaluate the potential of these amendments.

Initial investigations focused on *in vitro* studies, to determine if changes in pH and/or arsenic concentration affected the adsorption capabilities of the additives. The resulting isotherms demonstrated that all iron oxides adsorbed arsenic effectively at pH 5 but, with the exception of iron III sulphate (plus lime), As adsorption decreased under alkaline conditions (pH9).

Changes in the speciation of arsenic in iron oxide-treated soils were evaluated using a sequential extraction procedure. Test soils were initially incubated with each amendment, and then extracted using a sequence of reagents with increasing chemical action. These displaced As from different soil fractions. Results demonstrated that As was mostly released in stage three of the extraction procedure, which removed metals bound to iron and manganese fractions. Reduced As liberation was also evident in the magnesium chloride fraction (stage 1), which released metals from the exchangeable pool. This is important because this compartment contains plant available As. A range of leaching studies were then conducted to evaluate the mobility of arsenic in the amended contaminated soils. Tests demonstrated both the short and long-term efficiency of the iron oxides, which significantly reduced concentrations of arsenic in the leachates from all treated soils. Amended soils were also observed to contain higher levels of lead in their leachates, signifying that Fe-oxides potentially increased Pb mobility in treated soils.

Changes in plant-available As were monitored with greenhouse trials. These used spinach (*Spinacia oleracea*) and tomato (*Lycopersicon esculentum*) for short-term tests and ryegrass (*Lolium perenne*) for a longer-term evaluation in amended As contaminated soils. Concentrations of As in plant tissues were reduced in treated soils, and visual appearance of plants was improved when compared to those grown in untreated

substrates, indicating that the bioavailability of arsenic had been reduced. The overall conclusions were that whilst Fe-oxides may be used as effective *in situ* amendments to reduce labile As in soils, their effects on other elements, such as Pb, should not be ignored.

CHAPTER 1.

INTRODUCTION

1.1. Arsenic contaminated land

Arsenic (As) is the fifty-second most abundant element in the Earth's crust (Adriano, 1986) and belongs to subgroup V in the elemental table, having an atomic number of 33 and an atomic weight of 74.922. Arsenic has an outer electronic configuration of $4s^2\ 4p^3$. In its elemental state arsenic is a crystalline metalloid that may exist in its yellow, black, or grey (the most stable) allotropic forms (Peters *et al.*, 1996). It occurs naturally in mineral ores, with approximately 60% being arsenates, 20% sulphides and sulphosalts and the final 20% being arsenides, arsenites, oxides and elemental arsenic (Onishi, 1968). Arsenopyrite, (FeAsS) is the most common arsenic mineral, but arsenic is also a dominant constituent of 245 other species of mineral (National Academy of Sciences, 1977a).

Increased levels of arsenic have been associated with the presence of sulphide minerals such as pyrites and in this form it is very stable and insoluble. After exposure to air the pyrites oxidise, yielding water-soluble arsenic salts (Woolson, 1983a). As well as occurring naturally in mineral ores, arsenic is present in igneous rocks and sedimentary deposits. However, concentrations are higher in sedimentary rocks compared to igneous strata (Bhumbla and Keefer, 1994).

In a soil system, the main source of arsenic is the parent material from which it has been derived (Yan-Chu, 1994). There are numerous ways in which arsenic can exist in the soil environment, either as a mineral deposit, complexed with organic material or bound as an inorganic oxyanion to cations in the soil (Peters *et al.*, 1996). Due to its readiness to bind with sulphur ligands, arsenic is found associated with mineral deposits producing sulphides. These sulphide ore deposits may have arsenic concentrations of as much as 8000 mg/kg (National Academy of Sciences, 1977a). Therefore soils in mineralised areas will have increased concentrations of arsenic present within them and typical levels may vary between 0.1 to 40 mg/kg (Colbourn *et al.*, 1975), however an average of 5 to 6 mg/kg is more typical.

Atmospheric deposition is the greatest contributor of arsenic to the geochemical cycle (O'Neill, 1990). For atmospheric cycling 60% has been estimated to result from low-temperature volatilisation, followed by activity from volcanic regions (Chilvers and Peterson, 1987). As an outcome of volcanic activity, airborne particulate matter may contain volatile arsenic species (Woolson, 1983b) and therefore on a localised scale, such activity may be a dominant source of deposition (O'Neill, 1990). Natural reduction processes such as weathering and biological reduction of arsenic species by microorganisms usually occur in soil environments. Such reductions can create levels as high as 0.01 $\mu g/m^3$ (Onishi, 1968).

As a result of the industrial revolution in the United Kingdom, land contaminated with arsenic is ubiquitous. Due to industrialisation, soil, sediment and water sources have become contaminated with toxic metals and metalloids (Vangronsveld & Cunningham, 1998). Arsenic sources may be derived from aerial deposition from coal burning power plants and metal mining / refining and smelting. Arsenic is also present in ashes / clinter from coal combustion and fly ash. Therefore the soil is an important sink for arsenic compounds (Smith *et al.*, 1998).

Levels of arsenic present in the soil compartment depend not only on the geological composition of the area but also from the contributions of industry and agriculture. The mining and smelting of metals is the greatest contributor of arsenic input into the environment from anthropogenic sources. Smelting of copper (Cu) is the largest single anthropogenic input (approx. 40% of the total). Lead (Pb) and gold (Au) ores also contain arsenic and the smelting of these will produce by-products as either a solid waste or a gaseous emission. Emissions tend to be localised around the area adjacent to the smelter. For example in Tacoma, USA, airborne levels of arsenic adjacent to a smelter were found to be around 2.5 $\mu g/m^3$. However 8 miles away levels had decreased to 0.02 $\mu g/m^3$ (Nelson, 1977). Emissions can also vary depending on the degree of industrialisation of the country and the pollution control levels employed. In Virginia, USA an estimated 40, 000 mg/kg^{-1} arsenic has been reported close to old spoil-tip and tailings-dam materials, whilst in South West England over 20, 000 mg/kg^{-1} As have been reported (Peterson *et al.*, 1979).

The mining of ores, although not a great contributor to the total arsenic input into the environment, can have an important part to play on a local scale. Weathering of the

waste will result in leaching of arsenic into the groundwater and soils, and if the waste is to be moved to another region this spreads the contamination elsewhere (Grantham and Jones, 1977). Abandoned mines and industrial wastes linked to non-ferrous metal ore extraction are commonplace in the United Kingdom with mine spoil heaps being typical features in areas such as Central/North Wales and South West England (Lewis, 1967). Many spoil heaps are unstable and flooding has caused the redistribution of spoil onto agricultural land adjacent to derelict mine sites (Davies and Alloway, 1970). Levels of arsenic were found to be elevated above background measurements (7.69-8.97 mg As Kg^{-1}) in three ore smelting areas in England – Derbyshire, Cornwall and Somerset, that were studied by Li and Thornton (1993). They reported ranges of arsenic between 16 and 925 mg Kg^{-1}. Although most mining ceased at the end of the 19th century this emphasises the long-term problems associated with soil contamination from industrialisation (Smith *et al.*, 1998). An economically viable solution to reduce such pollution hazards and therefore enhance the value of these sites is required (Johnson *et al.*, 1977).

Arsenic present in sewage sludge originates mostly from surface run-off, via atmospheric deposition. Phosphate detergents add to the levels of arsenic present, as do industrial effluents. Pesticide residues will also increase levels, although arsenic is not now widely used for this purpose. Arsenic-based herbicides like sodium arsenite, arsenic acid and methane arsonic acid, have shown an increase in usage recently. A total of 90% of the arsenic pesticide industry is taken by the preservation of wood using ammoniacal copper chromium arsenate, and also for its use in the cotton industry (Woolson, 1983a; Ndiokwere, 1985).

The combustion of coal releases huge quantities of arsenic into the environment, and represents a major source of contamination. Due to the vast quantities of fly ash that are produced from coal-fired power stations, it is continually used as landfill (Beretka and Nelson, 1994). Levels of arsenic reaching 1500 mg/kg can be found in coal (Piver, 1983), but depending on its source there are differences in the concentrations encountered. For example in Eastern Europe, where hard coal is used, this has a higher level of arsenic than the soft variety used in North America (Benko and Simon, 1977).

Arsenic occurrence in soils becomes an environmental concern when the levels begin to affect human health and the environment (Vangronsveld & Cunningham, 1998). Plant growth and development in these areas is restricted due to phytotoxicicty of the high

levels of contamination, and this leaves the land biologically barren, and susceptible to erosion and leaching of arsenic off-site. The presence of As in most agricultural soils is due to the application of pesticides, herbicides and fungicides that are arsenic based. Compounds such as lead arsenate, copper acetoarsenite and sodium arsenate are used as pesticides and herbicides (WHO, 1981) and may accumulate in plants and so enter human food chains. The total amount of As present in soils will therefore be an important influence to plant growth and human health (Yan-Chu, 1994).

The development of natural plant populations at these contaminated sites may take many years, if not centuries to establish and so there is a need for intervention by man in order to create and maintain a healthy ecosystem in these contaminated areas.

Arsenic is well known for its toxicity and possible carcinogenic properties. The metalloid is phytotoxic, its chemical behaviour determining its uptake into plants and other soil biota (Sachs and Michaels, 1971; Otte *et al.*, 1991). However there are major differences between arsenic species with regards to their toxicity. The organo-arsenic compounds are less harmful than the inorganic compounds, and this difference separates arsenic from many of the common heavy metals.

Arsenic can be present in more than one oxidation state under a range of soil conditions, but exists preferentially as an oxyanion with a +3 or +5 oxidation state. There is a descending order of toxicity of arsenic compounds with elemental arsenic being most toxic, then arsenite, arsenate, monomethylarsenate (MMA) and dimethylarsenate (DMA) (WHO, 1981). Compounds in the trivalent state are generally more toxic than the pentavalent species and the pattern of toxicity can be represented as: $AsH_3 > As^{III} > As^{V} >$ RAs-X (Fowler, 1977).

In humans, the LD_{50} of arsenic poisoning has ranged from 1 to 5 mg As kg^{-1} (Fowle III *et al.*, 1991). In developing countries domestic coal use can cause a number of health problems related to arsenic poisoning. The residents of the Guizhou Province of China are affected by a variety of symptoms ranging from hyperkeratosis (scaly skin lesions) to Bowen's disease (dark, horny, precancerous lesions of the skin) (Finkelman *et al.*, 1999). Arsenic poisoning has developed here because the coals are highly mineralised and the residents use them on open stoves in poorly ventilated houses. Important dietary items, Chilli peppers, are also dried over the coals and may contain around 500 ppm arsenic within their tissues (Finkelman *et al.*, 1999). In Bengal, thousands of people have

developed toxicity symptoms through ingestion of arsenic contaminated ground water or consuming crops grown on contaminated land (Das *et al.*, 1996).

However, ingestion of arsenic via crops may be unlikely due to its low transfer from soil to plant. Further research must be carried out in order to assess this situation. Listed as a hazardous material, and a carcinogen, arsenic has been associated with cancer of the skin and lung tissues (National Academy of Sciences, 1977b). It has also been described as a teratogen, and can effectively cross the placental membrane and enter the metabolic system of a foetus. Arsenic is a cumulative substance, and may be deposited in the skin, hair, finger / toenails and bones (Leonard, 1991). Approximately 5-15 % of arsenic ingested by humans is absorbed (National Research Council of Canada [NRCC], 1978), with arsenic compounds being distributed in the lungs, kidney, spleen, gastrointestinal tract wall and liver within 24 hours of adsorption.

Arsenic in the environment may be present either through natural background sources or anthropogenic causes. However, one important sink for arsenic compounds in the environment is the soil. Arsenic from the soil system is only depleted slowly due to slow plant uptake and leaching, and will therefore accumulate readily. Owing to the increasing number of contaminated sites in the world, and arsenic toxicity to humans and animals, its dynamics are now being reviewed with possible management strategies in order to remediate these areas.

1.2. The Chemistry of Arsenic in Soils

The behaviour of arsenic is similar to that of phosphorus (P) in the soil environment. Phosphorus is chemically most similar to arsenic and will compete for binding sites in soils, however arsenic can form bonds more readily with sulphur and carbon compared to phosphorus. Under soil conditions arsenic is more mobile than P and can undergo changes in its oxidation state. Arsenic differs from phosphorus in that it can become volatilised by undergoing biological transformations. Arsenic chemistry is further complicated in that changes in redox potential (E_h) and pH can alter its chemical state in the soil solution. In an oxidized soil solution, thermodynamic calculations have shown that arsenic exists in the pentavalent state As(V), whilst in the trivalent state

As(III) it is found mainly in solutions that are anoxic. Masscheleyn, *et al* (1991b) demonstrated that 65-98% of arsenic found in the pentavalent (V) condition was found at higher redox levels (pe+pH>10), whereas the trivalent (III) state was found where redox conditions had been reduced. Under high redox conditions (Eh > 200 mV), arsenic solubility is low, and it exists predominantly as As^{5+}. With an increase in pH the level of mobile arsenic species in solution increases; this may also be brought about by reducing As^{V} to As^{III} (Masscheleyn *et al.*, 1991b).

Duel and Swoboda (1972b), discovered that, over time, As^{3+} became the predominant species in a flooded soil. The transition of As^{5+} to As^{3+} was not unexpected due to As^{III} being thermodynamically more stable than As^{V} under reducing conditions (Sadiq *et al.*, 1983). This was accompanied with the dissolution of iron oxyhydroxide minerals, that, under oxic conditions, have a strong affinity for As^{V}. The process occurs due to minerals like $FeAsO_4$ and Fe^{III} being reduced to the soluble form, Fe^{II}. The sorbed As^{V} is then released into the soil solution (Takamatsu *et al.*, 1982).

In a soil solution arsenic will exist as negatively charged oxyanions ($HAsO_4^{2-}$), however soil pH is important to arsenic chemistry. At pH 2 the most abundant species of As is $H_3AsO_4^{0}$, but such acidic soils are rarely found in nature. At pH 3 to 6, H_2AsO_4- is the more abundant species and as the pH increases to 7 and 8 H_2AsO_4- and $HAsO_4^{2}$- can be found. From pH 8 to 11 $HAsO_4$- becomes more abundant. Above pH 11 arsenic species such as AsO_4^{3-} are present, but are rarely found in nature (Sadiq, 1997). Therefore by altering the pH and redox conditions of a soil solution the ratio of arsenic (V) to As (III) can be altered (Smith *et al.*, 1998).

The presence of microorganisms (fungi and bacteria) may cause biotransformations of arsenic in soils (Sadiq, 1997). Numerous strains of soil bacteria have been isolated that accelerate the oxidation of arsenite to arsenate and are involved in the methylation of arsenic in soils (Boyle and Jonasson 1973; Jernelov, 1975; Mandl *et al.*, 1992; Weinberg, 1977). Methylation of oxyanions can form monomethylarsonic acid $CH_3AsO(OH)_2$, but the reactions that take place depend on the arsenic species and the microorganisms present (NRCC, 1978).

1.2.1. Soil properties

There are many factors that affect the sorption of As in a soil, but the most extensively studied has been that of soil properties. The amount of clay, and the nature of the mineral will control the amount of As in a soil. Studies by Johnson and Hiltbold (1969) demonstrated that of all the As present in the soil, 90% was associated with the clay fraction. Livesey and Huang (1981) investigated As(V) retention in four Saskatchewan surface soils. They found that sorption was related to ammonium oxalate-extractable Al and, to a smaller degree, the clay and iron (Fe) fraction.

Wauchope (1975) also investigated the adsorption of As(V) , and found that the arsenic species were correlated ($p< 0.01$) to the clay and Fe oxide contents of the soils. Iron oxide surfaces have been shown to be effectively involved in arsenic adsorption in soils (Bowell, 1994; ElBassam *et al.*, 1975; Harrison and Berkheiser, 1982; Lombi *et al.*, 1999; Lumsdon *et al.*, 1984; Norrish, 1975; Waychunas *et al.*, 1993; Woolson *et al.*, 1971) and therefore Fe coatings on clay surfaces and Fe in the soil may be significant in controlling arsenic adsorption-desorption processes.

Modification of arsenic-clay interactions may be brought about by clays being coated with Fe and Al oxides (Shuman, 1976; Schuthess and Huang, 1990; Naidu *et al.*, 1994). Fordham and Norrish (1979) reported that clay minerals were not as important, when compared to Fe oxides and titanium oxides, with regards to As adsorption in several acidic soils. In a further study, they controlled As adsorption using Fe oxides, with titanium oxides competing for As(V) only when the iron oxides had been removed. Elkhatib *et al.*, (1984b) studied arsenite adsorption in the A and B-horizons of five West Virginian soils, and found that iron oxides were associated with As^{III} adsorption. It has been suggested that the iron oxide/hydroxide surfaces may develop electrical charge due to hydration, specific adsorption, etc, and so arsenic adsorption onto Fe oxides may be explained on the basis of the type of charge (Sadiq, 1997). Manganese (Mn) oxides can also be involved in the adsorption of As^{III} and As^{V} (Oscarson *et al.*, 1983) and were found to be involved in the oxidation of the more toxic arsenite to arsenate (Oscarson *et al.*, 1981). Therefore if a soil is contaminated with As^{III}, the presence of Mn oxides, such as birnessite, can reduce the toxicity of arsenic by converting trivalent arsenic to the pentavalent state.

1.2.2. Arsenic adsorption / desorption in soils

As discussed previously the amount of arsenic in a soil solution depends both on the physical and chemical properties of the soil that will influence adsorption-desorption processes. The adsorption of arsenic in a soil has been shown to be dependent on the presence of adsorbing surfaces and also the concentrations of adsorbent (Elkhatib *et al.*, 1984a; Kabata-Pendias & Pendias, 1984). The ability of a soil to hold on to arsenic depends on the presence of iron (Fe) and aluminium (Al) oxides (ElBassam *et al.*, 1975), exchangeable calcium (Ca) and also the clay content. Arsenic has a high affinity for oxidic surfaces and will preferentially attach to Fe oxides (Akins & Lewis, 1976; Wauchope, 1975) and to a lesser degree Al oxides.

The adsorption of arsenic onto these surfaces is due to the charges on the oxides. The quantity of arsenic sorbed by Mn / Fe oxides is related to the pH_{pzc} (point at which there is a net zero charge on the mineral surface). The surfaces of many oxides change from being positively charged at low pH to negatively charged at high pH (Parfait, 1980), and the point at which this occurs is termed the PZC. Hydrous iron oxides at pH 7 -10 have a charge of zero. Adsorption has been shown to increase at low pH values and declines with an increase in the pH of a soil.

Aluminium oxide surfaces carry positive charges in soils that are acidic, but are negatively charged in neutral and alkaline conditions. Soil texture (Wauchope, 1975; Frost and Griffin, 1977), constituent minerals (Walsh *et al.*, 1977; Pierce and Moore, 1980) and competing ions will also exert their effects on the adsorption of arsenic.

Arsenic will also bind to Ca but not as strongly as to Fe. Clays are also important as binding agents, but the type and quantity in the soil is important. Clays are negatively charged silicate minerals, and will adsorb positively charged ions. Therefore due to arsenic being present as negatively charged oxyanions they will have a limited affinity to the metalloid. However, Greenland, (1975), Parks, (1967), and Wada and Okamura (1977), reported that many clays had a wide pH range and that arsenic adsorption was witnessed in acidic soils where the clay particles were positively charged. Tammes and de Lint, (1969) found that an increased clay content in a soil represented an increase in arsenic retention. However it was discovered by Dickens & Hiltbold (1967), that the various types of clay sorb arsenic differently. They found that kaolinite sorbed more

arsenic than vermiculite from solution, which in turn sorbed more As than montmorillonite. Conversely, Frost and Griffin (1977) found results that contradicted those of Dickens and Hiltbold, their research showed that montmorillonite sorbed both arsenate and arsenite more strongly than kaolinite from solution. Research by Goldberg and Glaubig (1988) demonstrated that arsenic was sorbed onto clay surfaces by chemisorption.

Other researchers have demonstrated that As was adsorbed by clays and that it was pH dependent. Soil pH is an important component with regards to adsorption properties and many researchers have found that arsenic adsorption increases with a fall in pH (Anderson *et al.*, 1976; Hingston *et al.*, 1971; Hsia *et al.*, 1992; Polemio *et al.*, 1982).

Apart from the surfaces of soil particles, other components in the soil play a part in arsenic adsorption. Phosphate ions have been shown by Hingston (1981), Peryea (1991), Roy *et al.*, (1984, 1986), and Woolson *et al.*, (1973) to adversely affect adsorption of arsenate. Large additions of P to a soil have been shown to displace up to 77% of the total As concentration, with the water soluble fraction being redistributed further down the profile (Woolson *et al.*, 1973).

Although phosphate will displace arsenic from soils, the desorption process is dependent on the soil type. This was discovered by Peryea (1991) who observed that, after adding phosphate to a volcanic soil, revealed that the arsenic concentration did not alter in solution. The volcanic soil had both a high anion-fixing and pH buffering capacity, which was due to the presence of allophanic minerals. Therefore only after large quantities of P are added to this type of soil may the arsenic concentration in solution be affected. The mechanism of arsenic sorption has also been studied. There is evidence for the formation of inner sphere complexes (specific adsorption) with the components of a soil (Hingston *et al.*, 1971; Anderson and Malotky, 1979). The use of X-ray absorption fine structure (EXAFS) spectroscopy has confirmed the formation of As^{5+} inner sphere complexes (Waychunas *et al.*, 1993). The use of wide-angle X-ray scattering showed similar complexes formed with ferrihydrite (Waychunas *et al.*, 1996), as did infrared spectroscopy for goethite (Lumsdon *et al.*, 1984). It was presumed by Waychunas and co-workers (1993, 1996) that As^{5+} adsorbs by forming binuclear, inner sphere complexes on ferrihydrite. However, monodentate complexes were also discovered, which accounted for up to 30% of the As-Fe correlations (Waychunas *et al.*, 1993). Arsenate and chromate

sorption onto goethite were studied by Fendorf *et al.*, (1997). By using EXAFS it was concluded that As^{5+} formed three different complexes on goethite. At low surface coverage the monodenate complex was favoured, but at higher surface coverage bidenate complexes were involved.

1.2.3. The importance of competing ions

Ions of both inorganic and organic nature exist within a soil system. They include Cl^-, SO_4^{2-}, PO_4^{2-} ions (Naidu and Rengasamy, 1993) and also those of organic nature such as exudates from plant roots and decomposing residues (Harter and Naidu, 1995). Competition exists between the ligand ions and arsenic for adsorption sites and this can affect the concentration of arsenic sorbed by the soil.

Investigations by Xu and co-workers (1988), involving competitive adsorption interactions using anions on pure mineral systems, have shown that at pH <7, the SO_4^{2-} anion (20 mg litre $^{-1}$) reduced arsenate (V) adsorption on alumina. Further increases in the concentration of SO_4^{2-} made little difference to the adsorption process (Xu *et al.*, 1988). Xu and co-workers (1988) also studied the presence of fulvic acid with regard to the adsorption of As^{V} on alumina at pH 3 and 7.5. They found that coulombic attraction might be the process via which arsenic is adsorbed. However fulvic acid may react directly with arsenic therefore reducing its adsorption (Thanabalasingam and Pickering, 1986).

A small number of studies have looked at organic matter and arsenic adsorption. Thanabalasingam and Pickering (1986), have shown that the process of adsorption involving both As valencies and humic acid was pH dependent. For As^{V} the highest adsorption was obtained at pH 5.5, whilst As ^{III} reached a maximum at pH 8.5. As humic acids become more soluble as pH increases, this decreases their ability to adsorb As from solution.

1.3. Remediation Methods

Due to the by-products of past industrialisation, a legacy of polluted sites now exists which are the subject of major concern for environmental protection in developed countries. However from the industrial revolution, development of the fossil fuel-based economy and growth of downstream chemical, manufacturing and engineering industries from the 1800's onward, are now the modern origins of the problem (Pollard *et al.*, 2001). Contaminated sites and the groundwater below them, used for industrial facilities or waste disposal often requires that unacceptable risks are assessed and managed so that the land can be reused for a new purpose (Pollard *et al.*, 2001). There are over 300,000 hectares of contaminated and derelict land in the United Kingdom and current remediation methods at such sites are environmentally invasive.

Without intervention these contaminated sites would remain barren, with no vegetative cover to protect them. The lack of cover would allow leaching of the soil, which may transport metals and metalloids into ground water sources and so contaminate them. The barren land presents another hazard to human populations from ingestion and inhalation of the contaminated soil from lateral dispersion of dust and particulates (Kabata-Pendias and Pendias, 1992).

Remediation of a contaminated site will depend upon (a) the site history and location, (b) the characteristics of the soil, (c) the chemical and physical state of the contaminants, (d) how polluted the site is, (e) the end use of the site, (f) finance available for remediation and (g) legal, environmental and social issues (Vangronsveld & Cunningham, 1998).

Remediation technology can be divided into either (1) removal of the contaminants from the soil, i.e. site decontamination techniques or (2) exposure to the contaminants is decreased, i.e. site stabilization techniques. Engineering approaches such as excavation of the contaminated material and disposal to a controlled landfill is a site decontamination technique, but the process has been criticised as it only transfers the contamination elsewhere (Wood, 2001). Further funds are then required to restore the site with vegetation. This type of remediation on a large scale would not be feasible due to the high costs involved and the safe disposal of the contaminated soil. Current remediation methods for soils contaminated with heavy metals are labour intensive, expensive and

environmentally invasive. Therefore low cost, environmentally safe alternatives are required to the current methods of remediation. Table 1.1 outlines the current remediation technologies available.

In situ metal inactivation is a technique whereby amendments are added to the contaminated soil in order to convert a soluble and highly mobile phase of a toxic metal into a more chemically stable phase. In doing so, this will reduce biological availability, plant toxicity and solubility. By reducing the toxicity of metals in the soil, vegetation will establish on the site, binding the soil and therefore stabilising it. Plants are important in that they prevent wind and water erosion to the soil and reduce leaching of the soil contaminants (Vangronsveld *et al.*, 1991, 1993).

Vangronsveld and Cunningham (1998) summarised the main objectives for *in situ* inactivation as:

- To alter the speciation of the trace element in the soil, thereby reducing the soluble and exchangeable fraction of the elements.

- Uptake of toxic metals by plants would be reduced and the vegetation cover would become stabilised.

- To reduce the exposure of soil-heterotrophic living organisms,

- To improve biodiversity.

In situ immobilisation includes both biological and physical / chemical processes. The chemical processes involved are, (i) complexation in solution, (ii) specific adsorption (clay, metal (hydr) oxides), (iii) ion exchange (clay), (iv) (Co) precipitation / dissolution, (v) solid solution formation (stable mix of two or more solids). The ultimate aim is to reduce metal solubility to a point where there is a limited 'sensitivity' for changes in physico-chemical soil parameters (Vangronsveld & Cunningham, 1998).

Table 1.1 Current remediation technologies available for remediation of contaminated land (Vangronsveld & Cunningham, 1998).

Remediation approach	**Comment**
Removal of metals from the soil	
Site decontamination techniques: Engineering Approaches	
Excavation & landfilling	Removal of the contaminated soil to a landfill, with backfilling of non-contaminated soil.
Soil washing	Removes solubilized contaminants using chemical extractants.
Thermal treatment	Rarely used
Electroreclamation	Electrokinetic process- current applied between cathode and anode.
Site decontamination techniques: Biological & Chemical approaches	
Microbially-based techniques	Only available to organic Contaminants
Phytoextraction	Plants that accumulate metals
Phytovolatilization	Plant –microbe associations
Reduce risk posed by contaminant	
Site stabilization techniques: Chemical & engineering approaches	
Soil & asphalt capping	Physical barrier to prevent leaching
In-place stabilisation/immobilisation	Mixing cement to stabilise
Vitrification	Conversion of matrix to solid glass-like material
Site stabilization techniques: Biological & Chemical approaches	
Phytorestoration	Revegetation
Phytoextraction	Hyperaccumulating plants
In situ metal inactivation (immobilisation)	Addition of inorganic amendments

There are three factors that are important when considering the quantity of trace element that will be sorbed on a solid phase: the nature of the solid, pH and the sorbed element and ligand concentration ratio. Together with these parameters, the presence of competing ions, type of element and concentration and ionic strength are also important influences. When choosing an additive to remediate a contaminated site, consideration must be given to the elements present, the soil characteristics and the proposed end use of the land once remediated (Vangronsveld & Cunningham, 1998).

1.4. Reasons for research

There are many techniques available for the remediation of contaminated land. As mentioned previously certain remediation techniques require extreme measures such as excavation of a site. Removal of the contaminated substrate appears to be a reasonable solution but because of the high costs involved with such an operation cheaper methods of remediation are required. The use of *in situ* ('soft') metal immobilisation techniques has gained increasing acceptance as a more viable approach to remediation. The low impact and cost of remediating a site with inorganic additives has made the technique very attractive. However the use of additives to remediate a site requires an extensive knowledge of the mechanisms involved for immobilisation of the element(s) in question. It is important to be able to predict the long-term efficiency of the additive in the soil and its durability. To date information on the effects of inorganic additives is still developing and is often incomplete (Mench *et al.*, 1998).

The uptake of metals into the food chain is of importance and so the bioavailability of the metal has to be considered together with its mobility in the soil. The idea of *in situ* remediation is to reduce the uptake of metals from the soil into the food chain therefore reducing their bioavailability. There are various ways of immobilising metals and practices such as incorporating inorganic additives like lime or phosphates to reduce metal mobility are common. However, such practices applied to arsenic contaminated land may be detrimental in that the additives will increase the metalloids mobility.

There are a number of techniques for the *in-situ* remediation of land contaminated with arsenic that involve either adsorption or fixation of the metalloid. The process of

solidification/stabilisation has been applied whereby cement and/or lime is/are added to the soil, which then becomes solidified. This has been shown to reduce the amount of arsenic leached from the soil to a level below 1 mg/l for landfill sites. Chemical fixation to prevent arsenic mobilisation has been carried out successfully at contaminated sites. For example iron sulphate and Portland cement have been used to form a barrier that halts the movement of arsenic, but also increases pH levels to alkaline conditions.

The addition of colloids such as clays, iron, manganese and aluminium oxides and hydroxides have been effective at reducing the mobility of arsenic in soils due to their adsorptive properties. An adsorption-oxidation system composed of goethite (α FeOOH) and birnessite has shown significant reduction in the toxicity of arsenic in contaminated soils (Sun and Doner, 1998). Iron oxide applied to garden soils has shown a decrease of as much as 50% in the water extractable arsenic concentrations, together with lower accumulation levels in plant tissues (Mench *et al.*, 1998). Other adsorbents such as aluminosilicates have been added to soils to reduce arsenic toxicity. Al-smectite was applied to a contaminated soil in Belgium that resulted in a 75% reduction in labile arsenic (Mench *et al.*, 1998). Studies have revealed that soils with increased clay content represented an increase in arsenic retention. There are nevertheless different types of clay and reported results regarding their adsorptive properties are often inconsistent. However montmorillonite and kaolinite have both shown arsenic adsorption (Frost and Griffin, 1977; Goldberg and Glaubig, 1988).

Amorphous iron hyroxide (am-Fe(OH_3)) also has an extremely high adsorptive capacity for arsenic, and steel shots have been used for arsenic immobilisation in contaminated garden soils (Vangronsveld *et al.*, 1994). Iron oxides may therefore adsorb toxic elements from the soil solution and occlude them. Steel shot, an industrial material contains mainly iron (97%) and corrodes and oxidises to produce iron oxides that have been shown to be effective in field trials at reducing the levels of arsenic in plant tissues (Mench *et al.*, 1998). In all cases, soil pH is an important factor for arsenic mobility and the rate and extent of adsorption usually increases with a decrease in soil pH (Hingston *et al.*, 1971).

The objective of this study was to evaluate various Fe-based additives with respect to their arsenic immobilising capabilities after incorporation into a variety of contaminated soils. A number of investigations were performed to test their effectiveness,

commencing with *in vitro* tests to determine their adsorption properties over a series of arsenic concentrations and selected pH conditions. Further studies investigated the partitioning of arsenic and a number of heavy metals in the selected soils using a sequential extraction scheme. Following on from these investigations, a variety of standard leaching tests were used to ascertain the stability of the additives in the soils, indicating their long-term potential and to try and understand the mechanisms involved during the leaching process. To complete the work, a series of plant trials were investigated in order to determine the bioavailability of arsenic within the remediated soils. This was an important consideration as they remain the last link, whereby toxic metals may accumulate and thereby enter the food chain. The trials would also help to establish if the addition of Fe-bearing additives produced any detrimental effects on plant growth.

CHAPTER 2.

SITE CHARACTERISATION AND GENERAL METHODS.

2.1. The collection and preparation of soil samples.

For the studies presented in this thesis, three contaminated soils were investigated. Surface soil samples (top 10cm) were collected from the following sites located in the North West of England. Each soil represented a different source of arsenic contamination. The soil from Kidsgrove (O.S. Grid Ref, SJ 844 543) was obtained from an embankment adjacent to a canal - here the soil had been contaminated with dredgings from the water course. Merton bank, St Helens (O.S. Grid Ref, SJ 523 961) soil may have been contaminated with low-level alkali waste, and also used as an unauthorised landfill site, however this is uncertain. Rixton clay pits near Warrington (O.S. Grid Ref, SJ 621 885) had some coal fly ash deposits, which contained elevated levels of arsenic.

2.2. Soil and site characterisation.

2.2.1. Kidsgrove (O.S. Grid Reference SJ 844 543)

The site is located to the north of Stoke-on-Trent. The British Waterways Board (BWB) owns the land, which is situated adjacent to a canal. Canal dredgings have been deposited onto adjoining land. The contaminants present in the canal dredgings may have accumulated via atmospheric deposition, or from use of pesticides or herbicides, which may have entered the canal via surface runoff from farmland. The soil is contaminated with a number of toxic metals, especially arsenic and cadmium. A pigment factory situated alongside the canal is a probable source of the large concentrations of cadmium present in the sludge.

2.2.2. Merton Bank, St Helens (O.S. Grid Reference SJ 523 961)

Merton Bank is located in the Pocket Nook area of St Helens, Merseyside. The area consists mainly of grassland, interspersed with plots of trees. To the South East, there is a known landfill site, Sankey Brook, which contains alkali waste. The contamination present at Merton Bank is low-level alkali waste, with some local pollution from the disused railway line. In 1872 Merton Bank alkali works was formed, operated by George Harris. However, in 1890, the business was taken over by the United Alkali Company Ltd, and closed down shortly afterwards. The land may also have been used as an unauthorised landfill site.

2.2.3. Rixton clay pits (O.S. Grid Reference SJ 621 885)

The clay pits are located near Warrington, east of Liverpool in NorthWest England. The site contains fly ash, which is an increasing waste problem due to the combustion of coal from coal-fired power stations (Smith *et al.*, 1998). This waste requires special care when disposed of, due to the high levels of arsenic present in it. Arsenic levels in coal can be large, reaching 1500 mg/kg (Piver, 1983). Therefore the burning of coal presents an increasing problem with regards to arsenic inputs into the environment. In coal combustion, trace elements such as Ni, Co, Cd, and Pb, present in the coal, are concentrated especially on the surface of the finest particles of fly ash due to volatilisation-condensation mechanisms that occur during burning (Natusch *et al.*, 1974 & Davidson *et al.*, 1974).

Due to the surface nature of the fly ash, heavy metals are immediately available for release into the aqueous environment as the trace metals are mainly concentrated on the surface of the fly ash (Prasad *et al.*, 1996). Natusch and co-workers (1974) demonstrated that elements that predominated on the fly ash surface, such as Co, Cd, Zn and Mn, showed a higher solubility in aqueous media. A small part of fly ash is used for construction material, roads and for backfill, however the major part is disposed of with great environmental risk (Prasad *et al.*, 1996). The environmental problems that arise from the disposal of fly ash are due to the leaching of metals from coal ash settling ponds,

resulting in phytotoxicity, soil contamination and ground and surface water pollution (Prasad *et al.*, 1996). Engineered control mechanisms, for example membrane systems, are expensive to construct (Prasad *et al.*, 1996) and therefore new remediation technologies such as *in situ* remediation may reduce the high costs associated with the disposal of this and other environmental wastes.

2.3. Preparation of soils for analysis

After collection, the soil samples were returned to the laboratory, air-dried for two weeks then crushed and sieved to a particle size of less than 4mm diameter. The drying process did not involve high temperatures, therefore preventing loss of components through evaporation. Additionally, higher drying temperatures may have caused transformations to occur to some elements in the soil that would have altered the original soil characteristics. The particle size (< 4mm) was recommended by the Dutch Environmental Agency column tests (NEN 7343) (Chapter 5) and therefore applied to all other investigations on soil leaching/speciation. The following analyses were then conducted on the soils:

2.4. Analysis of soil characteristics

The following physical and chemical characteristics of the soils from Kidsgrove, Rixton clay pits and Merton bank were determined:

- pH
- % weight loss at 110 °C (moisture content)
- % weight loss on ignition (organic matter content)

2.4.1. pH

pH is a measure of hydrogen-ion activity. A 20g soil sample was added to a glass beaker and 50ml deionised water was added. The mixture was then stirred thoroughly with a glass rod to homogenise the sample and left to stand for 1 hour at room temperature. The supernatant was tested using a PHM85 precision pH meter with a Radiometer GK2401C combination glass electrode. Table 4.1 shows the arithmetic mean values that were recorded from three replicates of each soil.

2.4.2. Organic Matter

Ashing expressed as loss-on-ignition is the term used to express a crude indication of the amount of organic matter present in a soil. The value obtained however is not a true measure due to loss of water bound to the clay minerals at the ashing temperature being included in the overall loss. The error is greater where a soil has a low organic matter content (Allen, 1989).

Approximately 1g of oven-dried soil was accurately weighed in a dry crucible. The sample was then placed in a muffle furnace at a temperature of 375°C and left overnight. Following removal from the furnace, the sample was cooled to room temperature in a desiccator, then re-weighed. Three replicates were recorded and a mean value was obtained (Table 4.1). Weight loss during combustion was thus recorded as percentage loss-on-ignition using the formula below:

$$\text{Loss-on-ignition (\%)} = \frac{\text{Weight loss (g)}}{\text{Oven-dry weight (g)}} \text{ X } 100$$

2.4.3. Moisture content of fresh soil.

A 10g sample of fresh soil was weighed and placed in an evaporating crucible. The soil was then dried at 100-110°C in an air–circulation oven for 24 hours. After reaching room temperature in a desiccator, the sample was re-weighed (Allen, 1989). All soil samples were analysed in triplicate and recorded as a mean value (Table 4.1). Percentage moisture was obtained using the formula below:

$$\text{Moisture (\%)} = \frac{\text{Loss in weight on drying (g)}}{\text{Initial sample weight (g)}} \times 100$$

2.5. Arsenic analysis using Hydride generation

For the detection of small concentrations of arsenic, in the range of μg l^{-1}, hydride generation is required. All solutions were filtered through Whatman GF/C fibreglass filter paper prior to analysis. For the determination of arsenic in all solutions, the samples were pre-reduced prior to analysis. This was accomplished by the addition of 1 ml concentrated hydrochloric acid (HCl) and 1ml of a reducing solution which contained 10% (w/v) potassium iodide (KI) and 5% (w/v) ascorbic acid to 1ml of sample. The reduction rate was improved by increasing the acid concentration. All solutions were then left to stand for 30 - 45 minutes. The above method allows for the conversion of As^{5+} in the sample to As^{3+} which provides increased sensitivity. As^{5+} can be determined with higher sensitivity if a larger reaction coil (500 μl) is used. Table 2.1 displays the operating conditions for the determination of arsenic using hydride generation with a Perkin Elmer 100 FIAS system. The principles behind the technique can be found in Appendix 1.

Table 2.1. Operating parameters for the analysis of arsenic with a Perkin Elmer100 FIAS system.

Parameter	Arsenic
Wavelength	193.7
Lamp	HCL
Slit (nm)	0.70nm (Low or Alt)
Cell temperature (quartz cell)	900°C
Flame	Very lean

A standard arsenic solution was prepared by the addition of 1.32g arsenic trioxide (III), dissolved in a minimum volume of 1M sodium hydroxide (NaOH) solution. The solution was then acidified with dilute hydrochloric acid (HCl) and diluted to 1 dm^3 in a volumetric flask. The hydrochloric acid was reagent grade and arsenic free. A 1cm^3 aliquot contained 1mg of arsenic and the necessary dilution of the stock solution was prepared to give a range of arsenic standards from 1 to 50 mg/l^{-1}. These were all diluted to volume with deionised water in volumetric flasks.

For analysis of arsenic using hydride generation, standard arsenic concentrations in the range of 10 to 60 $\mu g\ l^{-1}$ were made from 1 mg/l^{-1} standard arsenic solution. The standards were acidified with HCl and the reducing solution which contained 10 % (w/v) potassium iodide (KI) and 5% (w/v) ascorbic acid was also added to the arsenic standards.

2.6. Heavy metal analysis using inductively coupled plasma emission spectrometry (ICP-AES)

For the determination of heavy metals copper (Cu), cadmium (Cd), zinc (Zn) and lead (Pb) in the $mg\ l^{-1}$ range, a Philips simultaneous sequential PV8060 emission spectrometer was used. All solutions were filtered through GF/C fibreglass filter paper prior to analysis. For the determination of heavy metals using this technique a 10 ml analytical

sample was required to which 0.1 ml of a 100 mg/l^{-1} yttrium solution was added. The ICP- AES used yttrium as an internal standard. A small (0.02 ml) volume of concentrated HNO_3 was also added to acidify the solution. Appendix 1. outlines the principles behind the technique.

2.7. Total metals analysis by X-ray fluorescence spectrometry (XRF)

Each soil was analysed for total metal concentrations using a Spectro X-Lab energy-dispersive X-Ray Fluorimeter (XRF). XRF is a non-destructive analytical technique where the analysis is based on x-ray radiation being emitted from the atoms in a sample.

The sample for analysis was either prepared as a solid pellet or as a powder in cuvettes. The soil samples were initially dried in an oven at 40°C and then ground and pulverised in a ball mill to create a fine-grained material. A 4.000g sample was then weighed out, to which 0.9000g of wax was added. The sample and wax were then mixed thoroughly in the ball mill. The sample plus wax was then placed in a mechanical press and a pressure of 10 tons was applied, to create a pellet. Powdered samples for use in cuvettes were prepared in the same way by grinding the soil in a ball mill in the absence of wax. The cuvettes were covered by thin mylar film upon which the sample rested. Table 4.3 shows the mean total metal concentrations (μg g^{-1}) for the three soils. Table 4.2 shows the percentage iron, calcium and sulphur present in the three soils, which are related to the chemistry and behaviour of arsenic in the soil environment. Appendix 1. outlines the principles behind the technique.

2.8. Preparation of plant tissue samples for metal analysis

In the plant uptake experiments, plant material for digestion was collected at the end of the growing period. Leaves and stems were removed by cutting the base of the plant near to the soil with a sharp knife. All plant material was washed in deionised water to remove soil residues from the lower leaves and stems, before being oven dried at 60^{0}C

for three days. The material was then ground in a mechanical sample grinder (Cyclotec 1093 sample mill). After each sample had been ground, the grinder was thoroughly cleaned with a stiff brush to ensure the removal of the previous sample and so prevent contamination occurring. All samples were stored in polyethylene containers until analysis.

2.8.1. Microwave digestion of plant / soil material

The plant / soil samples were digested by microwave digestion technique using the MDS-81D microwave digestion instrument. The methods described are optimised conditions for plant and soil material following the manufacturers recommendations.

2.8.1.1. Leaves

A standard aliquot (0.5g) of dry finely ground plant material was weighed into a 100% Teflon digestion vessel (120 ml). Concentrated nitric acid (HNO_3) (9 ml) and hydrogen peroxide (H_2O_2) (1 ml) were added to the vessel in a fume cupboard. The vessels were allowed to stand for 15 minutes to allow any reactions to occur. Safety valves and caps were then placed on each vessel and tightened using the capping station. Each vessel was numbered, and the venting tubes were attached to the vessels. All vessels were placed on the turntable of the microwave and the fan and turntable were then activated.

The oven was programmed for 2 minutes 30 seconds at 100% power (stage 1) and 10 minutes at 80 % power (stage 2). Samples were removed on completion of the programme and checked visually for any loss of material or venting. Samples were then cooled to room temperature before being placed in a fume cupboard where they were manually vented. Samples were filtered using Whatman No. 1 filter papers, the solutions were decanted into 25 ml volumetric flasks and made up to volume with deionised water. Solutions were analysed via hydride AAS and ICP. Triplicate samples and blanks were digested. Bowens Kale was used as a standard reference plant material with every batch of digests.

2.8.1.2. Soil

Soils were oven dried at 60°C, sieved to a particle size of less than 4 mm diameter and 0.5g of soil was weighed into a digestion vessel. Concentrated nitric acid (HNO_3) (10 ml) was added to the vessels inside a fume cupboard, and these were allowed to stand for 15 minutes. The oven was programmed for 10 minutes at 100% power (stage 1) and 10 minutes at 80 % power (stage 2). Upon completion of the programme the vessels were treated as described above (2.8.1.1). The solutions were filtered and made up to volume in 25 ml volumetric flasks. Triplicate samples and blanks were digested and the results are presented in Table 4.4.

Between digests the Teflon vessels, safety valves, caps and venting tubes were washed with 10% Decon to decontaminate them. Following the wash, concentrated nitric acid (HNO_3) was added to the vessels and then washed out with deionised water. The vessels were then oven dried at 60°C.

2.9. Preparation of goethite (α - FeOOH) (an iron oxide) used in the investigations

For the preparation of goethite used in the investigations, the method of Atkinson *et al* (1967) was employed. A clear rust brown solution (pH 2) was formed by dissolving 50g purple $Fe(NO_3)_3.9H_2O$ (iron nitrate) in 800cm^3 distilled water. To the $Fe(NO_3)_3$ a solution of 2.5M KOH (200 cm^3) (potassium hydroxide) was added and the amorphous rust-brown precipitate formed was stirred vigorously, whilst adjusting the pH to 12.0 with NH_3 (aq) (ammonia). The precipitate was aged to form yellow coloured crystals by heating to 60°C in a water bath for 24 hours.

The solution was filtered using a vacuum pump and washed with deionised water to remove any adsorbed K^+ or NO_3^-. All washings were discarded. The precipitate was oven dried at 120°C and then crushed and sieved to a particle size of 180 μm. The material was kept in an oven to prevent water absorption. The precipitate was characterised by X-Ray Diffraction (XRD) (figure 3.3.a) and compared to the JCPDS powder file No. 17-536. This was necessary as the precipitate was prepared in the

laboratory and therefore the authenticity of the iron oxide had to be established prior to use.

The other additives used in the investigations were, Iron (II) sulfate heptahydrate (98+%) ($FeSO_4 \cdot 7H_2O$) and Iron (III) sulfate pentahydrate (97%) ($Fe_2(SO_4)_3 \cdot 5H_2O$) which were both obtained from Aldrich Chemical Supplies. Iron powder was obtained from Pometon (metal powders and granules), type 31051, which typically had a particle size of between 2- 4 mm diameter. Lime used in the studies was obtained from a local horticultural merchant.

CHAPTER 3.

ADSORPTION STUDIES USING IRON OXIDE ADDITIVES.

3.1. Introduction

A variety of iron oxides were selected as potential additives, based on their adsorptive properties for arsenic anions. These were initially characterised, prior to use in the investigations. Iron oxides have been shown to reduce the concentration of arsenic in solution, however the amount sorbed onto a solid phase is dependent upon the following; the nature of the solid, pH and the concentration ratio between the selected element and the ligand (Kabata-Pendias & Pendias, 1984). The concentration and type of element, ionic strength and the presence of competing ions in solution also influence the sorption process.

Arsenic chemistry in aqueous systems is complicated due to the element's four oxidation states (+5, +3, 0, -3) under varying redox and pH conditions (Ferguson & Anderson, 1974). Research has shown that an increase in pH will reduce the effect of adsorption onto geological materials such as amorphous aluminium hydroxides (Anderson *et al.*, 1976). However a low pH may cause dissolution of the metal hydroxides and therefore release any bound metals back into solution (Khourey *et al.*, 1983; Singh and Subramanian, 1984). The following investigation presents data on the adsorptive ability of iron oxides over varying pH conditions and arsenic concentrations. Firstly an overview of iron oxides and their adsorption processes will be described.

3.2. Natural occurrence of iron oxides

Iron is the fourth most abundant element and second most abundant metal in the Earth's crust, of which it forms 5% by weight (Moody, 1991). The principal ores of iron (III) oxide, are found as hematite, Fe_2O_3, and limonite, $2Fe_2O_3.3H_2O$, of tri-iron tetroxide, magnetite, Fe_3O_4, (highest proportion of iron), and iron (II) carbonate, siderite, $FeCO_3$ (Moody, 1991).

There are numerous oxides / oxyhydroxides of iron that exist naturally in soils, which are responsible for their red and brown tints. The oxides of iron are often referred to as hydrous oxides; these have a disordered structure and exist in the clay-size fraction (< 2μm) (Alloway, 1995). In the tropics, due to a more rigorous weathering environment, iron oxides are more abundant than clay minerals (Wild, 1988).

Iron oxides can occur as either concentric nodules, fillings in voids or as a mixture with clays that appear as coatings on soil particles. Of all the oxides present in a soil, i.e. Fe, Al, and Mn oxides, iron oxide minerals appear to be the most abundant. Sorption of trace metals by hydrous iron oxides is due to their high reactivity, due to the presence of hydroxyl groups, which form ideal templates for bridging trace metals (Mench *et al.*, 1998). At first, the precipitation of Fe is in the form of gelatinous ferrihydrite ($5Fe_2O_3.9H_2O$). However this dehydrates to form goethite (-FeOOH) that is more stable and more common in soils (O'Neill, 1985) than hematite (α-Fe_2O_3), which is found mainly in tropical soils.

3.3. Structure

The oxides of iron and manganese were initially thought to posses an amorphous structure, however they actually have small-sized scattering domains (Manceau *et al.*, 1992; Charlet & Manceau, 1993) that exist as a mix of cubic and hexagonal anionic packaging (Mench *et al.*, 1998). There are at least five separate local structures that have been accounted for:

- The hydrolysis and oxidation of Ferrous chloride or sulphate leads to the precipitation of ferric gels that have a local structure like that of lepidocrocite.
- The '2-line' gels – either with goethite-like (α FeOOH), or akaganeite-like (β FeOOH) local structures are made from ferric nitrate or chloride solutions.
- Goethite and akaganite, when aged by either neutral pH or heating, can be converted into a ferroxyhite-like form (δ FeOOH).
- Ferroxyhite forms can then be further transformed into hematite (Mench *et al.*, 1998).

Spadini *et al.*, (1994) described the '2-line ferrihydrite' (HFO) structure as a single and double octahedral chain mosaic of variable length ranging from 1 to *n* octahedra, linked at the corners of the chain.

3.4. Adsorption process

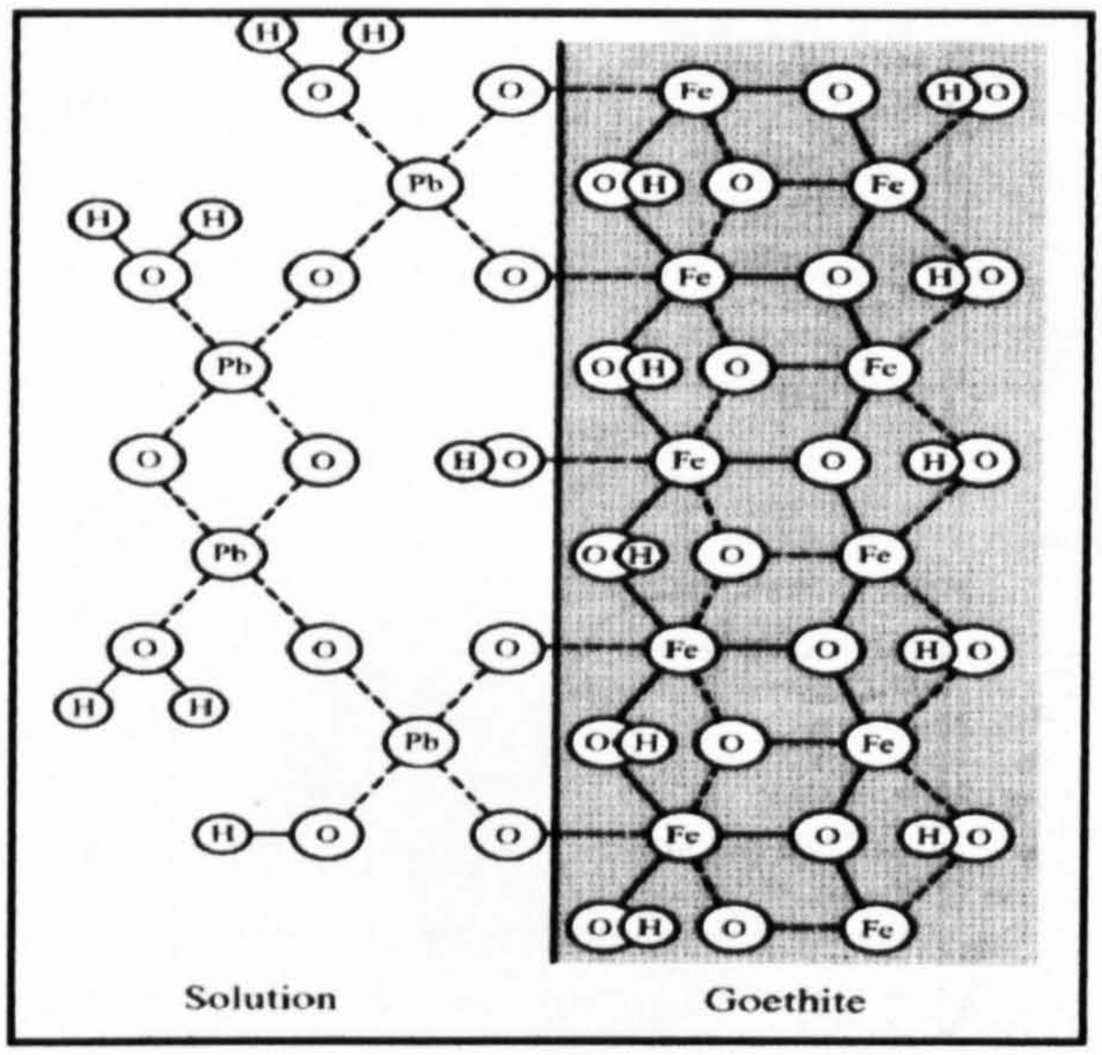
The chemical process of adsorption potentially controls the bioavailability and behaviour of metal contaminants in a soil. This process removes the contaminants from the liquid phase to a solid phase. Numerous mechanisms may be related to adsorption, including cation exchange, co-precipitation and complexation with organic material. However, specific adsorption, whereby there is an exchange of anions and cations with surface ligands forming partly covalent bonds with lattice ions, produces a far greater adsorption effect (Alloway, 1995).

Iron oxides co-precipitate and will scavenge (i.e. adsorb) anions such as AsO_4^{3-} and also cations, for example Cr, Zn and Ni, out of solution. This is due to a pH charge dependency, because the net charge on a mineral can change from being positive to negative with an increase in pH. In the lower pH range, increased protonation increases the positively charged sites and therefore arsenic anions are attracted to the iron oxide surface, whilst at higher pH, negatively charged sites dominate, repelling anions and so adsorption decreases (Hsia *et al.*, 1992). The point at which the minerals charge becomes zero is called a point of zero charge (PZC) or pH_{pzc} and differs for various hydrous oxide minerals. Mineral surfaces of Al oxides and hydroxides such as gibbsite, have positive surface charges in solutions with a pH less than 9.0, and so negatively charged aqueous species will be attracted to their surfaces, whilst the iron oxide goethite has a PZC of 7.3 – 7.8 (Krauskopf and Bird, 1995).

Adsorption involves the removal of a solute from the bulk solution, which is then attached to a mineral surface. A stable molecular unit called a surface complex is formed. Two common types exist, based on atomic arrangement and bonds between the mineral and solute. The first type, termed an inner-sphere complex, involves covalent or ionic bonds which are formed between the specific crystallographic site on the mineral surface and the solute species. There are no water molecules between the absorbed species and

the mineral surface. The second type is called an outer-sphere complex, which loosely attaches to the surface of the mineral with one or more water molecules located between the solute species and the mineral surface (Krauskopf and Bird, 1995). Figure 3.1 shows a diagrammatic representation of a multinuclear surface of lead bound by two inner-sphere surface complexes to goethite.

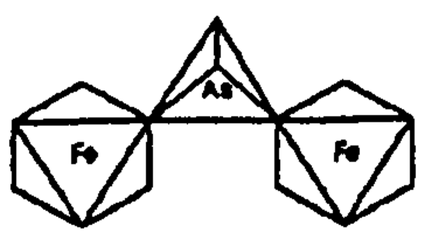
Figure 3.1. Diagrammatic representation of a multinuclear surface of lead bound by two inner-sphere surface complexes to goethite (Roe *et al.*, 1991).



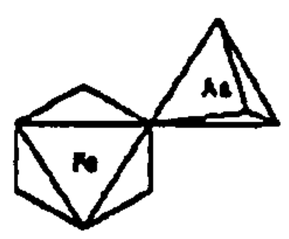
Surface complexation by trace metals may be varied for hydrous metal oxides. With $As_2O_4^{2-}$ for example, isolated inner-sphere surface complexes on ferrihydrite (HFO) are formed (Manceau *et al.*, 1992; Hargé, 1997; Spadini *et al.*, 1994). The formation of binuclear bidenate complexes on hydrous ferric oxides may occur for arsenate at high surface coverage, but at low surface coverage mononuclear monodenate complexes form. Figure 3.2 shows idealised surface complexes of arsenic with ferrihydrite. By attaching through double corner links, anions may attach to goethite and ferrihydrite by two single coordinated assemblages (Mench *et al.*, 1998). Three different stages have been shown to occur in the adsorption of metals by goethite. Firstly, surface adsorption occurs, followed by diffusion into the goethite particle. Thirdly, adsorption and fixation occur within the mineral (Brummer, 1986).

Figure 3.2. Idealised surface complexes of arsenic with ferrihydrite (Modified from Waychunas *et al.*, 1993).

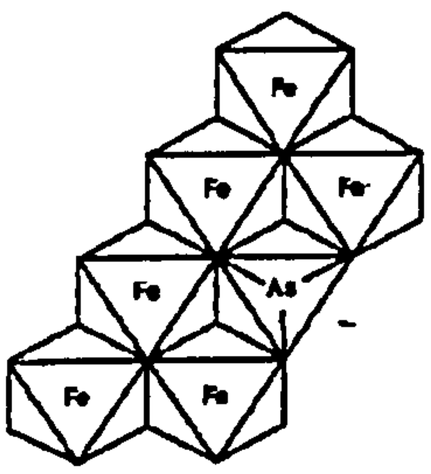
Shared edge complex



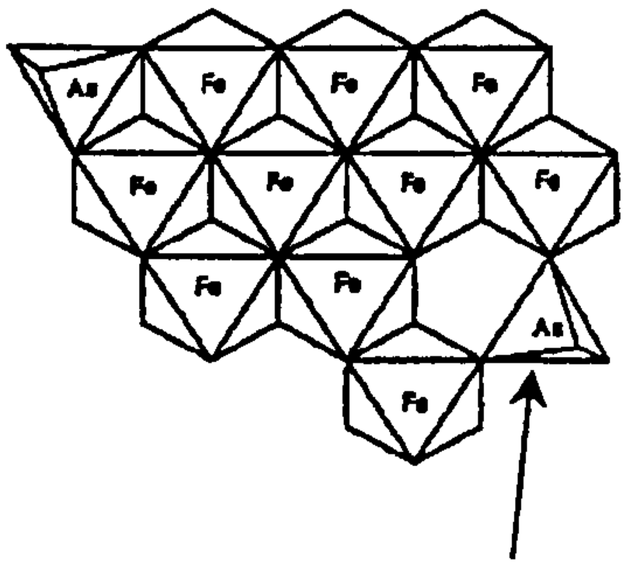
Shared corner complex



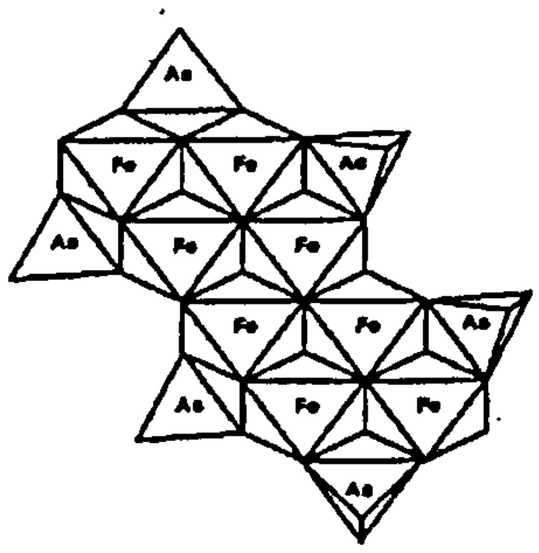
Isolated bidentate complex



Tridentate arsenate complex



Bidentate complex



Fe dioctahedral chain unit.

Iron grit (Steel shot) used in this investigation is of industrial origin, containing mainly iron (97%), plus resident impurities, for example, Mn (0.6 to 1%), C (0.8% to 1.2%), Si (0.8% to 1.2%) and Cr (0.2% to 0.5%) (Mench *et al.*, 1998). The grit corrodes and oxidises readily to form a variety of iron oxides such as lepidocrocite, maghemite and magnetite and manganese oxides in soils (Sappin-Didier, 1995). The grit forms oxides, which may coat particles of soil, enabling an increased surface for reaction with trace metals in the soil solution.

There is evidence to suggest that arsenic immobilisation occurs in soils treated with iron grit (steel shot). Greenhouse and field trials have shown reductions in plant arsenic uptake, and an arsenic contaminated garden soil was remediated effectively by steel shots (Vangronsveld *et al.*, 1994).

A further additive used in this study was Lime. This was included to determine its effects on the arsenic anion. Lime ($CaCO_3$), an alkaline material, is probably the oldest technique for immobilising cationic metals in the soil. Lime affects binding sites in the soil by binding H^+ ions that are attached to soil particles, thereby allowing the site to be accessible for cationic metals to attach and bind. Liming has been carried out in agriculture for over thirty years. For example, it was used to reduce copper (Cu) phytotoxicity in vineyards located in France by combining it with organic matter (Delas, 1963).

The addition of Dolomitic lime acts by precipitating metals in solution, by inducing hydrolysis of metals and / or carbonate coprecipitation. However although effective in the sort term for remediation of soils contaminated with metals, lime will increase the pH of a soil and this may mobilise anionic species such as arsenates (Mench *et al.*, 1998). Both iron II sulphate ($FeSO_4 \cdot 7H_2O$) and iron III sulphate ($Fe_2(SO_4)_3 \cdot 5H_2O$) were mixed with lime (1% w/w) and iron oxides were formed *in situ* by reaction of iron sulphate with the lime. Goethite was synthesised using the method described in Chapter 2. Section 3.5 discusses the characterisation of each additive.

3.5. Characterisation of additives.

A variety of inorganic additives were used to attempt to reduce the mobilisation of arsenic in solution. The selection of a soil additive must be chosen with respect to the total metal concentrations present and the characteristics of the soil in question. Further, the potential end use of the soil must be carefully considered (Mench *et al.*, 1998). As a result of applying additives, by spreading and tilling the material into the topsoil, it is hoped that chemical binding of the metals to the amendment will occur, therefore preventing mobilisation into the soil solution. Iron oxides have been shown to adsorb metals and prevent them from entering the soil solution, whilst electron-microprobe investigations have shown accumulation of metals in iron oxides (Hiller & Brummer, 1995).

Before addition of these materials to a soil, an understanding of the mechanisms involved in adsorption responsible for immobilisation was vital, although this knowledge

is often lacking, or embryonic, in such circumstances (Mench *et al.*, 1998). Prior to the soil studies the iron oxides were firstly characterised and then investigated using pure model systems, which would provide an insight into their adsorption capacity at varying pH and arsenic concentrations.

3.5.1 X-Ray Diffraction

To determine the identity and crystallinity of the compounds used in the following investigations, samples of the original materials were examined by X-ray diffraction. The JCPDS (Joint Committee on Powder Diffraction Standards) card index was used to identify the crystalline solids. The dry additives were analysed at room temperature using a Philips PW 1729 X powder diffractometer, which was run by APD (Automated Powder diffraction) software. The XRD powder patterns for the additives are shown in figures 3.3.a,b,c and d. No XRD pattern could be obtained for iron grit.

3.5.2. Thermal analysis

Differential thermogravimetric analysis (DTGA) was carried out using a Perkin Elmer TGA 7. A sample of the additive (5 mg), previously dried at 60 °C, was heated at a rate of 5 °C per minute over a temperature range of 20 °C to 850 °C. The loss in weight, and energy differentials were recorded. DTGA is used to measure the water content of a sample. From this information, identification of the iron oxide can be established. This is due to each iron oxide having its own specific decomposition pattern. Firstly water is lost from the sample followed by water loss of crystallisation. The iron oxyhydroxides then decompose into the iron oxide and water. For all the additives, the thermogravimetric curves reveal endothermic weight loss due to dehydration (Figures 3.4 a,b,c and d). A TGA analysis was unobtainable for iron grit.

3.5.3. Surface Area

The additives were analysed for their specific surface areas by a Quantachrome Nova 2000, using the Nova data analysis package. A sample (1.0 g), (previously oven dried at

60 °C), was dried at 240 °C, vacuumed, degassed and purged with nitrogen for 12 hours. Table 3.1 shows the specific surface areas for the additives used in the investigations.

3.5.4. Scanning Electron Microscopy

Approximately 3 milligrams of iron oxide was gold sputter coated on a metal target coated with an adhesive. A tungsten filament was used for the vacuum evaporation. The sample was held at a 45° angle to the electron beam and the iron oxide particles were photographed at an accelerating voltage of 25 kV on a Jeol JSM 840 scanning electron microscope at a magnification of 3500. The photographs are presented in plates 3.1 – 3.4.

3.6. Experimental batch adsorption investigations.

A standard arsenic solution was prepared by dissolving sodium arsenate ($Na_2HAsO_4 \cdot 7H_2O$ (1.3620g, A.R.)) in deionised water in a 1 dm^3 volumetric flask. The solution was then adjusted to the required pH (pH 5/9) with dilute (0.1 M) acetic acid (CH_3COOH) or dilute (0.1 M) sodium hydroxide (NaOH). 1 cm^3 contained 1 mg of arsenic, and the necessary dilution of the stock solution was prepared to give a range of arsenic standard solutions from 1 to 100 ppm. These were diluted to volume with deionised water in volumetric flasks and the pH readjusted if necessary. The pH of all solutions were measured with a Radiometer PHM85 precision pH meter fitted with a Radiometer GK2401C combination glass electrode.

Standard arsenic solutions were then added (100 cm^3) to polyethylene screw cap bottles (125 ml). The desired amendment was accurately weighed (1.00 g) and mixed with the standard arsenic solutions. All analyses were carried out in triplicate. The solutions were maintained at a constant temperature (25°C) in a re-circulating water bath for 30 days. This allowed for exchange processes to occur and equilibrium to be reached. Throughout the duration of the investigation the containers were regularly shaken to mix the additive with the solution. Following the 30-day incubation period, all samples were filtered through GF/C fibreglass filter paper into screw cap polyethylene containers and analysed for arsenic content by AAS using a Perkin Elmer 100 Atomic Absorption Spectrophotometer.

3.7 Results and Discussion

Characterisation of the additives using XRD analysis (figures 3.3a – 3.3d) identified their authenticity, but this was especially important for goethite, as this iron oxide had been synthesised in the laboratory and therefore identification was paramount, to ensure that the material produced was pure goethite. DTGA analysis (figures 3.4a - 3.4d) revealed different decomposition patterns for each amendment and from these, identification of the iron oxides was possible. Surface area (SA) studies (Table 3.1) showed that goethite had the largest surface area of 71.4 Sq m/g, whereas iron grit displayed the lowest measurement of 0.30 Sq m/g. From the surface area data it would be possible to explain differences in the effectiveness of the iron oxides in relation to arsenic sorption studies.

Although the SA results identified the potential area for adsorption to occur, scanning electron microscope studies revealed the surface structure in photographic form (Plates 3.1 – 3.4). These plates show the differences between the iron oxides and it can be seen that goethite (Plate 3.4) has a very different structure to that of the other iron oxides (Plates 3.1-3.3). Goethite's structure is amorphous when compared to iron III sulphate for example, which is very crystalline (Plate 3.1). These initial studies have revealed differences in the iron oxides structures that will help to explain any potential differences that may arise with regard to their adsorptive capabilities, which will be discussed below.

Adsorption data are most frequently represented as adsorption isotherms. The plot displays the quantity of adsorbate retained by a solid as a function of the concentration of that adsorbate in the solution phase that is at equilibrium with the solid (McBride, 1994). By addition of a known quantity of amendment to a known concentration of aqueous arsenic solution, adsorption isotherms were constructed (Figures 3.6 – 3.10). They were derived by calculating the equivalent fraction of ion in solution (As) and plotted against the equivalent fraction of ion in the amendment (Ac).

There are a variety of adsorption isotherms, which are classified into four types (Figure 3.5). From data obtained from the four iron oxides studied in the investigation the Langmuir isotherm was evident, and this suggests that there was a high affinity between the iron oxide surfaces and the arsenic anion. Chemisorption is usually associated with

Figure 3.3.a. XRD pattern for Goethite (α - FeOOH)

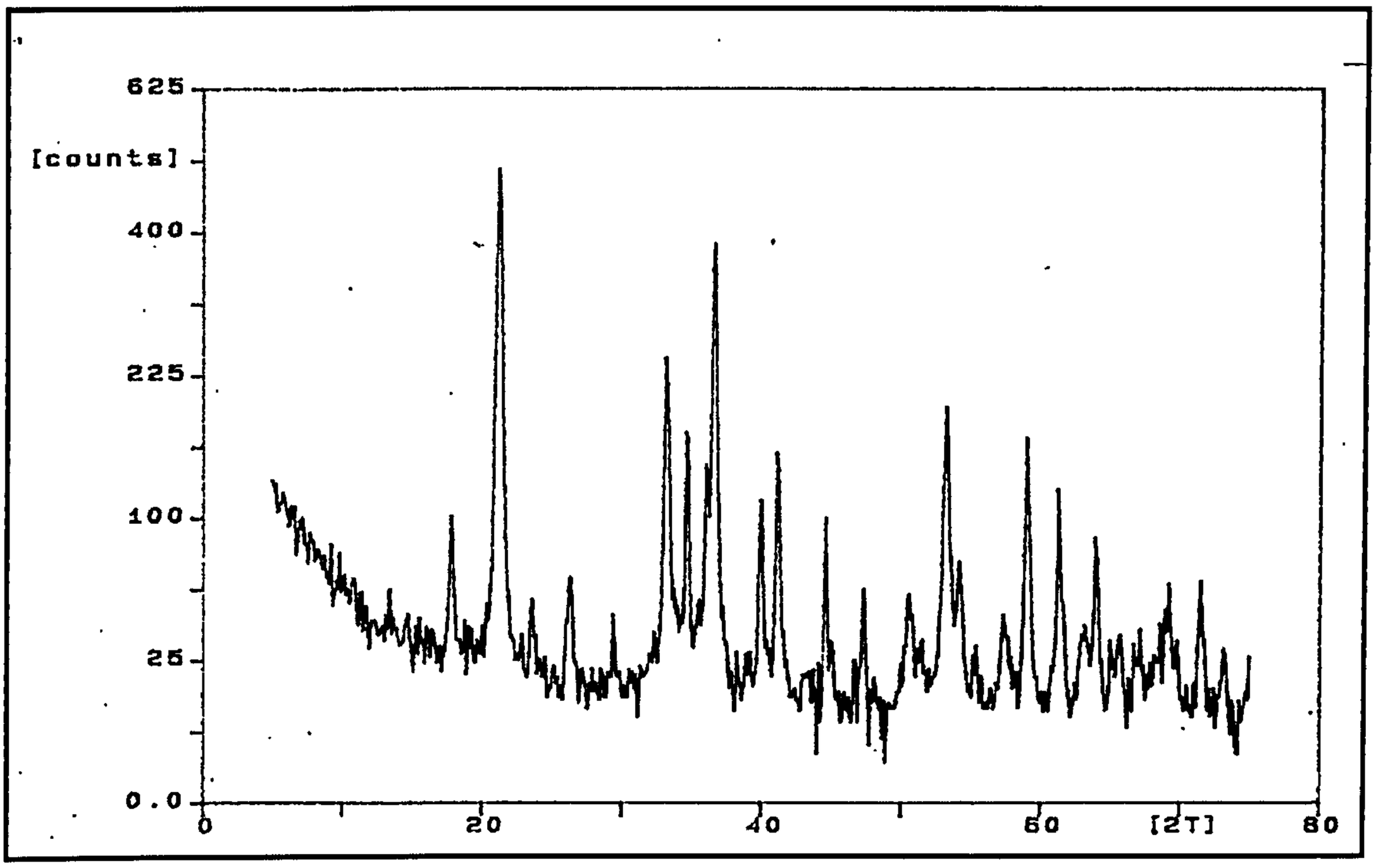


Figure 3.3.b. XRD pattern for Iron II sulphate and lime.

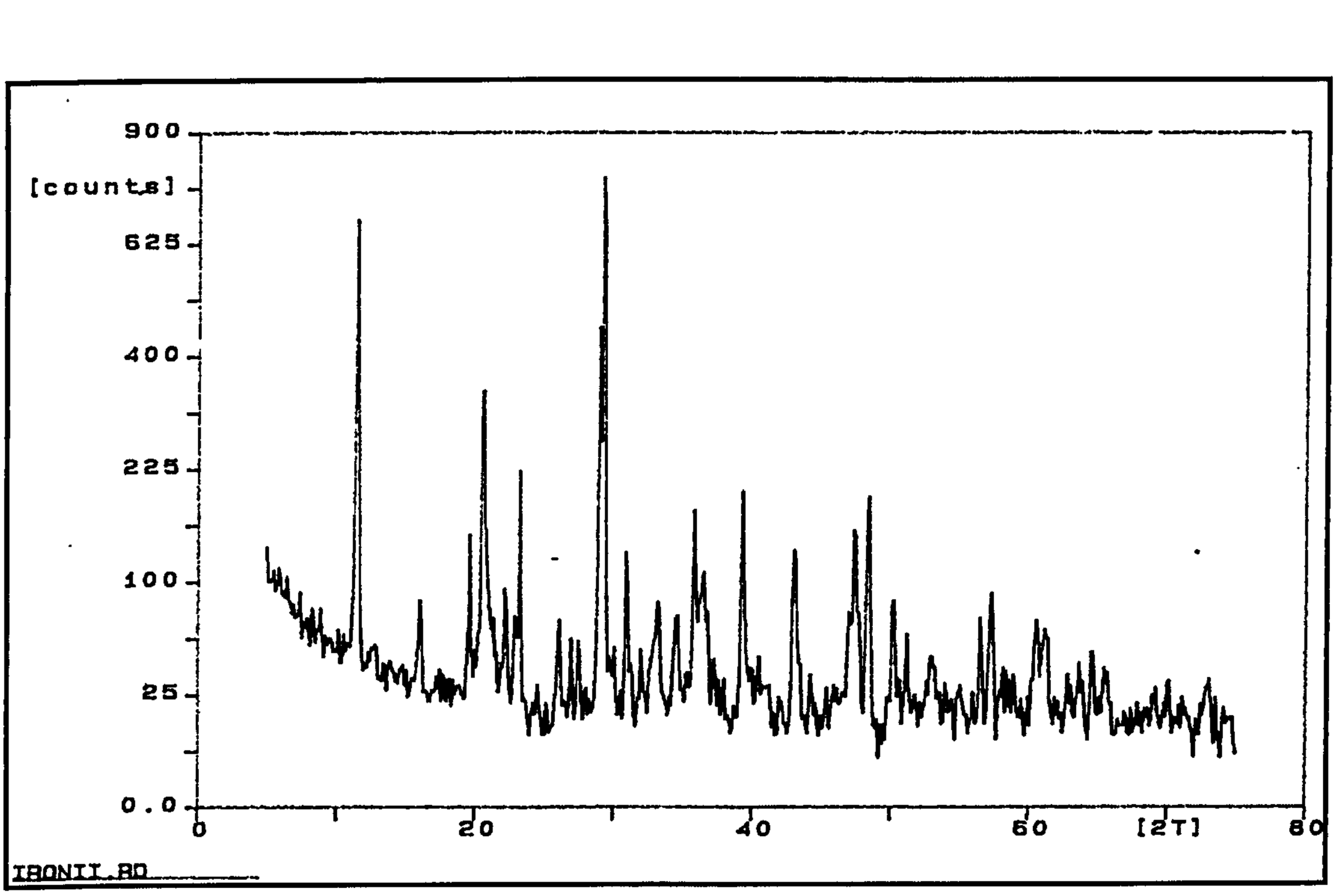


Figure 3.3.c. XRD pattern for Iron III sulphate and lime

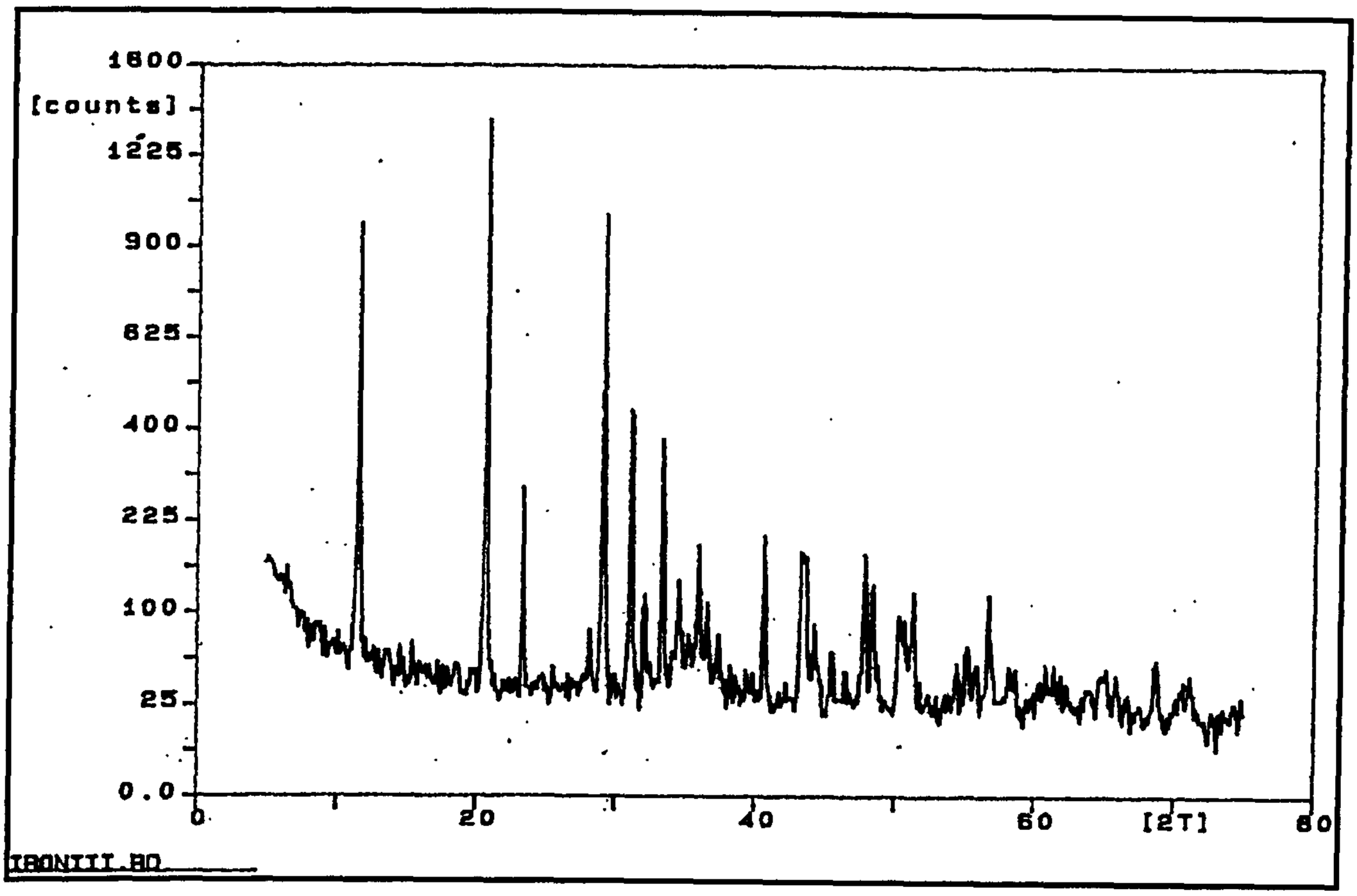


Figure 3.3.d. XRD pattern for Lime.

