STUDIES ON THE CHEMISTRY AND BEHAVIOUR OF ZINC IN SOIL

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SUMMARY

Chapter 1 includes a survey of dynamic equilibria of trace metals and the forms which exist in soil fractions. The forms of trace metals as influenced by environmental factors are also discussed. The types of studies used regarding trace metal behaviour in soil are also reviewed. The objectives of the thesis are to study the chemistry and behaviour of zinc in soil and also the changes in the distribution of this metal with plant uptake.

Chapter 2 lays emphasis on selective extraction procedures for measurement of soil zinc. The removal of zinc held by different mechanisms in the soil is affected by the nature of the extractant. Pairs of extractants used for the exchangeable, specifically sorbed, and organically bound-Zn fractions showed differences in the removal of zinc from the soil. 0.05M calcium chloride is suggested for the removal of exchangeable zinc in preference to M ammonium acetate (pH 7.0), as it released more zinc into solution. Being alike in charge the Ca^{2+} ion more readily displaced the exchangeable zinc from the soil than the NH_4^+ ion. Acetic acid (2.5%) is suggested for the extraction of specifically sorbed zinc compared to modified Morgan´s solution (ammonium acetate/acetic acid, pH 4.8). It extracted higher amounts of zinc from the soil probably due to its acid nature. Ammonium EDTA (0.05M) pH 7.0 is suggested for removing zinc from the organic fraction in preference to 0.1M sodium pyrophosphate, as the latter also affected the oxide pool. As well as individual extraction of zinc, sequential extraction techniques were also utilized to define the forms of zinc in soils. Two schemes were used, which showed differences in various pools of extractable zinc, especially in the oxalate extractable fractions. They also indicated the effect of a particular extractant on the extractability of the subsequent pool in the sequence. There may also be some risk of contamination, hence the use of individual extraction is suggested. Air-drying can also bring about slight changes in the amount of extractable zinc from the soil. In the air-dried samples the extractable zinc increased slightly with various extractants for different fractions compared to fresh samples. Seasonal variation, or depth of sample, can affect the extractability of zinc in various soil pools. Significantly more zinc was extracted in adsorbed, organically bound, and oxide bound Zn fractions of Dreghorn (Arkleston) soil during the winter season compared to the summer season, but these variations were nonsignificant in the case of calcium chloride extractable zinc. It is suggested that this readily available zinc fraction is not affected by plant uptake or seasonal variations, indicating its zinc content is maintained by equilibria with the other pools. In Dreghorn (Arkleston) subsoil lower amounts of zinc in all fractions were extracted compared to topsoil, suggesting the decrease of metal with depth. Seasonal variations have a lesser effect on the extractability of zinc fractions in subsoil compared to topsoil.

Chapter 3 investigates the influence of continuous cropping of ryegrass on the distribution of zinc in soil using a pot experiment, and assesses this by means of specific extractants. Calcium chloride, acetic acid, ammonium EDTA and acid oxalate were used to extract zinc associated with exchange sites, specific sorption sites, organic complexes and oxide materials respectively. It was found that all soil pools showed, directly or indirectly, a response to plant uptake of zinc, except calcium chloride extractable (exchangeable), which remained unchanged. Acetic acid and ammonium EDTA extractable zinc showed some decline with time, suggesting a response to plant uptake and maintaining the exchangeable pool. The oxide fraction, being a big reservoir, showed a greater decline, suggesting that the other soil pools are maintained by equilibrium with this soil fraction. Results showed that zinc in the immediate bioavailable pool was not affected by continuous growth of ryegrass, and it is suggested that equilibrium was maintained by the other soil pools. The amount of zinc taken up by grass is higher in soils with high zinc in readily available pools, rather than high total amounts, suggesting that total zinc is not a good indicator for plant uptake. Higher amounts of zinc accumulation in roots, compared to the tops, in soils with an adequate supply of zinc suggested the intermediate mobility of this metal within the plant.

Chapter 4 illustrates different aspects of zinc adsorption by soil. Data from adsorption studies in different soils showed that soils high in clay content adsorbed more zinc than sandy soils. Soils with high clay content provided more surface area, suggesting that the texture of soil plays an important role for the retention of zinc. Shaking time can also influence the adsorption of zinc by soils. Results showed that an increase in shaking time from 18 hours to 7 days resulted in only a slight increase in zinc adsorption, which was not significant. It is suggested that length of shaking time had no effect on zinc adsorption by soil. It has been observed that no more zinc was adsorbed by air-dried than fresh soils. Adsorption of zinc in the presence of sodium, potassium, ammonium, magnesium, and calcium salts in the form of sulphate and chloride as background electrolytes indicated some influence on zinc adsorption by soil, depending on the nature of the competing cation. Soils adsorbed highest amounts of zinc in the presence of sodium salts due to their dispersive effect and lowest levels in calcium salts due to their flocculating nature, irrespective of the anion form. All soils adsorbed more zinc in the presence of monovalent salts than divalent salts, suggesting that soil prefers to adsorb the divalent compared to monovalent cation. To some extent soils adsorbed more zinc from a sulphate system than chloride system but this is not considered a severe effect as the differences were negligible. No differences in the zinc adsorption maxima, obtained from Langmuir plots, were found when zinc activity was used instead of concentration. Data from the adsorption studies were also considered in terms of a precipitation-dissolution mechanism. When treated in this way, the results suggested that precipitation could not be dismissed as a possible mechanism for removal of zinc from solution. Two processes may occur, one involving the release of H^+ ions. There was also evidence of the involvement of iron in the precipitation mechanism.

CHAPTER I

TRACE METALS IN SOILS

1.1 INTRODUCTION

Those metals whose total concentration in the soil is normally less than 1,000 mg kg^{-1} are called trace metals. The chemistry of some of these metals changes, in that electrons are added to and removed from inner electron orbitals and they are called transition metals. While being soil micronutrients they fall into two categories, the essential micronutrients like Cu, Mn, Mo and Zn, which are beneficial to plants at normal concentrations in the plant (ranging from 0.1 mg kg^{-1} for Mo to 100 mg kg^{-1} for Mn; White 1987). At higher concentrations they may become toxic. Others have no benefit and are nonessential micronutrients (e.g. Pb, Cr, Cd and Ni) and are toxic when present in soil at levels greater than a few mg kg^{-1}.

A large number of the elements are required for growth and reproduction of plants and animals. Of these nutrients only a few are required in large amounts for agricultural production. Deficiencies of those remaining elements which are required in lesser amounts are most frequently related to specialised crops or certain types of soil. But as cropping systems become more intensive, changes in soil management practices frequently alter micronutrient availability, and depletion of nutrients not added in fertilizers becomes more rapid. As the demand for higher yields increases and the plant´s requirement for major elements is more efficiently met, other nutrients are more likely to become limiting. To obtain the higher yield and good quality of crops to meet human requirements, the use of NPK fertilizers, higher yielding plant varieties with increased nutrient demands, and the decreasing availability of farmyard manure (rich in trace metals) in areas where mixed farming has given way to intensive arable agriculture, have combined to increase the demands made on the soil in terms of its ability to supply trace metals to plants. In consequence, deficiency problems have become more common and attempts to solve these problems have necessarily required a better understanding of the soil chemistry of trace metals.

Trace metal distribution in terms of amounts of micronutrients in rocks and soils has been well described by Hodgson (1963), Phipps (1981) and Bohn et al. (1985). Table 1.1 indicates the total contents of trace metal ions in the lithosphere and in soils.

Table 1.1 Total contents of trace metal ions in the lithosphere and in soil.

Element	Average in lithosphere ($mg\ kg^{-1}$)	Soil Content ($mg\ kg^{-1}$)
Iron	50,000	10,000 -300,000
Manganese	1,000	200 - 3,000
Nickel	100	10 - 1,000
Chromium	100	5 - 3,000
Zinc	80	10 - 300
Copper	70	2 - 100
Cobalt	40	1 - 50
Lead	10	2 - 200
Molybdenum	2	0.2 - 5
Cadmium	0.2	0.01- 7

From: Bohn, McNeal and O´Connor, 1985 p 311

Following the work of McLaren and Crawford (1973a,b) on copper, trace elements are usually considered to occur in soils in many different fractions: (a) in the soil solution as ionic or complexed forms; (b) on normal exchange sites; (c) adsorbed on specific sorption sites, and not removed by reagents which are normally used for determining the exchangeable ions; (d) occluded in the soil oxide material; (e) associated in biological residues and living organisms; (f) held in the lattice structure of primary and secondary minerals. The equilibria and reactions between these forms are fundamental to an understanding of the soil chemistry of trace metals.

Lindsay (1979) described the soil as the "living phase" which includes living microorganisms and other forms of life. These living organisms are continually breaking down the organic residues and synthesising many of the products into their body tissue, while others are released to the surroundings. The manner in which the various constituents of the soil interact is represented diagrammatically in Figure 1.1.

The soil solution is the liquid phase by which the solid phases are enveloped. It is the medium from which all plants take their nutrients, and small amounts of plant constituents may also be released into the soil solution. Although the soil solution is affected by all of these reactions shown in Figure 1.1, its composition is ultimately controlled by the mineral phases of the soil. Different chemical extraction methods are commonly used for the distinction of different forms of metal by their defined soil pools. However, this is only on an experimental basis and the distinction between these forms of metals is not always clear cut.

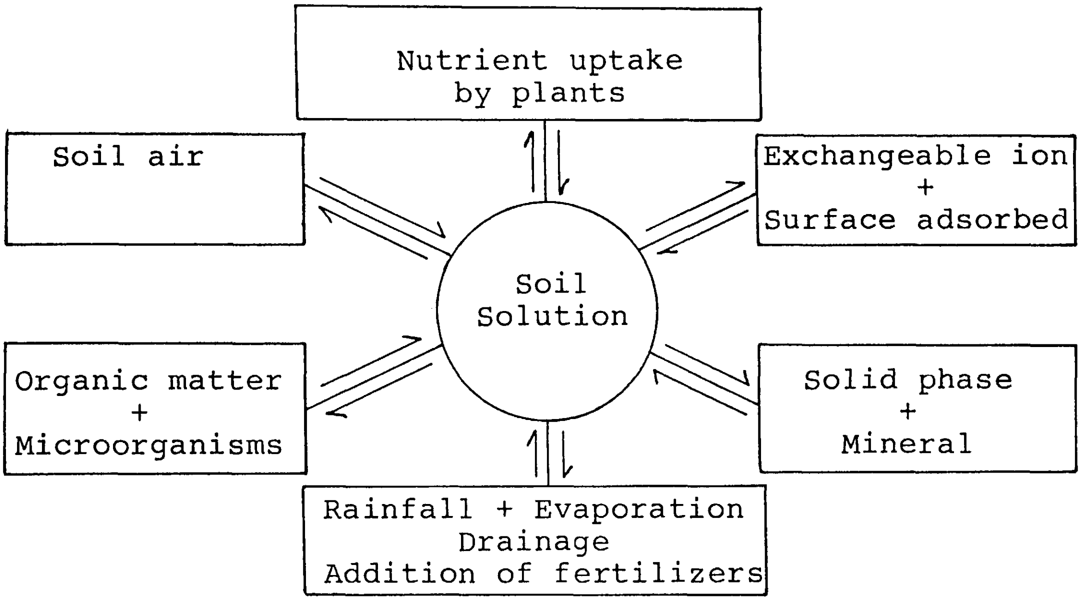


Figure 1.1 The dynamic equilibria that occurs in soils. From Lindsay (1979).

Zinc occupies a unique position among the elements essential for plants and animals. It was first realised in the nineteenth century that zinc is required for normal plant growth, but the acceptance of this element as an essential plant nutrient did not occur until the early 1930's (Giordano and Mortvedt, 1980). Zinc deficiency in agricultural crops grown on widely varying soils under a variety of management practices has been identified throughout the world, and is one of the most common micronutrient deficiencies. Lindsay (1972) reviewed the patterns of zinc deficiency. The first sign of zinc deficiency is usually an interveinal chlorosis. In crops like maize (Zea mays L) the interveinal areas broaden into chlorotic bands on either side of the midribs of the leaf.

Zinc deficiency is often referred to as "rosette", "little leaf", "mottle leaf", or "yellows". Soil is the major source for this element, and ultimately the parent materials that form soils. As modern agronomic practices have led to a wide occurrence of zinc deficiency in plants, the use of zinc fertilizers to correct the deficiency has become more common. The development and widespread use of atomic absorption spectrophotometry as a suitable method of measuring trace metals has resulted in considerable interest and research into the chemistry of zinc in soil. Soil tests to assess available zinc in soils are now commonplace. Although in the past much emphasis has been placed on deficiencies, possible zinc toxicity problems are becoming of increasing concern. This is due to activities such as land disposal of high metal content sewage sludges.

1.2 CHEMISTRY AND BEHAVIOUR OF TRACE METALS IN SOILS

1.2.1 Metals in soil solution

Lindsay (1979) described the soil solution, as the "liquid phase" that envelops the solid phase. While Russell (1973) defined soil solution as the water in soil containing soluble salts. Soil Science Society of America (1965) defined soil solution as "the aqueous liquid phase of the soil and its solutes consisting of ions dissociated from the surfaces of soil particles and of other soluble materials". Trace metals and other nutrients required by plants are supplied through this medium. Soil solution acts as a transport medium bringing the trace metals into contact with root surfaces where they may be absorbed. The movement of nutrients through the soil solution is by convection or by diffusion.

The liquid phase is one of the four component multiple-phase systems which the soil comprises. However it contains only a very small fraction of trace metals. Jenkins and Wyn Jones (1980) quoted the ranges of some micronutrient metal concentrations and their degree of complexing in soil solution, which are given in Table 1.2.

Table 1.2 Concentration and degree of complexing of some micronutrients in solution.

Element	Total element in soil solution (μM)	Degree of complexing (%)	(Mean)
Cobalt	0.007 - 0.2	8 - 50	25%
Zinc	0.03 - 3	28 - 99	50%
Manganese	0.02 - 68	84 - 99	90%
Copper	0.01 - 0.6	89 - 99.9	>90%

After Jenkins and Wyn Jones, 1980 p 13

Loneragan (1975) stated that in acid soils the dominant inorganic ions of Co, Cu, Mn and Zn in solution are divalent cations M^{2+}, although Fe^{3+} may exist. In neutral and alkaline soils the monovalent hydroxy cation $M(OH)^+$ would also be important. Much less is known of the concentrations and forms of Fe and Mo in soil solutions. Concentrations in soil solution reported for iron are from 0.4 to 5 µM, and for molybdenum from 0.02 to 0.08 µM. Most of the iron could be expected to be strongly complexed. The predominant inorganic form of Mo in soil solutions is believed to be divalent molybdate anion, MoO_4^{2-}. The monovalent anion, $HMoO_4^-$, would approach the concentration of the divalent ion in extremely acid soils.

According to Bohn et al. (1985) when ions and molecules interact, they can bond together and lose their separate identities by forming complex ions or ion pairs. Many transition metals are present in solutions as complex ions or ion pairs. Complex ions are usually defined as the combination of a central cation with one or more ligand. A ligand is any ion or molecule in the coordination sphere of the central ion, such as H_2O in the case of $Fe(H_2O)_6^{3+}$ (hexaquoiron (III) complex ion). Ion pairs are thought to form by ligand attachment outside the inner solvation sphere, as hydrated ions are linked electrostatically, and behave like a single unit. This is shown diagrammatically in Figure 1.2.

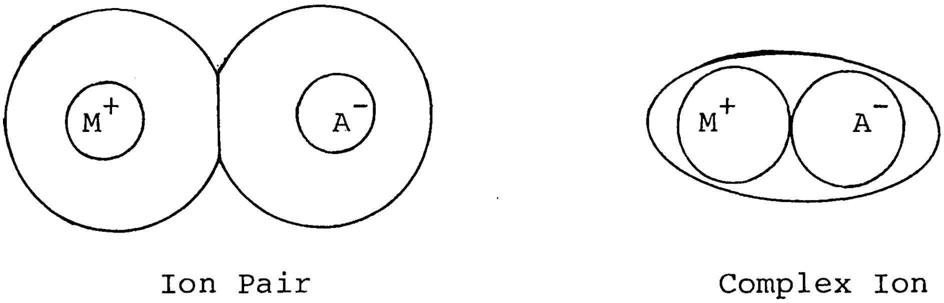


Figure 1.2 Diagram of an ion pair and complex ion. From Bohn et al. (1985) p 35.

The concentration of zinc in soil solution plus exchangeable-Zn is about 0.26% of the total amount of zinc in soil as reported by Mandal and Mandal (1986) in lowland rice field soils. Giordano and Mortvedt (1980) stated that the concentrations of zinc in soil solution are usually low, especially in alkaline soils. They reported values of about 75 ppb Zn were found in several acid soils from New York, while values of less than 2 ppb Zn were found in calcareous soils from Colorado. Approximately 60% of the solution-Zn was complexed by the soluble organic matter fraction. Lindsay (1979) described the different zinc species in soil solution. The predominant zinc species in solution below pH 7.7 is Zn^{2+}, although $ZnOH^{+}$ is more prevalent above this pH. The neutral species $Zn(OH)_2^0$ is the major species above pH 9.11, whereas the species $Zn(OH)_3^-$ and $Zn(OH)_4^{2-}$ are never major solution species in the pH range of soils. Zinc also forms complexes with chloride, phosphate, nitrate, and sulphate. The complex $ZnSO_4^0$ is very important in soils and can contribute significantly to total Zn in solution. Having sulphate in zinc fertilizer is often beneficial because this complex increases the solubility and mobility of Zn^{2+} in soils.

Shuman (1980) reported that the zinc held by ion exchange is in dynamic equilibrium with Zn^{2+} and that complexed by soluble organic matter in the soil solution.

1.2.2 Metals on exchange sites

Cations released by weathering and organic decay vary greatly in ion charge and size, and they respond differently to the ions and surfaces encountered in the soil. Some tend to remain in solution but to be associated with the surface of charged solid phases and are called the exchangeable ions, while some remain in bulk soil solution (soluble ions) which are poor competitors for surface charge. The exchangeable ions are defined as those released from soils by solutions of neutral salts. Salt solution also removes some anions from the soil but, because most soil colloids are negatively charged, the major reaction is the exchange of soil cations for the cations of the extracting solution. The sites from which cations can be released by the cation from a neutral salt solution are called exchange sites. The exchange sites can regulate the metal concentration in soil solution by their release of cations. Also, the metal ions they adsorb are readily exchangeable, so they can be taken up by the plants. The fraction of soil metals adsorbed on these sites varies and depends on the cation exchange capacity of a soil.

McLaren and Crawford (1973a) reported that the amount of copper held on these sites depended on the pH of the soil, decreasing in quantity with increasing pH. Soon and Bates (1982) reported that a low pH value increased the proportion of trace metals (Cd, Ni, Zn) in the exchangeable form of soil. Sims and Patrick (1978) reported that amounts of manganese and iron held on exchange sites were greatly affected by pH and redox potential. It is obvious from their results that at low pH and Eh more manganese and iron can exist on exchange sites. Manganese and iron in a silty clay loam soil decreased from 121 mg kg^{-1} and 1295 mg kg^{-1} at pH 4.5 to 96 mg kg^{-1} and less than 1 mg kg^{-1} at pH 7.5, respectively. While going from Eh +500 mV to -150 mV, manganese and iron increased from 22 mg kg^{-1} and 1 mg kg^{-1} to 169 mg kg^{-1} and 1226 mg kg^{-1} respectively. In the case of zinc, the exchangeable amount was decreased from 9 mg kg^{-1} at pH 4.5 to 1 mg kg^{-1} at pH 7.5. The amount of zinc held on exchange sites was inversely related to pH, but positively correlated with cation exchange capacity of soils (John 1974). Mandal and Mandal (1986) reported that average soluble plus exchangeable-Zn was 0.26% of the total amount of zinc in rice soils of West Bangal, and also claimed that soil having comparatively low pH values contained a higher amount of zinc in this form.

1.2.3 Metals on specific sorption sites

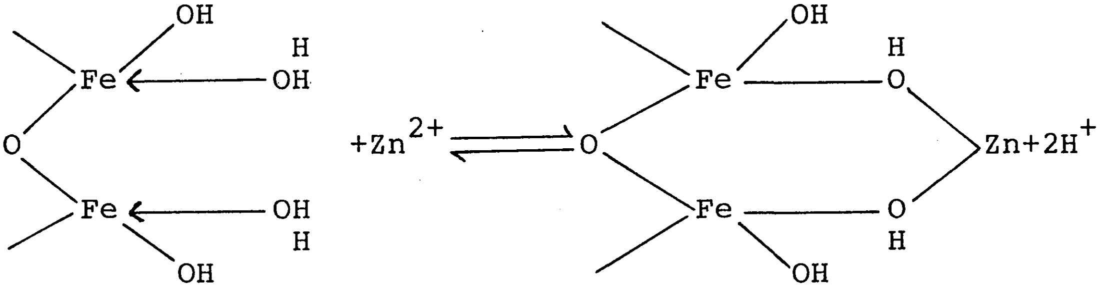
Specific sorption sites are well defined by McLaren and Crawford (1973b) as, the adsorption sites on soil and various soil constituent surfaces which adsorb cations that cannot be removed by reagents normally used for determining the exchangeable cations. Misra and Tiwari (1966) reported from their study that all of the copper and zinc added to black, red and alkali soils was not extracted by neutral normal ammonium acetate. This suggests that the exchange sites alone are not solely responsible for the uptake of copper and zinc by these soils.

McLaren and Crawford (1973b) reported from their study that organic matter and free manganese oxides were the dominant constituents contributing towards specific adsorption of copper in soils. They found the adsorption maxima of copper on various soil constituents were in the following order:
manganese oxides>organic matter>iron oxides>clay minerals. They also suggested that specific adsorption was the most important process in controlling the concentration of copper in soil solution. McLaren, Lawson and Swift (1986b) reported that the sorption of cobalt by soil components at pH 6.0 was greater with soil oxide than organic materials and clay minerals.