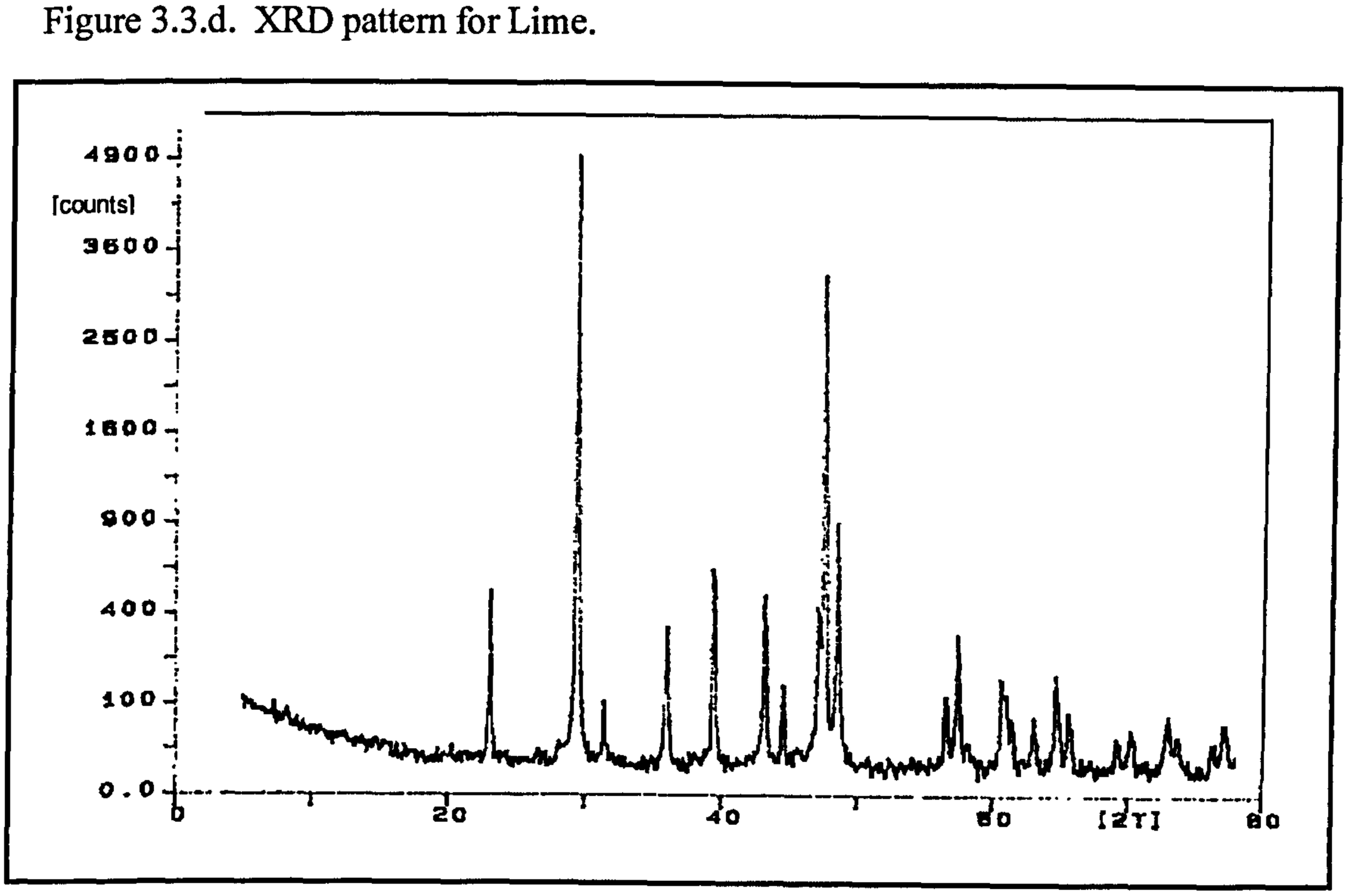


Figure 3.4.a. TGA for Goethite.

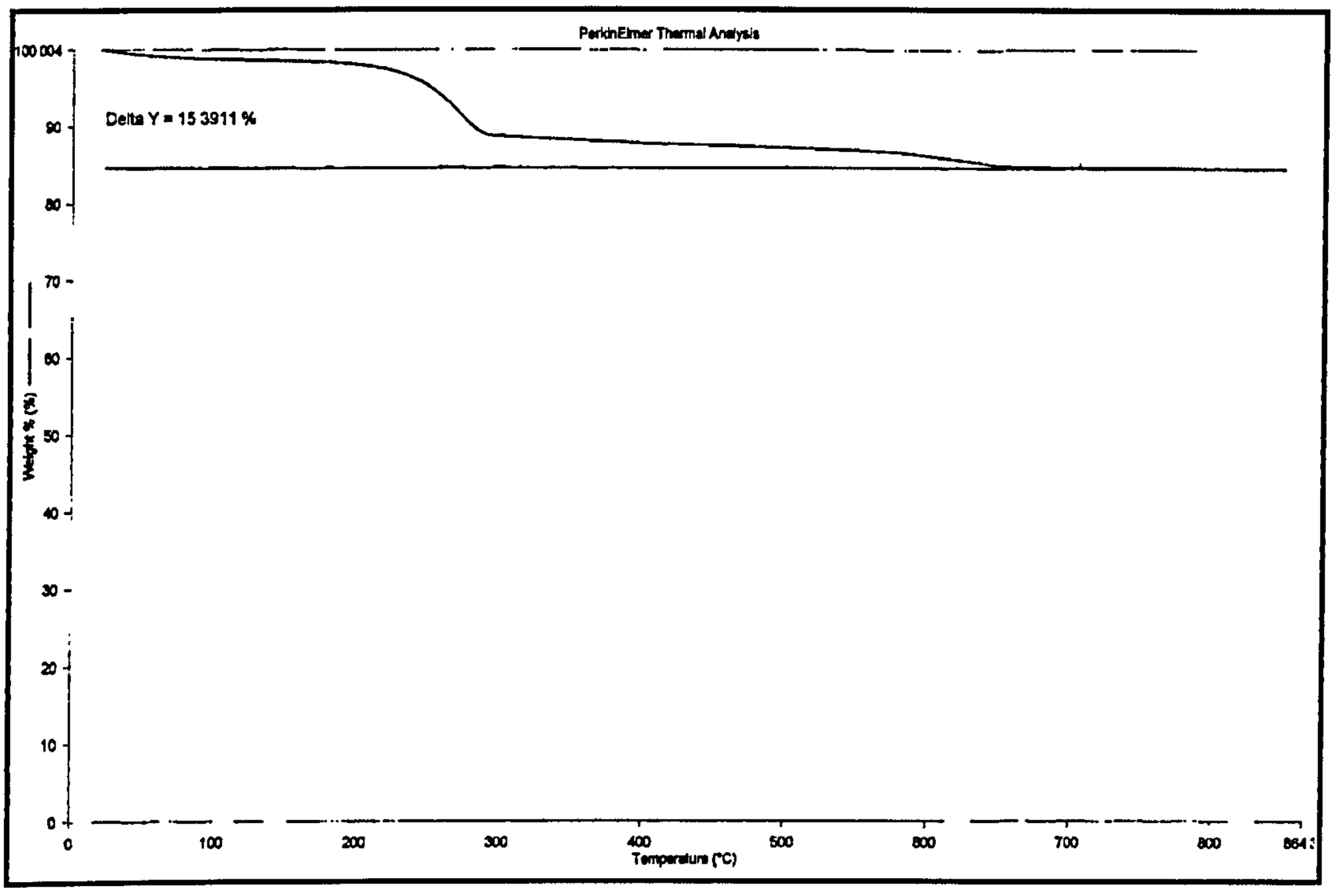


Figure 3.4.b. TGA for Iron II sulphate and Lime

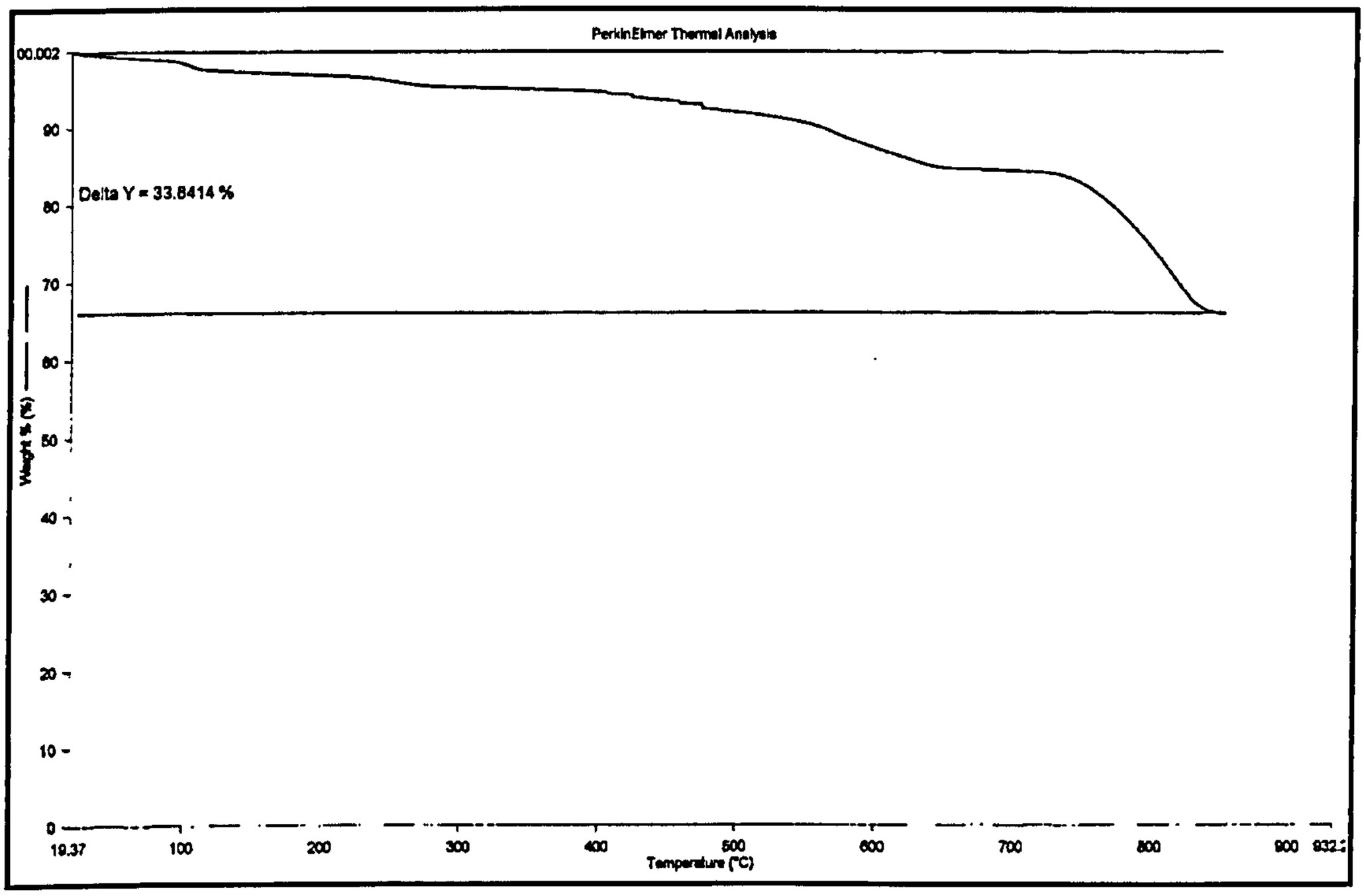


Figure 3.4.c. TGA for Iron III sulphate and lime.

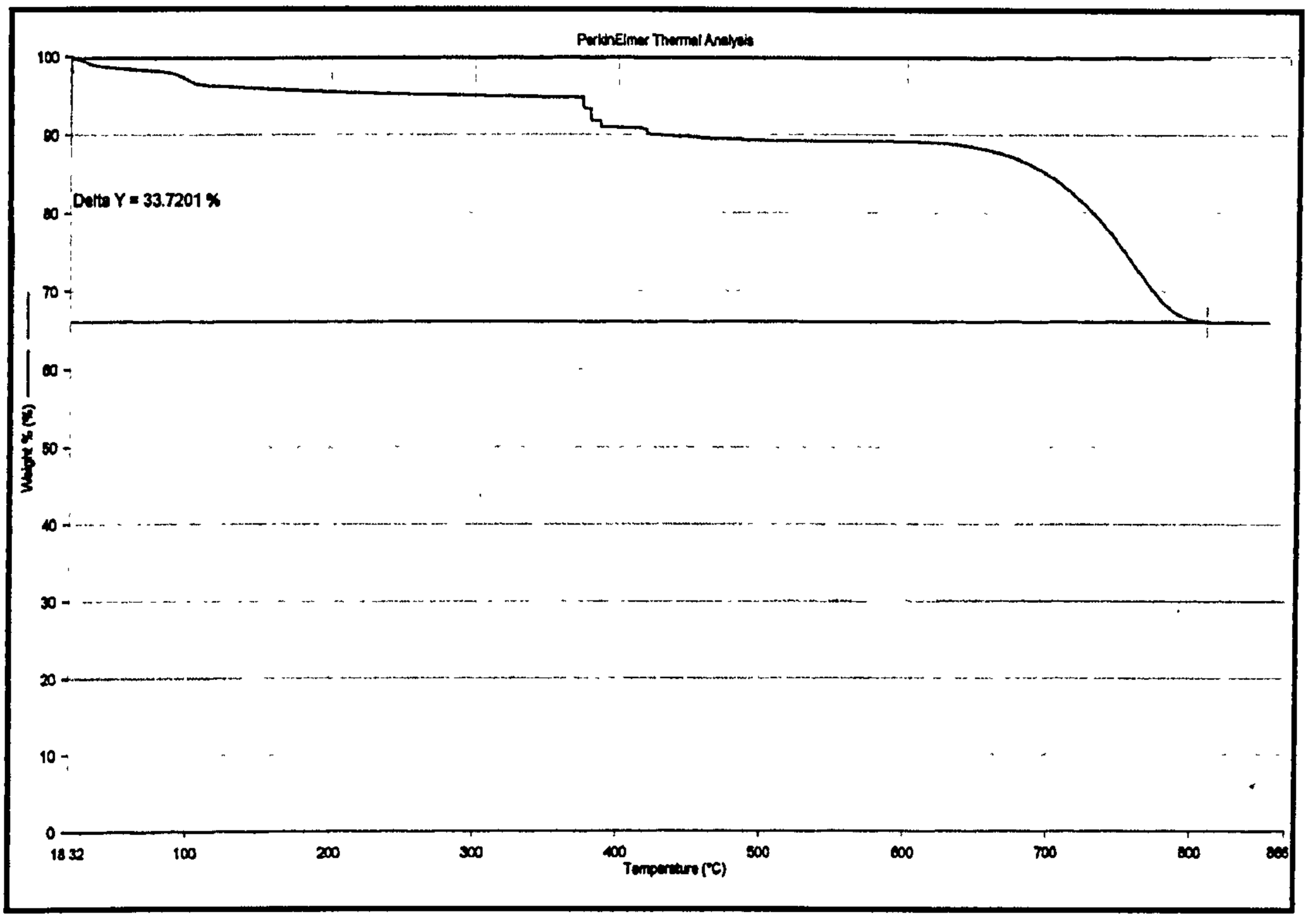


Figure 3.4.d. TGA for Lime.

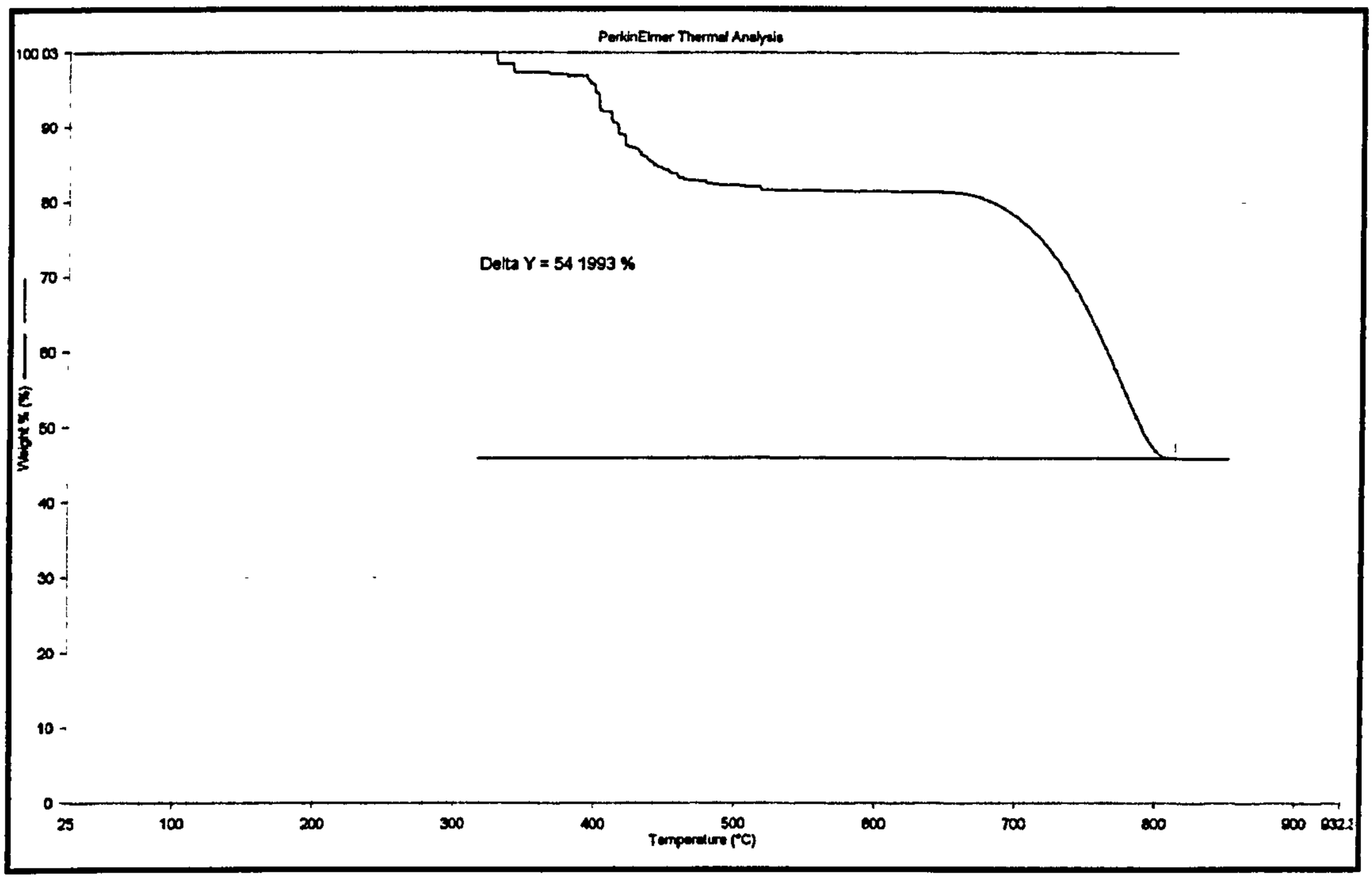


Table 3.1 Specific surface areas for the additives.

Additive	Surface Area (Sq m/g)
Goethite	71.4
Iron Grit	0.30
Iron II Sulphate & lime	18.4
Iron III Sulphate & lime	48.1

Figure 3.5. Adsorption isotherm classification (Modified from Giles *et al.*, 1960)

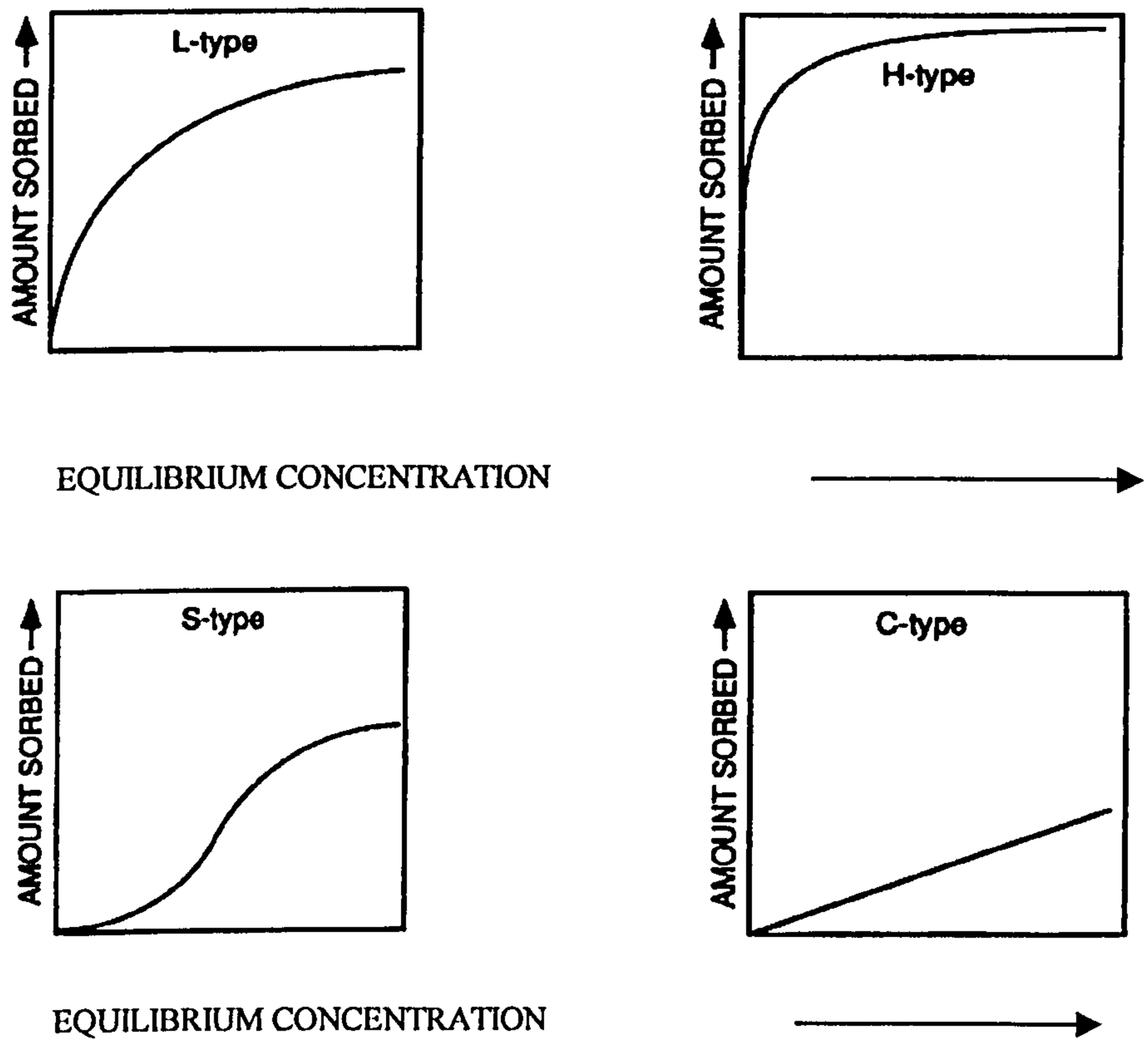


Figure 3.6. Arsenic adsorption onto Iron grit at pH 5 and 9 (n=3).

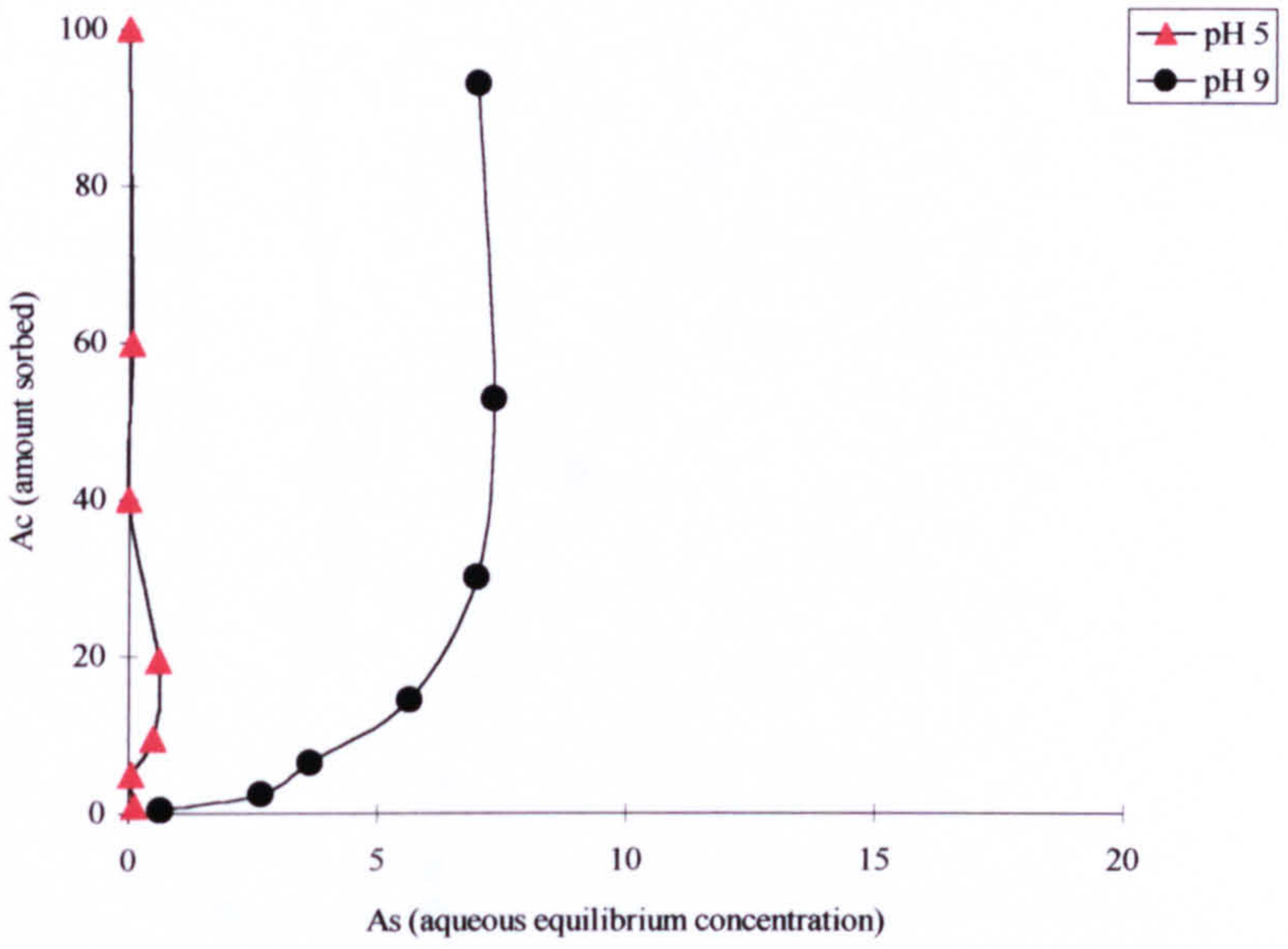


Figure 3.7. Arsenic adsorption onto goethite at pH 5 and 9 (n=3).

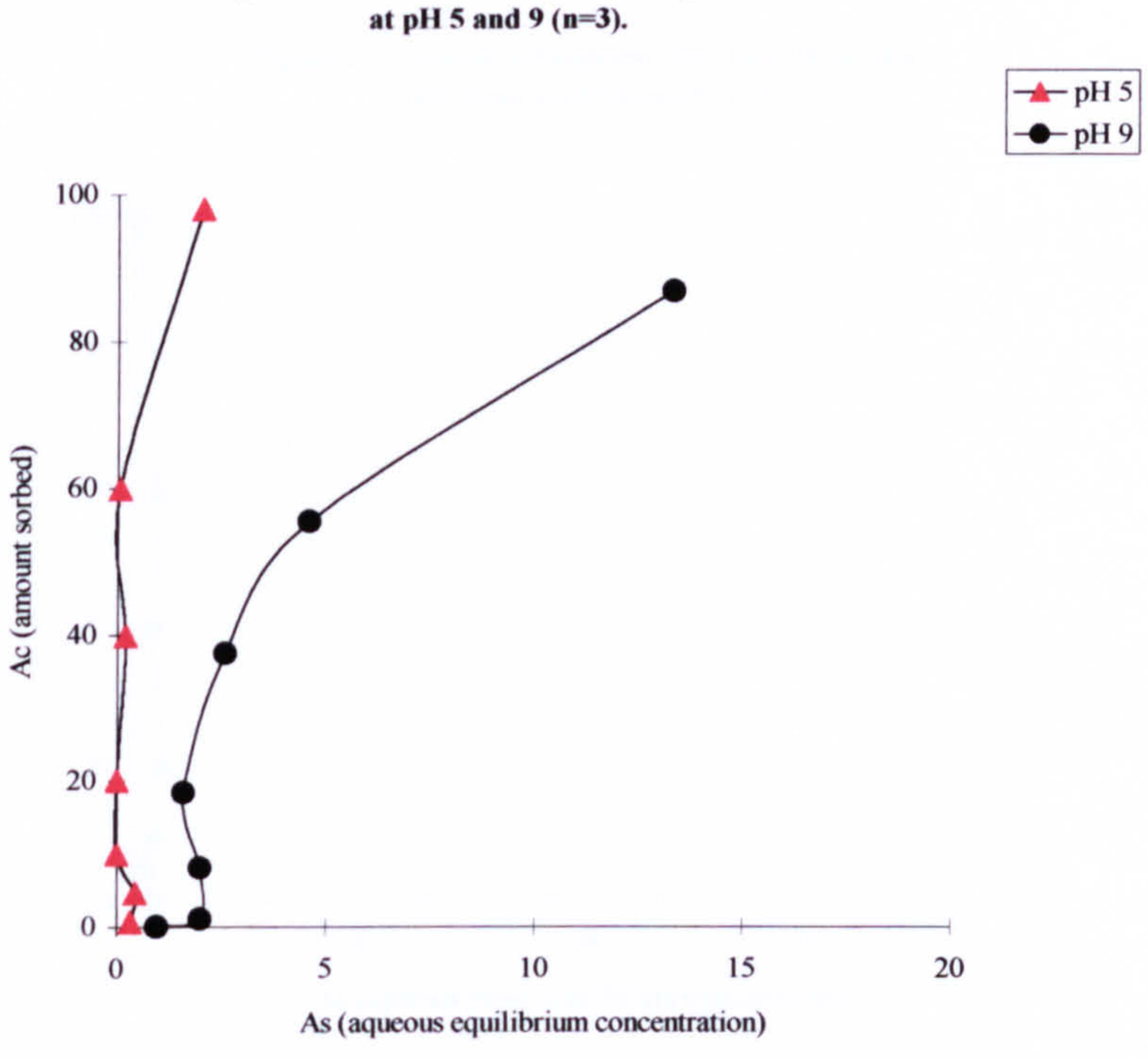


Figure 3.8. Arsenic adsorption onto Iron II Sulphate and Lime at pH 5 and 9 (n=3).

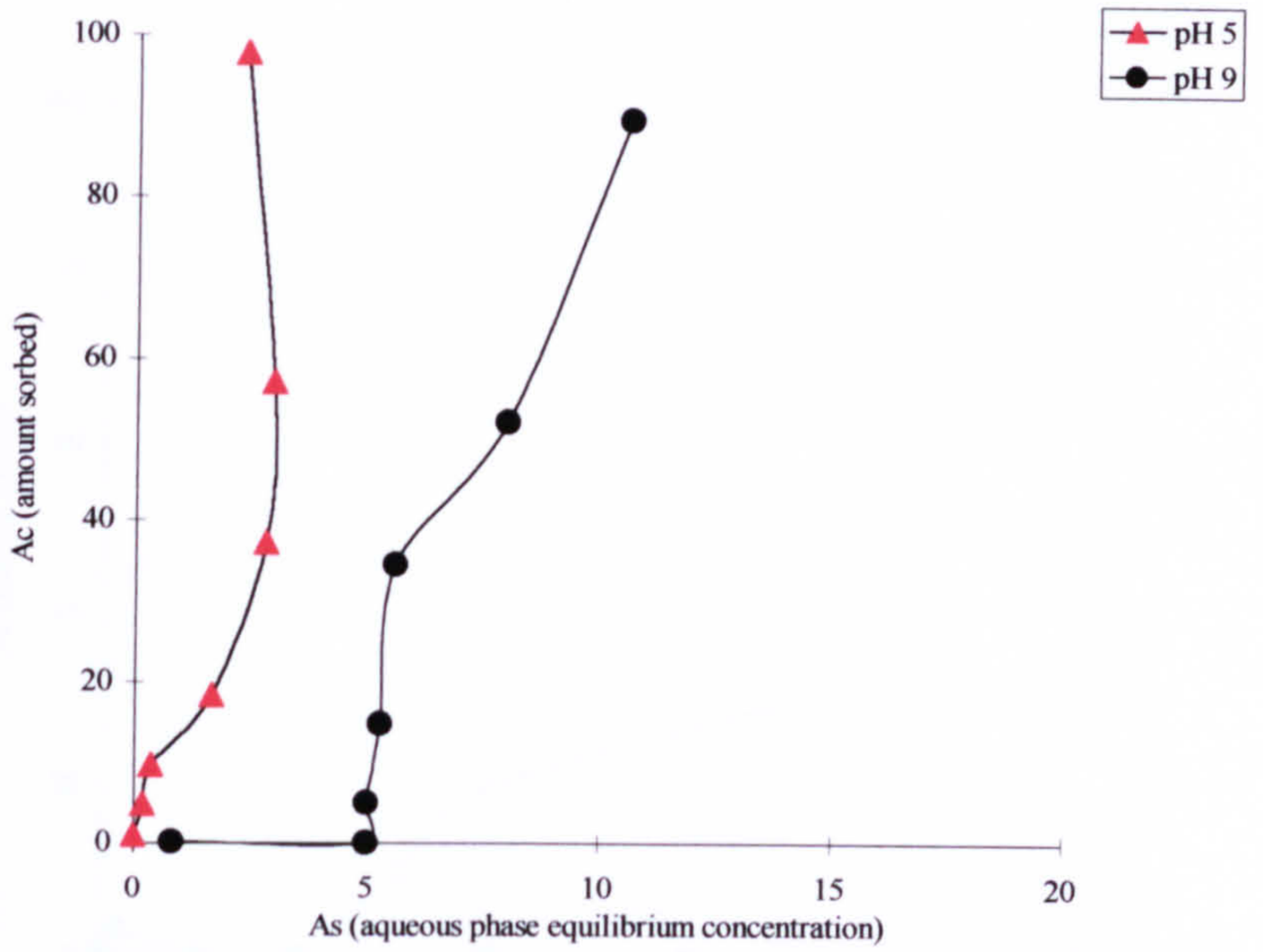


Figure 3.9. Arsenic adsorption onto Iron III Sulphate and Lime at pH 5 and 9 (n=3).

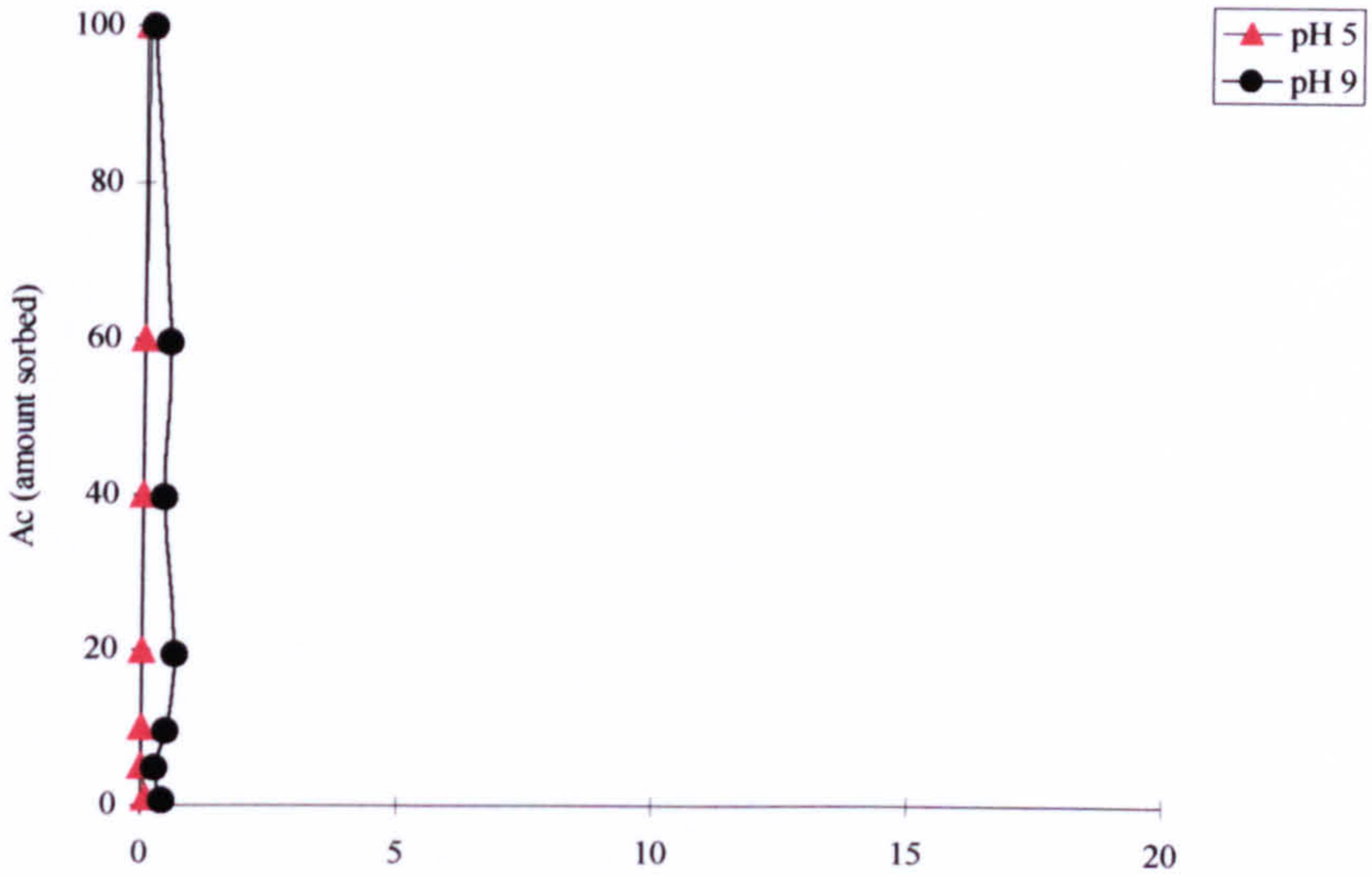


Figure 3.10. Arsenic adsorption onto lime at pH 5 and 9 (n=3).

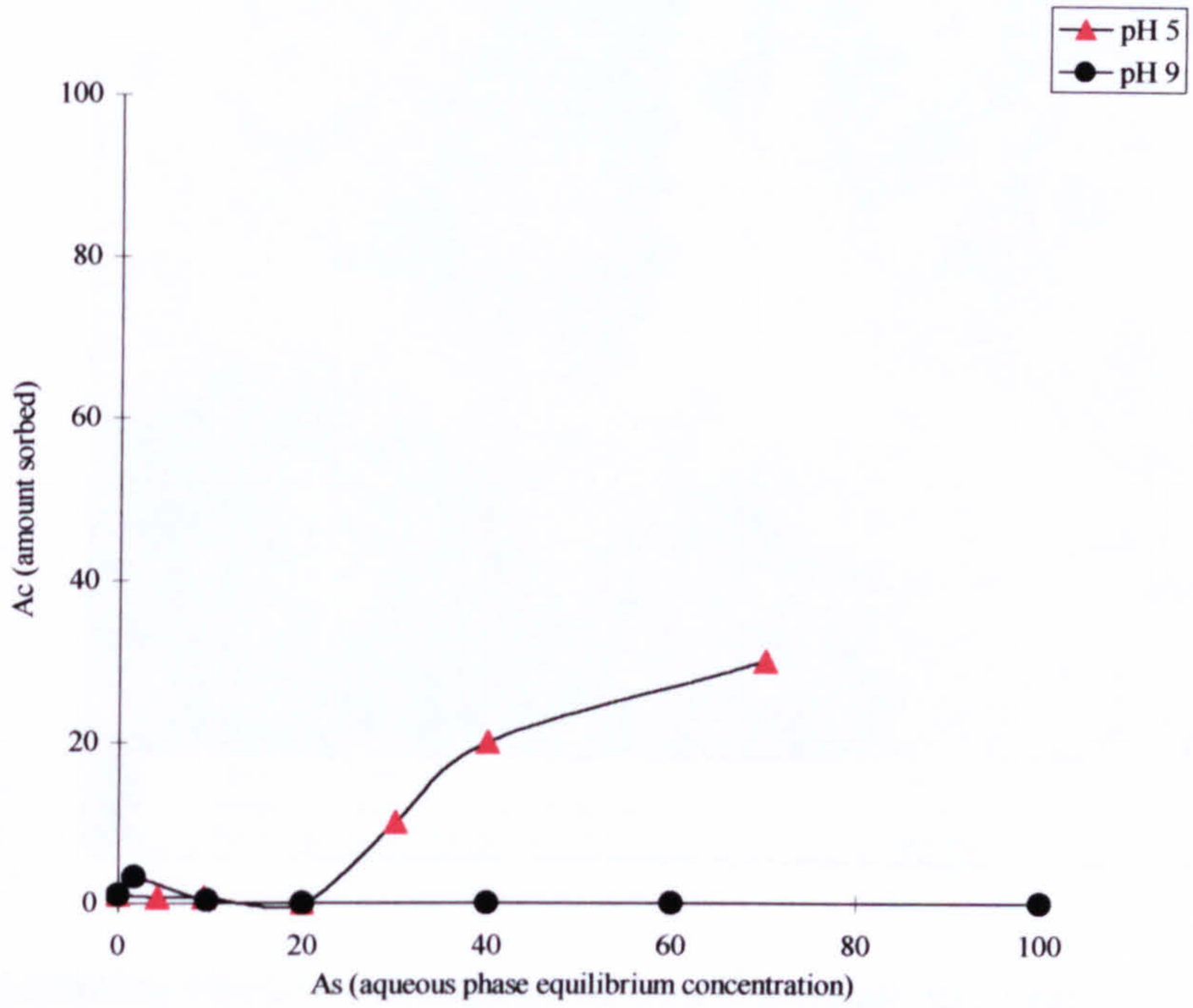


Plate 3.1. Scanning electron micrograph of iron III sulphate and lime, gold sputter coated. Magnification 3500.

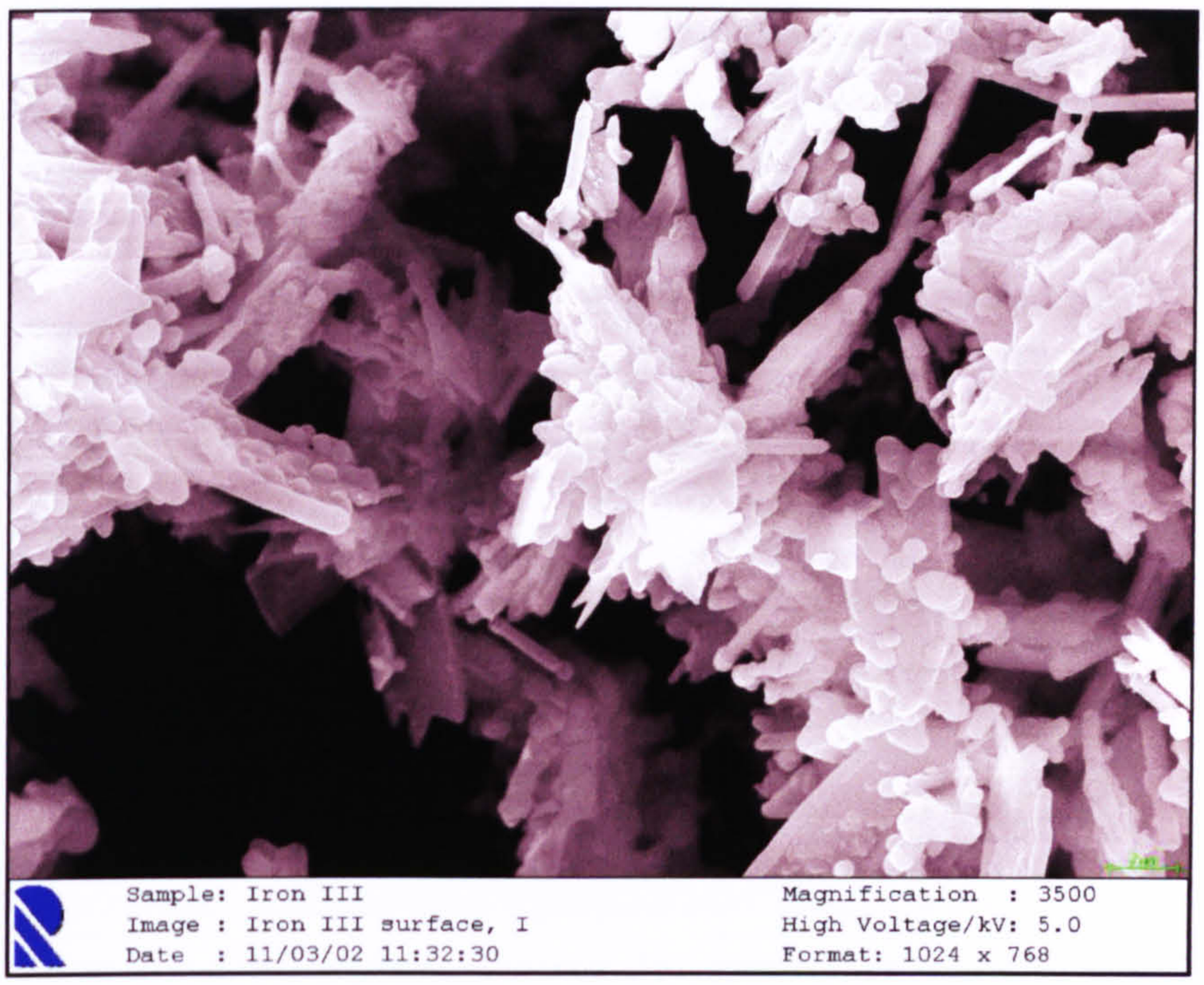


Plate 3.2. Scanning electron micrograph of iron II sulphate and lime, gold sputter coated. Magnification 3500.

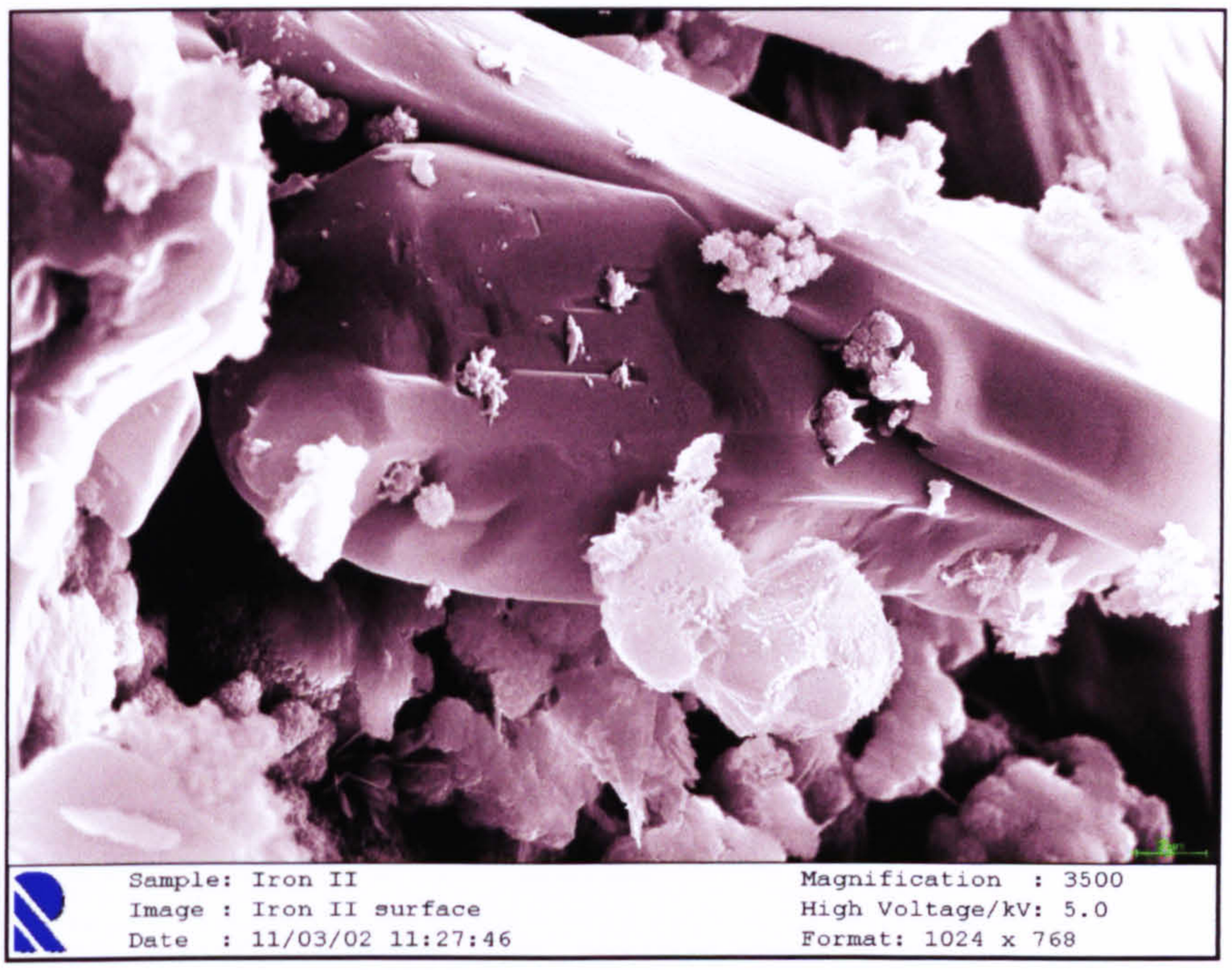


Plate 3.3. Scanning electron micrograph of rusted iron grit, gold sputter coated. Magnification 3500.

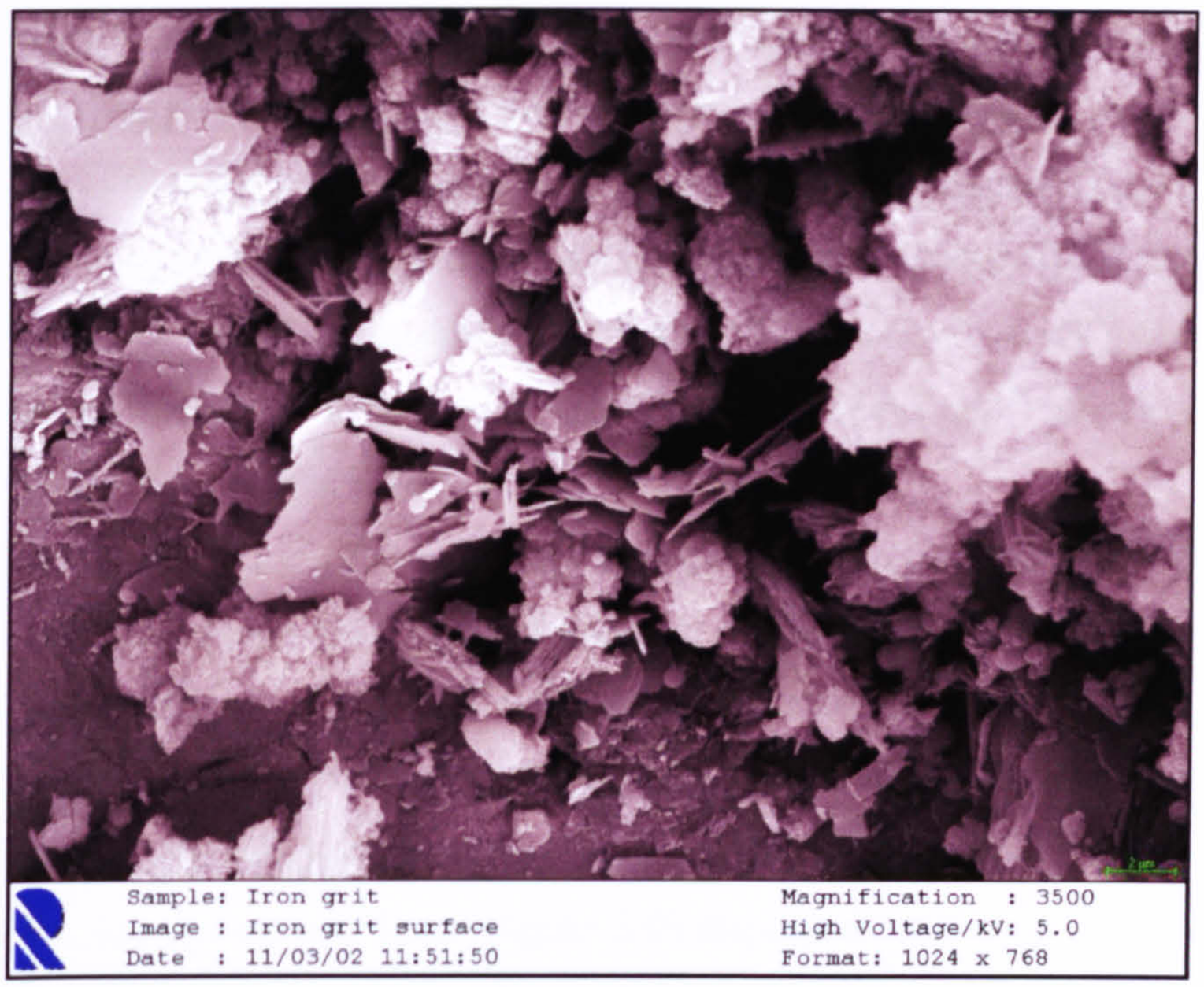
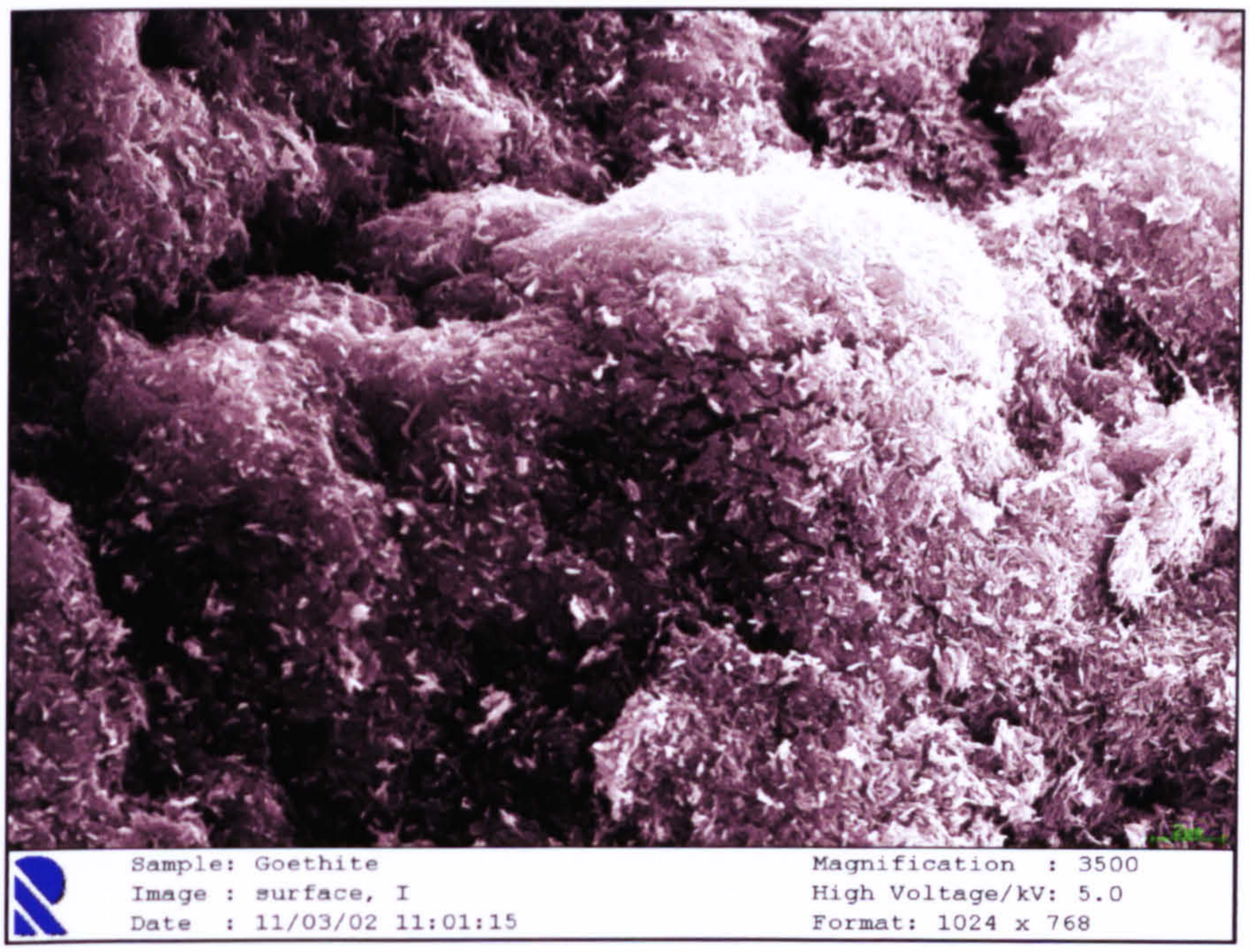


Plate 3.4. Scanning electron micrograph of goethite, gold sputter coated. Magnification 3500.



the Langmuir isotherm (McBride, 1994). The term chemisorption is a collective term for the effect of pure adsorption and also chemical reaction (Sadiq, 1997).

Figure 3.6 shows the adsorption of arsenic onto iron grit at pH 5 and 9. The isotherm constructed at pH 5 displayed a *H-type* curve. This type of curve indicates a very strong adsorbate-adsorbent interaction, i.e. chemisorption (McBride, 1994). The *H-type* curve, with its characteristic large initial slope, is an extreme *L-type* (Langmuir) curve and iron II sulphate, iron III sulphate and goethite also demonstrated this type of isotherm at pH 5 (Figures 3.7 – 3.9). It has been described that the formation of arsenic solid phases in soils may be due to the chemisorption of arsenic oxyanions on solid colloid surfaces, like iron oxide/hydroxides and carbonates (Sadiq, 1997).

At pH 9 the adsorption of arsenic onto iron grit decreased (Figure 3.6). Above pH 8 iron oxide surfaces would play a limited role in the adsorption of arsenic due to their surface charge, which at a low pH is positively charged and at higher pH becomes negatively charged (Sadiq, 1997). Therefore, above pH 8, the negatively charged arsenic oxyanions would be repelled from the iron oxide surfaces and remain in solution. However iron III sulphate and lime (Figure 3.9) displayed the *H-type* isotherm at pH 9, indicating that this iron oxide has an affinity for the negatively charged anions even at this increased pH. As discussed in section 3.4, iron oxides have a point at which their surfaces have a zero charge. This pH_{pzc} may be higher for iron III sulphate, allowing adsorption of arsenic onto its surface even at the higher pH encountered.

Figure 3.10 shows the isotherm constructed from data obtained using lime. The isotherm demonstrated that lime has a limited affinity for adsorption of arsenic especially at higher pH levels. There is however an adsorption effect at the lower pH and this may be the result of arsenic reacting with calcium to form calcium arsenate.

3.8. Conclusions

By constructing adsorption isotherms the effectiveness of the four iron oxides at adsorbing arsenic anions out of solution has been demonstrated. The most effective additives used in the investigation were iron III sulphate plus lime (Figure 3.9), which showed a very high affinity for arsenic at both pH's and iron grit at pH 5 (Figure 3.6).

This study has indicated that iron oxides are effective at adsorbing anions at a relatively low pH but with an increase to more alkaline conditions, adsorption was reduced. The isotherms cannot however be used to prove the adsorption mechanisms involved and must be regarded as curve-fitting models having a predictive capability (Sposito, 1989).

These investigations were model systems, involving a solution containing arsenic. In soils other factors will affect adsorption rates, for example the presence of competing ions such as phosphate. This may affect the iron oxides ability to adsorb arsenic if they are added to a soil containing high levels of fertilizer.

The additives have shown their ability to adsorb arsenic in a model aqueous system, but further studies are required to validate their effectiveness. Their fate in soil forms the subject of the next chapter.

CHAPTER 4.

METAL PARTITIONING AND SPECIATION IN IRON OXIDE-AMENDED SOILS.

4.1. Introduction

The ecotoxicity and mobility of metals in the environment depend strongly on their specific chemical forms or method of binding (Quevauviller, 1998). The definition of speciation may be described by the function of the 'species', for example 'plant available forms', 'exchangeable cations' or 'labile species' (Ure, 1996). That is, the form (physical or chemical) in which the element exists. Chemical speciation is important in environmental systems, because the form and amount of trace elements in a natural system such as soil dictate the behaviour of the trace metal (Davidson *et al.*, 1998). Determination of a chemical species is difficult in soils and sediments and only a few compounds have been accurately determined in sediment (Quevauviller, 1998). Ure (1990), placed speciation into three class types:

i) Functional speciation, the function of the species is defined.
ii) Operational speciation, the isolation procedure defines the species.
iii) Classical speciation, determination of oxidation states or chemical compounds are determined.

For trace element speciation of a soil sample, operational methods are normally utilised, such as sequential extractions, where different reagents partition the analyte content of the sample (Davidson *et al.*, 1999). The availability of metals in soils can depend on many factors, such as organic matter, pH, ion exchange, the plant species (Soon & Bates, 1982; Davies, 1992; Smith, 1994) and the presence of earthworms, whose activities in the soil may change bioavailable metal concentrations (Ma *et al.*, 2000). Sequential extraction schemes have been developed to differentiate between the different metal fractions in a soil sample.

Analysis of a soil using strong acid digest techniques or X-ray fluorescence spectrometry (XRF) is used to assess the 'total' element content of soil and will show the extent of heavy metal pollution accumulated (Ure, 1996). Many studies concerning metal

availability in the environment have concentrated on total metals, implying that all forms will have equal impact (Tessier *et al.*, 1979). However it is the chemical form of a metal that will determine its behaviour and mobilisation in the soil environment (Ramos *et al.*, 1994). Therefore, the total metal content of soil is not a reliable indicator of those metal concentrations that are available for plant uptake, as only a small proportion will be actually available (Davies, 1992). To understand the chemistry of heavy metals and their interaction with soil components such as clay minerals, organic matter and the soil solution, or to determine their availability to plants, the usual approach is to use selective chemical extractions (Ure, 1996). The uptake of metals by plants has become an environmental concern, because accumulation of metals in plants is a process by which they can enter the food chain (Zhang *et al.*, 1998).

By using a sequential extraction scheme such as that developed by Tessier and co-workers (1979), various extractants with increasing chemical action can be applied to a soil sample to partition metals in that sample into definable chemical forms. The information collected can be used to predict metal leaching rates, bioavailability and transformations that may occur within the soil system (Salomons and Forstner, 1980). Therefore complex information about the origin of metals, their mode of occurrence, mobilisation and transport, plus biological and physiochemical availability can be assessed (Tessier *et al.*, 1979). The chemicals used allow metal distribution to fall into five distinct stages. Tessier and co-workers selected each of these fractions that were likely to be affected by various environmental conditions (see below).

There are limitations to the extraction procedures, which have been questioned by a number of investigators. Shan and Chen (1993) showed that one of the limitations to Tessier's method was that none of the elements were completely and fully selectively removed due to elemental redistribution. However Zhang and co-workers (1998) compared Tessier's method with that of the Community Bureau of Reference (BCR) sequential extraction procedure. From their work it was determined that there was no significant difference between results obtained from the two methods for evaluating plant availability of the given soil metals.

As a result of their poor selectivity and re-adsorption problems, sequential extraction techniques cannot be used to determine specific geochemical associations, but they are still important for the assessment of land contamination (Davidson *et al.*, 1998).

The reagents employed in the extraction schemes are used to estimate the potentially available metal concentrations (Kheboian and Bauer, 1987). They include up to five extractants and follow a general protocol.

For the initial stage of the extraction, sodium or ammonium acetate or magnesium chloride (adjusted to pH 7) is added to the soil sample. These solutions affect the adsorption of trace metals in the exchangeable fraction of the soil by acting on the ion-exchange sites and displacing the ions in the sample. For example, changes in the ionic composition of water may affect sorption-desorption processes.

The second stage applies sodium acetate acidified to pH 5 with acetic acid. These reagents affect metals bound to carbonates and will dissolve a metal carbonate phase (Kunze, 1965; McLaren and Crawford, 1973). It has been shown that trace metals are associated with sediment carbonates (Gupta and Chen, 1975).

At stage three, hydroxy ammonium chloride in 25% acetic acid is added to the sample. This solution attacks metals bound to iron and manganese oxides. These exist as nodules, concretions, and cements or as a coating on particles. Oxides are efficient scavengers of heavy metals, but are thermodynamically unstable in anoxic conditions (i.e. low Eh).

Stage four consists of hydrogen peroxide and ammonium acetate. Hydrogen peroxide that has been acidified with nitric acid is used as a strong oxidising agent. These reagents will attack metals bound to organic matter and sulphides. It has been recognised that heavy metals may bind to various types of organic matter (i.e. humic and fulvic acids) and this is due to its properties such as peptisation and complexation (Tessier *et al.*, 1979). In natural waters organic matter can be broken down under oxidising conditions to release soluble trace metals (Tessier *et al.*, 1979).

The final stage of an extraction procedure is the addition of hydrochloric acid (HCl), nitric acid (HNO_3) and hydrofluoric acid (HF) to the sample. Concentrated acid affects the residual fraction and with the removal of the first four fractions this stage will contain the silicates and minerals that have held trace metals within their crystal structures. Under normal environmental conditions, these metals would not be released into solution, and would not be available for plant uptake. The use of strong acid is required to dissolve the silicate fraction that the previous reagents were too weak to achieve.

The first four stages of the extraction procedure are most important with regard to the mobility of trace metals in the soil solution and therefore their availability to plants. Changes in the chemistry of a soil may affect the metals bound in these fractions and therefore will determine their bioavailability. The use of strong acid extractants are useful to determine the total metal content of a soil, but cannot be applied in terms of the mobility of metals under natural conditions.

Until now most of the work done with sequential extractions has been employed for speciation of copper (Cu), chromium (Cr), lead (Pb), zinc (Zn) and nickel (Ni) in soil samples. It is necessary to understand how trace metals / metalloids are held within a soil system, especially one that has been remediated, as this information will determine the bioavailability of the elements after the addition of amendments to the soil. This information can then be applied to the remediation of the contaminated site.

The sequential extraction scheme developed by Tessier and co-workers (1979) was selected because of its wide application to metal partitioning in soils. By applying the sequential extraction scheme, the aim was to consider arsenic partitioning in three contaminated soils. The resulting fractionation would determine the effectiveness of the iron oxide amendments applied to the soils in order to reduce arsenic mobility.

4.2. Experimental

4.2.1. Preparation of reagents.

$MgCl_2$ (203.30 g, A.R.) was dissolved in deionised water and transferred to 1 litre volumetric flask. Solution pH was adjusted to pH 7.0.

CH_3COONa (82.03 g, A.R.) was dissolved in deionised water and transferred to 1 litre volumetric flask. Solution pH was adjusted to pH 5 by adding a few drops of 1 M acetic acid.

$NH_2OH.HCl$ (2.78 g, A.R.) in 25% CH_3COOH w/v was dissolved in deionised water and transferred to 1 litre volumetric flask. Solution pH was adjusted to pH 5 by adding a few drops of 1 M acetic acid.

CH_3COONH_4 (246.7 g, A.R.) was dissolved in deionised water and transferred to 1 litre volumetric flask.

HNO_3 (conc. A.R.), was purchased from Aldrich.

H_2O_2 (30% w/v), was purchased from Aldrich.

All other reagents were obtained from Merck, Poole, Dorset, UK.

4.2.2. Preparation of soil samples.

Soil samples collected from three areas of arsenic contamination, namely Kidsgrove (canal dredgings), Rixton clay pits (coal fly ash) and Merton Bank (landfill) (See Chapter 2 for details) were air-dried in the laboratory. The soils were ground in a mortar and pestle then sieved to a particle size of < 4 mm diameter. Soil background edaphic factors were analysed prior to this investigation using the methods outlined in Chapter 2 together with the total metal concentrations for each soil, which were obtained using XRF and nitric acid-extractable microwave digestion techniques. The results are

presented in tables 4.1 to 4.4. 100g of soil was placed in a (500ml) polyethylene container. Appropriate amendments were added at a rate of 1% w/w and mixed thoroughly to homogenise. The soil was then moistened to field capacity with deionised water. The soils plus amendments were then allowed to stand for one month at field capacity and room temperature in the polyethylene containers to allow iron oxides to form. The amendments added were lime, goethite, iron grit, iron II or iron III sulphate plus lime.

Table 4.1. Background edaphic factors. (Mean values for soil analysis, n=3, values in brackets represent the standard deviations).

Soil	pH	Moisture (%)	Organic matter (%)
Rixton	8.19 (±0.02)	11.95 (±6.87)	7.66 (±0.92)
Kidsgrove	7.40 (±0.03)	13.27 (±0.69)	15.40 (±0.94)
Merton Bank	6.47 (±0.09)	8.81 (±0.04)	14.00 (±1.07)

Table 4.2. XRF total iron, calcium and sulphur present in the contaminated soils. (Mean values for soil analysis (n=3), values in brackets represent the standard deviations).

Soil	Fe (%)	Ca (%)	S (%)
Rixton	6.88 (±0.29)	1.137 (±0.19)	0.1477 (±0.014)
Kidsgrove	18.88 (±0.15)	1.096 (±0.04)	0.234 (±0.006)
Merton Bank	3.544 (±0.94)	2.484 (±1.77)	0.379 (±0.006)

Table 4.3. XRF total metal concentrations (μg g^{-1}) (n=3, values in brackets represent the standard deviations).

Soil	Total metal concentrations (μg g^{-1})				
	Zn	Pb	Cu	Cd	As
Rixton	249.4 (±88.5)	128.86 (±16.2)	147.9 (±13.1)	5.73 (±1.19)	98.33 (±7.9)
Kidsgrove	1837.66 (±61.2)	336.33 (±15.9)	141.03 (±8.1)	1434 (±120)	361.16 (±40.9)
Merton Bank	170.7 (±53.9)	1412.1 (±1106.1)	222.8 (±122.6)	30.0 (±0)	778.4 (±408.6)

Table 4.4. Nitric acid-extractable total metal concentrations (μg g^{-1}) (n=3, values in brackets represent the standard deviations).

Soil	Total metal concentrations (μg g^{-1})				
	Zn	Pb	Cu	Cd	As
Rixton	32.5 (±2.40)	127.3 (±1.44)	68.7 (±2.84)	0.83 (±2.00)	78.01 (±15.53)
Kidsgrove	508.3 (±16.56)	259.3 (±18.01)	114.1 (±0.40)	36.2 (±2.00)	59.53 (±6.91)
Merton Bank	101.7 (±40.17)	359.5 (±124.10)	117.9 (±33.36)	1.65 (±0.34)	71.96 (±9.48)

4.2.3. Extraction procedure.

All stages of the extraction procedure were carried out in the centrifuge tube to minimise soil loss. The soil residues were washed with deionised water (10 cm^3) and shaken on a Griffin flask shaker for a period of 15 minutes, followed by centrifugation to remove any reagent left in the residue after each stage of the procedure.

4.2.3.1. Stage 1: Magnesium chloride

Each soil sample (2.000 g) was weighed into 50 cm^3 centrifuge tubes. To these were added $MgCl_2$ (8 cm^3, 1 M, pH 7.0). The mixture was then shaken at 25°C on a Griffin flask shaker. After 1 hour, the aqueous extract was separated from the soil residue by centrifugation (2500 rpm for 5 mins) using a Beckman GP centrifuge. The supernatant was decanted into a screw top polyethylene container (60 cm^3) until analysis.

4.2.3.2. Stage 2: Sodium acetate

CH_3COONa (25 cm^3, 1 M, pH 5) was then added to the soil residue from step 1. The mixture was shaken continuously on a Griffin flask shaker at 25°C. After 5 hours, the aqueous extract was separated from the soil residue as described above.

4.2.3.3. Stage 3: Hydroxy ammonium chloride in acetic acid.

To the residue from stage 2, $NH_2OH.HCl$ in 25% CH_3COOH w/v (20 cm^3, 0.04 M, pH 2) was added. The sample was then heated in a water bath (96 °C). After 6 hours the aqueous extract was separated from the soil residue as previously described.

4.2.3.4. Stage 4: Nitric acid, Hydrogen peroxide and ammonium acetate.

To the residue from stage 3, HNO_3 (3 cm^3, 0.02 M) and H_2O_2 (5 cm^3, 30% w/v) were added. The sample was heated in a water bath (85 °C). After 2 hours H_2O_2 (3 cm^3, 30% w/v) was added for a further 3 hours in the water bath (85 °C). After 3 hours, CH_3COONH_4 (5 cm^3, 3.2 M) was added to the sample and left to stand for 30 minutes

(25°C). The aqueous extract was separated from the soil residue as previously described. Table 4.5 outlines the extraction procedure.

4.2.3.5. Analysis.

Each supernatant was filtered through GF/C fibre glass filter paper to remove any fine suspended particles prior to analysis. The sample was then made up to volume with deionised water. Standards did not require matrix matching for arsenic analysis. Standard Cu, Cd, Zn, and Pb solutions were made up separately for each stage with the appropriate reagent to overcome interferences from the matrix prior to analysis by ICP. All solutions were analysed in triplicate using both standards and blanks in the same matrix.

Table 4.5. Scheme for sequential extraction. (Tessier *et al.*, 1979).

STAGE	FRACTION	REAGENT	VOLUME (CM^3)	CONDITIONS
1	Exchangeable	$MgCl_2$ 1mol L^{-1}	8	Shake for 1 hr @ 25 ^{0}C (pH7)
2	Carbonate-bound	CH_3COONa 1 mol L^{-1}	25	Shake for 5 hrs @ 25 ^{0}C (pH5)
3	Fe- Mn oxides-bound (reducible)	$NH_2OH.HCl$ 0.04 mol L^{-1} in 25% CH3COOH w/v	20	6hrs @ 96^{0}C water bath (pH2)
4	Organic matter-bound (oxidisable)	HNO_3 0.02 mol L^{-1} / 30% H_2O_2 (w/v) + 30% H_2O_2 (w/v) + CH_3COONH_4 3.2 mol L^{-1}	3 5 3 5	2 hrs @ 85^{0}C 3 hrs @ 85^{0}C 30 mins @ 25^{0}C
5[a]	Total	HNO_3 HCl HF H_2O	4 1 2 5	26 mins

[a]Determination of total metal content was performed independently on separate soil samples (see Chap. 2 & Tables 4.3 and 4.4).

4.3. Results and Discussion.

The sequential extraction scheme proposed by Tessier *et al.*, (1979) was applied to the three arsenic contaminated soils (see Chapter 2 for details). In this study the extraction scheme was used to assess the changes in arsenic mobility in untreated and iron oxide-amended soil and to assess the chemical forms of arsenic in the soils upon remediation. The chemical speciation of the predominant metal cations present in the test soils, namely copper, cadmium, zinc and lead were also considered. This was done to evaluate any changes in their mobility and speciation that resulted from the application of potentially arsenic-immobilising amendments. The concentrations of metals and arsenic extracted from the samples would also be affected by soil characteristics such as pH, organic matter content and soil texture.

The addition of iron oxides to all soils resulted in a reduction in arsenic mobility in stage one of the extraction procedure, i.e. the exchangeable metal fraction. In the Kidsgrove soil a 95% reduction was observed for arsenic in iron II amended soil compared to that of the untreated control. Iron II and III amendment of Rixton soil resulted in 94% and 75% reductions in mobile arsenic respectively. Similar results were obtained for the Merton Bank soil, with iron II and III producing 71% and 87% reductions in mobility respectively when compared to the untreated soil. The fact that reductions were observed in this fraction is of importance because it is in this form that the metalloid will be potentially most available to plants and groundwater.

4.3.1 Exchangeable metals

A dilute aqueous solution of magnesium chloride was used to determine the proportion of metals electrostatically bound in the soils. Magnesium chloride liberates exchangeable metals into solution, however ammonium acetate, previously used for this purpose, was discovered to attack metal carbonate complexes (Jackson, 1958; Wagemann *et al.*, 1977). This gave unusually high results for freely available ion exchangeable metal ions. Stage one of the extraction scheme liberated the most mobile metals present in the soils and its neutral pH would not affect the availability of those metals.

With the exception of Kidsgrove soil (Figure 4.1), arsenic present in the freely exchangeable form was observed to show the lowest concentrations when compared to the other fractions. Arsenic present in a soil may, depending on soil factors such as pH, soil texture or the presence of iron oxides, show limited mobility in this labile form. The soils in the investigation would have had a high redox potential and arsenic would have been present as arsenate. Arsenate displays an anionic nature that provides strong sorption in soils (Onken & Adriano, 1997). The greater concentration of arsenic found in the Rixton soil extraction (Table 4.6), compared to the other soils, may be due to the nature of the substrate, in that arsenic was liberated more in sandy soil and so leaching would have occurred more readily into the soil solution. It has been identified that arsenic mobility is of the order: sandy loam > silty clay loam > silty clay > clay (Fuller, 1978).

The mobility of zinc was found to be very low in this fraction and as will be discussed later was found to be associated strongly with another fraction. Lead however was observed to be highly mobile in the exchangeable fraction with the greatest percentage found in this stage compared to the other fractions (Figures, 4.7, 4.11 & 4.15). The addition of iron oxides had little effect immobilising this metal in soil and an increase in lead (mg/Kg) was observed in the exchangeable fraction in the presence of these additives (Table 4.10).

Both copper and cadmium were found to be highly mobile in this fraction (Figures, 4.4, 4.5, 4.8, 4.9, 4.12 & 4.13) for all soils. Cadmium has been shown to have a relatively high soil-plant concentration ratio (Jackson and Alloway, 1992) and this was reflected in the high concentrations observed in the exchangeable form.

4.3.2 Carbonate bound metals

Sodium acetate solution, acidified to pH 5, was used to release those metals bound to carbonates. A high percentage of arsenic was found associated with the carbonate fraction in lime-amended Kidsgrove soil (Figure 4.1). The carbonate fraction was observed to contain the second highest concentration of arsenic (the highest concentrations were found in stage three) in all the soils studied (Table 4.6). Lindsay (1979) discovered that carbonate minerals may be important in the adsorption of arsenic in alkaline soils, especially calcareous soils, but where unstable in acidic soils. It has been

identified that, after the exhaustion of iron, arsenic adsorption will be controlled by calcium levels in calcareous soils (Woolson *et al.*, 1971). The carbonate fraction may therefore have an important adsorption role in alkaline soils, as Parks (1967) demonstrated that calcium carbonates have an isoelectric point of between 7 and 10.

In Kidsgrove soil treated with lime, 347.74 ppb arsenic was extracted in stage 2, and adsorption of arsenic may be controlled by the carbonate fraction in this particular case. Table 4.6 shows that in the other soils treated with lime, an increase in extracted arsenic was observed.

The concentrations of copper, cadmium, zinc and lead were all relatively low in this fraction. However in Merton Bank soil, lead levels were increased when compared to the other extraction stages (Figure 4.15).

4.3.3 Metals bound to Iron and Manganese oxides.

There is a plethora of evidence in the literature, which demonstrates that iron oxide surfaces are involved with the adsorption of arsenic (Bowell, 1994; Khaodhiar *et al.*, 2000; Lumsdon *et al.*, 1984; Lombi *et al.*, 1999; Pierce and Moore, 1982; Sun and Doner, 1998; Wilkie and Hering, 1996). This stage of the extraction procedure released metals bound to iron and manganese oxides. Figures 4.1- 4.3 show that arsenic was largely bound to this fraction in all three soils. Adsorption of arsenic onto iron oxide surfaces is dependant on surface charge, with higher pH favouring a negative charge and lower pH producing a positive charge on these surfaces (Sadiq, 1997). The pH's of the three soils are presented in Table 4.1. Soil pH's were all below 8.6, which is the threshold at which the iron oxide surfaces are expected to be positively charged, and so capable of adsorbing arsenic oxyanions (Sadiq, 1997).

It was observed that addition of lime to either Rixton or Merton Bank soil resulted in a greater concentration of arsenic adsorbed on the iron oxide fraction in these soils (Table 4.6). An increase in soil pH caused by the addition of lime will have mobilised arsenic into solution, which may then have been re-adsorbed onto the available iron oxide surfaces.

Zinc was found to be mostly associated with this fraction. In strongly alkaline soils, zinc-hydroxy anions may form to increase solubility (McBride, 1994). The

Figure 4.1. Partitioning of arsenic in Kidsgrove soil using the Tessier sequential extraction method (n=3).

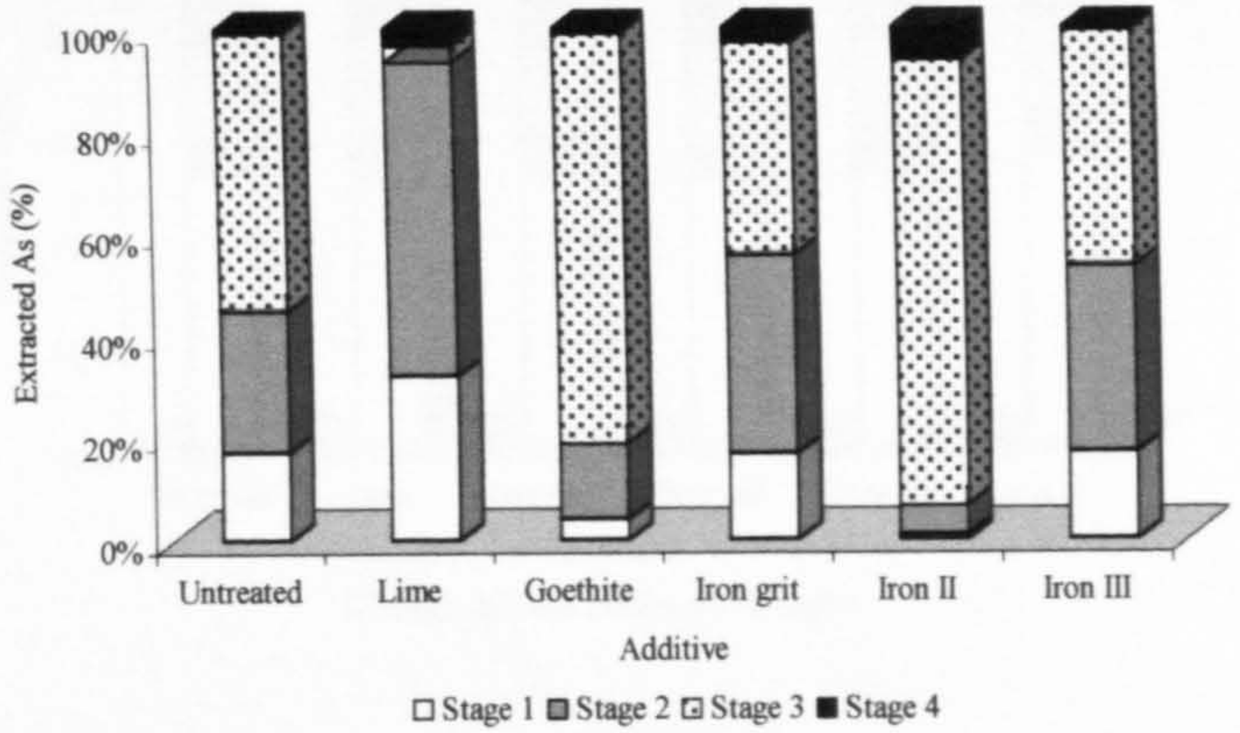


Figure 4.2. Partitioning of arsenic in Rixton soil using the Tessier sequential extraction method (n=3).

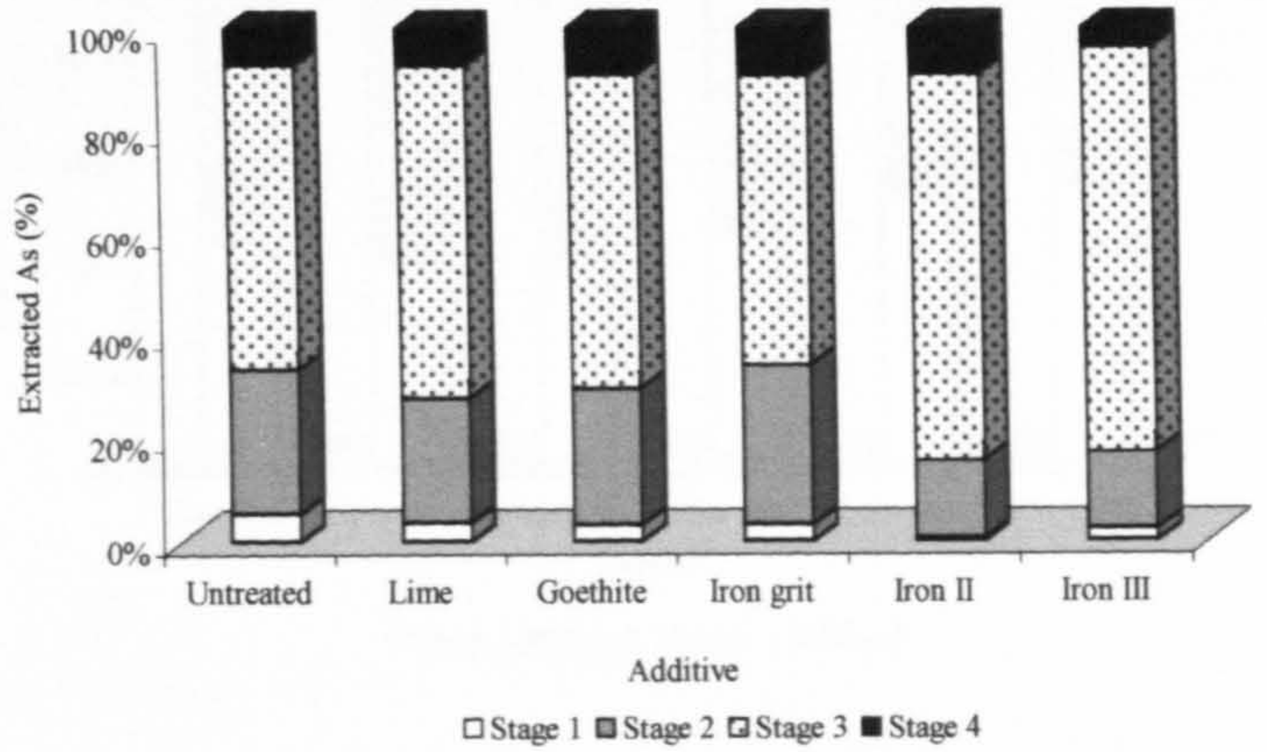


Figure 4.3. Partitioning of arsenic in Merton Bank soil using the Tessier sequential extraction method (n=3).

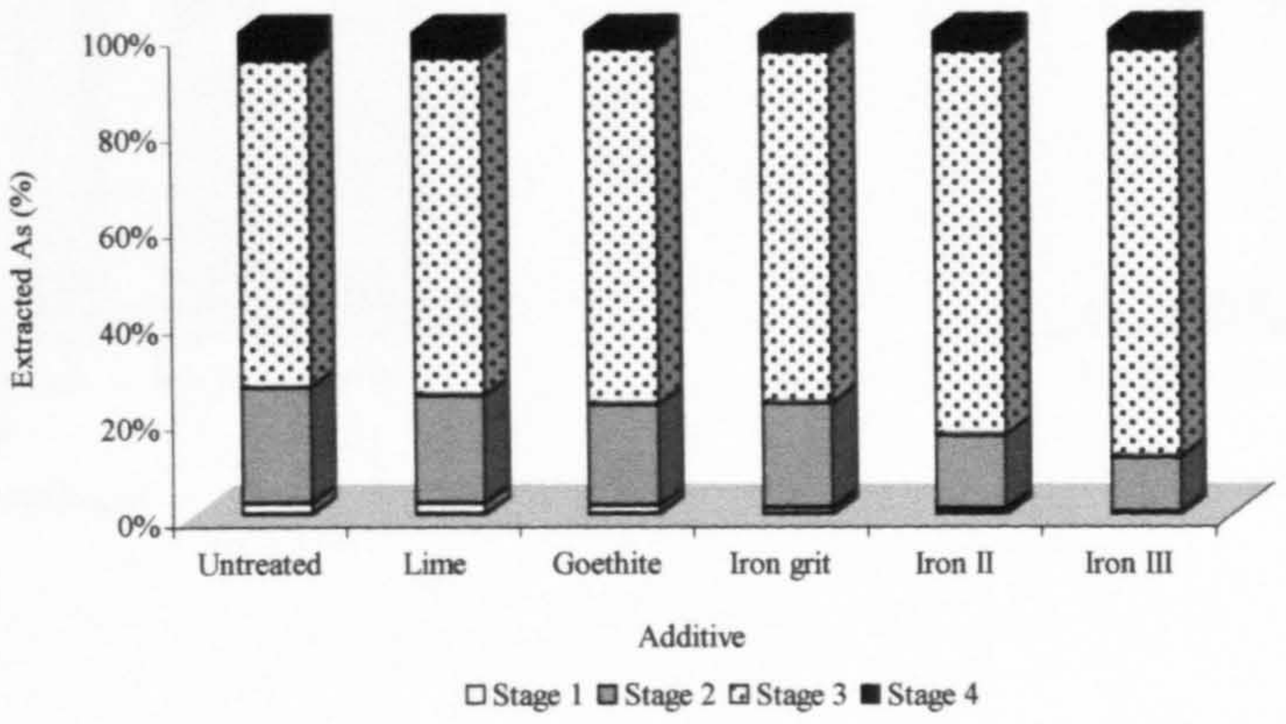


Figure 4.4. Partitioning of copper in Kidsgrove soil using the Tessier sequential extraction method (n=3).

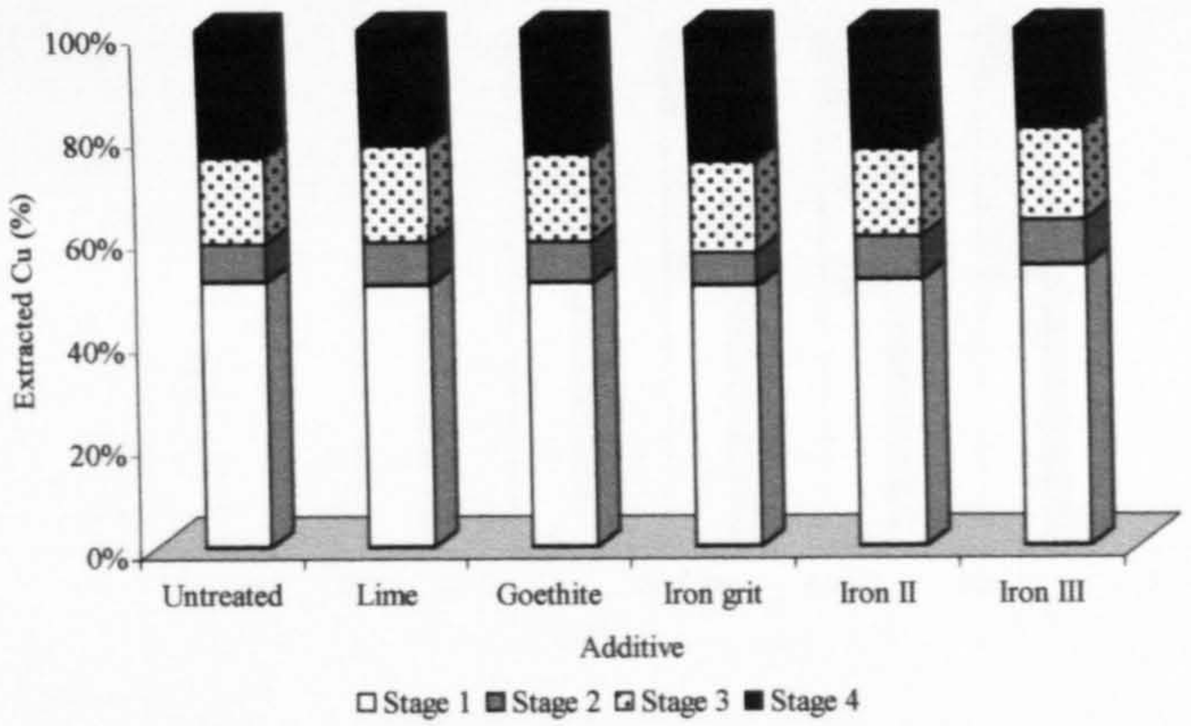


Figure 4.5. Partitioning of cadmium in Kidsgrove soil using the Tessier sequential extraction method (n=3).

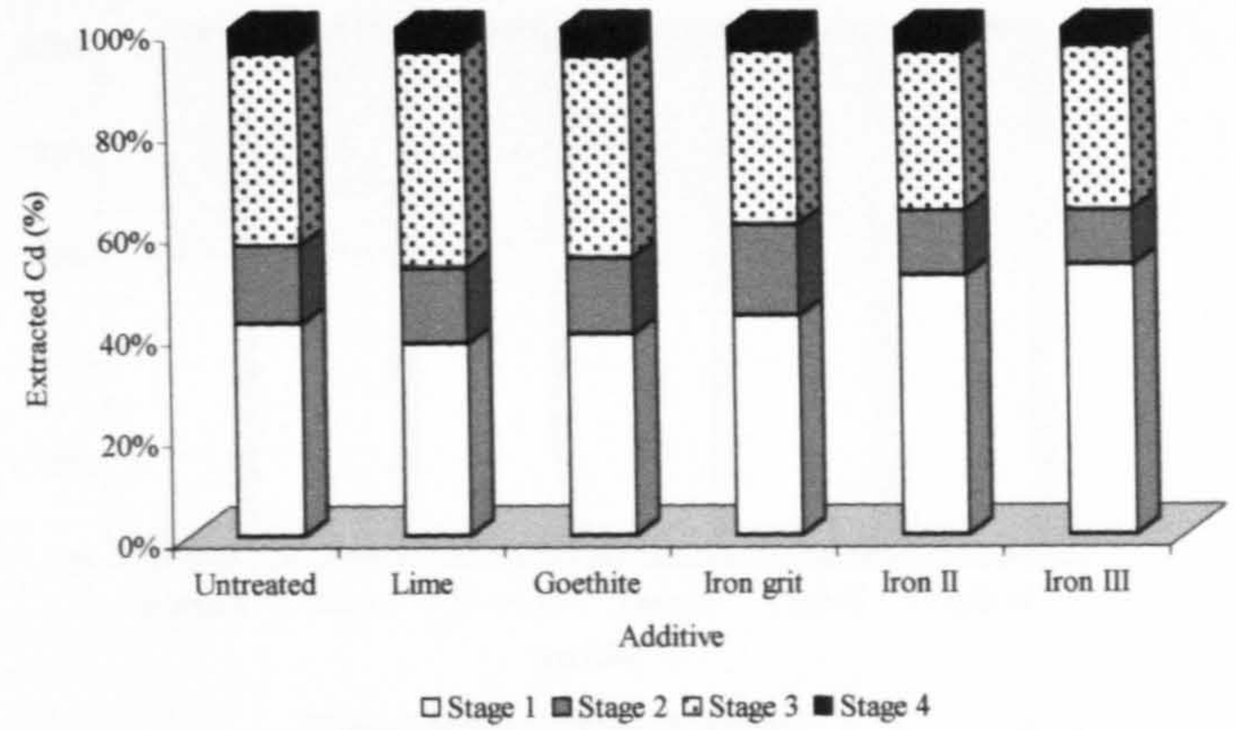


Figure 4.6. Partitioning of zinc in Kidsgrove soil using the Tessier sequential extraction method (n=3).

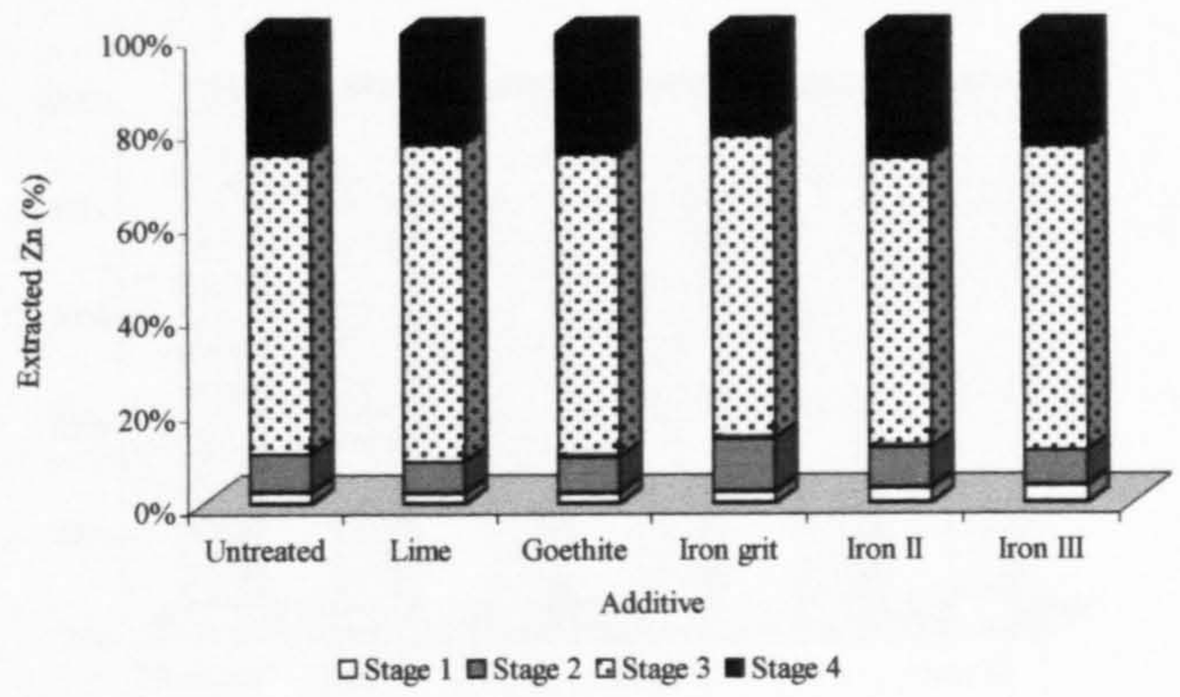


Figure 4.7. Partitioning of lead in Kidsgrove soil using the Tessier sequential extraction method (n=3).

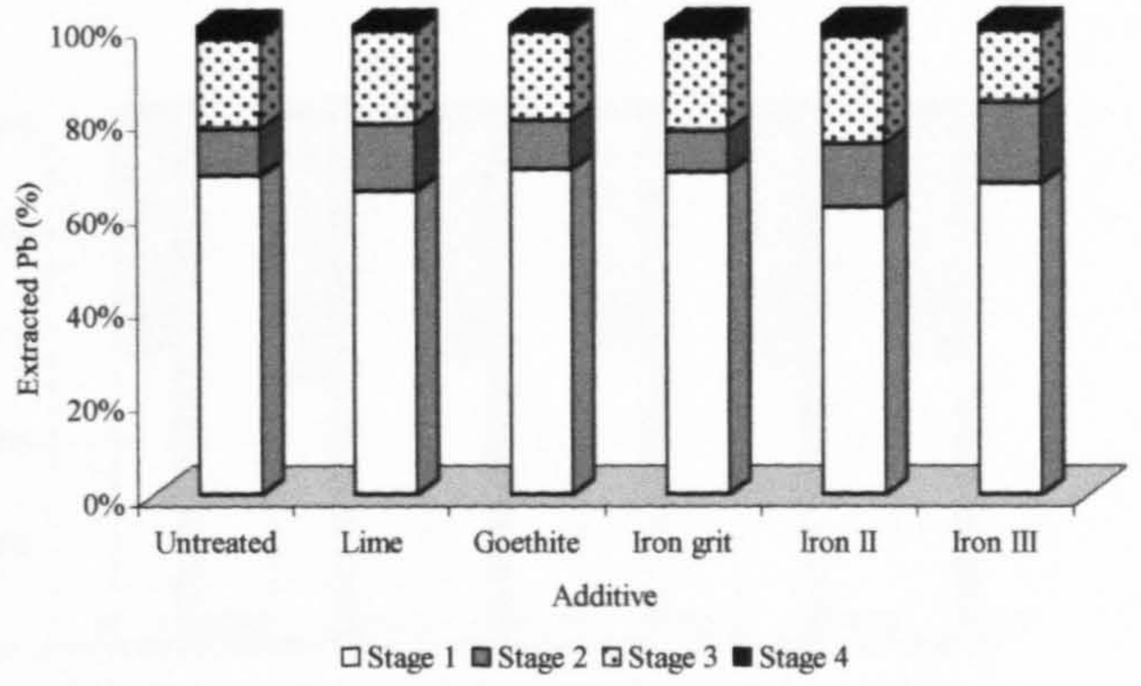


Figure 4.8. Partitioning of copper in Rixton soil using the Tessier sequential extraction method (n=3).

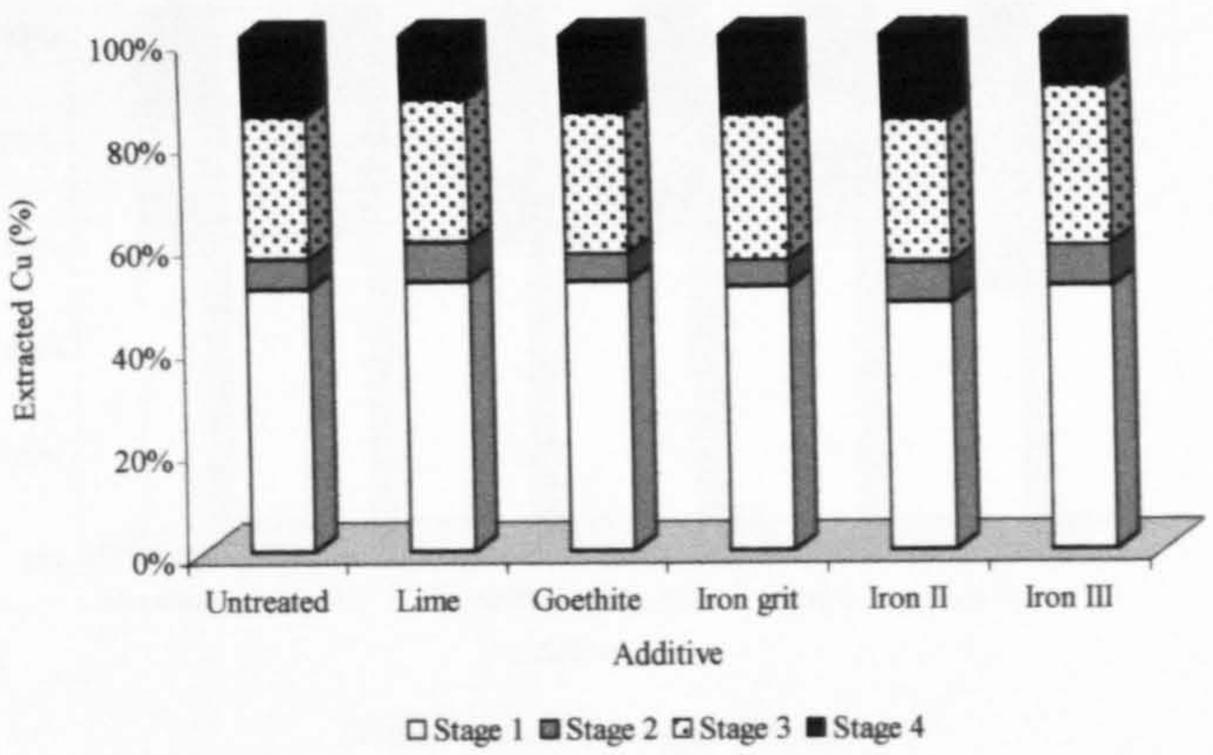


Figure 4.9. Partitioning of cadmium in Rixton soil using the Tessier sequential extraction method (n=3).

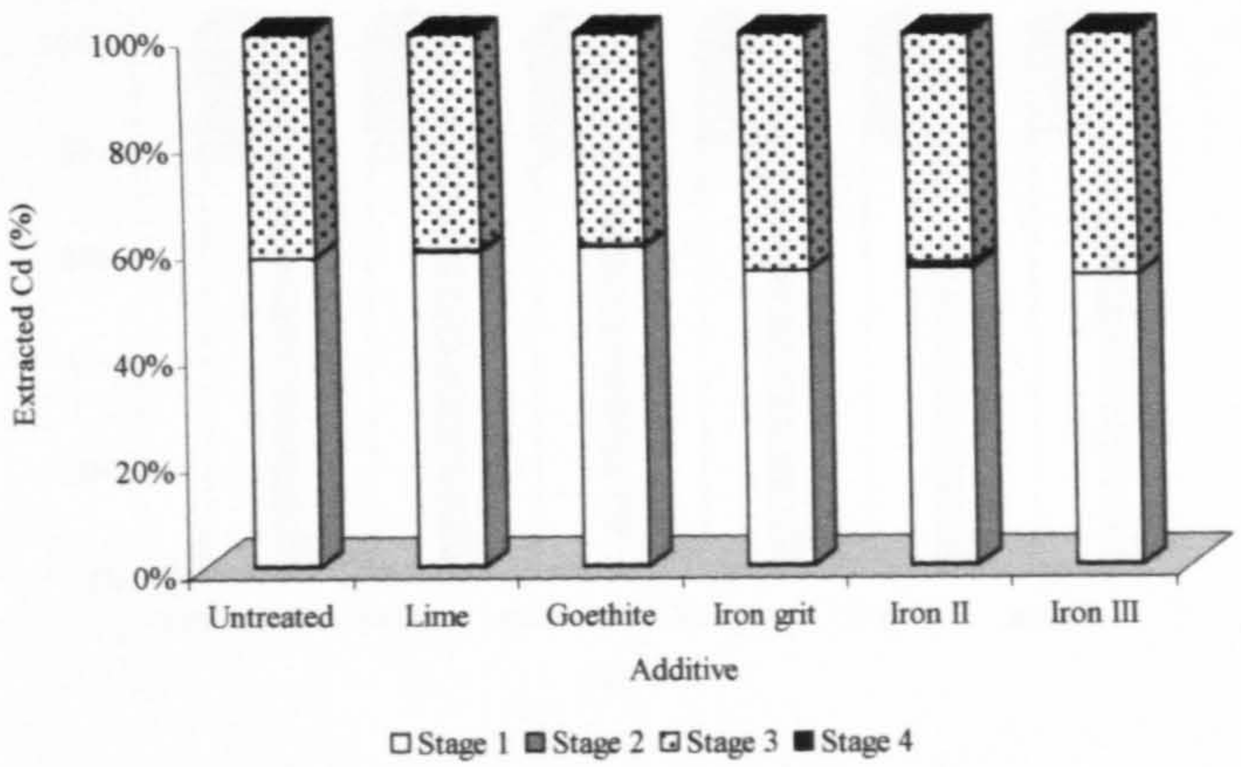


Figure 4.10. Partitioning of zinc in Rixton soil using the Tessier sequential extraction method (n=3).

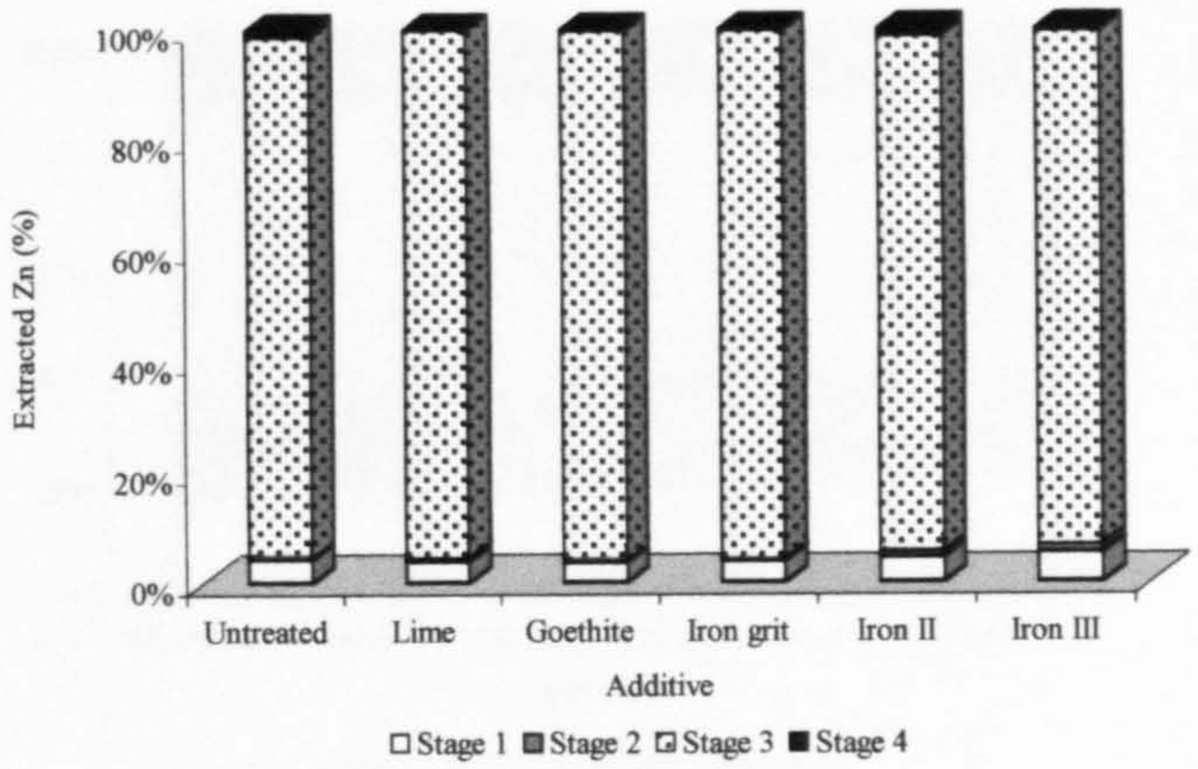


Figure 4.11. Partitioning of lead in Rixton soil using the Tessier sequential extraction scheme (n=3).

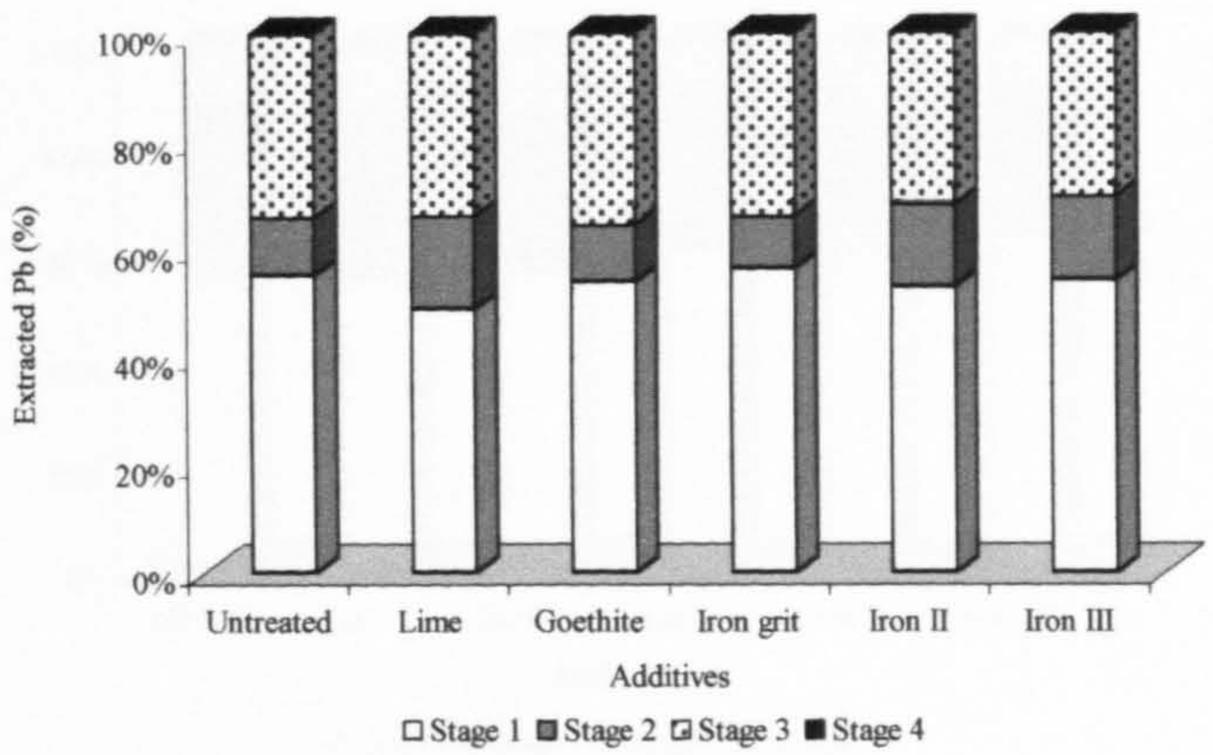


Figure 4.12. Partitioning of copper in Merton Bank soil using the Tessier sequential extraction method (n=3).

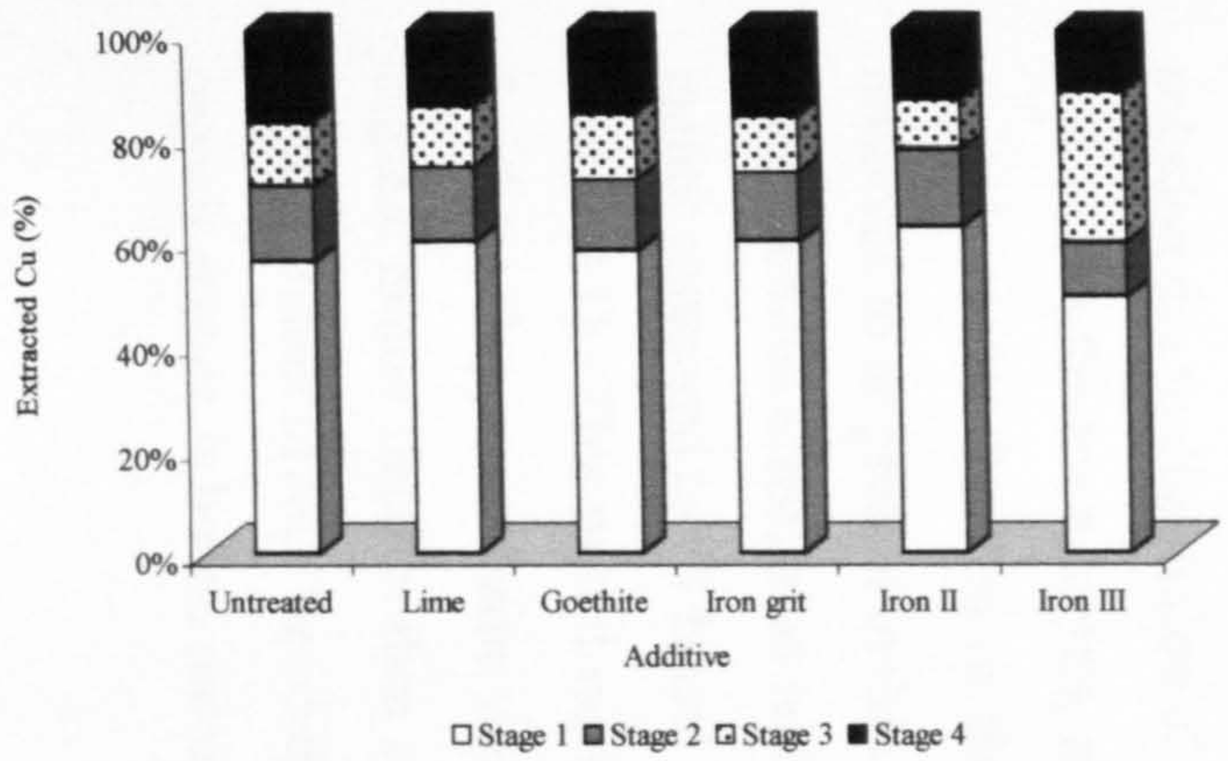


Figure 4.13. Partitioning of cadmium in Merton Bank soil using the Tessier sequential extraction method (n=3).

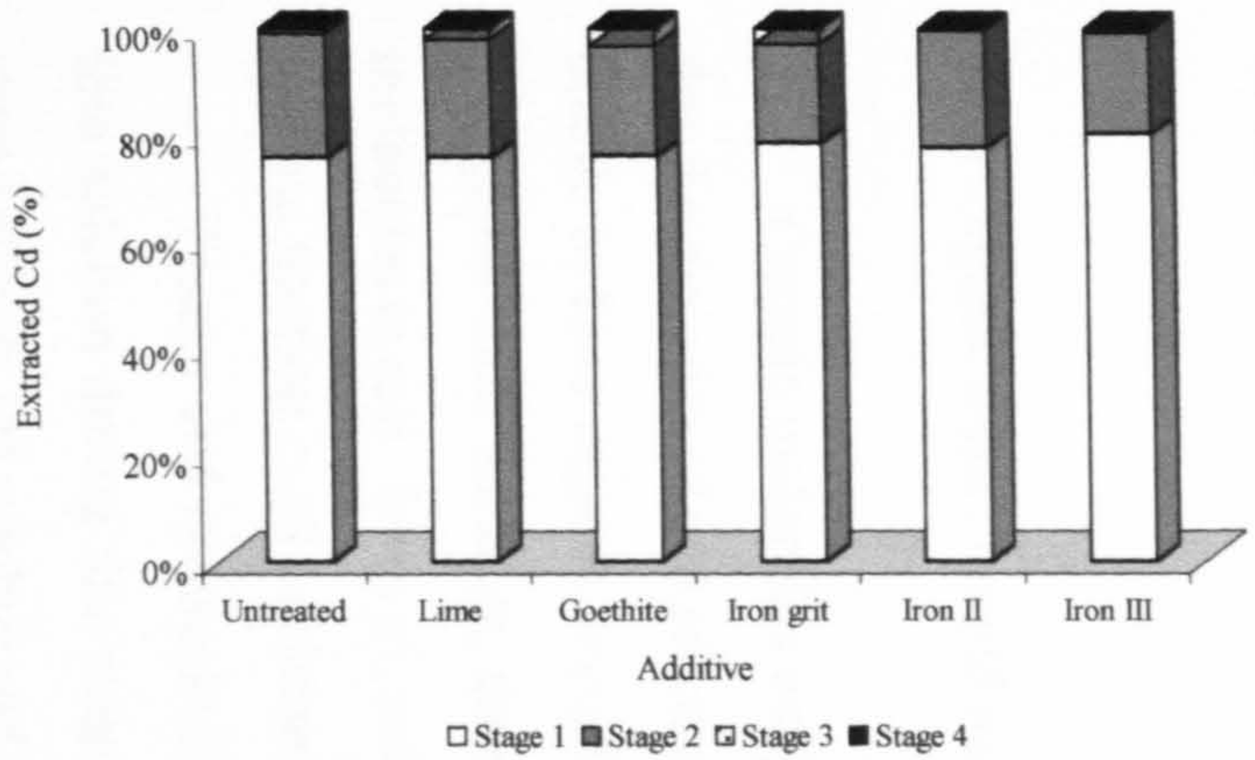


Figure 4.14. Partitioning of zinc in Merton Bank soil using the Tessier sequential extraction method (n=3).

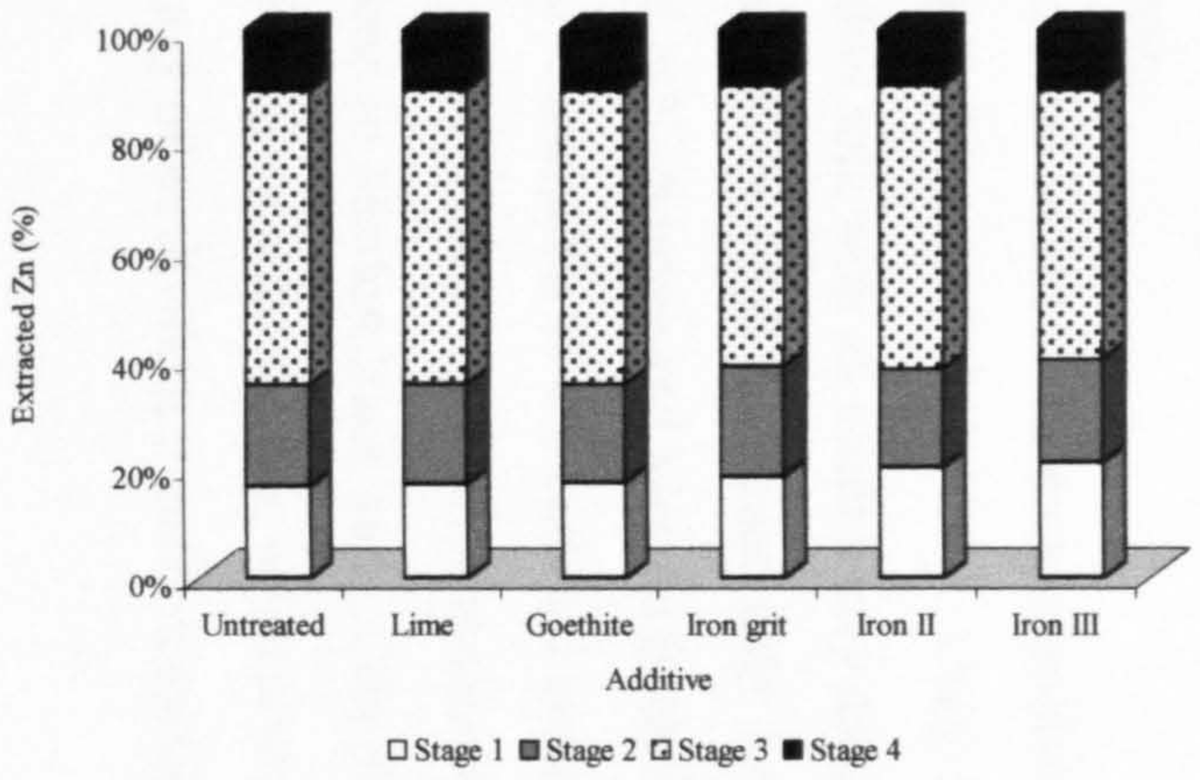
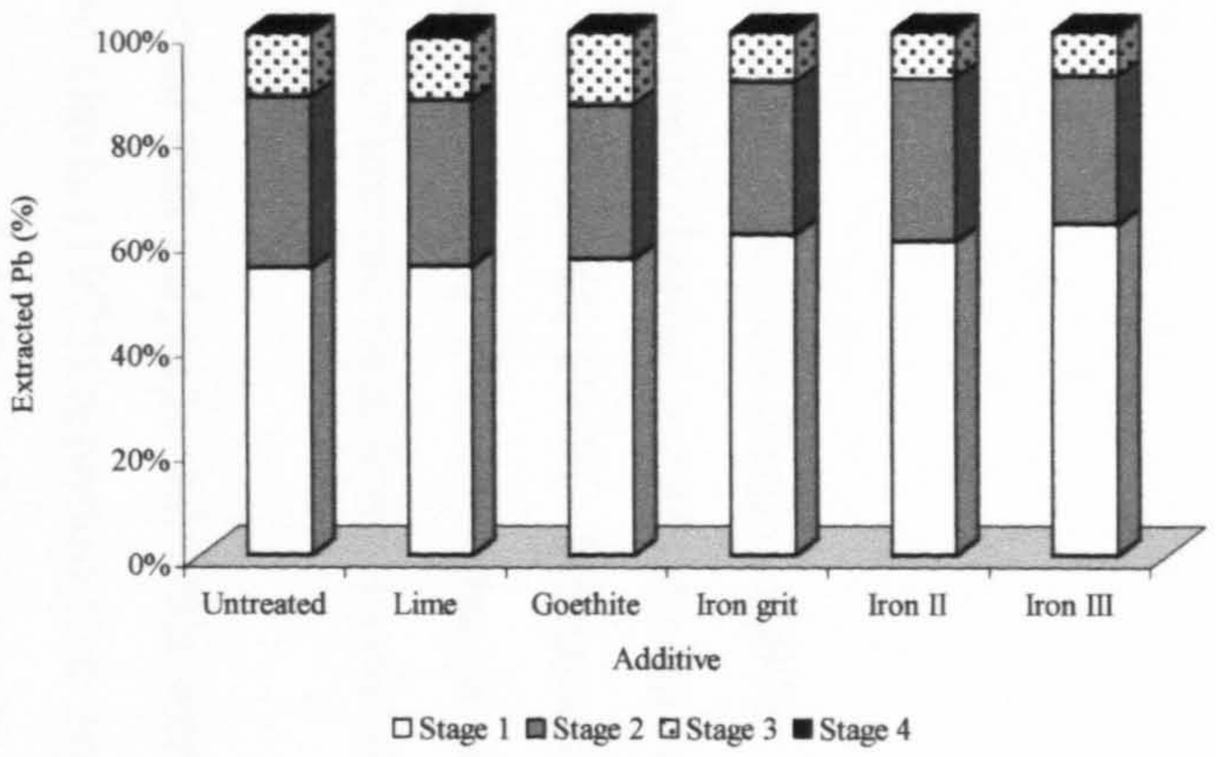


Figure 4.15. Partitioning of lead in Merton Bank soil using the Tessier sequential extraction method (n=3).



formation of zinc anions in Rixton soil may be a reason why zinc was mostly associated with the iron oxide fraction (Figure 4.10). It is considered that the principal matrix, which occludes the less abundant heavy metals, may be hydrous oxides of iron and manganese (Collins, 1981) and this may explain the high levels of zinc adsorbed in this fraction. The other heavy metals did not demonstrate the same increased level of adsorption in stage 3 as zinc.

4.3.4 Organic matter bound metals

Organic molecules carry a net negative charge in soils (Sadiq, 1997). It is known that the majority of soil arsenic species are negatively charged oxyanions and so arsenic is unable to form organic complexes (Johnson and Hiltbold, 1969). Because of the same charge on their surfaces, there is only a limited affinity between arsenic and organic molecules in soil. Even so, small concentrations of arsenic were found associated with the organic fraction in all untreated and amended soils.

Tessier and co-workers (1979) discovered that sulphide minerals were extracted into solution during this stage. Ferguson and Gavis (1972) reported that arsenic had a strong affinity for sulphur and a reduction in arsenic solubility under reducing conditions was affected by the formation of insoluble sulphides (Carbonell-Barrachina *et al.*, 1999). Table 4.2 shows the concentrations of sulphur present in the soils. Due of the presence of arsenic in this fraction, it may be assumed that the metalloid may have been extracted into solution due to dissolution of sulphide minerals.

For the trace metals, zinc and copper were found to be most associated with the organic matter fraction in the Kidsgrove soil (Figures 4.4 & 4.6). Only copper was observed to be present in this fraction in Rixton soil, with all other heavy metals showing a very limited association with organic matter. Rixton soil contained only 7.6 % organic matter compared to 15 % and 14 % observed in Kidsgrove and Merton Bank respectively (Table 4.1). This would explain the limited association of the cationic metals with this fraction. Copper and zinc were again found to be present in higher concentrations in the organic matter fraction than cadmium and lead in Merton Bank soil. Complexation via organic matter in soils limits the solubility of metal cations; copper, when complexed with organic matter, is bound more strongly than any other divalent transition metal (McBride,

1994). Lead and cadmium however showed limited associations with organic matter in all the soils studied.

Tables 4.11 to 4.13 show the cumulative total arsenic concentrations extracted and it is evident that Merton Bank soil contained the greatest concentrations. The soils treated with iron oxides showed reduced levels of total extracted arsenic compared to the untreated and lime treated soils. This may be due to the metalloid becoming incorporated into the iron oxide whereby even the treatment for stage three may not have extracted it into solution.

Total extracted copper, cadmium, zinc and lead concentrations are displayed in Tables 4.11- 4.13. The concentrations of extracted cadmium and zinc were greatest in Kidsgrove soil due to the higher levels of contamination present in comparison to the other substrates (Tables 4.3 and 4.4). Lead totals were greatest in those soils treated with iron II and III sulphate plus lime. The addition of these additives may have an adverse effect on the mobility of lead in soil and subsequent leaching studies and plant growth trials will determine if this effect is important.

4.3.5 Statistical Analysis

A general linear model (GLM) was used to carry out a multifactorial analysis of variance on the sequential extraction data to determine if soil, treatment and / or stage affected the concentration of arsenic and metals in the extracts of the three contaminated soils (Tables 4.14 – 4.18). An interaction term was also applied to determine if the soil and stage together affected the concentration of metalloid / metal extracted from a sample.

For arsenic, the statistical analysis showed a highly significant difference for the soil type used in the extraction procedure ($F = 117.58$, $P < 0.001$). Therefore the level of soil contamination will determine the concentration of extracted arsenic and was significantly different for each soil type. The effect of additive treatment on extracted arsenic was also significant ($F = 3.27$, $P = 0.007$), indicating that the addition of the treatments to all soils resulted in changes in the concentrations of arsenic extracted. The effect of different stages of the extraction procedure produced a significant difference in mean arsenic concentrations within each stage ($F = 252.40$, $P < 0.001$). The effect of soil type and stage of extraction together showed a highly significant result, and therefore

differences in extractable arsenic depended not only on soil type or stage of extraction, but on a combination of the two factors ($F = 55.95$, $P < 0.001$).

The multifactorial analysis for copper showed a significant difference for the soil type used in the extraction procedure ($F = 6.74$, $P < 0.001$). However the effect of additive treatment on copper concentrations in the soils was not significant ($F = 1.89$, $P = 0.097$), implying that the additives had little effect on copper partitioning. The stage of the extraction procedure was significant ($F = 656.88$, $P < 0.001$), as was the interaction of soil type and stage in copper extraction ($F = 14.56$, $P < 0.001$).

Cadmium showed similar results with a highly significant difference between the soil type and cadmium extracted ($F = 758.05$, $P < 0.001$). Additive effect was not significant ($F = 2.01$, $P = 0.079$), but the stage of the extraction procedure was significant ($F = 121.92$, $P < 0.001$). Interaction between the soil type and stage of extraction was significant in the partitioning of cadmium ($F = 104.97$, $P < 0.001$).

The multifactorial analysis for zinc showed a highly significant difference between the soil type and mean zinc concentrations ($F = 403.45$, $P < 0.001$). Treatment with the various additives was again not significant for this metal ($F = 0.25$, $P = 0.937$). The stage of extraction procedure was significant in extracting different mean concentrations of zinc ($F = 250.27$, $P < 0.001$), as was the interaction of both soil type and stage of extraction for the metal ($F = 125.05$, $P < 0.001$).

Differences in mean lead concentrations were found to be significant in the three soil types analysed ($F = 14.18$, $P < 0.001$). Treatment with the additives applied to the soils, were also found to be significant for this metal ($F = 5.95$, $P < 0.001$). The stage of the extraction procedure was highly significant for lead concentrations ($F = 1851.05$, $P < 0.001$), as was the interaction between soil type and stage of extraction procedure ($F = 95.41$, $P < 0.001$).

The statistical results have demonstrated that stage and treatment are significant in the extraction of the metalloid and metals from the soils. For arsenic, simple interpretation of the main effects of treatment and stage of extraction on its behaviour in the soils is reasonable, in that iron oxides were effective in immobilising arsenic and significant differences were obtained from the various extractions carried out. However, for the heavy metals, care must be taken in interpreting the results due to the large interaction terms observed in some cases. The statistical results nevertheless revealed that

treatment with the various additives was not significant for copper, cadmium and zinc but for lead the effect was found to be significant in all soils.

4.4. Conclusions

This study has demonstrated that arsenic retention in soil was mostly associated with the iron and manganese fraction. However the most important metals are those present in the exchangeable fraction, because they are the most mobile and so potentially more available for plant uptake. Addition of iron oxides to all soils reduced the concentration of arsenic in the exchangeable fraction, therefore altering its chemical form. This information is vital prior to remediation of a contaminated site because it demonstrates that the additives have the ability to reduce the mobile fraction of arsenic in the soil.

Arsenic retention in soils is related to the presence of iron and manganese oxides. It is well known that the ability of a soil to retain arsenic depends on the content of extractable amorphous and cryptocrystalline hydrous oxides of Fe and Al (Jacobs *et al.*, 1970; Livesey & Huang, 1981). Jacobs and co-workers (1970) demonstrated that removal of Fe and Al by oxalate treatment reduced the adsorption of arsenic in the soil. It is also important to note that arsenic will bind preferentially to Fe oxides, to a lesser extent on Al oxides and shows a secondary preference for H_2SO_4 – extractable calcium (Akins & Lewis, 1976; Wauchope, 1975).

Arsenic was found to be associated with the carbonate fraction, but not to the same extent as with stage 3. The carbonate mineral fraction will adsorb arsenic oxyanions in soils with a pH between 7 and 9 (Sadiq, 1997) and the soils demonstrated pH values within this range (Chapter 5, Tables 5.10-5.12). When iron oxide sites become exhausted, the metalloid will preferentially bind to calcium carbonates. The concentrations of arsenic associated with iron II and III sulphates and goethite with respect to stage 3 were always greater when compared to iron grit. This may be due to a reduced adsorption capacity compared to the other iron oxides and indeed the specific surface area result for iron grit reflects this (Chapter 3, Table 3.1). Greater association with the carbonate fraction, forming $Ca_3(AsO_4)_2$, may be a result of the lower adsorption capacity of iron grit.

The presence of arsenic in stage 4 may be due to the dissolution of sulphide minerals, which may have been affected due to the nature of the reagents used in the extraction scheme. The use of nitric acid may have affected the more strongly bound

forms of arsenic increasing liberation of the metalloid and therefore leaching it into solution.

Zinc was observed to be associated with the Fe/Mn fraction in all the soils investigated. Copper, which is generally associated with organic matter, was mainly present in the exchangeable fraction, together with lead and cadmium. The low organic matter content of the soils may be why there was a high concentration of these heavy metals in the initial stage of the extraction procedure and due to the heterogeneity of the soils this may be a factor in the results observed.

The application of sequential extraction schemes has been applied mostly to sediments, with the results obtained being susceptible to irreproducibility because of errors occurring between steps (Sahuquillo *et al.*, 1999). Sahuquillo and co-workers indicated that of a number of variables tested, the pH of extractants used in the scheme was of great importance. Davidson and co-workers (1999) also identified that the pH of certain reagents was an important source of variability. They also identified that the process of air-drying soil produced larger concentrations of metals than if the soil was field-moist (Davidson *et al.*, 1999). Therefore the relevance of results could be affected if the soils were air dried prior to extraction. Errors may also arise in carry-over from one step to the next during the various stages of the extraction procedure (Davidson *et al.*, 1994) and these must be taken into account when considering the results.

The results obtained from this study have revealed that arsenic concentrations in all soils were reduced in the first stage of the extraction scheme due to the addition of iron oxide additives, indicating that the initial form of arsenic was changed to a more chemically stable species in the soil. Such information is important before additives are applied in the field, not only to assess the element under investigation, but also to consider other toxic elements that may become more mobile after incorporation of the amendment. This was observed here, where lead was found to increase in the exchangeable fraction upon addition of iron II and III sulphates (Table 4.10), whilst an increase in cadmium was found in Kidsgrove soil during stage 1 with the addition of iron II and III treatments respectively (Table 4.8).

In the following chapters the durability of the amendments will be investigated in order to determine their effectiveness over the long-term, which will be investigated using a variety of leaching tests. The bioavailability of arsenic and heavy metals will also be considered using plant studies.

Table 4.6. Mean concentrations of arsenic (ppb) extracted sequentially from the three soils (n=3).

	KIDSGROVE				RIXTON				MERTON BANK			
	Stage 1	**Stage 2**	**Stage 3**	**Stage 4**	**Stage 1**	**Stage 2**	**Stage 3**	**Stage 4**	**Stage 1**	**Stage 2**	**Stage 3**	**Stage 4**
Untreated	85.92 (±144.52)	136.38 (±226.56)	268.88 (±311.02)	4.58 (±0.34)	214.74 (±74.44)	1102.66 (±295.60)	2331.66 (±522.20)	278.93 (±205.88)	112.28 (±5.47)	1163.33 (±77.18)	3272 (±669.94)	274.33 (±87.96)
Lime	182.43 (±202.30)	347.74 (±498.87)	18.06 (±5.53)	19.74 (±24.55)	146.01 (±28.25)	1007 (±107.50)	2667 (±192.80)	298.52 (±79.79)	115.78 (±4.72)	1113.93 (±115.37)	3515 (±1061.12)	259.70 (±39.25)
Goethite	24.86 (±24.85)	89.10 (±140.82)	487.44 (±409.67)	6.16 (±5.52)	100.20 (±28.17)	831.2 (±106.85)	1921.2 (±190.96)	284.85 (±78.86)	74.50 (±26.07)	896.73 (±30.87)	3515 (±700.74)	259.70 (±33.52)
Iron grit	34.39 (±52.87)	80.28 (±70.14)	85.22 (±102.32)	6.00 (±5.14)	85.78 (±27.27)	830.2 (±103.13)	1505.2 (±182.68)	246.38 (±76.36)	42.68 (±8.80)	784.2 (±80.67)	2618.33 (±507.74)	143.85 (±32.76)
Iron II	3.70 (±3.00)	24.68 (±32.01)	374.28 (±622.26)	27.65 (±29.06)	12.86 (±25.97)	533.00 (±98.01)	2618.33 (±168.29)	317.77 (±71.95)	32.12 (±4.12)	520 (±68.38)	2693.83 (±276.09)	134.57 (±20.60)
Iron III	95.25 (±140.37)	203.60 (±233.19)	258.50 (±270.00)	4.16 (±4.98)	53.69 (±22.51)	373.33 (±90.98)	1941.86 (±159.85)	94.36 (±66.28)	13.70 (±0.83)	404.73 (±45.96)	3033.33 (±125.06)	139.37 (±26.96)

Table 4.7. Mean concentrations of copper (ppm) extracted sequentially from the three soils (n=3).

	KIDSGROVE				RIXTON				MERTON BANK			
	Stage 1	**Stage 2**	**Stage 3**	**Stage 4**	**Stage 1**	**Stage 2**	**Stage 3**	**Stage 4**	**Stage 1**	**Stage 2**	**Stage 3**	**Stage 4**
Untreated	6.64 (±0.39)	0.96 (±0.17)	2.16 (±0.11)	3.13 (±0.85)	5.71 (±0.13)	0.64 (±0.39)	3.08 (±0.43)	1.70 (±0.17)	6.82 (±0.43)	1.75 (±0.11)	1.48 (±0.65)	2.1 (±1.17)
Lime	6.94 (±0.25)	1.14 (±0.26)	2.56 (±0.33)	3.03 (±0.97)	5.57 (±0.32)	0.80 (±0.45)	2.95 (±0.39)	1.27 (±0.07)	7.20 (±0.29)	1.72 (±0.28)	1.38 (±0.80)	1.71 (±0.98)
Goethite	6.31 (±0.57)	0.96 (±0.07)	2.09 (±0.21)	2.94 (±0.87)	5.89 (±0.37)	0.62 (±0.53)	3.05 (±0.47)	1.65 (±0.32)	7.11 (±0.20)	1.65 (±0.21)	1.53 (±0.69)	1.93 (±1.23)
Iron grit	6.59 (±0.16)	0.84 (±0.12)	2.28 (±0.26)	3.33 (±0.71)	5.88 (±0.38)	0.58 (±0.42)	3.24 (±0.57)	1.73 (±0.61)	7.03 (±0.33)	1.54 (±0.06)	1.26 (±0.62)	1.92 (±0.86)
Iron II	6.73 (±0.12)	1.08 (±0.21)	2.18 (±0.17)	3.01 (±0.77)	5.92 (±0.21)	0.94 (±0.55)	3.42 (±0.62)	1.97 (±0.39)	7.6 (±0.43)	1.78 (±0.14)	1.16 (±0.74)	1.60 (±0.72)
Iron III	7.32 (±0.42)	1.19 (±0.05)	2.40 (±0.13)	2.58 (±0.96)	6.12 (±0.41)	0.95 (±0.41)	3.66 (±0.21)	1.17 (±0.65)	7.61 (±0.20)	1.59 (±0.16)	4.47 (±3.68)	1.8 (±1.32)

Table 4.8. Mean concentrations of cadmium (ppm) extracted sequentially from the three soils (n=3).

	KIDSGROVE				RIXTON				MERTON BANK			
	Stage 1	**Stage 2**	**Stage 3**	**Stage 4**	**Stage 1**	**Stage 2**	**Stage 3**	**Stage 4**	**Stage 1**	**Stage 2**	**Stage 3**	**Stage 4**
Untreated	39.81 (±1.56)	14.55 (±1.27)	35.89 (±10.17)	4.77 (±0.09)	0.99 (±0.11)	0.00 (±0)	0.72 (±0.22)	0.00 (±0)	1.42 (±0.12)	0.43 (±0.2)	0.01 (±0.01)	0.00 (±0)
Lime	39.43 (±2.13)	15.48 (±1.97)	44.35 (±17.07)	4.96 (±1.01)	0.91 (±0.15)	0.003 (±0.005)	0.63 (±0.07)	0.00 (±0)	1.50 (±0.09)	0.44 (±0.08)	0.04 (±0.06)	0.00 (±0)
Goethite	37.97 (±2.24)	14.32 (±0.89)	38.09 (±8.76)	5.33 (±0.40)	0.97 (±0.17)	0.00 (±0)	0.65 (±0.05)	0.00 (±0)	1.52 (±0.06)	0.42 (±0.07)	0.06 (±0.05)	0.00 (±0)
Iron grit	37.49 (±1.74)	15.66 (±2.05)	29.91 (±9.89)	3.93 (±0.68)	0.96 (±0.09)	0.00 (±0)	0.78 (±0.08)	0.00 (±0)	1.47 (±0.12)	0.35 (±0.01)	0.05 (±0.09)	0.00 (±0)
Iron II	58.23 (±2.74)	14.58 (±1.04)	36.26 (±10.91)	5.26 (±0.70)	1.00 (±0.1)	0.01 (±0.02)	0.77 (±0.07)	0.00 (±0)	1.66 (±0.11)	0.48 (±0.06)	0.003 (±0.005)	0.00 (±0)
Iron III	63.39 (±2.88)	12.98 (±0.39)	39.07 (±13.62)	4.3 (±0.17)	1.10 (±0.19)	0.00 (±0)	0.92 (±0.09)	0.00 (±0)	1.68 (±0.04)	0.40 (±0.07)	0.01 (±0.02)	0.00 (±0)

Table 4.9. Mean concentrations of zinc (ppm) extracted sequentially from the three soils (n=3).

	KIDSGROVE				RIXTON				MERTON BANK			
	Stage 1	**Stage 2**	**Stage 3**	**Stage 4**	**Stage 1**	**Stage 2**	**Stage 3**	**Stage 4**	**Stage 1**	**Stage 2**	**Stage 3**	**Stage 4**
Untreated	1.29 (±0.06)	4.53 (±0.31)	35.52 (±10.10)	14.09 (±0.50)	0.32 (±0.11)	0.01 (±0.02)	7.05 (±0.64)	0.10 (±0.08)	0.85 (±0.06)	0.95 (±0.08)	2.74 (±0.23)	0.55 (±0.18)
Lime	1.23 (±0.07)	4.14 (±0.22)	35.38 (±13.57)	13.94 (±1.12)	0.27 (±0.11)	0.04 (±0.08)	6.71 (±0.38)	0.00 (±0)	0.89 (±0.03)	0.95 (±0.07)	2.80 (±0.42)	0.55 (±0.11)
Goethite	1.22 (±0.11)	4.20 (±0.18)	35.38 (±11.84)	13.94 (±1.25)	0.27 (±0.10)	0.01 (±0.02)	7.05 (±0.48)	0.02 (±0.02)	0.90 (±0.01)	0.93 (±0.13)	2.77 (±0.13)	0.56 (±0.10)
Iron grit	1.21 (±0.03)	5.85 (±1.17)	33.27 (±9.70)	11.20 (±1.46)	0.26 (±0.08)	0.02 (±0.02)	6.55 (±0.18)	0.02 (±0.02)	0.86 (±0.04)	0.92 (±0.03)	2.39 (±0.25)	0.46 (±0.12)
Iron II	1.70 (±0.09)	4.77 (±0.21)	34.04 (±10.06)	14.62 (±0.67)	0.32 (±0.06)	0.07 (±0.06)	6.81 (±0.40)	0.09 (±0.06)	0.97 (±0.06)	0.86 (±0.03)	2.49 (±0.13)	0.48 (±0.04)
Iron III	2.05 (±0.28)	4.19 (±0.26)	36.89 (±14.71)	13.74 (±0.89)	0.37 (±0.09)	0.10 (±0.07)	6.50 (±0.25)	0.02 (±0.04)	0.98 (±0.005)	0.88 (±0.13)	2.3 (±0.23)	0.50 (±0.04)

Table 4.10. Mean concentrations of lead (ppm) extracted sequentially from the three soils (n=3).

	KIDSGROVE				RIXTON				MERTON BANK			
	Stage 1	**Stage 2**	**Stage 3**	**Stage 4**	**Stage 1**	**Stage 2**	**Stage 3**	**Stage 4**	**Stage 1**	**Stage 2**	**Stage 3**	**Stage 4**
Untreated	24.36 (±1.78)	3.54 (±0.62)	6.95 (±2.35)	0.98 (±0.40)	20.00 (±0.95)	3.83 (±0.70)	12.37 (±1.40)	0.00 (±0)	23.54 (±1.31)	14.05 (±0.26)	5.23 (±1.20)	0.05 (±0.08)
Lime	25.43 (±0.43)	5.64 (±1.63)	7.83 (±3.15)	0.44 (±0.43)	18.37 (±1.14)	6.41 (±0.99)	12.75 (±1.22)	0.00 (±0)	24.50 (±1.29)	14.13 (±1.38)	5.34 (±0.96)	0.39 (±0.36)
Goethite	23.25 (±2.01)	3.47 (±0.48)	6.42 (±2.90)	0.42 (±0.21)	19.99 (±1.23)	3.92 (±1.51)	13.19 (±0.65)	0.00 (±0)	25.65 (±0.60)	13.38 (±2.42)	6.32 (±2.88)	0.07 (±0.12)
Iron grit	23.98 (±1.81)	3.02 (±0.97)	7.11 (±2.07)	0.87 (±0.17)	20.47 (±1.26)	3.52 (±1.05)	12.38 (±1.19)	0.00 (±0)	24.33 (±1.29)	11.56 (±0.24)	3.85 (±1.11)	0.00 (±0)
Iron II	25.48 (±1.03)	5.79 (±1.50)	9.49 (±7.64)	1.10 (±0.26)	21.62 (±0.86)	6.16 (±1.57)	13.05 (±0.92)	0.00 (±0)	27.06 (±1.86)	14.12 (±0.13)	4.09 (±0.54)	0.02 (±0.04)
Iron III	29.51 (±1.96)	7.67 (±0.58)	6.84 (±2.32)	0.58 (±0.32)	23.56 (±2.32)	6.74 (±1.61)	13.26 (±0.75)	0.00 (±0)	28.00 (±0.80)	12.55 (±1.44)	3.76 (±0.79)	0.05 (±0.08)

Table 4.11. Cumulative concentration of arsenic and heavy metals extracted sequentially from Kidsgrove soil.

Treatment	Arsenic (µg/kg)	Copper (mg/kg)	Cadmium (mg/kg)	Zinc (mg/kg)	Lead (mg/kg)
Untreated	495.76	12.89	95.02	55.43	35.83
Lime	567.97	13.67	107.22	54.69	39.34
Goethite	607.56	12.3	95.71	54.74	33.56
Iron grit	205.89	13.04	86.99	51.53	34.98
Iron II	430.31	13.00	114.33	55.13	41.86
Iron III	561.51	13.49	119.74	56.87	44.6

Table 4.12. Cumulative concentration of arsenic and heavy metals extracted sequentially from Rixton soil.

Treatment	Arsenic (µg/kg)	Copper (mg/kg)	Cadmium (mg/kg)	Zinc (mg/kg)	Lead (mg/kg)
Untreated	3927.99	11.13	1.71	7.48	36.2
Lime	4118.53	10.59	1.54	7.02	37.53
Goethite	3137.45	11.21	1.62	7.35	37.1
Iron grit	2667.56	11.43	1.74	6.85	36.37
Iron II	3481.96	12.25	1.78	7.29	40.83
Iron III	2463.24	11.9	2.02	6.99	43.56

Table 4.13. Cumulative concentration of arsenic and heavy metals extracted sequentially from Merton bank soil.

Treatment	Arsenic (µg/kg)	Copper (mg/kg)	Cadmium (mg/kg)	Zinc (mg/kg)	Lead (mg/kg)
Untreated	4821.94	12.15	1.86	5.09	42.87
Lime	5004.41	12.01	1.98	5.19	44.36
Goethite	4745.93	12.22	2.00	5.16	45.42
Iron grit	3589.06	11.75	1.87	4.63	39.74
Iron II	3380.78	12.14	2.14	4.8	45.29
Iron III	3591.13	15.47	2.09	4.66	44.36

Table 4.14. General Linear Model for Arsenic.

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Soil	2	32756561	32756561	16378281	117.58	0.000
Treat	5	2280266	2280266	456053	3.27	0.007
Stage	3	105473685	105473685	35157895	252.40	0.000
Soil*Stage	6	46763151	46763151	7793858	55.95	0.000
Error	199	27719965	27719965	139296		
Total	215	214993628				

Table 4.15. General Linear Model for Copper.

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Soil	2	6.542	6.542	3.271	6.74	0.001
Treat	5	4.594	4.594	0.919	1.89	0.097
Stage	3	956.859	956.859	318.953	656.88	0.000
Soil*Stage	6	42.427	42.427	7.071	14.56	0.000
Error	199	96.626	96.626	0.486		
Total	215	1107.048				

Table 4.16. General Linear Model for Cadmium.

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Soil	2	30485.3	30485.3	15242.6	758.05	0.000
Treat	5	201.9	201.9	40.4	2.01	0.079
Stage	3	7354.3	7354.3	2451.4	121.92	0.000
Soil*Stage	6	12664.3	12664.3	2110.7	104.97	0.000
Error	199	4001.4	4001.4	20.1		
Total	215	54707.2				

Table 4.17. General Linear Model for Zinc.

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Soil	2	7404.5	7404.5	3702.2	403.45	0.000
Treat	5	11.7	11.7	2.3	0.25	0.937
Stage	3	6889.7	6889.7	2296.6	250.27	0.000
Soil*Stage	6	6885.4	6885.4	1147.6	125.05	0.000
Error	199	1826.1	1826.1	9.2		
Total	215	23017.3				

Table 4.18. General Linear Model for Lead.

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Soil	2	81.1	81.1	40.5	14.18	0.000
Treat	5	85.0	85.0	17.0	5.95	0.000
Stage	3	15871.9	15871.9	5290.6	1851.05	0.000
Soil*Stage	6	1636.2	1636.2	272.7	95.41	0.000
Error	199	568.8	568.8	2.9		
Total	215	18243.0				

CHAPTER 5.

A COMPARISON OF LEACHING TESTS TO DETERMINE ARSENIC MOBILITY IN IRON OXIDE AMENDED SOILS.

5.1. Introduction

Due to the industrial revolution in the United Kingdom, land contaminated with arsenic is ubiquitous. The persistence of arsenic within the soil environment and its toxicity to plants and animals is therefore of concern. The soil is an important sink for arsenic compounds, which accumulate rapidly due to slow depletion by plant uptake, leaching and erosion (Smith *et al.*, 1998). The chemical behaviour of arsenic will determine its uptake by plants and soil biota (Sachs and Michaels, 1971; Otte *et al.*, 1991). Therefore a better understanding of arsenic chemistry within a soil system will lead to a more improved management of arsenic contaminated sites.

Soil is a key component of terrestrial ecosystems, both natural and agricultural (Alloway, 1995). It is an active system that is subject to short-term fluctuations, such as alterations in pH, moisture status and redox conditions. Other factors that may affect the soil are changes in environmental conditions and management strategies. Adjustments in soil properties can therefore affect the form and bioavailability of metals (Alloway, 1995), as was demonstrated in the previous chapter by incorporating Fe-bearing additives to soils in order to change the partitioning of arsenic. However, these factors must be considered carefully before decisions on the management of contaminated land are made.

The most common approach to remediate a contaminated site is excavation and landfilling which is then followed, by using engineered barriers. This technique is however environmentally disruptive and extremely expensive (Vangronsveld and Cunningham, 1998). Alternatives for the remediation of metal contaminated soils include *in situ* biological remediation, (for example, phytoextraction and phytovolatilization) and physical and chemical stabilisation, which include techniques such as vitrification, asphalt capping and the application of inorganic amendments to a contaminated soil, which again are *in situ* remediation techniques.

Among the range of common inorganic additives that can be applied to an arsenic contaminated soil (lime, phosphate, clays, zeolites and manganese oxides), iron oxides were chosen due to the previous *in vitro* and speciation studies identifying their efficiency at adsorbing arsenic. The iron oxide surfaces are known to be effectively involved in the adsorption of arsenic in soils (ElBassam *et al.*, 1975; Jacobs *et al.*, 1970; Lumsdom *et al.*, 1984; Waychunas *et al.*, 1993). Carbonella-Barrachina and co-workers (1999) discovered that water-soluble iron concentrations were highly correlated with dissolved total arsenic suggesting that iron hydrous oxides play an important part in controlling arsenic adsorption-desorption reactions in sludge. Among the range of iron oxides chosen for these studies, ferrous sulphate was selected because when tested with certain other iron oxides such as hematite in soils, it was discovered that it bound arsenic more strongly (Artiola *et al.*, 1990).

Lime has been used to immobilise heavy metals, however its application to soil contaminated with arsenic may result in an increase in the metalloids solubility, because lime will increase the soil pH. Although a slight adsorption affect was observed in chapter 3, where calcium arsenate ($Ca_3(AsO_4)_3$) may have been formed *in vitro*, changes in the soil environment, for example reaction with CO_2 , can lead to the formation of $CaCO_3$ and so release of arsenic (Robins, 1981). Therefore it has been added to the list of amendments used in the following investigation in order to assess this hypothesis.

Numerous methods for the *in situ* remediation of metal contaminated soils have been proposed. The main objective of an *in situ* remediation technique is to change the speciation of trace elements in the soil, making them less soluble and so preventing leaching to groundwater, making them less bioavailable for plant uptake. However, the overall concentration of the contaminants does not change. The majority of national guidelines for the remediation of metal contaminated soils are based on total metal concentrations, although a number of regulatory authorities are using the more realistic approach of risk based assessment for setting target criteria for the cleanup of contaminated soils and leachates.

To test the effectiveness of the iron oxide bearing additives a number of leaching tests were carried out. Leaching tests are used to predict the fate of those metals that are mobile in the soil profile and so be potentially absorbed by plants under natural conditions, i.e. by employing water as the medium to remove the metals instead of strong acids. The environmental problems associated with the leaching of toxic elements like

arsenic from contaminated substrates such as fly ash deposits is of concern. Leaching tests can help to estimate the potential availability of trace metals and when used in conjunction with inorganic soil additives will provide an estimation of how effective the material is at reducing the trace metal in the leachate.

The aim of this study was to use different leaching tests to evaluate the mobility of trace elements present in a range of contaminated soils and to determine the changes in arsenic and other heavy metal concentrations in the leachates of contaminated soils when treated with iron oxides. The use of *in situ* remediation (immobilisation) for metal contaminated soil is not popular because it still requires validation of long-term stability data. There are a number of leaching methods proposed to evaluate mobilisation of heavy metal/As contaminated soils. These studies range from simple one-hour water extraction techniques to elaborate column studies that take up to three weeks to complete.

The three leaching tests used were, the UK Environmental Agency (UKEA) method, the American Society of Testing and Materials (ASTM) method and the Dutch Environmental Agency Column Test (NEN 7343). The three leaching methods would demonstrate both the short and long-term efficiency of the iron oxides as possible arsenic immobilising agents.

5.2. Experimental

All soils were air dried and treated with 1% w/w amendment. The amendments used were: goethite, iron grit, iron II sulphate + lime, iron III sulphate + lime and lime. An untreated soil was used as a control. The soils were mixed thoroughly in order to obtain even distribution of the additives applied to them and then they were allowed to equilibrate for one month at room temperature and field moisture capacity in screw top polyethylene containers prior to analysis using the leaching methods outlined below:

5.2.1. UK Environmental Agency Leaching Test (UKEA):

The UKEA test provides an analysis of those metal fractions immediately available to plants in a soil system. The test provides an idea of how efficient the additives are at

immobilising arsenic and shows the leaching of metals from a soil sample under natural conditions.

Typically, a 10g sample of soil was leached with deionised water (50 cm^3) for 1 hour, during which time the soil was occasionally agitated. The leachate was filtered through GF/C fibreglass filter paper and analysed.

5.2.2. American Society of Testing and Materials Leaching Test (ASTM):

The ASTM test is similar to the UKEA, only the test is more vigorous, and does not represent the natural conditions found in soil.

Typically, a 25g sample of soil was leached with 100 cm^3 deionised water for 48 hours with continuous agitation on a Griffin flask shaker. The leachate was then filtered and analysed.

5.2.3. Dutch Environmental Agency Leaching Test (NEN 7343):

The following procedure was taken from NEN 7343 (Accelerated Dutch Leaching Test). Typically, a 20cm long glass column (5 cm internal diameter) was filled with contaminated soil to a height of four times the internal diameter and leached with acidified deionised water (acidified to pH4 with concentrated nitric acid (HNO_3) of Analytical Reagent grade, having a conductivity of 1µs/cm). The soil was leached from the base of the column and upwards by a peristaltic pump, which provided a continuous flow of water at a rate of 0.1 cm^3 per minute. The glass columns (XK 50), were purchased from Pharmica Biotech (Plates 5.1a,b and 5.2). The columns were fitted with acrylic jackets, which allowed the investigations to be maintained at a constant temperature. All the leaching columns were fitted with Whatman pre-filters having a pore size of 1.5µm. Whatman membrane filters having a pore size of 0.45µm were fitted at the top of each column. All tubing material was polyethylene.