The specific adsorption of divalent Cd, Co, Cu, Pb, and Zn on goethite was measured by Forbes, Posner and Quirk (1976), who found the affinities of these metal ions for the oxide surface increased in the order
Cd<Co<Zn<Pb<Cu.

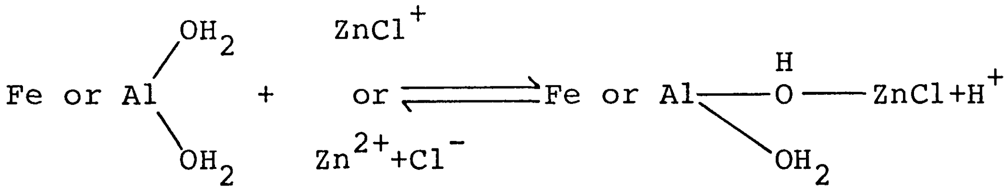
Knezek and Ellis (1980) mentioned that a strong adsorption of Zn by clay, that could not be reversed by use of neutral salt extraction, has been reported by many research workers. The mechanism of the adsorption is unknown, but possible explanations have ranged from octahedral layer substitution to specific binding sites. Hodgson (1963) observed that the specific adsorption was not by the substitution into the octahedral layer since the mineral would need to be destroyed to release the zinc and most of the adsorbed zinc could be replaced by non-destructive dilute acid extraction.

It is obvious that more recent research work may provide a better explanation about zinc adsorption on the oxide surface. Quirk and Posner (1975) proposed a model that the adsorption of Zn(II) at an oxide surface may be represented as a bridging ligand between two neutral sites:



They observed such adsorption can be viewed as a growth or an extension of the surface and its properties would accord with the lack of complete reversibility. Kalbasi, Racz and Loewen-Rudgers (1978) later proposed two possible mechanisms for zinc adsorption by aluminium and iron oxide surfaces:

1.



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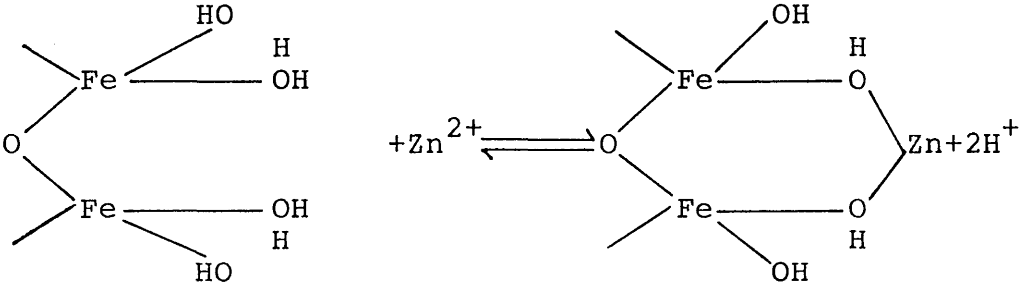
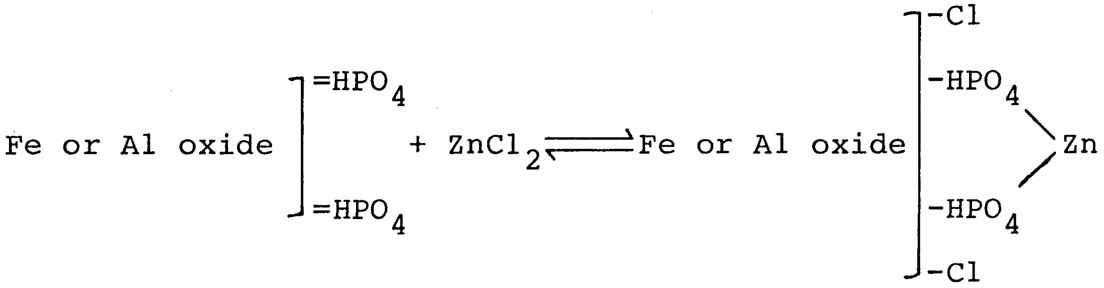


It is obvious from their study that specific adsorption involved the adsorption of Zn^{2+} and release of two H^+ ions for each mole of Zn^{2+} adsorbed and accounted for 60-90 percent of total Zn adsorption by Fe_2O_3. They further concluded that specific adsorption of Zn by Al_2O_3 and Fe_2O_3 may be responsible for the frequently reported fixation and unavailability of zinc added to soils. Elsokkary (1979) also reported that CEC, free Fe_2O_3 and clay content were the dominant soil variables contributing towards specific Zn adsorption.

Stanton and Burger (1967) mentioned from a study by the first author that various hydrous oxides of iron and aluminium can sorb zinc through the medium of adsorbed polyvalent phosphate ions, which has been postulated as follows:



$$\text{Fe or Al oxide}\left]\begin{matrix}=HPO_4\\ \\ =HPO_4\end{matrix}\right. + ZnCl_2 \rightleftharpoons \text{Fe or Al oxide}\left]\begin{matrix}-Cl\\ -HPO_4\\ \\ -HPO_4\\ -Cl\end{matrix}\right.\!\!\!\!\!\!\!\!\;\;\;\;\; \left.\vphantom{\begin{matrix}a\\a\\a\end{matrix}}\right\rangle Zn$$

They further suggested from their results that zinc bound to hydrated iron oxides in soil through this mechanism is unavailable to the plants.

1.2.4 Metals associated with organic matter

The role of organic matter in the reactions of metals has been studied and emphasized by many workers.

Hodgson (1963) suggested four ways to assess the contribution of organic matter to the chemistry of trace metals in soils:

(i) The association of organic matter content with the distribution and availability of metals in soils,

(ii) the effect of organic matter removal on the reactivity of soils with metals,

(iii) a direct attempt to assess the amount of an element present in the organic form, and

(iv) characterization of organic matter and its reaction sites.

He also observed three classes of systems distinguishing the reactions between organic matter and metals:

(i) Association between metals and high molecular weight organic compounds such as lignins which are essentially immobile and serve to immobilize metals associated with them,

(ii) association between metals and short-chain organic acids and bases which serve to promote the solubility and movement of metals and

(iii) formation of insoluble salts of metals with other complexing agents which appear to be soluble themselves.

Organic matter contributes significantly to the cation exchange capacity of soils and participates in metal ion binding by the functional groups involved. Hodgson (1963) reviewed some oxygen containing functional groups in a poorly drained podzol soil. The carbonyl (=C=O) groups in surface soil and carboxyl (-COOH) groups in subsoil were in great abundance. A series of phenolic and carboxylic acids were used as models by Lewis and Broadbent (1961a) who reported that copper was adsorbed as $CuOH^+$ by carboxyl groups, whereas the phenols complex the divalent cupric ion. Lewis and Broadbent (1961b), and Schnitzer and Skinner (1966) in their subsequent research, using actual organic matter extracts of soils did not clearly identify the forms of copper bound and did not confirm the importance of carboxyl and phenolic groups in binding copper to soil organic matter. An important aspect of the interaction between Cu, Fe, and Zn and organic matter complexes involving binding with fulvic acid, was reported by Schnitzer and Skinner (1966), who found the order of stabilities of the complexes formed was $Cu^{2+}>Fe^{2+}>Zn^{2+}$.

It is evident that metal ions can be strongly bound with organic matter. In general, copper is the most strongly bound. The stabilities of metal-organic complexes increase with the increase of pH, up to the point where the complexes break up. The log K (stability constant) of metal-organic complexes increased from pH 3.5 to pH 5.0, (Schnitzer and Skinner 1966,1967).

Lindsay (1972) observed two important ways by which organic matter can interact with zinc. First, soluble Zn can be mineralized and made available to plants. Second, zinc can be bound into organic constituents that are immobile in soils, constituting a fixation mechanism from which zinc is not readily released. Randhawa and Broadbent (1965) found at least three sites responsible for binding of zinc in humic acids. The least stable fraction of zinc was believed to be associated with phenolic (>OH) and weakly acidic carboxyl (-COOH) groups. The more stable fraction of zinc was linked to strongly acidic carboxyl (-COOH) groups, less than 1% of the zinc was strongly bound, but the importance of this fraction is that it represents a preferential binding of zinc. The log K (stability constant) values for Zn-fulvic acid complexes were 1.73 at pH 3.5 and 2.4 at pH 5.0, (Schnitzer and Skinner, 1966), indicating the increase in stability of complexes with the increase of pH. Shuman (1975) reported that soils high in organic matter had higher adsorptive capacities and higher binding energies for zinc than soils low in organic matter. Stevenson (1977) found that mixed complexes are formed, one being of phthalic acid type; other possible combinations include a COOH and a phenolic OH group binding of zinc by humic acid.

1.2.5 Metals associated with oxide materials

Secondary manganese oxides and iron oxides formed during the weathering process from primary minerals present reactive surfaces for the adsorption of metals. These oxides exist in soils, and have great ability to adsorb other trace metals. The metals adsorbed in this way are largely occluded as the precipitate continues to develop. Stanton and Burger (1967) reported that in the absence of phosphate ions, only the most strongly-crystalline hydrated iron oxides, such as goethite, fix zinc in soils against plant uptake. Iyengar, Martens and Miller (1981) reported that approximately 25% of total Zn was extracted with acid-ammonium oxalate indicating the association of Zn with soil sesquioxide, and about 15% of total copper occluded by free oxide was reported by McLaren and Crawford (1973a). Kalbasi and Racz (1978) also suggested that iron and aluminium oxides are major matrices for zinc in coarse, medium-to-fine and very fine textured soils. Cavallaro and McBride (1984) gave evidence that the oxide component of soil clay was more significant than the organic component in metal sorption and fixation, as pretreatment of the clays to oxidize organic matter by NaOCl did not decrease the metal sorption. Iu, Pulford and Duncan (1981) reported the oxide fraction is important under waterlogged conditions, providing high adsorptive capacity surfaces to bind Zn and Cu, as the result of breakdown of lattices due to the reduction of manganese and iron oxides. Shuman (1977) reported that Zn adsorption was 10 times greater for fresh iron and aluminium oxides (amorphous) than for aged oxides.

One of the major mechanisms of metal ion holding by oxides is specific adsorption, which has already been mentioned in Section 1.2.3. There has also been found an exchange of metal ions within lattice structures during adsorption. The zinc removed with ammonium oxalate under uv radiation was more closely associated with free aluminium oxides than with free iron oxides in the soils studied by Iyengar, Martens and Miller (1981). They explained this close association between ammonium oxalate-Zn and free aluminium oxide by some soil zinc being present in hydroxy-Al interlayers of 2:1 layer silicates, and that the zinc was released during partial dissolution of the interlayer material. McKenzie (1975) reported that cobalt was incorporated into the surface layers of the crystal lattice of manganese oxides, resulting in the release of manganese into soil solution.

Coprecipitation is considered another factor which binds the trace metals into the oxide lattice. Kalbasi and Racz (1978) observed that presence of iron and aluminium cations in solution markedly lowered the pH at which precipitation of zinc ions occurred, indicating that zinc was occluded and coprecipitated with iron and aluminium oxides.

1.2.6 Precipitates of metals

When the concentration of metals in soil solution reaches saturation point, they form precipitates by the association of certain anions, such as hydroxide, carbonate, phosphate, sulphate and sulphide. It is the way the oxides of these metals respond to change in pH, oxidation potential, and the presence of soluble complexing agents, which is important to the movement and availability of these metals to plants.

Knezek and Ellis (1980) stated that copper hydroxide forms readily in aqueous media if sufficient Cu^{2+} is present and the pH of the solution is increased.

Zinc hydroxide is so soluble that it is not considered to be an important compound in soil. Even at pH 8.0 more than 1 mg l^{-1} Zn^{2+} would exist in a solution in equilibrium with $Zn(OH)_2$. They also suggested that in acid media hydrogen ions react with reduced sulphur species to form the very stable H_2S. But under reducing conditions with pH values greater than 7.0, metal sulphides readily form. On examination of stability constants, they further claimed that CuS could readily form, ZnS and FeS would be intermediate and MnS would be the least likely to form of the four metal sulphides.

Singh and Sekhon (1977) reported that zinc at high applied concentrations (100 mg kg^{-1}) was probably precipitated as hydroxide by alkaline soil. Shuman (1977) observed that zinc precipitated as $Zn(OH)_2$ at pH 8.0, causing the sharp apparent increase in Zn adsorption by iron and aluminium oxides. Pulford (1986) suggested that the concentration of Zn in soil solution is controlled by a precipitation mechanism. Gupta, Elshout and Abrol (1987) claimed that precipitation reactions controlled the Zn solubility in alkali soil.

Some common minerals of copper and zinc are listed below:-

Cu: tenorite (CuO), malachite ($Cu_2(OH)_2CO_3$), azurite ($Cu_3(OH)_2(CO_3)_2$), chalcocyanite ($CuSO_4$), and cuperite (Cu_2O).

Zn: zincite (ZnO), smithsonite ($ZnCO_3$), franklinite ($ZnFe_2O_4$), willemite (Zn_2SiO_4), zinkosite ($ZnSO_4$), and hopeite ($Zn_3(PO_4)_2.4H_2O$).

The solubilities of these above mentioned minerals in relation to Eh and pH have been well explained by Lindsay (1979).

1.3 FACTORS AFFECTING THE AVAILABILITY OF TRACE METALS IN SOIL TO PLANTS

The degree of availability of trace metals is determined by the amount and forms of trace metals in soil and the ability of plants to absorb metals. There are various factors in the natural environment which contribute to the availability of metals, such as; pH, organic matter, microbiological activity, oxidation and reduction, rhizosphere activity and antagonistic reaction of metals.

1.3.1 pH

The solubility of minerals in soil is greatly related to the change in pH. The effect on solubilities of minerals has been well compiled by Lindsay (1979). He observed the activity of Fe^{3+} and Al^{3+} maintained by oxides decreases 1000-fold for each unit increase in pH, while the solubilities of most of the zinc minerals decrease 100-fold for each unit increase in pH. Copper and manganese have also been found to decrease in solubility as pH increases.

The adsorption sites on oxides and organic matter are pH dependent (Randhawa and Broadbent 1965, Shuman 1975, Sims and Patrick 1978, and Cavallaro and McBride

1984). Kinniburgh and Jackson (1982) reported that Zn adsorption on iron hydrous oxide gel is pH dependent. They claimed that Zn adsorption at pH 6.5 was about 10 times greater than at pH 5.5. Soluble Zn may increase at high pH (>7.5) as solubilized organic complexes are released into soil solution (Saeed and Fox 1977, and McBride and Blasiak 1979). Hargrove (1986) reported that Al-organic matter complexes may be solubilized in the pH range of 5 to 7 and may therefore be subject to plant uptake. Lagerwerff (1971) found that increasing soil pH from 5.9 to 7.2 resulted in decrease in trace metal content of radish. He suggested that this might have been due to a decrease in solubility and/or mobility of these metals.

The change of pH can also affect the availability of trace metals through microbial activities and chelate stabilities. Sims and Patrick (1978) reported that micronutrients (Fe, Mn, Zn, and Cu) adsorbed on cation exchange resin decreased as pH increased, while those adsorbed on anion exchange resin increased with pH. They suggested the covalently bonded hydrogen on the functional groups of organic matter fluctuated with pH, causing increase (at high pH) in sites of negative charge and more micronutrient complexes with organic matter. They also gave an alternative explanation that the microbial activity was greater at pH 6.0 and 7.5 than pH 4.5 causing greater alteration of soil organic matter with increases in reactive sites for metals. Schnitzer and Skinner (1967) listed the order of stabilities of soil fulvic acid-metal complexes. At pH 3.5 the order was $Ni^{2+} > Pb^{2+} > Co^{2+} > Mn^{2+}$, and at pH 5.0 the order changed to $Pb^{2+} > Ni^{2+} > Mn^{2+} \geq Co^{2+}$. They also reported all log K (log stability constant) values were higher at pH 5.0 than at pH 3.5, which can be ascribed to increased ionization of functional groups, especially carboxyls, with increase in pH. The log K values of complexes at pH 3.5 were 3.47, 3.09, 2.20, and 1.47, while at pH 5.0, values were 4.14, 6.13, 3.69 and 3.78 for Ni, Pb, Co and Mn respectively.

In spite of above mentioned effects, pH may alter plant uptake of metal through a change in the ability of the plant's roots to absorb ions, or to transport them to the tops once absorbed. Hodgson (1963) observed in the case of Cu, Zn and Co, the amounts of these elements extracted with chemical solvents varied more with soil pH than the amounts removed by plants. This is presumably due to an increased efficiency in the process of plant uptake at higher pH values.

1.3.2 Organic matter

Trace metal association with organic matter has been pointed out in section 1.2.4. Organic matter exists in soil in a dynamic equilibrium. Through chemical, enzymatic, and metabolic transformations, it is continuously subjected to polymerization and degradation processes, and thus more susceptible to changes in metal uptake than the inorganic soil fraction. Zunino and Martin (1977a) suggested that naturally-occurring soil organic matter binds metal ions, so that substantial losses by percolation of free metal ions and organic-metal complexes are avoided. In addition, soil organic matter saturated with metal ions may constitute the most important pool of trace metals available to biological systems.

The presence of organic matter may promote the availability of certain trace metals by supplying soluble complexing agents that maintain the metals in solution. On the other hand, some organic soils commonly show a deficiency of certain metals, e.g. copper. Loneragan (1975) reported that a mixture of humic acid and fulvic acid complexed manganese from oxides and hydroxides. Such reactions may be very important in keeping these metals in soluble forms in alkaline soils. Shuman (1986) reported that increasing of lime rates decreased the exchangeable Zn and increased organic fraction Zn and Mn. This increase in zinc and manganese in organic fraction as lime rates increased may be due to a greater ability of the organic matter to complex metals. This shows that pH does not influence metals in some fractions in the same manner as it does plant availability. Shuman (1986) also showed that iron decreased in both the exchangeable and organic fractions as lime rates increased. Albasel and Cottenie (1985) reported that the addition of lime reduced drastically the uptake of heavy metals, and the addition of chelating agents increased the uptake. MacLean (1974) reported the depressive effect of mulch and peat amendments in soils on zinc soluble in 0.01M $CaCl_2$

suggesting the formation of insoluble complexes of metal with humic acid. Whereas the corresponding, but favourable effect of alfalfa amendment, and of the high organic matter content of one of the soils used, supports the presence of soluble complexes of zinc.

1.3.3 Microbiological Agents

The availability of trace metals from organic matter mostly depends on the microbial activity, as metals are released by the decomposition of organic matter. The most important microbiological effects on the availability of trace metals involve the oxidation and reduction of iron and manganese. Hodgson (1963) reviewed five ways that microorganisms may affect the availability of metals in the soil:-

(i) Releasing inorganic ions during the decomposition of organic matter.

(ii) Immobilizing ions by incorporation into microbial tissue.

(iii) Oxidizing a metal, generally to a less available form.

(iv) Reducing oxidized form of a metal under limited oxygen conditions.

(v) Indirect transformations, changing pH or oxidation potential.

Zunino and Martin (1977b) reported that the microbial ecology of soil may markedly influence the maximum binding ability characteristics of the naturally occurring soil organic matter due to their effect on its formation or decomposition. They may strongly influence the metal translocation and availability in soils.

Changes in microbial activities during and after flooding greatly differ from the aerobic condition. Tate (1979) showed that activity decreased approximately 65 percent from the levels detected prior to flooding. Another effect of microbial activity under waterlogged conditions is that it uses organic or inorganic constituents as electron acceptors when oxygen is depleted. The reduced condition of a soil is almost entirely dependent on these reactions.

The microbial decomposition of organic complexing agents that serve to stabilize reduced forms of iron and manganese provides indirect means of promoting oxidation of these metals. Such decompostion can also cause the conversion of other metals to less available forms.

If the oxygen supply is decreased, soil microorganisms are forced to utilize weaker electron acceptors. The next strongest electron acceptor, nitrate, is reduced to N_2 and N_2O. After this has been exhausted, Mn(III-IV) and Fe(III) hydroxides can be reduced and $Mn^{2+}$and Fe^{2+} concentrations increase in soil solution. Under strong reducing conditions sulphate can be reduced to sulphur or sulphide, if the supply of the above electron acceptors is still inadequate, microorganisms can make use of some of the energy stored in organic compounds by reducing carbon to methane.

Zinc deficiency is often quite pronounced on old corral sites and barnyards. It is believed that rapid growth of microorganisms may at least temporarily tie up available zinc (Lindsay 1972). The effect of microorganisms on other trace metals is principally through decomposition of organic bound forms or through direct competition for nutrients.

1.3.4 Oxidation and reduction

Plant growth is greatly related to the state of oxidation or reduction in soils. In aerated soils, the process of oxidation is mainly that of addition of oxygen. When there is a shortage of oxygen the oxidation is the loss of electrons by a substance, while reduction is gain of electrons. Oxidation and reduction always occur together because a substance can only donate electrons if another substance can accept them. The tendency of a substance to gain or lose electrons, to be reduced or oxidized, can be measured by redox potential (Eh).

The oxidizing system will have relatively positive Eh values and reducing systems lower or negative Eh values. It also follows that for a given ratio of (Ox)/(Red), the lower the pH the higher the Eh value at which reaction occurs. Aerobic soils have Eh values between 0.3 and 0.8v, but reproducible values are only obtained in anaerobic soils, in which the potential ranges from 0.3 to -0.4v (White 1987).

Schwab and Lindsay (1983b) reported that manganese solubility was apparently controlled by manganese oxides at high redox and by $MnCO_3$ (rhodocrosite) at redoxes below pe + pH = 15 (pe=Eh/0.059v). Fe^{2+} activity is controlled by $FeCO_3$ (siderite) below pe + pH = 8 and by $Fe_3(OH)_8$ (ferrosic hydroxide) above pe + pH = 8 (Schwab and Lindsay 1983a).

Under waterlogged conditions of soil, the amount of soluble and exchangeable manganese and iron increased with decrease of redox potential (Gotoh and Patrick 1972, 1974). Iron reduction and consequent dissolution was favoured by reducing conditions and lower pH values. Whereas significant reduction of iron occurred at +300mv at pH 5, the redox potential had to fall to between +300mv and +100mv in order to result in reduction at pH 6 or 7. At pH 8, a redox potential of -100mv was necessary for iron reduction to occur. Sims and Patrick (1978) also reported that greater amounts of Fe, Mn, Zn, and Cu were found in either the exchangeable or organic fractions at low Eh than at high Eh. Metals occluded by oxides, hydroxides and in the residual fractions generally were greater at high than low Eh, hence indicating that micronutrients precipitated and occluded as oxides and hydroxides were solubilized by soil reduction. Iu, Pulford and Duncan (1981) observed that under waterlogged conditions, Eh decreased and acid soil pH values increased, resulting in a lowering of soluble, exchangeable and organically bound Zn and Cu. There were increases in the levels of these metals held by specific adsorption and by oxide materials, suggesting the breakdown of oxides of iron and manganese, providing surfaces with high adsorptive capacity for Zn and Cu.

Sajwan and Lindsay (1986) reported that under controlled redox conditions in the laboratory, decreasing pe + pH from 14.99 to 4.00 decreased the zinc content of rice plants from 39 to 9 mg kg^{-1}. This shows the effect of redox on the availability of metals to plants.

1.3.5 Rhizosphere activity

Plant roots can excrete a great variety of chemical substances, and alter their immediate chemical environment. These substances can affect the availability of metals through their influence on microorganisms or through a direct interaction with soil constituents. Bromfield (1958b) reported that the roots of both oat and vetch plants released substances which dissolved δ-MnO_2. The substances were readily decomposed by microorganisms; they became more effective as the pH fell below 7 and also as their concentration increased. Oat plants grown under sterile conditions on agar slopes were able to obtain manganese from manganese oxides, this and root washings of oat plants which dissolved manganese oxides are the evidence for these substances (Bromfield 1958a).

Brown, Holmes and Tiffin (1961) studied soyabeans which were both susceptible and non-susceptible to iron deficiency. They reported that iron-deficient, non-susceptible soyabean roots had more reductive capacity to reduce Fe^{3+} in solution than an iron-sufficient, non-susceptible variety and an iron-deficient susceptible variety. They further concluded that cutting off tops of the plants or placing them in the dark decreased the reductive capacity of the roots. More iron was absorbed by the chlorotic than non- chlorotic plants. Reuszer (1962) observed the presence in plant roots of exoenzymes capable of dephosphorylating certain organic phosphorus compounds, and gave a general discussion of how the chemical environment is altered by roots.

1.3.6 Antagonistic reaction of metals

All the above mentioned factors are considered to be mainly responsible for the changes in metal availability, but antagonistic reactions between metal ions can also be important. High concentrations of added ions could affect metal uptake. For example, addition of Ca to a test solution decreased the absorption of Zn, Mn and Cd, and also inhibited drastically the translocation of Mn and Zn, but accelerated the translocation of Cd in excised barley roots (Kawasaki and Moritsugu, 1987). Raya et al. (1974) reported low supply of iron increased manganese uptake and translocation, but excessive iron supply increased only manganese uptake.

At concentrations of $10^{-4}M$, both $FeCl_2$ and $MnCl_2$ depressed zinc uptake in roots and translocation to shoots in rice seedlings. Uptake was depressed to a lesser extent with calcium (Giordano, Noggle and Mortvedt 1974). This suggests that high solution concentrations of reduced Fe and Mn, which developed in paddy culture, may cause zinc deficiency. Sajwan and Lindsay (1986) also observed zinc deficiency in submerged paddy rice soils. From their study they explained that increased reduction and solubilization of iron and manganese had an antagonistic effect on the availability and uptake of zinc.

1.4 TYPES OF STUDY ON SOIL TRACE METALS

A lot of research studies have been directed towards the correlation of plant uptake of trace metals with soil content and their transformation in soil. These mostly depend on the ability to analyse different forms in which metals are held in soil and metals in plant tissues. If any one skill or area of expertise can be regarded as essential to the increased understanding of plant-metal interactions, it must be chemical analysis. There are different techniques and chemical methods for studying the trace metals in soils.

1.4.1 Selective extraction

Trace metals are held in the soil in different pools. McLaren and Crawford (1973a) distinguished five pools in which copper can occur in soil:
(1) in soil solution as ionic or complexed forms, (2) on exchange sites, (3) held in biological residues and living organisms, (4) occluded in soil oxide materials and (5) in the lattice structure of primary and secondary minerals.

The total amount of metal in soil is not directly correlated to nutritional aspects, because plants may take up just a small portion. Different pools of metal in soil have a different category of lability and bioavailability.

LeClaire et al. (1984) proposed that soluble, exchangeable and organic zinc pools are labile, inorganic zinc precipitates are quasilable and bioavailable, but the resistant mineral zinc pool is nonlabile and is not bioavailable.

For each pool of extractable metal many workers have used different types of extractants depending on the ability to extract certain types of metal from a wide variety of soils. Separation of various forms of metals in soils has been useful in studying the retention of metals by the soil and their release to the plant. Many and varied extractants for exchangeable trace metals have been used, since the amounts in this fraction are usually most closely related to plant uptake. Stewart and Berger (1965) found that 1M $MgCl_2$ solution was a suitable predictor of zinc uptake. Zinc concentrations in corn and in oats grown on different samples were best correlated with amounts extracted by 1M $MgCl_2$, acidic CH_3COONH_4, and 1M KCl (John 1974). More recently, Neilsen, Hoyt and MacKenzie (1986) reported that much smaller amounts of exchangeable zinc were extracted by M CH_3COONH_4 (pH 7.0) than by M $MgCl_2$ from acid soils. McLaren and Crawford (1973a), and Elsokkary (1979) used 0.05 M $CaCl_2$ for the extraction of exchangeable Cu and Zn. For exchangeable Cd, Zn and Ni, 1M CH_3COONH_4 was used by Soon and Bates (1982) and Mandal and Mandal (1986). Shuman (1985) used 1M $Mg(NO_3)_2$ for exchangeable ions instead of 1M $MgCl_2$ (Shuman 1979), while Miller, Martens and Zelazny (1986) used 0.5M $Ca(NO_3)_2$. Selvarajah, Pavanasasivam and

Nandasena (1982) used 1M CH_3COONH_4 (pH 4.6), 0.01M $CaCl_2$ and 0.2M $MgSO_4$ for the extraction of exchangeable Zn and Cu. They suggested that more zinc was extracted by the ammonium acetate (pH 4.6) than the other two salt solutions. This may be due to its acidic nature which made it able to extract some precipitated forms of zinc in paddy soils.

Metals specifically sorbed by inorganic sites also have a high correlation with plant uptake, although small amounts of metals are held in this fraction. McLaren and Crawford (1973a) reported very small amounts of solution-plus-exchangeable copper are present in soil, and suggested that these forms of copper are in equilibrium with specifically adsorbed forms constituting the bulk of the "available" copper reserves. This accounted for only 1 - 2 percent of the copper in 24 soils, representing a range of British soil types. The extractant used was 2.5% acetic acid. Elsokkary (1979) extracted more zinc than expected by acetic acid, and explained these higher levels probably resulted from the dissolution of some precipitated zinc. Under waterlogged conditions acetic acid extractable Zn and Cu increased with time, possibly because specific inorganic adsorption sites preferentially took up zinc and copper at the expense of the organic sites (Iu, Pulford and Duncan 1981). Selvarajah, Pavanasasivam and Nandasena (1982) used 0.05M HCl for this fraction of soil zinc and copper. John (1974) extracted more "plant available" Zn with Morgan´s solution (7% sodium acetate and 3% acetic acid, pH 4.8) than acidic ammonium acetate.

A wide variety of extractants have been used by many workers to extract the trace metals bound by organic sites. McLaren and Crawford (1973a) indicated that the bulk of "available" Cu reserves were in the organic fraction, extracted by 0.1M $K_4P_2O_7$. This reagent was also used for copper and zinc specifically sorbed by organic sites by Sims and Patrick (1978), Elsokkary (1979) and Miller, Martens and Zelazny (1986). Shuman (1983, 1985) proposed an alternative organic matter oxidant, and used sodium hypochlorite (NaOCl) pH 8.5 for the extraction of organic matter fraction Mn, Cu, Fe, and Zn instead of H_2O_2 (Shuman 1979). Lindsay and Norvell (1978) proposed an extractant consisting of 0.005M DTPA (diethylenetriaminepentaacetic acid), 0.1M triethanolamine and 0.01M $CaCl_2$ (pH 7.3) to extract plant available Zn, Fe, Mn and Cu in near neutral and calcareous soils. Haynes and Swift (1983) concluded from their study that the 0.005M DTPA soil test was not suitable for use over a wide range of soil pH values. It was also used for zinc by John (1974). McLaren, Lawson and Swift (1986a) used 0.4M di-sodium EDTA for organically bound cobalt extraction. Kennedy and Brown (1981) suggested HEDTA (hydroxyethylenediaminetriacetic acid) and DTPA were good chelators for zinc extraction from soils below pH 7.0, as did Norvell (1984). Murthy (1982) and Mandal and Mandal (1986) used 0.05M $(CH_3COO)_2Cu$ for zinc extraction in wetland and lowland rice soils. For Cd, Ni and Zn, 0.125M $(CH_3COO)_2Cu$ was used by Soon and Bates (1982).

In extracting the trace metals associated with oxides, or held by oxide materials, many extractants have been used. Shuman (1979) used a solution of 0.2M ammonium oxalate and 0.2M oxalic acid pH 3.0 for trace metals associated with hydrous iron oxide. Nielson, Hoyt and MacKenzie (1986) used this solution for iron and aluminium oxide associated Zn, and reported 1.3 to 15% of total Zn in this fraction in orchard soils. McLaren and Crawford (1973a) used acid oxalate (oxalic acid 0.1M, ammonium oxalate 0.175M, pH 3.25) for copper occluded by free oxides, while Levesque and Mathur (1986) used aqueous $CaCl_2$ + hydroquinone. Murthy (1982) used 0.2M acidified ammonium oxalate for Zn bound by amorphous sesquioxides and dithionite-citrate-bicarbonate for Zn bound by crystalline-sesquioxides. He extracted 1.8 to 6.8%, and 4.2 to 5.8% of total Zn respectively from wetland rice fields, and the same extractants were used by Mandal and Mandal (1986) who reported that 0.41 to 90% of the total Zn was extracted by citrate-bicarbonate-dithionite from lowland rice soils. Soon and Bates (1982) used 1M HNO_3 for occluded metals and precipitates such as oxides and carbonates.

Although the total concentrations of trace metals in the soil are not good indicators of their availability to higher plants, their distribution in the soil profile provides useful information towards the understanding of soil development and of nutrient cycling in the soil-plant ecosystem. Furthermore, the total concentrations can give a good guide to determine the percentage of the total amount in each individual pool of trace metals in soils. The major extracting methods used to determine the total concentration of trace metals are acid digestion methods. McLaren and Crawford (1973a) used hydrofluoric acid and perchloric acid digestion to extract copper from soil. Nakos (1983) for total concentrations of Mn, Zn, and Cu in certain forest soils also used the $HClO_4$-HF digestion method. Mills and Zwarich (1975) used nitric acid and perchloric acid to digest soil for total concentration of Cd, Cu, Ni and Zn. This was also used by Mandal and Mandal (1986) for total Zn.

1.4.2 Sequential extraction

Individual extracting solutions do not give good enough discrimination between the various pools of metal held by the soils, e.g. acetic acid which is normally used for extracting the specifically adsorbed metal, would remove soluble and exchangeable metal as well; ammonium oxalate would remove soluble + exchangeable + specific sorbed + organic metal forms + oxide fractions. To better understand the separate forms of trace metals held by the soil (Hodgson 1963, LeRiche and Weir 1963, and McLaren and Crawford 1973a), and also, the dynamics of how elements move from one chemical form to another in response to changing soil conditions, sequential extraction techniques can be used. In this extraction procedure the same soil sample is used for successive forms of metal extraction. Miller, Martens and Zelazny (1986) suggested that the sequential extraction methodology has a unique capability to describe these forms and monitor their potential transformation.

Sequential extraction schemes have not been standardized yet, and each worker uses his own scheme, or some modification to one developed by another. There are some early schemes which have been used as models for recent ones (LeRiche and Weir 1963, and McLaren and Crawford 1973a). Shuman (1979) proposed a fractionation scheme to find methods to distinguish chemical and physical forms of Zn, Mn, and Cu in soils. This scheme included exchangeable, organic matter, iron oxide, sand, silt and clay fraction for these metals. Neilsen, Hoyt and MacKenzie (1986) used the proposed fractionation scheme of Shuman (1979) to determine exchangeable Zn by 1M $MgCl_2$, zinc associated with organic matter by H_2O_2, iron and aluminium oxide associated by acidified ammonium oxalate (pH 3.0), residual Zn by aqua regia, $HF-HNO_3$ and HCl. Unlike the procedure of Shuman (1979), they determined residual Zn on the total residue following the iron and aluminium oxide zinc extraction, instead of partitioning into sand, silt and clay residual fractions. Shuman (1985) modified his sequential extraction procedure based on the earlier one (Shuman 1979), because he noted two problems with his previous scheme. The most obvious was that H_2O_2, used to extract the organic fraction, increased the manganese value of this fraction in soils having high amounts of manganese oxide, by dissolving some manganese oxides. This also caused the trace metals associated with manganese oxides to be released in the organic fraction. To overcome this problem, an alternative organic matter oxidant, NaOCl, was proposed by Shuman (1983). The second problem was crystalline iron oxides which could not be dissolved using dithionite. An alternative extractant, ascorbic acid and oxalic acid, for crystalline iron oxides has been proposed (Shuman 1982). In the new scheme Shuman (1985) used NaOCl for organic fractions and included two further fractions, the manganese oxides and the crystalline iron oxides. Miller, Martens and Zelazny (1986) suggested a sequential extraction scheme to characterize trace metals in agricultural, polluted, and waste amended soils. They extracted different forms of metals with the extractants as, soluble by H_2O, exchangeable by 0.5M $Ca(NO_3)_2$, acid soluble by 0.44M CH_3COOH + 0.1M $Ca(NO_3)_2$, manganese oxide occluded by 0.1M $NH_2OH.HCl$ + 0.1M HNO_3, organic bound by 0.1M $K_4P_2O_7$, amorphous iron oxide occluded by oxalate reagent, crystalline iron oxide occluded by oxalate reagent at 85°C under ultraviolet irradiation, and residual by aqua regia + HF. They also observed that $NH_2OH.HCl$ (acidified hydroxylamine hydrochloride) had little effect on organically bound metals, and should be used before $K_4P_2O_7$. Soon and Bates (1982) used a scheme for Cd, Ni, and Zn in polluted soils, using 1M CH_3COONH_4, 0.125M $(CH_3COO)_2Cu$ and 1M HNO_3 for extracting the soluble + exchangeable, organic bound, and chemisorbed or occluded metals and precipitates such as oxides and carbonates respectively. Iyengar, Martens and Miller (1981) used the scheme developed by McLaren and Crawford (1973a) with some modification for soil zinc extraction. They used 0.1M $NH_2OH.HCl$ in 0.01M HNO_3 for the extraction of Zn bound with manganese oxide in addition, before using acid oxalate. Sposito, Lund, and Chang (1982) used the sequential extraction scheme to estimate the quantities of Ni, Cu, Zn, Cd and Pb in exchangeable, sorbed, organic, carbonate, and sulphide forms for the soils amended with sewage sludge.

Murthy (1982) proposed a fractionation scheme of soil zinc in wetland rice soils, distinguishing four zinc fractions; (1) zinc in soluble organic complexes and exchange positions; (2) zinc in amorphous iron and aluminium oxides; (3) zinc in crystalline oxides of iron and aluminium; and (4) residual fraction, mainly in clay structures. He used copper acetate for the first, acidified ammonium oxalate pH 3 for the second, and dithionite- citrate-bicarbonate for the third fractions respectively. The residual fraction was found by the difference between total Zn and the sum of the above three fractions. Mandal and Mandal (1986) used a fractionation scheme for soil zinc in lowland rice soil with little modification of Murthy´s (1982) scheme. They used a separate extractant, ammonium acetate for soluble and exchangeable Zn fraction and copper acetate for the complexed Zn fraction. A flow chart of their scheme showing the sequence of extractions is represented in Figure 1.3, as an example of this type of procedure.

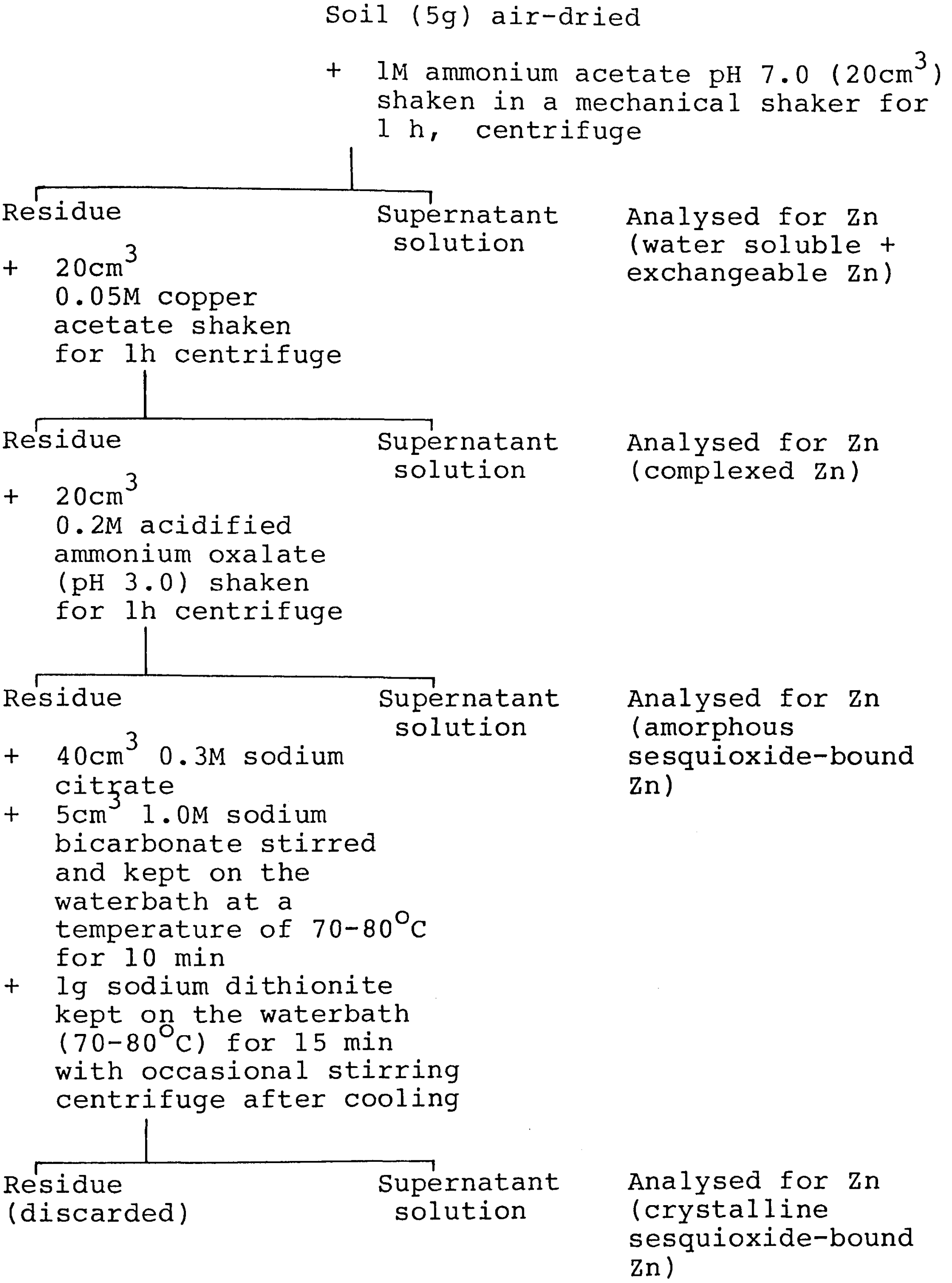


Figure 1.3 Flowchart showing the sequence of extractions made to partition different fractions of soil zinc. (Mandal and Mandal 1986).

1.4.3 Adsorption study

An adsorption study is done by putting the metal on to soil, which is the opposite of soil extraction. A known amount of metal in solution is equilibrated with known weight of soil, and the amount adsorbed determined by measuring the amount left in the solution. Adsorption simply refers to when a chemical species passes from one bulk phase to the surface of another, where it accumulates without penetrating the structure of the second phase (Burchill, Greenland and Hayes 1981). Sposito (1984) quoted that adsorption is the process through which a net accumulation of a substance occurs at the common boundary of two contiguous phases. An adsorption isotherm shows the amount of adsorbate (solute) sorbed as a function of its equilibrium concentration, and has been used for many years to investigate the nature of various types of adsorption phenomena. Shuman (1975) observed that the Langmuir adsorption isotherm was derived for the adsorption of gases on solids and has since been used also to describe the relationship between the adsorption of ions by a solid and the concentration of the ion in solution. The Langmuir equation which he presented is:

$$\frac{c}{x/m} = \frac{1}{kb} + \frac{c}{b}$$

where c = equilibrium concentration of adsorbate (mg l^{-1})

x/m = amount adsorbed (mg g^{-1})

b = adsorption maximum (mg g^{-1})

k = a constant related to bonding energy (l mg^{-1})

If adsorption conforms to the Langmuir equation, plotting c/(x/m) versus c yields a straight line with a slope 1/b and intercept 1/kb. The Langmuir constant k is the reciprocal of the slope (1/b) and the intercept (1/kb).