Eluate samples were collected over a three-week period (Table 5.1) and preserved by the addition of 0.5ml of concentrated HNO_3 A.R. grade, in 60 ml polyethylene screw-cap collection flasks prior to analysis. The concentration of arsenic in the leachate was determined by HG-AAS. Copper, cadmium, zinc and lead concentrations were determined by ICP-AES analysis.

Plate 5.1.a. A column used in the Dutch & modified column leaching tests.

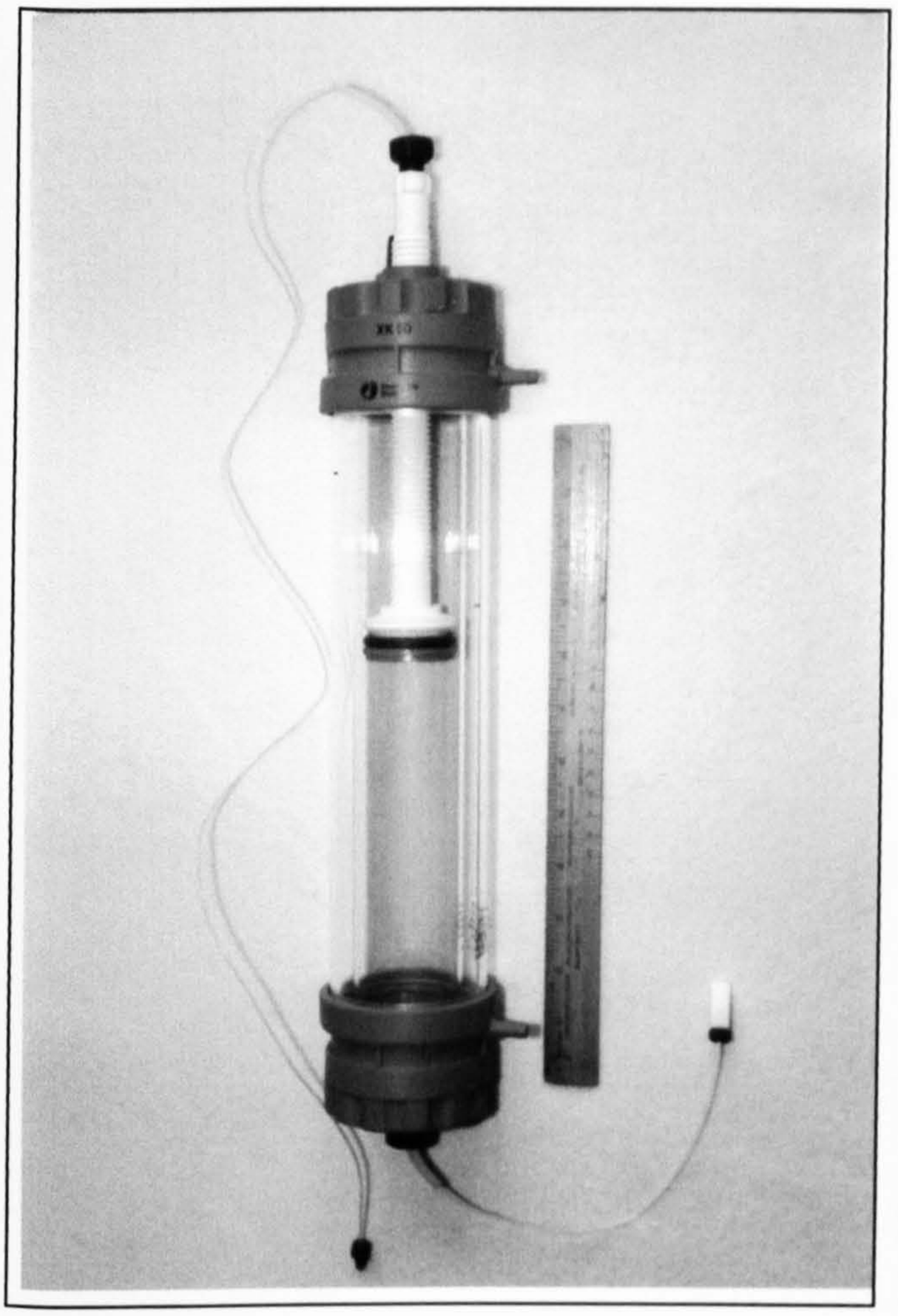


Plate 5.1.b. Dismantled column

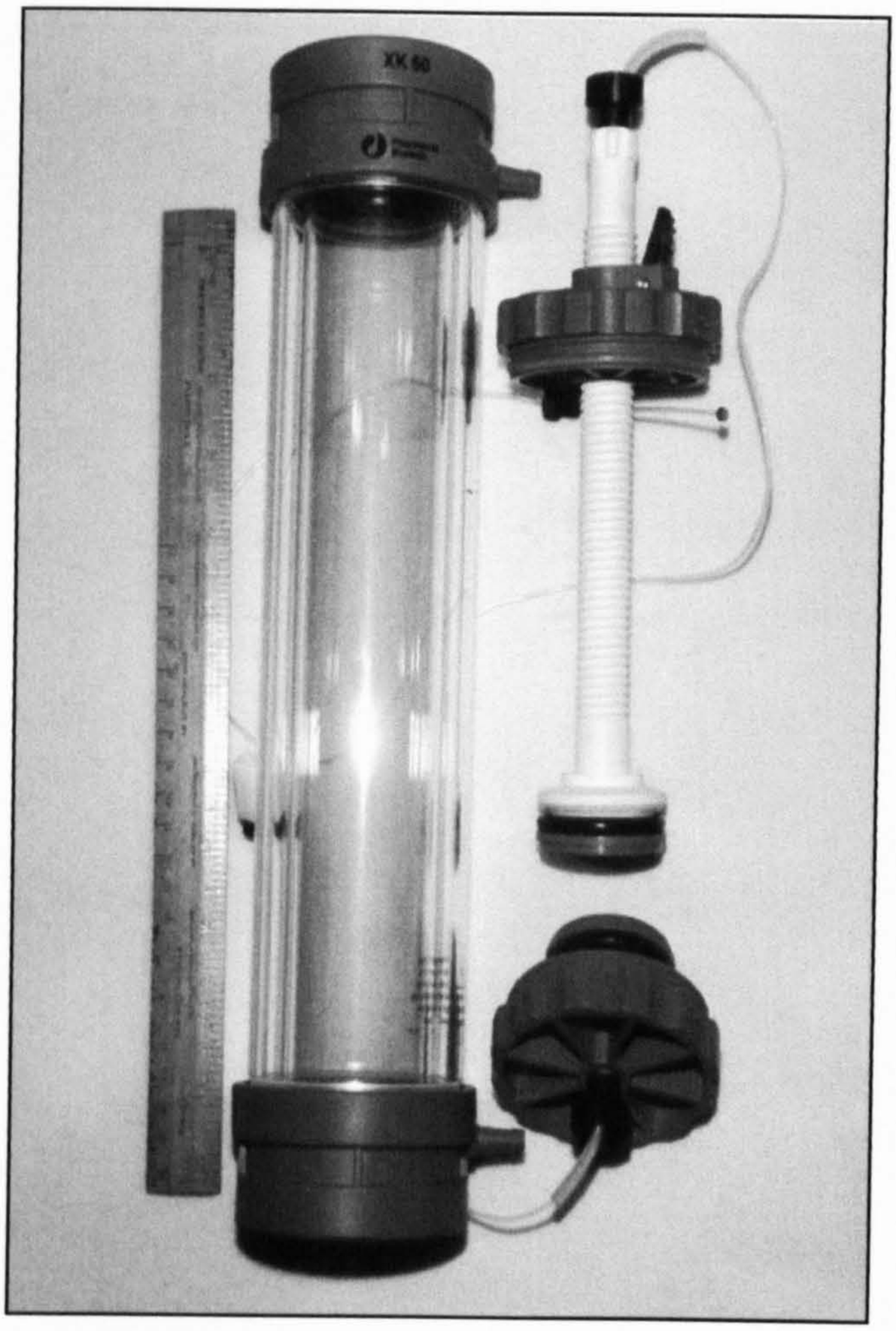


Table 5.1. Eluate volumes collected during the Dutch leaching tests.

Fraction (K)	Volume (ml)
1	30
2	30
3	90
4	150
5	300
6	900
7	1500

Plate 5.2. Experimental set up of the accelerated Dutch leaching test (NEN 7343) and modified column tests.

5.2.4. Modified Column Leaching Test:

The test procedure was similar to the Dutch test, however the soil was leached at a continuous flow rate of 1 cm^3 per minute. The fraction volumes collected are presented in Table 5.2.

Table 5.2. Eluate volumes collected during the Modified column leaching tests.

Fraction (K)	Volume (ml)
1	300
2	300
3	900
4	1500
5	3000
6	9000
7	15000

5.3. Results

Differences in leached arsenic (μg/kg) from the UK Environmental Agency and ASTM leaching tests for treated and untreated soils are presented in Table 5.3. Mean arsenic concentrations were reduced dramatically by the addition of iron III sulphate (+ lime) to all three soils in the UKEA leaching tests. Leachate collected from untreated Kidsgrove soil was found to be 73.2 μg/kg arsenic, which was reduced to 19 μg/kg in the iron III treated soil. This produced a 74% reduction in arsenic being leached (Table 5.6). Leachate collected from Rixton soil contained 367 μg/kg arsenic, which was reduced to 27 μg/kg with the addition of iron III, giving a 92% reduction in leachable arsenic (Table 5.6). Similar reductions were obtained from the Merton Bank soil (Table 5.3).

Comparable reductions in arsenic concentration were observed with the ASTM test for Merton bank and Rixton soil, showing reductions of 83.8% and 88.13% respectively (Table 5.6). However there was only a 5.8% reduction observed in Kidsgrove soil (Table 5.6). Iron II demonstrated a 94% reduction in arsenic from Rixton soil using the ASTM method, which was the greatest reduction in leached arsenic observed from the three soils with this test.

Addition of lime to Merton bank soil led to an increase of 7.45% and 7.79% arsenic in the leachates collected from the UKEA and ASTM tests respectively. The tests

however showed reductions in arsenic compared to the untreated soils, when lime was applied to Kidsgrove and Rixton substrates (Table 5.6).

Total leached arsenic (μg/kg) for each soil collected from the Dutch test can be seen in Figure 5.1 and Table 5.4. Goethite reduced leached arsenic from 48.74 μg/kg in Kidsgrove untreated soil to 40.69 μg/kg. A similar reduction in the same soil was observed with iron III, reducing the total leached arsenic to 41.22 μg/kg. Greater reductions were observed in Rixton soil, with iron II and III reducing total leached arsenic from 4467 μg/kg to 174.1 μg/kg and 126.55 μg/kg respectively (Table 5.4). Decreases in total leached arsenic were also observed with iron II and III compounds in Merton Bank soil (Figure 5.1).

Figures 5.6-5.8 indicate the percentage reductions in arsenic for selected fractions during the Dutch test. A trend in percentage arsenic reduction was observed in Rixton and Merton Bank soils. Over the course of the leaching tests iron III showed the greatest reductions (over 80%), followed by iron II, goethite and iron grit. This step-wise reduction demonstrates the efficiency of iron III compared to the other iron oxides. Kidsgrove soil did not show the same patterns in reduction (figure 5.8), with goethite being more efficient in the K4 and K7 fractions. Figures 5.3-5.5 show the changes in leached arsenic over the course of the Dutch tests. From the graphs, iron II and III have demonstrated their efficiency at reducing arsenic in the leachates collected during the tests. Merton Bank and Rixton soil both displayed a gradual increase in arsenic mobility in the untreated and lime treated soils. Both goethite and iron grit immobilise the metalloid, but not to the same extent as iron II and III.

Figure 5.2 shows the total leached arsenic collected for each soil from the modified column test. An increase in water leaching through the column produced a dramatic increase in total leached arsenic from the substrates. Untreated Kidsgrove soil leached a total of 3077 μg/kg arsenic which was reduced to 524 μg/kg in the iron III amended soil (Table 5.5), producing an 83% reduction. Greater reductions were observed in Rixton and Merton Bank soils amended with iron III, giving 87% and 92% reductions in total leached arsenic respectively.

Changes in the percentage reduction of arsenic leached over the course of the tests are depicted in figures 5.12-5.14. Rixton and Merton bank soils demonstrated similar patterns that were observed in the Dutch test. Iron oxides applied to Kidsgrove soil during

Figure 5.1. Total leached arsenic (ug/kg) for each soil from the Dutch test.

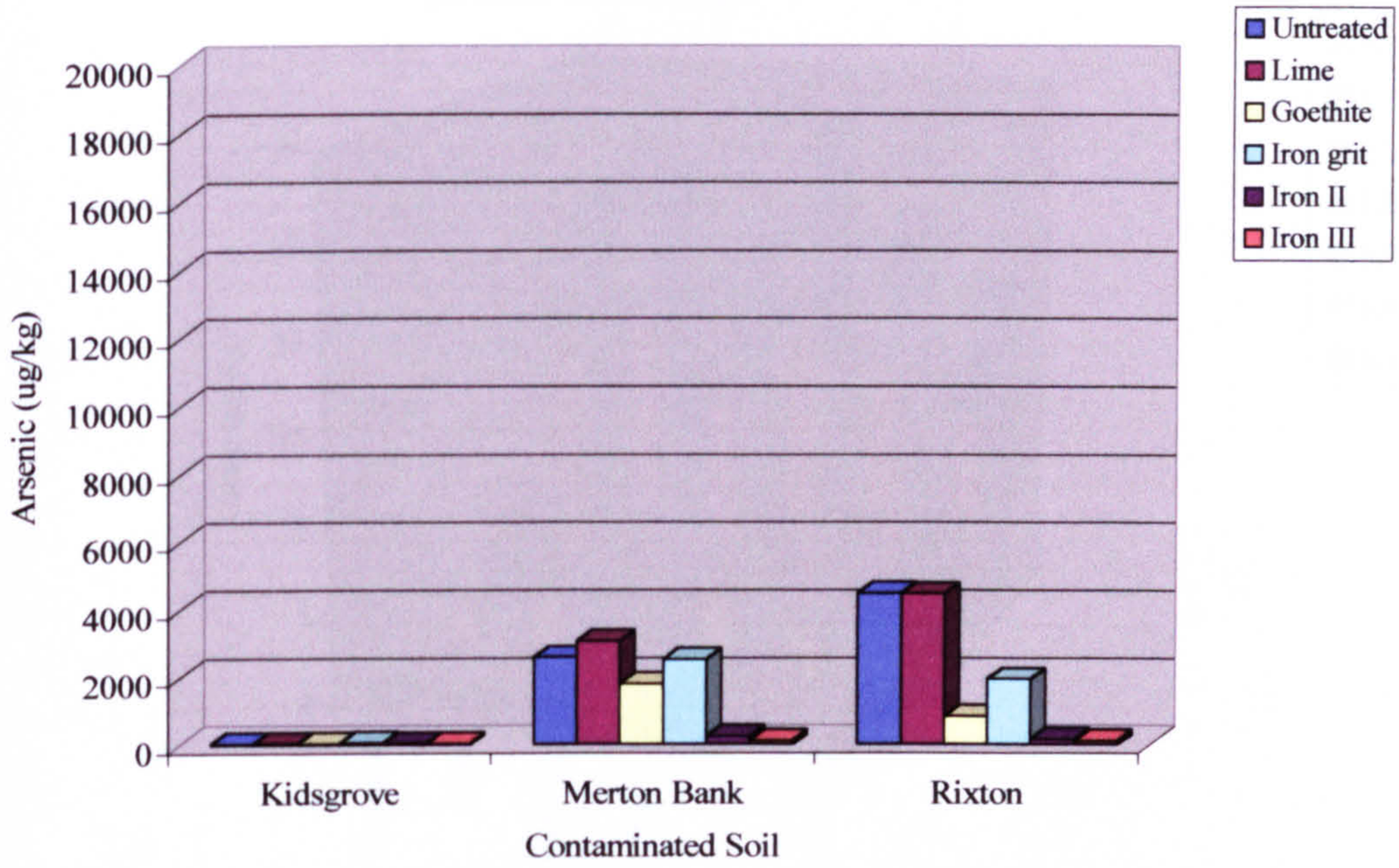


Figure 5.2. Total leached arsenic (ug/kg) for each soil from the modified column test (n=3).

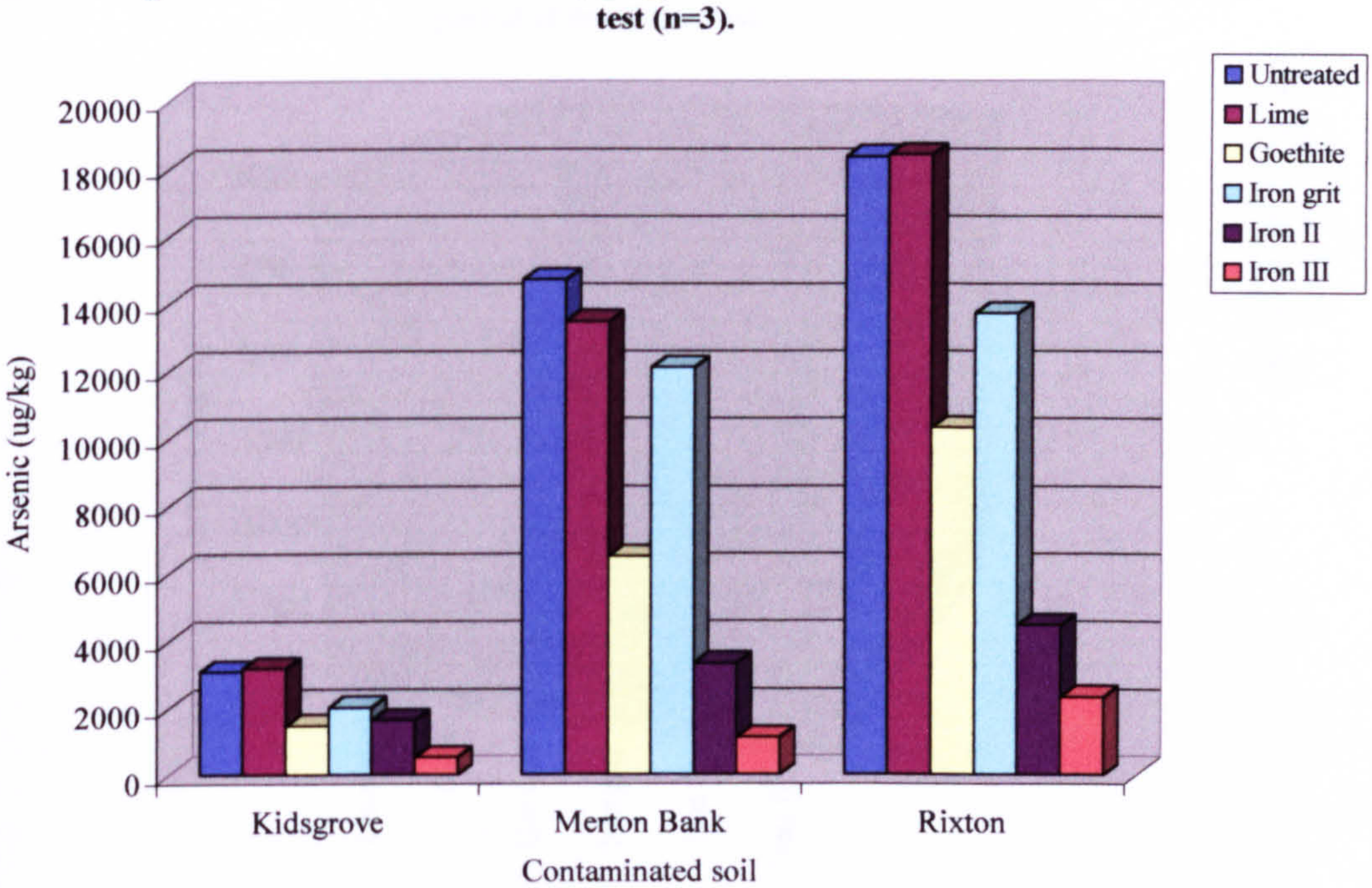


Figure 5.3. Changes in Kidsgrove soil arsenic (ug/kg) leached from each fraction over the time period of the Dutch test

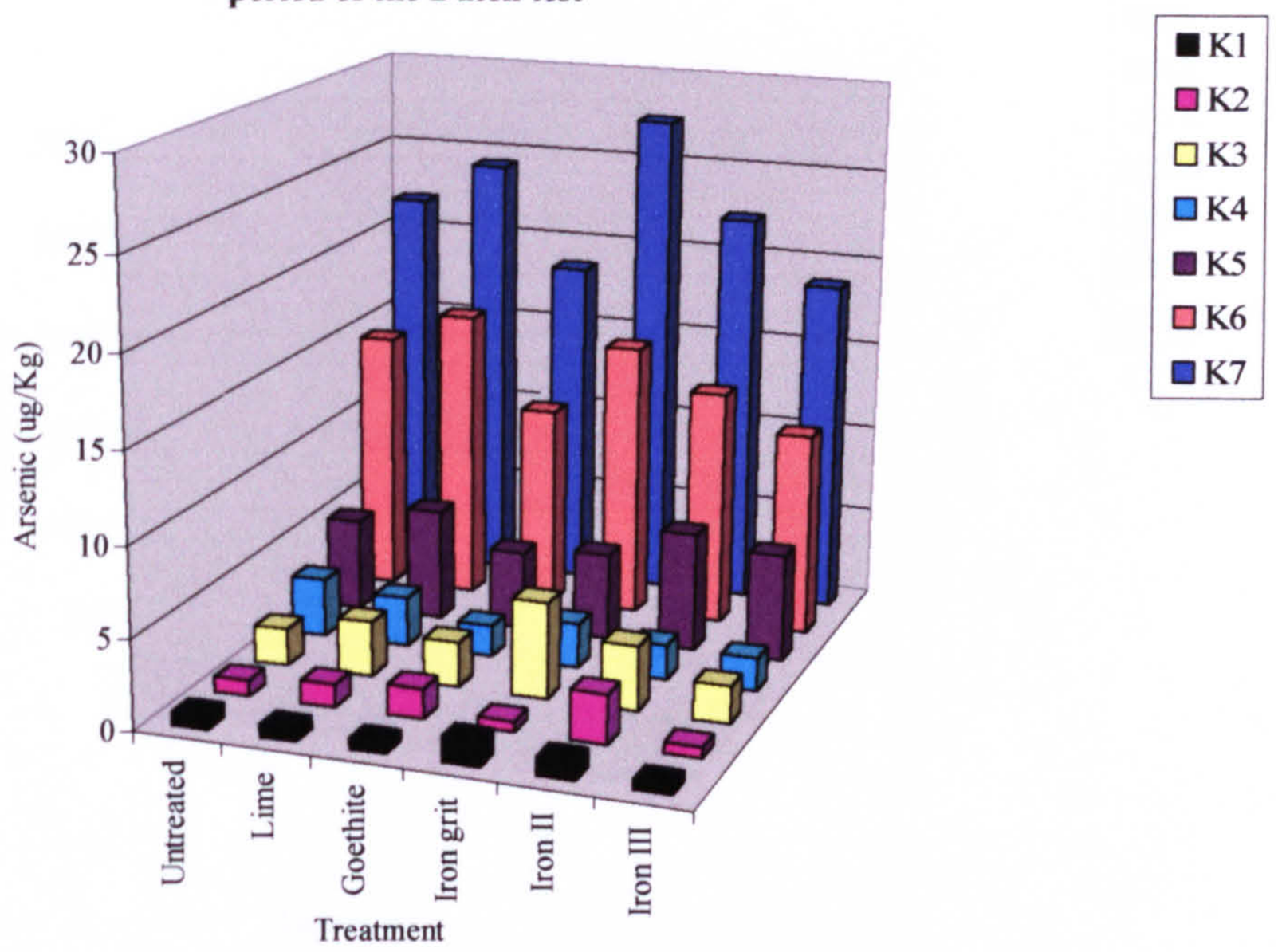


Figure 5.4. Changes in Rixton soil arsenic (ug/kg) leached from each fraction over the time period of the Dutch test.

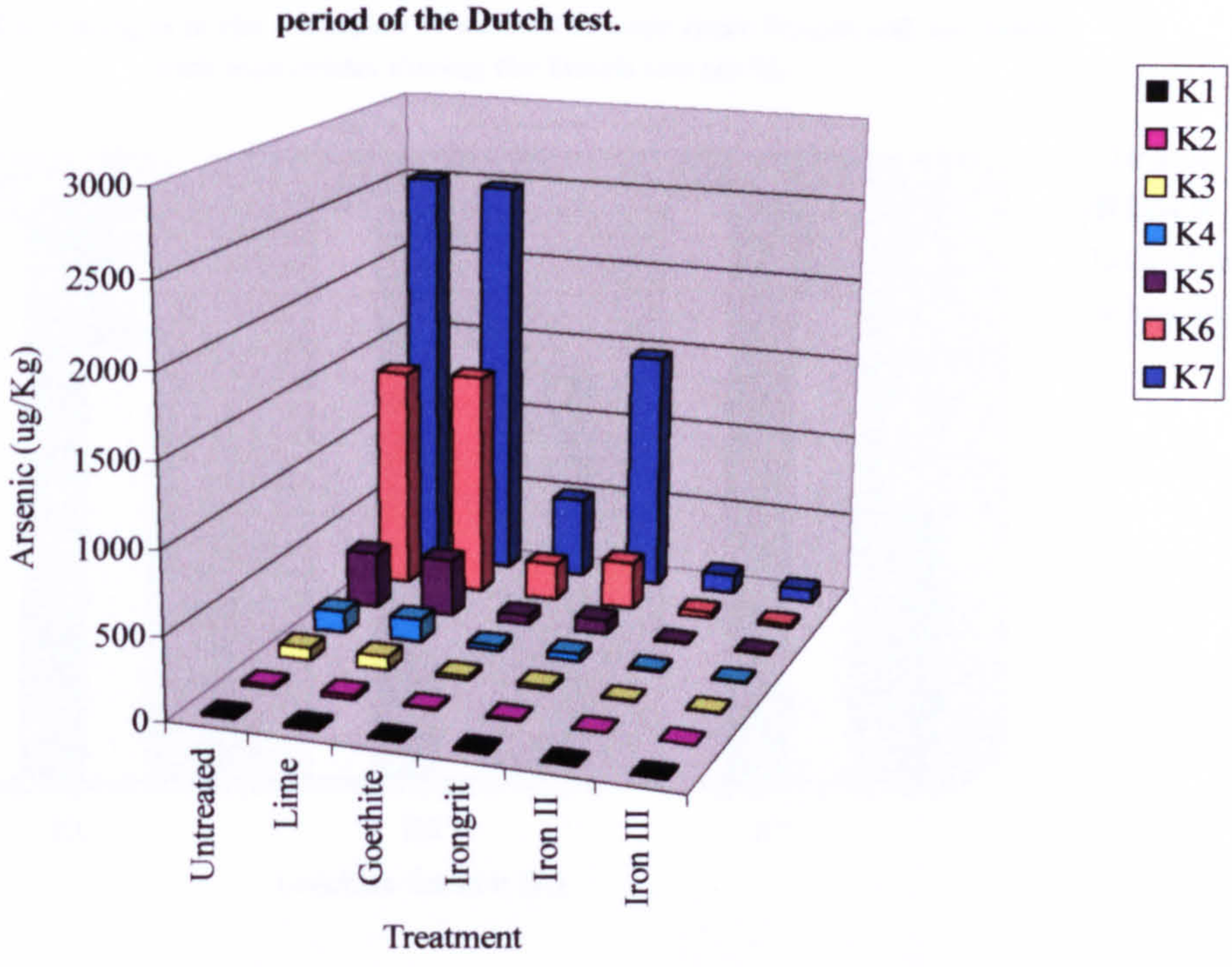


Figure 5.5. Changes in Merton Bank arsenic (ug/kg) leached from each fraction over the time period of the Dutch test

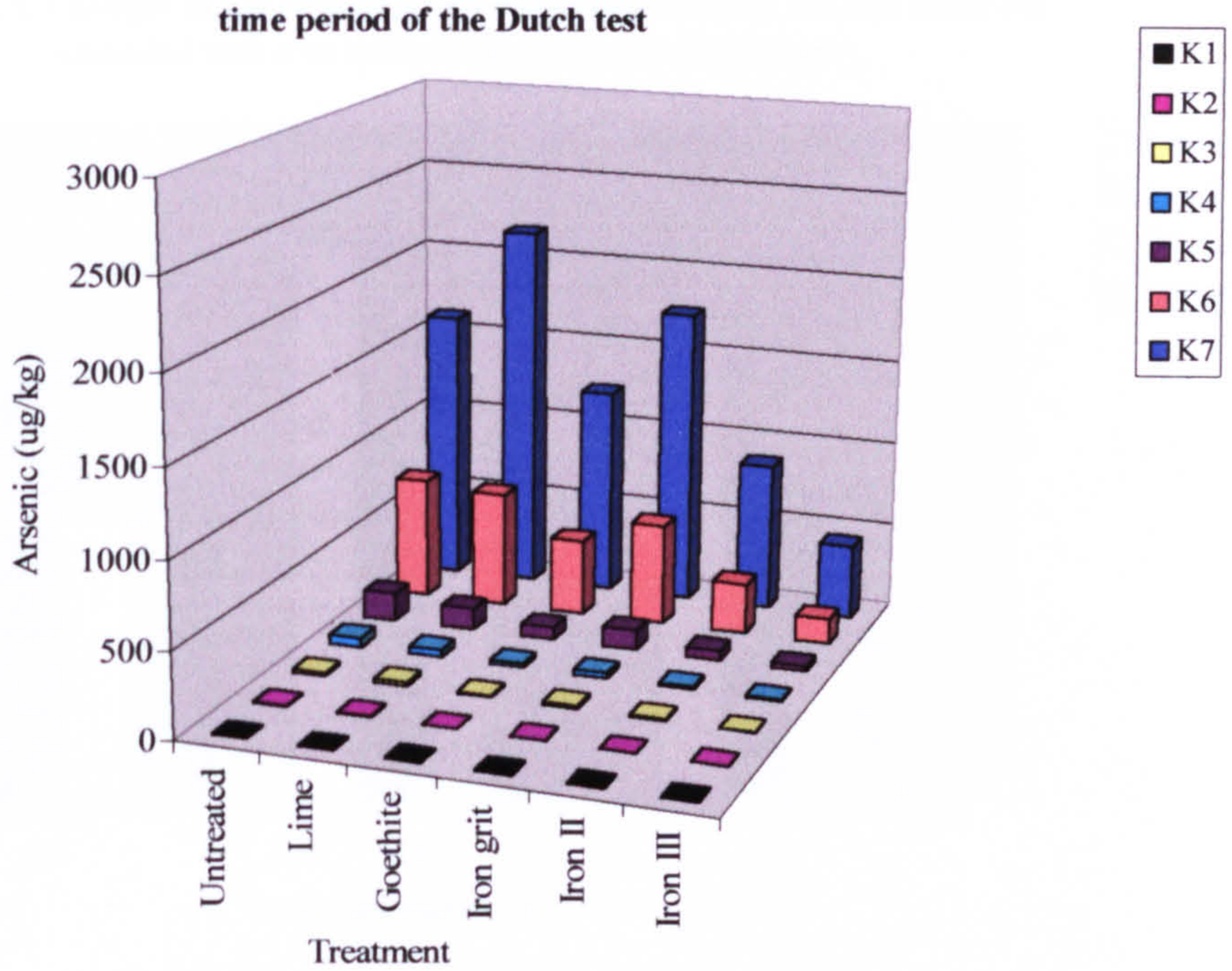


Figure 5.6. Changes in the reduction of leached arsenic from Rixton soil amended with iron oxides during the Dutch test (n=2).

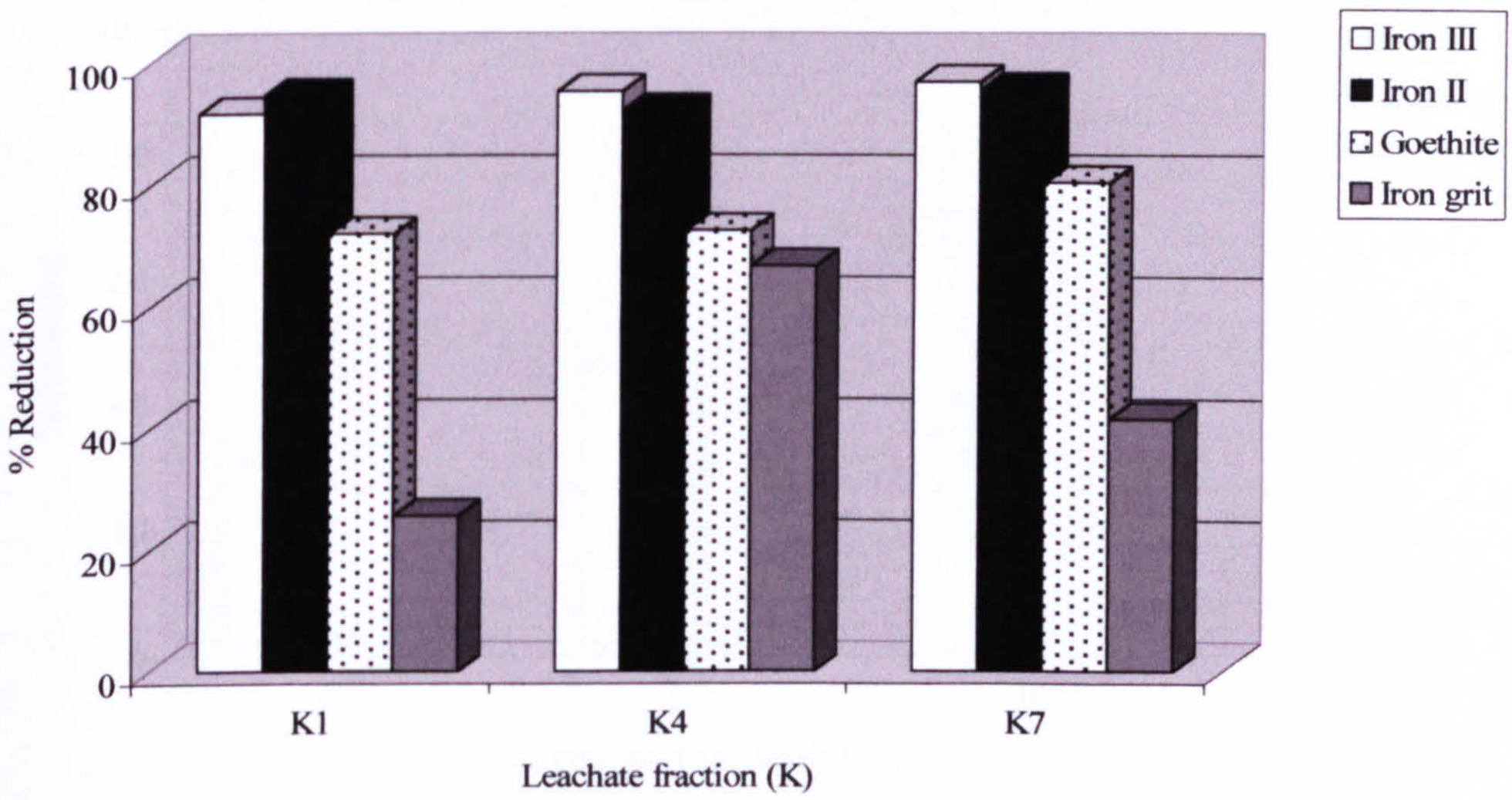


Figure 5.7. Changes in the reduction of leached arsenic from Merton Bank soil amended with iron oxides during the Dutch test (n=1).

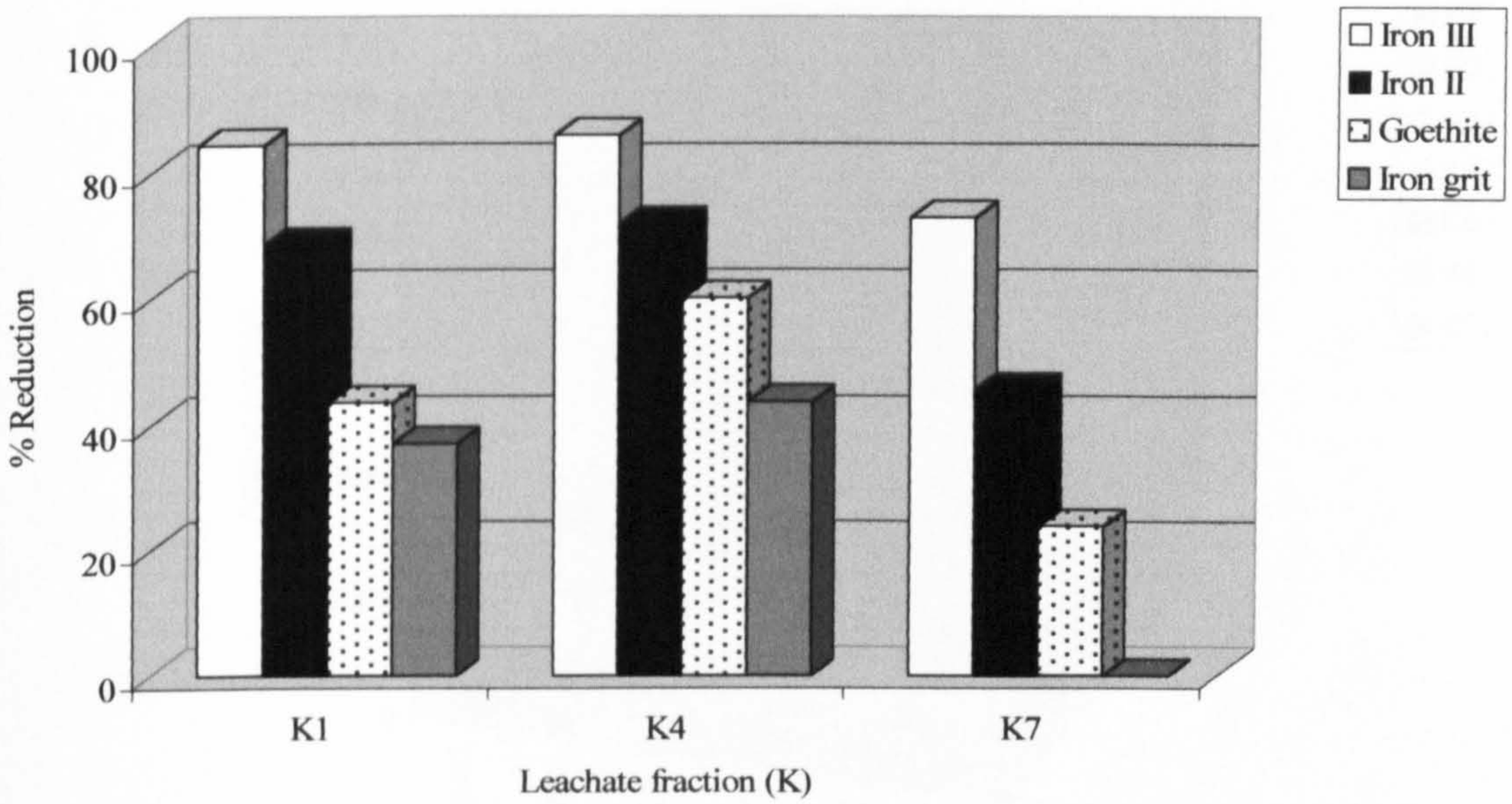


Figure 5.8. Changes in the reduction of leached arsenic from Kidsgrove soil amended with iron oxides during the Dutch test (n=1).

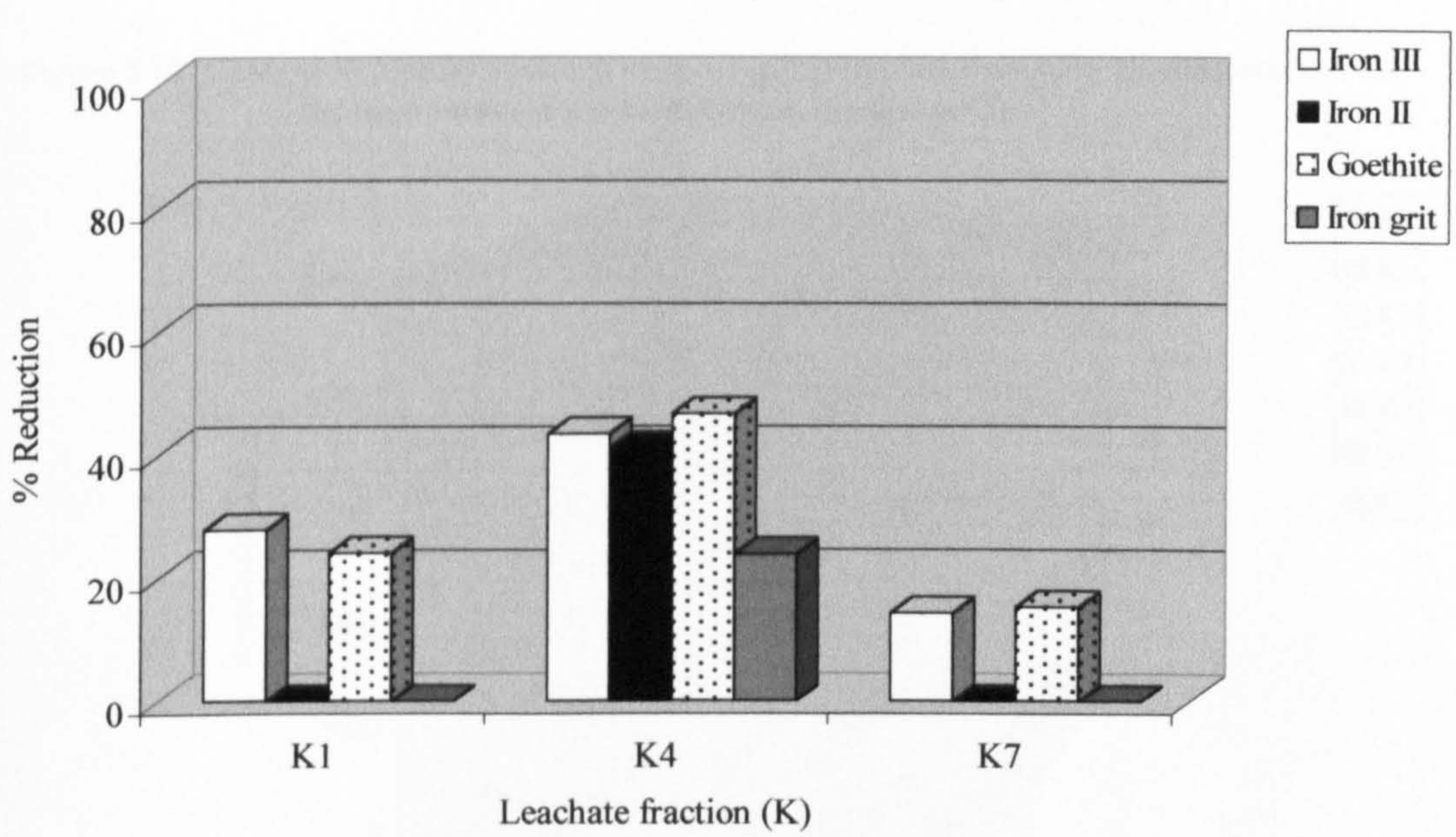


Figure 5.9. Changes in Rixton soil arsenic (ug/kg) leached from each fraction over the time period of the modified column test (n=3).

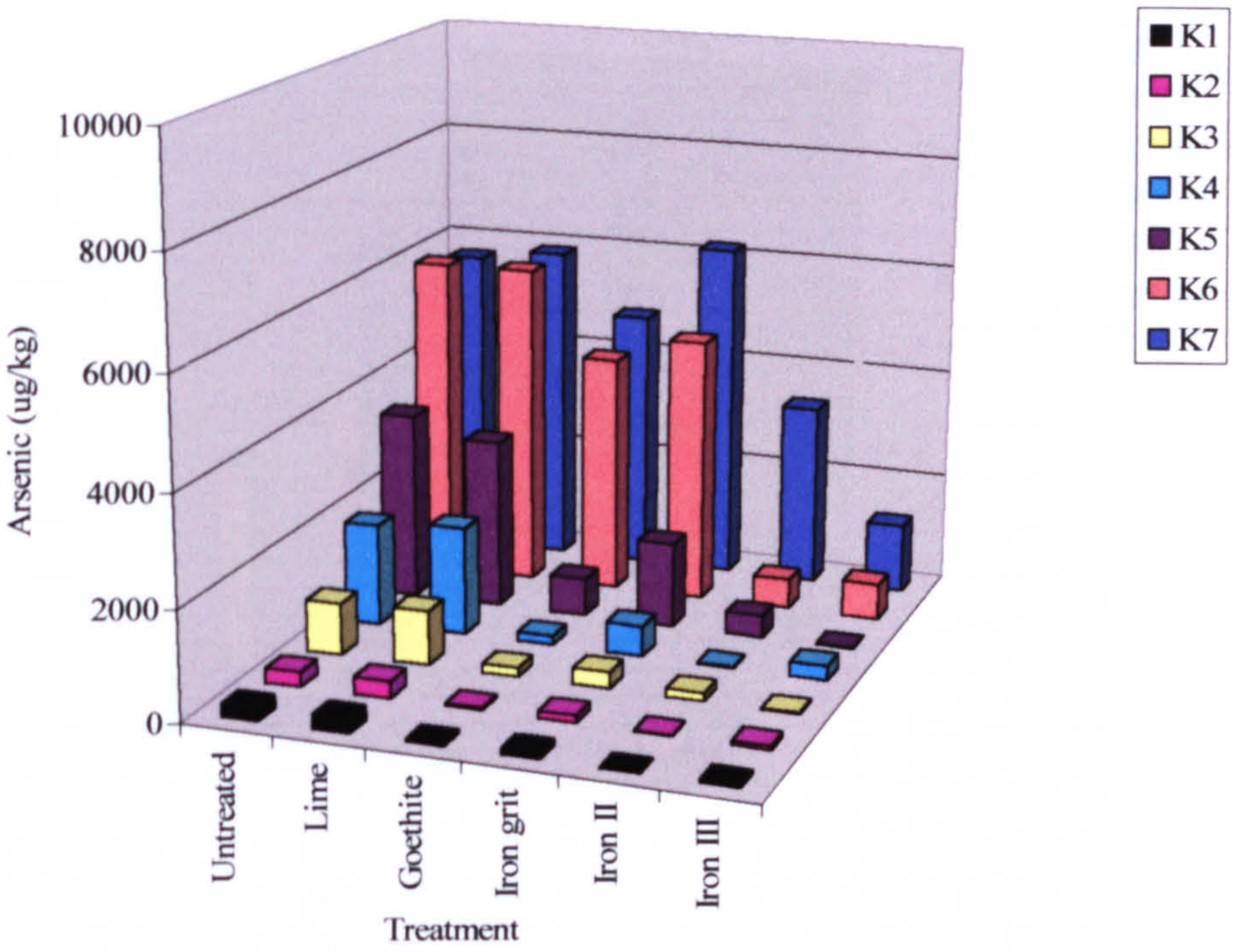


Figure 5.10. Changes in Merton bank soil arsenic (ug/kg) leached from each fraction over the time period of the Modified column test (n=3).

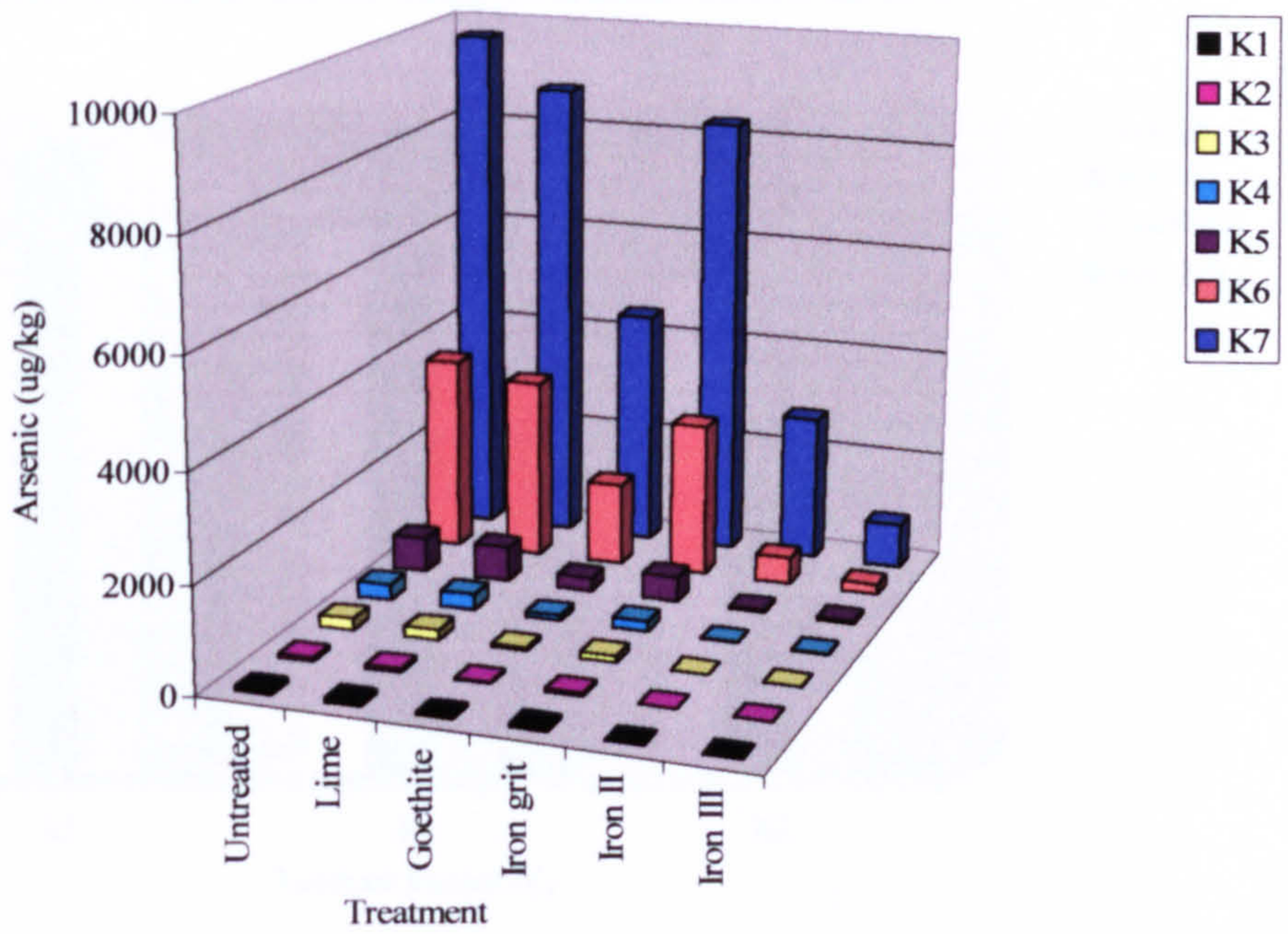


Figure 5.11. Changes in Kidsgrove soil arsenic (ug/kg) leached from each fraction over the time period of the modified column test (n=3).

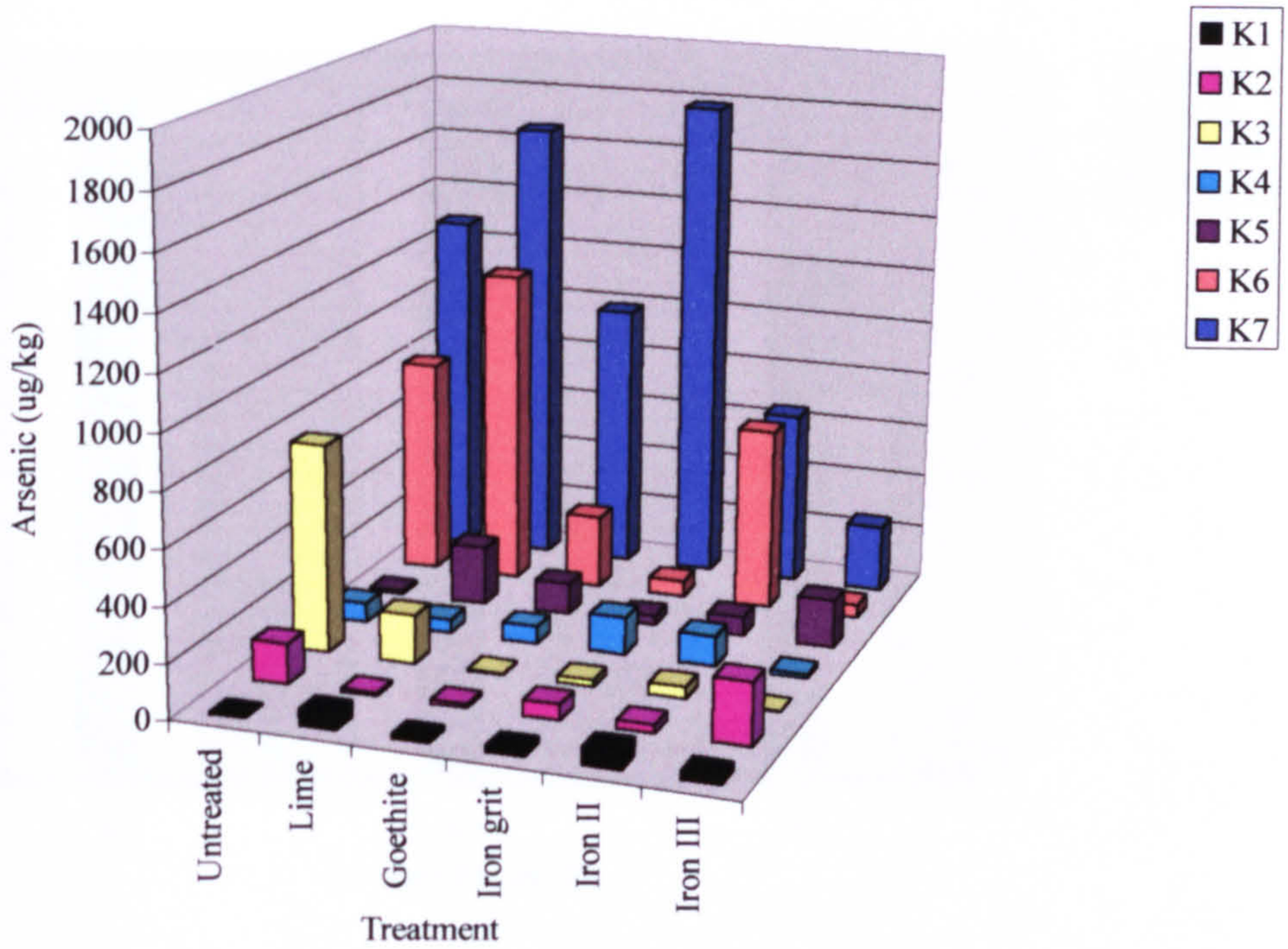


Figure 5.12. Changes in the reduction of leached arsenic with the iron oxide additives from Rixton soil during the modified column test (n=3)

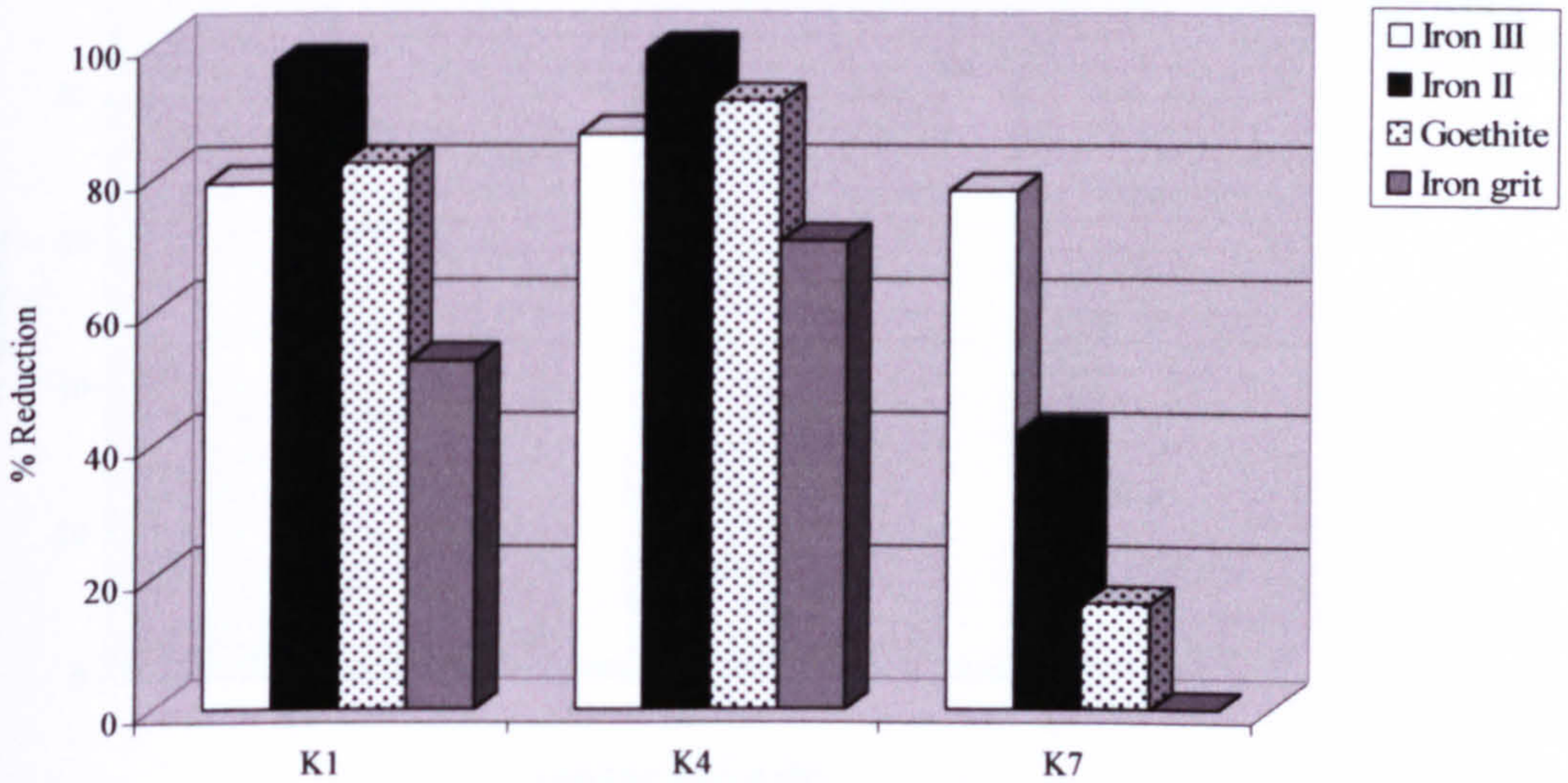


Figure 5.13. Changes in reduction of leached arsenic from Merton Bank soil during the modified column test (n=3)

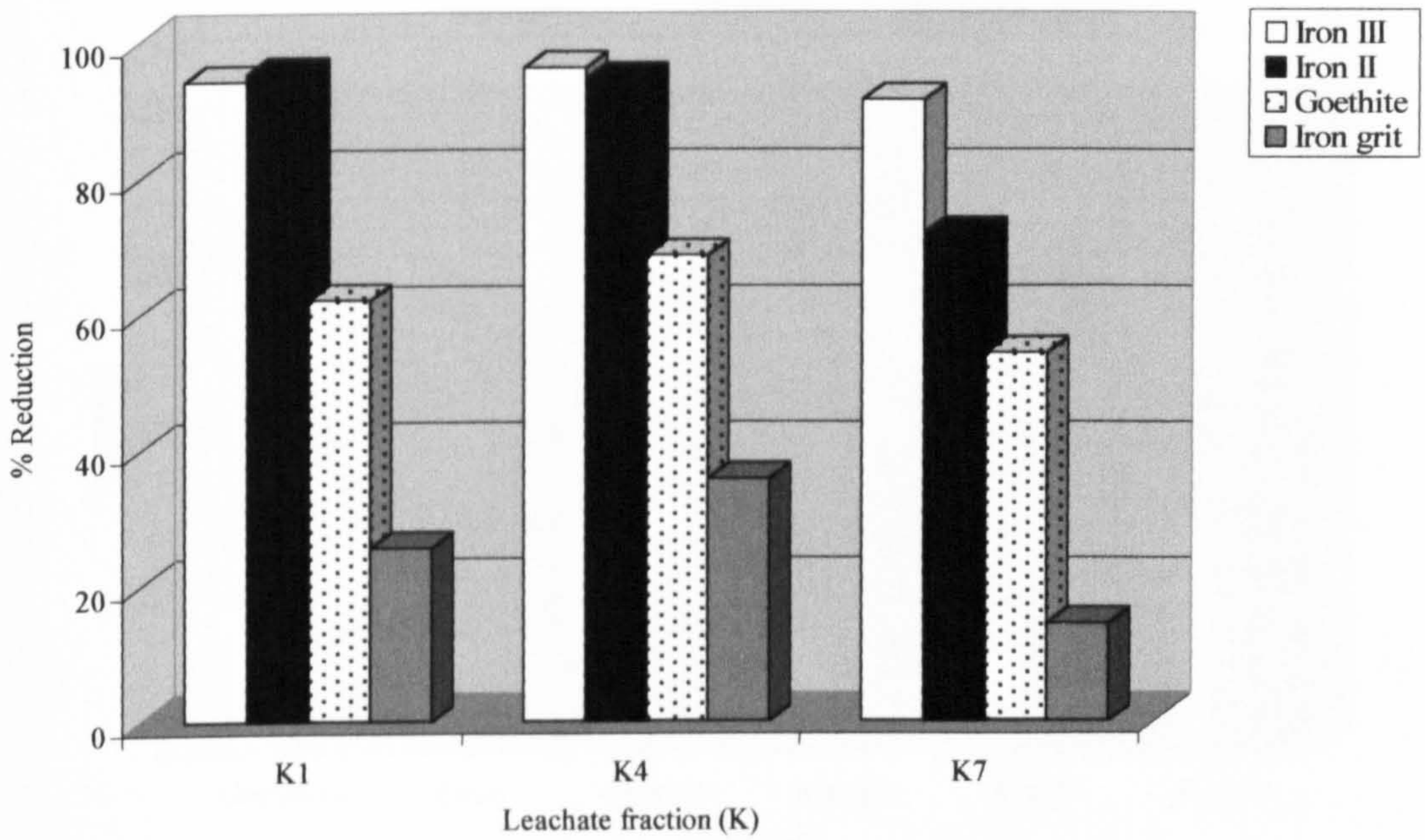


Figure 5.14. Changes in the reduction of leached arsenic from Kidsgrove soil during the modified column test (n=3).

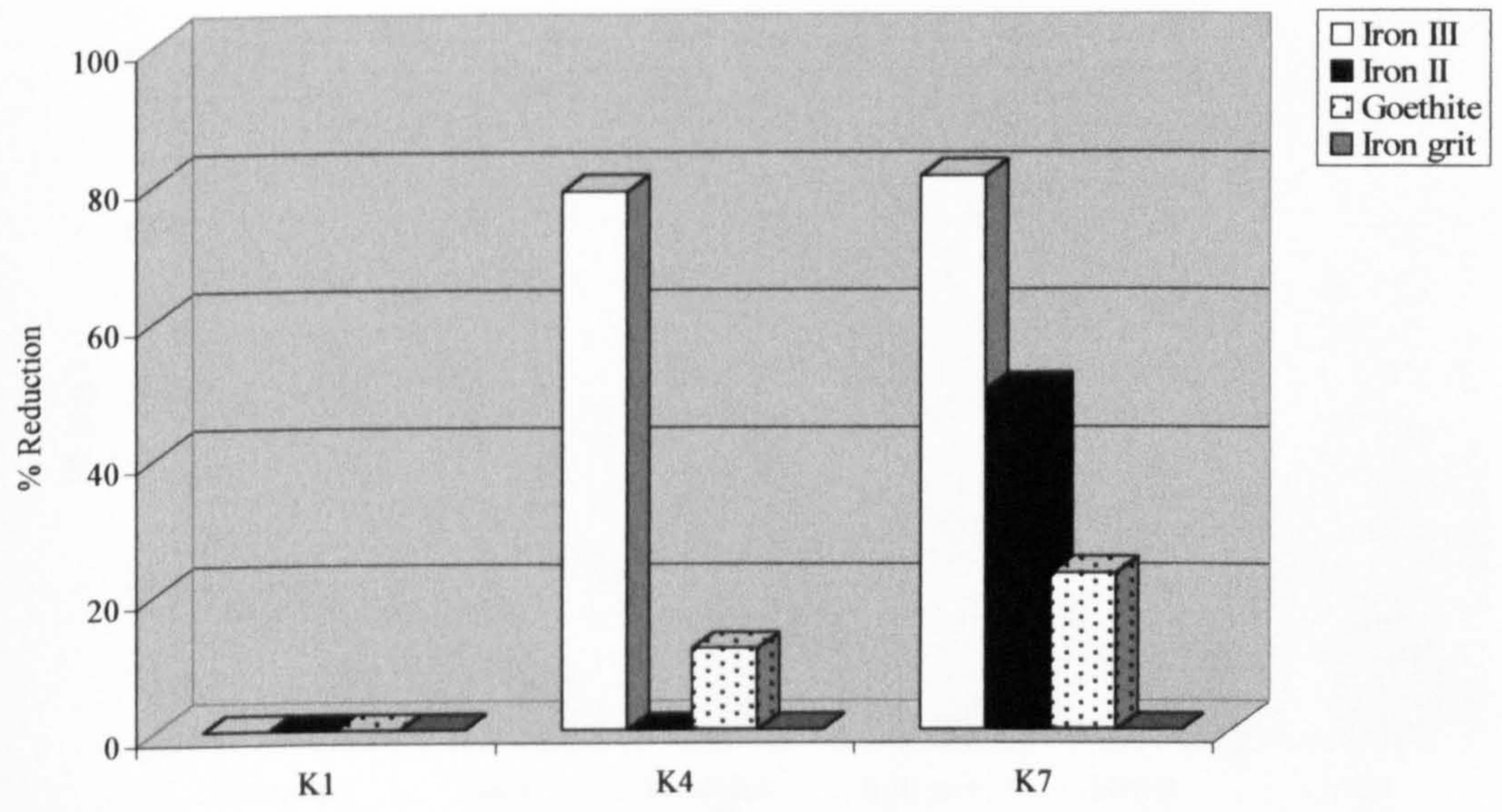


Figure 5.15. Effect of additives on lead solubility during the modified column test (n=3).

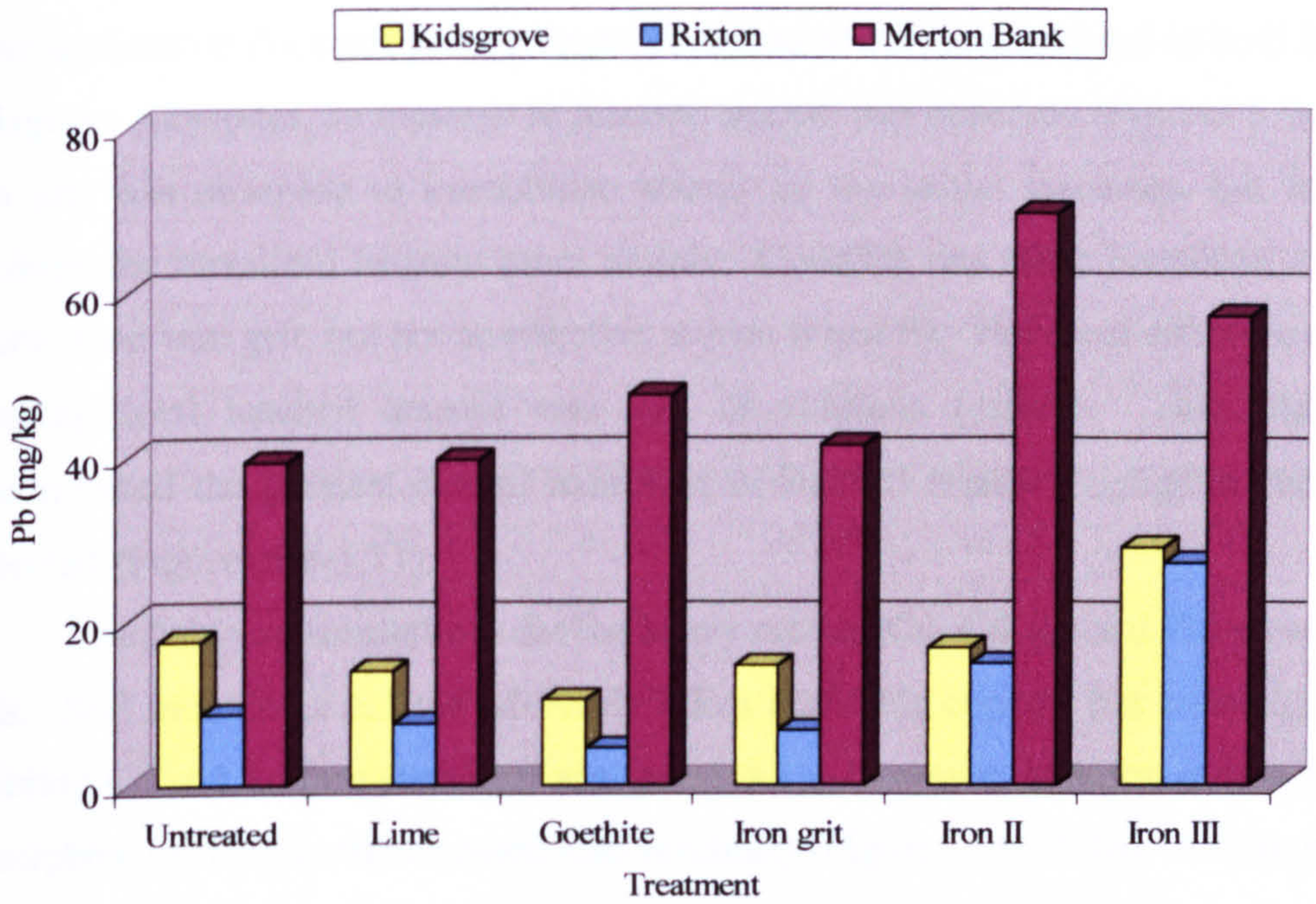
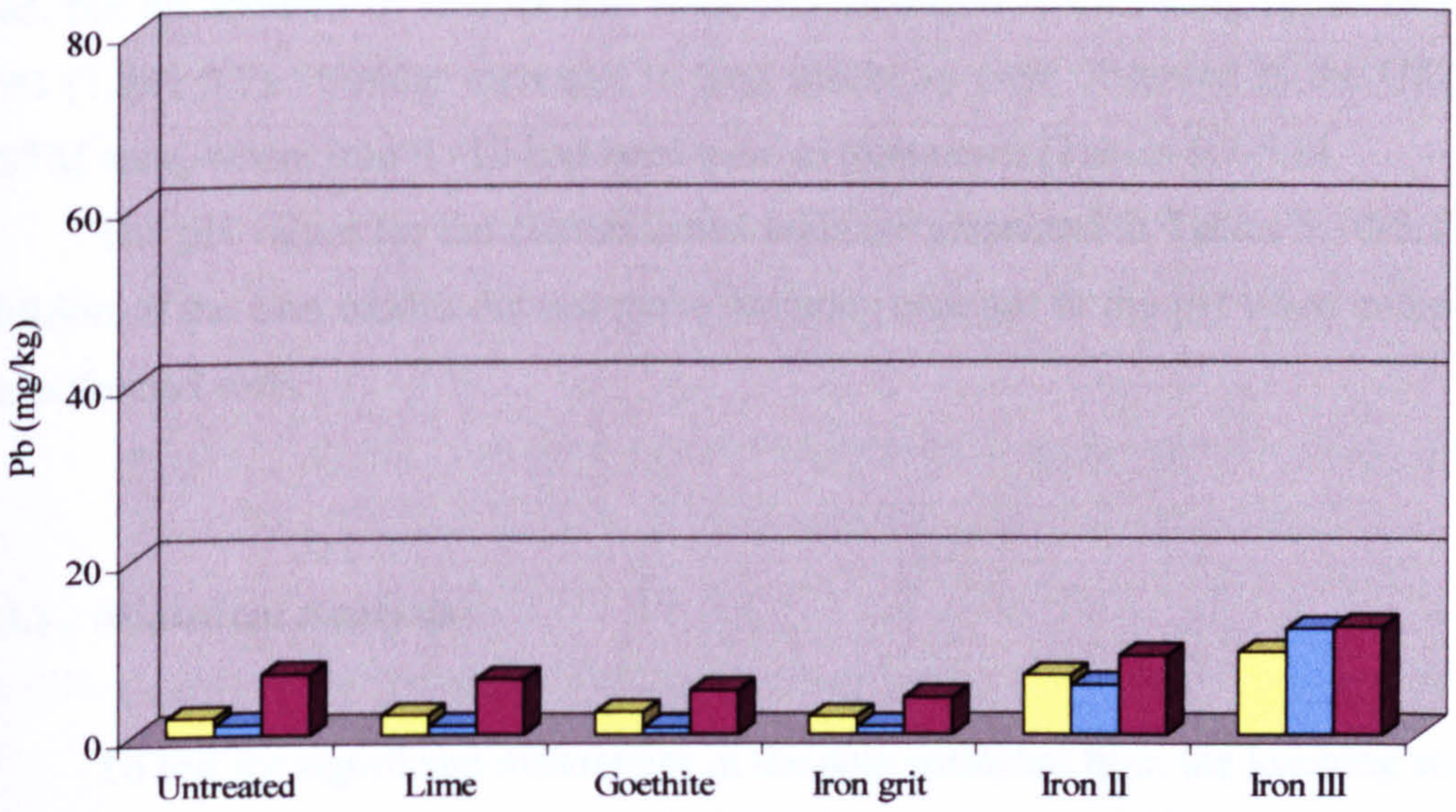


Figure 5.16. Effect of additives on lead solubility during the UKEA test (n=3).



the first fraction (K1) showed no reduction in arsenic compared to the untreated soil. However the later fractions showed that iron III sulphate was immobilising arsenic.

Figures 5.9-5.11 show the changes in leached arsenic (µg/kg) collected from each fraction. Overall a similar pattern can be seen for each soil during the course of the tests. Lime application does not prevent immobilisation of the metalloid and in both Rixton and Kidsgrove substrates, an increase in leached arsenic was observed (Figures 5.9 and 5.11). Iron grit was observed to immobilise arsenic in the initial leachates, but in the final fractions the metalloid became more mobile. Goethite was more beneficial at reducing arsenic than iron grit, but not as effective as iron II and III. The most effective additive at reducing total leached arsenic was iron III sulphate (+lime). This additive also demonstrated the greatest overall reduction in leached arsenic (µg/kg) in each fraction collected (Figures 5.9-5.11).

Leachable concentrations for the heavy metals (Cu, Cd, Zn and Pb) were low in all soils. Soil treatments did not adversely affect leachable copper, but were significant in affecting Cd and Zn (see statistical analysis, 5.3.1). However, addition of iron II and iron III sulphate (+ lime) both increased lead solubility (Figures 5.15-5.16). Addition of iron II sulphate to Merton Bank soil increased lead in the leachate collected from the Modified column test, from 39.3 mg/kg to 69.6 mg/kg, therefore producing a 77% increase in leachable lead (Figure 5.15). Untreated Kidsgrove soil was found to leach 17.49 mg/kg lead, but on addition of iron III lead solubility increased to 28.88 mg/kg, an increase of 65% (Table 5.9). Similar increases in lead solubility were observed in the UKEA and ASTM tests, where iron II / III had been used as treatments (Tables 5.7-5.8).

The pH values for the contaminated soils are presented in Tables 5.10-5.13. The addition of the iron oxides did not make dramatic changes to the pH when compared to the untreated soils.

5.3.1. Statistical Analysis

To test for significant differences in the data collected from the leaching studies, a multifactorial analysis of variance using a general linear model (GLM) was carried out similar to that used for the sequential extraction scheme. This would determine if soil or treatment affected the concentration of arsenic and heavy metals leached from the soils

using the standard methods (Tables 5.14-5.28). An interaction term was also applied to the data in order to determine if the soil and treatment together affected the concentration of leached metalloid / metal.

Arsenic leached from the soils in the UK EA water extract tests showed a significant difference between the concentration of arsenic leached and the soil type ($F = 14.06$, $P < 0.001$). A significant difference was also obtained for arsenic concentration and the effect of treatment on arsenic leachability ($F = 4.58$, $P = 0.002$). However, the interaction of soil type and treatment was not significant ($F = 1.51$, $P = 0.178$). Arsenic leached from the soils using the ASTM method showed a significant difference between the different soil types ($F = 120.68$, $P < 0.001$) and treatment effect ($F = 28.63$, $P < 0.001$). There was also a significant difference when the interaction of soil type and treatment were combined ($F = 19.25$, $P < 0.001$). The modified column test produced significant differences for both soil type ($F = 30.24$, $P < 0.001$) and treatment effect ($F = 16.63$, $P < 0.001$) and a significant difference was obtained when the interaction of both soil type and treatment were combined ($F = 2.57$, $P = 0.019$).

A significant difference was obtained between the concentration of copper leached during the UK EA tests and soil type ($F = 4.51$, $P = 0.018$), however treatment effect was not significant for copper concentrations ($F = 2.44$, $P = 0.053$) and the interaction of both soil type and treatment were non significant ($F = 1.32$, $P = 0.259$). Soil type ($F = 230.43$, $P < 0.001$) and treatment ($F = 23.40$, $P < 0.001$) were both significant however for copper concentrations observed using the ASTM method of extraction, as were the interaction of both effects ($F = 5.66$, $P < 0.001$). Copper extracted using the column leaching test was significantly different for soil type ($F = 33.73$, $P < 0.001$), but treatment effect on copper concentrations was not significant in this test ($F = 2.08$, $P = 0.091$), as was the interaction effect ($F = 0.59$, $P = 0.814$).

Cadmium leachate concentrations were significantly different for soil type ($F = 82.76$, $P < 0.001$), treatment effect ($F = 80.13$, $P < 0.001$) and the interaction of both effects ($F = 32.56$, $P < 0.001$) for the UK EA leaching tests. For the ASTM method significant differences were also obtained for soil type ($F = 153.55$, $P < 0.001$), treatment ($F = 64.92$, $P < 0.001$) and the interaction term ($F = 38.94$, $P < 0.001$). The column leaching test also showed significant differences for copper leachates with soil type ($F = 15.51$, $P < 0.001$) treatment ($F = 13.07$, $P < 0.001$) and the interaction term ($F = 6.30$, $P < 0.001$).

Zinc leachability with the UK EA test, was significantly different between soil types ($F = 3.43$, $P = 0.043$) and with treatment effect ($F = 15.91$, $P < 0.001$). However the effect of interaction of both soil type and type of treatment was not significant ($F = 1.67$, $P = 0.126$). The ASTM method produced significant differences for soil type ($F = 343.12$, $P < 0.001$) treatment effect ($F = 41.61$, $P < 0.001$) and the interaction of both ($F = 10.23$, $P < 0.001$) on zinc concentrations. For the column tests, soil type was significant ($F = 37.63$, $P < 0.001$), as were the different treatments ($F = 7.91$, $P < 0.001$), although the interaction of both produced no significant differences ($F = 2.10$, $P = 0.051$).

The effect of soil type on lead concentrations extracted using the UK EA method was significant ($F = 75.27$, $P < 0.001$) as was the type of treatment ($F = 122.13$, $P < 0.001$). The interaction of both soil type and treatment were also significant for lead leachability ($F = 4.09$, $P < 0.001$). Significant differences were also obtained for lead with the ASTM method for soil type ($F = 563.34$, $P < 0.001$), treatment effect ($F = 58.64$, $P < 0.001$) and the interaction of both effects ($F = 13.25$, $P < 0.001$). Soil type was again significant ($F = 37.28$, $P < 0.001$) for lead concentrations in the leachates collected from the column studies, as was the effect of treatment ($F = 2.70$, $P = 0.036$). However the interaction of both produced a non-significant result ($F = 0.58$, $P = 0.816$).

To conclude, the statistical analysis established that firstly the effect of soil type was significant on metalloid / metal leachate concentrations. Secondly, the effect of different additive treatments was significant in affecting arsenic leachate concentrations, whilst the heavy metals cadmium, zinc and lead were significantly affected by the treatments but copper was not. Finally the interaction of both soil type and treatment were significant for arsenic leachates with the exception of the UK EA water extract tests. However for the heavy metals, the combined effect of soil and treatment was significant for cadmium only in the column tests.

5.4. Discussion

It has been reported that land contaminated with heavy metals such as copper and cadmium may be remediated by the addition of lime and synthetic zeolites (Rebedea, 1997). In such circumstances the effect of adding these materials to a soil contaminated with arsenic may actually increase mobility of the metalloid within the soil system. Sites

contaminated with arsenic will require alternative approaches in order to prevent mobilisation of the metalloid. In this investigation iron oxides and lime were considered in order to remediate soils that were contaminated with high levels of arsenic.

The Dutch leaching test can be used to predict the long-term behaviour of heavy metals/As in a contaminated soil. By studying the chemical composition of soil, analysis of the soil solution can be determined. The soil solution is in direct contact with plant roots and will provide important information with regard to the effectiveness of the additives. The results of this study have indicated that whilst all the iron oxides investigated immobilised arsenic in the soil system, the compounds of iron II / III sulphate (+ lime) which form iron oxides *in situ*, were the most efficient. Arsenic has been shown to have a high affinity for oxidic surfaces, preferentially attaching itself to iron oxides (Atkins & Lewis, 1976; Wauchope, 1975), that will co-precipitate and scavenge (adsorb) anions such as arsenate from the soil solution. They are capable of this due to a pH dependent charge, which is negative in alkaline conditions but positive in acidic solutions. However, the pH that exists where there is no net charge, the point of zero charge (PZC) is in the range of 7-10 for iron oxides (Alloway, 1995). Tables 5.10-5.12 depict the changes in pH from the soils during the leaching tests. The pH range for all contaminated soils fell between the range of 7-10 during the column and standard leaching tests and this would help to explain the effective immobilisation of arsenic.

Lime has the affect of increasing the soil pH and it has been used to reduce the bioavailability of heavy metals through increased soil adsorption (Rebedea, 1997). In this study lime was used to detect if its pH affected the mobility of arsenic. The results of the column tests indicated that lime did increase arsenic mobility in solution, but in certain cases it was found to reduce arsenic concentrations. It is known that arsenic will bind to calcium (Ca^{2+}) but not as efficiently as to iron, possibly by forming complexes with arsenic anions and therefore reducing its mobilisation.

There was a broad agreement in the relative changes in arsenic leachability between the tests. Although the leaching times for each test were different, the additives affected arsenic in much the same way, with iron II and III always providing the greatest reductions. However there were differences in the concentrations of arsenic leached between the UK and ASTM tests and this was related to a time dependant factor.

The short-term tests, although efficient at indicating the concentration of metals leached, only represent the effect of the additives over a short time scale. The vigorous

shaking of soil and water during the ASTM tests does not represent natural leaching conditions either. The Dutch leaching test therefore, can be used to assess the efficacy of a treatment over a longer time scale and be used to simulate the long-term behaviour of metals in soils under more natural leaching conditions. Therefore the test will provide a more realistic assessment of the effects of water leaching compared to the short-term data in the UKEA and ASTM methods. The Dutch test was modified, whereby the soil was leached to an even greater extent (Modified column tests). Results demonstrated that even when leaching conditions were intensified the iron oxides remained stable, i.e. they adsorbed arsenic out of the soil solution and prevented it from being leached.

Addition of the soil treatments did not adversely affect leachable copper, cadmium and zinc concentrations but lead was mobilised in the presence of iron II and III sulphate. The patterns for leachable lead were the same for all three tests. Identification of increased lead solubility was important, because when treating a contaminated site for a particular element, other metals present in the substrate must also be monitored to ensure that their speciation is not altered. Lead is frequently associated with arsenic where soils have been contaminated with lead arsenate ($PbAsO_4$) pesticides, for example in orchards (Anastasia and Kender, 1973) and Peryea and Creger (1994) found that the movement of these two elements was greater in soils with low organic matter and clay content. The association of these two elements with regard to pesticide application is of importance here because identification of past land use and soil characteristics is vital before any remediation programme is initiated.

5.5. Conclusions.

The leaching studies demonstrated that iron oxides produced *in situ* were more effective at immobilising soluble arsenic in contaminated soils compared to goethite. The order of preference for arsenic adsorption was determined as Fe^{3+} > Fe^{2+}> Iron grit > Goethite > Lime. Column leaching tests also demonstrated that arsenic immobilised by iron oxide treatments were stable not only in the short-term (UKEA and ASTM tests) but also over a longer time scale. Therefore when considering the leachability of a metal from a contaminated site the choice of leaching test is important. Although results from

standard short-term tests agree with the column tests it is important to determine the effects over the longer time scale, thereby indicating the additives durability.

Careful consideration must also be given to complete soil chemistry when remediating a contaminated site. In this study, metals present in the soils demonstrated that they will behave differently, for example arsenic and lead mobility, when the soil chemistry is changed by application of inorganic additives.

The nature of the soil is also important in terms of remediation. Fly ash (Rixton) used in this investigation was very sandy in texture compared to the other soils and was also lower in organic matter content. The sorptive capacity of a soil is important for its role in binding arsenic (Woolson *et al.*, 1971). If a soil is sandy or contains a low clay capacity, it is less likely that arsenic will bind when compared to one which has high organic matter, is silty or clay-like (Fraust *et al.*, 1987a,b). It has been shown that arsenic has a shorter residence time in soils that are sandier, especially when the pH is more alkaline (Gullens *et al.*, 1979; Masscheleyn *et al.*, 1991b). The physical and chemical properties of a soil, such as texture and pH are therefore important when considering remediation.

The leaching studies demonstrated that arsenic mobility was reduced by addition of Fe-bearing additives. These are consequently very important for the reduction of arsenic in soil leachates. The column investigations represented a close approximation to a soil in the field and from these studies predictions can be made as to the effects on plant uptake in such situations. In the next chapter trials involving plant development in amended soils will be considered with regard to additive effects on arsenic uptake and plant growth.

Table 5.3. Standard leaching tests for the three soils (n=3). Figures in brackets represent standard deviations. Leached arsenic (ug/kg) from Un/treated soils.

	KIDSGROVE		RIXTON		MERTON BANK	
	UK EA	**ASTM**	**UK EA**	**ASTM**	**UK EA**	**ASTM**
Untreated	73.2 (± 9.01)	17 (± 0.20)	367 (± 70.34)	682 (± 25.71)	460 (± 1.55)	413.4 (± 2.52)
Lime	28 (± 0.56)	9.05 (± 0.45)	325 (± 31.32)	656 (± 43.42)	494.2 (± 0.55)	446 (± 0.45)
Goethite	30 (± 1.12)	15.09 (± 0.41)	207 (± 18.89)	263 (± 24.90)	522 (± 4.04)	255.3 (± 1.09)
Iron grit	19.7 (± 1.24)	23 (± 0.04)	301 (± 34.05)	171 (± 8.99)	245 (± 1.46)	63.1 (± 0.50)
Iron II	23 (± 1.60)	22 (± 2.31)	47.4 (± 5.81)	41 (± 1.77)	77 (± 0.40)	99.2 (± 0.32)
Iron III	19 (± 1.00)	15.7 (± 0.77)	27 (± 4.79)	81 (± 33.04)	40 (± 0.12)	67 (± 1.22)

Table 5.4 . Leached arsenic (µg/kg) from the Dutch test.

	UNTREATED	LIME	GOETHITE	IRON GRIT	IRON II	IRON III
Kidsgrove	48.74	54.63	40.69	57.36	51.36	41.22
Rixton	4467	4458.5	842.55	1935.5	174.1	126.55
Merton Bank	2576	3052	1783	2519	243.6	117.75

Table 5.5. Leached arsenic (µg/kg) from modified column test (n=3). Figures in brackets represent the standard deviations.

	UNTREATED	LIME	GOETHITE	IRON GRIT	IRON II	IRON III
Kidsgrove	3077 (± 1039.22)	3178 (± 2135.57)	1468 (± 1743.32)	2009 (± 2861.54)	1631 (± 1686.79)	524 (± 338.68)
Rixton	18331 (± 3013.80)	18399 (±1468.48)	10276 (±2131.19)	13676 (±3598.60)	4463 (± 3656.41)	2330 (± 2517.53)
Merton Bank	14681 (±3514.4)	13443 (± 2592.69)	6472 (±2488.44)	12075 (± 5298.13)	3317.3 (±2392.90)	1111.2 (±491.49)

Table 5.6. Effect of additives on contaminated soils (% change in leachable arsenic, µg/kg).

	KIDSGROVE		RIXTON		MERTON BANK	
	UKEA	ASTM	UKEA	ASTM	UKEA	ASTM
Lime	- 62.1	- 45.7	- 11.5	- 3.7	+ 7.45	+ 7.79
Goethite	- 59.45	- 9.53	- 43.75	- 57.06	+ 13.5	- 38.3
Iron grit	- 59.73	+ 34.77	- 18.1	- 74.91	- 46.77	- 84.7
Iron II	- 69.19	+ 29.61	- 87.11	- 94.00	- 83.3	- 76
Iron III	- 74.34	- 5.87	- 92.6	- 88.13	- 91.3	- 83.8

Table 5.7. Copper, cadmium, zinc and lead concentrations (mg/kg) present in the leachates of the UK EA leaching test (n=3).

Figure in brackets represent the standard deviations.

	KIDSGROVE				RIXTON				MERTON BANK			
	Copper	Cadmium	Zinc	Lead	Copper	Cadmium	Zinc	Lead	Copper	Cadmium	Zinc	Lead
Untreated	0.2 (±0.02)	0.13 (± 0.01)	0.1 (±0.003)	2 (±0.08)	0.13 (±0.03)	0	0.2 (± 0.04)	1.21 (±0.21)	0.71 (±0.002)	0.3 (±0.002)	0.3 (±0.01)	7.0 (± 0.05)
Lime	0.2 (±0.01)	0.1 (± 0.001)	0.1 (±0.003)	2.2 (±0.13)	0	0	0.03 (±0.007)	1.05 (±0.28)	0.36 (±0.01)	0.21 (±0.006)	0.23 (±0.01)	6.3 (± 0.05)
Goethite	0.25 (±0.02)	0.2 (± 0.1)	0.11 (±0.01)	2.5 (±0.12)	0	0	0.03 (±0.01)	0.8 (±0.15)	0.50 (±0.01)	0.2 (± 0.006)	0.2 (±0.004)	5.02 (± 0.05)
Iron grit	0.22 (±0.02)	0.12 (± 0.01)	021 (±0.05)	2.01 (±0.06)	0.1 (±0.01)	0	0.04 (±0.01)	0.9 (±0.16)	0.4 (±0.008)	0.11 (± 0.01)	0.14 (±0.002)	4.2 (± 0.06)
Iron II	1 (±0.04)	1.2 (± 0.05)	0.4 (±0.02)	6.7 (±0.29)	0.5 (±0.03)	0.2 (±0.02)	0.2 (±0.01)	5.64 (±0.21)	0.83 (±0.04)	0.3 (± 0.01)	0.3 (± 0.01)	9.0 (± 0.21)
Iron III	1 (±0.02)	2.3 (±0.09)	1 (± 0.01)	9.4 (±0.13)	1.3 (±0.07)	0.5 (± 0.03)	0.5 (± 0.04)	12.05 (±0.43)	1.19 (±0.01)	0.44 (± 0.01)	0.4 (±0.003)	12.3 (± 0.19)

Table 5.8. Copper, cadmium, zinc and lead concentrations (mg/kg) present in the leachates of the ASTM leaching test (n=3).

Figure in brackets represent the standard deviations.

	KIDSGROVE				RIXTON				MERTON BANK			
	Copper	Cadmium	Zinc	Lead	Copper	Cadmium	Zinc	Lead	Copper	Cadmium	Zinc	Lead
Untreated	0.33 (±0.04)	0.22 (±0.02)	0.12 (±0.01)	3.1 (±0.14)	0.09 (±0.03)	0.02 (±0.01)	0.02 (±0.003)	0.96 (±0.16)	1.51 (±0.03)	0.56 (±0.01)	0.48 (±0.008)	13.85 (±0.22)
Lime	0.5 (±0.007)	0.3 (±0.01)	0.2 (±0.001)	4.3 (±0.03)	0.112 (±0.02)	0.04 (±0.01)	0.02 (±0.01)	1.25 (±0.15)	1.39 (±0.02)	0.52 (±0.008)	0.45 (±0.007)	13.15 (±0.09)
Goethite	0.31 (±0.04)	0.21 (±0.02)	0.12 (±0.01)	3.4 (±0.19)	0.08 (±0.03)	0.02 (±0.01)	0.01 (±0.004)	0.91 (±0.18)	1.54 (±0.08)	0.62 (±0.04)	0.49 (±0.02)	13.80 (±0.57)
Iron grit	0.3 (±0.02)	0.3 (±0.01)	0.11 (±0.01)	3.02 (±0.11)	0.17 (±0.07)	0.07 (±0.03)	0.03 (±0.01)	1.21 (±0.31)	1.51 (±0.04)	0.61 (±0.02)	0.49 (±0.009)	13.82 (±0.21)
Iron II	1 (±0.04)	1.3 (±0.03)	0.34 (±0.01)	8.7 (±0.21)	0.65 (±0.009)	0.19 (±0.01)	0.25 (±0.01)	6.60 (±0.05)	1.46 (±0.02)	0.57 (±0.009)	0.48 (±0.005)	13.61 (±0.08)
Iron III	1.3 (±0.05)	2 (±0.07)	0.5 (±0.02)	11.8 (±0.51)	1.03 (±0.03)	0.33 (±0.01)	0.32 (±0.01)	9.19 (±0.21)	1.54 (±0.02)	0.60 (±0.01)	0.49 (±0.007)	14.18 (±0.09)

Table 5.9. Copper, cadmium, zinc and lead concentrations (mg/kg) present in the leachates of the modified column test (n=3).

Figure in brackets represent the standard deviations.

	KIDSGROVE				RIXTON				MERTON BANK			
	Copper	Cadmium	Zinc	Lead	Copper	Cadmium	Zinc	Lead	Copper	Cadmium	Zinc	Lead
Untreated	1.32 (± 0.96)	0.68 (± 0.36)	0.42 (± 0.24)	17.49 (± 10.14)	0.64 (± 0.75)	0.32 (± 0.45)	0.04 (± 0.04)	8.64 (± 6.19)	3.9 (± 1.55)	1.3 (± 0.50)	1.3 (± 0.38)	39.3 (± 13.28)
Lime	0.83 (± 0.41)	0.58 (± 0.23)	0.30 (± 0.16)	13.92 (± 4.17)	0.36 (± 0.31)	0.15 (± 0.16)	0.08 (± 0.01)	7.49 (± 2.41)	3.5 (± 1.60)	1.01 (± 0.36)	1.13 (± 0.48)	39.6 (± 15.23)
Goethite	0.66 (± 0.20)	0.47 (± 0.15)	0.27 (± 0.13)	10.43 (± 3.75)	0.19 (± 0.19)	0.12 (± 0.17)	0.03 (± 0.02)	4.52 (± 5.61)	4.9 (± 2.75)	1.6 (± 0.91)	1.6 (± 0.71)	47.5 (± 23.55)
Iron grit	1.42 (± 0.97)	0.72 (± 0.44)	0.48 (± 0.24)	14.52 (± 6.13)	0.41 (± 0.52)	0.23 (± 0.36)	0.09 (± 0.05)	6.64 (± 6.50)	4.2 (± 2.82)	1.3 (± 0.94)	1.2 (± 0.78)	41.44 (± 24.38)
Iron II	1.01 (± 0.23)	1.45 (± 0.14)	0.48 (± 0.31)	16.67 (± 1.28)	1.20 (± 0.73)	0.49 (± 0.36)	0.37 (± 0.20)	14.73 (± 7.88)	6.8 (± 3.76)	2.3 (± 1.23)	2.2 (± 0.99)	69.6 (± 31.92)
Iron III	2.42 (± 0.37)	5.94 (± 2.19)	2.35 (± 0.94)	28.88 (± 6.90)	2.61 (± 1.01)	1.01 (± 0.60)	0.57 (± 0.02)	26.98 (± 9.05)	5.5 (± 2.13)	2.03 (± 0.71)	2.03 (± 0.60)	57.13 (± 22.92)

Table 5.10. Changes in pH of fractions collected from Kidsgrove soil during the modified column test (n=3). Figures in brackets represent the standard deviation.

	KIDSGROVE						
	K1	K2	K3	K4	K5	K6	K7
UNTREATED	7.38 (±0.11)	7.82 (±0.12)	8.06 (±0.19)	7.88 (±0.16)	7.88 (±0.11)	7.73 (±0.15)	7.21 (±0.46)
LIME	7.44 (±0.11)	8.02 (±0.17)	7.96 (±0.07)	8.00 (±0.18)	8.02 (±0.19)	7.70 (±0.15)	7.27 (±0.48)
GOETHITE	6.57 (±0.52)	7.83 (±0.02)	8.07 (±0.03)	7.97 (±0.14)	7.88 (±0.14)	7.77 (±0.11)	7.33 (±0.43)
IRON GRIT	6.78 (±0.54)	7.75 (±0.08)	7.87 (±0.18)	7.81 (±0.17)	7.73 (±0.25)	7.65 (±0.18)	7.24 (±0.38)
IRON II	7.75 (±0.19)	8.08 (±0.20)	7.98 (±0.29)	7.80 (±0.10)	7.85 (±0.28)	7.71 (±0.23)	7.31 (±0.35)
IRON III	7.83 (±0.10)	7.93 (±0.05)	7.93 (±0.11)	7.98 (±0.13)	7.94 (±0.13)	7.78 (±0.08)	7.34 (±0.42)

Table 5.11. Changes in pH of fractions collected from Rixton soil during the modified column test (n=3). Figures in brackets represent the standard deviation.

	RIXTON						
	K1	K2	K3	K4	K5	K6	K7
UNTREATED	8.19 (±0.05)	8.34 (±0.03)	7.78 (±0.32)	7.69 (±0.21)	7.71 (±0.25)	7.31 (±0.06)	7.32 (±0.24)
LIME	8.12 (±0.31)	8.23 (±0.18)	7.85 (±0.23)	7.50 (±0.28)	7.73 (±0.22)	7.47 (±0.34)	7.33 (±0.20)
GOETHITE	8.25 (±0.32)	8.24 (±0.27)	7.90 (±0.23)	7.52 (±0.53)	7.65 (±0.16)	7.53 (±0.28)	7.51 (±0.18)
IRON GRIT	8.17 (±0.22)	8.13 (±0.20)	8.22 (±0.07)	7.63 (±0.22)	7.62 (±0.0.26)	7.45 (±0.21)	7.26 (±0.12)
IRON II	7.85 (±0.08)	7.76 (±0.09)	8.19 (±0.25)	8.01 (±0.16)	8.01 (±0.08)	7.67 (±0.23)	7.33 (±0.15)
IRON III	7.81 (±0.17)	7.90 (±0.16)	7.86 (±0.09)	8.02 (±0.23)	8.00 (±0.12)	7.59 (±0.16)	7.32 (±0.10)

Table 5.12. Changes in pH of fractions collected from Merton Bank soil during the modified column test (n=3). Figures in brackets represent the standard deviation.

	MERTON BANK						
	K1	K2	K3	K4	K5	K6	K7
UNTREATED	7.77 (±0.28)	7.83 (±0.31)	7.86 (±0.11)	7.57 (±0.10)	7.68 (±0.16)	7.74 (±0.35)	7.83 (±0.11)
LIME	7.90 (±0.29)	7.64 (±0.52)	7.83 (±0.27)	7.67 (±0.07)	7.67 (±0.16)	7.91 (±0.28)	7.88 (±0.46)
GOETHITE	8.02 (±0.34)	7.82 (±0.39)	7.81 (±0.46)	7.67 (±0.15)	7.68 (±0.17)	7.92 (±0.24)	7.92 (±0.23)
IRON GRIT	7.78 (±0.37)	7.75 (±0.30)	7.64 (±0.56)	7.76 (±0.09)	7.60 (±0.07)	7.84 (±0.29)	7.57 (±0.47)
IRON II	7.69 (±0.18)	7.84 (±0.39)	7.93 (±0.21)	7.81 (±0.07)	7.61 (±0.15)	7.73 (±0.26)	7.83 (±0.35)
IRON III	7.85 (±0.16)	7.93 (±0.05)	8.05 (±0.18)	7.87 (±0.08)	7.91 (±0.06)	7.98 (±0.20)	7.78 (±0.35)

Table 5.13. pH values for the three contaminated soils from the UK EA and ASTM tests (n=3). Figures in brackets represent the standard deviation.

	KIDSGROVE		RIXTON		MERTON BANK	
	UK EA	**ASTM**	**UK EA**	**ASTM**	**UK EA**	**ASTM**
Untreated	6.44 (±1.31)	7.60 (±0.10)	6.57 (±0.33)	8.13 (±0.12)	7.35 (±0.01)	7.52 (±0.09)
Lime	7.02 (±0.95)	7.87 (±0.22)	7.31 (±0.11)	8.26 (±0.15)	7.31 (±0.04)	7.52 (±0.02)
Goethite	6.56 (±1.34)	8.02 (±0.06)	6.65 (±0.71)	8.00 (±0.05)	7.32 (±0.04)	7.37 (±0.05)
Iron grit	6.41 (±1.11)	7.63 (±0.21)	6.26 (±1.06)	8.18 (±0.05)	7.33 (±0.04)	7.36 (±0.04)
Iron II	4.47 (±0.24)	7.60 (±0.23)	6.5 (±0.21)	8.00 (±0.06)	7.25 (±0.01)	7.37 (±0.08)
Iron III	7.09 (±0.15)	7.39 (±0.15)	5.37 (±0.35)	7.93 (±0.06)	7.24 (±0.02)	7.33 (±0.13)

Table 5.14. General Linear Model for arsenic leached from modified column tests.

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Soil	2	645699904	672717504	336358752	30.24	<0.001
Treatment	5	938769762	924743744	184948736	16.63	<0.001
Site*Treat	10	285637504	285637504	28563750	2.57	0.019
Error	36	400477504	400477504	11124375		
Total	53	2270584576				

Table 5.15. General Linear Model for arsenic leached from EA water extract tests.

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Soil	2	11917.5	11917.5	5958.8	14.06	<0.001
Treatment	5	9709.3	9709.3	1941.9	4.58	0.002
Site*Treat	10	6380.4	6380.4	638.0	1.51	0.178
Error	36	15254.6	15254.6	423.7		
Total	53	43261.8				

Table 5.16. General Linear Model for arsenic leached from the ASTM tests.

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Soil	2	58577.7	58577.7	29288.8	120.68	<0.001
Treatment	5	34744.1	34744.1	6948.8	28.63	<0.001
Site*Treat	10	46728.2	46728.2	4672.8	19.25	<0.001
Error	36	8737.3	8737.3	242.7		
Total	53	148787.2				

Table 5.17. General Linear Model for copper leached from modified column tests.

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Soil	2	165.267	165.267	82.633	33.73	<0.001
Treatment	5	25.460	25.460	5.092	2.08	0.091
Site*Treat	10	14.376	14.376	1.438	0.59	0.814
Error	36	88.206	88.206	2.450		
Total	53	293.308				

Table 5.18. General Linear Model for cadmium leached from modified column tests.

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Soil	2	17.6786	17.6786	8.8393	15.51	<0.001
Treatment	5	37.2563	37.2563	7.4513	13.07	<0.001
Site*Treat	10	35.9141	35.9141	3.5914	6.30	<0.001
Error	36	20.5206	20.5206	0.5700		
Total	53	111.3696				

Table 5.19. General Linear Model for zinc leached from modified column tests.

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Soil	2	16.8119	16.8119	8.4059	37.63	<0.001
Treatment	5	8.8365	8.8365	1.7673	7.91	<0.001
Site*Treat	10	4.6862	4.6862	0.4686	2.10	0.051
Error	36	8.0413	8.0413	0.2234		
Total	53	38.3760				

Table 5.20. General Linear Model for lead leached from modified column tests.

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Soil	2	14845.5	14845.5	7422.8	37.28	<0.001
Treatment	5	2685.6	2685.6	537.1	2.70	0.036
Site*Treat	10	1163.0	1163.0	116.3	0.58	0.816
Error	36	7168.7	7168.7	199.1		
Total	53	25862.9				

Table 5.21. General Linear Model for copper leached from the EA water extract tests.

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Soil	2	0.18005	0.18005	0.09002	4.51	0.018
Treatment	5	0.24306	0.24306	0.04861	2.44	0.053
Site*Treat	10	0.26293	0.26293	0.02629	1.32	0.259
Error	36	0.71868	0.71868	0.01996		
Total	53	1.40472				

Table 5.22. General Linear Model for cadmium leached from the EA water extract tests.

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Soil	2	0.116127	0.116127	0.058063	82.76	<0.001
Treatment	5	0.281084	0.281084	0.056217	80.13	<0.001
Site*Treat	10	0.228448	0.228448	0.022845	32.56	<0.001
Error	36	0.025256	0.025256	0.000702		
Total	53	0.650915				

Table 5.23. General Linear Model for zinc leached from the EA water extract tests.

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Soil	2	0.0032656	0.003256	0.0016328	3.43	0.043
Treatment	5	0.0378817	0.0378817	0.0075763	15.91	<0.001
Site*Treat	10	0.0079580	0.0079580	0.0007958	1.67	0.126
Error	36	0.0171387	0.0171387	0.0004761		
Total	53	0.0662439				

Table 5.24. General Linear Model for lead leached from the EA water extract tests.

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Soil	2	5.4583	5.4583	2.7292	75.27	<0.001
Treatment	5	22.1409	22.1409	4.4282	122.13	<0.001
Site*Treat	10	1.4846	1.4846	0.1485	4.09	<0.001
Error	36	1.3052	1.3052	0.0363		
Total	53	30.3891				

Table 5.25. General Linear Model for copper leached from the ASTM tests.

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Soil	2	0.808257	0.808257	0.404129	230.43	<0.001
Treatment	5	0.205202	0.205202	0.041040	23.40	<0.001
Site*Treat	10	0.099213	0.099213	0.009921	5.66	<0.001
Error	36	0.063138	0.063138	0.001754		
Total	53	1.175810				

Table 5.26. General Linear Model for cadmium leached from the ASTM tests.

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Soil	2	0.207139	0.207139	0.103570	153.55	<0.001
Treatment	5	0.218937	0.218937	0.043787	64.92	<0.001
Site*Treat	10	0.262656	0.262656	0.026266	38.94	<0.001
Error	36	0.024281	0.024281	0.000674		
Total	53	0.713013				

Table 5.27. General Linear Model for Zinc leached from the ASTM tests.

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Soil	2	0.0826148	0.0826148	0.0413074	343.12	<0.001
Treatment	5	0.0250491	0.0250491	0.0050098	41.61	<0.001
Site*Treat	10	0.0123174	0.0123174	0.0012317	10.23	<0.001
Error	36	0.0043340	0.0043340	0.0001204		
Total	53	0.1243153				

Table 5.28. General Linear Model for lead leached from the ASTM tests.

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Soil	2	66.6535	66.6535	33.3267	563.34	<0.001
Treatment	5	17.3469	17.3469	0.7836	58.64	<0.001
Site*Treat	10	7.8359	7.8359	0.0592	13.25	<0.001
Error	36	2.1297	2.1297			
Total	53	93.9660				

CHAPTER 6.

THE EFFECT OF ADDITIVES ON PLANT GROWTH IN ARSENIC CONTAMINATED SOIL.

6.1 Introduction

A number of metals termed micronutrients are essential for the growth of plants. These include iron, zinc, copper, manganese, magnesium, molybdenum, and possibly nickel. At suboptimal concentrations they affect plant growth, producing deficiency symptoms such as leaf bleaching and growth inhibition. At supraoptimal concentrations these micronutrients become phytotoxic and stunt growth (Clijsters *et al.*, 1999). However there are other metals, for example cadmium, chromium, lead, selenium and mercury which are non essential to plant growth, but the plant accumulates (Raskin *et al.*, 1994). These can be taken up by the plant and potentially be directly ingested by humans.

Arsenic may enter the agricultural soil environment via the use of pesticides, herbicides and fungicides. It may also be deposited from point emission sources such as coal combustion, tannery wastes or wood preservation factories. Past use of lead arsenate insecticide in apple orchards, may present a source of arsenic contamination in vegetables grown in that area some time later (Kenyon *et al.*, 1979; Aten *et al.*, 1980). The concentration and chemical form of arsenic in the soil will have an influence on plant growth and therefore animal and human health (Yan-Chu, 1994). Arsenic exists primarily in the soil environment as either arsenate [$As^{(V)}$] or arsenite [$As^{(III)}$] (Masscheleyn *et al.*, 1991b). However methyl arsonic acid (MMAA) and dimethyl arsinic acid (DMAA) may also exist.

There are many factors that influence the uptake of arsenic by a plant, including species (Walsh and Keeney, 1975), the presence of competing ions (Khattak *et al.*, 1991), concentration of arsenic in the soil (NAS, 1977a), and soil properties including pH, clay content (Von Endt *et al.*, 1968), as well as redox potential and iron oxides. The total concentration of arsenic in the soil is a poor indicator of the fraction of arsenic that is plant-available (Sheppard, 1992). The uptake of arsenic is therefore dependent on the plant available fraction in the soil (Duel and Swoboda, 1972a). It has also been suggested that arsenic uptake in plants may be affected by the presence of mycorrhizal fungi (Covey *et al.*, 1981; Benson *et al.*, 1981).

Arsenic accumulation within edible plant tissue is generally low (Vaughan, 1993; O'Neill, 1995). Research has shown that the largest quantities of plant arsenic residues are found in the roots, intermediate concentrations are found in leaves and stems (above ground vegetative parts) and the smallest amount of arsenic is to be found in seeds and fruits (Walsh and Keeney, 1975; Carbonell-Barrachina, 1992; Carbonell-Barrachina, 1995). There is considerable variation in sensitivity to arsenic among plant species (Jacobs *et al.*, 1970; Jiang and Singh, 1994). It has been shown that various plants can accumulate levels of arsenic greater than 0.1% of their dry weight, levels that would kill other plants. This demonstrates that plant species differ, not only in their tolerance to arsenic, but also to their absorption capabilities (Carbonell-Barrachina, *et al.*, 1997). Woolson (1973), grew a variety of vegetable crops in three contaminated soils and found plant sensitivity followed the order green beans > lima beans ≅ spinach > radish > tomato > cabbage.

The Chinese Brake fern (*Pteris vittata* L.) was the first plant discovered to hyperaccumulate arsenic within its above ground tissues (Ma *et al.*, 2001). Recent work by Fitz and co-workers (in press) discovered a close relative known as the Cretan Brake fern (*Pteris cretica* L.) which also hyperaccumulates the metalloid. The Cretan brake fern was found to accumulate mean arsenic concentrations of 2365 mg kg^{-1} in its fronds, whilst *P. vittata* accumulated 2038 mg kg^{-1}. The concentration factor of arsenic present in the shoot/root was 14:1 in *P. cretica* and 36:7 in *P. vittata* (Fitz *et al.*, in press). However *P. vittata* was found growing on copper rich soils in South Central Africa, where it showed no hyperaccumulation of this element (Brooks and Malaisse, 1985).

Plant absorption of metals from the soil solution depends on metabolic processes within the root. Alteration of the soil solution at the root surface may result from the interaction of the plant with the soil environment. Not only does the root absorb water and ions, it also modifies its immediate environment by excreting substances that are chemically active. Coating the root tip is a gelatinous material called mucigel, which may be pectin and this material together with amino acids, HCO_3^- ions, organic acids and H^+ ions is excreted from roots. These may affect the release of metals from soil colloids. Root exudates may enhance the activity of microorganisms and these could affect metal bioavailability by competing with the plant root for their absorption and causing their release from soil colloids (Lepp, 1981).

Increasing concentrations of arsenic in the soil solution may interfere with the uptake of essential nutrients, such as phosphate (Meharg & Macnair, 1990). Elevated arsenic concentrations may also interfere with plant metabolism. Arsenite is toxic to radicular membranes (Sachs & Michaels, 1971). This is due to reactions with sulfhydryl groups of proteins (Speer, 1973), which then causes disruption to the functioning of the root and cellular death (Orwick *et al.*, 1976).

The effects of arsenic toxicity in plants are reduced water mobility, root plasmolysis followed by necrosis of the leaves and prevention of seed germination. Arsenic does not appear to be involved in any specific metabolic reactions in plants and is therefore not essential to their growth (Marin *et al.*, 1993). At increased internal concentrations, arsenic has been shown to obstruct metabolic pathways in plants, inhibiting their growth and sometimes causing death (Marin *et al.*, 1993). Phosphate absorption by plants shares the same uptake system as that of arsenic. Therefore if a soil contained high concentrations of arsenic, plant phosphate uptake may be compromised (Meharg *et al.*, 1994). Arsenate being a chemical analogue of phosphate may interfere with the process of oxidative phosphorylation (Terwelle & Slater, 1967).

Due to the relationship of skin cancer and angiosarcoma with the ingestion of arsenic, this establishes the metalloid as a human carcinogen (Pershagan, 1981; Léonard and Lauwerys, 1980). The reason for this may be related to the cumulative dose of arsenic (WHO, 1981). Therefore because of these carcinogenic properties, plants grown in soil contaminated with arsenic would be the first link in the food chain, which may eventually reach humans. Remediation of land contaminated with arsenic would be a step forward in preventing this transfer.

The work described below investigated survival and biomass production of three test plants grown on three different arsenic contaminated substrates. Soils were tested for pH, moisture content, organic matter content, arsenic and heavy metal content (water and nitric acid extractable) at the start of the investigation, then each soil was amended with one of the following iron oxide bearing additives, goethite, iron grit, iron (II) sulphate, iron (III) sulphate (plus lime) or lime at a concentration of 1% (w/w) dry weight, together with untreated soil and compost as controls.

The ability of plants to absorb arsenic from the soil differs between species, and in this investigation spinach (*Spinacia oleracea var.* Spinnaker), tomato (*Lycopersicon esculentum var.* Moneymaker) and ryegrass (*Lolium perenne var.* Rambo) were grown in

a glasshouse study, in the contaminated soils together with the iron oxide based additives described above. The plants were selected because of their differences in arsenic uptake, biomass production and use as food crops.

Tomato, *Lycopersicon esculentum* was chosen due to its reported tolerance to arsenic pollution (Wauchope, 1983). In a previous study a concentration of 2 mg L^{-1} As was not phytotoxic to the tomato plant (Carbonell-Barrachina *et al.*, 1997). Spinach, *Spinacia oleracea* however, accumulates metals within its tissues, which was identified from previous investigations on this plant species (personal communication). Perennial ryegrass was grown due to its importance in the food chain. Arsenic absorbed by grass would be consumed by grazing livestock and so eventually reach man. The ryegrass study would also demonstrate the uptake of arsenic over one growing season and the changes in uptake of arsenic and other metals would be observed by regular harvesting of the grass. These microcosm investigations would demonstrate changes in arsenic uptake in relation to the physiological development of the grass.

6.2. Experimental

6.2.1. Materials and methods

Plant trials using mono-and dicotyledonous plants were investigated in order to determine the effectiveness of the iron oxides on improving plant growth, and reducing arsenic and heavy metal uptake when applied to the contaminated soils. Each test soil was amended with 1% w/w (d.w.) iron oxide-bearing additives and lime. Untreated soil samples and compost were used as controls during the study.

For the tomato and spinach study, plastic 1 Kg pots (16cm diameter) were filled with contaminated soils with or without the amendments. The additives were combined with the soil in larger containers and thoroughly mixed using a trowel prior to being added to the 1 Kg pots, in order to obtain an even distribution of the amendment and were left in these pots for seven days to allow the additives to equilibrate and form iron oxides.

Tomato (*Lycopersicon esculentum*) and spinach (*Spinacia oleracea*) seeds were sown in John Innes compost. Two weeks after germination, seedlings were transplanted into the contaminated soils (4 seedlings/pot, 4 pots per treatment). The plants were harvested after three months.

For the microcosm study, Perennial ryegrass (*Lolium perennne*) was sown (20g seed / pot) in 5 Kg plastic pots (32cm diameter) and the soils amended at a rate of 1% w/w. (d.w). The resulting growth was harvested every three weeks from late March 2000 onwards over a four-month period. The plant growth trials were carried out in a controlled greenhouse environment with regular daily watering.

6.2.2 Harvesting and analysis of plant material

In the plant uptake experiments using Tomato or Spinach, plant material for digestion was collected at the end of the growing period (three months). Leaves and stems were removed by cutting the base of the plant near to the soil with a sharp knife. The fresh weight of the above ground vegetative material was weighed and all plant material was washed in deionised water to remove soil residues from the lower leaves and stems, then oven dried at 60 °C for three days. The material was weighed, then ground in a mechanical sample grinder (Cyclotec 1093 sample mill). After each sample was ground, the grinder was thoroughly cleaned with a stiff brush to ensure the removal of the previous sample and so prevent contamination occurring. All samples were stored in polyethylene containers prior to analysis.

For the microcosm studies, above-ground plant growth was collected over a period of one growing season. The grass was harvested using stainless steel scissors and the material was cut from approximately 1 cm above the soil. The material was weighed, washed, then oven dried as above.

All plant material was analysed in triplicate for the concentrations of arsenic and heavy metals. The biomass obtained was weighed (fresh and dry) to give a yield figure for each group of plants. For the microwave digestion of plant material see Chapter 2 (section 2.8.1.1).

6.3. Growth observations

Due to the need for continual watering of the potted plants, regular observations were made during the growing period. A photographic record was also taken for all the treatments (Plates 6.1-6.9).

6.4. Statistical analysis

A one-way analysis of variance (ANOVA) combined with the Dunnett's test was used to test for differences between spinach and tomato mean metal concentrations and treatment type for each soil. A balanced one-way analysis of variance was used to test for differences in arsenic uptake compared with soil type and treatment type in perennial rye grass.

6.5. Results

6.5.1. Plant productivity: Spinach and Tomato.

Plants grown in the unamended, contaminated soils all developed classic symptoms of heavy metal toxicity. Plant growth was stunted and the lower leaves developed chlorosis followed by necrosis. Tomato plants developed a dark purple colouration to the leaves and were very stunted in growth when compared to those grown in compost (Plates 6.1,6.4,6.6).

The dry matter yields for spinach and tomato trials are presented in Figures 6.1-6.6. All untreated soils showed reduced plant growth compared to the compost controls. A visual analysis of the plant trials is presented in plates 6.1-6.6 (Spinach & Tomato).

In the unamended coal fly ash soil, spinach growth was very poor (Plate 6.5). All amendments, with the exception of goethite, resulted in poor stunted plant growth. This may be due, not only to the fact that the Rixton soil has highly elevated levels of toxic metals, but also the low organic matter content of the soil (7.6 %). The soil may therefore have had a reduced nutrient and metal binding capacity, which could have affected plant growth. Similar results were obtained with tomato in Rixton soil, with only the addition of goethite producing higher dry matter yields (Figure 6.4).

The dry weight of Tomato material collected from those pots amended with iron II or iron III sulphate plus lime and iron grit, were lower than that of the unamended control. These additives were therefore producing detrimental effects towards tomato plant growth in this soil.

Spinach grown in amended Kidsgrove soil showed very poor growth, even for those plants that were grown in goethite-amended soil. All the plants demonstrated

Plate 6.1. Effect of iron oxides on tomato plant growth in Kidsgrove soil.
(Photograph of tomato plants was taken three months after sowing date, prior to harvesting).

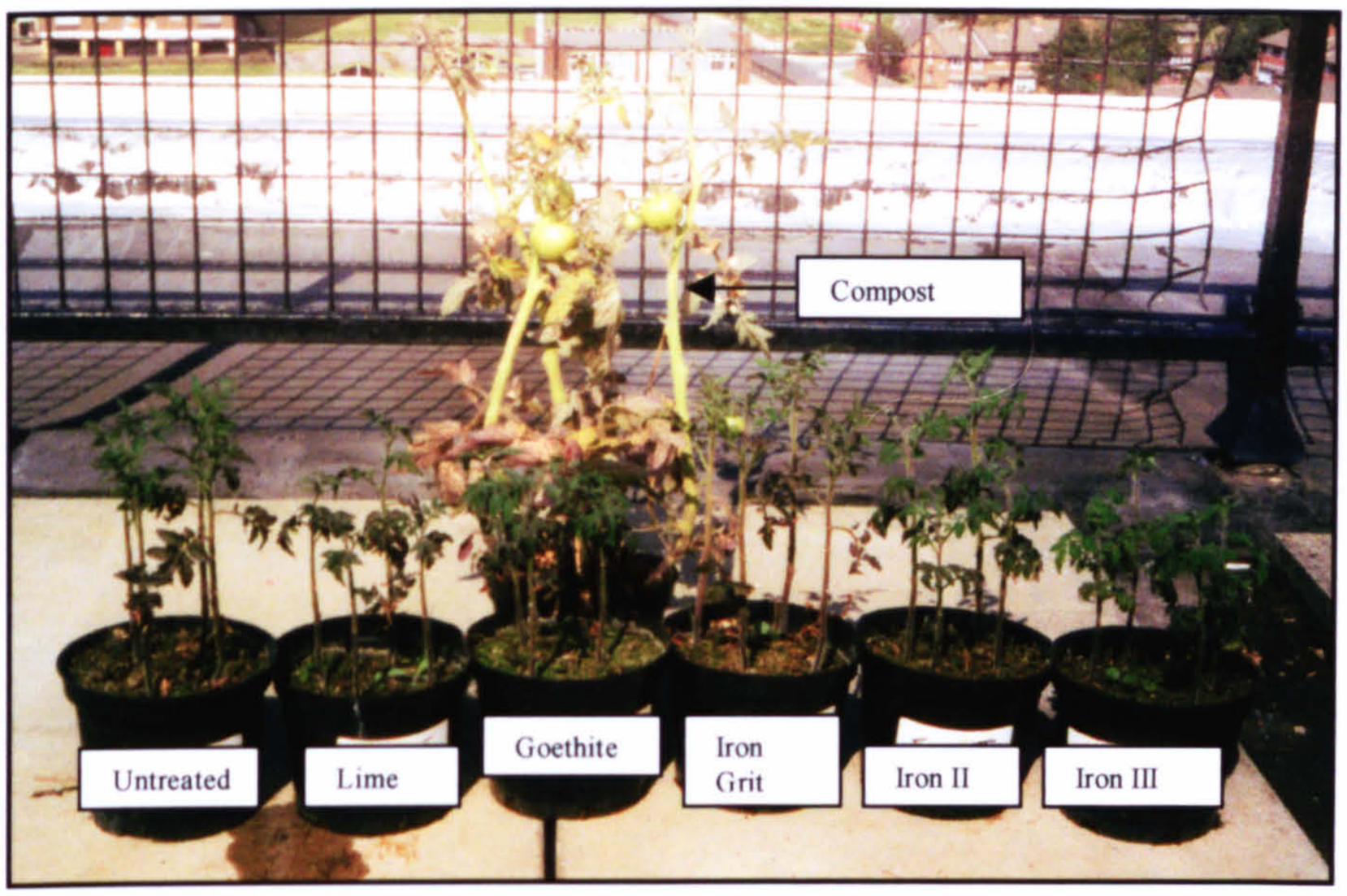


Plate 6.2. Effect of iron oxides on spinach plant growth in Kidsgrove soil.
(Photographs of spinach plants were taken three months after sowing date, prior to harvesting).

Plate 6.3. Effect of iron oxides on spinach plant growth in Merton Bank soil.
(Photograph of spinach plants was taken three months after sowing date, prior to harvesting).

Plate 6.4. Effect of iron oxides on tomato plant growth in Merton Bank soil.
(Photographs of tomato plants were taken three months after sowing date, prior to harvesting).

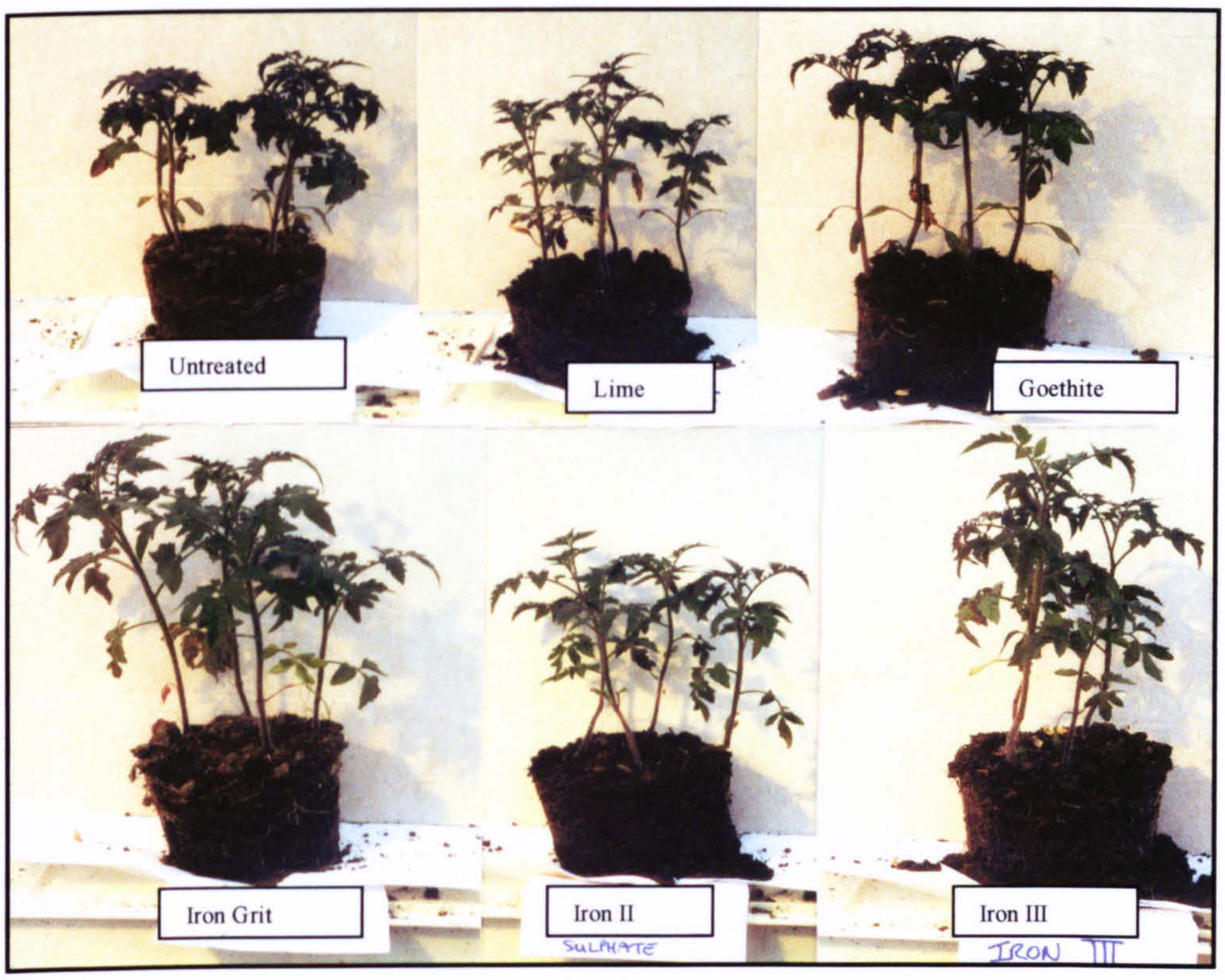


Plate 6.5. Effect of iron oxides on spinach plant growth in Rixton soil.
(Photographs of spinach plants were taken three months after sowing date, prior to harvesting).

Plate 6.6. Effect of iron oxides on tomato plant growth in Rixton soil.
(Photographs of tomato plants were taken three months after sowing date, prior to harvesting).

Plate 6.7. The effect of iron oxides on perennial rye grass growth in Merton Bank soil. (Photographs were taken nine weeks after sowing date).

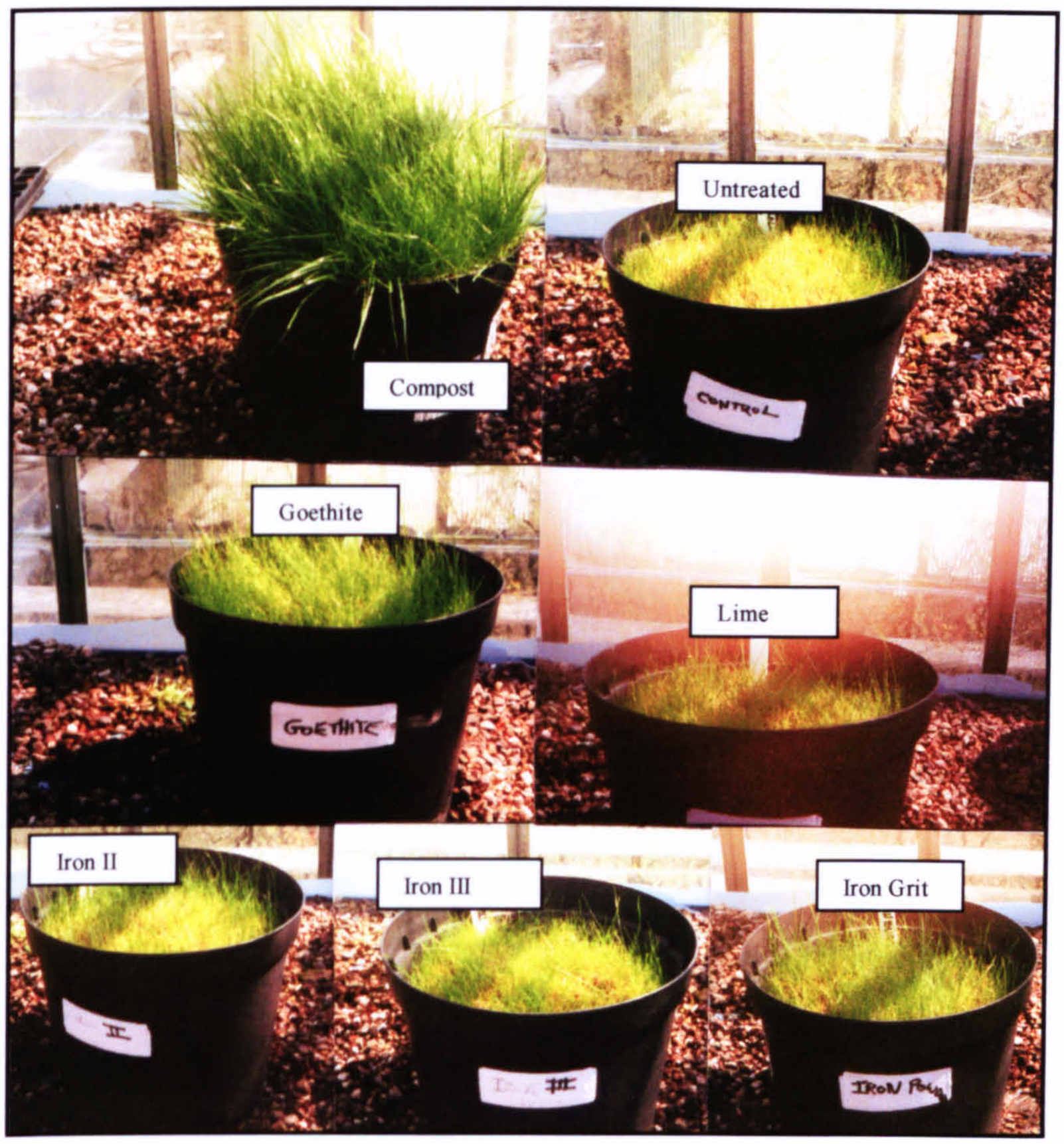


Plate 6.8. The effect of iron oxides on perennial rye grass growth in Kidsgrove soil. (Photograph was taken nine weeks after sowing date).

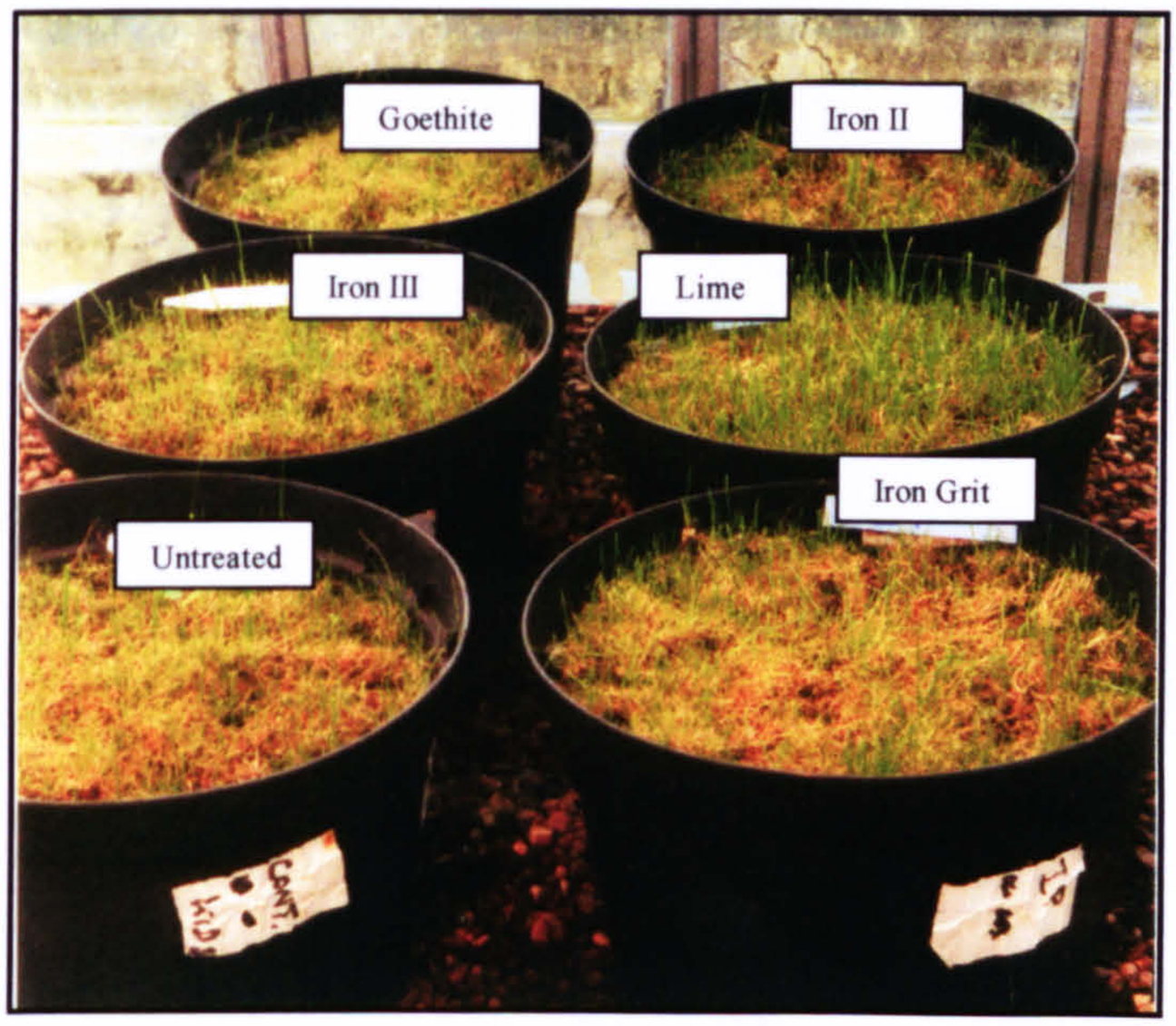
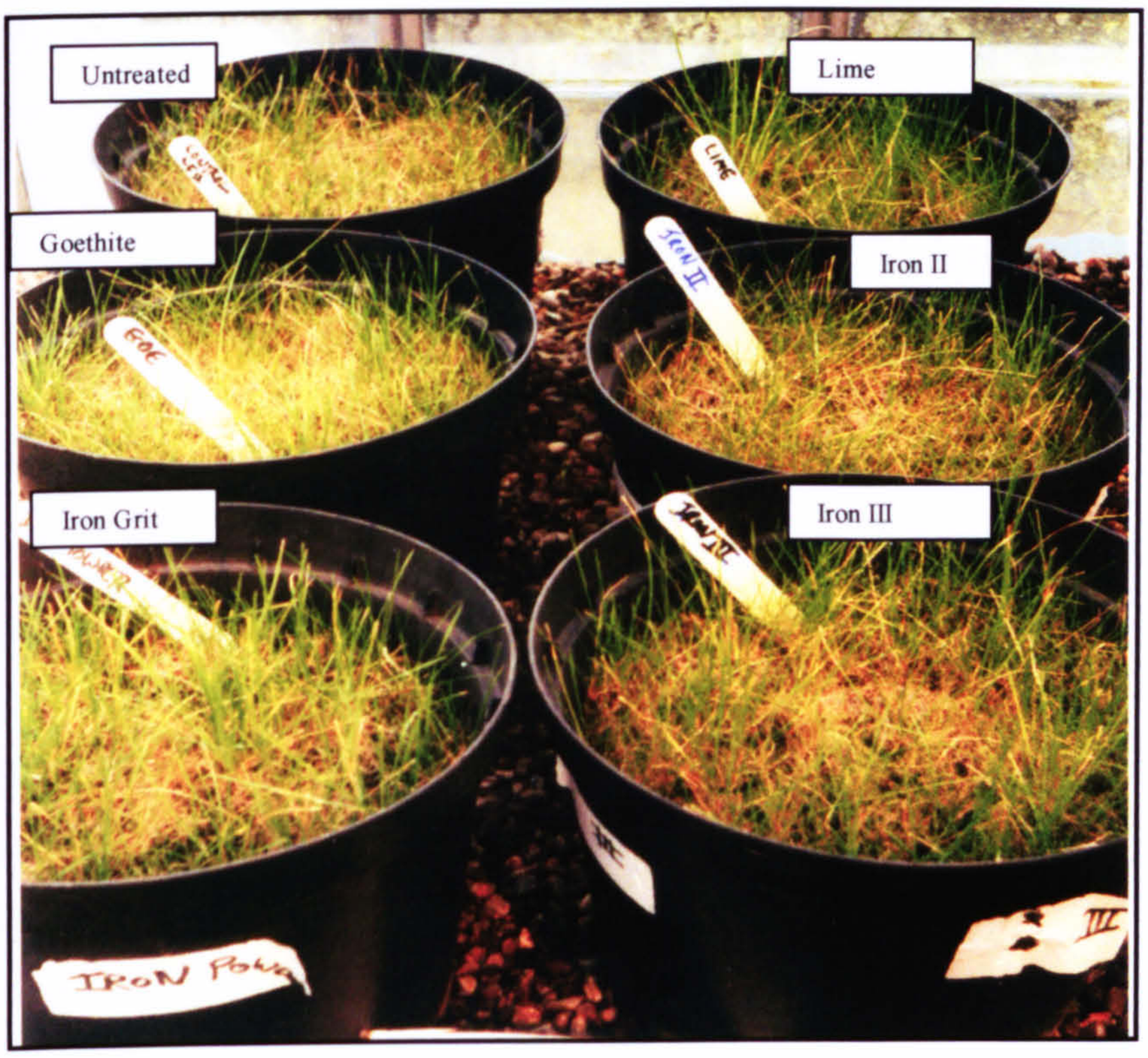


Plate 6.9. The effect of iron oxides on perennial rye grass growth in Rixton soil. (Photograph was taken nine weeks after sowing date).



stunted growth with chlorosis being evident on the lower leaves. Tomato plants achieved a greater biomass when grown in Kidsgrove than in Rixton soil (with the exception of the goethite amended soil). This may have been due to the higher levels of organic matter present in the Kidsgrove soil (15.4%), providing a greater nutrient status and metal binding capacity.

Iron grit produced the greatest total shoot dry weight in tomato plants when applied to the Kidsgrove soil, followed by goethite. The other additives produced similar results to the unamended control. Despite the fact that iron grit and goethite were found to increase the dry mass of tomato plants, the overall quality of the test crop was poor and stunted. This may have been the result of increased levels of heavy metals such as cadmium, zinc and lead found in this soil. The dry weight of tomato plants grown in Kidsgrove soil amended with iron (III) sulphate and lime was lower than that of the untreated plants. Similar findings were obtained for those plants grown in iron II-amended Kidsgrove soil. The iron oxides produced detrimental effects on plant growth in this soil, similar to that observed for Rixton.

A similar trend was observed in the Merton Bank soil, with highest biomass being obtained from spinach and tomato plants grown in contaminated soils amended with goethite and iron grit. Addition of iron (II) sulphate to the soil produced a detrimental effect on spinach growth in Merton Bank soil. All spinach plants grown in the Merton Bank soil showed visible signs of heavy metal toxicity, especially with the lime treatment.

In both spinach and tomato growth trials it was evident that an increase in plant growth was observed when goethite was applied to the soils. Addition of iron grit was effective at reducing arsenic solubility in Merton Bank soil, producing higher biomass production in both spinach and tomato compared to those grown in the unamended soils.

The plant trials demonstrated that not all iron oxides have a beneficial effect on plant growth, when applied as additives to arsenic contaminated soils. The iron oxide bearing additives, iron grit, iron II sulphate ($FeSO_4 \cdot 7H_2O$) and iron III sulphate ($Fe_2(SO_4)_3 \cdot 5H_2O$) plus lime, resulted in poor plant growth in most cases with respect to spinach and tomato trials. Goethite was the exception, especially in the spinach trials, producing greater plant biomass. The addition of lime showed similar results to that of the unamended control soils. Plant trial results have demonstrated that the iron oxide goethite has the ability to improve soil conditions for plant growth.

6.5.2. Microcosm plant growth (Perennial ryegrass).

Ryegrass growth was collected over a period of one growing season. During this period a total of five harvests were collected. Growth towards the end of the growing period was slow, possibly due to the toxicity of the soils or nutrient depletion affecting growth rate. Changes in grass dry weight are presented in figures 6.7-6.9.

A compost control was used in the study to compare changes in growth rate of grass grown in the polluted soils. The dry weight of ryegrass grown in compost was initially very high, which then decreased gradually over the growing period as nutrients were possibly depleted.

Untreated Rixton soil showed the greatest reduction in dry weight production over the growing period (figure 6.7), with the lowest biomass for the last harvest collected. Grass growth was slow and the sward was straw-like in texture, with chlorosis being evident. Plant growth towards the end of the study was located around the perimeter of the pot. Kidsgrove untreated soil (plate 6.8) showed similar phytotoxic signs on the ryegrass as Rixton soil had. Initial plant dry weight was greater than Rixton and this may be due to higher organic matter content in the soil. For the untreated soils, Merton Bank produced the greatest dry matter overall (figure 6.9). This may be the result of organic matter content combined with a near neutral pH (Table 4.1).

Goethite was the most beneficial treatment applied to Rixton soil. This additive produced the highest biomass, in comparison to the other treatments over the harvesting period. The other iron oxide additives all produced lower initial dry weights than untreated Rixton soil. However, dry matter production for the final harvests were greater than the untreated soils. The grass in the treated soils was beginning to grow mostly around the edges of the pots towards the end of the investigation.

A similar trend was observed in the treated Kidsgrove soils, with goethite producing a high dry weight increase at the beginning of the study. Final dry weights though were improved for the iron II and III amended pots. Soil amended with lime showed a greater final mass than that of the untreated soil. Lime has been used to immobilise cations in polluted soils. Kidsgrove soil was highly contaminated with cadmium and other heavy metals as well as arsenic and the application of lime may well have immobilised the cationic metals, binding them with the organic matter. In doing so it will have reduced the phytotoxic effects on ryegrass growth. Grass grown in the lime-

amended soil was greener in colour than the other treatments, which were showing yellowing of the leaves (plate 6.8). Merton Bank soil presented similar findings with the goethite treatment, however the untreated soil produced the greatest final dry weight of grass. Iron grit, iron II and III treatments also produced greater final dry weights than the goethite treatment. The phytotoxic symptoms of chlorosis were not as apparent on the leaves in this soil (plate 6.7) as they were in Rixton and Kidsgrove substrates.

The microcosm studies demonstrated that the iron oxide, goethite, has the ability to improve soil conditions for plant growth. Iron oxide bearing additives were also beneficial at improving polluted soil quality for grass in the early stages of growth. Lime too had a positive effect on grass growth in the Kidsgrove soil and it is therefore important to determine all contaminants present before embarking on a method of remediation.

6.5.3. Accumulation of metals in spinach and tomato.

Arsenic accumulation in the plants.

The use of iron oxides as a treatment for the immobilisation of arsenic in soils has proved effective for both spinach and tomato plants, reducing, in most cases, the levels of arsenic uptake when compared to plants grown in the unamended soils (Figures 6.10-6.15). Arsenic levels in spinach leaves were found to be greater than those in tomato plants. This indicates that different plant species have the ability to prevent arsenic uptake. Tables 6.1 –6.6 present the total uptake of metals in the plants (spinach and tomato). Total metal uptake was calculated by dividing the metal concentration in the leaves by the dry matter yield for each treatment therefore converting the mg/kg dry weight value into mg / plant.

Goethite was the most beneficial additive used in the investigations. When applied to Rixton soil, there was a 98% reduction in arsenic uptake by spinach. Application of goethite to all three soils displayed the best reduction of arsenic in the shoots of both plant species. Spinach grown in Merton bank soil, amended with goethite contained 0.91 $\mu g\ g^{-1}$ arsenic in the leaves, compared to 1.6 $\mu g\ g^{-1}$ in the leaves of plants grown in the untreated soil (Figure 6.10). The addition of goethite produced a 69% reduction in the uptake of arsenic by spinach. A 98% reduction in arsenic uptake was observed when spinach was

grown in Rixton soil. A concentration of 3.52 μg g^{-1} was present in the untreated plants compared to 0.58 μg g^{-1} in those grown in goethite-treated soil (Figure 6.12). Spinach plants grown in Kidsgrove soil showed 83% and 79% reductions in arsenic uptake compared to plants grown in untreated soil, when goethite and iron grit were applied to the soil respectively (Table 6.1).

Tomato plants grown in Merton Bank soil exhibited large reductions in arsenic uptake when iron II, III and goethite were applied to the soil. The addition of iron II and iron III sulphate produced 90% and 79% reductions in arsenic uptake respectively when compared to the untreated plants. The concentration of arsenic present in the leaves of tomato plants grown in iron II amended soil was 0.09 μg g^{-1} compared to 0.98 μg g^{-1} in the untreated plants, whilst the addition of goethite revealed an 82% reduction when compared to the untreated plants.

Tomato plants grown in Kidsgrove soil presented lower reductions in arsenic uptake (61% reduction with iron grit and 42% with iron III sulphate plus lime). Goethite displayed the best immobilisation of arsenic in Rixton soil reducing tomato leaf concentrations from 1.48 μg g^{-1} to 0.38 μg g^{-1} (Figure 6.15) producing a 94% reduction in arsenic uptake. Addition of Iron II sulphate to Rixton soil resulted in a 55% reduction in arsenic uptake in tomato plants.

All test plants accumulated arsenic within their leaves, when grown in the untreated contaminated soils and this would explain the poor growth rates obtained from these plants. Although the iron oxide producing additives reduced arsenic uptake into the above ground tissues, in some cases there were still significant levels present. However biomass production by the plant will affect the observed concentrations.

A one-way analysis of variance was used to test for differences between metal concentrations and treatments for spinach and tomato plants grown in the three soils. The ANOVA was combined with a Dunnett's test. This was used to provide confidence intervals for the differences between means, using a family error rate, which is the maximum probability of obtaining one or more confidence intervals that do not contain the true difference between level means.

Highly significant differences ($P < 0.001$) were obtained with respect to the As/heavy metal concentrations in the test plants that were grown in soils treated with the additives (Table 6.10). The ANOVA combined with Dunnett's test showed that in most

cases the metal concentrations in the test plants were significantly affected by the addition of the iron oxides and lime to the contaminated soils.

For spinach grown in Merton bank soil there were significant differences (from Dunnett's test) ($P<0.001$) between the metalloid concentration in the leaves and additives in the soil versus the untreated control soil. There was a significant increase when lime was added to the soil compared to the untreated control. Significant decreases were obtained using the Dunnett's test when goethite and III were applied respectively.

Spinach grown in Rixton soil showed significant differences (from Dunnett's test) ($P<0.001$) between arsenic concentration in the leaves and additives in the soil versus the untreated control soil. All iron oxide additives demonstrated a significant decrease in arsenic levels in the leaves using the Dunnett's test. Similar findings were observed for Kidsgrove soil ($P<0.002$), with the exception of the iron III treatment.

Tomato plants grown in Merton bank soil showed significant differences (from Dunnett's test) ($P<0.001$) between arsenic concentration in the leaves and additives in the soil versus the untreated control soil. This demonstrated that all the treatments produced a significant decrease in arsenic accumulation in the test plants when compared to untreated Rixton soil. A significant increase in arsenic accumulation was observed when lime was used as a treatment in Rixton soil. No significant differences were obtained for tomato plants grown in Kidsgrove soil ($P>0.05$) and there were no observable differences with Dunnett's test either.

Copper accumulation in the plants.

Copper uptake in spinach and tomato was most notably reduced by addition of goethite to the soils. A 94% reduction was obtained in spinach plants grown in Rixton soil amended with goethite. A copper concentration of 18.99 $\mu g\ g^{-1}$ was found in the leaves of untreated spinach plants, compared to 12.88 $\mu g\ g^{-1}$ in those grown in goethite-amended soil (Figure 6.17). Similar reductions were obtained in plants grown in the other soils. Tomato plants were found to take up less copper when goethite was applied to Rixton soil (Table 6.4) and when grown in Merton bank soil displayed a 71% reduction in copper uptake, whilst only a 39% reduction was obtained for those plants grown in Kidsgrove soil.

Lime and iron II both produced increases in accumulation of copper in the leaves of spinach grown in Merton Bank. Plants grown in lime and iron II amended Merton Bank soil accumulated higher levels of copper in their leaves, 22 μg g^{-1} and 21.9 μg g^{-1} respectively compared to the untreated control of 18.82 μg g^{-1} (Table 6.5).

For spinach grown in Merton bank soil there were significant differences (from the Dunnett's test) ($P<0.001$) between the metal concentration in the leaves and additives in the soil versus the untreated control soil. A significant increase with goethite was observed using Dunnet's test, when compared to the untreated control. Spinach grown in Kidsgrove soil showed a significant difference with the analysis of variance ($P<0.001$), but the Dunnett's test revealed no differences between the additives and the untreated control. Goethite also demonstrated a significant decrease in copper uptake when applied to Rixton soil. However all other treatments showed no significant differences when compared to the untreated control using Dunnett's test.

There was a significant difference ($P<0.001$) between treatments for tomato plants grown in Merton Bank soil. Dunnett's test showed a significant decrease in copper when tomato plants were grown in contaminated soil amended with iron II. There were significant increases however when iron III was applied to the soil. Dunnett's test revealed no significant differences in copper in tomato plants grown in Kidsgrove soil, however the analysis of variance test was significant ($P=0.029$). Plants grown in Rixton soil revealed that there was a significant difference between them ($P=0.06$), however the Dunnett's test revealed no differences between the additives and the untreated control.

Cadmium accumulation in the plants.

Cadmium levels were highest in plants grown in Kidsgrove soil, due to it containing highly elevated levels of this metal. Spinach grown in goethite amended Rixton soil exhibited a 94% reduction in cadmium uptake (Table 6.3). However the same plants grown in lime amended Rixton soil showed increases in cadmium levels in the leaves, 4.28 μg g^{-1} as opposed to 3.62 μg g^{-1} in the untreated control plants. Iron II produced a similar effect with spinach leaves containing 4.5 μg g^{-1} (Table 6.3). Spinach grown in Merton Bank soil amended with lime, goethite, iron grit and iron II, all increased the tissue concentrations of cadmium, when compared to the untreated control (Table 6.5).

Kidsgrove soil amended with goethite exhibited a 60% reduction in cadmium uptake in spinach (Table 6.1). The other additives all increased the concentrations of cadmium in the spinach leaves, with 93.85μg g^{-1} in the tissues of those plants grown in iron grit amended soil (Figure 6.18).

An 85% reduction in cadmium uptake was observed in tomato plants grown in iron II amended Merton Bank soil, when compared to the control. Cadmium was reduced from 3.86 μg g^{-1} in untreated control plants to 0.56 μg g^{-1} with iron II (Table 6.6). When goethite and iron grit were incorporated into Kidsgrove soil, a 42% reduction in cadmium uptake by tomato plants was achieved.

Dunnett's test revealed that there were no significant differences between the untreated control and amended Merton Bank soils. Significant decreases were observed in goethite and iron III amended Kidsgrove soils, with a significant increase in cadmium uptake in iron II and iron grit amended soils. There were no significant differences in spinach plants grown in Rixton soil ($P=0.368$).

For tomato plants in Merton bank soil, no significant differences were observed ($P=0.129$). Significant decreases were observed in Kidsgrove soil amended with goethite and iron grit respectively ($P<0.001$). No significant differences were observed in cadmium uptake in the amended Rixton soil ($P=0.840$).

Zinc accumulation in the plants.

For Rixton soil, the addition of goethite reduced zinc uptake in spinach by 96% (Figure 6.3). A 56% reduction in zinc availability was recorded when goethite was applied to Kidsgrove soil. Spinach plants grown in Merton Bank soil all showed increased levels of zinc in their tissues (Figure 6.16). Tomato plants grown in soil from Rixton produced similar results, in that all the additives increased zinc concentrations in the plants tissues (Figure 6.20). Addition of iron II sulphate to Merton Bank soil resulted in a 78% reduction in zinc uptake in tomato plants, reducing tissue concentrations from 23.04 μg g^{-1} to 5.09 μg g^{-1}. A decrease in zinc uptake of 42% was seen in tomato plants grown in iron grit-amended Kidsgrove soil, whilst with the exception of iron III, zinc tissue concentrations were all reduced in tomato plants grown in the other treatments (Table 6.2).

All treatments demonstrated a significant increase ($P<0.001$) in zinc uptake in spinach plants grown in Merton Bank soil when compared to the untreated control using Dunnett's test. Decreases were observed in all but the iron grit treatment, which showed an observable increase compared to the untreated control in zinc uptake in Kidsgrove soil ($P<0.001$). Dunnett's test revealed significant decreases for all but iron III (a significant increase) amended soil, when zinc concentrations were compared to the Rixton untreated control soil ($P<0.001$).

The zinc concentration in tomato plants grown in Merton Bank soil was observed to significantly decrease in iron II amended soil ($P<0.001$). Only iron grit in Kidsgrove soil produced a significant decrease in zinc uptake using Dunnett's test ($P<0.001$). Plants grown in amended goethite, iron II and III Rixton substrates all displayed significant increases of this metal when compared to the untreated control in the Dunnett's test ($P<0.001$).

Lead accumulation in the plants.

Lead uptake decreased by 94% and 57% in spinach plants grown in goethite-amended Rixton and Merton Bank soils respectively (Table 6.3). Tissue lead concentrations were higher in spinach grown in iron II and III amended Rixton soil (77.45 $\mu g\ g^{-1}$with iron II and 73.08 $\mu g\ g^{-1}$ with iron III) compared to the untreated soil (71.11$\mu g\ g^{-1}$) (Table 6.3). Addition of lime was observed to increase lead tissue concentrations of spinach plants grown in all three soils (Figures 6.16-6.18). Application of iron II to Merton Bank soil resulted in a 73% reduction in lead uptake in tomato plants. The tissue concentration of lead in the untreated soil was 79.1$\mu g\ g^{-1}$, whereas with iron II, lead levels had been reduced to 21.34 $\mu g\ g^{-1}$ (Table 6.6). The Lead tissue concentration in tomato plants grown in Kidsgrove soil was 61.15 $\mu g\ g^{-1}$. With the addition of goethite and iron grit, lead concentrations were reduced to 48.15 $\mu g\ g^{-1}$ and 46.42 $\mu g\ g^{-1}$ respectively (Figure 6.21). Addition of lime to the three soils produced higher lead tissue concentrations than the untreated controls. For example, the addition of lime to Merton Bank soil gave rise to 86.91 $\mu g\ g^{-1}$ in the leaves of tomato plants compared to 79.1 $\mu g\ g^{-1}$ in the untreated plants (Figure 6.19). Iron III application produced increased lead tissue

levels across all soils when compared to the untreated plants. In tomatoes grown in iron III –amended Rixton soil, the lead tissue concentration was 70.78 μg g^{-1} compared to only 56.86 μg g^{-1} in the untreated plants (Figure 6.20).

Dunnett's test revealed a significant decrease in lead concentrations in the leaves of spinach ($P<0.001$) grown in Merton Bank soil amended with either goethite or iron III sulphate. Significant increases compared to the untreated control were observed in plants grown in soils amended with iron II, iron grit and lime respectively. The Dunnett's test for spinach grown in Kidsgrove soil revealed again that goethite produced a significant decrease in lead uptake into the plants, and that iron II showed a significant increase ($P<0.001$). Similar results were obtained for the plants grown in Rixton soil ($P<0.001$).

Dunnett's test revealed that for tomato plants grown in Merton Bank soil amended with iron II, a significant decrease in leaf lead levels was observed ($P<0.001$). However lime, iron grit and Iron III all showed significant increases when compared to the untreated control. For plants grown in Kidsgrove soil, Dunnett's test revealed significant decreases with goethite and iron grit amended soils, but showed that lead uptake was significantly increased in the presence of lime, iron II and III ($P<0.001$). Dunnett's test showed that apart from iron grit and iron II (non significant results), the additives showed significant increases in lead concentrations in the above ground tissues of tomato plants when grown in Rixton soil ($P<0.001$).

Application of iron oxides to the polluted soils resulted in not all the plants responding well to the treatments. Even with addition of the iron oxides plant growth was stunted in most cases. However, the application of the iron oxides did reduce arsenic uptake into the leaves, when compared to the untreated plants.

Growth observations have shown that the application of goethite to an arsenic polluted soil was the most effective and beneficial treatment in terms of improved growth rates, decreased metal uptake and reduced metalloid concentration in the leaves. The other iron oxides may be effective at immobilising arsenic, but in a soil contaminated with other phytotoxic metals, the results have shown that plant growth is affected by their addition. This may be due to their effects at mobilising other toxic metals present in these soils.

Overall, the results indicated that the addition of iron oxides did reduce arsenic uptake in spinach and tomato plants when compared to the untreated control plants.

However differences in soil properties, for example texture and pH, will affect arsenic toxicity, as will differences between the plant species themselves.

6.5.4. Accumulation of arsenic by perennial ryegrass.

All iron oxide treatments reduced the total arsenic concentrations in the leaves of the perennial ryegrass when compared to the untreated and lime amended soils (figures 6.22-6.24). Rye grass grown in Kidsgrove soil treated with iron II and III showed reduced uptake of arsenic in the leaves at the final two harvests. With addition of iron II and III there was a 99% and 98% reduction in arsenic uptake respectively when compared to the grass grown in the untreated soil for the last harvest (Figure 6.22 & 6.26).