When the development of Langmuir adsorption equation was critically examined by Harter and Baker (1977), they concluded that the equation which soil scientists have been using is in the wrong form. The error is of no great importance when used to obtain a calculated adsorption maximum for comparison to other adsorbent properties. However it does become importamnt when used to understand adsorption dynamics and bonding strengths. The commonly reported curvilinear nature of the c/x/m vs. c plots was simply the result of not considering the effect of desorbed ions in the equilibrium solution. When the equation was corrected by considering desorbed ions, the isotherm became linear. In addition, the constant b of the Langmuir equation was not simply related to the bonding energy of the adsorbed ion, but to the ratio of adsorbed and desorbed ion bonding energies.

If data do not conform to the Langmuir equation, the less demanding Freundlich equation can often be used successfully. Bohn et al. (1985) mentioned that Freundlich found that adsorption data from many dilute solutions could be fitted to an equation of the form;

$$\frac{x}{m} = kc^{1/n}$$

where k and n are empirical constants and other terms are defined previously. The equation was originally empirical, without theoretical foundation. It implies, however, that the energy of adsorption decreases exponentially as the fraction of covered surface increases. The Langmuir equation, on the other hand, implies that the energy of adsorption on a uniform surface is independent of surface coverage. The Freundlich equation can be derived theoretically by assuming that the decrease in energy of adsorption with increasing surface coverage is due to surface heterogeneity. The linear form of the Freundlich equation is,

$$\log \frac{x}{m} = \frac{1}{n} \log c + \log k$$

The Freundlich equation has the limitation that it does not predict a maximum adsorption capacity. Despite its shortcoming, this equation is a common adsorption equation and is included in several models for predicting pesticide behaviour in soil. Many investigators have used this equation for zinc adsorption studies in soils as well as by iron hydrous oxide gel (Kuo and Mikkelsen 1979, Shukla and Mittal 1979, Kinniburgh and Jackson 1982, and Kurdi and Doner 1983).

In soil, adsorption is known to regulate the concentration of trace metal ions in soil solution. Trace metal adsorption study has great importance due to the increase in deficiency problems in some soils under certain conditions or the increasing toxicity problem by industrial activity and land application of sewage sludge in some areas. The adsorption of trace metals by soils has importance in determining their availability to the plant and their movement through the soil.

Many investigators have used different aspects for trace metals adsorption studies. Joshi (1986) used different textured arid soils for Cu adsorption study, and found that sandy loam soils have higher values of adsorption maxima and bonding energy constants than sandy soils. Zinc adsorption studies on calcareous and alkaline soils, in which zinc deficiency is the most common problem, have been conducted by Udo, Bohn and Tucker (1970), Kuo and Mikkelsen (1979), and Singh and Abrol (1985) and by acid soils, in which the toxicity of trace metals is a greater problem to plants, by Saeed and Fox (1977), McBride and Blasiak (1979), Kuo and Baker (1980), and Cavallaro and McBride (1984).

Some have used this approach to study the influence of pH, which is very important to trace metal adsorption, and determined a decrease in Zn solubility with increasing pH (Shuman 1975, Saeed and Fox 1977, McBride and Blasiak 1979, Harter 1983, and Gupta, Elshout, and Abrol 1987). Bruemmer et al. (1983) reported that below pH 7 zinc concentration in soil solution is controlled by adsorption -desorption reactions with soil clay and whole soils. The adsorption of trace metals on solid phase surfaces, such as clay minerals and hydrous oxides, particularly iron and aluminium oxides, have been studied by Bingham, Page, and Sims (1964), Kinniburgh, Jackson, and Syers (1976), Shuman (1976, 1977), Kalbasi, Racz, and Loewen-Rudgers (1978), and Inskeep and Baham (1983).

Shuman (1975) reported that zinc adsorption data for four soils conformed to the Langmuir adsorption isotherm, when the curves were resolved into two linear portions representing two different types of adsorption site. He also observed that the adsorption sites for the lower part had very high bonding energy coefficients and low adsorptive capacities compared with the adsorption sites of the part of the curve corresponding to higher zinc concentration in the equilibrium solution. Pulford (1986) using different salts as background electrolytes for zinc adsorption by seven soils also described the split Langmuir isotherm in the same way as Shuman (1975).

Many researchers used this type of study to see the effects of different anions present in the equilibrating solution and the ionic strength of that solution. Kinniburgh and Jackson (1982) used a 1M $NaNO_3$ solution as background electrolyte for Zn adsorption by iron oxides, and Shuman (1986) used 0.005, 0.01, 0.05 and 0.1M $NaNO_3$ for Zn adsorption by soils. Shuman (1986) also used different anions, SO_4^{2-}, Cl^- and NO_3^- at an ionic strength of 0.01M for all the anions with Na^+ as the cation. He observed that Zn adsorption using NO_3^- at ionic strengths of 0.005 and 0.01M was the same, but the adsorption at 0.05 and 0.1M was lower than for the other ionic strengths. The SO_4^{2-} ion produced higher adsorption than NO_3^- or Cl^- ions which yielded the same isotherm at pH 6.0. Elrashidi and O´Connor (1982) found no differences in Zn^{2+} adsorption on a sandy loam soil at pH 7.6 using

Cl^-, NO_3^- and SO_4^{2-} anion species. Singh and Abrol (1985) used saturated soils with 1M NaCl and 0.5M $CaCl_2$ for Zn adsorption, and observed that Zn adsorption for Ca-saturated soil followed the Langmuir isotherm up to an equilibrium concentration of 20 µM for the lower part and 62 µM for the upper part of the curve, whereas for an Na-soil the Langmuir isotherm was a single curve up to 42 µM. At low levels of zinc application, Ca-soil adsorbed 2.7 times less zinc, though held with higher affinity, than at higher zinc concentrations and 1.7 times less than that of Na-soil.

1.4.4 Solution/Precipitation study

Precipitation is simply an accumulation of a substance to form a new bulk solid phase (Sposito 1984). This is one of the mechanisms which controls the movement of the trace metals in soil solution.

Shuman (1975) in his study on the pH influence on Zn adsorption, observed that at pH 8.0 for all sandy and high clay soils within each depth the retention of zinc was similar. He assumed that chemical precipitation took place and that the retention of zinc was due to fixation as a solid rather than to soil adsorption. At the same pH value zinc probably precipitated as $Zn(OH)_2$ causing the sharp apparent increase in Zn adsorption by iron and aluminium hydrous oxides reported by Shuman (1977). Shukla and Mittal (1979) showed that a very high adsorption maximum value in part II, compared to part I, of the Langmuir isotherms, even for a sandy soil, might be attributed to predominantly precipitation reaction instead of adsorption. The pH of both the soils used was above 8.0 which could have favoured precipitation of zinc as $Zn(OH)_2$ at high equilibrium zinc concentrations.

Precipitation - dissolution reactions of zinc are more likely at pH values above 7.0 (Udo, Bohn, and Tucker 1970, and Bruemmer et al. 1983). Lindsay (1979) suggested that franklinite ($ZnFe_2O_4$) could control the zinc solubility at pH values found in most soils. Sadiq and Enfield (1984a,b) produced models of various nickel minerals in soils and they confirmed by their experimental data the formation of nickel ferrite ($NiFe_2O_4$) in various soils. Pulford (1986) also suggested from his study that precipitation is a mechanism for controlling zinc concentration in soil solution if iron is not ignored. Singh and Abrol (1985) suggested that zinc solubility at pH higher than 7.9 was controlled by precipitation of zinc as $Zn(OH)_2$ or $ZnCO_3$ in sodic soils. It is also obvious from the study of Gupta, Elshout, and Abrol (1987) that at high pH value precipitation reaction controlled zinc solubility.

1.5 AIMS OF PROJECT

The main objective of this project is to understand better the chemistry and behaviour of trace metals regarding their distribution and solubility in the soil and availability to plants. Zinc was used as a study example for trace metals through the use of selective extraction and adsorption studies.

A pot experiment as well as field experiment studies were carried out to see the effect of plant growth and seasonal changes on the distribution of zinc in various soil pools by using different extractants.

CHAPTER 2

SELECTIVE EXTRACTION PROCEDURES FOR MEASUREMENT OF SOIL ZINC

2.1 INTRODUCTION

Knowledge of the total amount of zinc in soil provides only limited information as this can seldom be correlated with availability to plants and does not show how the zinc is bound in the soil. The soil zinc may be present (Hodgson 1963);

(i) in soil solution as ionic or organically complexed species;

(ii) on exchange sites of reactive soil components;

(iii) complexed by solid phase organic matter;

(iv) occluded in oxides and hydroxides of Al, Fe and Mn;

(v) entrapped in primary and secondary minerals.

Various extractants have been proposed for estimating the zinc bound in different soil forms and have been discussed in Section 1.4.1.

Different investigators used various extractants to study the different aspects of soil zinc. Zinc in the soil has different categories of lability and bioavailability. The soluble, exchangeable, and organic zinc pools are labile and bioavailable, but the resistant mineral zinc pool is non-labile and is not bioavailable (LeClaire et al. 1984). Several extractants have been used to estimate the plant available zinc in soils. John (1974) examined 27 samples from different horizons of Canadian soils for extractable zinc with 0.1M $CaCl_2$, acidic 1M CH_3COONH_4 (pH 4.8), Morgan's solution (7% sodium acetate, 3% acetic acid) and DTPA ((0.005M DTPA, 0.1M TEA, 0.01M $CaCl_2$), and obtained an average of 0.69, 1.64, 1.99, and 3.77 mg kg^{-1} Zn respectively. Haq, Bates, and Soon (1980) extracted zinc from 46 surface mineral soils of southern Ontario, an average of 0.1, 5.9, 67, 57, and 48 mg kg^{-1} by using H_2O, CH_3COONH_4, CH_3COOH, EDTA and DTPA extractants respectively.

The same extractants may not be suitable for soils of different physico-chemical characteristics. All the extractants cannot be used for routine analysis. Extraction of zinc with DTPA + $CaCl_2$ has been used by Lindsay and Norvell (1978) for near-neutral to calcareous soils and by Gupta and Mittal (1981) for non-calcareous soils. Gupta and Mittal (1981) suggested the use of 0.1M HCl as it was cheaper than DTPA + $CaCl_2$. HEDTA + calcium acetate pH 6.0 (Kennedy and Brown 1981) has been proposed for extracting plant available zinc for soils below pH 7.0.

Instead of individual extraction of zinc from a specific pool, many researchers have proposed various sequential extraction schemes. Sequential extraction techniques are being utilized to define chemical forms of elements in soils. There is no perfect scheme to extract zinc from various soil pools, because each researcher uses his own scheme or some modification of one developed by another. Various sequential extraction schemes used by different investigators have been well described in Section 1.4.2. Shuman (1979) reported an average of 14.0, 14.1, and 41.0 mg kg^{-1} soil Zn in exchangeable, organic and iron oxide fractions respectively by using a sequential extraction scheme. Neilsen, Hoyt and MacKenzie (1986) using a sequential fractionation scheme observed that, of the total zinc, 0.3 - 23.2% was in the exchangeable fraction, 0.5 - 29.7% associated with organic matter, 1.3 - 15% associated with iron and aluminium oxides and 45.6 - 92% in the residual fraction. Mandal and Mandal (1986) reported 0.26, 0.74, 1.58, 0.71 and 90% of the total Zn was water soluble plus exchangeable, organically complexed, amorphous sesquioxide, crystalline sesquioxide, and residual Zn fraction respectively in lowland rice soil.

Most of the work has been done regarding zinc extraction by various extractants and by using different sequential extraction schemes, but a few attempts have been made to study the extraction of zinc under moist and air-dried conditions, as well as the seasonal effect on the different extractable zinc pools in soil. Rule and Graham (1976) measured labile pools of zinc using DTPA under both air-dried and field moist conditions, and found that there was a slight increase in extractable Zn in air-dried compared to moist soil. The extractability of zinc in soils varies considerably from one part of the year to another. The majority of information on this subject comes from seasonal fluctuations of plant composition. Seasonal changes are accompanied by variations in microbial activity, moisture, and temperature which can affect the decomposition of organic matter (Hodgson 1963).

Work in this chapter mostly concentrates on selective extraction, by using different extactants as individual extraction methods and sequential extraction schemes as a means of bringing soil zinc into solution before analysis by atomic absorption spectrophotometry. Some selective extractants are used to study the seasonal effect using Dreghorn (Arkleston) field soil on the extractability of Zn in various soil pools, and also used for air-dried and fresh soil zinc bound in different soil forms.

2.2 CHARACTERISTICS OF STUDY SOILS

The following five soils were used which provided a wide range of pH, organic matter, clay, and iron oxide contents (Table 2.1):

1. Dreghorn (Auchincruive)
2. Dreghorn (Arkleston)
3. Midelney (topsoil)
4. Midelney (subsoil)
5. Zn contaminated soil

Table 2.1 Properties of test soils

Soil Series	pH water[1]	pH $CaCl_2$[1]	% LOI[2]	% Clay[3]	% iron oxide[4]
1. Dreghorn (Auchincruive)	5.8	4.8	5.0	8.1	0.40
2. Dreghorn (Arkleston)	5.6	4.8	5.0	15.7	0.39
3. Midelney (topsoil)	7.4	7.0	8.4	40.4	0.59
4. Midelney (subsoil)	8.0	7.5	3.2	53.0	0.41
5. Zn contaminated soil	6.3	5.6	10.1	24.4	0.82

1. pH measured in given solution at given ratio using a combination pH electrode.
2. Loss on ignition, 450°C for 6h.
3. Clay content measured by pipette method.
4. Oxalate extractable iron oxide, measured by oxalate extraction described in Section 2.4.1.

2.3 ANALYSIS

For all experimental studies regarding this project, the zinc and iron concentrations in the adsorption study, and zinc in the extraction study were determined by using flame atomic absorption spectrophotometry (Perkin-Elmer 370A and 306). For zinc determination the wavelength used was 213.9 nm and slit setting at 0.7 nm, and for iron, the wavelength was 248.3 nm and slit setting at 0.2 nm. Two separate hollow cathode lamps were used as light sources by setting to their recommended maximum current. The air-acetylene flame was used for all zinc and iron determinations. All zinc and iron measurements were made by using their standards ranging from 0 - 1.5 mg Zn l^{-1} and 0 - 5 mg Fe l^{-1} respectively. All dilutions of standards and samples were made up in the appropriate extracting solution or background electrolyte in adsorption study to overcome the background interferences.

2.4 EXTRACTION OF ZINC FROM VARIOUS SOIL POOLS BY USING DIFFERENT EXTRACTANTS

2.4.1 Method

Soils 1 to 4 (Table 2.1, Section 2.2) were used in this experiment. 5 g of each air-dried soil was weighed in 4-ounce glass bottles, using four replicates, and 50 cm^3 of extractant was added to each bottle, and shaken for 18 hours by using end-over-end shaker at room temperature. Two blanks having no soil were also run along with samples for each extractant. The suspensions were filtered through Whatman filter paper no. 40, size 15.0 cm, and filtrates were collected in 100 cm^3 polyethylene bottles to measure zinc in the extracts. The reagents used were all of analytical grade. The following extractants were used for extracting specified forms of zinc:

(i) H_2O (deionized water): water soluble.

(ii) 0.05M $CaCl_2$: Soluble + Exchangeable.

(iii) 1M ammonium acetate (pH 7.0): Soluble + Exchangeable.

(iv) 2.5% acetic acid: Soluble + Exchangeable + Adsorbed.

(v) 0.5M ammonium acetate/0.5M acetic acid (pH 4.8) (modified Morgan´s solution): Soluble + Exchangeable + Adsorbed.

(vi) 0.05M NH_4EDTA (pH 7.0): All above pools + Organic.

(vii) 0.1M $Na_4P_2O_7$ (sodium pyrophosphate): All above pools + Organic.

(viii) Acid oxalate (0.1M oxalic acid, 0.175M ammonium oxalate pH 3.25) (Tamm´s solution): All above pools + Free oxide.

(ix) Acid mixture (H_2SO_4 + HNO_3): Total Zn.

For the determination of total Zn an acid mixture was used to dissolve the sample. The air-dried soil samples were ground very finely with an agate (zinc free) mortar and pestle. 100 mg of each sample, in duplicate, were placed in the acid-washed teflon dissolution bombs with screw tops. 5 cm^3 Aristar H_2SO_4 and 4 cm^3 Aristar HNO_3 were added to these bombs. The bombs were sealed with screw lids and kept at 200^0C for 2.5 hours over the sandbath, then removed and thoroughly cooled. Approximately 20 cm^3 of deionized water was added to each bomb and the digest filtered through Whatman filter paper no. 50, size 11.0 cm, into 50 cm^3 volumetric flasks, and then the volume was made up to the mark with deionized water. Two blank solutions containing only the acids were made with the same procedure and analysed together with the samples.

Zinc standards were made in each separate extractant to reduce the effect of background electrolyte, while for total zinc determination, standards had the same volume of acids included.

The objective of this experiment was to select extractants for extractable Zn from exchangeable, adsorbed and organic pools.

2.4.2 Results and discussion

The mean values of extractable Zn as well as total Zn for the four soils with respect to each extractant are given in Table 2.2.

Table 2.2 Mean content of extractable zinc (oven dry basis) with various extractants

mg kg^{-1} (sd),
and % of total Zn

Soil Series	H_2O	$CaCl_2$	ammonium acetate	acetic acid	Mod Morgan´s solution	NH_4EDTA	$Na_4P_2O_7$	acid oxalate	Total Zn
Dreghorn (Auchincruive)	0.206 (0.0) 0.27%	0.31 (0.0) 0.40%	0.33 (0.05) 0.43%	4.58 (0.11) 5.94%	3.16 (0.13) 4.10%	6.66 (0.19) 8.64%	6.76 (0.24) 8.77	14.25 (0.35) 18.49%	77.05
Dreghorn (Arkleston)	0.33 (0.05) 0.26%	4.65 (0.06) 3.64%	1.25 (0.05) 0.98%	16.37 (0.10) 12.82%	10.2 (0.10) 7.99%	16.4 (0.10) 12.84%	25.2 (0.10) 19.74%	49.4 (0.25) 38.69%	127.68
Midelney (topsoil)	0.21 (0.0) 0.19%	0.42 (0.0) 0.37%	0.26 (0.06) 0.23%	3.49 (0.26) 3.09%	2.94 (0.09) 2.60%	9.37 (0.20) 8.29%	9.50 (0.20) 8.40%	18.7 (0.17) 16.54%	113.03
Midelney (subsoil)	0.00	0.00	0.00	0.78 (0.0) 0.81%	0.7 (0.06) 0.73%	1.85 (0.06) 1.92%	2.1 (0.05) 2.18%	10.9 (0.12) 11.32%	96.25

Although water extractable Zn is associated with Zn^{2+} which determines the immediate bioavailability (LeClaire et al. 1984), due to the very low concentrations in this pool most investigators combine water soluble Zn with the exchangeable fraction. It is clear from Table 2.2 that zinc values in the water extractable fraction are very small, ranging from 0.00 - 0.33 mg kg^{-1}, while Haq, Bates and Soon (1980) reported the water soluble Zn in contaminated soils from 0.00 - 3.38 mg kg^{-1}.

The values of zinc (Table 2.2) indicate some difference within the same pool extracted by two different types of extractant. Student´s t test was applied to the data given in Table 2.2 to compare two different extractants used for the same pool of zinc; ie. calcium chloride versus ammonium acetate; acetic acid versus modified Morgan´s solution; and NH_4EDTA versus sodium pyrophosphate.

This test showed that $CaCl_2$ extractable Zn was significantly higher than ammonium acetate for Dreghorn (Arkleston) and Midelney (topsoil), but non-significant for Dreghorn (Auchincruive) and Midelney (subsoil). It is known that soil prefers to hold divalent cations than monovalent cations, hence Ca^{2+} ion, being alike in charge to the zinc ion, might more readily displace the exchangeable zinc from the soil than the NH_4^+ ion. The presence of chloride ions in the solution, which would promote formation of soluble $ZnCl_2^0$ (John 1974), is the second reason for getting the higher values of extractable Zn with $CaCl_2$. These factors give good support for further experimental use of $CaCl_2$.

Acetic acid extracted significantly higher amounts of zinc than the modified Morgan´s solution for all four soils. The comparison of acetic acid and modified Morgan´s solution extractable Zn confirmed that a significant increase in the amount of zinc extracted with acetic acid is due to its acidic nature. These results agree with John (1974) who reported that 0.05M HCl, 0.0125M H_2SO_4 solubilized and removed more zinc, averaging 3.37 mg kg^{-1}, from soil due to its higher acidic nature than Morgan´s solution, (7% sodium acetate, 3% acetic acid), which extracted an average zinc value of 1.99 mg kg^{-1}. This evidence makes the acetic acid extractant the preferred one to use for further work.

The amount of sodium pyrophosphate extractable Zn was significantly higher than NH_4EDTA for Dreghorn (Arkleston) and Midelney (subsoil), but non-significant in the case of Dreghorn (Auchincruive) and Midelney (topsoil). The extractable Zn for Dreghorn (Arkleston) soil with $Na_4P_2O_7$ averaged 25.2 mg kg^{-1} which was much higher than with NH_4EDTA which averaged 16.4 mg kg^{-1}. This might be due to the dissolution of some oxide bound Zn, as the amount of acid oxalate extractable Zn for this soil (Arkleston) was high compared to the other three soils. This increase in $Na_4P_2O_7$ extractable Zn may relate to the high amount of free oxide bound Zn in the Dreghorn (Arkleston) soil, which may be a result of industrial pollution, as this soil is found close to a motorway and an industrial site. In the case of Midelney (subsoil) this difference is attributed to low levels of organic matter present. To remove organically bound metals, hydrogen peroxide (H_2O_2), pyrophosphate ($K_4P_2O_7$), and sodium hypochlorite (NaOCl) have been used by various investigators (Sims and Patrick 1978, Shuman 1979, 1983 and 1985, Iyengar et al. 1981, and Miller et al. 1986). Peroxide and hypochlorite both partially dissolve manganese oxides (Shuman 1983), and cause microelements associated with these oxides to be released with the organic fraction (Shuman 1985). The partial dissolution of manganese oxides by $K_4P_2O_7$ has been reported by Iyengar et al. (1981). McLaren, Lawson and Swift (1986a) used EDTA and $Na_4P_2O_7$ for organically bound cobalt, and also reported that at least some of the pyrophosphate extractable manganese is derived from easily reducible inorganic forms, using their comparative study of extractable Co, Mn and Fe by various extractants. Sodium pyrophosphate ($Na_4P_2O_7$) also dissolves some iron oxides (Shuman 1982). Haq, Bates and Soon (1980) reported greater mean values for extractable Zn (57 mg kg^{-1}) with EDTA than DTPA (48 mg kg^{-1}). While DTPA dissolved some iron and aluminium oxides and caused the release of some zinc from these oxides (Jahiruddin et al. 1986), EDTA was reported as a good chelator extractant for metals (Norvell 1984).