Grass grown in Rixton soil amended with iron II showed an 85% reduction in arsenic uptake in the first harvest. However this increased to 96% in the final cut when compared to the grass grown in untreated Rixton soil (Figure 6.23 & 6.25). Application of goethite showed a 90% reduction during the third harvest, but this was reduced to 73% in the final harvest. The addition of lime to Rixton soil resulted in the grass accumulating a greater level of arsenic within its tissues (958.68 mg/pot) compared to 581.65 mg/pot in the untreated Rixton soil.

The concentration of arsenic in the leaves of grass grown in iron II amended Merton Bank soil over the five harvests was greatly reduced when compared to grass grown in the untreated soil (Figure 6.24). The addition of iron II produced a 92% reduction in arsenic uptake in the second harvest (Table 6.9.b. & figure 6.24). Plant arsenic uptake increased until the third harvest and was then observed to fall in the final cut (Figure 6.27). As with the other soils, the addition of lime resulted in an increase in the concentration of arsenic present in the leaves, reaching a peak of 1.9 mg/kg^{-1} in the leaves from the third harvest (Figure 6.24 & 6.27).

For the perennial ryegrass, a balanced analysis of variance was used to test for differences in the uptake of arsenic between the different harvests and also the different treatments (Table 6.11-6.13).

There was a significant difference between the different harvests collected and arsenic uptake (mg/pot) by the ryegrass when grown in the Rixton substrate ($F_{[4,24]} = 3.61$, $P = 0.019$). A significant difference was also observed between the different treatments

and arsenic uptake in Rixton soil ($F_{[6,24]}$ = 3.31, P= 0.016). There was no significant difference between harvest and arsenic uptake in ryegrass grown in soil from Kidsgrove ($F_{[4,24]}$ = 2.53, P= 0.097). There was also no significant difference between treatments and arsenic uptake in Kidsgrove soil ($F_{[6,24]}$ = 1.66, P= 0.175). A significant difference was seen in the uptake of arsenic by ryegrass grown in Merton Bank soil and the different harvests collected ($F_{[4,24]}$ = 7.71, P= 0.000). There were also significant differences between arsenic uptake and the application of the additives to the Merton Bank soil ($F_{[6,24]}$ = 6.73, P= 0.000) (Tables 6.11-6.13).

Figure 6.1. Spinach total shoot dry weight/pot grown in Rixton soil.

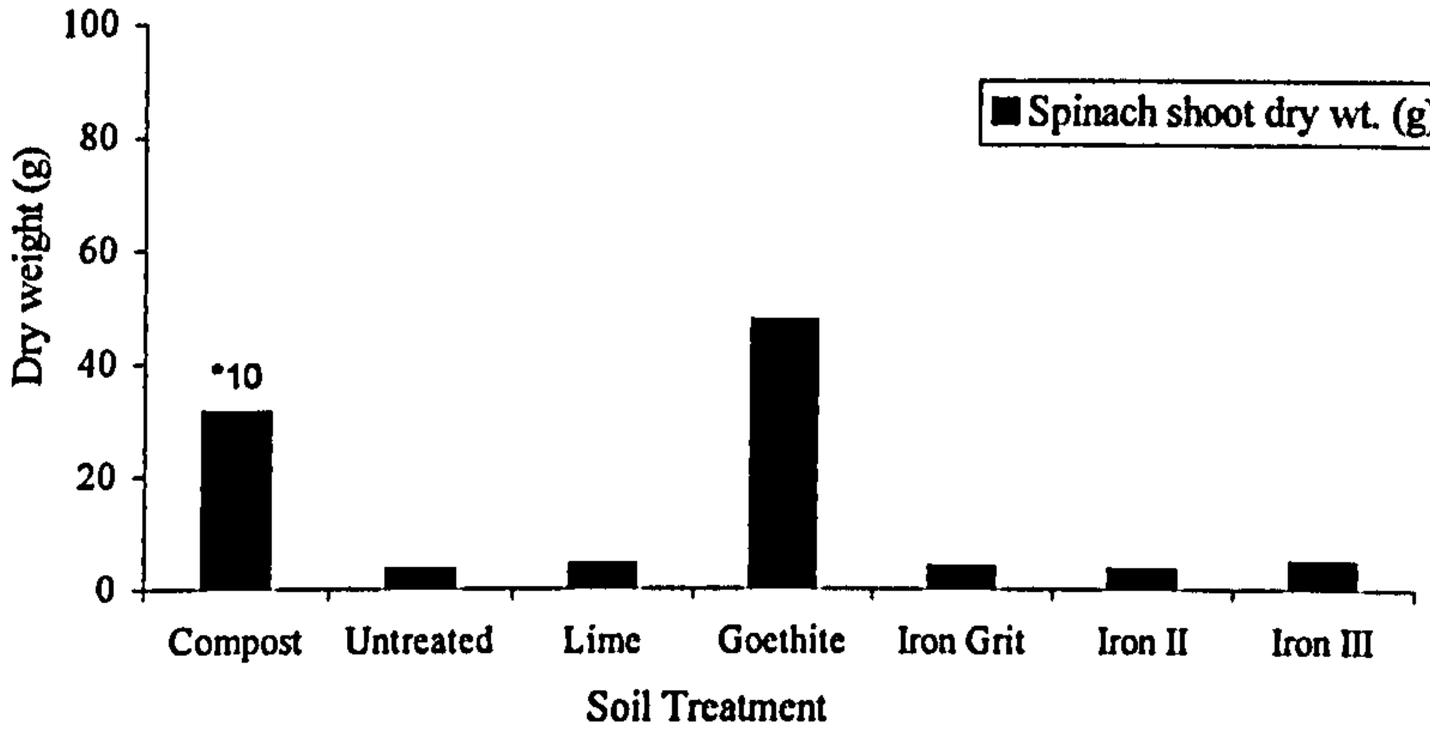


Figure 6.2. Spinach total shoot dry weight/pot grown in Kidsgrove soil.

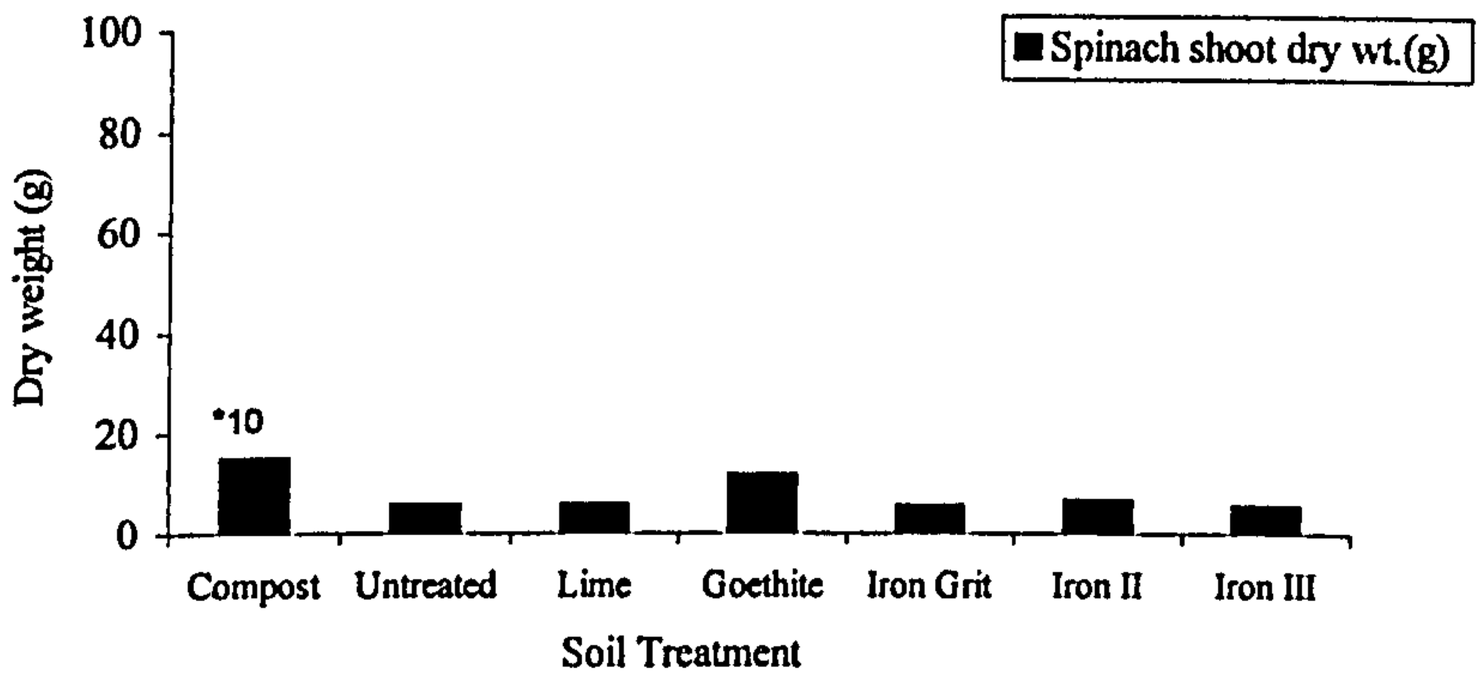


Figure 6.3. Spinach total shoot dry weight/pot grown in Merton Bank soil.

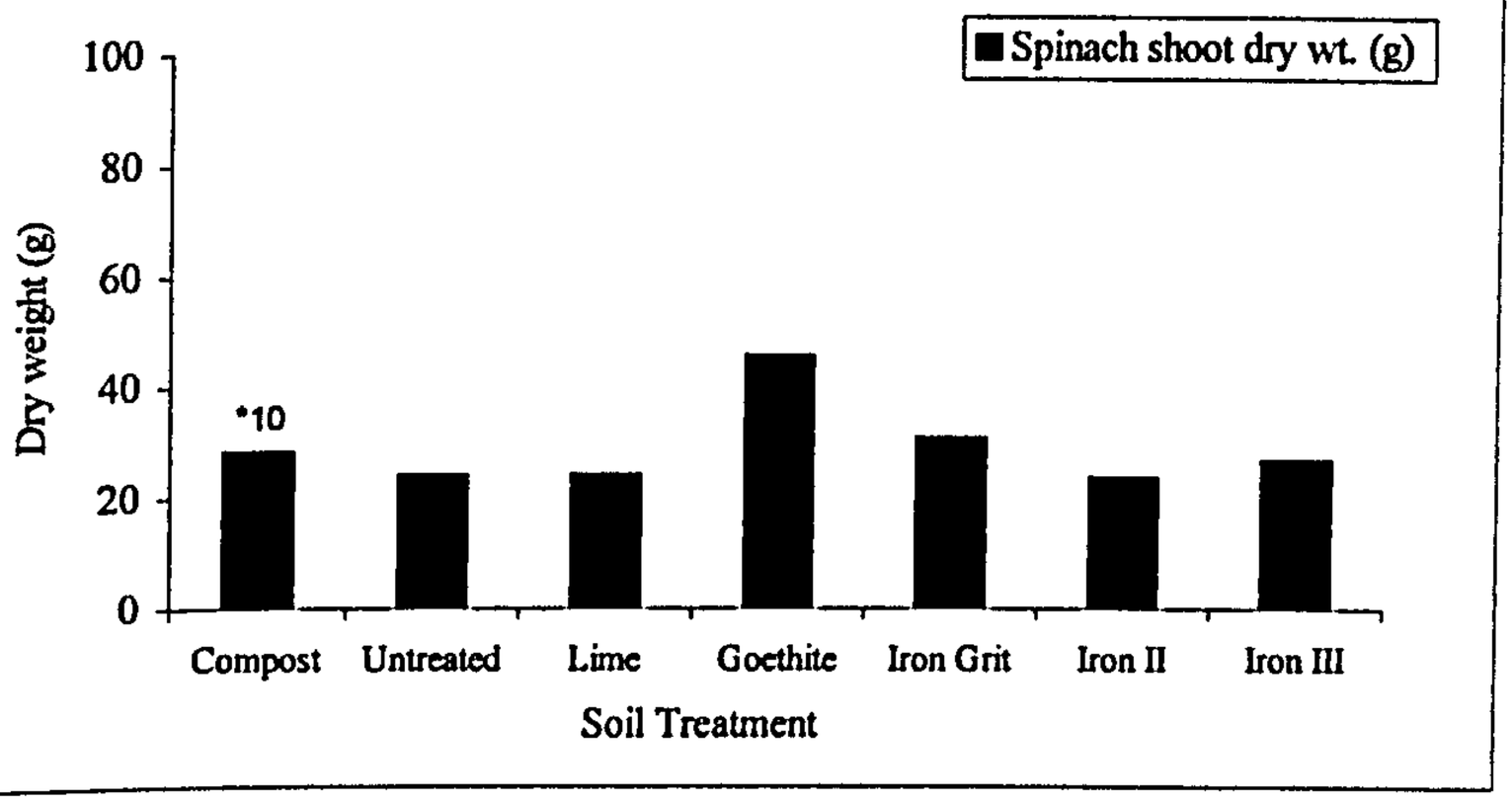


Figure 6.4. Tomato total shoot dry weight/pot grown in Rixton soil.

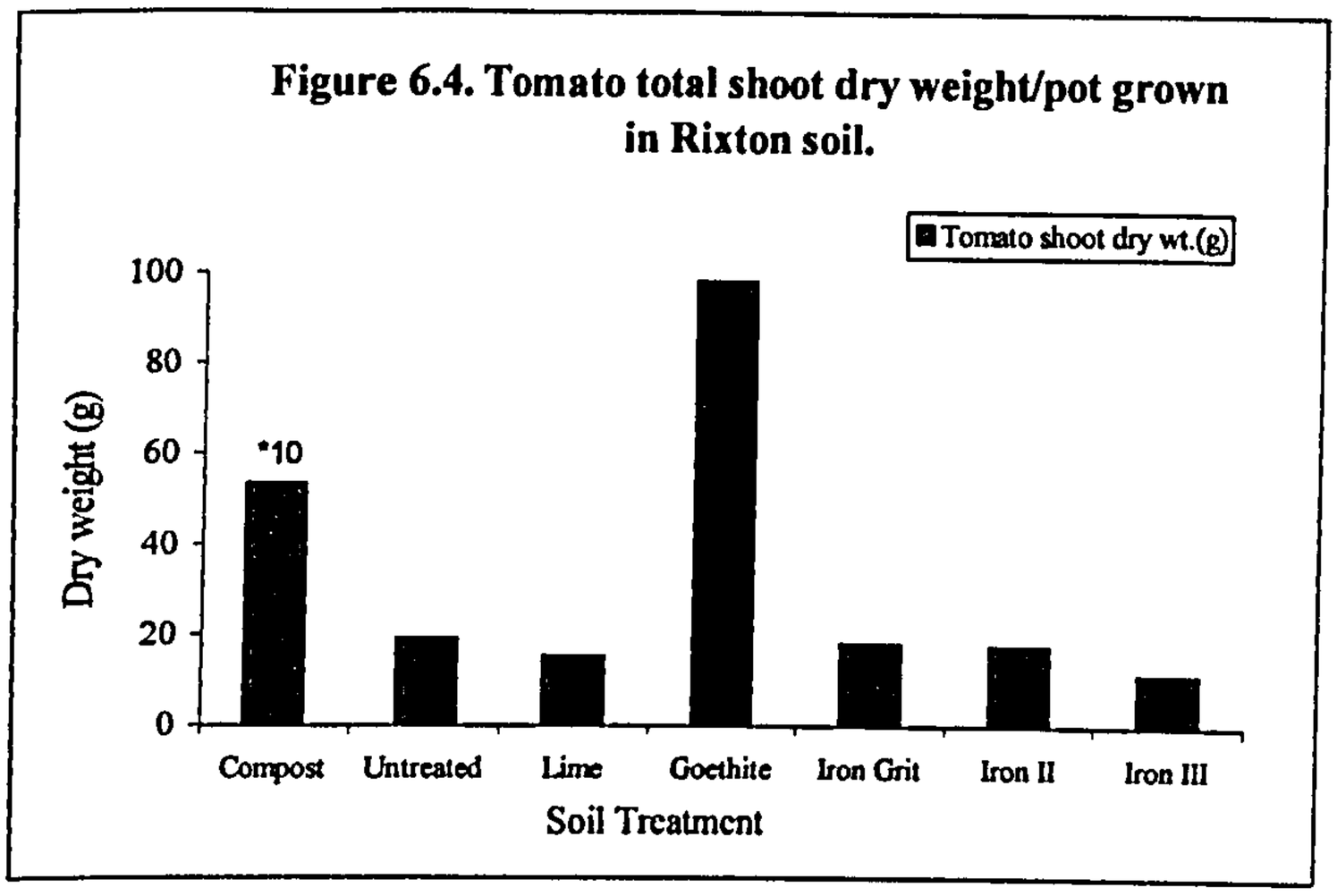


Figure 6.5. Tomato total shoot dry weight/pot grown in Kidsgrove soil.

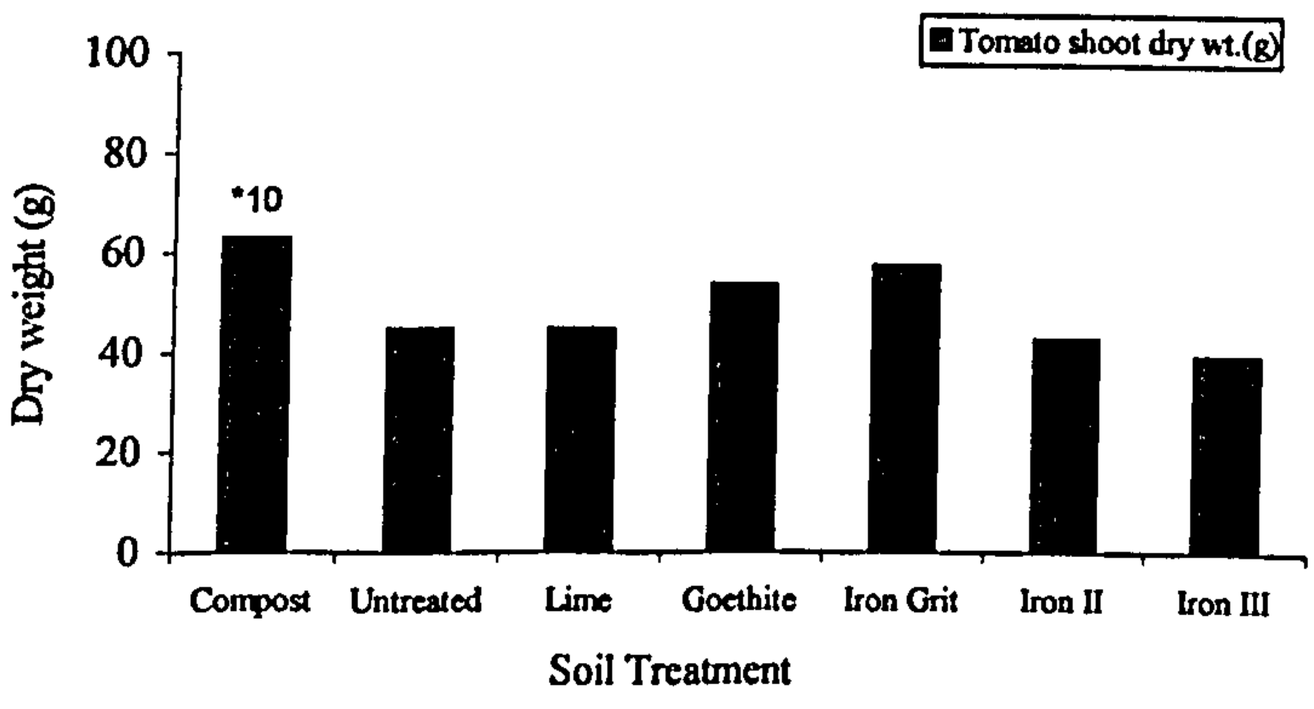


Figure 6.6. Tomato total shoot dry weight/pot grown in Merton bank soil.

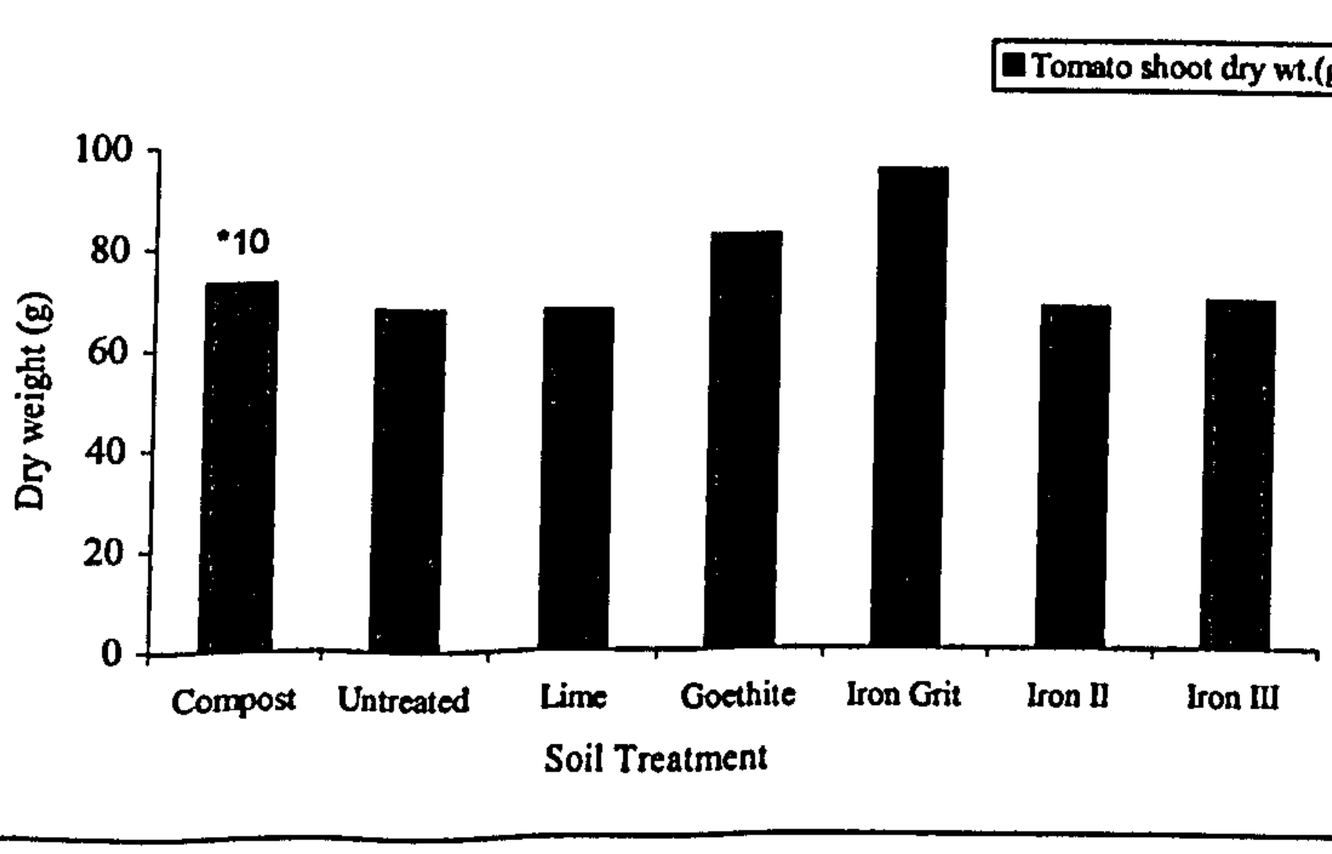


Figure 6.7. Changes in total shoot dry weight of perennial rye grass grown in Rixton soil over five harvests.

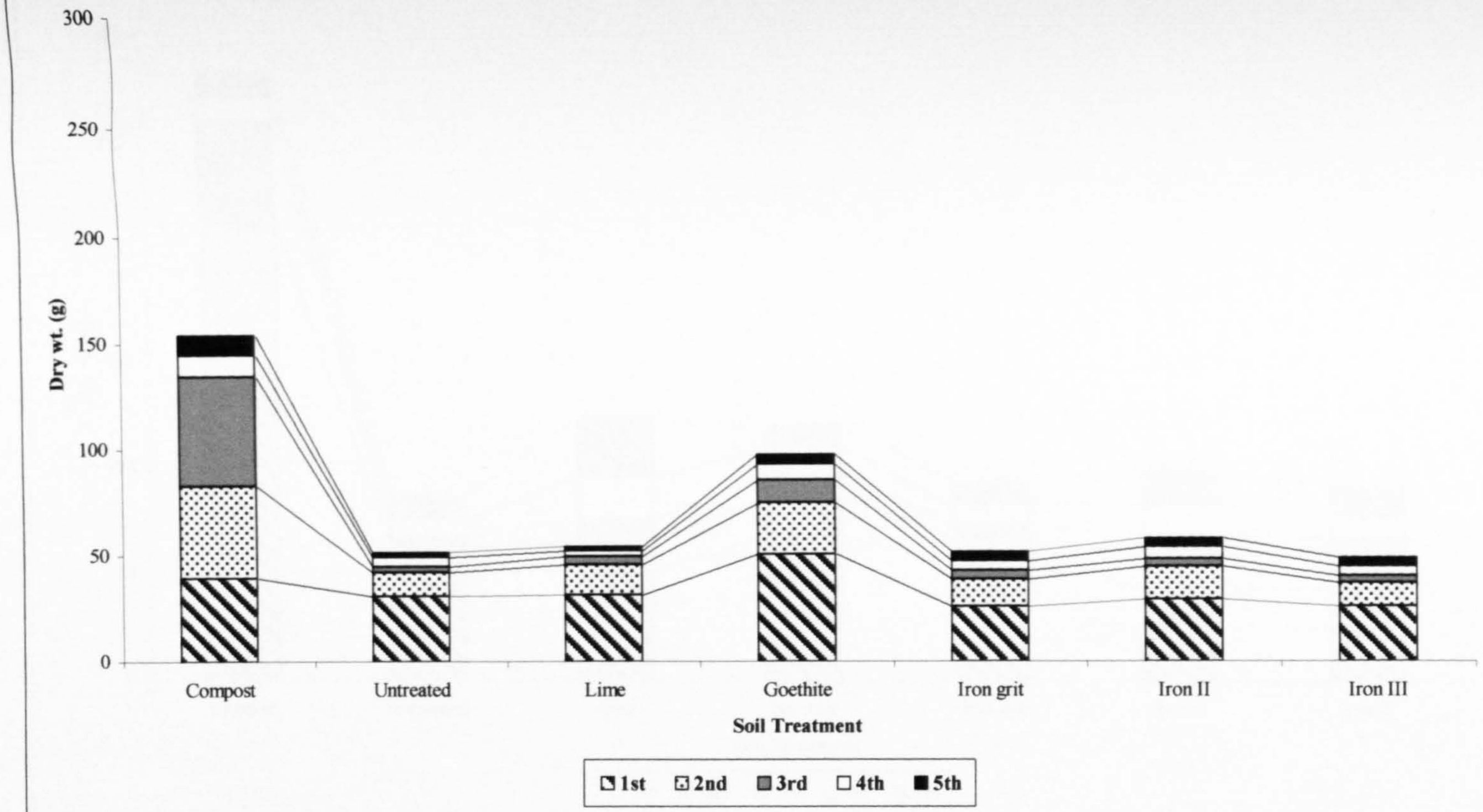


Figure 6.8. Changes in total shoot dry weight of perennial rye grass grown in Kidsgrove soil over five harvests.

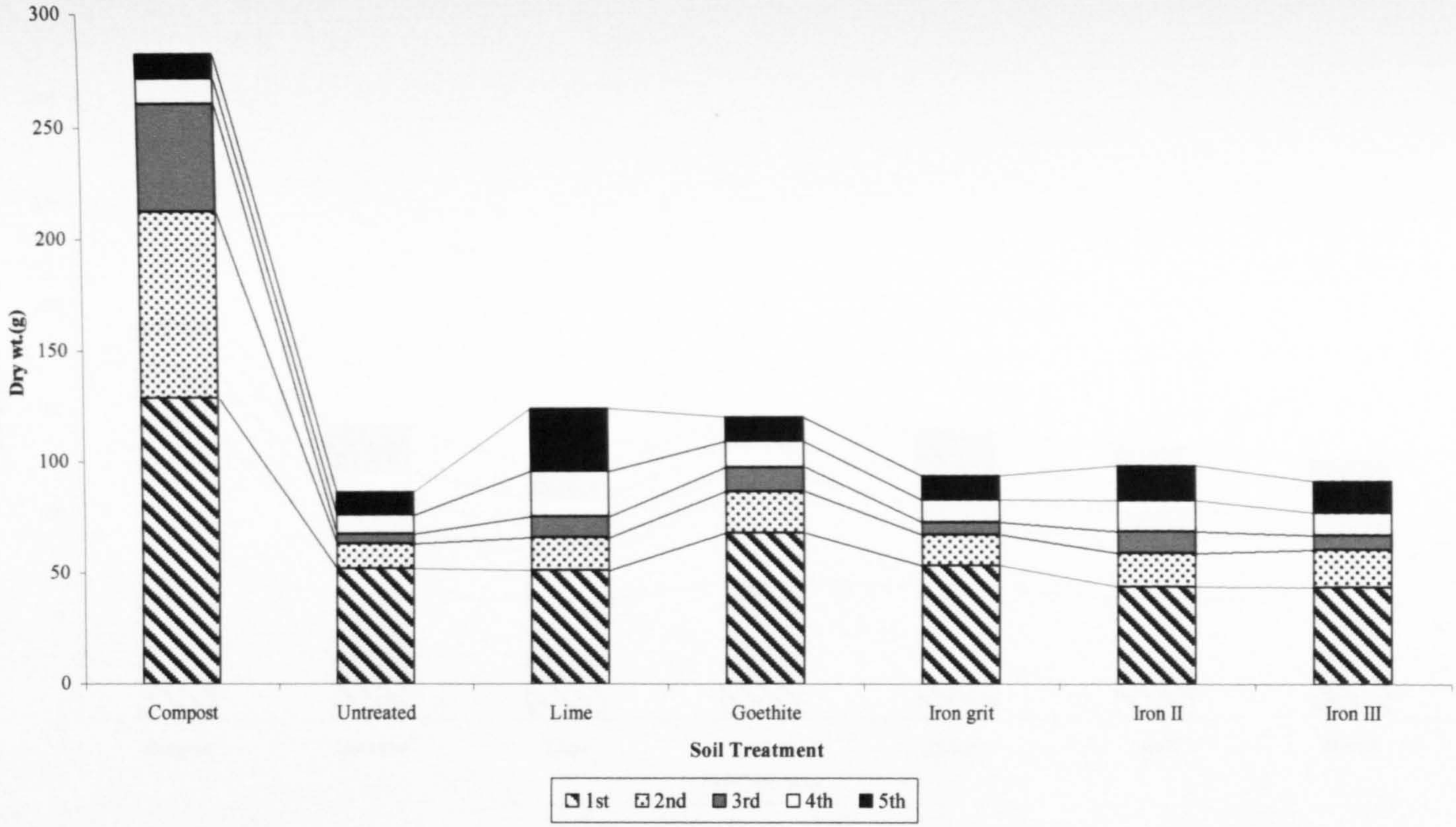


Figure 6.9. Changes in total shoot dry weight of perennial rye grass grown in Merton Bank soil over five harvests.

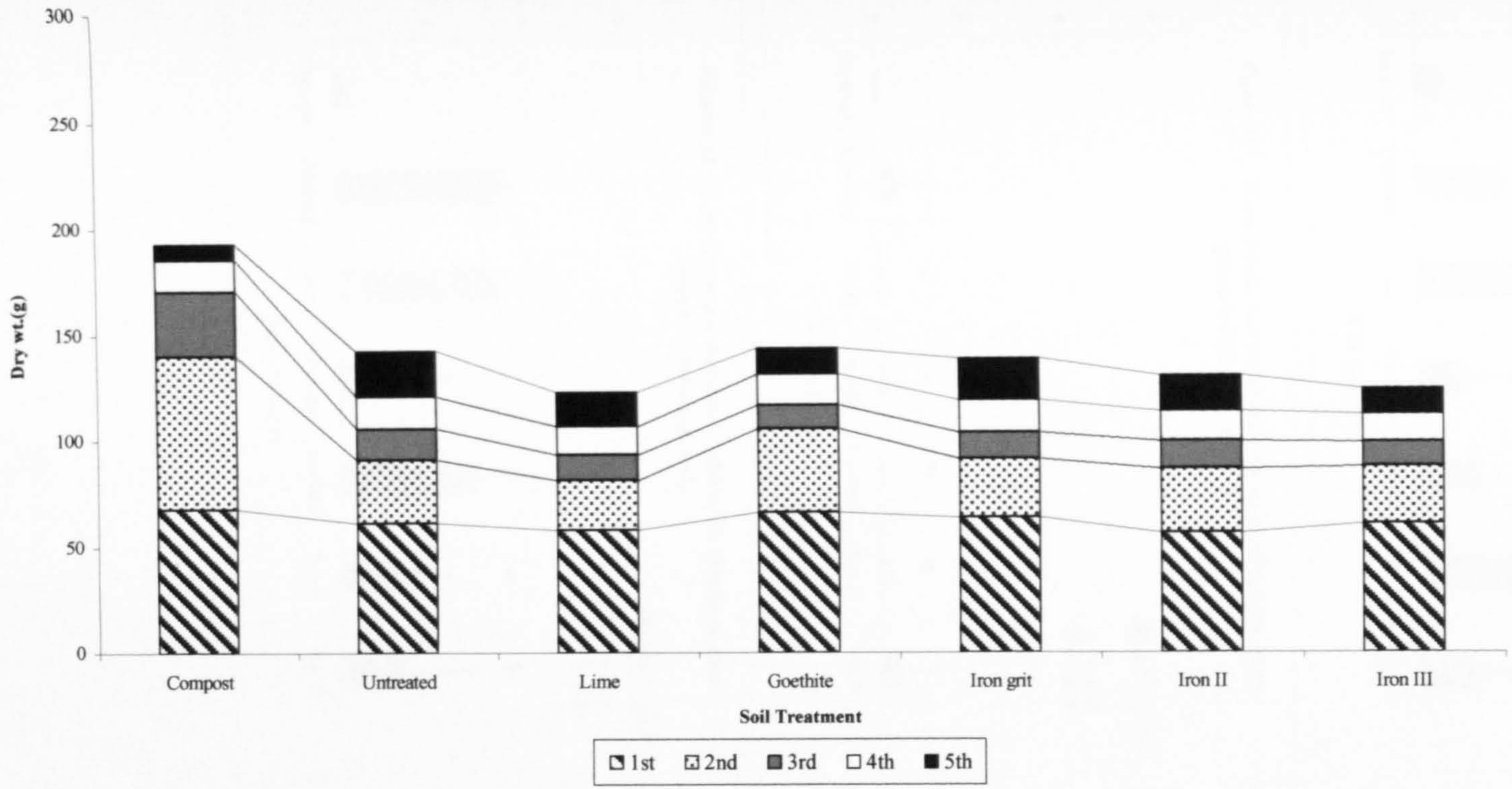


Figure 6.10. Mean arsenic concentrations in the leaves of spinach plants grown in Merton Bank soil (n=3).

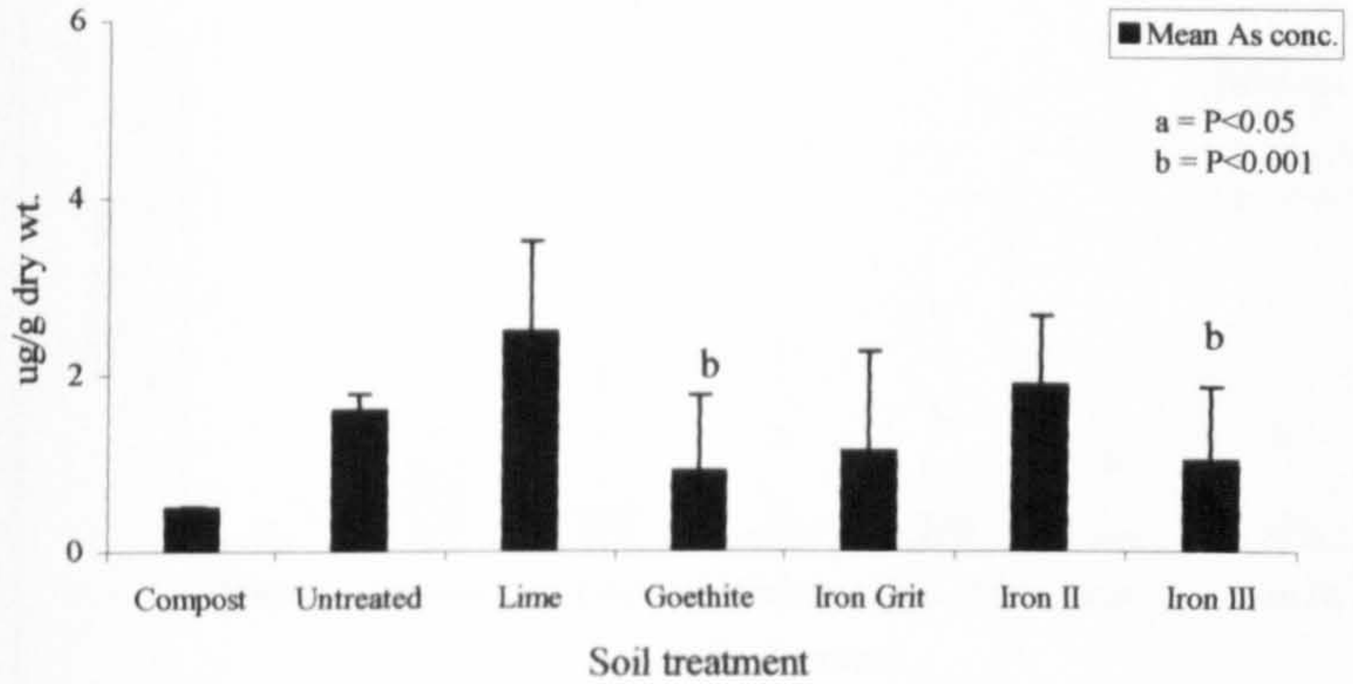


Figure 6.11. Mean arsenic concentrations in the leaves of spinach plants grown in Kidsgrove soil (n=3).

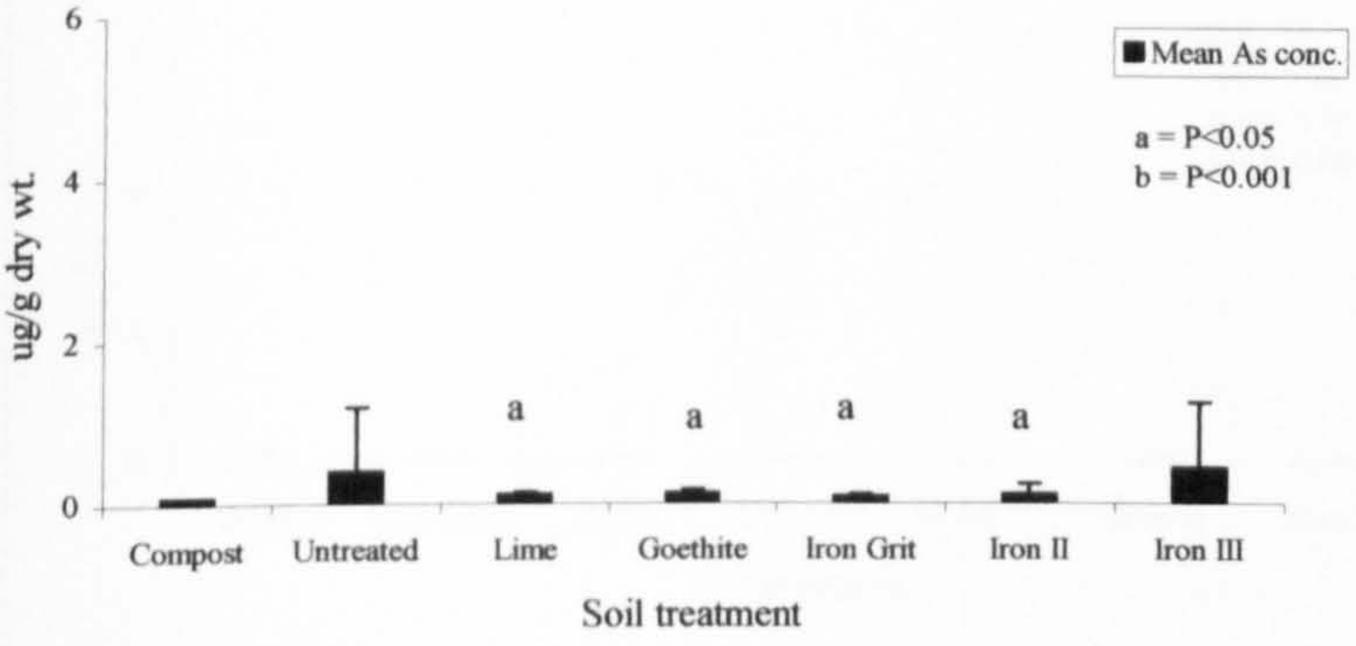


Figure 6.12. Mean arsenic concentrations in the leaves of spinach plants grown in Rixton soil (n=3).

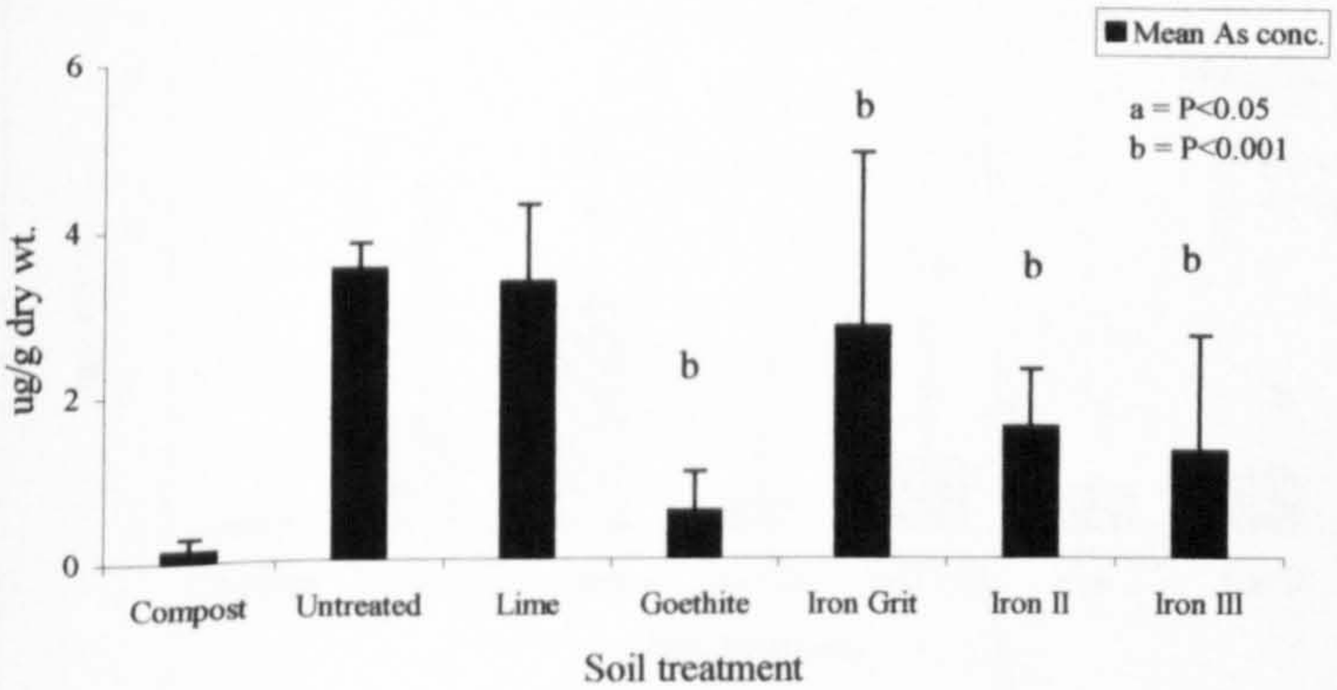


Figure 6.13. Mean arsenic concentrations in the leaves of tomato plants grown in Merton Bank soil (n=3).

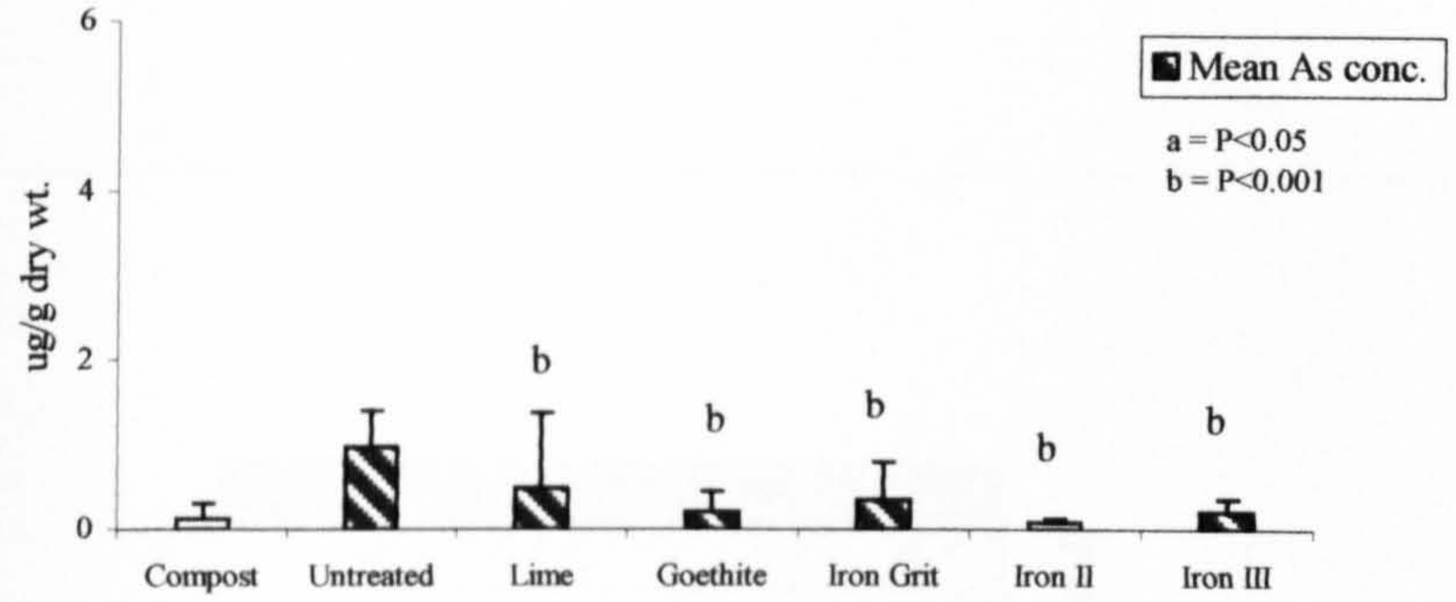


Figure 6.14. Mean arsenic concentrations in the leaves of tomato plants grown in Kidsgrove soil (n=3).

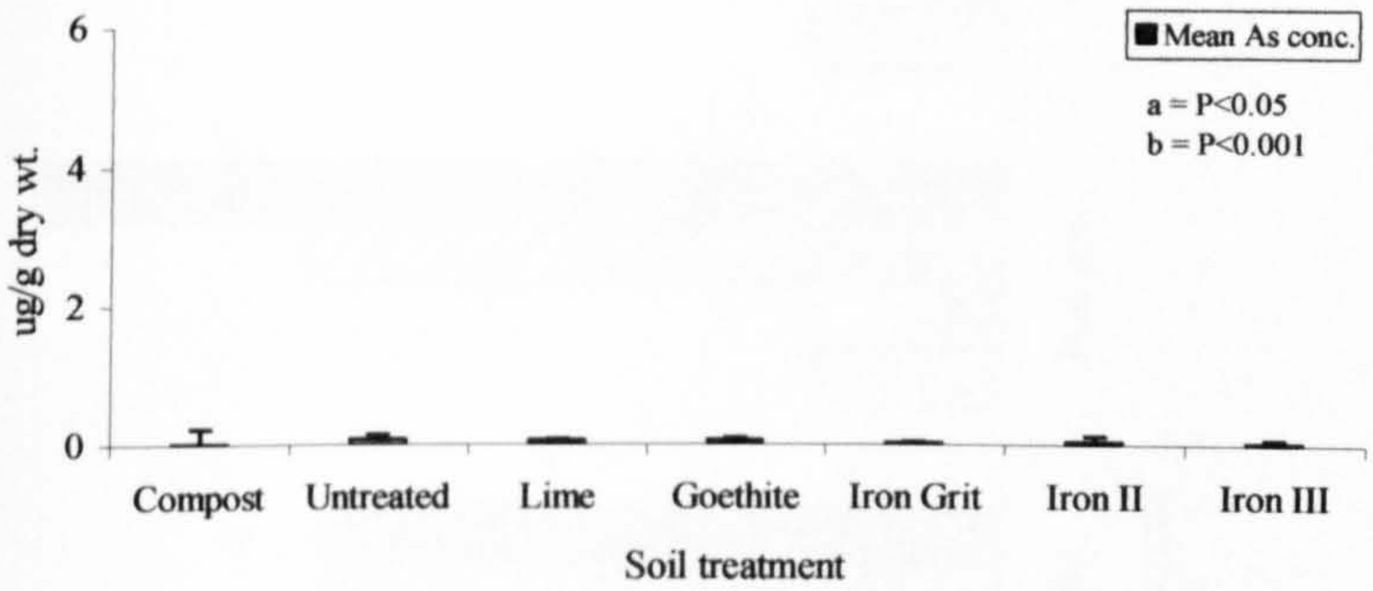


Figure 6.15. Mean arsenic concentrations in the leaves of tomato plants grown in Rixton soil (n=3).

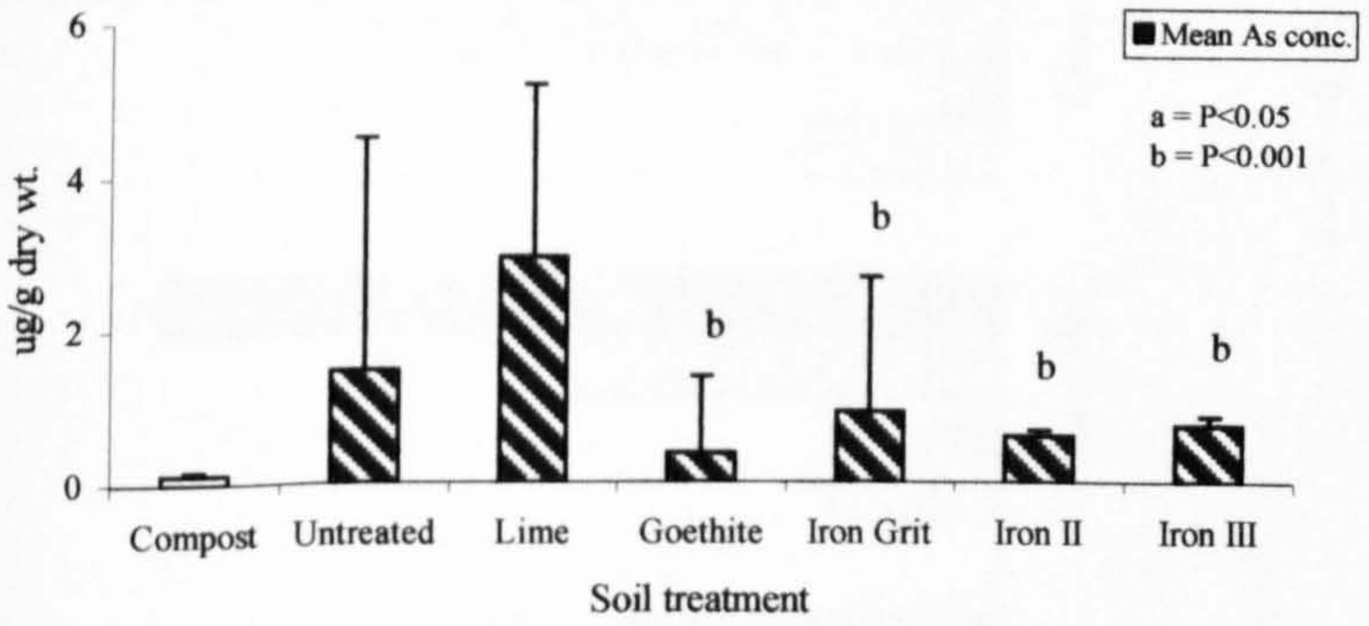
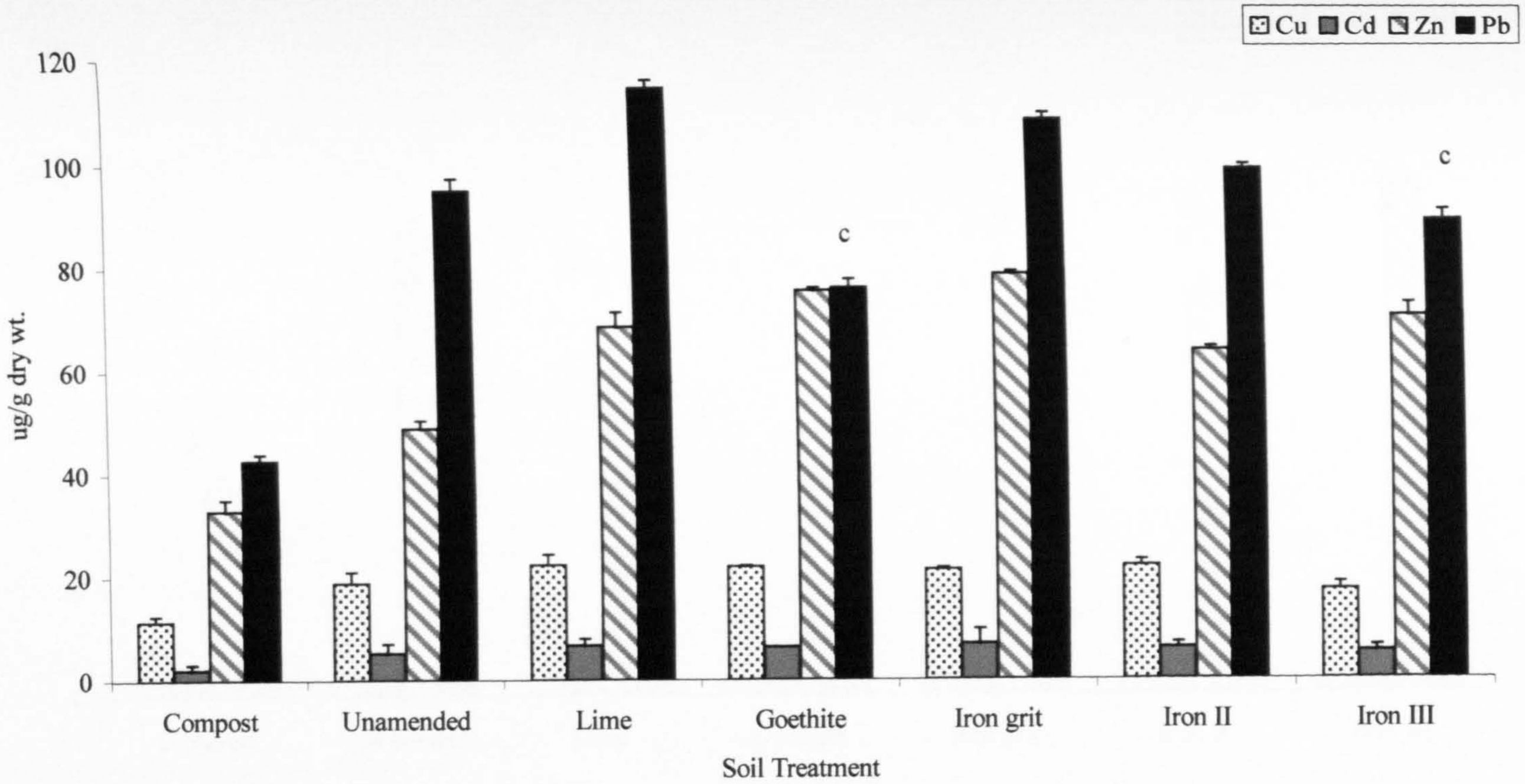


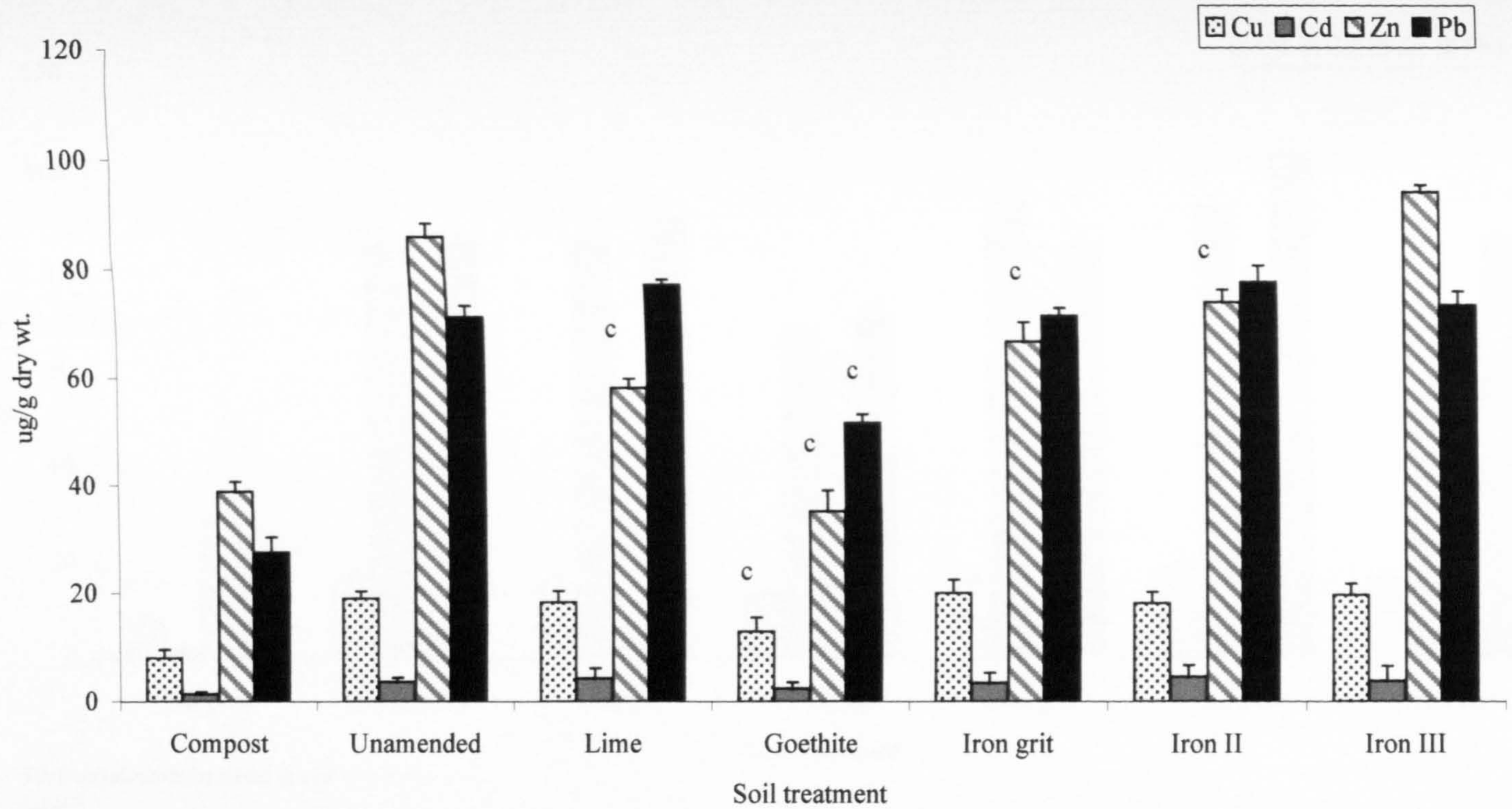
Figure 6.16. Mean heavy metal concentrations in the leaves of spinach grown in Merton Bank soil (n=3).



Total metal concentrations in soil (ug/g):
Cu 84.6
Cd 30
Zn 451
Pb 162

a = P < 0.05
b = P < 0.01
c = P < 0.001

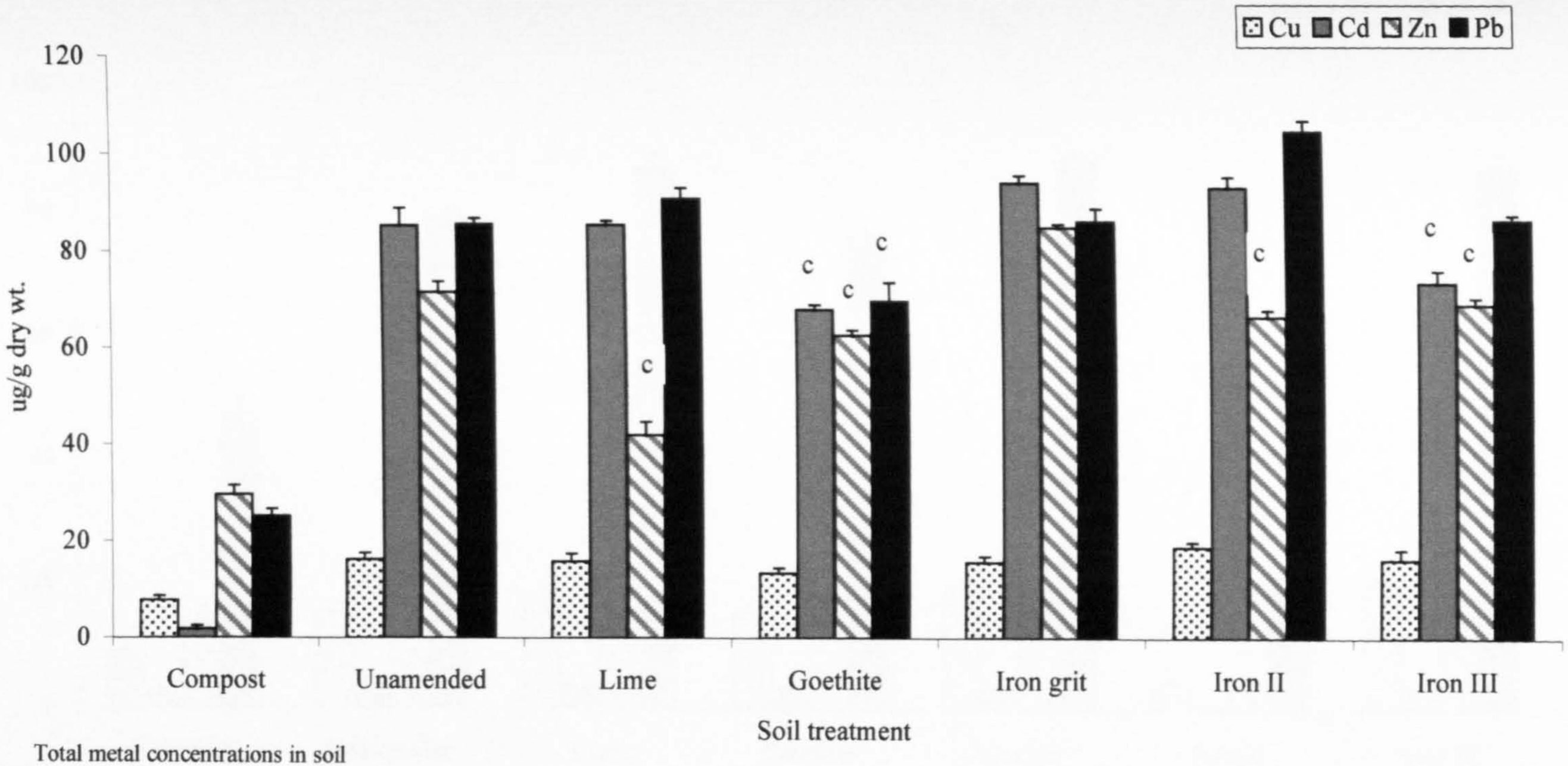
Figure 6.17. Mean heavy metal concentrations present in the leaves of spinach plants grown in Rixton soil (n=3).



Total metal concentrations in soil (ug/g):
Cu 160
Cd 5.0
Zn 228
Pb 122

a = $P < 0.05$
b = $P < 0.01$
c = $P < 0.001$

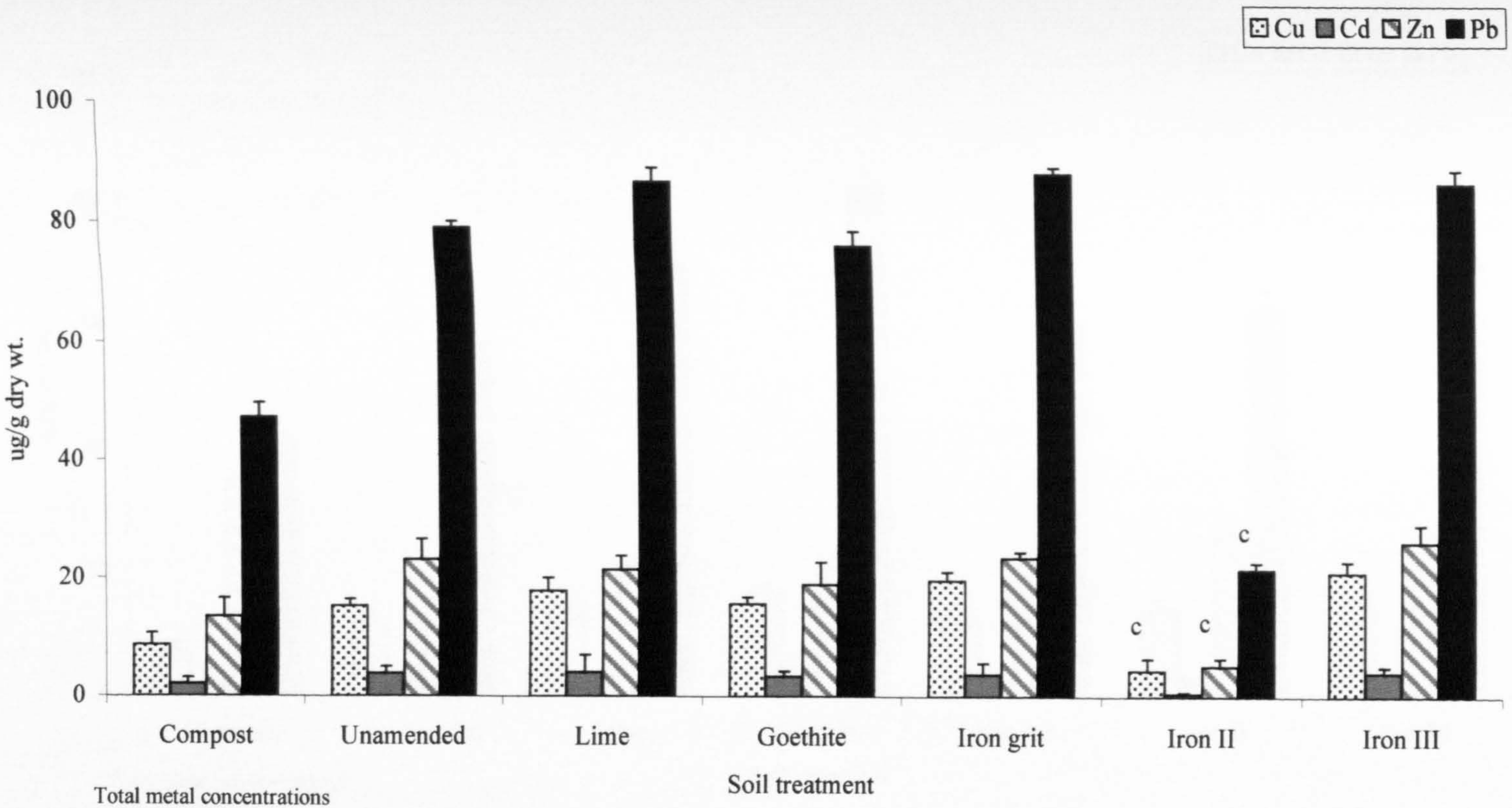
Figure 6.18. Mean heavy metal concentrations present in the leaves of spinach plants grown in Kidsgrove soil (n=3).



Total metal concentrations in soil (ug/g):
Cu 125
Cd 1104
Zn 1538
Pb 313

a = P < 0.05
b = P < 0.01
c = P < 0.001

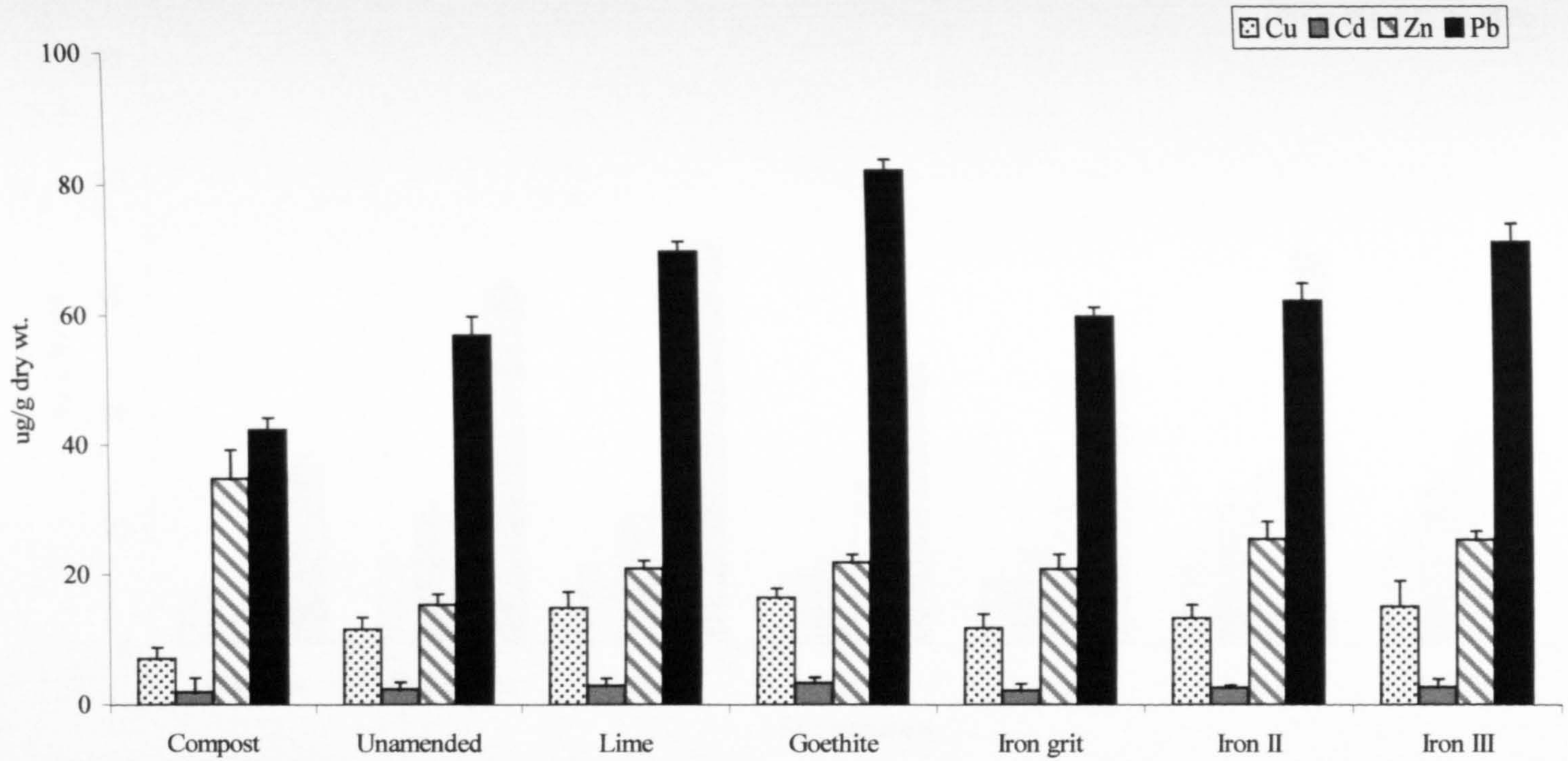
Figure 6.19. Mean heavy metal concentrations present in the leaves of tomato plants grown in Merton Bank soil (n=3).



Total metal concentrations in soil (ug/g):
Cu 84.6
Cd 30
Zn 451
Pb 162

a = P < 0.05
b = P < 0.01
c = P < 0.001

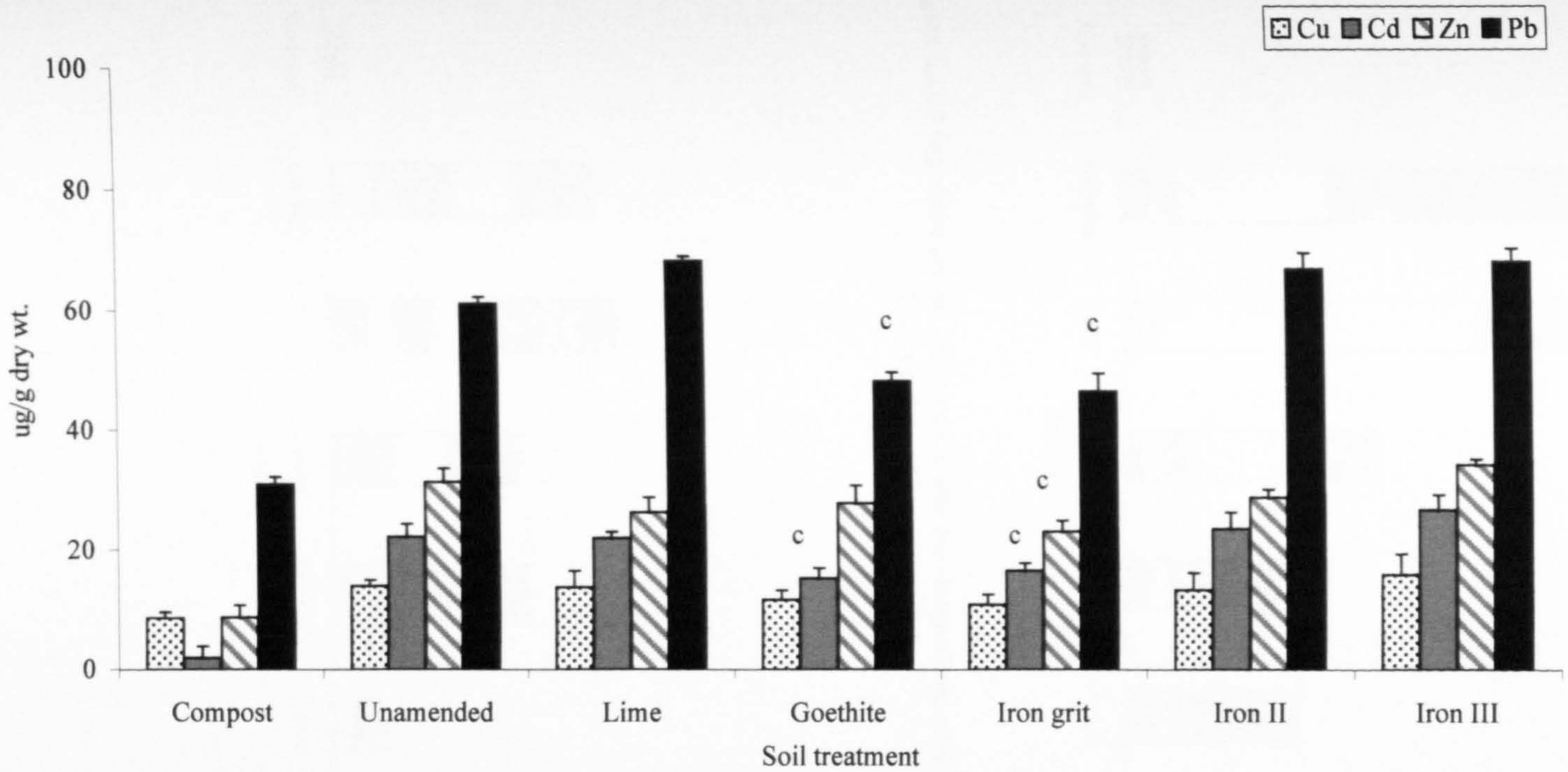
Figure 6.20. Mean heavy metal concentrations present in the leaves of tomato plants grown in Rixton soil (n=3).



Total metal concentrations in soil (ug/g):
Cu 160
Cd 5.0
Zn 228
Pb 122

a = $P < 0.05$
b = $P < 0.01$
c = $P < 0.001$

Figure 6.21. Mean heavy metal concentrations present in the leaves of tomato plants grown in kidsgrove soil (n=3).



Total metal concentrations in soil (ug/g):
Cu 125
Cd 1104
Zn 1538
Pb 313

a = $P < 0.05$
b = $P < 0.01$
c = $P < 0.001$

Figure 6.22. Progressive arsenic accumulation with time in the shoots of rye grass grown in Kidsgrove soil over 15 weeks (n=3).

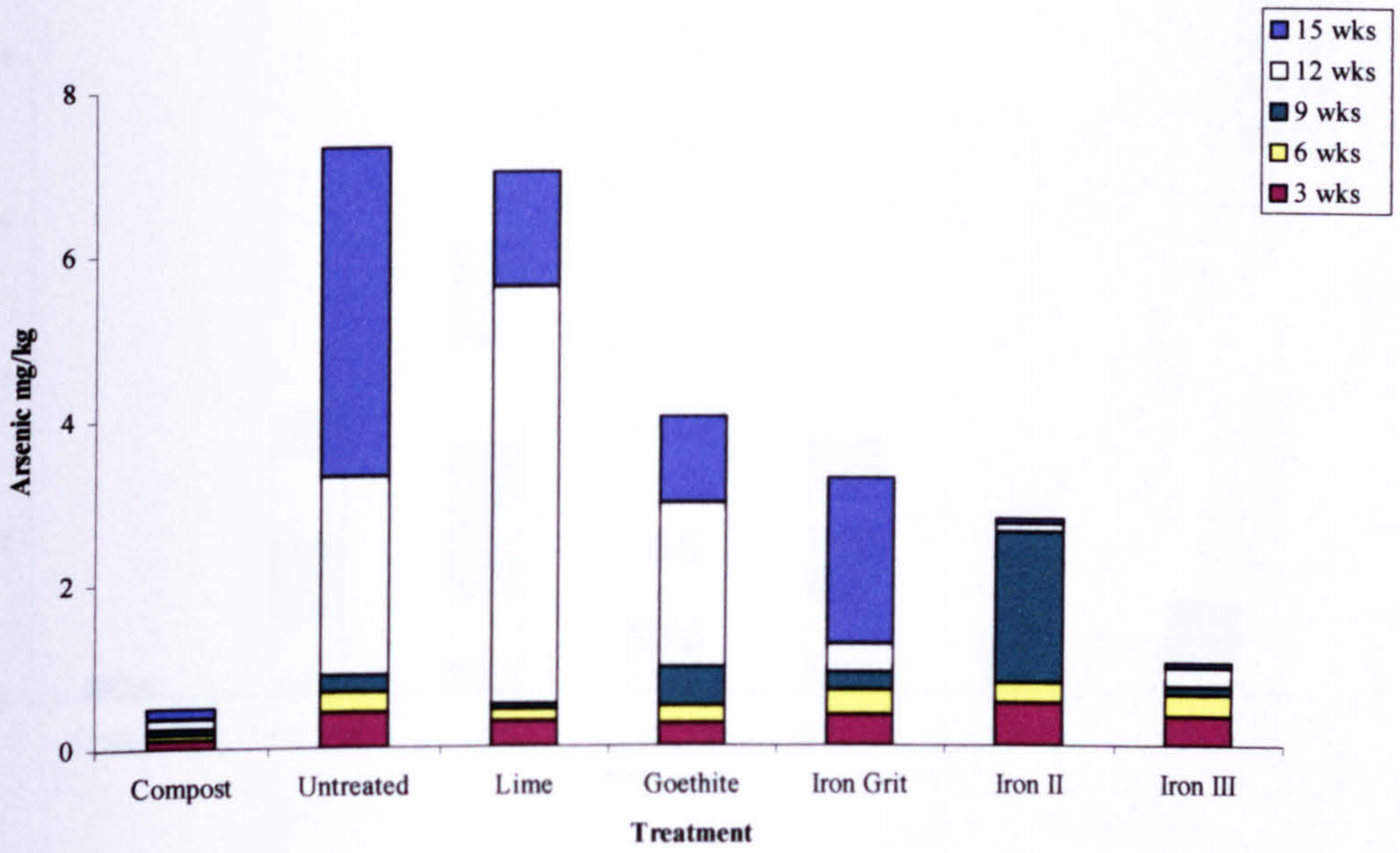


Figure 6.23. Progressive arsenic accumulation with time in the shoots of rye grass grown in Rixton soil over 15 weeks (n=3).

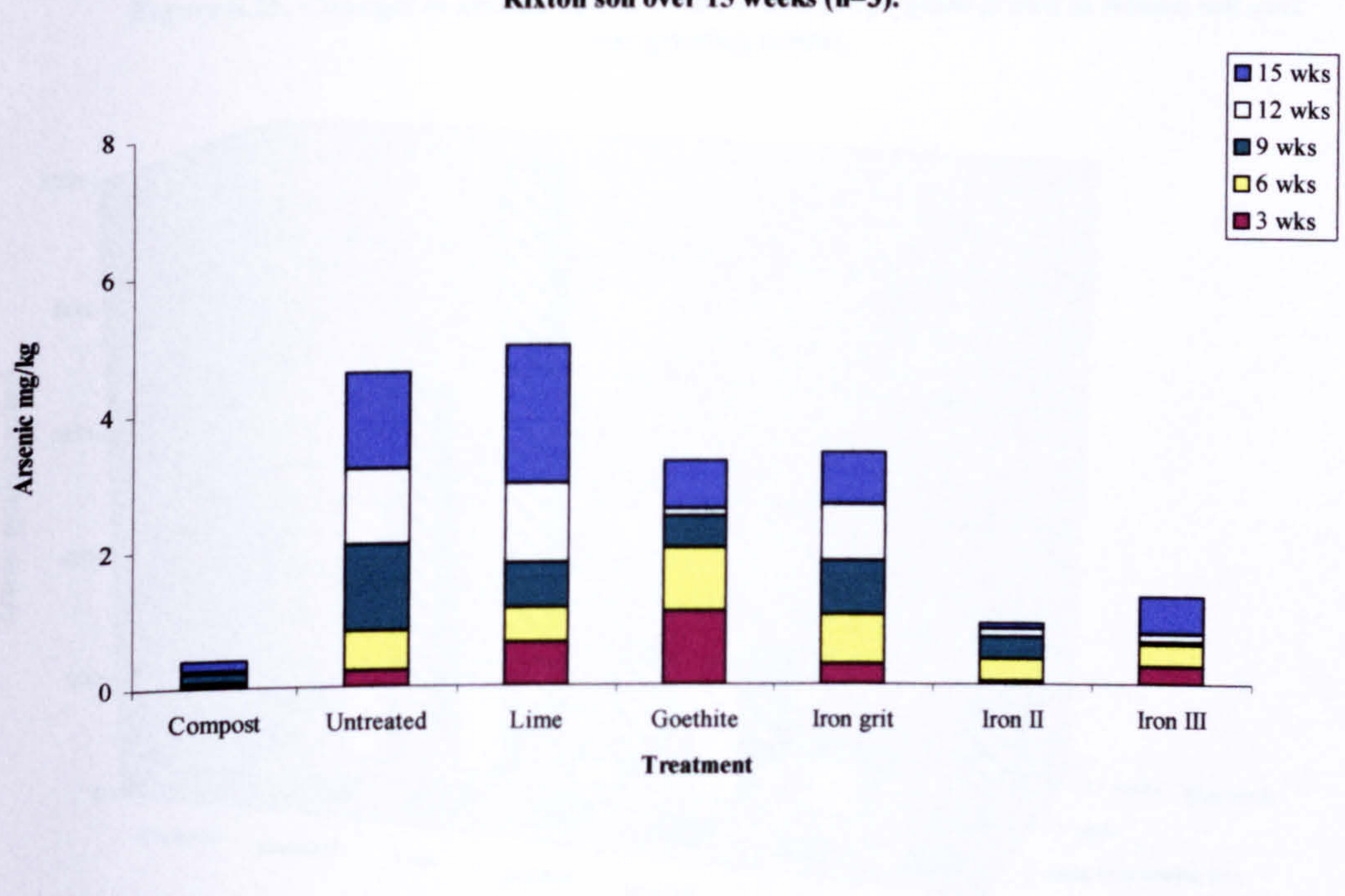


Figure 6.24. Progressive arsenic accumulation with time in the shoots of rye grass grown in Merton Bank soil over 15 weeks (n=3).

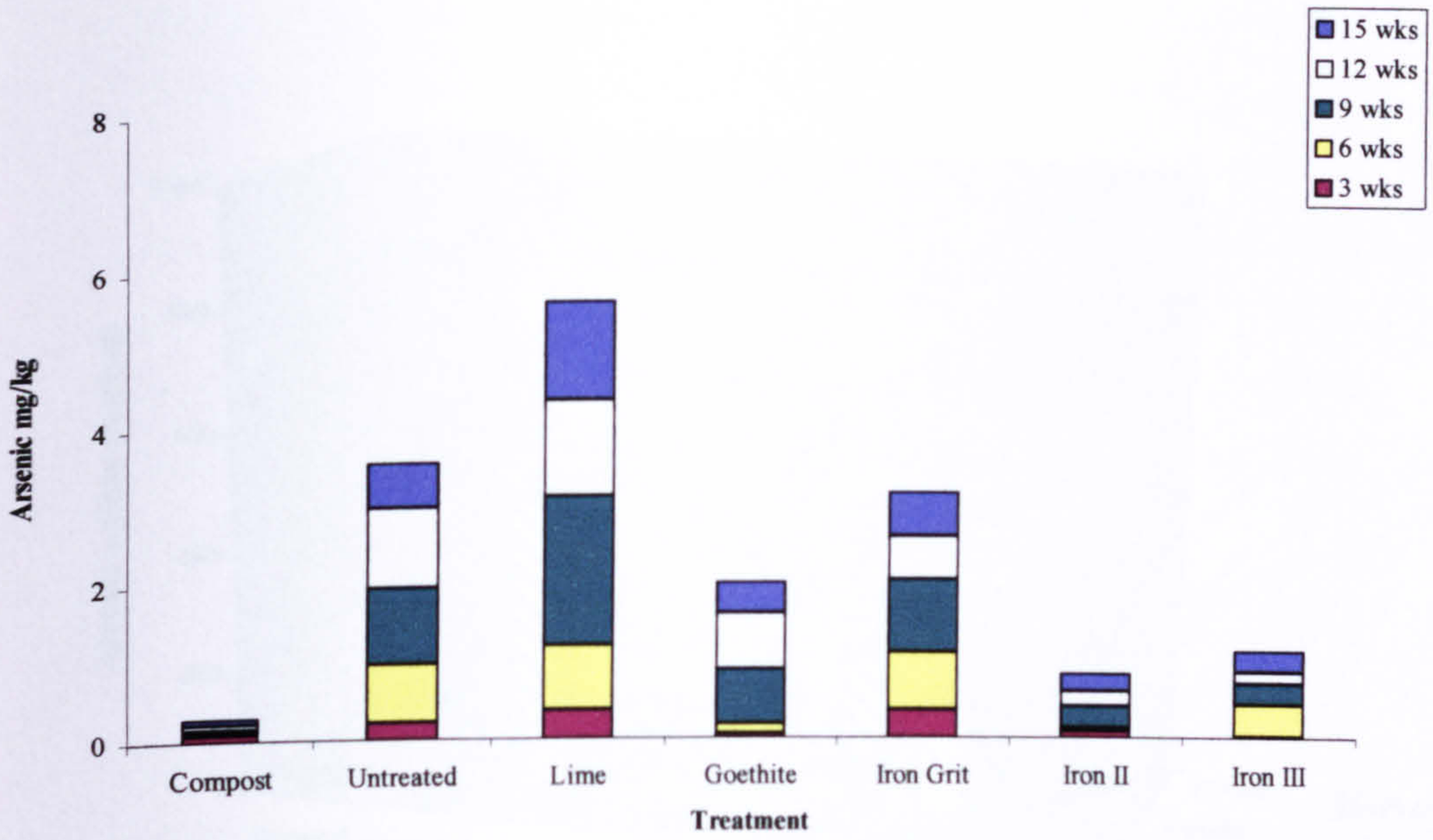


Figure 6.25. Changes in arsenic uptake in the shoots of rye grass grown in Rixton soil over one growing season.

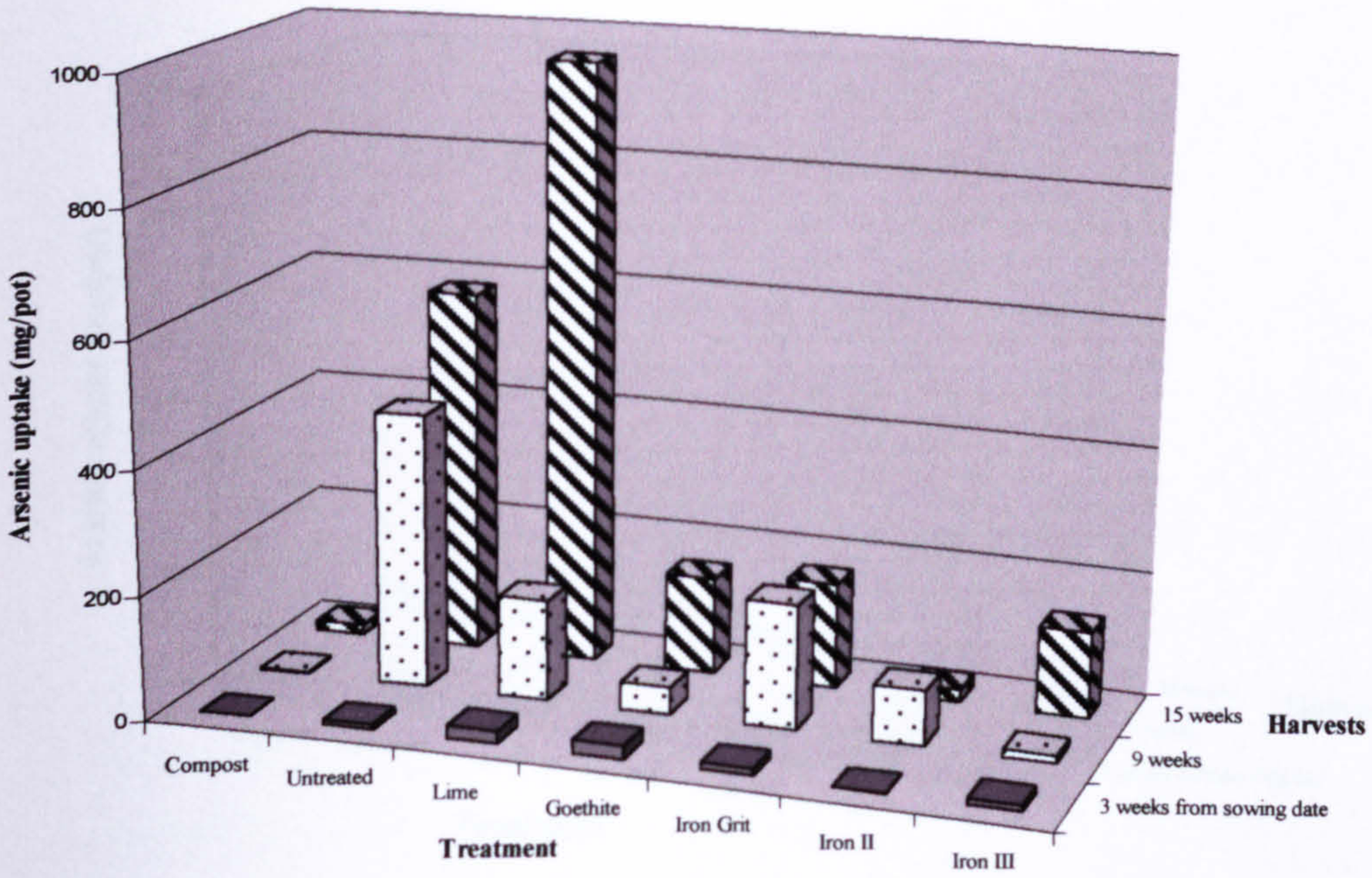


Figure 6.26. Changes in arsenic uptake in the shoots of rye grass grown in Kidsgrove soil over one growing season

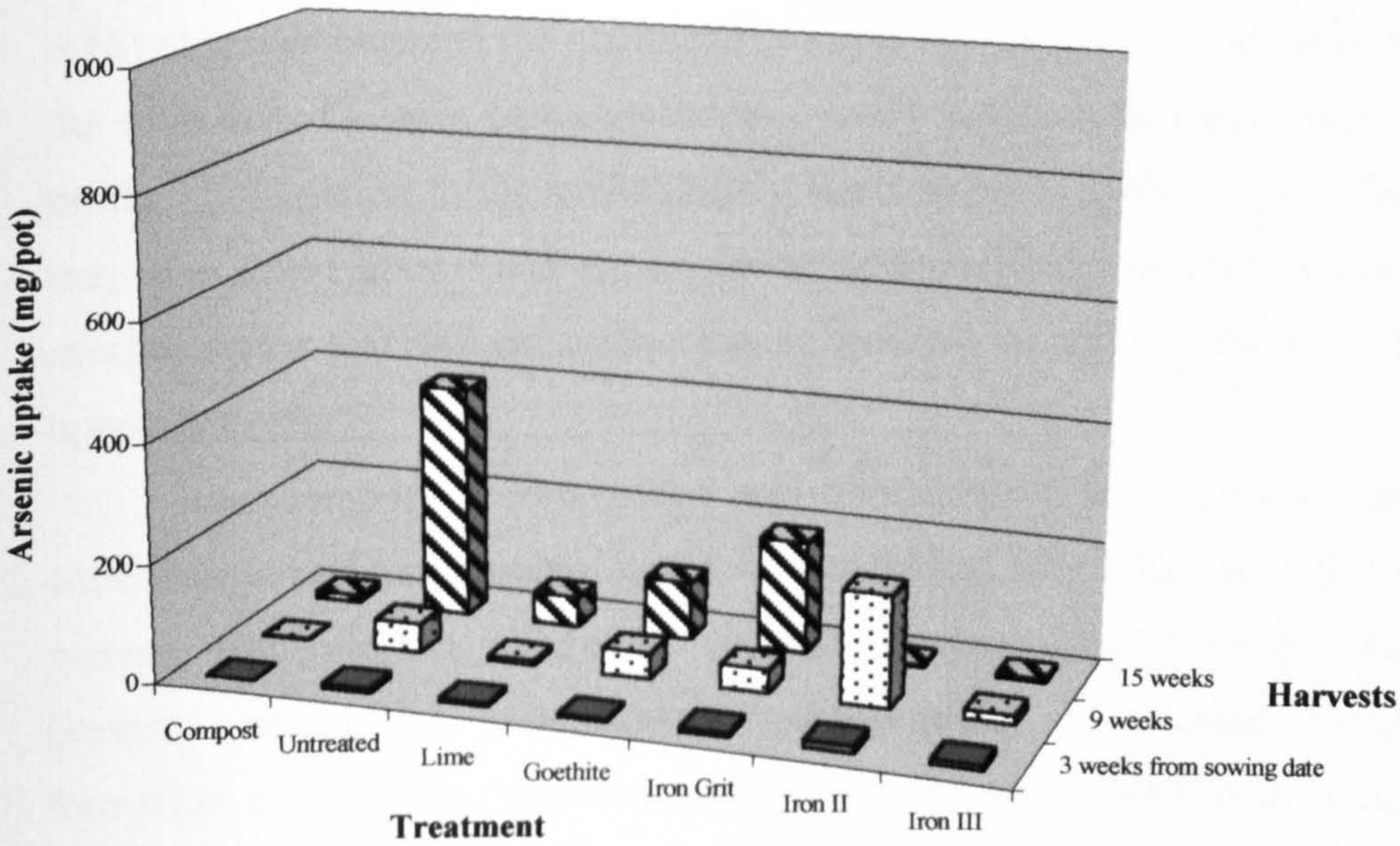
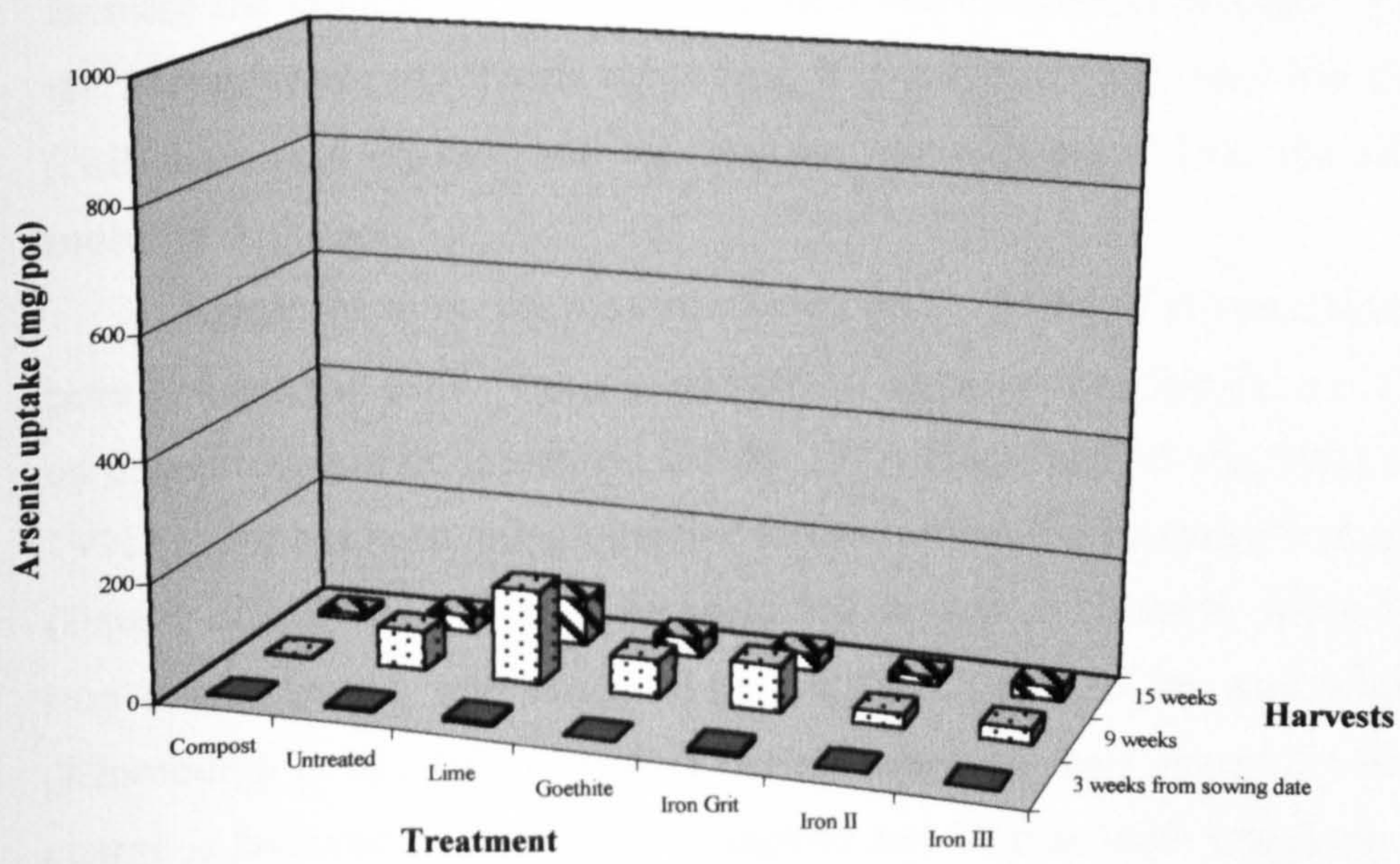


Figure 6.27. Changes in arsenic uptake in the shoots of rye grass grown in Merton Bank soil over one growing season



6.6. Discussion

The plant investigations demonstrated a successful reduction in uptake and accumulation of arsenic when grown in iron oxide-amended soils. Application of the additives to contaminated soils showed their ability to adsorb and immobilise the metalloid. There were however differences in shoot arsenic concentrations (Figures 6.10-6.15) observed between the plants and this may be attributed to the variation in soil types, the mobility of arsenic being greater in a sandy substrate than in a loamy soil, therefore producing variation in the availability of labile arsenic. Differences in the plant species may also affect uptake and accumulation of metal(loids) in shoot tissues. Soil pH is another factor that will determine arsenic mobility in soil and therefore availability for uptake into plants.

Incorporation of iron oxides into contaminated soil does not change the total concentration of toxic metals available, but instead alters their mobility within the soil system. However, this will depend on soil type, type of iron oxide and the metal species present. Arsenic has been shown to co-precipitate and become immobilised by the formation of insoluble, hydrated iron oxides, and so its behaviour in the soils will be related to their presence (Ferguson and Gavis, 1972; Masscheleyn *et al.*, 1991a).

Addition of lime to the contaminated substrates resulted in some cases to increase the accumulation of arsenic in plant shoots. Lime will increase the pH of the soil, and so increase the mobility of arsenic. This effect was apparent in perennial ryegrass grown in the Merton Bank and Rixton substrates. Kidsgrove soil may have had a buffering effect (N.B. high iron content) and this may be why addition of lime did not affect arsenic mobility in the soil.

Extensive work has been conducted on the effect of pH on arsenic adsorption in pure systems and soils. These investigations demonstrated that pH had a large influence on arsenic adsorption (Frost and Griffin, 1977; Pierce and Moore, 1980; Xu *et al.*, 1988, 1991) and it has been recognised that arsenic adsorption increases with a decrease in pH (Hsia *et al.*, 1992). Soil pH's are presented in chapters 2 and 5. It has been shown that iron oxides have a zero charge at pH ranging from 7 to 10, with a mean around 8.5 (Kinniburgh *et al.*, 1976). Higher pH favours a negative charge whilst a net positive charge is favoured by a low pH. Kidsgrove and Merton Bank soils both displayed pH's below 8.00, whilst that of Rixton soil was above 8.00, and so was more alkaline. This

may explain the higher concentrations of arsenic found in the shoots of spinach and tomato grown in the Rixton substrate and the increased uptake of arsenic in the ryegrass investigations when compared to the other soils. The additives may have been capable of adsorbing arsenic from the soil solution, due to their zero charge, but adsorption effectiveness may have declined due to the higher pH at Rixton.

A notable difference was the variation in arsenic accumulation in the shoots of spinach and tomato. Spinach accumulated higher levels of arsenic in its shoots than tomato. The tomato plant is reported as being tolerant to arsenic pollution (Wauchope, 1983), and it may be assumed that different plants possess mechanisms in their uptake of water and nutrients that either avoid toxic metals or accumulate them readily. When a plant absorbs toxic metals the most widespread mechanism in plant tolerance is to reduce the upward translocation of the metal to the shoots and therefore accumulation occurs within the roots (Meharg and Macnair, 1990).

In this study, analysis of plant roots was impractical because of the difficulty in obtaining clean root surfaces free of soil contamination. It may be hypothesised that tomato plants prevented upward translocation of arsenic by storing the metalloid in the root system. Burló and co-workers (1999) suggested that compartmentalisation of arsenic occurred in the roots of tomato plants and this mechanism was effective at reducing its toxic effects on growth and metabolism. It may be for this reason that tomato plants displayed lower levels of arsenic within their shoots when compared to spinach. Walsh and Keeney (1975) noted that arsenic uptake by plants was influenced, among other factors, by the plant species and this was demonstrated in this investigation by the greater uptake of arsenic in spinach compared to tomato plants.

Arsenic has not been shown to be an essential plant nutrient, although it is essential for animal metabolism (Lepp, 1981). The phytotoxic effects of arsenic are indicative of a sudden decrease in water mobility, as suggested by root plasmolysis and discoloration of leaves followed by leaf wilting and necrosis of leaf tips and margins (Machlis, 1941; Macnair and Cumbes, 1987; O'Neill, 1995). This occurs due to oxidative stress; it has been demonstrated that exposure of plants to inorganic arsenic results in the generation of reactive oxygen species (ROS) (Hartley-Whitaker *et al.*, 2001), brought about by the conversion of arsenate to arsenite which occurs readily in plants (Meharg and Hartley-Whitaker, 2002).

Addition of goethite to all contaminated soils exhibited the most beneficial effects, producing more vigorous plant growth in comparison to untreated controls. Increases in dry matter yields were observed for all plants grown in soil amended with this iron oxide, but most notably with spinach (Figures 6.1-6.3).

Plant growth may not only have been affected by arsenic toxicity, but also by removal of essential elements from the soil solution due to incorporation of the additives. Phosphorus (as phosphate) is an important component to a number of compounds in plant cells (Taiz and Zeiger, 1991). Phosphate and arsenate have been shown to share a general pathway by a common carrier into plant roots. Arsenate acts as a phosphate analogue, which is transported across the plasma membrane by phosphate co-transport systems (Ullrich-Eberius *et al.*, 1989). This phosphate/arsenate plasma carrier has a higher affinity for phosphate than arsenate (Meharg and Macnair, 1990). Phosphorus being chemically similar to arsenic will also compete with arsenic species for binding sites (Peters *et al.*, 1996), such as the surfaces of iron oxides.

It may be speculated that addition of iron oxides to the soils affected phosphate availability, adsorbing phosphate out of the soil solution and thereby preventing plant uptake of this essential macronutrient. Determination of phosphate in the soil compartment was not analysed in this investigation, but characteristic symptoms of phosphorus deficiency include stunted growth and dark greenish-purple colouration occurring in the leaves. The purple colouration is induced by the production of anthocyanins, which may be formed in excess when phosphate levels decline (Taiz and Zeiger, 1991).

Tomato plants demonstrated similar leaf colouration together with stunted growth. Iron oxide addition may promote nutrient deficiencies. It has been shown that arsenate sensitivity is strongly linked to phosphate nutrition and an increase in phosphate status will lead to a reduction in arsenate uptake, by suppression of the high-affinity phosphate/arsenate uptake system (Meharg and Macnair, 1991, 1992). Due to possible depletion of phosphate in the amended soils, arsenic uptake may have become enhanced in the plants, therefore magnifying its toxicity.

Incorporation of an additive may also introduce contamination to an already toxic soil. Iron grit (steel shots) has been shown to contain nickel (Ni) that may be released upon acidification of the soil (Mench *et al.*, in press). Contaminants present in an amendment may affect plant growth, even when the original contaminant has been

immobilised. Therefore contamination level in an amendment can be an important aspect (Mench *et al.*, in press).

Lead uptake in some instances was augmented in both spinach and tomato. This may be related to its solubility, which was observed to increase when iron II and III sulphate were incorporated into the soils. Lead concentrations were also found to be greater in the same treated soils which were identified in the leaching studies (Chapter 5) and this could be a possible limiting factor in the remediation of arsenic contaminated soil with these particular additives. Lead concentrations were observed to increase in some of the test plants, but in most cases the levels were not excessively greater than the untreated controls. In tomato, compartmentalisation of lead, like that of arsenic, may be a factor controlling this metal, although as discussed earlier root analysis was not possible. We can only speculate that lead may be stored in the root free space and so this may have prevented the metal from being translocated to the shoots.

Spinacia oleracea was observed to accumulate high concentrations of arsenic in the untreated controls whilst *Lycopersicon esculentum* had the ability to prevent upward transport of arsenic and so avoid accumulation in its shoots. Availability of the metalloid was however probably reduced in the soil solution due to attenuation by amendments. Their efficiency nevertheless depends on soil chemistry, especially pH, and for this reason field trials are necessary to demonstrate their long-term stability under natural environmental conditions. The biomass increase obtained from plants grown in goethite-amended soil was very encouraging and further research into this additives application would prove very interesting.

Despite the above, a possible detrimental effect of applying additives to contaminated soil in which crops for human consumption or grazing material for livestock are to be grown is that the shoots still contained concentrations of arsenic that would be transferred to higher levels of the food chain. Cultivation of plants in arsenic contaminated soil was improved by the incorporation of goethite, preventing stunted growth and necrosis associated with this toxic element (Plates 6.5, 6.6). Nevertheless, arsenic shoot concentrations were still present above safe levels.

For example, spinach yield (g/pot) was greater in goethite-amended Rixton soil than with any other treatment (Table 6.3) but total arsenic uptake was observed to be 12.21 mg/treatment (in 4 treated pots). Incorporation of goethite produced healthy plants compared to those cultivated in untreated soil (Plate 6.5). An important point to illustrate

is that addition of iron oxide treatments may produce plants that appear vigorous in comparison to those grown in untreated soil, but transfer of arsenic into the food chain via these amended plants was still possible. Spinach harvested from goethite-amended Rixton soil contained levels of arsenic, which would be transferred into the human food chain.

For remediation purposes the issue here would be, once treated, what is the final use of the land? For example, land to be used by livestock would require different control measures as opposed to an area that was not grazed. Ryegrass grown in goethite-amended Merton Bank soil produced the greatest total yield (Table 6.9.f.). Even so, over one growing season total uptake of arsenic was greater (146.7 mg/pot) than in grass grown with iron II (51.12 mg/pot) and III (72.31 mg/pot) amended soils. In relation to the final land use, incorporation of soil additives must be viewed with caution. Plants may appear healthy, producing high yields, but the shoots may still contain concentrations of toxic metal(loids) that would accumulate in the food chain over time.

Goethite was discovered to be most beneficial additive for healthy plant growth, but in the leaching studies (Chapter 5), iron III was observed to be the most effective amendment. Iron III did not produce high plant productivity as was expected and was detrimental in some cases to plant growth, producing lower yields than the untreated soils. Table 6.9.f however shows that application of iron III to Merton Bank soil reduced total arsenic uptake in ryegrass. Total yield (g/pot) was lower than the untreated control, but the concentration of arsenic in the shoots had been reduced by 69% and arsenic uptake had also been reduced (6.9.f.). With iron III, reduction in yield was observed to be only 13%, but uptake of arsenic had been reduced by 62%. This can be compared to goethite, were yield was increased by only 1% compared to the untreated plants, and arsenic uptake had only been reduced by 23% (Table 6.9.f).

A similar scenario was observed in iron III-amended Rixton soil (6.8.f) were total yield was reduced by 5.8%, but increased by 89% with goethite compared to the untreated plants. However, arsenic uptake had been reduced by 80% with goethite and 83% with iron III.

Application of iron III brought about a decrease in total yield but was beneficial in reducing the transfer of arsenic into the shoots. Goethite produced an increase in yield, but arsenic uptake was greater in comparison. In all cases however arsenic was present in the shoots regardless of soil treatment and this would indicate that it was available for transfer into the food chain. Field trials would present further data with regard to this

problem because plants grown in pots eventually become deprived of nutrients over time and this may have a bearing on the elements being absorbed by roots such as the case with arsenate and phosphate.

6.7. Conclusions

Results from the plant investigations demonstrated the efficiency of iron oxides in reduction of arsenic accumulation in a variety of test crops grown in contaminated soil. Rixton soil had a high pH and low organic matter content and development of plants in this medium was not ideal, due in part, to the low nutrient content, but also high pH that would have provided conditions favourable for arsenic mobilisation. This worse case scenario demonstrated the efficiency of Fe-bearing additives in attenuating arsenic and thereby reducing its uptake and accumulation in the shoots of the test plants under these poor soil conditions. The low nutrient status of these soils together with high concentrations of arsenic may have increased arsenic uptake even in the presence of the additives because of the phosphate/arsenate uptake system discussed earlier.

Although goethite and iron grit proved efficient in arsenic removal from the soil solution, it may be necessary to add compost to soils such as fly ash because of their low organic matter content. This would improve soil conditions for plant growth and added in combination with Fe-bearing additives may improve the soils markedly.

The investigations employed in this chapter confirmed the efficiency of iron oxides at an application rate of 1% w/w. At an increased application rate (e.g. 5% w/w) this may result in more efficient reductions in arsenic uptake thereby reducing its transfer into the food chain. However careful consideration must also be given to the complete soil chemistry, as metals behave differently, for example, arsenic and lead. At greater application rates the effects on lead solubility observed in this study and the preceding leaching investigations may be enhanced. This would be detrimental to plant growth, even if attenuation of arsenic from the soil solution were achieved. Another side effect of increasing the application rate may be the effect of reducing the availability of certain essential elements in the soil, which are vital to plant development, such as major nutrients like phosphate. This and other problems discussed above must be considered if Fe-bearing additives are to be employed as remediation tools.

The observations concluded from this study are the result of greenhouse investigations, and so it would be necessary to conduct field trials in order to determine the true efficiency of the iron oxides under natural conditions.

Table 6.1. Effect of additives on yield, mean metal concentration (n=3) and metal uptake in spinach plants grown in Kidsgrove soil.

		Concentration in Leaves					Plant Uptake				
Treatment	**Yield g/pot**	**As**	**Cu**	**Cd**	**Zn**	**Pb**	**As**	**Cu**	**Cd**	**Zn**	**Pb**
		mg/kg Dry Wt.					mg/treatment (4 pots)				
Compost	151.96	0.08 (±0.01)	7.76 (±1.02)	1.87 (±0.83)	29.71 (±1.96)	25.15 (±1.54)	0.52	51.06	12.31	195.51	165.50
Untreated Soil	5.88	0.4 (±0.79)	16.11 (±1.40)	85.35 (±3.55)	71.55 (±2.27)	85.51 (±1.29)	68.03	2739.79	14515.31	12168.37	14542.52
Lime	5.94	0.12 (±0.01)	15.71 (±1.65)	85.37 (±1.11)	41.85 (±2.81)	90.77 (±2.29)	20.20	2644.78	14372.05	7045.45	15281.14
Goethite	11.80	0.13 (±0.04)	13.30 (±1.21)	67.90 (±1.14)	62.48 (±1.14)	69.61 (±3.86)	11.02	1127.12	5754.24	5294.9	5899.15
Iron Grit	5.75	0.08 (±0.03)	15.64 (±1.28)	93.85 (±1.62)	84.71 (±0.91)	86.02 (±2.60)	13.91	2720	16321.74	14732.17	14960
Iron II	6.77	0.11 (±0.14)	18.73 (±1.05)	92.89 (±2.19)	66.27 (±1.59)	104.22 (±2.33)	16.25	2766.62	13720.83	9788.77	15394.38
Iron III	5.69	0.44 (±0.81)	16.14 (±2.12)	73.29 (±2.65)	68.85 (±1.43)	86.14 (±1.07)	77.33	2836.55	12880.49	12100.17	15138.84

Table 6.2. Effect of additives on yield, mean metal concentration (n=3) and metal uptake in tomato plants grown in Kidsgrove soil.

		Concentration in Leaves					Plant Uptake				
Treatment	**Yield g/pot**	**As**	**Cu**	**Cd**	**Zn**	**Pb**	**As**	**Cu**	**Cd**	**Zn**	**Pb**
		mg/kg Dry Wt.					mg/treatment (4 pots)				
Compost	630.17	0.01 (±0.23)	8.54 (±1.05)	2.03 (±1.92)	8.75 (±2.06)	31.02 (±1.23)	0.016	13.55	3.22	13.88	49.22
Untreated Soil	44.86	0.08 (±0.07)	13.95 (±0.96)	22.16 (±2.16)	31.37 (±2.25)	61.15 (±1.20)	1.78	310.96	493.98	699.28	1363.13
Lime	44.7	0.07 (±0.01)	13.65 (±2.80)	21.97 (±1.13)	26.20 (±2.54)	68.18 (±0.89)	1.60	305.37	491.49	451.90	1525.28
Goethite	53.73	0.06 (±0.03)	11.63 (±1.62)	15.23 (±1.75)	27.78 (±2.90)	48.15 (±1.44)	1.12	216.45	283.45	517.03	896.15
Iron Grit	57.6	0.04 (±0.01)	10.80 (±1.70)	16.43 (±1.26)	22.98 (±1.82)	46.42 (±3.05)	0.69	187.5	285.24	398.95	805.90
Iron II	42.96	0.05 (±0.08)	13.21 (±2.88)	23.42 (±2.74)	28.71 (±1.36)	66.74 (±2.59)	1.16	307.49	545.16	668.29	1553.53
Iron III	39.4	0.04 (±0.05)	15.79 (±3.42)	26.52 (±2.60)	34.10 (±1.05)	67.88 (±2.19)	1.02	400.76	673.09	865.48	1722.84

Table 6.3. Effect of additives on yield, mean metal concentration (n=3) and metal uptake in spinach plants grown in Rixton soil.

		Concentration in Leaves					Plant Uptake				
Treatment	**Yield g/pot**	**As**	**Cu**	**Cd**	**Zn**	**Pb**	**As**	**Cu**	**Cd**	**Zn**	**Pb**
		mg/kg Dry Wt.					mg/treatment (4 pots)				
Compost	313.6	0.14 (±0.15)	8.05 (±1.65)	1.35 (±0.49)	38.85 (±1.91)	27.57 (±2.89)	0.45	25.66	4.30	123.88	87.91
Untreated Soil	3.7	3.52 (±0.31)	18.99 (±1.45)	3.62 (±0.95)	85.87 (±2.46)	71.11 (±2.18)	951.35	5132.4	978.37	23208.1	19218.9
Lime	4.4	3.35 (±0.93)	18.24 (±2.20)	4.28 (±1.85)	57.86 (±1.80)	77.08 (±0.97)	905.41	4929.73	1156.76	15637.84	20832.43
Goethite	47.5	0.58 (±0.47)	12.88 (±2.57)	2.38 (±1.23)	35.00 (±3.85)	51.43 (±1.60)	12.21	271.16	50.11	736.84	1082.74
Iron Grit	4	2.81 (±2.08)	19.86 (±2.58)	3.44 (±1.80)	66.33 (±3.63)	71.16 (±1.50)	702.8	4965	860	16582.5	17790
Iron II	3.6	1.58 (±0.71)	18.01 (±2.17)	4.5 (±2.22)	73.61 (±2.41)	77.45 (±3.20)	438.88	5002.77	1250	20447.22	21513.88
Iron III	4.9	1.29 (±1.40)	19.53 (±2.08)	3.83 (±2.77)	93.96 (±1.30)	73.08 (±2.60)	263.26	3985.7	781.63	19175.51	14914.28

Table 6.4. Effect of additives on yield, mean metal concentration (n=3) and metal uptake in tomato plants grown in Rixton soil.

		Concentration in Leaves					Plant Uptake				
Treatment	**Yield g/pot**	**As**	**Cu**	**Cd**	**Zn**	**Pb**	**As**	**Cu**	**Cd**	**Zn**	**Pb**
		mg/kg Dry Wt.					mg/treatment (4 pots)				
Compost	533	0.12 (±0.05)	7.05 (±1.80)	2.03 (±2.08)	34.79 (±4.51)	42.31 (±1.95)	0.23	13.23	3.81	65.27	79.38
Untreated Soil	19.3	1.48 (±3.03)	11.54 (±1.91)	2.36 (±1.18)	15.32 (±1.64)	56.86 (±2.93)	76.68	597.93	122.28	793.78	2946.11
Lime	15.5	2.94 (±2.26)	14.84 (±2.46)	2.96 (±1.08)	20.85 (±1.30)	69.62 (±1.62)	189.67	957.41	190.97	1345.16	4491.61
Goethite	98.2	0.38 (±1.00)	16.34 (±1.50)	3.38 (±0.86)	21.79 (±1.22)	81.86 (±1.64)	3.87	166.39	34.42	221.89	833.60
Iron Grit	18.2	0.93 (±1.76)	11.63 (±2.25)	2.18 (±1.05)	20.72 (±2.36)	59.58 (±1.41)	51.09	639.01	119.78	1138.46	3273.63
Iron II	17.8	0.61 (±0.07)	13.25 (±2.13)	2.61 (±0.40)	25.35 (±2.66)	61.89 (±2.71)	34.27	744.38	146.63	1424.16	3476.96
Iron III	11.5	0.74 (±0.13)	15.01 (±3.94)	2.74 (±1.18)	25.23 (±1.38)	70.78 (±2.85)	64.35	1305.22	238.26	2193.91	6154.78

Table 6.5. Effect of additives on yield, mean metal concentration (n=3) and metal uptake in spinach plants grown in Merton Bank soil.

		Concentration in Leaves					Plant Uptake				
Treatment	**Yield g/pot**	**As**	**Cu**	**Cd**	**Zn**	**Pb**	**As**	**Cu**	**Cd**	**Zn**	**Pb**
		mg/kg Dry Wt.					mg/treatment (4 pots)				
Compost	283.85	0.5 (±0.01)	11.51 (±1.14)	2.13 (±1.25)	32.91 (±2.26)	42.69 (±1.28)	1.76	40.55	7.50	115.94	150.29
Untreated Soil	24.19	1.6 (±0.18)	18.82 (±2.19)	5.23 (±1.90)	48.86 (±1.56)	94.89 (±2.28)	66.14	778.01	216.21	2019.84	3922.69
Lime	24.22	2.5 (±1.01)	22.2 (±2.12)	6.72 (±1.24)	68.36 (±2.91)	114.35 (±1.62)	103.22	916.59	277.45	2822.46	4721.31
Goethite	45.71	0.91 (±0.86)	21.87 (±0.26)	6.33 (±0.12)	75.21 (±0.67)	75.85 (±1.65)	19.91	478.45	138.48	1645.37	1659.37
Iron Grit	31.09	1.131 (±1.14)	21.19 (±0.36)	6.87 (±2.83)	78.29 (±0.69)	107.77 (±1.33)	36.37	681.56	220.97	2518.17	3466.38
Iron II	23.88	1.9 (±0.78)	21.9 (±1.15)	6.04 (±1.03)	63.45 (±0.78)	98.11 (±0.99)	79.56	917.08	252.93	2657.04	4108.45
Iron III	27.02	1.03 (±0.84)	17.04 (±1.46)	5.20 (±1.25)	69.85 (±2.50)	88.14 (±1.98)	38.12	630.64	192.45	2585.12	3262.03

Table 6.6. Effect of additives on yield, mean metal concentration (n=3) and metal uptake in tomato plants grown in Merton Bank soil.

		Concentration in Leaves					Plant Uptake				
Treatment	**Yield g/pot**	**As**	**Cu**	**Cd**	**Zn**	**Pb**	**As**	**Cu**	**Cd**	**Zn**	**Pb**
		mg/kg Dry Wt.					mg/treatment (4 pots)				
Compost	729.89	0.13 (±0.17)	8.64 (±2.01)	2.19 (±1.05)	13.45 (±3.12)	47.18 (±2.53)	0.18	11.84	3.00	18.43	64.64
Untreated Soil	67.77	0.98 (±0.42)	15.15 (±1.19)	3.86 (±1.19)	23.04 (±3.48)	79.1 (±1.06)	14.46	223.55	56.95	339.97	1167.18
Lime	67.5	0.49 (±0.89)	17.67 (±2.30)	4.04 (±2.96)	21.32 (±2.35)	86.91 (±2.36)	7.26	261.77	59.85	315.85	1287.55
Goethite	82.32	0.21 (±0.23)	15.50 (±1.26)	3.41 (±0.94)	18.85 (±3.81)	76.11 (±2.47)	2.55	188.28	41.42	228.98	924.56
Iron Grit	95.22	0.35 (±0.45)	19.43 (±1.50)	3.71 (±1.96)	23.27 (±1.08)	88.15 (±1.11)	3.67	204.05	38.96	244.38	925.75
Iron II	68.13	0.09 (±0.04)	4.38 (±2.08)	0.56 (±0.26)	5.09 (±1.39)	21.34 (±1.22)	1.32	64.28	8.22	74.71	313.22
Iron III	69.55	0.21 (±0.15)	20.74 (±2.03)	4.05 (±1.09)	25.88 (±3.00)	86.66 (±2.25)	3.02	298.20	58.23	372.11	1246.01

Table 6.7.a. Effect of additives on yield, mean arsenic concentration (n=3) and arsenic uptake in rye grass shoots grown in Kidsgrove soil for the 1st harvest.

1st Harvest (3 weeks) Treatment	Yield (g/pot)	Concentration in shoots (mg/kg Dry wt.)	Plant uptake (mg/pot)
Compost	128.5	0.09 (±0.05)	0.77
Untreated	51.5	0.42 (±0.48)	8.10
Lime	50.7	0.30 (±0.21)	5.95
Goethite	67.5	0.26 (±0.06)	3.88
Iron grit	52.9	0.36 (±0.26)	6.92
Iron II	43.3	0.50 (±0.06)	11.73
Iron III	43.2	0.34 (±0.26)	7.85

Table 6.7.b. Effect of additives on yield, mean arsenic concentration (n=3) and arsenic uptake in rye grass shoots grown in Kidsgrove soil for the 2nd harvest.

2nd Harvest (6 weeks) Treatment	Yield (g/pot)	Concentration in shoots (mg/kg Dry wt.)	Plant uptake (mg/pot)
Compost	83.77	0.07 (±0.01)	0.84
Untreated	11.33	0.24 (±0.01)	21.80
Lime	14.83	0.14 (±0.06)	9.20
Goethite	18.74	0.20 (±0.06)	11.13
Iron grit	13.76	0.29 (±0.06)	21.44
Iron II	15.00	0.23 (±0.07)	15.96
Iron III	16.56	0.26 (±0.15)	16.22

Table 6.7.c. Effect of additives on yield, mean arsenic concentration (n=3) and arsenic uptake in rye grass shoots grown in Kidsgrove soil for the 3rd harvest.

3rd Harvest (9 weeks) Treatment	Yield (g/pot)	Concentration in shoots (mg/kg Dry wt.)	Plant uptake (mg/pot)
Compost	48.24	0.05 (±0.009)	1.22
Untreated	4.47	0.21 (±1.01)	47.52
Lime	9.29	0.06 (±0.04)	7.13
Goethite	10.89	0.47 (±0.56)	43.70
Iron grit	5.51	0.21 (±0.05)	39.68
Iron II	9.84	1.84 (±0.55)	187.01
Iron III	6.73	0.10 (±0.03)	15.29

Table 6.7.d. Effect of additives on yield, mean arsenic concentration (n=3) and arsenic uptake in rye grass shoots grown in Kidsgrove soil for the 4th harvest.

4th Harvest (12 weeks) Treatment	Yield (g/pot)	Concentration in shoots (mg/kg Dry wt.)	Plant uptake (mg/pot)
Compost	11.14	0.12 (±0.31)	11.48
Untreated	8.49	2.41 (±1.31)	284.43
Lime	20.59	5.08 (±1.15)	247.12
Goethite	11.6	1.99 (±0.53)	171.99
Iron grit	10.23	0.34 (±0.16)	34.04
Iron II	13.83	0.10 (±0.02)	7.68
Iron III	9.86	0.22 (±0.07)	23.00

Table 6.7.e. Effect of additives on yield, mean arsenic concentration (n=3) and arsenic uptake in rye grass shoots grown in Kidsgrove soil for the 5th harvest.

5th Harvest (15 weeks) Treatment	Yield (g/pot)	Concentration in shoots (mg/kg Dry wt.)	Plant uptake (mg/pot)
Compost	10.95	0.12 (±0.21)	11.37
Untreated	10.22	4.01 (±0.07)	392.85
Lime	28.08	1.40 (±0.25)	49.95
Goethite	10.93	1.06 (±0.90)	97.30
Iron grit	10.77	2.02 (±1.16)	188.26
Iron II	15.8	0.06 (±0.10)	3.82
Iron III	14.12	0.07 (±0.03)	5.02

Table 6.7.f. Total yield, arsenic concentration (n=3) and arsenic uptake in rye grass shoots grown in Kidsgrove soil over one growing season.

Totals Treatment	Yield (g/pot)	Concentration in shoots (mg/kg Dry wt.)	Plant uptake (mg/pot)
Compost	282.6	0.45	25.68
Untreated	86.01	7.29	754.7
Lime	123.5	6.98	319.4
Goethite	119.7	3.98	328
Iron grit	93.17	3.22	290.3
Iron II	97.77	2.73	226.2
Iron III	90.47	0.99	67.38

Table 6.8.a. Effect of additives on yield, mean arsenic concentration (n=3) and arsenic uptake in rye grass shoots grown in Rixton soil for the 1st harvest.

1st Harvest (3 weeks) Treatment	Yield (g/pot)	Concentration in shoots (mg/kg Dry wt.)	Plant uptake (mg/pot)
Compost	39.2	0.02 (±0.06)	0.75
Untreated	30.7	0.23 (±0.04)	7.54
Lime	31.2	0.61 (±0.42)	19.80
Goethite	50.2	1.06 (±1.06)	21.30
Iron grit	25.5	0.28 (±0.12)	11.12
Iron II	28.9	0.03 (±0.02)	1.11
Iron III	25.6	0.25 (±0.10)	9.77

Table 6.8.b. Effect of additives on yield, mean arsenic concentration (n=3) and arsenic uptake in rye grass shoots grown in Rixton soil for the 2nd harvest.

2nd Harvest (6 weeks) Treatment	Yield (g/pot)	Concentration in shoots (mg/kg Dry wt.)	Plant uptake (mg/pot)
Compost	43.6	0.04 (±0.01)	1.04
Untreated	11.0	0.57 (±0.04)	52.46
Lime	14.1	0.50 (±0.42)	36.08
Goethite	24.2	0.92 (±1.39)	38.24
Iron grit	12.8	0.72 (±0.51)	56.62
Iron II	15.2	0.32 (±0.19)	21.19
Iron III	10.8	0.32 (±0.23)	30.04

Table 6.8.c. Effect of additives on yield, mean arsenic concentration (n=3) and arsenic uptake in rye grass shoots grown in Rixton soil for the 3rd harvest.

3rd Harvest (9 weeks) Treatment	Yield (g/pot)	Concentration in shoots (mg/kg Dry wt.)	Plant uptake (mg/pot)
Compost	51.5	0.13 (±0.30)	2.71
Untreated	2.9	1.27 (±0.14)	438.21
Lime	4.1	0.65 (±0.22)	160.67
Goethite	10.7	0.46 (±0.11)	43.38
Iron grit	4.0	0.79 (±0.20)	198.20
Iron II	3.7	0.32 (±0.12)	87.77
Iron III	3.4	0.03 (±0.01)	11.51

Table 6.8.d. Effect of additives on yield, mean arsenic concentration (n=3) and arsenic uptake in rye grass shoots grown in Rixton soil for the 4th harvest.

4th Harvest (12 weeks) Treatment	Yield (g/pot)	Concentration in shoots (mg/kg Dry wt.)	Plant uptake (mg/pot)
Compost	10.35	0.03 (±0.14)	2.95
Untreated	4.25	1.09 (±0.73)	258.31
Lime	2.62	1.16 (±0.67)	443.51
Goethite	7.46	0.10 (±0.16)	13.86
Iron grit	4.64	0.82 (±0.07)	178.17
Iron II	5.95	0.12 (±0.07)	21.59
Iron III	4.43	0.11 (±0.24)	25.58

Table 6.8.e. Effect of additives on yield, mean arsenic concentration (n=3) and arsenic uptake in rye grass shoots grown in Rixton soil for the 5th harvest.

5th Harvest (15 weeks) Treatment	Yield (g/pot)	Concentration in shoots (mg/kg Dry wt.)	Plant uptake (mg/pot)
Compost	9.37	0.14 (±0.24)	15.62
Untreated	2.43	1.41 (±0.52)	581.65
Lime	2.12	2.03 (±0.83)	958.68
Goethite	4.61	0.71 (±0.84)	155.18
Iron grit	4.5	0.76 (±0.85)	169.01
Iron II	4.11	0.08 (±0.10)	20.64
Iron III	4.03	0.55 (±0.24)	138.70

Table 6.8.f. Total yield, mean arsenic concentration (n=3) and arsenic uptake in rye grass shoots grown in Rixton soil over one growing season.

Totals Treatment	Yield (g/pot)	Concentration in shoots (mg/kg Dry wt.)	Plant uptake (mg/pot)
Compost	154	0.36	23.07
Untreated	51.28	4.57	1331
Lime	54.14	4.95	1619
Goethite	97.17	3.25	272
Iron grit	51.44	3.37	613.1
Iron II	57.86	0.87	76.04
Iron III	48.26	1.26	215.6

Table 6.9.a. Effect of additives on yield, mean arsenic concentration (n=3) and arsenic uptake in rye grass shoots grown in Merton Bank soil for the 1st harvest.

1st Harvest (3 weeks) Treatment	Yield (g/pot)	Concentration in shoots (mg/kg Dry wt.)	Plant uptake (mg/pot)
Compost	67.59	0.08 (±0.04)	1.24
Untreated	60.89	0.21 (±0.06)	3.51
Lime	57.37	0.36 (±0.51)	6.31
Goethite	65.76	0.04 (±0.05)	0.61
Iron grit	63.11	0.34 (±0.45)	5.53
Iron II	55.82	0.07 (±0.36)	1.31
Iron III	60.13	0.01 (±0.02)	0.27

Table 6.9.b. Effect of additives on yield, mean arsenic concentration (n=3) and arsenic uptake in rye grass shoots grown in Merton Bank soil for the 2nd harvest.

2nd Harvest (6 weeks) Treatment	Yield (g/pot)	Concentration in shoots (mg/kg Dry wt.)	Plant uptake (mg/pot)
Compost	72.47	0.02 (±0.01)	0.32
Untreated	29.79	0.74 (±0.27)	25.14
Lime	23.56	0.82 (±0.27)	35.02
Goethite	39.31	0.13 (±0.15)	3.40
Iron grit	27.66	0.73 (±0.30)	26.59
Iron II	30.32	0.05 (±0.10)	1.84
Iron III	26.93	0.40 (±0.08)	14.99

Table 6.9.c. Effect of additives on yield, mean arsenic concentration (n=3) and arsenic uptake in rye grass shoots grown in Merton Bank soil for the 3rd harvest.

3rd Harvest (9 weeks) Treatment	Yield (g/pot)	Concentration in shoots (mg/kg Dry wt.)	Plant uptake (mg/pot)
Compost	30.54	0.04 (±0.01)	1.41
Untreated	14.72	0.97 (±0.31)	65.97
Lime	12.22	1.90 (±0.75)	155.92
Goethite	11.26	0.69 (±0.13)	61.64
Iron grit	12.27	0.93 (±1.01)	76.33
Iron II	12.88	0.27 (±0.15)	20.96
Iron III	11.42	0.26 (±0.20)	23.55

Table 6.9.d. Effect of additives on yield, mean arsenic concentration (n=3) and arsenic uptake in rye grass shoots grown in Merton Bank soil for the 4th harvest.

4th Harvest (12 weeks) Treatment	Yield (g/pot)	Concentration in shoots (mg/kg Dry wt.)	Plant uptake (mg/pot)
Compost	14.81	0.06 (±0.05)	4.14
Untreated	15.08	1.03 (±0.96)	68.44
Lime	13.06	1.24 (±0.53)	95.41
Goethite	14.65	0.72 (±0.93)	49.43
Iron grit	15.48	0.54 (±0.15)	35.10
Iron II	13.86	0.18 (±0.11)	13.49
Iron III	12.79	0.14 (±0.04)	11.21

Table 6.9.e. Effect of additives on yield, mean arsenic concentration (n=3) and arsenic uptake in rye grass shoots grown in Merton Bank soil for the 5th harvest.

5th Harvest (15 weeks) Treatment	Yield (g/pot)	Concentration in shoots (mg/kg Dry wt.)	Plant uptake (mg/pot)
Compost	7.64	0.06 (±0.05)	9.10
Untreated	21.63	0.57 (±0.57)	26.60
Lime	16.33	1.25 (±0.07)	77.05
Goethite	12.25	0.38 (±0.29)	31.59
Iron grit	19.73	0.56 (±0.56)	28.85
Iron II	16.83	0.22 (±0.04)	13.52
Iron III	12.16	0.27 (±0.24)	22.29

Table 6.9.f. Total yield, mean arsenic concentration (n=3) and arsenic uptake in rye grass shoots grown in Merton Bank soil over one growing season.

Totals Treatment	Yield (g/pot)	Concentration in shoots (mg/kg Dry wt.)	Plant uptake (mg/pot)
Compost	193.1	0.26	16.21
Untreated	142.1	3.52	189.7
Lime	122.5	5.57	369.7
Goethite	143.2	1.96	146.7
Iron grit	138.3	3.1	172.4
Iron II	129.7	0.79	51.12
Iron III	123.4	1.08	72.31

Table 6.10. ANOVA (one-way) with Dunnett's Test.

Treatment	**F**	**P**
As / Mert / spin	35.28	<0.001
As / Mert / Tom	24.87	<0.001
As / Rixt / Spin	75.68	<0.001
As / Rixt / Tom	16.19	<0.001
As / Kids / Spin	6.66	0.002
As / Kids / Tom	1.16	0.380
Cu / Rixt / Spin	12.68	<0.001
Cu / Rixt / Tom	5.01	0.006
Cu / Kids / Spin	17.45	<0.001
Cu / Kids / Tom	3.35	0.029
Cu / Mert / Spin	22.30	<0.001
Cu / Mert / Tom	31.94	<0.001
Cd / Rixt / Spin	1.19	0.368
Cd / Rixt / Tom	0.44	0.840
Cd / Kids / Spin	714.39	<0.001
Cd / Kids / Tom	48.88	<0.001
Cd / Mert / Spin	3.18	0.035
Cd / Mert / Tom	2.03	0.129
Zn / Rixt / Spin	214.56	<0.001
Zn / Rixt / Tom	18.68	<0.001
Zn / Kids / Spin	311.92	<0.001
Zn / Kids / Tom	47.07	<0.001
Zn / Mert / Spin	228.18	<0.001
Zn / Mert / Tom	20.06	<0.001
Pb / Rixt / Spin	196.59	<0.001
Pb / Rixt / Tom	92.89	<0.001
Pb / Kids / Spin	362.32	<0.001
Pb / Kids / Tom	158.15	<0.001
Pb / Mert / Spin	632.81	<0.001
Pb / Mert / Tom	384.20	<0.001

NB:
Mert = Merton Bank
Rixt = Rixton
Kids = Kidsgrove

Spin = spinach
Tom = tomato

Table 6.11. Balanced analysis of variance for rye grass grown in Rixton soil.

Source of variation	DF	SS	MS	F	P
Cut /As uptake	4	345098	86274	3.61	0.019
Treatment/ As uptake	6	474262	79044	3.31	0.016
Error	24	573145	23881		
Total	34	1392505			

Table 6.12 . Balanced analysis of variance for rye grass grown in Kidsgrove soil.

Source of variation	DF	SS	MS	F	P
Cut /As uptake	4	69574	17394	2.53	0.097
Treatment/ As uptake	6	68341	11390	1.66	0.175
Error	24	164832	6868		
Total	34	302747			

Table 6.13. Balanced analysis of variance for rye grass grown in Merton Bank soil.

Source of variation	DF	SS	MS	F	P
Cut /As uptake	4	12822.7	3205.7	7.71	<0.001
Treatment/ As uptake	6	16786.5	2797.8	6.73	<0.001
Error	24	9978.1	415.8		
Total	34	39587.4			

CHAPTER 7.

CONCLUSIONS AND SUGGESTIONS FOR FUTURE WORK.

The work in this thesis was undertaken to evaluate the effectiveness of iron oxide bearing additives on the attenuation of arsenic in a variety of contaminated soils, with a view to changing the speciation and in turn the bioavailability of the metalloid, therefore rendering it immobile in the soil. Addition of all iron oxides used in this work achieved immobilisation of arsenic to some extent when their effects on arsenic leaching and bioavailability were compared to unamended control soils. The fate of arsenic in soil after amendment was predicted using a number of investigations from simple *in vitro* tests to long-term leaching and plant growth studies.

Iron oxides were characterised by XRD, TGA, surface area and SEM. They were then tested for their potential adsorption capabilities at varying pH levels using *in vitro* batch tests. These demonstrated that the iron oxides were efficient at adsorbing arsenic at a relatively low pH, but alkaline conditions caused a decrease in their efficacy. To determine the forms by which arsenic was held in the soils, a sequential extraction procedure was used to study the association between the different fractions after addition of the amendments. The investigation demonstrated that after iron oxide addition, the percentage of exchangeable arsenic was reduced. Iron II and III were most efficient showing reductions of 94% and 75% respectively in arsenic extractability in the exchangeable fraction of Rixton soil for example. The study also determined that arsenic was mainly bound to the iron oxide fraction, so reducing arsenic in the exposure pathway i.e. the soil solution.

However, in order to determine their true effectiveness over a longer time scale, a variety of leaching tests were compared. These involved short leaching trials from 60 minutes to vigorous soil shaking for 48 hours and long-term tests that involved columns of soil, which were slowly percolated with water for approximately three weeks. The potential durability of the additives was then compared. Addition of all iron oxides resulted in marked reductions in the mobility of arsenic, with the most effective treatments being iron II and III sulphate plus lime. These produced over 80% reductions in leached arsenic from Rixton soil in the Dutch test compared to the untreated control. Iron oxides

were found to be stable in the soils during the column tests, reducing arsenic in the leachates. The Dutch and modified column tests simulated leaching over an extended period of time, which was more realistic in relation to natural soil conditions in comparison to the more conventional UKEA and ASTM methods. Overall additive effectiveness (i.e. reduction of arsenic in solution) can be represented as, iron III > iron II > goethite > iron grit with respect to the adsorption studies and leaching investigations.

Plant studies determined the effect of incorporating iron oxides to contaminated soil in order to reduce the bioavailability of arsenic to plants and to assess the affect of iron oxides themselves on plant growth. These identified that goethite was the most beneficial additive in relation to plant growth (biomass), whilst also reducing arsenic uptake. The statutory limit for arsenic concentration in fruits, crops and vegetables is 1mg kg^{-1} on a fresh weight (fw) basis (Mitchell and Barr, 1995), whilst the accepted health limits for human consumption is also 1mg kg^{-1} arsenic (National Food Authority, 1993).

Levels of arsenic in spinach and tomato plants grown in Rixton soil amended with goethite were 0.58 mg kg^{-1} (dw) and 0.38 mg kg^{-1} (dw) respectively, compared to the untreated controls of 3.52 mg kg^{-1} (dw) and 1.48 mg kg^{-1} (dw) respectively. Levels of phytotoxic metals / metalloids in crops is of concern and addition of iron oxides was shown here in most cases to reduce arsenic concentrations within the plant tissues when compared to the untreated control plants. Microcosm studies using perennial ryegrass showed the stability of the additives during one growing season, where regular harvests were collected to monitor bioavailability with time. The results demonstrated that addition of goethite increased plant biomass when compared to unamended controls, but arsenic concentrations in the shoots of goethite treated plants were still higher than iron II and III sulphate treatments. Reasons for these differences will be discussed below, but these studies demonstrated the durability of the additives over one growing season.

Goethite ($\alpha FeOOH$) was prepared in the laboratory prior to incorporation in the soils, whereas iron grit, iron II and III sulphates only formed iron oxides once mixed with the soils and in contact with water. When iron grit was added to soil, it would have oxidized readily to form various iron oxides. Similarly, iron II and III reacted with the application of lime, added with these compounds, to form iron oxides *in situ*. The differences in arsenic binding observed in this work, between iron sulphate compounds and goethite, may be due to the formation of iron oxides *in situ* by the iron sulphates whereas goethite was already pre-formed when applied to the soils.

Surface area studies indicated that goethite possessed a higher surface area than iron II and III sulphates, but goethite was observed to be less effective at immobilising arsenic in the leaching tests. Other soil factors may have affected the ability of goethite to adsorb arsenic, especially pH. The surfaces of oxides change from being positively charged at low pH to negatively charged at high pH (Parfait, 1980) and have a point at which this change occurs, i.e. they have a net zero charge (pzc) (Bowell, 1994). The pzc for goethite is 7.6-8.1 (Parks and DeBruyn, 1962) and the leachate pH levels observed from the soils were mostly between 7-8.

It may be hypothesised that the point of zero charge for iron II and III sulphates were higher than that of goethite, so they were more effective adsorbing agents at the pH levels encountered in the test soils. Adsorption isotherms presented in chapter 3 indicated that in the case of iron III, adsorption of arsenic was occurring even at pH 9. This would indicate that at the higher pH observed in Rixton soil, for example, iron III would be more effective at attenuating arsenic than goethite. The factors affecting arsenic binding in this study could be attributed to firstly, *in situ* formation of iron oxides, which may have resulted in a higher surface coverage in the soil as the compound rusted to form the iron oxides, therefore dispersing and coating other soil particles which then created a larger surface area as opposed to addition of pre-formed iron oxides such as goethite. Secondly, the pzc of the mineral surfaces may have affected arsenic sorption, depending on soil pH.

Iron grit corrodes rapidly in the presence of water to form numerous iron oxides. Although this compound formed iron oxides *in situ*, its effectiveness was poor in comparison to iron II and III. Surface area studies demonstrated that this additive produced a low surface area when oxidised (Chapter 3). It may have been for this reason that iron grit demonstrated the smallest reductions in arsenic retention during the leaching tests, as all available sites had become saturated and further anion adsorption was prevented. Mench and co-workers (1998) identified that particle size was a significant factor in reducing Cd and Zn availability in the Louis Fargues soil. Steel shot with a larger particle size was shown to be less effective in reducing the heavy metals in ryegrass shoots compared to finer steel shots, even though both materials had the same chemical composition. The grit particle size (Chapter 2, section 2.9) used in the previous investigations may be responsible for the poorer reductions in arsenic retention when compared to the other additives. With iron grit application, sorption sites, particle size and addition rates may all be limiting factors. In these investigations all additives were

applied at a rate of 1% w/w to the soils. It may be necessary to increase the application rate of the grit whilst reducing the particle size, in order that adsorption rates may be enhanced.

A possible side effect of this however may be the toxicity of the material itself. It has been reported that steel shots (iron grit) contain Ni (Mench *et al.*, in press) and this may become a potential toxic element in the soil if application rates were increased, especially if the final outcome of the remediation process was to revegetate the area of contamination. However, the content of nickel in iron grit used in this report was found to be < 1.0 μg/g, when analysed by XRF and could not have affected plant growth. Varying sources of additives such as iron grit may be an important consideration, in that not every batch may be identical. An increase in application of a potential additive may also affect soil texture, which in turn may affect plant growth. The mixing of steel shots must also be adequate, as the formation of iron oxide nuggets must be avoided (Mench *et al.*, in press). Dispersion of the iron grit due to mixing would result in more efficient scavenging of anions and so help reduce arsenic in the soil solution. These factors may all have contributed to reduce the arsenic immobilising effects of iron grit encountered in the previous studies.

Mench and co-workers (in press) outlined the necessary requirements of *in situ* amendments. These should be inexpensive, readily available, easy to apply and safe to handle, soil structure and fertility should not be affected, they should be compatible to plants for the purpose of revegetation, be suitable for a range of contaminants and finally be in compliance with statutory regulations.

The application of an amendment to soil in order to immobilise a toxic element may inadvertently affect the solubility of other elements that previous to this treatment, were immobile and so affect the speciation of the contaminant in the soil. In the previous studies it was observed that addition of iron II or III sulphates (plus lime) to soil resulted in an increased concentration of lead in the leachates. Fixation of arsenic by application of these additives was very effective, but an unfortunate side effect of their use was the increase in lead solubility.

Lead arsenate ($PbHAsO_4$) was a very common insecticide used in deciduous fruit tree orchards before the introduction of DDT (dichlorodiphenyltrichloroethane) in 1947 (Peryea, 1991). With frequent application of the compound, soils became increasingly contaminated with both arsenic and lead. Lead was found to be relatively immobile in

orchard soils and non-phytotoxic, whereas the arsenic was both mobile and phytotoxic (Benson, 1976). The increase in lead mobilisation would be a factor in the remediation of such soils with iron II or III sulphate.

Levels of nitric acid-extractable lead observed in our soils were relatively low. The normal range of lead in soils is 2-300 $\mu g\ g^{-1}$, whilst the critical range is 100- 400 $\mu g\ g^{-1}$ (Alloway, 1995). Soils highly contaminated with lead arsenate would therefore present a more serious problem if the solubility of lead increased in the soil solution as a result of amendment addition. The increase in lead solubility may produce a negative effect on the revegetation of the area or increase lead leaching to groundwater, and these are not desired outcomes of remediating contaminated land.

The above limitation serves to illustrate that before the remediation of a contaminated site, a comprehensive survey of the soil must be undertaken to outline all the contaminants present and the additive effects must be studied on all other toxic elements present, not just the primary contaminant(s). A detailed knowledge of site history and collection of site records must be undertaken to establish all possible toxic wastes that may have been disposed of on the land. Historic sources of contamination must also be considered and are often thought to be the most important concern (Kibblewhite, 2001). Addition of any *in situ* treatment must be viewed with caution due to possible changes in the speciation of other elements present, which may be altered after application of the additive has been initiated.

Although certain elements may become more available in the soil solution as a result of additive incorporation, other essential elements may be immobilised. If a plant has a nutrient deficiency symptom, this is due to metabolic disorders resulting from an insufficient supply of an essential element (Taiz and Zeiger, 1991). Phosphate is a component of sugar phosphates, nucleic acids, coenzymes etc, and has a key role in reactions in which ATP is involved (Taiz and Zeiger, 1991). As described in Chapter 6, tomato plants developed a dark greenish-purple colouration to their leaves. The plants also produced slender stems, with older leaves developing necrosis. These symptoms are related to phosphate deficiency in the soil and the competitive relationship between phosphate and arsenate is well documented (Peryea and Kammereck, 1997; Meharg and Macnair, 1991, 1992).

Phosphate and arsenate exhibit similar physicochemical behaviour in soils and directly compete for specific adsorption sites on soil particles (Hingston *et al.*, 1971;

Woolson, 1983a). There is considerable evidence that phosphate is adsorbed on the surface of free iron oxides in acid soils (Nye and Tinker, 1977) and indeed, phosphate adsorption by synthetic Fe-oxides has been used as a model system to study specific adsorption of anions (Elkhatib *et al.*, 1984a). It has also been shown by methods such as infrared spectroscopy, whereby phosphate forms a bridging binuclear complex on goethite surfaces (Atkinson *et al.*, 1974; Russell *et al.*, 1974).

It may be speculated that addition of iron oxides II and III resulted in the immobilisation of phosphate resulting in the deficiency symptoms observed. Although not determined in the investigations, immobilisation of phosphate may have been the result of the reduced biomass observed in tomato plants. Reductions in tomato plant biomass were observed in iron II and III –amended Kidsgrove and Rixton soils, producing lower biomass production compared to untreated plants. Although the phytotoxic effects of arsenic were probably the main reason for poor plant growth, essential elements in the soil compartment may also have been adsorbed and rendered unavailable to the plants.

Throughout the plant studies, goethite remained the most effective of all the iron oxide additives in relation to plant health and biomass production. In contrast to this, it was not as efficient in the leaching tests. The *in vitro* tests established that pre-formed goethite, was not as effective, but *in vivo* investigations demonstrated that because of the detrimental effects of the other additives formed *in situ*, goethite was much more efficient because it did not mobilise lead and probably did not affect soil texture as the other additives had.

By forming iron oxides *in situ* the resultant dispersal of iron II or III sulphate and lime in the soil may have affected soil texture and therefore produced unfavourable conditions for plant root growth. This factor together with the high surface area coverage in soil and possible phosphate binding may have resulted in the low biomass production when these compounds were incorporated in the soils.

Goethite on the other hand was already pre-formed and may not have affected soil texture in the same way. Iron grit however formed oxides *in situ*, but the detrimental effects observed with iron II and III were not observed with this material. The grit corrodes *in situ* but the effect on soil texture may not be the same. Indeed, during the batch sorption investigations it was observed that iron II and III formed a slurry which in soil may have hardened, covering soil particles, whereas iron grit formed oxides of iron

around the grit particles themselves. These differences may have attributed to changes in the soil and affected the normal functioning of root systems.

The first two priorities that Mench and co-workers (in press) outlined as important requirements of amendments were that the material should be inexpensive and readily available. Although goethite proved effective, its production in the laboratory was time consuming and for these investigations using simple batch adsorption tests, column leaching studies and plant trials, numerous batches had to be continually prepared and then characterised to establish authenticity.

For the reclamation of a large industrial site or mine spoil, the quantity of goethite required would be huge and the cost of production would probably outweigh its effects as a beneficial amendment. For these reasons goethite application on a large scale would be unrealistic. Application of iron grit or iron II/III sulphate (and lime) would be cost effective, but if the establishment of a plant community was the final outcome iron II and III sulphate would be possibly detrimental as discussed previously. However, only a field trial would determine this and it may be that the plant species used here required high levels of essential nutrients to promote growth whereas other species may be more tolerant to poor soil conditions.

In the majority of studies such as this, it is recommended that for future work increased application rates of the additive(s) is/are investigated. However, in this case the potential arsenic binding capacity of iron II and III sulphate were so great (as observed in the leaching tests) that a reduction in the application rate to 0.5% may still produce the strong arsenic binding effect, but with a reduction in application rate detrimental effects on plant growth may be reduced. Addition of iron grit to the soils could be increased to 2%, as the surface area investigation showed that this additive had the lowest surface area of all the iron oxide treatments. This approach however has already been applied to soils with ryegrass, where it was discovered that shoot phosphorous levels were reduced and dry matter production was found to decrease by up to 20% compared to the untreated soil (Mench *et al.*, 1998).

The sites studied all showed differences in soil composition and structure. An important point to discuss here is that Kidsgrove soil contained highly elevated levels of iron (approx. 18%) (Chapter 4, Table 4.2). The concentrations of arsenic observed during the leaching tests (Chapter 5) indicated that Kidsgrove soil did not leach high levels of the contaminant when compared to the other substrates. The presence of high levels of iron

already present in the soil may have naturally remediated the site and so maintained the low levels of arsenic observed in previous studies.

The site was also highly contaminated with cadmium and XRF analysis indicated concentrations around 1434 μg g^{-1}. The toxicity of this heavy metal may not have affected plant growth because of the high iron levels already present. Although our investigations studied the bioavailability of both arsenic and heavy metals on a variety of plants, it is important to note here that the site was already vegetated with trees and an understory of grass, bramble, etc. High levels of iron may be an important factor at this location by allowing the development of ground cover plants and the survival of tree species in soil that contains high levels of cadmium and arsenic.

A similar situation existed at both Rixton clay pits and Merton Bank where trees and a variety of ground cover plants had colonised the sites. This is important because at first glance the level of arsenic contamination at these sites would be cause for concern. However with the natural vegetation already present binding the soil due to the establishment of roots, the soil is protected from lateral wind erosion and leaching to groundwater due to the vegetation cover. At these sites, although our studies have demonstrated that immobilisation of arsenic can be achieved by addition of iron oxides, it must be remembered that they are already in a stabilised condition because of the natural vegetation cover.

Future Work.

The application of inorganic additives to contaminated land has demonstrated the efficiency of iron oxides at immobilising arsenic and removing it from the exposure pathway (the soil solution). However, the long-term stability of the treatments are in question. Field trials would be required to assess the efficiency of the additives in the environment, because here they will be exposed to weathering over time, which in glasshouse pot experiments could not be predicted. Monitoring of trial sites over time would establish the success of the amendments and determine how persistent they were in relation to attenuating arsenic and reducing its bioavailability. The effect of pH is important with regard to the long-term efficiency of adsorption by iron oxides. Environmental changes may increase the pH of a soil causing arsenic binding to be

reduced. Only with long-term field trials can such information regarding additive stability be ascertained.

A variety of soil types including clays, loam and sand and different contamination sources should be investigated to determine the efficiency of iron oxides in the field. We studied three contaminated soils that already had established plant communities growing on them. Sites such as mine tailings with an end point to establishing a vegetation cover would be a suitable field study for these additives. Soil type is an important consideration, as arsenic has been deemed more mobile in sandy environments, whilst in loam soils higher levels of organic matter may affect the immobilisation of the metalloid.

The work demonstrated that certain iron oxide-bearing additives produced a mobilising effect on lead therefore altering its speciation in the soil. Future work may focus on identifying other ameliorants that, when applied in conjunction with iron II or III sulphates would bind any mobile lead and counteract this potentially detrimental effect. Application of apatite may reduce the bioavailability of lead (Ruby *et al.*, 1994) and when combined with iron II/III (plus lime) may adsorb both lead and arsenic. Lime was applied with iron II/III, but did not adversely affect arsenic mobility. However Boisson *et al.*, (1999) discovered that application of hydroxyapatite increased the uptake of arsenic in bean and maize plants especially in the roots and may be related to PO_4^{2-} concentrations in the soil.

The presence of phosphate may influence arsenic mobility and adsorption rates on iron oxide surfaces because of the associated competitive effect. However, O'Reilly and co-workers (2001) demonstrated that desorption of arsenate from goethite by PO_4^{2-} was significantly unaffected, even though the phosphate solution was three times stronger than that of arsenate. The arsenate ion is larger than phosphate and therefore interacts more strongly with the surface OH groups (O'Reilly *et al.*, 2001). For this reason desorption of arsenate may not be affected by addition of apatite and remediation of both lead and arsenic may be achievable.

The application of phosphate may also be of importance where plants are to be established in arsenic contaminated soil, because increases in phosphate application lead to reduced arsenate uptake, due to suppression of the high-affinity phosphate/arsenate uptake system (Meharg and Macnair, 1991, 1992). Investigations could focus initially on incorporation of Fe-bearing additives to the soils, followed by application of apatite or applying varying concentrations of phosphate at intervals over the growing season. By

applying phosphate at regular intervals this would potentially maintain the suppression of the phosphate/arsenate uptake system. It was demonstrated in the plant trials, that even with iron oxide incorporation, arsenic concentrations were still present in the shoots and so phosphate application may reduce these levels even further.

The use of isotopes to examine the lability of metals in contaminated soils may be investigated. The technique would be used to understand the mechanisms controlling metal availability in a soil amended with iron oxides. A radioactive arsenic spike added to a sample of remediated soil, would rapidly exchange with any surface bound arsenic in the sample and the concentration of the element may be calculated. The only stable and naturally occurring isotope of arsenic is ^{75}As (www.webelements.com). However it has a number of radioisotopes (radioactive isotopes), ^{73}As having the longest half-life of 80.3 days, decaying as β emissions (www.webelements.com). This method, applied across a pH gradient, would help determine the effect of bioavailability of the metalloid in relation to its attenuation by the iron oxide. Since the mobility of arsenic is affected by pH, if the remediated soil was to become alkaline over time, this in turn would affect its mobilisation. Identifying how strongly sorbed arsenic had become with the additive may help to determine its long-term efficiency.

Recently a number of arsenic accumulating plants have been identified, including ferns such as the Silver fern (*Pityrogramma calomelanos*) (Francesconi *et al.*, 2002), and the Chinese Brake fern (*Pteris vittata* L.) (Fitz *et al.*, in press). Both ferns demonstrated that they can hyperaccumulate arsenic from the soil in which they grow. These species are mainly tropical and subtropical in distribution and so their efficacy in temperate regions is unknown. By using *in situ* remediation at a site contaminated with arsenic together with phytoremediation using native fern species an attempt may be made to combine the two processes in order to remediate the contaminated site. Although iron oxides immobilised arsenic in the soils in this investigation, they did not totally prevent leaching of the metalloid or uptake into plant shoots.