The difference in extractable Zn between the two extractants, and above evidence about dissolution of some oxides by different workers, made NH_4EDTA the preferable extractant to use for organically bound Zn.

Most workers used acid oxalate (Tamm's solution) for the extraction of free oxide bound metals. Elsokkary (1979) for zinc, reported the value in this fraction ranging from 10.00 - 21.75 mg kg^{-1} Zn in alluvial soils. Haq, Bates and Soon (1980) reported 6 - 191 mg kg^{-1} extractable Zn with acid oxalate in contaminated soils. The mean results in Table 2.2 for extractable Zn with acid oxalate ranged from 10.9 - 49.4 mg kg^{-1}, indicating a large amount of zinc is present in this fraction.

Total soil Zn is not directly related to plant availability, but its determination can provide knowledge about soil development, and also useful information for the distribution of soil zinc within different soil pools on a percentage basis. The results in Table 2.2 revealed the total concentrations in four different soils, extracted by using H_2SO_4-HNO_3 mixture, ranged from 77.05 - 127.68 mg Zn kg^{-1}. Elsokkary (1979) used HNO_3-$HClO_4$ mixture for total Zn and reported 39.15 - 98.50 mg Zn kg^{-1} in 29 Egyptian alluvial soils. Archer and Hodgson (1987) also used the HNO_3-$HClO_4$ acid mixture for total trace metal determination of soils in England and Wales, and reported total Zn values ranged from 3.9 to 975.0 mg kg^{-1}. Iyengar et al. (1981) reported total Zn 19 - 160 mg kg^{-1} after digesting 19 different soils in an aqua-regia/HF mixture. The total concentrations in different horizons of 26 soils of southern Ontario in HNO_3-$HClO_4$ and HF mixture (Whitby, Gaynor and MacLean 1978), were reported ranging 40 - 163 mg kg^{-1}, 35 - 140 mg kg^{-1} and 40 - 128 mg kg^{-1} Zn for Ap, B and C horizons respectively.

It is obvious from this study that every pair of extractants used for zinc extraction from the same soil pool either had different extracting ability or affected the other pools as well as their specific pool. The following extractants, in addition to H_2O, acid oxalate (Tamm´s solution pH 3.25), and acid mixture (H_2SO_4 + HNO_3), were selected for future work on the basis of giving good results and also having good support from the above discussion, i.e. 0.05M $CaCl_2$ for exchangeable Zn, 2.5% acetic acid for specifically adsorbed Zn, and 0.05M NH_4EDTA (pH 7) for organically bound Zn in soils.

2.5 SEQUENTIAL EXTRACTION PROCEDURE FOR ZINC

2.5.1 Method

Two soils, Dreghorn (Auchincruive) and Midelney (topsoil), were used with four replicates for the extraction of zinc by sequential extraction procedures, which are given in the following flow diagrams, Figures 2.1 and 2.2.

For exchangeable Zn, 10 g air-dried soil was extracted by using two extractants, 20 cm^3 of 0.05M $CaCl_2$ or 20 cm^3 of 1M CH_3COONH_4 (pH 7.0) as two separate sets. After shaking for 18 hours using end-over-end shaker at room temperature, the suspensions were filtered through Whatman no. 40 filter papers. The solutions from both extractants were preserved for zinc measurement in 100 cm^3 polyethylene bottles. Soil residues, after washing with deionized water, were carried through the acetic acid and ammonium acetate/acetic acid (modified Morgan's solution) extractions respectively.

Specifically adsorbed Zn was extracted from the soil residue after $CaCl_2$ extraction by 50 cm^3 2.5% acetic acid, and the residue after 1M ammonium acetate (pH 7.0) extraction by 50 cm^3 modified Morgan's solution (0.5M ammonium acetate, 0.5M acetic acid, pH 4.8). After 18 hours shaking using end-over-end shaker, the suspensions were filtered through Whatman no. 40 filter papers into 100 cm^3 polyethylene bottles. The residues of soil were discarded.

For organically bound Zn extraction, 5 g of air-dried soil was shaken for 18 hours with 50 cm^3 of 0.1M $Na_4P_2O_7$ or 0.05M NH_4EDTA as two separate sets. Then the suspensions were filtered and preserved for measurement of zinc as before.

Zinc bound with free oxides in the residue from pyrophosphate and EDTA extractions were extracted by 50 cm^3 Tamm's oxalate (pH 3.25) solution, with 18 hours shaking by end-over-end shaker. The suspensions were filtered through Whatman filter paper no. 40, then solutions were collected in 100 cm^3 polyethylene bottles for zinc measurement. The residues of soil were discarded. Two blanks having no soil were also run with samples for each extraction. All zinc standards were made with the different extractants used for sequential extraction, for measuring zinc in the different extracts by flame atomic absorption spectrophotometry.

The aim of this experiment was to see the residual effect of different types of extractants on the extractability of zinc.

Figure 2.1 Flow diagram for the sequential extraction method

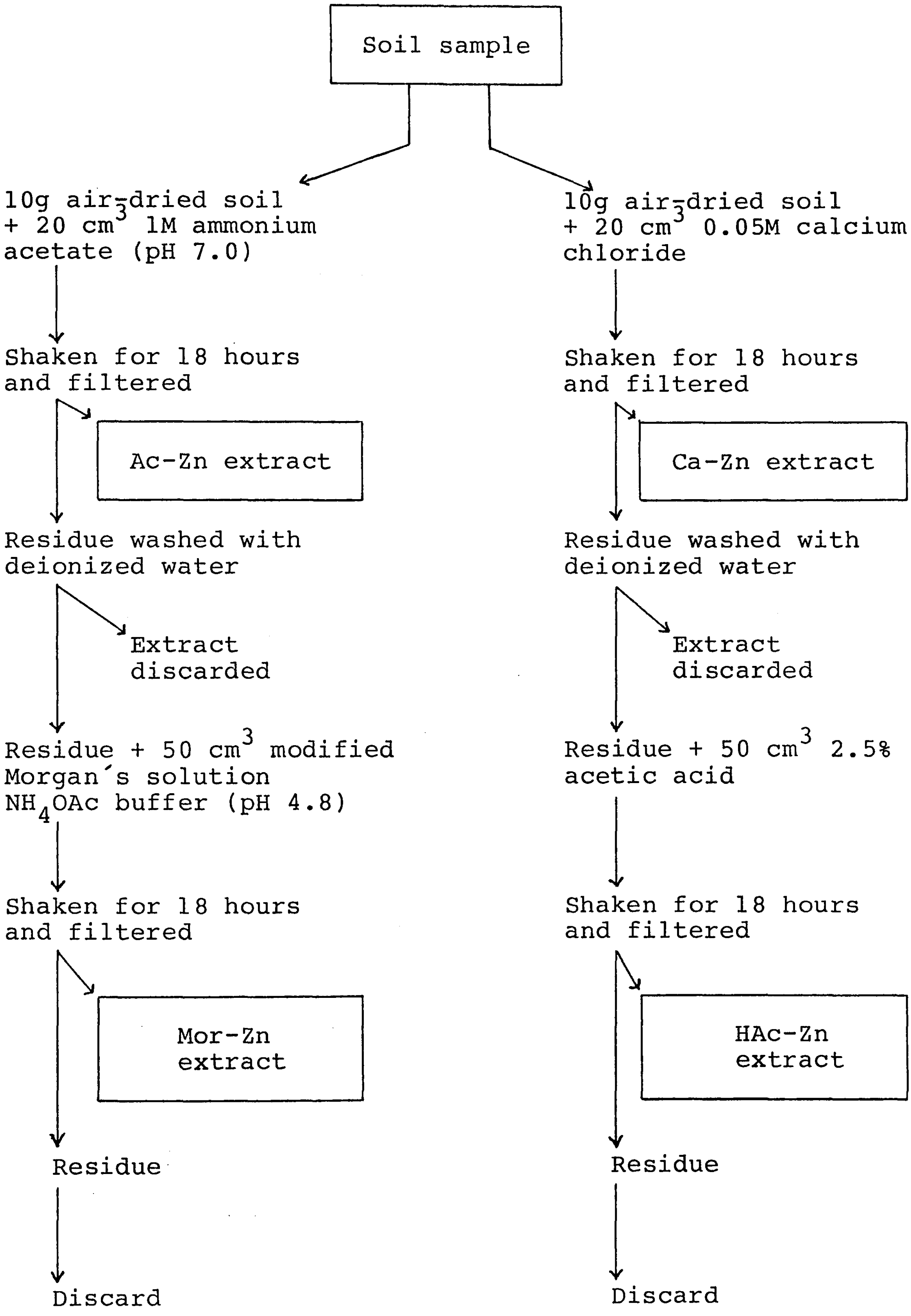
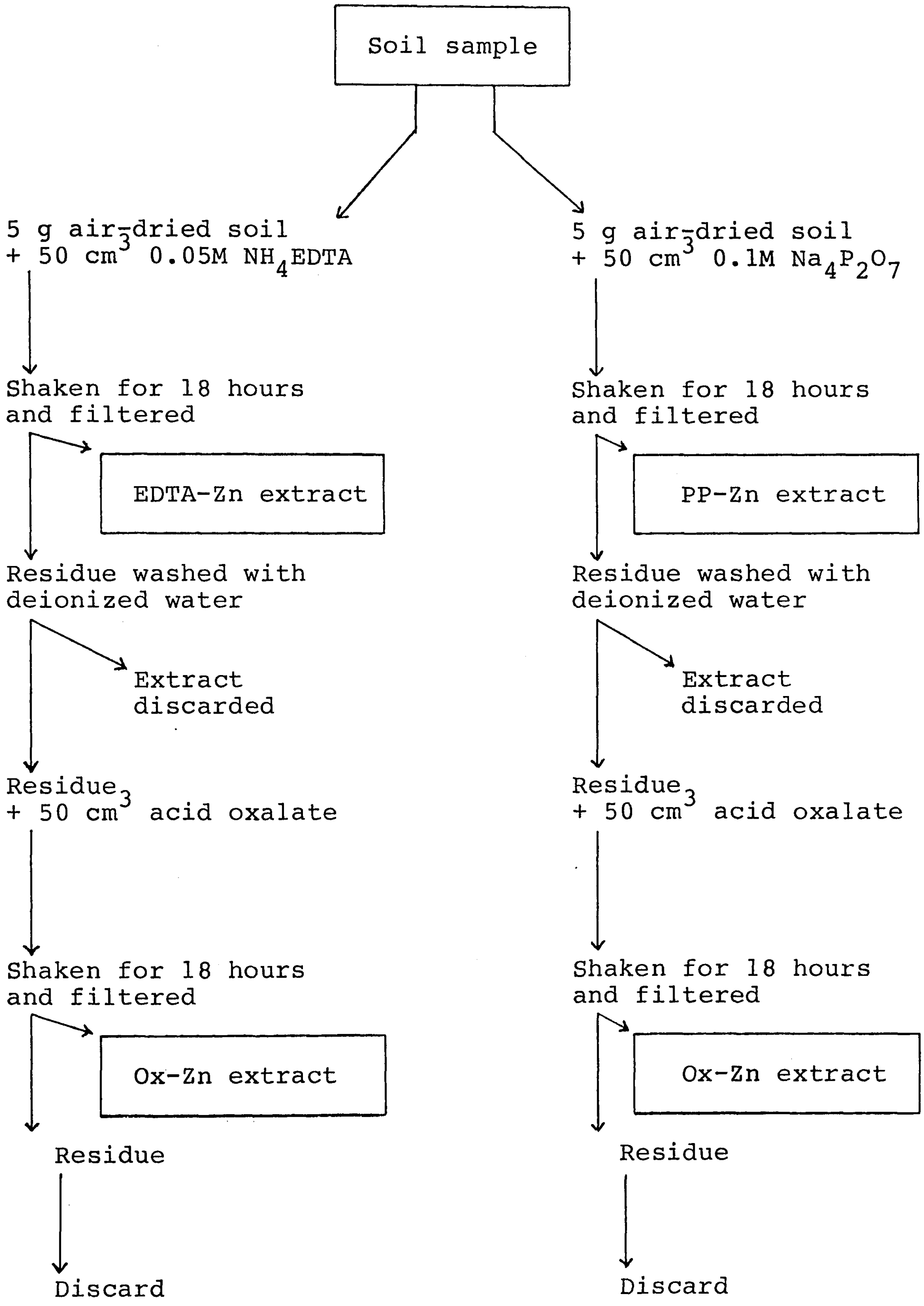


Figure 2.2 Flow diagram for the sequential extraction method



2.5.2 Results and discussion

Exchangeable Zn extracted by 0.05M $CaCl_2$ was 0.19 mg kg^{-1} (Dreghorn) and 0.22 mg kg^{-1} (Midelney) (Table 2.3). These figures represent 0.25% and 0.19% of the total Zn in the two soils respectively. Ammonium acetete extractable Zn was 0.11 mg kg^{-1} in both soils. This comprised 0.10% of the total Zn in the Midelney soil, and 0.14% in Dreghorn. A comparison using Student's t test showed that $CaCl_2$ extracted significantly more zinc than ammonium acetate in both soils. These values for exchangeable Zn agreed with results of Iyengar et al. (1981), who reported 0.05M $CaCl_2$ extractable Zn ranged from 0.02 - 0.58 mg kg^{-1}, and with Mandal and Mandal (1986) who reported 1M ammonium acetate extractable Zn constituting only 0.17 - 0.38% of the total amount of zinc in soils. Neilsen et al. (1986) reported that much smaller amounts of zinc were extracted by 1M ammonium acetate (pH 7.0) than by 1M $MgCl_2$ from acid soils. The reason for extracting the more zinc from the soil with calcium chloride compared to the ammonium acetate is already mentioned in Section 2.4.2.

Specifically adsorbed Zn concentrations extracted by 2.5% acetic acid were, 1.87 mg kg^{-1} (Midelney) and 2.82 mg kg^{-1} (Dreghorn). Amounts of zinc removed by ammonium acetate/acetic acid were 1.69 mg kg^{-1} and 1.75 mg kg^{-1} for Midelney and Dreghorn respectively. These figures constituted 1.65%, 3.66%, 1.49% and 2.27% of the total soil zinc extracted from the two soils. The concentrations of zinc extracted were significantly higher with acetic acid than the modified Morgan's solution. The percentage values of specifically adsorbed Zn agreed with values of Iyengar et al. (1981), who reported an average 3.3% of total soil Zn extracted by acetic acid. The increase in the amount of specifically adsorbed Zn by the acetic acid extractant compared to the modified Morgan's solution may be due to its higher acidic nature as reported by John (1974) and mentioned already in Section 2.4.2.

Zinc associated with the organic matter fraction was 6.38 mg kg^{-1} (Dreghorn) and 9.73 mg kg^{-1} (Midelney) extracted by 0.05M NH_4EDTA (pH 7.0), and 6.46 mg kg^{-1} and 9.86 mg kg^{-1} respectively extracted by 0.1M $Na_4P_2O_7$. These differences between extractants were not significant using Student's t test. After deducting the amount of zinc in the acetic acid fraction (Table 2.2, Section 2.4.2) these constituted 2.34%, 5.20%, 2.67% and 5.64% of the total amount of soil zinc respectively. The concentration of zinc in this fraction agreed with results of Iyengar et al. (1981) who reported 0.01 - 4.24 mg kg^{-1} Zn extracted by pyrophosphate, while Shuman (1979, 1985) reported 0.30 - 3.41 and 0.62 - 5.16 mg kg^{-1} Zn extracted by H_2O_2 and NaOCl respectively. Murthy (1982) reported 0.7 - 6.1 mg kg^{-1}, and Mandal and Mandal (1986) observed 0.74% of total soil Zn in this fraction.

Although the amount of zinc extracted with $Na_4P_2O_7$ was slightly higher than zinc extracted by NH_4EDTA, it had a greater residual effect on the zinc extracted by the acid oxalate extractant used in sequence. It has been observed that pyrophosphate partially dissolved iron and manganese oxides (Iyengar et al. 1981 and Shuman 1982).

Free oxide bound Zn extracted by acid oxalate (pH 3.25) was 8.67 mg kg^{-1} (Dreghorn) and 10.84 mg kg^{-1} (Midelney) when removed following NH_4EDTA extraction. The values for the two soils following pyrophosphate extraction were 11.01 mg kg^{-1} and 12.52 mg kg^{-1} respectively. These figures comprised 11.25%, 9.59%, 14.29% and 11.08% of the total soil Zn respectively. The Student´s t test revealed that significantly more zinc was extracted by acid oxalate after the $Na_4P_2O_7$ than after NH_4EDTA, although $Na_4P_2O_7$ had already extracted slightly more zinc than NH_4EDTA. The concentrations of zinc in this fraction were higher than the values of 0.44 - 4.75 mg kg^{-1} Zn reported by Shuman (1979), 1.8 - 6.8% of total Zn by Murthy (1982), 0.93 - 2.22% of total Zn in this fraction by Mandal and Mandal (1986), but lower than reported by Iyengar et al. (1981), which comprised about 25% of total Zn in this fraction. This increase in the amount of acid oxalate fraction Zn after $Na_4P_2O_7$ may be due to dispersive effects by sodium ions on the soil, providing more oxide surfaces to release zinc in solution.

Due to this fluctuation in the values of acid oxalate Zn, and the risk of some contamination in this extraction procedure, the use of individual extraction of zinc from different pools with selective extractants was preferred for further work.

Table 2.3 Mean values of zinc extracted by sequential extraction

Scheme 1 (Figure 2.1)

mg kg^{-1} (oven dry), (sd)
and as % of total Zn

	Dreghorn (Auchincruive)	Midelney (topsoil)
0.05M $CaCl_2$	0.19 (0.01) 0.25%	0.22 (0.01) 0.19%
2.5% acetic acid	2.82 (0.05) 3.66%	1.87 (0.03) 1.65%
M ammonium acetate	0.11 (0.01) 0.14%	0.11 (0.01) 0.10%
Modified Morgan's solution	1.75 (0.04) 2.27%	1.69 (0.05) 1.49%

Scheme 2 (Figure 2.2)

0.05M NH_4EDTA	6.38 (0.08) 2.34%	9.73 (0.18) 5.20%
Acid oxalate	8.67 (0.27) 11.25%	10.84 (0.16) 9.59%
0.1M $Na_4P_2O_7$	6.46 (0.13) 2.67%	9.86 (0.21) 5.64%
Acid oxalate	11.01 (0.44) 14.29%	12.52 (0.13) 11.08%

2.6 ZINC EXTRACTION FROM AIR-DRIED VERSUS FRESH SOILS

2.6.1 Method

Fresh soils were passed through a 2 mm stainless steel sieve, and subsamples from each were air-dried and preserved in glass bottles, while fresh subsamples were kept in the fridge at $4^{o}C$. To determine the extractable Zn, extractants used were H_2O, 0.05M $CaCl_2$, 2.5% acetic acid, 0.05M NH_4EDTA (pH 7.0), acid oxalate (pH 3.25) (Tamm´s solution), and H_2SO_4/HNO_3 mixture. The extractants used were all of analytical grade reagent standard.

For all determinations of zinc except total Zn (acid mixture), 5 g soil on oven dry basis was taken from each air-dried and fresh sample and weighed into 4-ounce glass bottles in duplicate. 50 cm^3 of the extractant was added, then shaken for 18 hours by using end-over-end shaker at room temperature, approximately $20^{o}C$. Suspensions were filtered through Whatman no. 40 filter papers and solutions were collected in 100 cm^3 polyethylene bottles to analyse for zinc in each extract. Two lots of each extracting solution were used as blanks in these measurements by treating them in the same way, but without soil.

Total Zn was measured by an acid digestion procedure. For both air-dried and fresh samples, 0.1 g very finely ground soil was taken on oven dry basis in acid washed teflon dissolution bombs. 5 cm^3 Analar H_2SO_4 and 4 cm^3 Analar HNO_3 was added to these bombs. The procedure described in Section 2.4.1 was followed.

The objective of this experiment was to measure the different pools of zinc in both air-dried and fresh condition, and also to see any effect of air drying the soil sample from its original fresh condition.

2.6.2 Results and discussion

The mean values of zinc extracted with some selected extractants for fresh soil, as well as air-dried samples are given in Table 2.4, indicating a small increase in some zinc pools for air-dried soils.

Dreghorn (Arkleston) soil extractable Zn remained the same in all pools for both moist and air-dried conditions, and Dreghorn (Auchincruive) soil zinc was slightly lower for $CaCl_2$, but there was some increase with acetic acid for air-dried samples. There was no change with NH_4EDTA and acid oxalate extractable Zn for both sample conditions. Midelney (topsoil) air-dried sample zinc increased in all pools, except the soluble and exchangeable fractions. While Midelney (subsoil) zinc values decreased with EDTA and acid oxalate in air-dried soil, but remained the same in all other pools for both soil conditions. The zinc contaminated soil gave higher zinc in all other pools except water and acid oxalate for air-dried than moist sample condition.