By combining the two techniques, a contaminated site may be "cleaned up" by firstly preventing mobilisation of the metalloid and secondly by removal of fronds that had accumulated arsenic within them. The technique known as phytoextraction, acts to remove the contaminant source. Attempts to find native species that accumulated arsenic would be the first step to such an investigation. As the plant species would have to be tolerant of the contamination the understory plant population at Rixton clay pits, which

consisted of ferns, would be an ideal starting location. Tolerance of the plant species to arsenic could be used to achieve restoration of other sites that are devoid of vegetation. Plants would accomplish this by reducing wind and rain erosion, so stabilising the site, limit the exposure of soil to excess leaching to ground water and also reduce exposure of the area to humans.

There is a requirement for more studies in the field focusing on the long-term effects of amendments in relation to their stability in the environment. This work has provided an insight into the effects of iron oxides on arsenic leaching and bioavailability rates and the methods, in particular the column studies, have shown the effectiveness of these additives over an extended time period. However, monitoring their effects in the environment is of more importance and with the current increase in demand for land and housing these studies will hopefully provide an insight for future development of *in situ* immobilisation techniques.

Arsenic chemistry in soils is complicated, especially when attenuation is required. Due to its mobility in alkaline conditions, the frequently used methods to attenuate heavy metals, for example liming or zeolite application, are ineffective treatments and serve only to increase the problem because of the induced pH increase. Addition of organic matter, as in compost application, has also given rise to increased levels of arsenic in leachates (Mench *et al.*, in press) and so the prospect of applying organic matter to contaminated soils which are often poor in quality is a problem if plant communities are to be established.

The organic residues provide essential nutrients, which maybe absent under these poor soil conditions. The application of fertilizers represents another problem because results are often conflicting. Phosphate has been shown to enhance arsenic mobility (Peryea and Kammereck, 1997) and this can increase the uptake of arsenic by certain plant species because it can substitute for phosphate and the plant assumes a P deficiency (Gulz and Gupta, 2001). However, Meharg and Macnair (1991, 1992) demonstrated that an increase in the phosphate status helped to reduce arsenic uptake. Therefore in the remediation of land contaminated with arsenic these and other factors must be considered if attenuation is to be successful in relation to the establishment of a plant community.

In conclusion, this study has provided an insight into the numerous effects that can be induced by applying inorganic additives to contaminated soil. An important consideration drawn from this report was that before any additive can be used as a

remediation tool, it must be demonstrated that the compound does not affect any other contaminants within the soil matrix. The *in vitro* tests indicated that certain iron oxides were more effective at immobilising arsenic from solution, however, when these were used *in vivo* their detrimental effects (mobilisation of lead) outweighed their beneficial properties. The effect of additives on soil texture and macronutrient availability may also be cause for concern, were revegetation is the desired outcome. Each contaminated site will provide diverse soil properties, therefore reflecting different problems in relation to remediation. Finally, an insight into the long-term efficiency of iron oxides has been established with column leaching tests and ryegrass microcosm studies, but field data would present a more complete picture.

REFERENCES

Adriano, D.C. 1986. Arsenic. *Trace elements in the terrestrial environment*. New York: Springer-Verlag. Pp. 46-72.

Akins, M.B., and Lewis, R.J. 1976. Chemical distribution and gaseous evolution of arsenic-74 added to soils as DSMA-74 Arsenic. *Soil Sci Am J.* 40: 655-658.

Allen, S.E. 1974. *Chemical Analysis of Ecological Materials*. London, Blackwell. pp. 565.

Allen, S.E. 1989. *Chemical Analysis of Ecological Materials.* Oxford, Blackwell Scientific Publishers. pp. 368.

Alloway, B.J. 1995. *Heavy Metals in Soils*. 2nd Edition. London, Blackie Academic and Professional. pp 368.

Anastasia, F.B. and Kender, W.J. 1973. The influence of soil arsenic on the growth of lowberry bush. *J. Environ. Qual.* 2: 335-337.

Anderson, M.A., Ferguson, J.F., and Gavis, J. 1976. Arsenate adsorption on amorphous aluminium hydroxide. *J. Colloid Interface Sci.* 54: 391-399.

Anderson, M.A., and Malotky, D.T. 1979. The adsorption of protolizable anions on hydrous oxides at the isoelectric pH. *J. Colloid Interface Sci.* 72: 413-427.

Artiola, J.F., Zabcik, D. and Johnson, S.H. 1990. In situ treatment of arsenic contaminated soil from a hazardous industrial site: Laboratory studies. *Waste Manag.* 10: 73-78.

Aten C.F., Bourke J.B., Martine J.H and Walton J.C. 1980. Arsenic and lead in an orchard environment. *Bull. Environ. Contam. Toxicol.* 24: 108-115.

Atkinson, R.J., Posner, A.M., and Quirk, J.P. 1967. Adsorption of potential-determining ions at the ferric oxide-electrolyte interface. *The Journal of Physical Chemistry.* 71: 550-558.

Atkinson, R.J., Parfitt, R.L. and Swart, R. St. C. 1974. Infrared study of phosphate adsorption on goethite. *J. Chem. Soc. Faraday Trans.* 70: 1472-1479.

Benko, V., and Simon, K. 1977. Health aspects of burning coal with a high arsenic content, arsenic in hair, urine and blood of children residing in a polluted area. *Environ Res.* 13: 378-385.

Benson, A.A., Cooney, R. V., and Herrera-Lasso, J. M. 1981. Arsenic metabolism in algae and higher plants. *J. Plant Nutrition.* 3: 285-292.

Benson, N.R. 1976. Retardation of apple tree growth by soil arsenic residues. *J.Am. Soc. Hortic. Sci.* 101: 251-253.

Beretka, J., and Nelson, P. 1994. The current state of utilisation of fly ash in Australia. In: Ash – A Valuable Resource. *South African Coal Ash Association.* 1: 51-63.

Bhumbla, D.K. and Keefer, R.F. 1994. Arsenic mobilization and bioavailability in soils. In: *Arsenic in the Environment. Part I. Cycling and Characterization*, Ed. J. O. Nriagu. John Wiley and Sons, New York, NY. Pp. 51-82.

Boisson, J., Ruttens, A., Mench, M. and Vangronsveld, J. 1999. Evaluation of hydroxyapatite as a metal immobilising soil additive for the remediation of polluted soils. Part 1. Influence of hydroxyapatite on metal exchangeability in soil, plant growth and plant metal accumulation. *Environ. Pollut.* 104: 225-233.

Bowell, R.J. 1994. Sorption of arsenic by iron oxides and oxyhydroxides in soils. *Applied Geochemistry.* 9: 279-286.

Boyle, R.W. and Jonasson, I.R. 1973. The geochemistry of arsenic and its use as an indicator element in geochemical prospecting. *J. Geochem. Explo.* 2: 251-296.

Brooks, R.R. and Malaisse, F. 1985. *The Heavy Metal-Tolerant Flora of South Central Africa.* Balkema, Rotterdam, NL.

Brummer, G.W. 1986. In: *The Importance of Chemical Speciation in Environmental Processes.* Springer-Verlag, Berlin. Pp. 169-192.

Burló, F., Guijarro, A. A., Carbonell-Barrachina, D., Valero, D. and Martinez-Sanchez, F. 1999. Arsenic species: Effects on and accumulation by tomato plants. *J. Agric. Food Chem.* 47: 1247-1253.

Carbonell-Barrachina, A. 1992. Absorción y distribución de arsénico en *Lycopersicon esculentum* Mill. Efectos nutricionales y morfológicos. *Tesis de Licenciatura,* Universidad de Alicante, Alicante, Spain. pp 150.

Carbonell-Barrachina, A. 1995. Estudio de la dinámica en el suelo y del comportamiento agroquimico del metaarsenito como fungicida. *Tesis Doctoral,* Universidad de Alicante, Alicante, Spain. pp 185.

Carbonell-Barrachina, A. A., Burló, F., Burgos-Hernández, A., López, E., and Mataix, J. 1997. The influence of arsenite concentration on arsenic accumulation in tomato and bean plants. *Scientia Horticulturae*. 71: 167-176.

Carbonella-Barrachina, A.A., Jugsujinda, A., Burlo, F., Delaune, R.D. and Patrick, JR, W.H. 1999. Arsenic chemistry in municipal sewage sludge as affected by redox potential and pH. *Water Res.* 34: 216-224.

Charlet, L. and Manceau, A. 1993. Structure, formation and reactivity of hydrous oxide particles: insights from X-ray adsorption spectroscopy. In: *Environmental Particles. Environmental Analytical and Physical Chemistry.* Eds. J. Buffle, and H.P. van Leeuwen. Boca Raton: Lewis Publishers. Pp. 117-164.

Chilvers, D.C., and Peterson, P.J. 1987. Global cycling of arsenic. In: *Lead, Mercury, Cadmium and Arsenic in the Environment*. Eds. T.C. Hutchinson and K.M. Meema. John Wiley and Sons, New York, NY. Pp. 279-301.

Clijsters H., Cuypers A. and Vangronsveld J. 1999. Physiological responses to heavy metals in higher plants; Defence against oxidative stress. *Z. Naturforsch.* 54c: 730-734.

Colbourn, P., Alloway, B.J. and Thornton, I. 1975. Arsenic and heavy metals in soils associated with regional geochemical anomalies in Southwest England. *Sci Total Environ.* 4: 359-63.

Collins, J.C. 1981. Zinc. In: *Effect of Heavy Metal Pollution on Plants.* Vol. 1. *Effects of Trace Metals On Plant Function.* Ed. N.W. Lepp. Applied Science Publishers. Pp 145-169.

Covey, R. P., Koch, B. L., and Larsen, H. J. 1981. Influence of vesicular arbuscular mycorrhizae on the growth of apple and corn in low-phosphorous soil. *Phytopathology* 71: 712-715.

Das, D., Samantha, G., Mandal, B.K., Chowdhury, T.R., Chanda, C.R., Chowdhury, P.R., Basu, G.K., and Chakraborti, D. 1996. Arsenic in groundwater in six districts of West Bengal, India. *Environ Geochem and Health.* 18: 5-15.

Davidson, C.M., Duncan, A.L. Littlejohn, D. Ure, A.M. and Garden, L.M. 1998. A critical evaluation of the three-stage BCR sequential extraction procedure to assess the potential mobility and toxicity of heavy metals in industrially-contaminated land. *Analytica Chimica Acta.* 363: 45-55.

Davidson, C.M., Ferreira, P.C.S. and Ure, A.M. 1999. Some sources of variability in application of the three-stage sequential extraction procedure recommended by BCR to industrially-contaminated soil. *Fresenius J. Anal. Chem.* 363: 446-451.

Davidson, C.M., Thomas, R.P., McVey, S.E., Perala, R., Littlejohn, D. and Ure, A.M. 1994. Evaluation of a sequential extraction procedure for the speciation of heavy metals in sediments. *Analytica Chimica Acta.* 291:277-286.

Davidson, R.S., Natusch, D.F.S. and Wallace, J.R. 1974. Trace elements in fly ash; dependence of concentration on particle size. *Environ. Sci. Technol.* 8: 1107.

Davies, B.E. 1992. Inter-relationships between soil properties and the uptake of cadmium, copper, lead and zinc from contaminated soils by radish (*Raphanus sativus* L.). *Water Air Soil Pollut.* 63: 331-342.

Davies, B.E. and Alloway, B.J. 1970. Polluted soils. In: *Soils of North Cardiganshire, Memoir of Soil Survey in Great Britain.* Ed. C.C. Rudeforth. Pp. 141-143.

Delas, J. 1963. La toxicite du cuivre accumule dans les sols. *Agrochimica.* VII: 257-288.

Dickens, R., and Hiltbold, A.E. 1967. Movement and persistence of methanearsonate in soil. *Weed Sci.* 15: 299-304.

Duel, L.E. and Swoboda, A.R. 1972a. Arsenic toxicity to cotton and soybeans. *J.Environ. Qual.* 1: 317-320.

Duel, L.E., and Swoboda, A.R. 1972b. Arsenic solubility in a reduced environment. *Soil Sci Am Proc.* 36: 276-278.

ElBassam, N., Keeppel, H. and Tietjen, C. 1975. Arsenic Transfer in Soils. *Abstr. ESNA Environ Pollut.* P.1.

Elkhatib, E.A., Bennett, O.L., and Wright, Z. 1984a. Kinetics of arsenite sorption in soils. *Soil Sci. Soc. Am. J.* 48: 758-762.

Elkhatib, E.A., Bennett, O.L., and Wright, R.J. 1984b. Arsenite sorption and desorption in soils. *Soil Sci. Soc. Am. J.* 48: 1025-1030.

Fendorf, S., Eick, M.J., Grossl, P., and Sparks, D.L. 1997. Arsenate and chromate retention mechanisms on goethite. I. Surface structure. *Environ. Sci. Technol.* 31: 315-320.

Ferguson, J.F. and Anderson, M.A. 1974. Chemical forms of arsenic in water supplies and their removal. In: *Chemistry of Water Supply, Treatment and Distribution.* Ed. A. J. Rubin. Ann Arbor Science Publishers. Pp. 137 –158.

Ferguson, J.F. and Gavis, J. 1972. A review of the arsenic cycle in natural waters. *Water Res.* 6: 1259-1274.

Finkelman, R.B., Belkin, H.E. and Zheng, B. 1999. Health impacts of domestic coal use in China. *Proc. Natl. Acad. Sci. USA.* 96: 3427-3431.

Fitz, W.J., Wenzel, W.W., Kollensperger, G., Nurmi, J., Stipek, K., Fischerova, Z., Ma, L.Q. and Stingeder, G.J. in press. Arsenic hyperaccumulator Cretan Brake fern may enhance phytoextraction of arsenic towards temperate climates. *J. Environ. Qual. (Submitted).*

Fordham, A.W., and Norrish, K. 1979. Arsenate-73 uptake by components of several acidic soils and its implications for phosphate retention. *Aust. J. Soil Res.* 17: 307-316.

Fowle III, J.R., Abernathy, C.O., Mass, M.J., McKinney, J.D., North, D.W., Ohanian, E.V., and Uthus, E. 1991. Arsenic research needs. *Trace Subst. Environ. Health.* 25: 257-271.

Fowler, B.A. 1977. Toxicology of Environmental Arsenic. In: *Toxicology of Trace Elements.* Eds. R.A. Goyer and M.A. Mehlman. John Wiley and Sons, New York, NY. Pp. 79-122.

Francesconi, K., Visoottiviseth, P., Sridokchan, W., and Goessler, W. 2002. Arsenic species in an arsenic hyperaccumulating fern, *Pityrogamma calomelanos*: a potential phytoremediator of arsenic-contaminated soils. *Sci. Total Environ.* 284: 27-35.

Fraust, S.D., Winka, A.J. and Belton, T. 1987a. An Assessment of chemical and biological significance of arsenical compounds in the Maurice River drainage basin (N.J.). I. Distribution in water and river and lake sediments. *J. Environ. Sci. Health.* A22: 209-37.

Fraust, S.D., Winka, A.J. and Belton, T. 1987b. An Assessment of chemical and biological significance of arsenical compounds in the Maurice River drainage basin (N.J.). II. Partitioning of arsenic into bottom sediments. *J. Environ. Sci. Health.* A22: 239-62.

Frost, R.R., and Griffin, R.A. 1977. Effect of pH on adsorption of arsenic and selenium from landfill leachate by clay minerals. *Soil Sci. Soc. Am. J.* 41: 53-57.

Fuller, W.H. 1978. Investigation of landfill leachate pollutant attenuation by soils. EPA-600/2-28-158. U.S. Environmental Protection Agency. Office of Research and Develpoment, Cincinnati, OH.

Giles, C.H., MacEwan, T.H., Nakhwa, S.N. and Smith, D. 1960. Studies in adsorption. Part XI. A system of classification of solution adsorption isotherms, and its use in diagnosis of adsorption mechanisms and in measurement of specific surface areas of solids. *J. Chem. Soc.* 540: 3973-3993.

Goldberg, S., and Glaubig, R.A. 1988. Anion sorption on a calcareous montmorillonitic soil – Arsenic. *Soil Sci. Am. J.* 52: 1297-1300.

Grantham, D.A. and Jones, J.F. 1977. Arsenic contamination of water wells in Nova Scotia. *J. Am. Water Works Assoc.* 69: 653-657.

Greenland, D.J. 1975. Charge characteristics of some kaolinite – iron hydroxide complexes. *Clay Miner.* 10: 407- 416.

Gullens, J., Champ, D.R. and Jackson, R.E. 1979. Influence of redox environments on the mobility of arsenic in ground water. In: *Chemical modelling in aqueous solution.* Washington, DC: American Chemical Society, ACS Symp. Ser. 7. P. 81.

Gulz, P. and Gupta, S.K. 2001. Is it possible to improve arsenic uptake in sunflower by adding phosphate to As contaminated soils? In: *Proc. 6th ICOBTE Conference*. Ed. L. Evans. University of Guelph, Ontario, Canada. P.319.

Gupta, S.K. and Chen, K.Y. 1975. Partitioning of trace metals in selective chemical fractions on nearshore sediments. *Environ. Lett.* 10: 129-158.

Hargé, J.C. 1997. *Spéciation comparée du zinc, du plomb et du manganèse dans des sols contaminés.* PhD thesis, Université Joseph Fourier, Grenoble, France. pp 178.

Harter, R.D., and Naidu, R. 1995. Role of metal-organic complexation in metal sorption by soils. *Adv. Agron.* 55: 219-264.

Hartley-Whitaker, J., Ainsworth, G. and Meharg, A.A. 2001. Copper and arsenate induced oxidative stress in *Holcus lanatus* L. clones with differential sensitivity. *Plant, Cell and Environment*. 24: 713-722.

Harrison, J.B., and Berkheiser, V.E. 1982. Anion interactions with freshly prepared hydrous iron oxides. *Clays Clay Miner.* 30: 97-102.

Hiller, D.A. and Brummer, G.W. 1995. Mikrosondenuntersuchungen an unterschiedlich stark mit Schwermetallen belasteten Böden. 1. Methodische grundlagen und Elementanalsen an pedogenen Oxiden. Z Pflanzenernähr Bodenk. 158: 147-156.

Hingston, F.J. 1981. A Review of Anion Adsorption, In: *Adsorption of Inorganics at Solid-Liquid Interface*. Eds. Anderson, M.A. and Rubin, A.J. Ann Arbor Science Publication, Ann Arbor, USA. Pp. 51-90.

Hingston, F.J., Posner, A.M., and Quirk, J.P. 1971. Competitive adsorption of negatively charged ligands on oxide surfaces. *Discuss. Faraday Soc.* 52: 334-342.

Howard, A.G. 1997. (Boro)Hydride techniques in trace element speciation. *J. Anal. Atomic Spectrometry.* 12: 267-272.

Hsia, T.H., Lo, S.L., and Lin, C.F. 1992. As (V) adsorption on amorphous iron oxide: Triple layer modelling. *Chemosphere.* 25: 1825 - 1837.

Jackson, A.P. and Alloway, B.J. 1992. The transfer of cadmium from agricultural soils to the human food chain. In: *Biogeochemistry of Trace Metals.* Ed D.C. Adriano. Lewis Publishers. Pp 109-158.

Jackson, M.L. 1958. *Soil Chemical Analysis.* Prentice-Hall, Englewood Cliffs, N.J. pp 498.

Jacobs, L.W., Syere, J.K. and Keeney, D.R. 1970. Arsenic sorption by soils. *Soil Sci. Soc. Am. Proc.* 34: 750-754.

Jernelov, A. 1975. Microbial Alkylation of Metals. Proc. Conf. *On Heavy Metals in the Environment*, Toronto, P.845.

Jiang, Q. Q., and Singh, B. R. 1994. Effect of different forms and sources of arsenic on crop yield and arsenic concentration. *Wat. Air Soil Poll.* 74: 321-343.

Johnson, L.R., and Hiltbold, A.E. 1969. Arsenic content of soil and crops following use of methanearsonate herbicides. *Soil Sci. Soc. Am. Proc.* 33: 279-282.

Johnson, M.S., McNeilly, T. and Putwain, P.D. 1977. Revegetation of metalliferous mine spoil contaminated by lead and zinc. *Environ. Pollut.* 12: 261-277.

Kabata-Pendias, A., and Pendias, H. 1984. *Trace Elements in the Biological Environment.* Wyd. Geol. Warsaw, Poland, pp. 300.

Kabata-Pendias, A., and Pendias, H. 1992. *Trace Elements in Soils and Plants.* Boca Raton: CRC Press. pp. 365.

Kenyon D.J., Elfving, D.C., Pakkala, I.S., Bache, C.A. and Lisk, D.J. 1979. Residues of lead and arsenic in crops cultured on old orchard soils. *Bull. Environ. Contam. Toxicol.* 22: 221-223.

Khaodhiar, S., Azizian, M.F., Osathaphan, K. and Nelson, P.O. 2000. Copper, chromium, and arsenic adsorption in an iron-oxide-coated sand, background electrolyte system. *Wat. Air Soil Pollut.* 119: 105-120.

Khattak, R.A., Page, A. L., Parker, D.R. and Bakhtar, D. 1991. Accumulation and interactions of arsenic, selenium, molybdenum and phosphorous in alfalfa. *J. Environ. Qual.* 20: 165-168.

Kheboian, C. and Bauer, C.F. 1987. Accuracy of selective extraction procedures for metal speciation in model aquatic sediments. *Analytical Chemistry.* 59: 1417-1423.

Khourey, C.J., Matisoff, G., Strain, W.H. and Varnes, A.W. 1983. Toxic metal mobility in ground water systems as influenced by acid rain. *Trace Subst. Environ. Health.* 17: 174 - 180.

Kibblewhite, M. 2001. Identifying and dealing with contaminated land. In: *Assessment and Reclamation of Contaminated Land; Issues in Environmental Science and Technology* No.16. Eds R.E. Hester and R.M. Harrison. Pp 45-64.

Kinniburgh, D. G., Jackson, M. L. and Syers, J. K. 1976. Adsorption of alkaline earth, transition, and heavy metal cations by hydrous oxide gels of iron and aluminium. *Soil Sci. Soc. Am. J.* 40: 796-799.

Krauskopf, K.B. and Bird, D.K. 1995. *Introduction to Geochemistry.* 3rd Ed. Mc Graw-Hill, Inc. pp. 647.

Kunze, G.W. 1965. *Methods of Soil Analysis*. Ed. C.A. Black. American Society of Agronomy, Madison, Wis. Pp. 568-577.

Leonard, A. 1991. Arsenic. In: *Metals and Their Compounds in the Environment. Occurrence, Analysis, and Biological Relevance.* 2nd ed. Eds, E. Merian, in cooperation with Clarkson *et al*. Weinheim, VCH. Pp. 751-773.

Léonard, A. and Lauwerys, R. R. 1980. Carcinogenicity, teratogenicity and mutagenicity of arsenic. *Mutat. Res.* 75: 49-62.

Lepp, N.W. 1981. *Effect of Heavy Metal Pollution on Plants: Effects of Trace Metals on Plant Function*. Applied Science Publishers: London, UK. Vol. 1. pp 352.

Lewis, W.J. 1967. *Lead Mining in Wales*. Cardiff, University of Wales Press. pp. 415.

Li, X. and Thornton, I. 1993. Arsenic, antimony and bismuth in soil and pasture herbage in some old metalliferous mining areas in England. *Environ. Geochem. Health.* 15: 135-144.

Lindsay, W.L. 1979. *Chemical Equilibria in Soils*. John Wiley and Sons, New York. pp 449.

Livesey, N.T., and Huang, P.M. 1981. Adsorption of arsenate by soils and its retention to selected chemical properties and anions. *Soil Sci.* 131: 88-94.

Lombi, E., Wenzel, W.W., and Sletten, R.S. 1999. Arsenic adsorption by soils and iron-oxide-coated sand: Kinetics and reversibility. *J. Plant Nutr. Soil Sci.* 162: 451- 456.

Lumsdon, D.G., Fraser, A.R., Russell, J.D., and Livesey, N.T. 1984. New infrared band assignments for the arsenate ion adsorbed on synthetic goethite (α-FeOOH). *J. Soil Sci.* 35: 381-386.

Ma, L. Q., Komar, K.M., Tu, C., Zhang, W., Cai, Y. and Kennelley, E.D. 2001. A fern that hyperaccumulates arsenic. *Nature.* 409: 579.

Ma, Y., Dickinson, N.M. and Wong, M.H. 2000. The effects of earthworm inoculation on metal bioavailability: Potential use for phytoremediation of Pb/Zn mine spoils. In: *Proceedings of Remade Lands: International Conference on the Remediation and Management of Degraded lands.* Freemantle, Western Australia. Eds A. Brion and R.W. Bell. Pp 33-35.

Machlis, L. 1941. Accumulation of arsenic in the shoots of Sudan grass and bush beans. *Plant Physiol.* 16: 521-544.

Macnair, M.R. and Cumbes, Q. 1987. Evidence that arsenic tolerance in *Holcus lanatus* L. is caused by an altered phosphate uptake system. *New Phytol.* 107: 387-394.

Manceau, A., Charlet, L., Boisset, M.C., Didier, B. and Spadini, L. 1992. Sorption and speciation of heavy metals on hydrous Fe and Mn oxides. From microscopic to macroscopic. *Appl. Clay Sci.* 7: 201-223.

Mandl, M., Matulová, P., and Dočekalová, H. 1992. Migration of arsenic (III) during bacterial oxidation of arsenopyrite in chalcopyrite concentrate by Thiobacillus ferrooxidans. *Appl. Microbiol. Biotechnol.* 38: 429 - 431.

Marin, A. R., Pezeshki, S. R., Masscheleyn, P. H. and Choi, H. S. 1993. Effect of dimethylarsenic acid (DMAA) on growth, tissue arsenic, and photosynthesis of rice plants. *J. Plant Nutr.* 16: 865-880.

Masscheleyn, P.H., DeLaune, R.D. and Patrick, W.H. Jr. 1991a. Arsenic and selenium chemistry as affected by sediment redox potential and pH. *J. Environ. Qual.* 20: 522-527.

Masscheleyn, P.H., Delaune, R.D., and Patrick, W.H. Jr. 1991b. Effect of redox potential and pH on arsenic speciation and solubility in a contaminated soil. *Environ. Sci. Technol.* 25: 1414-1418.

McBride, M.B. 1994. *Environmental Chemistry of Soils.* Oxford University Press. pp 406.

McLaren, R.G. and Crawford, D.V. 1973. Studies on soil copper. I. The fractionation of copper in soils. *J. Soil Sci.* 24: 172-181.

Meharg, A.A. and Hartley-Whitaker, J. 2002. Arsenic uptake and metabolism in arsenic resistant and nonresistant plant species. *New Phytol.* 154: 29- 43.

Meharg, A. A. and Macnair, M. R. 1990. An altered phosphate uptake system in arsenate-tolerant *Holcus lanatus* L. *New Phytol.* 116: 29-35.

Meharg, A.A. and Macnair, M.R. 1991. The mechanisms of arsenate tolerance in *Deschampsia cespitosa* (L.) Beauv and *Agrostis capillaris* L. *New Phytol.* 119: 291-297.

Meharg, A.A. and Macnair, M.R. 1992. Suppression of the high-affinity phosphate-uptake system – a mechanism of arsenate tolerance in *Holcus lanatus* L. *Journal of Experimental Botany.* 43: 519-524.

Meharg, A. A., Naylor, J. and Macnair, M. R. 1994. Phosphorus nutrition of arsenate-tolerant and nontolerant phenotypes of velvet-grass. *J. Environ. Qual.* 232: 234-238.

Mench, M., Vangronsveld, J., Lepp, N. and Bleeker, P. (in press). Use of amendments to attenuate trace element exposure: Sustainability and failures. In: *Natural Attenuation of Trace Element Availability in Soils.* Eds. R. Hammon and M. McLaughlin.

Mench, M., Vangronsveld, J., Lepp, N.W. and Edwards, R. 1998. Physico-chemical aspects and efficiency of trace element immobilization by soil amendments. In: *Metal-Contaminated Soils; In Situ Inactivation and Phytorestoration.* Eds. J. Vangronsveld and S.D. Cunningham. Springer-Verlag. Pp. 151-182.

Mitchell, P. and Barr, D. 1995. The nature and significance of public exposure to arsenic: a review of its relevance to South West England. *Environ. Geochem. Health.* 17: 57-82.

Moody, B. 1991. *Comparative Inorganic Chemistry.* 3rd Ed. Edward Arnold publishers. pp 562.

Naidu, R., and Rengasamy, P. 1993. Ion interactions and constraints to plant nutrition in Australian sodic soils. *Aust. J. Soil Res.* 31: 801-819.

Naidu, R., Bolan, N.S., Kookana, R.S., and Tiller, K.G. 1994. Ionic-strength and pH effects on the sorption of cadmium and the surface charge of soils. *Eur. J. Soil Sci.* 45: 419-429.

National Academy of Sciences (NAS). 1977a. Arsenic. The national research council. National Academy of Sciences, Washington, DC, USA. P. 332.

National Academy of Sciences (NAS). 1977b. "Medical and Biologic Effects of Environmental Pollutants: Arsenic." National Research Council, Washington, D.C. *Cited in* Leonard, A. (1991). Arsenic. In: *Metals and Their Compounds in the Environment. Occurrence, Analysis and Biological Relevance.* 2nd ed. Eds. E. Merian, in cooperation with Clarkson *et al.* Weinheim, VCH. Pp. 751-773.

National Food Authority. 1993. "Australian Food Standards Code: March, 1993." Australian Govt. Pub. Service, Canberra.

National Research Council of Canada (NRCC). 1978. "Effects of arsenic in the Canadian Environment". Ottawa, Canada. NRCC no. 15391.

Natusch, D.F.S., Wallace, J.R. and Evans, C.A. 1974. Toxic trace elements preferential concentration in respirable particles. *Science* . 183: 202-204.

Ndiokwere, C.L. 1985. The dispersal of arsenic, chromium and copper from a wood treatment factory, and their effect on soil, vegetation and crops. *Intern. J. Environ. Studies.* 24: 231-234.

Nelson, K.W. 1977. Industrial contributions of arsenic to the environment. *Environ. Health Perspect.* 19: 31- 34.

Norrish, K. 1975. The Geochemistry and Mineralogy of Trace Elements, In: *Trace Elements in Soil-Plant-Animal System.* Eds. D.D.J. Nicholas, and A.R. Egan. Academic Press, New York, P.55.

Nye, P.H. and Tinker, P.B. 1977. *Solute Movement In The Soil-Root System: Studies In Ecology.* Blackwell Scientific. Vol 4. pp 342.

O'Neill, P. 1985. *Environmental Chemistry.* George Allen and Unwin, London. pp 232.

O'Neill, P. 1990. Arsenic. In: *Heavy Metals in Soils.* 2nd ed. Ed. B.J. Alloway. Blackie, London. Pp. 83-99.

O'Neill, P. 1995. Arsenic. In: *Heavy Metals in Soils.* 2nd ed. Ed. B.J. Alloway. Blackie, London. Pp. 105-121.

Onken, B.M. and Adriano, D.C. 1997. Arsenic availability in soil with time under saturated and subsaturated conditions. *Soil Sci. Soc. Am. J.* 61: 746-752.

Onishi, H. 1968. Arsenic. In: *Handbook of Geochemistry.* Ed. K.H. Wedepohl. New York: Springer-Verlag.

O'Reilly, S.E., Strawn, D.G. and Sparks, D.L. 2001. Residence time effects on arsenate adsorption / desorption mechanisms on goethite. *Soil Sci. Soc. Am. J.* 65: 67-77.

Orwick, P. L., Schrieber, M. M., Hodges, T. K. 1976. Adsorption and efflux of chloro-s-triazines by Setaria roots. *Weed Res.* 16: 139-144.

Oscarson, D.W., Huang, P.M., Defosse, C., and Herbillon. 1981. Oxidative power of Mn (IV) and Fe(III) oxides with respect to As (III) in terrestrial and aquatic environments. *Nature*. 291: 50-51.

Oscarson, D.W., Huang, P.M., Liaw, W.K., and Hammer, U.T. 1983. Kinetics of oxidation of arsenite by various manganese dioxides. *Soil Sci. Soc. Am. J.* 46: 644-648.

Otte, M.T., Dekkers, M.J., Rozema, J. and Broekman, R.A. 1991. Uptake of arsenic by *Aster tripolium* in relation to rhizosphere oxidation. *Can. J. Bot.* 69: 2670-2677.

Parfait, R.L. 1980. Chemical properties of variable charge soils. In: *Soils with Variable Charge*. Ed. B.K.G. Theng. *New Zealand Society of Soil Science*. Pp. 167-194.

Parks, G.A. 1967. Aqueous surface chemistry of oxides and complex oxide minerals. Isoelectric point and zero point of charge. *Advances in Chem. Ser.* 67: 121- 160.

Parks, G.A. and DeBruyn, P.J. 1962. The zero point of charge of oxides. *J. Phys. Chem.* 66: 967-973.

Pershagan, G. 1981. The Carcinogenicity of Arsenic. *Environ. Health Perspect.* 40: 93-100.

Peryea, F.J. 1991. Phosphate induced release of arsenic from soils contaminated with lead arsenate. *Soil Sci. Soc. Am. J.* 55: 1301-1306.

Peryea, F.J. and Creger, T.L. 1994. Vertical distribution of lead and arsenic in soils contaminated with lead arsenate pesticide residues. *Wat. Air Soil Poll.* 78: 297-306.

Peryea, F.J. and Kammereck, R. 1997. Phosphate-enhanced movement of arsenic out of lead arsenate-contaminated topsoil and through uncontaminated subsoil. *Wat. Air Soil Poll.* 93: 243-254.

Peters, G.R., McCurdy, R.F. and Hindmarsh, J.T. 1996. Environmental aspects of arsenic toxicity. *Critical Rev. In Clinic. Lab. Sci.* 33: 457-493.

Peterson, P.J., Benson, L.M., and Porter, E.K. 1979. Biogeochemistry of arsenic on polluted sites in SW England. In: *Heavy Metals in the Environment, London, September 1979*. CEP Consultants Ltd., Edinburgh. Pp. 198-201.

Pierce, M.L., and Moore, C.B. 1980. Adsorption of arsenite and arsenate on amorphous iron hydroxide from dilute aqueous solutions. *Environ. Sci. Technol.* 14: 214-216.

Pierce, M.L. and Moore, C.B. 1982. Adsorption of arsenite and arsenate on amorphous iron hydroxide. *Water Res.* 16: 1247-1253.

Piver, W.T. 1983. Mobilization of arsenic by natural and industrial processes. *Top. Environ. Health.* 6: 1-50.

Polemio, M., Bufo, S.A., and Senesi, N. 1982. Minor elements in south-east Italy soils: A survey. *Plant and Soil.* 69: 57-66.

Pollard, S.J.T., Lythgo, M. and Duarte-Davidson, R. 2001. The extent of contaminated land problems and the scientific response. In: *Assessment and Reclamation of Contaminated Land; Issues in Environmental Science and Technology.* No.16. Eds. R.E. Hester and R.M. Harrison. Royal Society of Chemistry Publishers. Pp. 1-19.

Prasad, B., Banerjee, N.N. and Dhar, B.B. 1996. Environmental assessment of coal ash disposal: A review. *Journal of Scientific and Industrial Research.* 55: 772-780.

Quevauviller, P.H. 1998. Operationally defined extraction procedures for soil and sediment analysis I. Standardization. *Trends in Analytical Chemistry.* 17: 289-298.

Ramos, L., Hernandez, L.M. and Gonzalez, M.J. 1994. Sequential fractionation of copper, lead, cadmium and zinc in soils from or near Donana National park. *J. Environ. Qual.* 23: 50-57.

Raskin I., Kumar N., Dushenkov S. and Salt D. 1994. Phytoremediation – A novel strategy for the removal of toxic metals from the environment using plants. *Current Options in Biotechnology*. 5: 285-290.

Rebedea, I. 1997. *An Investigation Into The Use Of Synthetic Zeolites For In Situ Land Reclamation.* Ph.D. Thesis. Liverpool John Moores University. pp 244.

Robins, R.G. 1981. The solubility of metal arsenates. *Metal. Trans. B.* 12B: 103-109.

Roe, A.L., Hayes, K.E., Chisholm-Brause, C., Brown, G.E., Parks, G.A., Hodgson, K.O. and Leckie, J.O. 1991. X-ray adsorption study of lead complexes at α-FeOOH/water interfaces. *Langmuir.* 7: 367-373.

Roy, W.R., Anisworth, C.C., Griffin, R.A. and Krapac, I.G. 1984. Development and Application of Batch Adsorption procedures for Designing Earth Landfill Liners, In: *Proc. Ann. Madison Waste Conf.* University of Wisconsin, Madison. Pp. 309-398.

Roy, W.R., Hassett, J.J., and Griffin, R.A. 1986. Competitive coefficients for the adsorption of arsenate, molybdate, and phosphate mixtures by soils. *Soil Sci. Soc. Am. J.* 50: 1176-1182.

Ruby, M.V., Davis, A. and Nicholson, A. 1994. In situ formation of lead phosphates in soils as a method to immobilize lead. *Environ. Sci. Technology*. 28: 646-654.

Russell, J.D., Parfitt, R.L., Fraser, A.R. and Farmer, V.C. 1974. Surface structures of gibbsite, goethite and phosphated goethite. *Nature* 248: 220-221.

Sachs, R.M., and Michaels, I.L. 1971. Comparitive phytotoxicity among four arsenical herbicides. *Weed Sci.* 19: 558-564.

Sadiq, M. 1997. Arsenic chemistry in soils: An overview of thermodynamic predictions and field observations. *Wat. Air and Soil Poll.* 93: 117-136.

Sadiq, M., Zaidi, T.H., and Mian, A.A. 1983. Environmental behaviour of arsenic in soils: Theoretical. *Wat. Air Soil Poll.* 20: 369-377.

Sahuquillo, A., Lopez-Sanchez, J.F., Rubio, R., Rauret, G., Thomas, R.P., Davidson, C.M. and Ure, A.M. 1999. Use of a certified reference material for extractable trace metals to assess sources of uncertainty in the BCR three-stage sequential extraction procedure. *Analytica Chimica Acta.* 382: 317-327.

Salomons, W. and Forstner, U. 1980. Trace metal analysis on polluted sediments. Part II: Evaluation of Environmental Impact. *Environmental Technology Letters.* 1: 506-517.

Sappin-Didier, V. 1995. *Utilization de composés inorganiques pour diminuer les flux de métaux dans agrosystémes pollués: étude des mécanismes impliqués par I'emploi d'un composé du fer.* PhD thesis, Analytical Chemistry and Environment, Bordeaux I University, France. pp 189.

Schuthess, C.P., and Huang, C.P. 1990. Adsorption of heavy metals by silicon and aluminium surfaces on clay minerals. *Soil Sci. Soc.Am. J.* 54: 679-688.

Shan, X.Q. and Chen, B. 1993. Evaluation of sequential extraction for speciation of trace metals in model soil containing natural minerals and humic acid. *Anal. Chem.* 65: 802-807.

Sheppard, S.C. 1992. Summary of phytotoxic levels of soil arsenic. *Wat. Air Soil Poll.* 64: 539-550.

Shuman, L.M. 1976. Zinc adsorption isotherms for soil clays with and without iron oxides removed. *Soil Sci. Soc. Am. J.* 40: 349-352.

Singh, S.K. and Subramanian, V. 1984. Hydrous Fe and Mn oxides – Scavengers of heavy metals in the aquatic environment. *Crit. Rev. Environ. Control.* 14: 33-90.

Smith, E., Naidu, R. and Alston, A.M. 1998. Arsenic In The Soil Environment: A Review. *Advances in Agronomy*. 64: 149-195.

Smith, S.R. 1994. Effect of soil pH on availability to crops of metals in sewage sludge-treated soils. I. Nickel, copper and zinc uptake and toxicity to ryegrass. *Environ. Pollut.* 85: 321-327.

Soon, Y. K. and Bates, T.E. 1982. Chemical pools of cadmium, nickel and zinc in polluted soils and some preliminary indications of their availability to plants. *Int. J. Environ. Anal. Chem.* 35: 241-251.

Spadini, L., Manceau, A., Schindler, P.W. and Charlet, L. 1994. Structure and stability of Cd^{2+} surface complexes on ferric oxides. 1. Results from EXAFS Spectroscopy. *J. Colloid and Interface Science.* 168: 73-86.

Speer, H. L. 1973. The effect of arsenate and other inhibitors on early events during the germination of lettuce seeds (*Lactuca sativa* L.). *Plant Physiol.* 52: 129-133.

Sposito, G. 1989. *The Chemistry of Soils.* Oxford University Press. pp 277.

Sun, X. and Doner, H. E. 1998. Adsorption and oxidation of arsenite on goethite. *Soil Sci.* 163: 278-287.

Taiz, L. and Zeiger, E. 1991. *Plant Physiology*. Benjamin / Cummings Publishing Company. pp 565.

Takamatsu, T., Aoki, H., and Yoshida, T. 1982. Determination of arsenate, arsenite, monomethylarsonate and dimethylarsenite in soil polluted with arsenic. *Soil Sci.* 133: 239-246.

Tammes, P.M., and de Lint, M. M. 1969. Leaching of arsenic from soil. *Neth. J. Agric. Sci.* 17: 128-132.

Terwelle, H. F. and Slater, E. C. 1967. Uncoupling of respiratory-chain phosphorylation by arsenate. *Biochim. Biophys. Acta.* 143: 1-17.

Tessier, A., Campbell, P.G.C. and Bisson, M. 1979. Sequential extraction procedure for the speciation of particulate trace metals. *Analytical Chemistry.* 51: 844-851.

Thanabalasingam, P., and Pickering, W. F. 1986. Arsenic sorption by humic acids. *Environ. Pollut. Ser. B.* 12: 233-246.

Thompson, M. and Walsh, J.N. 1989. *Handbook of ICP Spectroscopy.* 2nd Ed. Blackie. P 33.

Ullrich-Eberius, C.L., Sanz, A. and Novacky, A.J. 1989. Evaluation of arsenate- and vanadate-associated changes of electrical membrane potential and phosphate transport in *Lemna gibba* G1. *Journal of Experimental Botany.* 40: 119-128.

Ure, A.M. 1990. Trace elements in soil: Their determination and speciation. *Fresenius J. Anal. Chem.* 337: 577-581.

Ure, A.M. 1996. Single extraction schemes for soil analysis and related applications. *Sci. Total Environ.* 178: 3-10.

Vandercasteele, C. and Block, C.B. 1993. *Modern Methods for Trace Element Determination.* John Wiley and Sons. pp. 330.

Vangronsveld, J., Carleer, R. and Clijsters, H. 1994. Transfer of metals and metalloids from soil to man through vegetables cultivated in polluted gardens: risk assessment and methods for immobilization of these elements in soils. Ed. S.P. Varnavas. In: *Environmental Contamination.* Edinburgh: CEP Consultants. Pp. 142-145.

Vangronsveld, J. and Cunningham, S.D. 1998. Introduction to the concepts. In: *Metal-Contaminated Soils: In Situ Inactivation and Phytorestoration.* Eds. J. Vangronsveld and S.D. Cunningham. Springer-Verlag and R.G. Landes. Pp. 1-15.

Vangronsveld, J., Van Assche, F., Clijsters, H. 1991. Reclamation of a 'desert-like' site in the North East of Belgium: Evolution of the metal pollution and experiments in situ. In: *Proc Int Conf Heavy Metals in the Environment.* Ed. J.G. Farmer. Edinburgh: CEP Consultants. Pp. 58-61.

Vangronsveld, J., Van Assche, F., Sterckx, J. et al. 1993. Rehabilitation studies on an old non-ferrous waste dumping ground: Effects of metal immobilization and revegetation. In: *Proc Int Conf Heavy Metals in the Environment.* Eds. R.J. Allen and J.O. Nriagu. Edinburgh: CEP Consultants. Pp. 563-566.

Vaughan, G. T. 1993. Investigation Report CET/LHIR 148: The environmental chemistry and fate of arsenical pesticides in cattle tick dip sites and banana plantations. CSIRO, Division of Coal and Energy Technology, Centre for Advanced Analytical Chemistry, Sydney, Australia.

Von Endt, D.W., Kearney, P.C., Kaufman, D.D. 1968. Degradation of monosodium methanearsonic acid by soil microorganisms. *J. Agr. Food. Chem.* 16: 17-20.

Wada, K. and Okamura, Y. 1977. Measurements of Exchange Capacities and Hydrolysis as Means of Characterizing Cation and Anion Retention by soils, Proc. Int. Seminar on Soil Environ. Fert. Manage. Intensive Agri. Tokyo. Pp. 811-815.

Wagemann, R., Brunskill, G.J. and Graham, B.W. 1977. Composition and reactivity of some river sediments from the Mackenzie Valley, N.W.T., Canada. *Environ. Geol.* 1: 349-358.

Walsh L.M. and Keeney D.R. 1975. Behaviour and phytotoxicity of inorganic arsenicals in soils; Ed. Woolson, E.A. Arsenical Pesticides 7; *American Chemical Society*: Washington, D.C. Pp 35-52.

Walsh, L.M., Sumner, M.E., and Keeney, D.R. 1977. Occurrence and distribution of arsenic in soils and plants. *Environ. Health Perspect.* 19: 67-71.

Wauchope, R.D. 1975. Fixation of arsenical herbicides, phosphate and arsenate in alluvial soils. *J. Environ. Qual.* 4: 355-358.

Wauchope, R. D. 1983. Uptake, translocation and phytotoxicity of arsenic in plants. In *Arsenic: Industrial, Biomedical, Environmental Perspectives.* Eds. W. H. Lederer and R. J. Fensterheim. Van Nostrand Reinhold Company: New York; Pp 348-374.

Waychunas, G.A., Fuller, C.C., Rea, B.A., and Davis, J.A. 1996. Wide angle X-ray scattering (WAXS) study of "two-line" ferrihydrite structure: Effect of arsenate sorption and counterion variation and comparison with EXAFS results. *Geochim. et Cosmochim. Acta.* 60: 1765-1781.

Waychunas, G.A., Rea, B.A., Fuller, C.C., and Davis, J.A. 1993. Surface chemistry of ferrihydrite: Part 1. EXAFS studies of the geometry of coprecipitated and adsorbed arsenate. *Geochim. et Cosmochim. Acta.* 57: 2251-2269.

Weinberg, E.D. 1977. *Microorganisms and Minerals*. Marcel Dekkar Inc. New York, pp.492.

WHO: 1981. World Health Organization. *Environmental Health Criteria* 18: Arsenic. Geneva, p.174.

Wild, A. 1988. *Russell's Soil Conditions and Plant Growth.* 11th Ed. Longman, London. pp. 991.

Wilkie, J.A. and Hering, J.G. 1996. Adsorption of arsenic onto hydrous ferric oxide: effects of adsorbate /adsorbent ratios and co-occurring solutes. *Colloids and Surfaces A: Physicochemical and Engineering Aspects.* 107: 97-110.

Wood, P. 2001. Remediation methods for contaminated sites. In: *Assessment and Reclamation of contaminated Land; Issues in Environmental Science and Technology.* No.16. Eds. R.E. Hester and R.M. Harrison. Royal Society of Chemistry Publishers. Pp. 115-139.

Woolson, E. A. 1973. Arsenic phytotoxicity and uptake in six vegetable crops. *Weed Sci.* 21: 524-527.

Woolson, E.A. 1983a. Emissions, cycling and effects of arsenic in soil ecosystems. *Top. Environ. Health.* 6: 51-139.

Woolson, E.A. 1983b. Man's perturbation of the arsenic cycle. In: *Arsenic, Industrial, Biomedical, Environmental Perspectives*. Eds. W.H. Lederer and R.J. Fensterheim. New York: Van Nostrand. P.393.

Woolson, E.A., Axely, J.H. and Kearney, P.C. 1971. The chemistry and phytotoxicity of arsenic in soils. I. Contaminated field soils. *Soil Sci. Am. Proc.* 35: 938-943.

Woolson, E.A., Axely, J.H., and Kearney, P.C. 1973. The chemistry and phytotoxicity of arsenic in soils: Effects of time and phosphorus. *Soil Sci. Am. Proc.* 37: 254-259.

www.webelements.com. Accessed May 2002.

Xu, H., Allard, B., and Grimvall, A. 1988. Influence of pH and organic substance on the adsorption of As(V) on geologic materials. *Wat. Air Soil Poll.* 40: 293-305.

Xu, H., Allard, B., and Grimvall, A. 1991. Effects of acidification and natural organic materials on the mobility of arsenic in the environment. *Wat. Air Soil Poll.* 57-58: 269-278.

Yan-Chu, H. 1994. Arsenic distribution in soils. In: *Arsenic in the Environment. Part I. Cycling and Characterization*, Ed. J. O. Nriagu. John Wiley and Sons, New York, NY. Pp 17-50.

Zhang, T., Shan, X. and Li, F. 1998. Comparison of two sequential extraction procedures for speciation analysis of metals in soils and plant availability. *Commun. Soil Sci. Plant Anal.* 29: 1023-1034.

APPENDIX 1.

1.1. X-ray fluorescence spectrometry.

XRF is a non-destructive analytical technique whereby analysis is based on x-ray radiation being emitted from the atoms in the sample. It is said to have a zero starting point, in that preliminary analysis or knowledge of the sample is not necessary, and therefore a completely unknown sample can be analysed.

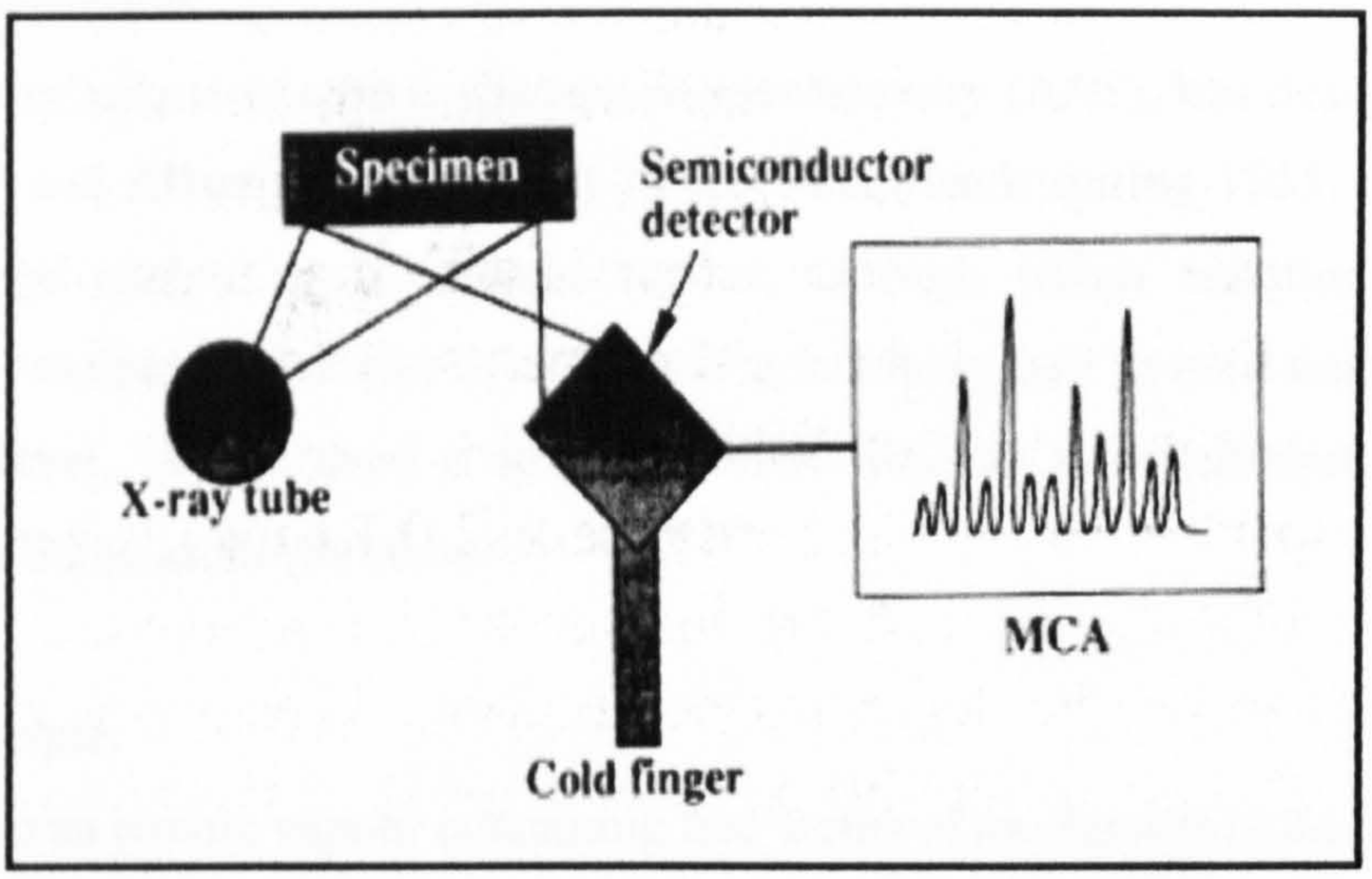
1.1.2. Instrumentation

X-rays are produced when high-energy electrons decelerate, or electron transitions take place in the inner shells of atoms. Producing a wavelength between 10^{-3} and 10nm, x-rays are electromagnetic radiation. When an atom of an element is bombarded with a (primary) beam of X-rays, excitation occurs resulting in the emission of secondary (fluorescent) X-rays whose energy and wavelength are characteristic of that element. Elements of higher atomic number emit shorter wavelength radiations and so higher energies.

This is due to the wavelength being inversely proportional to the square of the atomic number and the energy. A diffraction crystal (acting as a monochromator) isolates the desired line and by means of an X-ray sensitive detector the intensity is measured at a known angle. For a given element this intensity is proportional to the concentration in the sample pellet (Allen, 1974). The X-ray radiation is divided into Bremsstrahlung and characteristic radiation. Energy levels of the individual electron levels and the difference in energy between them are specific to the atoms.

With energy-dispersive X-ray fluorescence (EDXRF), X-rays are measured by a detector that produces pulses proportional to the energy of the impinging X-rays, and which is connected to a multi-channel analyser (Vandecasteele & Block, 1993). All elements are measured simultaneously, regardless of their energy levels. For each incident X-ray photon the detector generates a pulse of electric current having an amplitude proportional to the photon energy. A multi-channel analyser (MCA) receives the output which is amplified and subsequently analysed (figure 1.1) (Vandecasteele & Block, 1993).

Figure 1.1. Energy-dispersive spectrometer. Reproduced by permission of Philips Electronics NV. (Vandecasteele & Block, 1993).



A disadvantage to EDXRF is the limited energy resolution (especially in the low energy area), therefore producing low sensitivity. The Spectro X-lab creates a high excitation intensity available, by optimising the excitation radiation from the tube. This is accomplished by modifying the tube radiation, using three different targets:

- Polarization targets
- Secondary targets
- Combination targets

Polarized radiation is used to excite fluorescence radiation. Polarized radiation scattering is minimised, therefore reducing the scattering background. Due to this method, a more improved signal to background ratio is achieved, and also, a shorter analysis time is created due to this. Secondary targets can be excited to self-radiation. Improved excitation is achieved for certain groups of elements due to this monoenergetic radiation. Alteration of the target material allows changes to the excitation energy, and with it the groups of elements to be investigated. Polarization of the primary x-ray radiation also occurs by combination targets. This allows a wider range of elements to be analysed.

1.2. Atomic Absorption Spectrometry

1.2.1. Introduction

The technique of atomic absorption spectrometry (AAS), was designed by Walsh in Australia and Alkemade and Milatz in the Netherlands during 1955. Their method presented the analyte as an atomic vapour, through which radiation of the right wavelength was passed in order to excite the atoms from their ground state to an excited electronic level. Walsh used a hollow cathode lamp as the excitation source, and a combustion flame as the atomizer.

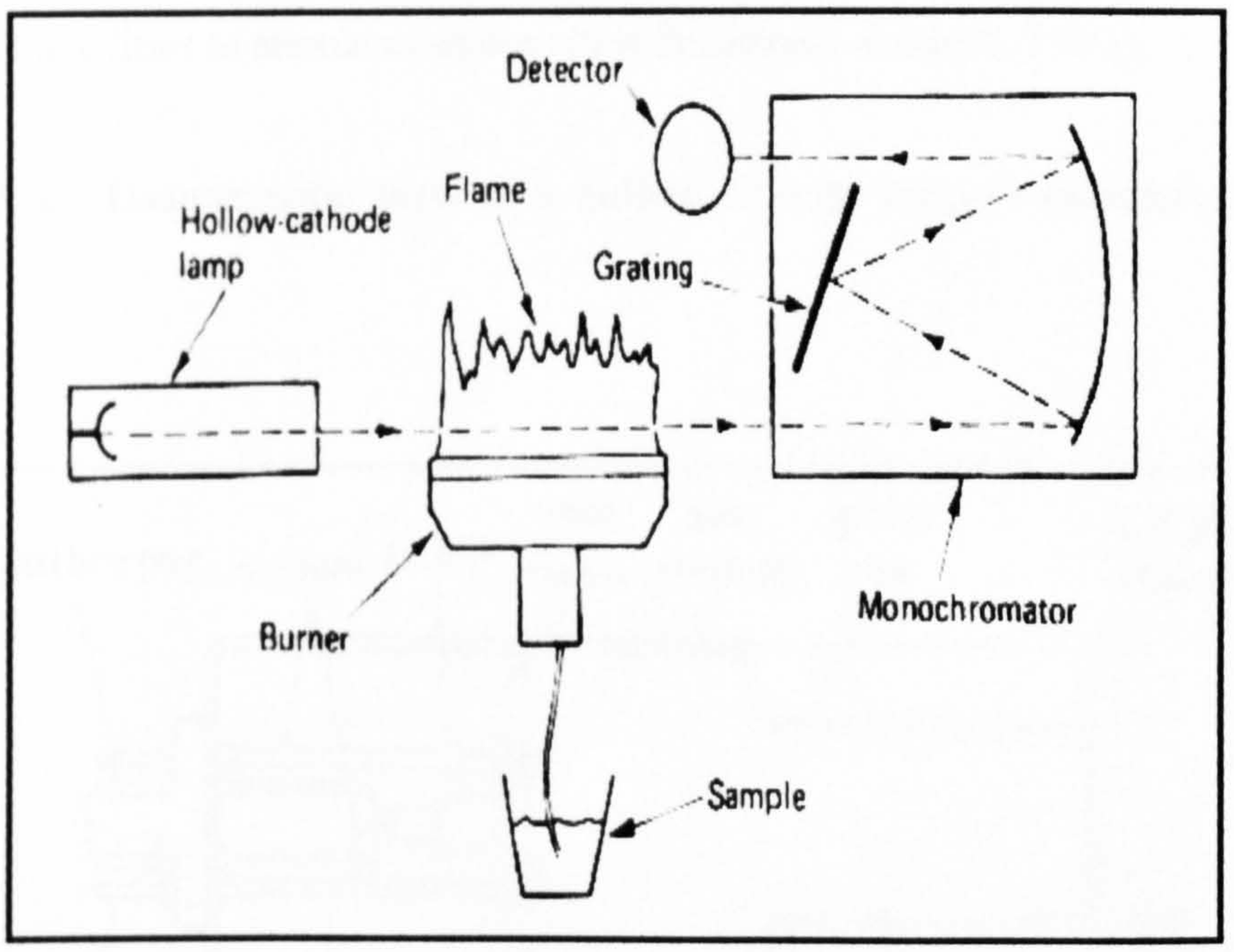
1.2.2. Principle.

When an atomic vapour containing free atoms of an element in the ground state is illuminated by a light source that radiates light of a frequency characteristic of the element present in the vapour, radiation will be attenuated at certain frequencies (Vandecasteele & Block, 1993). The absorbed energy promotes the ground state atom E_o to a higher energy state, the exicted state E_1. Absorption is a quantitative measure for the ground state concentration in the vapour.

1.2.3. Apparatus.

The basic flame atomic absorption spectrometer consists of a radiation source, the hollow cathode lamp, the atomization device, either flame or furnace, a monochromator, a detector (photomultiplier) and a recording system. The instrumentation functions as follows; the hollow cathode lamp emits a characteristic sharp line spectrum of the particular element being studied. The radiation from the lamp is chopped (modulated) to eliminate the background signal, which is produced from the radiation from the sample itself. The beam passes through the atom cell, and the atoms absorb some of the light from the source. The monochromator selects the desired spectral line, whereby the isolated line falls on the detector. Here the light is converted to an electrical signal. Amplification of the modulated signal occurs due to a selective amplifier and the signal is recorded by a readout device (eg. Chart recorder). Figure 1.3 shows the main components of a flame atomic absorption spectrometer.

Figure 1.3. Diagrammatic view of a basic flame atomic absorption system (Vandecasteele & Block, 1993).



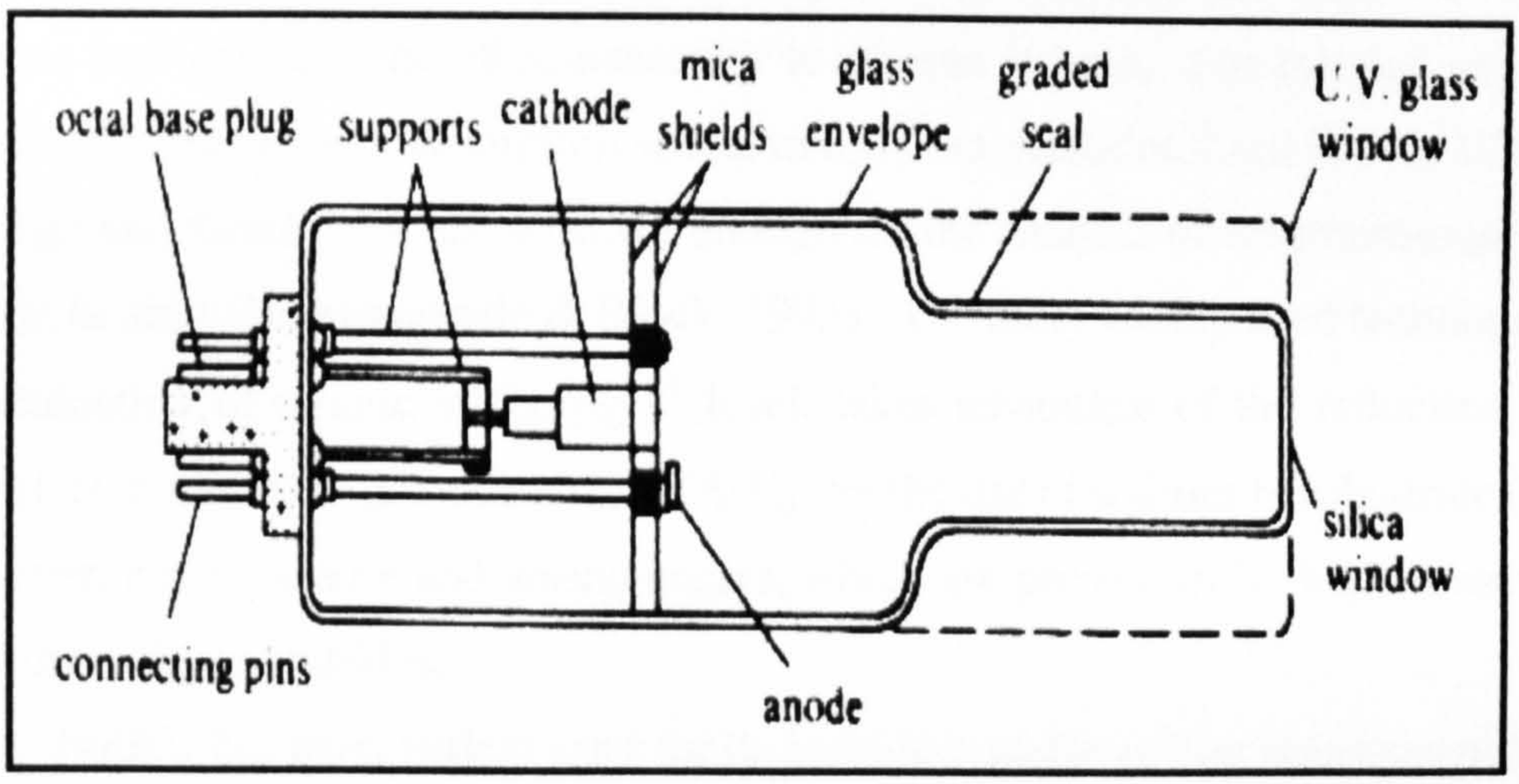
1.2.4. Radiation source

Radiation sources may be one of two types. Either continuum sources or line sources. The hollow-cathode lamp, belongs to the latter, and is the more frequently used in AAS. Line sources emit radiation which is intense and at a maximum wavelength as the absorption maximum. A chief advantage of the line source is the high intensity within a narrow bandwidth. A disadvantage is the need for a different source for every element analysed. The line source used most frequently for AAS is the hollow-cathode lamp (HCL) (Vandecasteele & Block, 1993).

The hollow-cathode lamp is made of a glass container with a quartz window. Inside the container is the cathode which is a hollow cylinder covered with the element or alloy of the particular element under observation. A tungsten anode can be seen in figure 1.4. Argon or neon are present as an inert gas inside the container, which is under vacuum (100-200 Pa). A voltage is maintained between the electrodes of around 300V,

producing a current of about 1-50mA. Ionisation of the inert gas takes place and positive gas ions are moved towards the cathode. A process called sputtering occurs whereby collision energy of the atoms at the cathode are transformed into gaseous atoms. Collision with electrons and ions excite the metal atoms, thereby emitting the characteristic lines of atomic emission. (Vandecasteele & Block, 1993).

Figure 1.4. Diagrammatic view of a hollow-cathode lamp (Vandecasteele & Block, 1993).



1.2.5. Flame Atomic Absorption Spectrometry (FAAS).

In the early development of AAS, the flame was used solely as an atomisation source. The sample solution is nebulized into the flame, were the solvent evaporates and the compounds dissociate into their atoms. A premix chamber type nebulizer is used on most commercial AA spectrometers, whereby the oxidant gas causes a decrease in pressure and the sample is drawn up, causing the formation of fine droplets. These are mixed with more oxidant and fuel and pass into the burner head and then flame. Larger droplets also form but these are deposited and pass down the drain. A large proportion of the sample (85-90%) is discarded in this way. The energy supplied by the flame is directly proportional to the flame temperature. If the energy supplied is small, then atoms will not be formed. If the energy is to great then ions will be formed rather than atoms.

Achieving a ratio between the oxidant gas and the fuel gas therefore alters the temperature of the flame. A flame were excess fuel is used is called 'fuel rich'. Lean flames are much hotter the fuel rich flames, and such a flame is produced when enough oxidant is used to react efficiently with all of the fuel (Vandecasteele & Block, 1993).

1.3. Arsenic analysis by Hydride generation Atomic Absorption Spectrometery.

For the detection of small concentrations of arsenic in the range of $\mu g\ l^{-1}$, hydride generation is required. During this work hydride generation was used routinely as an analysis tool and it is therefore necessary to discuss it here. For the determination of arsenic by flame atomic absorption spectroscopy, the detection limit is only of the order of 1mg/l and therefore is not sensitive enough for the analysis of environmental levels of arsenic in soils (Vandecasteele & Block, 1993). The most widely used technique for the determination of arsenic at the $\mu g\ l^{-1}$ level, takes advantage of the reduction of some arsenic compounds to gaseous arsines (AsH_3) by the use of sodium borohydride ($NaBH_4$). However, arsenobetaine and arseno-sugars, which are present in biological samples, do not form volatile hydrides.

$NaBH_4$ has been widely used for its hydride transfer and reducing properties. It is used for the conversion of aqueous species into volatile hydrides (*hydride* generation) (Howard, 1997). The hydride technique involves the reaction of an acidified sample with the reducing agent ($NaBH_4$), which subsequently forms hydrides. For example, by reducing a sample to As^{III} (by the addition of potassium iodide (KI) and ascorbic acid) the addition of $NaBH_4$ forms arsine, and is represented in figure 1.5.

Figure 1.5. Formation of arsine by sodium borohydride.

$$3BH_4^- + 3H^+ + 4H_3AsO_3 \longrightarrow 3H_3BO_3 + 4AsH_3 + 3H_2O$$

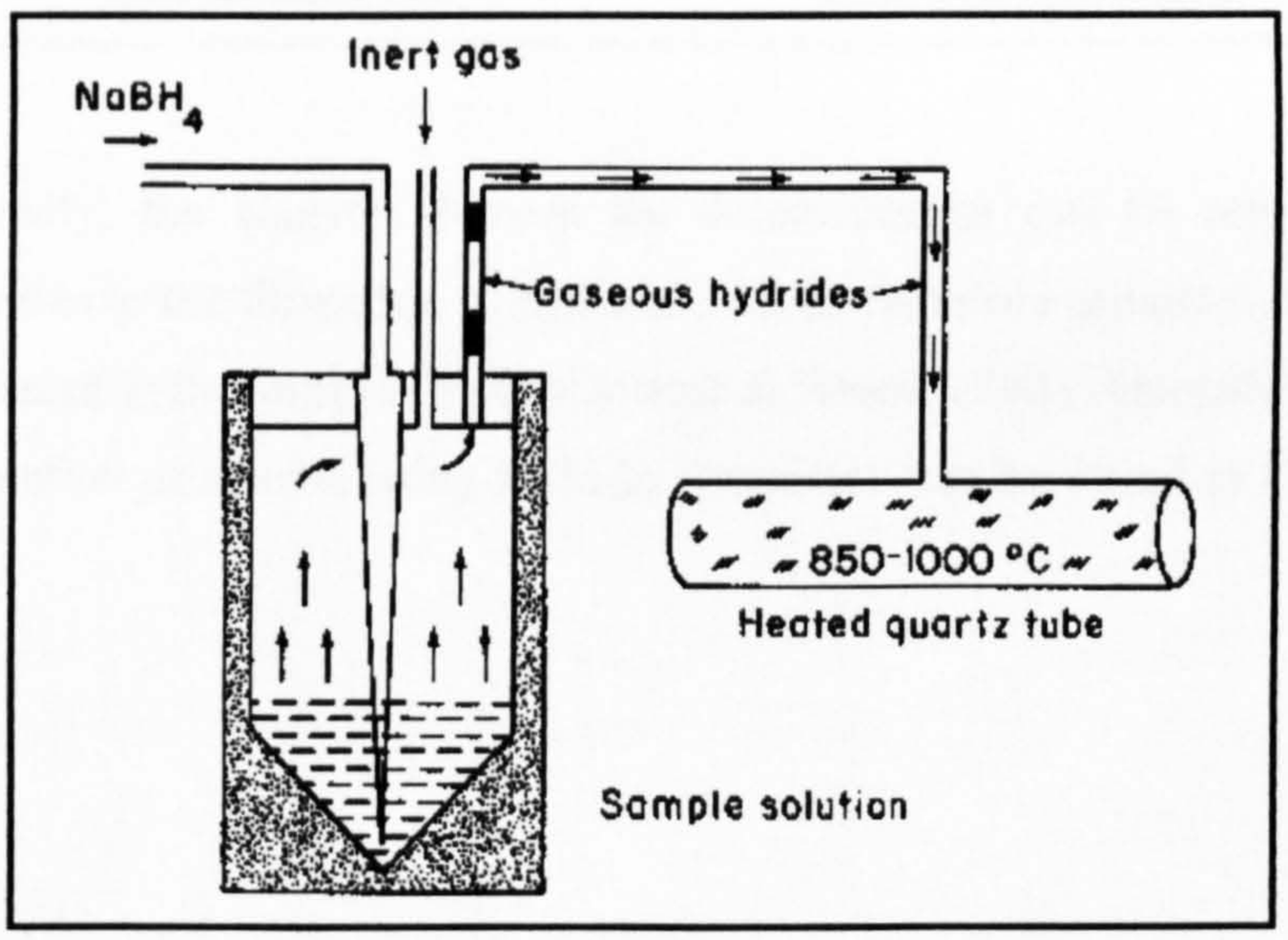
(Howard, 1997)

For the reaction to proceed quickly, the target species must not be negatively charged. The reaction appears to be pH sensitive in that for arsenic speciation analyses, the arsenate must be fully protonated, before it can be converted to arsine. Therefore the reaction is carried out in 1 –2 M hydrochloric acid.

The reaction in figure 1.5 produces a volatile hydride that is transported to a quartz cell by a carrier gas (figure 1.6), of either argon or nitrogen. Once in the quartz cell (figure 1.7) the hydrides are decomposed and converted to gaseous metal atoms whereby the atomic absorption signal in measured by the amount of light absorbed (Vandecasteele & Block, 1993). The quartz cell can be either heated electrically or by flame. It is assumed that atomization of the hydride takes place due to collisions with free hydrogen radicals (Vandercasteele and Block, 1993).

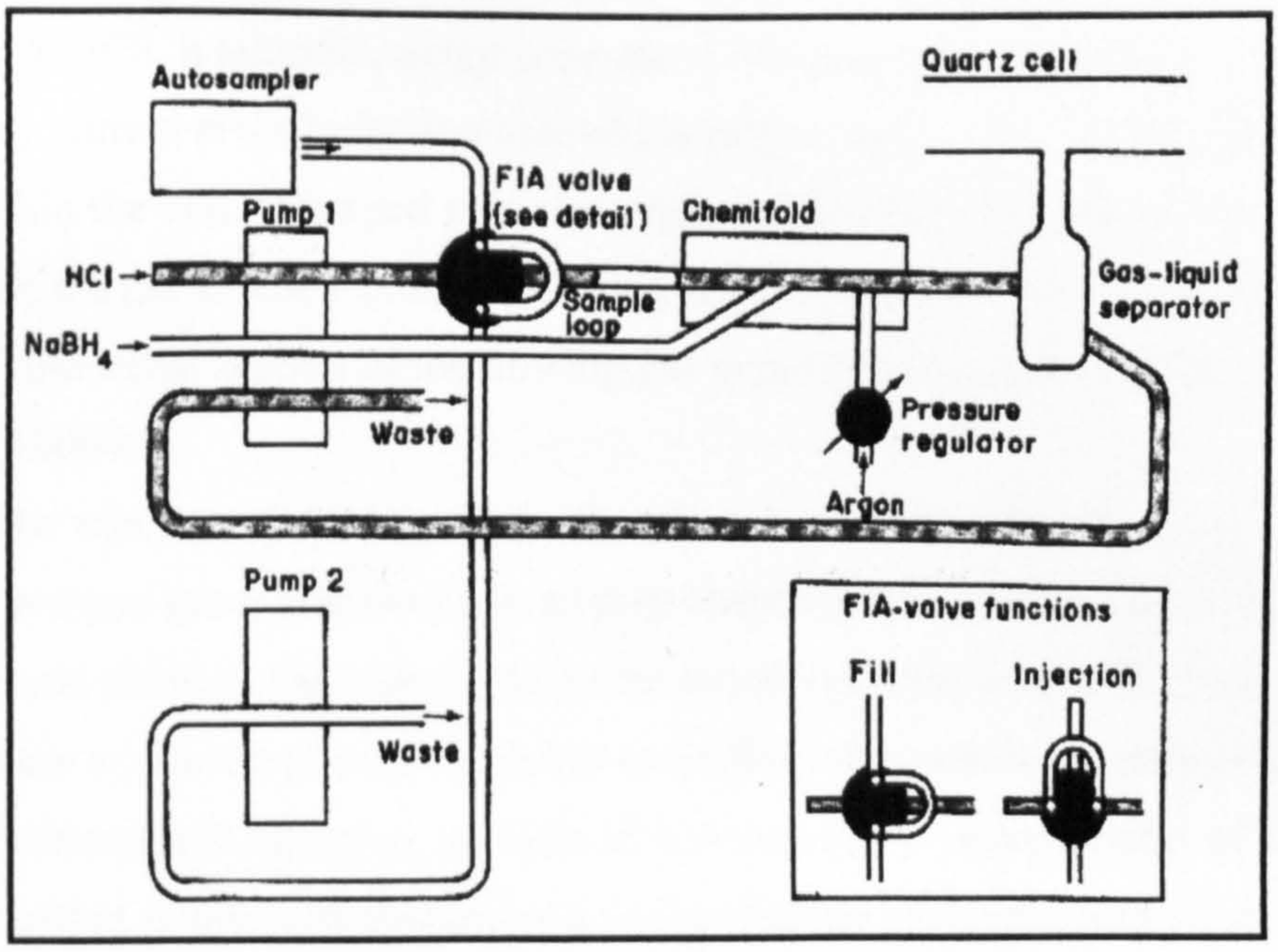
Two types of system exist for hydride generation. Normal batch systems whereby the whole sample is reduced and the hydride formed is delivered to an absorption tube, and continuous flow systems were the use of a gas/liquid separator is employed to strip the hydride from the solution and is then delivered to the quartz cell. Continuous systems have two versions, continuous flow and FI. A continuous flow system with a flame heated quartz cell was employed for the determination of arsenic in this report.

Figure 1.6. A system for the production and atomisation of gaseous hydrides. (Vandecasteele & Block, 1993.)



The advantages hydride generation offers for determination of arsenic in environmental samples are firstly, it has superior sensitivity, being 10 –100 times lower than furnace AAS (Vandecasteele & Block, 1993). The limit of determination for arsenic using hydride is 0.01 μg/l, whereas with graphite furnace the limit of determination is 0.3 μg/l (Vandecasteele and Block, 1993).

Figure 1.7. FIA system for hydride generation techniques (Perkin-Elmer, Norwalk, CT,USA) (Vandercasteele and Block, 1993).



Secondly, the analyte element for determination can be removed from any interference due to the formation of hydrides, which therefore separates it from any other materials present in the sample (Vandecasteele & Block, 1993). Operating conditions for the determination of arsenic using hydride generation can be found in Chapter 2, Table 2.2.

1.4. Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES).

The Philips PV 8060 ICP-AES (the ICP) is a simultaneous / sequential instrument which has twenty six fixed channels which can be operated in the simultaneous mode and a scanner for sequential determination of other elements.

1.4.1. The ICP Source Unit.

A plasma is a gas in which a considerable proportion of the atoms have been ionised. In ICP, a radiofrequency generator (RF generator) is used to produce a high frequency current at the induction coil which in turn results in a rapidly varying magnetic field within the coil. Charged particles produced in the argon gas flowing through the coil cause the gas to heat rapidly, producing further ionisation and consequent heating of the gas. Inductive heating of the flowing gas maintains the plasma temperature between 6000 to 10000 K.

The sample is introduced into the plasma via the nebuliser, where the resulting aerosol in argon gas is transferred to a spray chamber in which the larger liquid particles are removed allowing the argon to carry the remaining sample into the plasma. The high temperature within the plasma causes the excitation of the elements present in the sample and the subsequent emission of light at a wavelength characteristic of the emitting element and at an intensity proportional to the quantity of the element present.

The spectrometer is of the Paschen-Runge type with the entrance and exit slits and the grating positioned on the circumference of a circle (The Rowland Circle). The light emitted from the plasma is delivered from the ICP source unit to the spectrometer, via the transfer optics. The light passes through the entrance slit and on to the grating, which disperses (and reflects) the different wavelengths back to the appropriate exit slits. Behind each slit is a photomultiplier tube the output of which is processed by the spectrometers electronics, and the microcomputer for final output of the data. Figure 1.8 is a representation of the spectrometer section of the PV 8060 ICP. As before, light from the plasma passes through the entrance slit to the concave primary grating and after dispersion the different wavelengths are reflected through the exit slits to the photomultipliers via the light guides (Thompson and Walsh, 1989).

Figure 1.8. Diagrammatic representation of the Philips PV 8060 ICP (Thompson and Walsh, 1989).