The results suggest that this ambiguous increase in air-dried samples of some soils may be either due to the death and decay of organisms by drying the samples, causing some tissue zinc to be released, or may be due to experimental error, which suggests there was no effect of drying the sample. The observed differences were so small that little significance could be placed on them.

Table 2.4 Air-dried versus fresh soil zinc extracted with some selected extractants

Soils	Extractable Zn (mg kg^{-1})											
	H_2O		0.05M $CaCl_2$		2.5% acetic acid		0.05M NH_4EDTA		Acid oxalate		Total Zn	
	F	AD	F	AD	F	AD	F	AD	F	AD	F	AD
Dreghorn (Arkleston)	0.2	0.2	1.9	1.9	7.35	7.35	8.9	8.8	22.95	23.2	77.5	77.5
Dreghorn (Auchincruive)	0.2	0.2	0.95	0.85	3.5	4.1	4.3	4.35	14.7	14.7	75.00	80.00
Midelney (topsoil)	0.00	0.00	0.00	0.00	3.35	3.85	13.4	14.05	28.7	29.2	105.00	102.50
Midelney (subsoil)	0.00	0.00	0.00	0.00	0.75	0.75	2.95	2.0	12.75	12.3	95.00	97.5
Zn contaminated soil	0.8	0.7	14.8	15.93	86.0	89.13	116.7	117.95	235.95	233.45	557.5	552.5

AD = Air-dried

F = Fresh

2.7 EFFECT OF CROPPING ON THE SOIL ZINC POOL IN DREGHORN (ARKLESTON) SOIL

2.7.1 Method

Soil samples of Dreghorn Series were collected from under barley cultivation at Arkleston Farm, Paisley in February, May, August and October 1986, and April 1987. Soil was taken by stainless steel core from four different sites of the field in area of approximately 10 x 10 m. These core samples were divided visually into topsoil (0 - 25 cm) and subsoil (29 - 40 cm), discarding the 4 cm of soil around the boundary. Soil samples were air-dried, passed through 2 mm stainless steel sieve and stored in glass bottles for analysis. 5 g air-dried soil was shaken with 50 cm^3 of the extractant for 18 hours by using end-over-end shaker at room temperature, and filtrate was collected in polyethylene bottles through Whatman filter paper no. 40. Two blanks for each extractant were also run along with the samples under the same procedure for zinc determination. In this study the following selective extractants were used for different pools of Zn; (i) 0.05M $CaCl_2$, (ii) 2.5% acetic acid, (iii) 0.05M NH_4EDTA, (iv) acid oxalate (Tamm's solution), and (v) H_2SO_4 + HNO_3 acid mixture.

Total Zn was determined by digesting 0.1 g air-dried very fine ground soil with 5 cm^3 Analar H_2SO_4 and 4 cm^3 Analar HNO_3 under the procedure mentioned in Section 2.4.1. All Zn standards were made in the separate extractant used for extracting the different zinc fractions from the soil.

The purpose of this study was to investigate the effect of cropping and time on the distribution of zinc in different soil fractions and also compare the amount of zinc within the topsoil and subsoil.

2.7.2 Results and discussion

Summarized mean extractable zinc values, as well as percentage of total zinc values, for sixteen replicates in the case of topsoil and ten replicates in the case of subsoil collected at four random sites are given in Table 2.5. These figures show that extractable Zn decreased with the depth of the samples at each sampling date. All values for extractable Zn with different extractants, as well as total content, were considerably higher in topsoil than in subsoil, and are in agreement with results of John (1974), who observed that the extractable Zn with seven extractants as well as total Zn content in seven British Columbia (Canada) alluvial soil profiles declined with increasing depth of sampling within the profile. Whitby, Gaynor and MacLean (1978) reported the mean concentrations of DTPA extractable Zn ranged from 0.44 - 6.71 and 0.04 - 0.67 mg kg^{-1} for Ap and C horizons respectively, and total Zn content ranged from 40 - 163, 35 - 140, and 40 - 128 mg kg^{-1} for Ap, B and C horizons respectively in soils of Ontario (Canada). Nakos (1983) using forest soils in Greece observed that zinc concentration showed no clear pattern of change with soil depth.

Table 2.5 Mean values of Dreghorn (Arkleston) soil zinc with some selected extractants at different sampling dates

	mg Zn kg^{-1} soil and (%) on oven dry basis				
Topsoil (date)	0.05M $CaCl_2$	2.5% acetic acid	0.05M NH_4EDTA	acid oxalate	Total
2/86	2.06NS (2.58)	7.37a (9.24)	9.3a (11.66)	19.72a (24.72)	79.77a
5/86	2.16NS (2.98)	6.95ab (9.57)	8.89ab (12.25)	19.74a (27.19)	72.6abc
8/86	2.11NS (2.98)	6.25c (8.82)	7.64cd (10.78)	16.13c (22.76)	70.86bc
10/86	1.59NS (2.34)	6.31bc (9.30)	7.4d (10.90)	18.26b (26.90)	67.88c
4/87	1.54NS (2.05)	6.57bc (8.77)	8.32bc (11.10)	20.71a (27.63)	74.95ab
Subsoil (date)					
2/86	0.37NS (1.54)	1.41NS (5.83)	1.59NS (6.62)	4.18ab (17.41)	24.01NS
5/86	0.60NS (1.93)	2.1NS (6.74)	2.39NS (7.67)	6.34a (20.35)	31.16NS
8/86	0.08NS (0.34)	0.68NS (2.89)	1.08NS (4.6)	2.9b (12.34)	23.5NS
10/86	0.43NS (1.89)	1.74NS (7.63)	2.04NS (8.94)	5.08ab (22.27)	22.81NS
4/87	0.21NS (0.85)	1.84NS (7.44)	2.18NS (8.82)	5.03ab (20.34)	24.73NS

Figures in a column with the same letter following are not significantly different at the 5% level using a Scheffe LSD test.

The observed results revealed that the relatively higher amount of extractable Zn from the topsoil than from subsoil is probably due to the greater association of metals with organic matter, and its decay in the topsoil, which has a favourable effect on zinc extractability. John (1974) mentioned the surface accumulation of zinc by its acquisition from the deeper horizons by plant roots, decay of organic matter and subsequent immobilization at the surface.

An F test was applied to this data for topsoil and subsoil to see if there were any differences in the mean values for each pool of extractable Zn at different sampling times. This test showed that for topsoil variations in $CaCl_2$ extractable Zn were nonsignificant, EDTA and oxalate extractable Zn highly significant at 0.1% level, acetic acid extractable Zn significant at 1% level, and total Zn significant at 5% level. For subsoil, only the oxalate extractable Zn was significantly different, at 5% level, while the variation in the other soil fractions of extractable Zn were nonsignificant at the different sampling times. These F values were also used to obtain the Scheffe least significant difference (LSD) between the mean values at different dates. For topsoil as well as subsoil the figures (Table 2.5) with the same following letter are not significantly different at 5% level. The LSD values were: acetic acid 0.64 mg kg^{-1}, EDTA 0.84 mg kg^{-1}, oxalate 1.16 mg kg^{-1} and total Zn 6.87 mg kg^{-1} for topsoil and oxalate 3.39 mg kg^{-1} for subsoil. The topsoil is considered a root zone from which plants mostly take their nutrients from the readily available fractions. The exchangeable Zn fraction is highly labile, bioavailable and readily available to plants (LeClair et al. 1984). From Table 2.5, this pool showed a nonsignificant difference between the times of sampling. It indicates that this fraction of soil zinc is maintained from the release of some zinc from other soil pools. Some decline was also observed during the cropping season in acetic acid extractable Zn and this showed some significant differences. This fraction is also available to plants and this decline may be attributed to some portion taken up by plants. Some may be specifically fixed and some may have been released to maintain the exchangeable fraction during the cropping time. EDTA extractable Zn represents a reservoir of potentially bioavailable zinc (LeClair et al. 1984). Oxalate extractable Zn is considered a big reservoir due to the high amount of zinc present in this fraction. These two fractions of zinc showed a highly significant difference, indicating the release of zinc from these fractions to maintain the levels in the adsorbed and exchangeable Zn fractions. The total soil Zn which is not directly related to plant growth showed some significant difference. These variations may be either due to the different sites of sampling within the field or due to experimental error.

In the case of subsoil, the variation in the mean values for all the zinc fractions at the different sampling times was nonsignificant using the Scheffe LSD test, except for the oxalate fraction. There was a decline in some pools during the period of sampling in summer, which was not significant. This may be due to leaching of metals or parent material variations within the field.

These mean values of summarized data are also presented graphically in Figures 2.3a and 2.3b for topsoil and subsoil respectively, showing a clear picture of cropping effects on different forms of zinc in soil. It is obvious from Figure 2.3a that during the cropping season there was a decline in all zinc fractions except $CaCl_2$. After the growing season, there was a rise in acetic acid, EDTA and oxalate Zn, but not $CaCl_2$ extractable Zn as a result of an increase in organic residues after harvesting the crop and decomposition of organic matter. Iyengar et al. (1981) quoted that a decrease in plant available soil Zn during decomposition of organic matter paralleled the decreases in amounts of both water soluble and exchangeable soil Zn. Hodgson (1963) reported that zinc availability was high during rainy cool weather, and flax seeded in June suffered most from zinc deficiency.

It is concluded from this study that seasonal fluctuations or cropping can affect the extractability of zinc in different soil fractions, but not the readily available (soluble + exchangeable) Zn fraction. It is also observed that extractability of zinc decreased with depth at all sampling times in soil. The organic matter plays an important role in maintaining the amounts of extractable Zn in this soil.

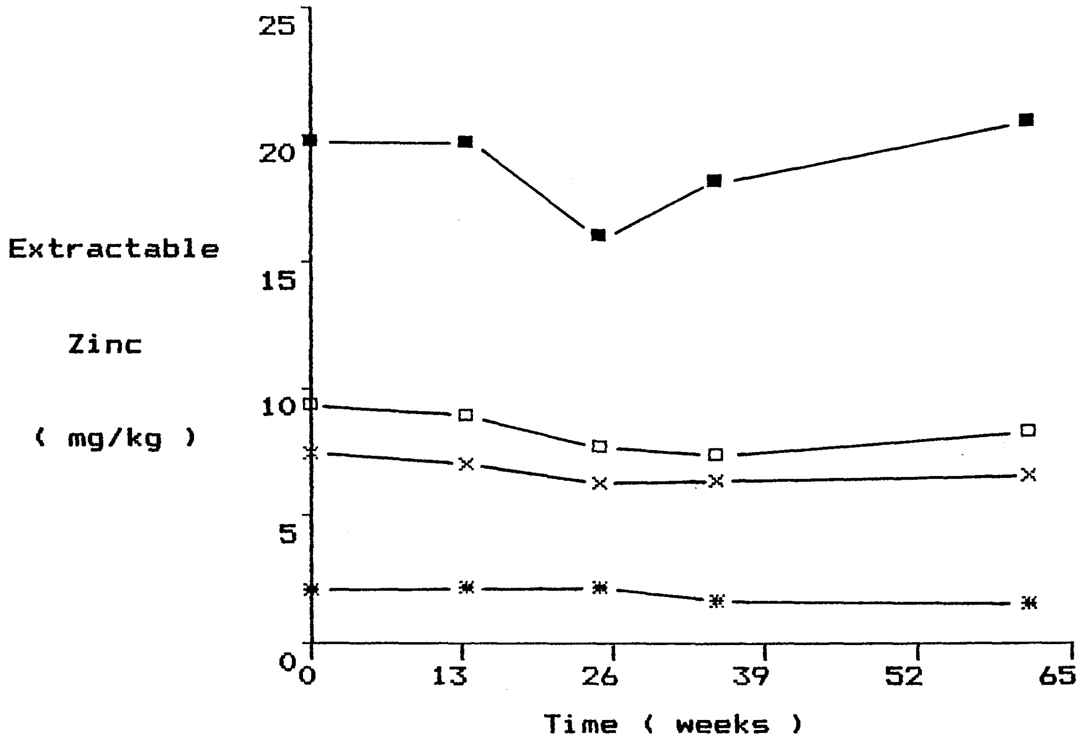


Fig. 2.3a Extractable zinc in various soil pools of Dreghorn (Arkleston) topsoil.

Calcium chloride Zn (*); Acetic acid Zn (X);
Ammonium EDTA Zn (□); Acid oxalate Zn (■).

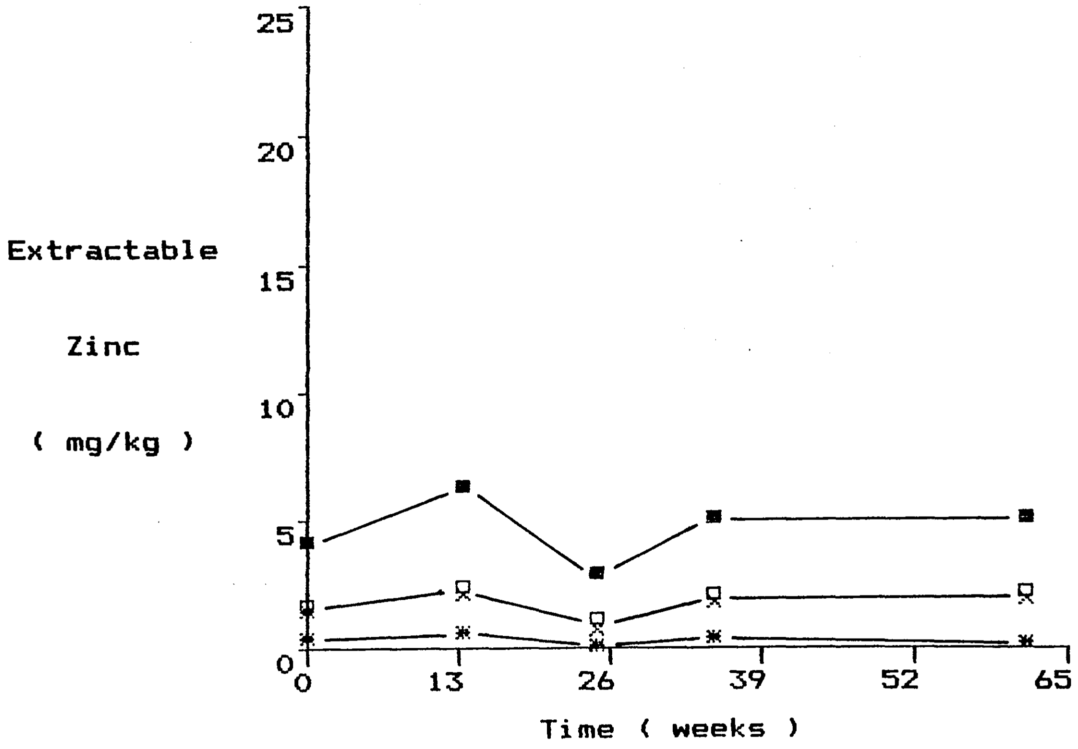


Fig. 2.3b Extractable zinc in various soil pools of Dreghorn (Arkleston) subsoil.

Calcium chloride Zn (*); Acetic acid Zn (X);
Ammonium EDTA Zn (□); Acid oxalate Zn (■).

CHAPTER 3

POT EXPERIMENT

3.1 INTRODUCTION

Amongst the micronutrients, zinc deficiency is observed in field crops on many kinds of soils in different parts of the world (Giordano and Mortvedt 1974, Forno et al. 1975, Sakal et al. 1984), and was well reviewed by Lindsay (1972). This phenomenon has also been noticed in the developing countries during the last decade as a result of modern agricultural technology for increasing food production per unit area. There are many other reasons involved in causing zinc deficiency e.g. imbalances of micronutrients in the soils due to fertility depletion through intensive cultivation of high yielding varieties; increased use of chemically pure, micronutrient-free fertilizers; decreased recycling of crop residues; and limited use of animal manures. On the other hand in some contaminated soils receiving sewage sludge, toxicity of zinc is a major problem (Sposito et al. 1983, Albasel and Cottenie 1985). Both of these aspects have been a focal point of study and recommendations have been made to rectify their adverse effect on crops.

Knowledge about the distribution of zinc between various soil forms, as well as its availability to plants, is considered essential. Different soils containing similar total amounts of a metal can vary greatly in its availability to plants. Total zinc in soil is not directly related to plant availability, and different soil forms of zinc are considered responsible for meeting plant requirements. Zinc in the different soil fractions also varies in plant availability. Iyengar et al. (1981) mentioned that the zinc present in water-soluble, exchangeable, and adsorbed fractions is readily available to plants, while zinc associated with primary and secondary soil materials is relatively unavailable to plants. Chandi and Takkar (1982) indicated from their study that weakly adsorbed and organic matter fractions are the deciding factors in the zinc nutrition of crops. Hence changes in these pools would reflect their influence on the zinc nutrition and the crop yields.

Crops feed differentially on various fractions and remove variable quantities of zinc from the soils. Diverse effects of cropping systems on labile zinc fractions were observed by Chandi and Takkar (1982). They reported that a wheat-groundnut rotation caused an increase in the exchangeable Zn of 25%, and that the maximum decrease was 50% in wheat-maize and raya-mash rotations. Although in the raya-mash rotation the weakly adsorbed and moderately adsorbed zinc appreciably increased, in other rotations these fractions markedly decreased. In sharp contrast to the above, the wheat-groundnut and wheat-rice rotations caused a decrease in organic matter bound Zn, while in other rotations this fraction of zinc increased.

The purpose of the present study was to determine the effect of continuous cropping on the distribution of zinc in various soil pools, and the relationship of amounts of zinc in these pools with plant uptake. A pot experiment was conducted in the greenhouse using ryegrass as a test crop grown in five different soils to study the above objective.

3.2 METHODS

The five soils described in Section 2.2 were used in this experiment. Fresh samples of the soils were collected in Spring 1986. Four soils were sampled approximately 0 - 20 cm deep, and Midelney (subsoil) was taken from below 20 cm depth. All fresh soils were passed through a 2 mm stainless steel sieve.

3.2.1 Pot culture technique

400 g (on oven dry basis) of each fresh soil was weighed into 10.0 cm internal-diameter plastic pots fitted with saucers. For all soils there were 17 replicates in which grass was grown, and 3 replicates having no grass, in a latin square design having four blocks (see next page). 0.5 g perennial ryegrass seed (Lolium perenne) was sown in each pot. Deionized water was supplied via the saucers, and this watering procedure was adopted throughout the experiment, except in some cases when the surfaces of Midelney (topsoil and subsoil) pots remained dry, then additional water was added to the top of the pot.

Layout for pot experiment

Design = latin square

Block 1

D4	C3	A1	E5	B2
E2	D1	B4	A3	C5
A5	E4	C2	B1	D3
C1	B5	E3	D2	A4
B3	A2	D5	C4	E1

Block 2

C5	E2	D1	B4	A3
D3	A5	E4	C2	B1
B2	D4	C3	A1	E5
A4	C1	B5	E3	D2
E1	B3	A2	D5	C4

Block 3

A1	D4	E5	B2	C3
B4	E2	A3	C5	D1
C2	A5	B1	D3	E4
E3	C1	D2	A4	B5
D5	B3	C4	E1	A2

Block 4

B1	A5	C2	D3	E4
E5	D4	A1	B2	C3
C4	B3	D5	E1	A2
D2	C1	E3	A4	B5
A3	E2	B4	C5	D1

A = Dreghorn (Arkleston)

B = Midelney (topsoil)

C = Midelney (subsoil)

D = Dreghorn (Auchincruive)

E = Zn contaminated soil

After the germination of grass, fertilizer was applied as NPK and Mg in solution, at the rate of 100, 50, 100, and 5 mg per pot respectively. The source of nutrients were NH_4NO_3 for N, KH_2PO_4 and KCl for P and K, and $MgSO_4 \cdot 7H_2O$ for Mg. The magnesium was included to prevent an acute deficiency which might arise during the intensive cropping (Arnold and Close 1961).

After each harvest the same dose of nutrients was applied to the cropped pots in solution from the top using a 10 cm^3 pipette. During the winter, supplementary lighting was provided by large fluorescent tubes held 0.75 m above the pots. It was observed that the lighting allowed the grass to grow at about half the mid-summer rate. Yield was measured from block 1 up to the 4th harvest by cutting the grass 3.0 cm above the soil for all except Midelney (subsoil) which was cut 4.0 cm above the soil. In order to enhance the vegetative growth of grass, this height was increased by 1.0 cm from the 5th harvest for each soil. This initial difference of one cm in height for Midelney (subsoil) was due to its compaction with watering and so the soil level was below the edge of the pots. The block of 25 pots used for yield measurement and grass zinc analysis was discarded after the 4th cutting as growth had ceased, and later three replicates (one for each of blocks 2, 3 and 4) were used for yield and grass zinc measurements. Three pots for all soils, one from each block (2, 3 and 4) were sacrificed at the 1st, 3rd, 6th and 8th harvest to measure zinc in soil, plant roots and stubble, while subsamples from control pots were also taken at the same time. Grass tops, stubbles and roots were dried in an oven at 80°C for 48 hours before measuring the yield.

As the pots were sacrificed the stubbles were harvested above the soil surface by stainless steel scissors, and the contents of each pot were air-dried, then the roots were picked out by hand and by sieving the soil. Roots were thoroughly washed with deionized water to remove soil particles before drying in an oven and the yield measured. All plant material was ground manually in separated portions by using a porcelain mortar and pestle to avoid zinc contamination by the use of electric grinder.

3.2.2 Analytical procedure

All zinc determinations were made with a flame atomic absorption spectrophotometer using appropriate standards. Zinc in different soil fractions, as well as total zinc, was determined before cropping in both air-dried and fresh conditions. At each sampling time, 5.0 g air-dried soil was extracted with 50 cm^3 of each extractant, ie. H_2O, 0.05M $CaCl_2$, 2.5% acetic acid, 0.05M NH_4EDTA (pH 7.0), and acid oxalate (Tamm´s solution), for water soluble, exchangeable, specific adsorbed, organic bound, and free oxide fraction Zn respectively. Extraction was for 18 hours shaking at room temperature using an end-over-end shaker. The suspension was filtered through Whatman no. 40 filter paper and collected in 100 cm^3 polyethylene bottles . Two blanks for each extractant were also run through for zinc analysis with the samples.

Plant material was extracted by the wet pressure digestion method adopted by Adrian (1973) and used for calcium determination by Adrian and Stevens (1977). About 0.5 g ground plant tissue was weighed into 60 cm^3 polypropylene bottles with screw caps. 4 cm^3 of concentrated nitric acid and 2 cm^3 of concentrated perchloric acid were delivered to these bottles via 100 cm^3 burettes (0.10 cm^3 divisions), which enhanced the speed and accuracy with which acids could be added. The bottles were swirled to soak all the sample with acid, and kept for 24 hours for predigestion loosely capped in the fume cupboard. Predigestion is essential as the bottles could burst if heated immediately. After that the bottle caps were screwed on tightly, the bottles placed in plastic trays (twelve on each) having 1 inch depth of water to provide constant heating to each bottle. They were then placed on the water bath in a fume cupboard for $3\text{-}3^1/_2$ hours at 65°C temperature. After cooling the bottles, 2 cm^3 of deionized water was added, the bottles recapped, replaced on the water bath, and the heating continued for a further 2 hours to expel the excess of volatile acid. The bottles were then thoroughly cooled, 15 cm^3 of deionized water was then added to each, and the contents were filtered through Whatman no. 540, size 11.0 cm filter paper into 50 cm^3 volumetric flasks. The volume was made up with deionized water and shaken thoroughly. Some content from the flask was transferred to 4 dram glass bottles, and stored in the refrigerator for analysis. The blanks having no plant sample were run through with the samples under the same procedure. The standards used for zinc determination were also made with the same volume of acids. All reagents used were of analytical grade.

3.3 RESULTS AND DISCUSSION

The results of work done in this study are discussed separately to show a clear picture about the distribution of zinc within the soil as well as its uptake by plants.

3.3.1 Soil zinc

Mean values of zinc extracted by different extractants from soil in the grass pots sampled at different harvesting times are presented in Table 3.1. Water soluble Zn is not given in this table as the amount present in this fraction was very low. Statistical analysis of the data by an F test showed that there were significant changes in the various pools of zinc in all five soils. These differences were significant at 0.1% level for all soils and extractants, except EDTA - Zn in Midelney (subsoil) which is significant at the 1% level.

The results in Table 3.1 reveal that $CaCl_2$ extractable Zn increased gradually with time for all soils, except Midelney (topsoil) and Midelney (subsoil), which gave no measureable zinc in this fraction.

Table 3.1 Mean values of soil Zn in grass pots with different extractants

	Zn mg kg^{-1} (oven dry basis)				
Soil	0 weeks	10 weeks	18 weeks	36 weeks	48 weeks
$CaCl_2$ extractable					
1	1.90d	2.49c	3.06b	3.36a	3.31ab
2	0.88c	1.40b	1.70a	1.70a	1.62ab
3	0.00	0.00	0.00	0.00	0.00
4	0.00	0.00	0.00	0.00	0.00
5	15.55c	25.54b	25.01b	34.99a	36.69a
Acetic acid extractable					
1	7.35a	7.36a	7.11a	6.30b	5.66b
2	3.90a	3.58ab	3.57ab	2.94bc	2.59c
3	3.68a	3.87a	3.70a	2.81b	2.60b
4	0.75b	1.09a	1.14a	0.78b	0.56c
5	88.12a	81.25b	78.94b	78.14bc	73.67c
EDTA extractable					
1	8.83ab	9.20a	8.68b	8.22c	7.67d
2	4.33ab	4.50a	4.25b	3.74c	3.62c
3	13.83a	13.17a	12.37b	11.51c	11.27c
4	2.32ab	2.53a	2.41ab	1.87ab	1.64b
5	117.53a	108.84b	99.52c	98.02c	97.06c
Oxalate extractable					
1	23.12a	19.26b	17.83b	17.66b	17.56b
2	14.70a	12.44b	11.19c	11.22c	11.16c
3	29.03a	27.00b	23.66c	23.37c	23.09c
4	12.45a	11.23b	10.47c	10.04cd	9.62d
5	234.27a	225.40b	210.75c	205.70d	199.39e

1 = Dreghorn (Arkleston)
2 = Dreghorn (Auchincruive)
3 = Midelney (Topsoil)
4 = Midelney (Subsoil)
5 = Zn contaminated soil

Figures in a row with the same letter following are not significantly different at 5% level using a Scheffe LSD Test.

A Scheffe LSD test showed the significance of the changes in extractable zinc between successive sampling times. As is well known, $CaCl_2$ extractable Zn is readily available for plant uptake. But there are various reasons which may have caused the increase in the amount of extractable Zn in this fraction.

(1) It has already been mentioned in Chapter 2 Section 2.7.2 that this pool of zinc was not reduced by plant uptake and the equilibrium was easily maintained by replenishing the zinc from other soil pools.

(2) Washing of some roots present in soil can release substances which may dissolve some oxides and cause the release of oxide bound zinc into the solution. Bromfield (1958 a, b) observed that root washing of oat and vetch plants released substances which dissolved manganese oxide. The release into solution of some zinc bound to oxides has been reported by Shuman (1982).

(3) Some zinc, which had been adsorbed during the growing time, may be released from the surface of roots by the exchange process because of intimate contact that exists between roots and soil particles. Tisdale et al. (1985) observed that soil colloids are not the only component to exhibit cation exchange properties but plant roots themselves possess this property. They suggested that ions (such

as H^+ ions) may exchange with those held on the surface of clay and organic matter in soils.

(4) Some zinc may be released into the $CaCl_2$ extractable pool from dead root tissue.

Acetic acid extractable Zn (specifically adsorbed) is also readily available for plant uptake. The amounts of zinc extracted from this pool decreased gradually over the sampling period in all soils, except Midelney (subsoil) where some increase was observed initially. Results given indicate the clear pattern of loss from this fraction. The Scheffe LSD test showed that the decrease between the initial zinc (0 week), 1st (10 week) and 2nd (18 week) sampling times was non-significant for three of these soils. The Zn contaminated soil showed a significant decrease over weeks 0 to 10. Between the 2nd (18 week) and 3rd (36 week) sampling times, three soils showed a significant decrease in acetic extractable Zn. The decrease in this fraction in Dreghorn (Auchincruive) and the Zn contaminated soil was not significant. Changes in acetic acid extractable Zn between the last two sampling times showed a non-significant decrease for four soils, but was significant for Midelney (subsoil).

Zinc extracted with NH_4EDTA declined gradually with time of sampling in all soils. This fraction represents a reservoir of potentially bioavailable zinc (LeClair et al. 1984). The Scheffe LSD test showed a non-significant decrease for four soils between the initial zinc (0 week) and the 1st (10 week) sampling time but there was a significant decrease in this fraction in the Zn contaminated soil. The decrease between the 1st (10 week) and 2nd (18 week) sampling times was significant for all soils, except Midelney (subsoil). From the 2nd to the 3rd sampling times the decrease was significant for three of the soils, but not for the Midelney (subsoil) and the Zn contaminated soil, while the differences between the 3rd (36 week) and the 4th (48 week) sampling times were non-significant in all soils except for Dreghorn (Arkleston). This decline in organically bound Zn may be either due to direct uptake by the plants or due to movement to maintain the levels in the exchangeable fraction.

Acid oxalate extractable Zn showed some decline from initial zinc (0 week) to 4th (48 week) sampling time. This fraction of soil is considered a big reservoir, as a large amount of zinc is present in it. The Scheffe LSD test showed a significant decrease between the initial (0 week) and 1st (10 week) sampling times for all five soils. While this significant decrease was also observed between the 1st (10 week) to 2nd (18 week) sampling times for all soils except Dreghorn (Arkleston). It was non-significant between 3rd (36 week) and 4th (48 week) sampling times for all soils except Zn contaminated soil. This significant decline between the initial zinc (0 week), 1st (10 week) and 2nd (18 week) sampling times for all soils suggested that zinc taken up by plants from the readily available pools was replenished by this oxide fraction. The soils which showed a significant decrease in EDTA extractable Zn at each sampling time, did not give a significant decline for the last three sampling periods in oxalate extractable Zn. It is most obvious from the Zn contaminated soil, which showed a significant decline in oxalate extractable Zn between all sampling times, but which showed non-significant differences from 1st (10 week) to 3rd (36 week) sampling times in acetic acid extractable Zn. The early significant difference between 1st (10 week) and 2nd (18 week) in EDTA extractable Zn, and non-significant differences between the last three successive samplings indicates that available pools were maintained by oxide fraction Zn.

Mean values of extractable zinc with different extractants in the ungrassed control pots at different sampling times are represented in Table 3.2. This summarized data revealed a gradual decrease in extractable zinc at each sampling time. An F test showed that there were significant differences in the various pools of zinc in all five soils except in $CaCl_2$ extractable Zn for Dreghorn (Arkleston) and in EDTA-Zn for Midelney (subsoil), where these differences were not significant. All of these differences were at 0.1% level for all five soils except in acetic acid extractable Zn for the Dreghorn (Auchincruive) soil where the difference was at 1% level.

Table 3.2 Mean values of zinc in soils of control pots with different extractants

	Zn mg kg^{-1} (oven dry basis)				
Soil	0 weeks	10 weeks	18 weeks	36 weeks	48 weeks
$CaCl_2$ extractable					
1	1.90NS	1.84NS	1.67NS	1.63NS	1.55NS
2	0.88b	1.02b	1.12a	1.09a	1.01ab
3	0.00	0.00	0.00	0.00	0.00
4	0.00	0.00	0.00	0.00	0.00
5	15.55a	12.86b	11.34b	11.79b	12.63b
Acetic acid extractable					
1	7.35a	7.49a	7.41a	6.84ab	6.35b
2	3.90a	3.73ab	3.94a	3.38ab	3.19b
3	3.68a	3.76a	4.08a	3.60b	3.21b
4	0.75c	1.01ab	1.15a	0.98b	0.86bc
5	88.12a	83.36b	83.10bc	82.43bc	79.17c
EDTA extractable					
1	8.83ab	9.34a	8.94ab	8.56bc	8.13c
2	4.33bc	4.51a	4.45ab	4.18cd	4.12d
3	13.83a	13.36ab	12.87bc	12.69bc	12.42c
4	2.32NS	2.61NS	2.61NS	2.25NS	2.20NS
5	117.53a	113.21a	108.14b	107.26b	105.69b
Oxalate extractable					
1	23.12a	19.85b	19.94b	20.89b	20.59b
2	14.70a	13.33b	12.52b	13.08b	13.14b
3	29.03a	27.95b	25.81d	26.78c	26.98c
4	12.45a	11.64b	11.10bc	10.99bc	10.78c
5	234.27a	235.85a	221.19b	223.24b	221.73b

1 = Dreghorn (Arkleston)
2 = Dreghorn (Auchincruive)
3 = Midelney (Topsoil)
4 = Midelney (Subsoil)
5 = Zn contaminated soil

Figures in a row with the same letter following are not significantly different at 5% level using a Scheffe LSD Test.

Using the Scheffe LSD test, it has been observed that this decline with time of sampling was significantly different to a varying extent for all soils with different extractants. For Dreghorn (Arkleston) in $CaCl_2$, and for Midelney (subsoil) in EDTA, these differences were not significant. This decline in extractable zinc in soil of ungrassed pots may be either due to the loss by leaching or to the fixation by clay minerals.

In order to study any changes in the various zinc pools, the mean zinc removed by one extractant was subtracted from each replicate extraction for the next strongest extractant. So, for example, the organic zinc pool is given by EDTA-Zn minus acetic acid-Zn. The mean value of each zinc pool in the control pots was then deducted from each replicate of the equivalent pool in the grass pots. The mean changes in each pool of zinc are shown in Table 3.3.

Table 3.3 Changes in zinc pools due to plant growth in pots

		Zn mg kg^{-1} (oven dry basis)			
Soil	Zinc pool	10 weeks	18 weeks	36 weeks	48 weeks
1	soluble and exchangeable	0.64c	1.39b	1.73a	1.76a
2		0.38b	0.58ab	0.61a	0.61a
3		0.00	0.00	0.00	0.00
4		0.00	0.00	0.00	0.00
5		12.68b	13.67b	23.21a	24.06a
1	specifically adsorbed	-0.78c	-1.69b	-2.27a	-2.45a
2		-0.53c	-0.95b	-1.05ab	-1.21a
3		0.11c	-0.38b	-0.79a	-0.61ab
4		0.08d	-0.01c	-0.20b	-0.30a
5		-14.79b	-17.83b	-27.50a	-29.56a
1	organically bound	-0.01NS	0.04NS	0.20NS	0.23NS
2		0.14NS	0.17NS	0.00NS	0.10NS
3		-0.30b	-0.12c	-0.39b	-0.54a
4		-0.16NS	-0.19NS	-0.18NS	-0.26NS
5		-2.26NS	-4.46NS	-4.95NS	-3.13NS
1	oxide bound	-0.45b	-1.85ab	-2.89a	-2.57a
2		-0.88a	-1.13a	-1.42a	-1.48a
3		-0.76b	-1.65ab	-2.23ab	-2.74a
4		-0.33NS	-0.43NS	-0.57NS	-0.60NS
5		-6.08b	-1.82c	-8.30b	-13.71a

1 = Dreghorn (Arkleston)
2 = Dreghorn (Auchincruive)
3 = Midelney (Topsoil)
4 = Midelney (Subsoil)
5 = Zn contaminated soil

Figures in a row with the same letter following are not significantly different at 5% level using a Scheffe LSD Test.

This data shows an increase in soluble plus exchangeable zinc ($CaCl_2$-Zn) with time, for the three soils in which this fraction was measurable. The specifically sorbed zinc pool (acetic acid-Zn minus $CaCl_2$-Zn) showed a decline with time for three of the soils (Dreghorn Arkleston, Dreghorn Auchincruive and the Zn contaminated soil), while the two Midelney soils exhibited an initial increase in this pool, followed by a decline. Differences in the specifically sorbed pool were not significant between 36 weeks and 48 weeks, except for the Midelney (subsoil), suggesting that this pool of zinc had come to equilibrium. Changes in the organic zinc pool (EDTA-Zn minus acetic acid-Zn) were not significant, except for Midelney (topsoil) where there was no clear pattern. In this soil an initial decrease was followed by an increase at 18 weeks, with a further decrease thereafter. The oxide zinc pool (oxalate Zn minus EDTA Zn) showed a significant decrease with time for all soils, except Midelney (subsoil).

The changes observed in the various pools of zinc suggest that zinc was removed from the specifically sorbed and oxide pools into the exchangeable pool in order to maintain an available source of zinc for plant uptake.

A clear picture showing the variation in extractable zinc in the soil in the grass pots, without deducting the mean zinc in the control pots, with each extractant is represented diagrammatically for each soil in Figures 3.1a, b, c, d and e.

Figure 3.1 Zinc extracted from soil in grass pots for:

a) Dreghorn (Arkleston)

b) Dreghorn (Auchincruive)

c) Midelney (topsoil)

d) Midelney (subsoil)

e) Zinc contaminated soil

0.05M calcium chloride	(*)
2.5% acetic acid	(×)
0.05M ammonium EDTA	(□)
acid oxalate	(■)

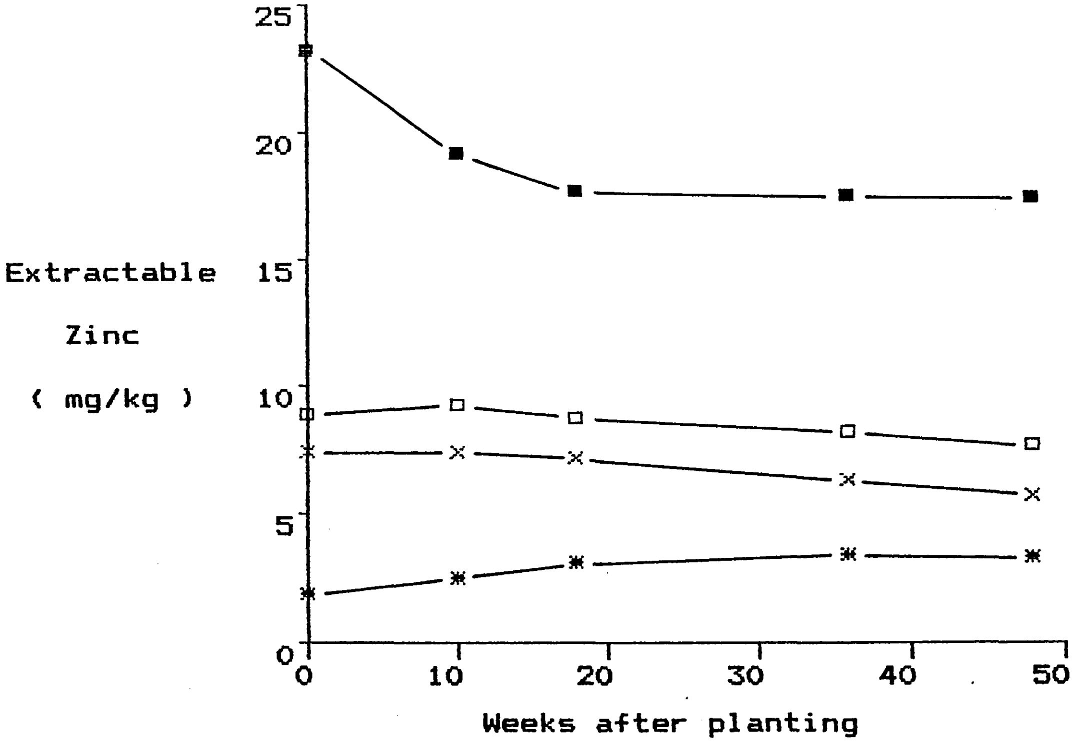


Fig. 3.1a Dreghorn (Arkleston).

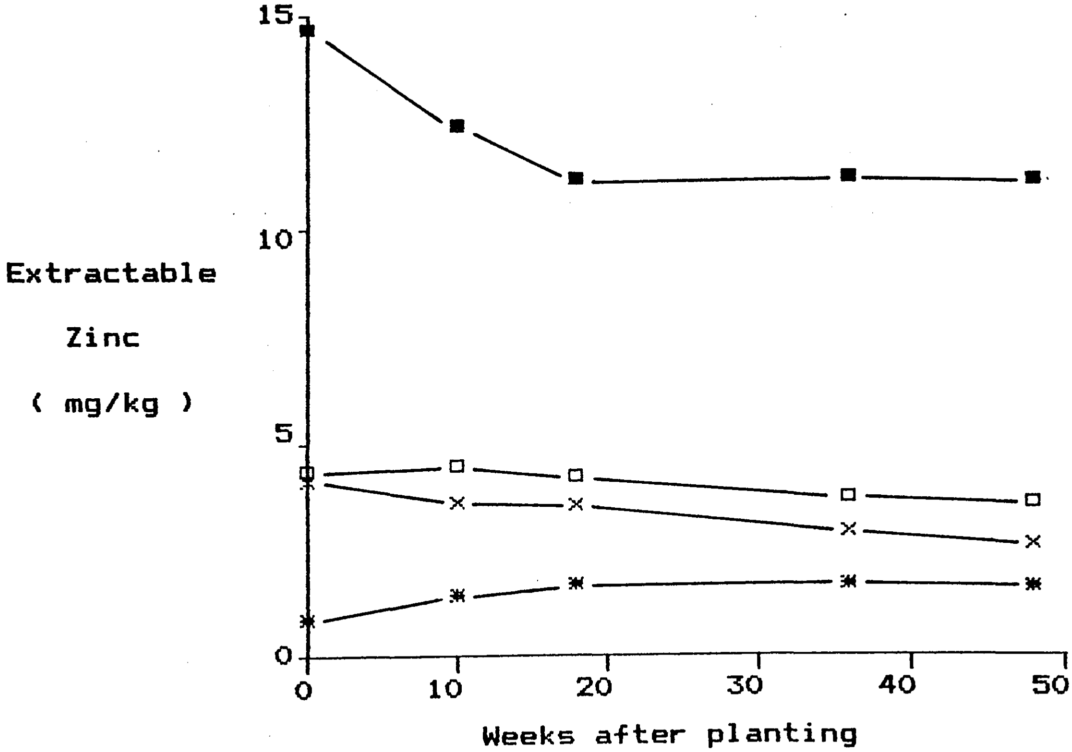


Fig. 3.1b Dreghorn (Auchincruive).

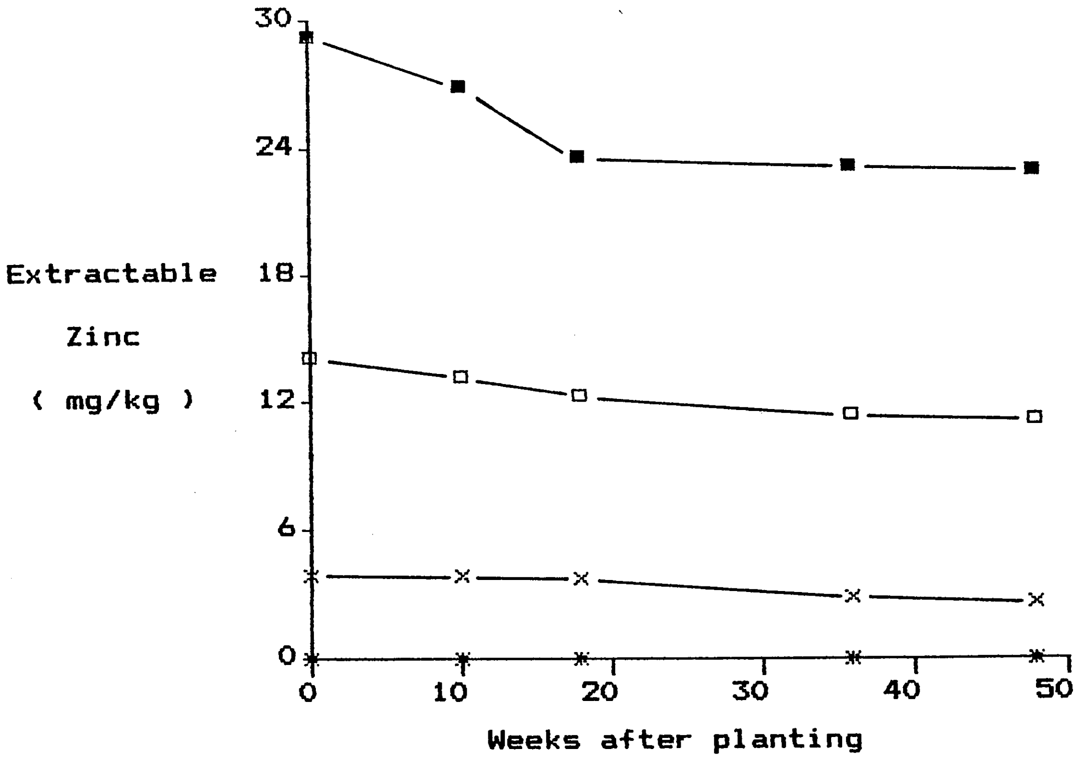


Fig. 3.1c Midelney topsoil.

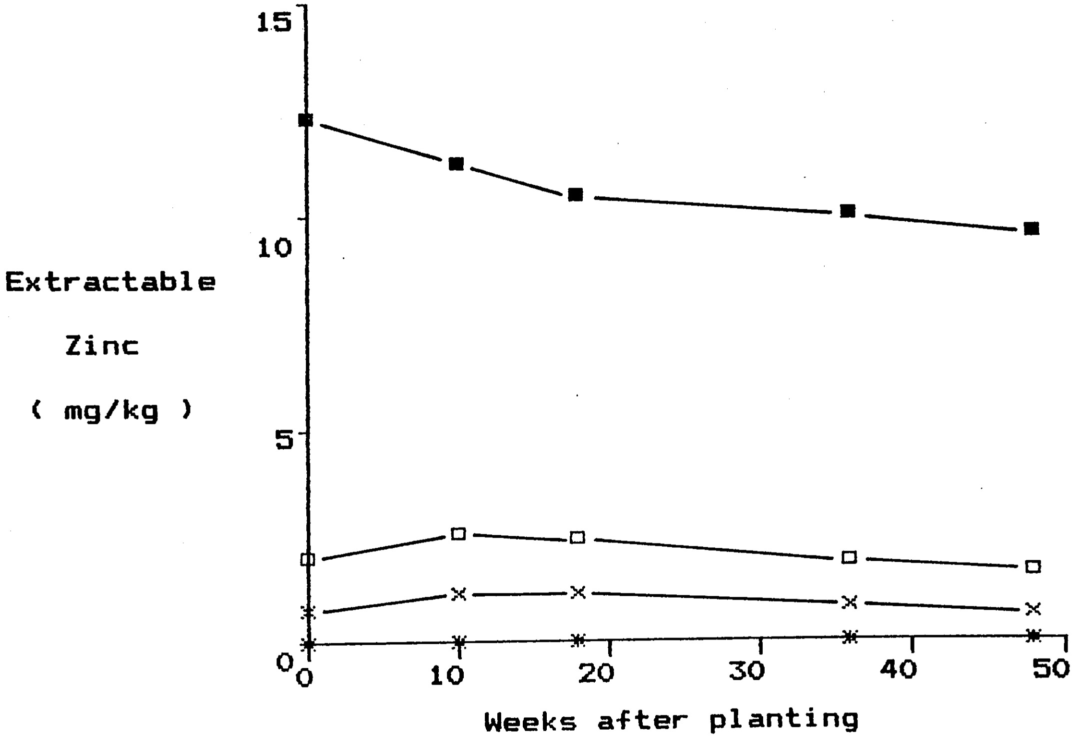


Fig. 3.1d Midelney subsoil.

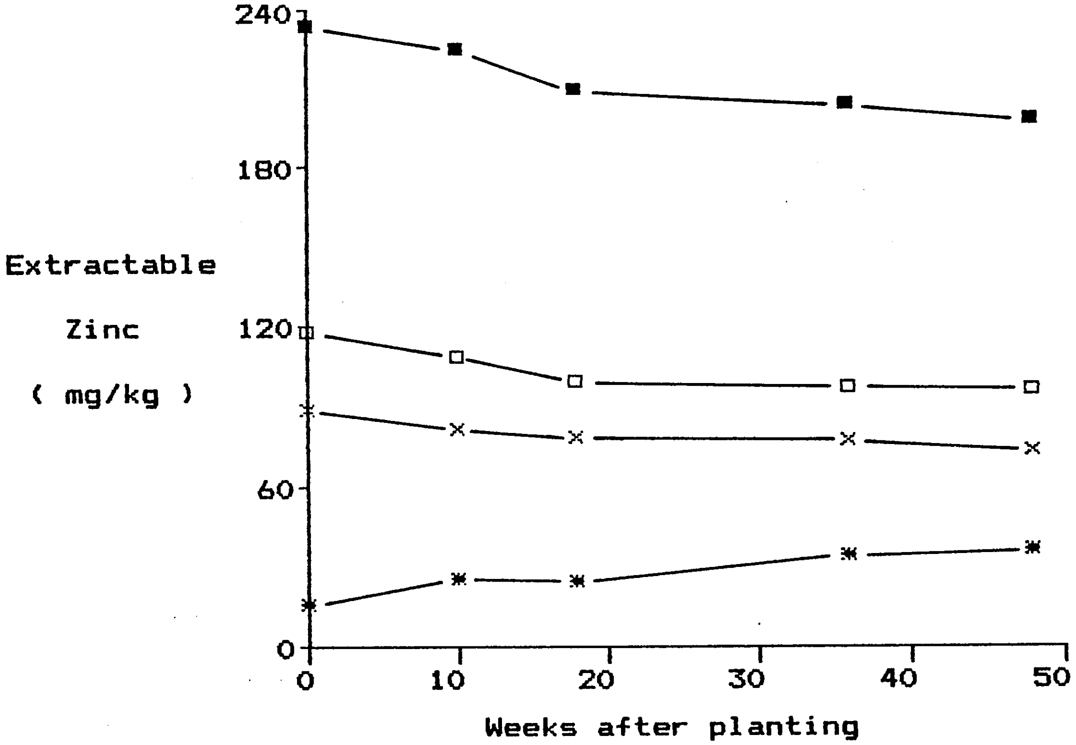


Fig. 3.1e Zinc contaminated soil.

3.3.2 Yield of grass

The mean yield (g/pot) of plant material as tops, stubble and roots for each soil at different harvesting times is represented in Table 3.4. The small decline in tops yield at the 22 week harvest may be due to the 1 cm increase in the height of the stubble at cutting times, which is obvious from the increase of their yield at each harvesting. In general Table 3.4 indicates a uniform plant growth throughout the period and no clear response of tops yield was observed regarding the amounts of Zinc present in soils.

Differences between the five soils in yields of tops and stubble are not obvious, but differences in the root yields are clear. The Midelney (topsoil) and Midelney (subsoil) gave lower yields of roots as compared to the other three soils, but were the same as each other. This may be due to their heavy texture, which inhibited the development of roots, and an enhancing effect on top growth in these soils may be due to higher water holding capacities.

Table 3.4 Plant material yield at different harvesting times (weeks)

Soil		g/pot and (SD)							
		10 weeks 1	14 weeks 2	18 weeks 3	22 weeks 4	28 weeks 5	36 weeks 6	42 weeks 7	48 weeks 8
Dreghorn (Arkleston)	Tops	3.9 (0.2)	2.3 (0.1)	2.2 (0.1)	1.4 (0.3)	2.4 (0.1)	2.7 (0.2)	2.3 (0.1)	2.3 (0.0)
	Stubbles	2.0 (0.4)	-	2.0 (0.5)	-	-	2.9 (0.3)	-	4.4 (0.2)
	Roots	6.2 (0.3)	-	7.5 (1.6)	-	-	6.3 (0.1)	-	7.1 (0.3)
Dreghorn (Auchincruive)	Tops	4.2 (0.2)	2.2 (0.1)	2.1 (0.2)	1.4 (0.4)	2.4 (0.2)	2.5 (0.3)	2.0 (0.1)	2.0 (0.1)
	Stubbles	2.0 (0.1)	-	2.0 (0.4)	-	-	3.0 (0.4)	-	4.0 (0.5)
	Roots	6.5 (0.5)	-	9.3 (0.3)	-	-	7.9 (1.9)	-	7.0 (0.7)
Midelney (Topsoil)	Tops	4.0 (0.1)	2.5 (0.2)	2.2 (0.1)	1.8 (0.2)	2.8 (0.0)	2.7 (0.2)	2.7 (0.1)	2.4 (0.0)
	Stubbles	1.8 (0.2)	-	2.1 (0.1)	-	-	3.0 (0.2)	-	3.7 (0.2)
	Roots	3.2 (0.1)	-	2.9 (0.2)	-	-	2.9 (0.2)	-	2.4 (0.1)
Midelney (Subsoil)	Tops	3.6 (0.2)	2.4 (0.2)	2.2 (0.2)	1.8 (0.3)	2.1 (0.2)	1.9 (0.2)	2.3 (0.2)	1.9 (0.1)
	Stubbles	1.9 (0.1)	-	2.2 (0.2)	-	-	2.9 (0.4)	-	3.9 (0.0)
	Roots	3.1 (0.2)	-	2.7 (0.4)	-	-	2.8 (0.8)	-	2.1 (0.1)
Zinc contaminated soil	Tops	4.0 (0.3)	2.5 (0.2)	2.5 (0.2)	1.9 (0.4)	2.4 (0.2)	2.8 (0.2)	2.3 (0.2)	2.4 (0.1)
	Stubbles	1.8 (0.2)	-	1.9 (0.1)	-	-	3.0 (0.4)	-	3.8 (0.5)
	Roots	6.0 (0.1)	-	7.0 (0.5)	-	-	6.2 (0.9)	-	4.9 (0.7)

The cumulative yield (g) of grass (tops), as well as the plant material (tops + stubble + roots) for each soil are represented in Figures 3.2 and 3.3 respectively. The Figure 3.2 indicates cumulative tops yield in Midelney (topsoil) was high as compared to the other soils, but opposite results were seen in the cumulative yield of plant material shown by Figure 3.3 due to the lower yield of roots. Dreghorn (Arkleston), Dreghorn (Auchincruive) and Zn contaminated soil showed approximately the same result for plant material by promoting root development, being light and well structured soils. Growth rates of grass tops for each soil calculated from Figure 3.2, are 0.33, 0.34, 0.37. 0.39 and 0.41 g/pot per week for Midelney (subsoil), Dreghorn (Auchincruive), Dreghorn (Arkleston), Zn contaminated soil and Midelney (topsoil) respectively. But to some extent growth rate changed when whole plant material was taken into account. The growth rates of plant material (tops + stubble + roots) calculated from Figure 3.3 are 0.33, 0.37, 0.39, 0.44 and 0.45 g/pot per week for Dreghorn (Auchincruive), Midelney (subsoil), Zn contaminated soil, Dreghorn (Arkleston) and Midelney (topsoil) respectively.

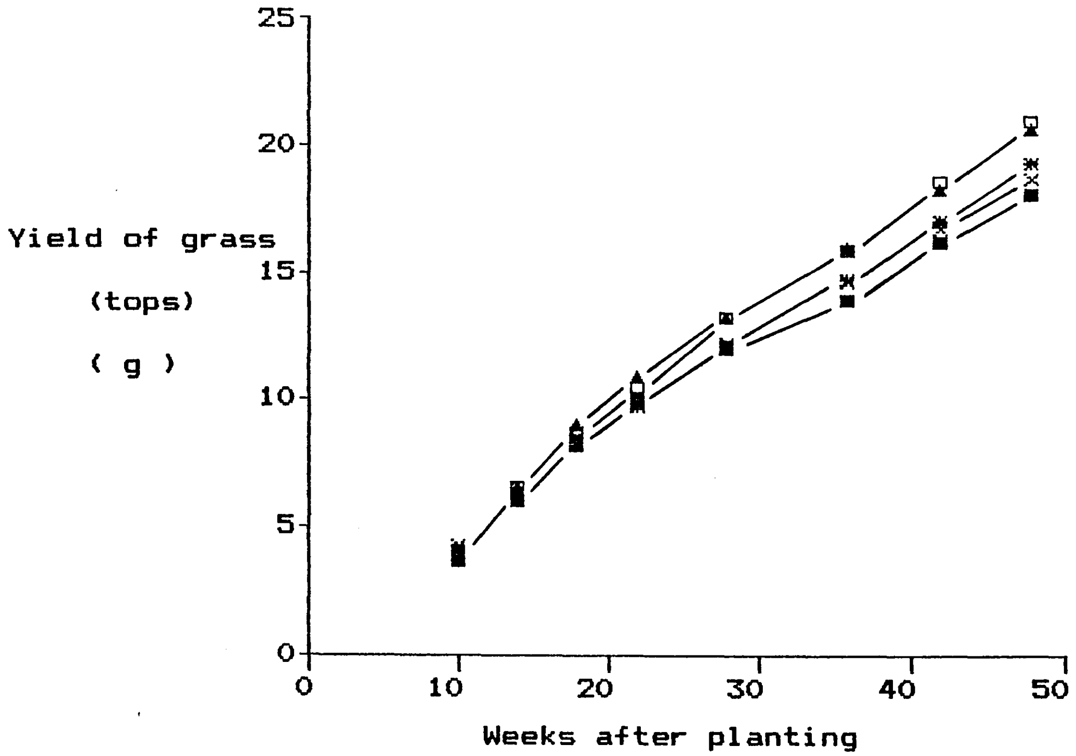


Fig. 3.2 Cumulative yield of grass (tops).

Dreghorn (Arkleston) (*); Dreghorn (Auchincruive) (x);
Midelney topsoil (□); Midelney subsoil (■);
Zinc contaminated soil (▲).

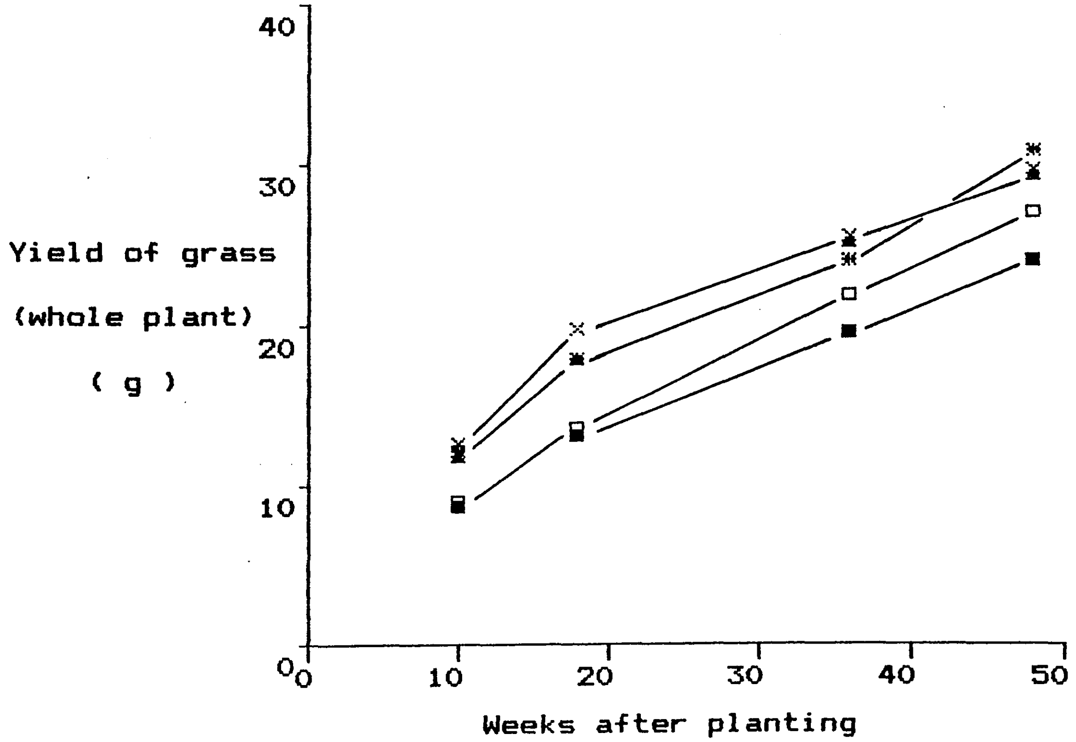


Fig. 3.3 Cumulative yield of grass (tops+stubble+roots).

Dreghorn (Arkleston) (*); Dreghorn (Auchincruive) (x);
Midelney topsoil (□); Midelney subsoil (■);
Zinc contaminated soil (▲).

3.3.3 Zinc in plant material

Mean values of zinc concentration in plant material are given in Table 3.5. Summarized data indicates that all the soils responded differently to zinc uptake. Zinc concentration in tops for the Zn contaminated soil was much higher compared to the other four soils, due to the luxury supply of zinc. The zinc levels observed during this study are much lower than the values reported by Albasel and Cottenie (1985). They observed the zinc content of ryegrass grown on uncontaminated Belgian soil ranged from 58 to 118 mg kg^{-1}, but grown on Zn-contaminated soil were higher, up to 18,000 mg kg^{-1}. They also suggested that ryegrass appeared to be much more tolerant than Bent grass. An upper critical zinc level ranging from 370 - 560 mg kg^{-1} in 4 - 5 month old ryegrass leaves was reported by MacNicol and Beckett (1985). In all three soils zinc concentration in tops was increased from the 1st harvest at 10 weeks after planting to the 14 week harvesting, except Midelney (topsoil) and Midelney (subsoil). A continuous increase was observed in zinc concentration in tops up to the 22 week harvest for all five soils, and a decline occurred after that.

Table 3.5 Concentration of Zinc in plant material at different harvesting times (weeks)

Soil		10 weeks 1	14 weeks 2	18 weeks 3	mg/kg and (SD) 22 weeks 4	28 weeks 5	36 weeks 6	42 weeks 7	48 weeks 8
Dreghorn (Arkleston)	Tops	28.5 (1.7)	50.5 (1.2)	54.0 (0.7)	66.3 (1.7)	63.2 (3.1)	65.6 (2.7)	58.5 (2.0)	50.6 (3.7)
	Stubbles	28.2 (1.5)	-	53.1 (1.3)	-	-	80.3 (4.6)	-	76.1 (0.9)
	Roots	70.3 (1.7)	-	63.0 (2.4)	-	-	88.1 (3.4)	-	73.2 (5.9)
Dregnorn (Auchincruive)	Tops	23.2 (0.9)	37.9 (1.4)	39.6 (2.5)	48.8 (1.2)	40.8 (3.6)	39.0 (2.2)	42.0 (1.0)	40.9 (1.0)
	Stubbles	20.0 (1.1)	-	28.7 (1.7)	-	-	47.5 (4.0)	-	60.8 (6.9)
	Roots	47.8 (0.9)	-	46.8 (1.2)	-	-	44.8 (3.4)	-	43.4 (0.8)
Midelney (Topsoil)	Tops	33.6 (1.4)	37.6 (1.5)	42.2 (1.5)	44.9 (1.3)	46.3 (2.5)	41.4 (1.6)	33.9 (1.6)	40.2 (0.8)
	Stubbles	25.1 (0.9)	-	30.2 (1.6)	-	-	36.9 (3.6)	-	34.8 (1.5)
	Roots	53.5 (1.1)	-	63.4 (4.3)	-	-	63.4 (2.2)	-	61.2 (3.0)
Midelney (Subsoil)	Tops	11.2 (0.5)	10.2 (0.4)	17.9 (10.9)	14.0 (0.9)	10.6 (1.5)	10.6 (0.6)	7.3 (0.5)	6.3 (0.6)
	Stubbles	9.0 (1.0)	-	6.5 (0.6)	-	-	10.6 (0.6)	-	7.9 (0.1)
	Roots	12.0 (1.0)	-	13.9 (1.0)	-	-	11.6 (1.1)	-	10.6 (0.6)
Zinc contaminated soil	Tops	85.5 (2.4)	146.3 (3.8)	187.3 (7.3)	230.3 (5.6)	228.0 (15.5)	165.6 (7.6)	216.6 (19.8)	212.4 (17.8)
	Stubbles	94.5 (4.5)	-	213.0 (3.2)	-	-	325.2 (12.9)	-	421.9 (33.2)
	Roots	349.7 (14.1)	-	427.2 (15.7)	-	-	497.0 (68.1)	-	511.9 (37.8)

The zinc concentration in stubble increased with the time of harvesting, indicating the accumulation of zinc in the older part of the plant. In the case of roots most of the zinc was accumulated in this part of the plant, showing generally the intermediate mobility of this element within a plant. Carroll and Loneragan (1968) reported that roots usually accumulate luxury levels of zinc if the supply is adequate. They observed from their study of growing clover, lucerne, oat and wheat, in different zinc solutions, zinc concentrations were below 12 ppm in the tops and 15 ppm in the roots for all species grown for 46 days at 0.01 µM zinc, and above 15 ppm in the tops and 17 ppm in the roots at 0.05 µM zinc. At a concentration in external solution of 6.25 µM zinc, zinc concentration in roots increased to a much greater extent than zinc in tops. In lucerne, zinc concentration ranged from 215 to 553 ppm in tops and from 1,049 to 2,146 ppm in roots. The same observations were reported by Lindsay (1972), that roots often show much higher zinc contents than tops, particularly if the plants are grown in a medium of high available zinc. Lindsay (1972) also suggested that zinc is intermediate in its mobility within the plants compared to that of other nutrients. Concentration of zinc in tops is also represented graphically in Figure 3.4.

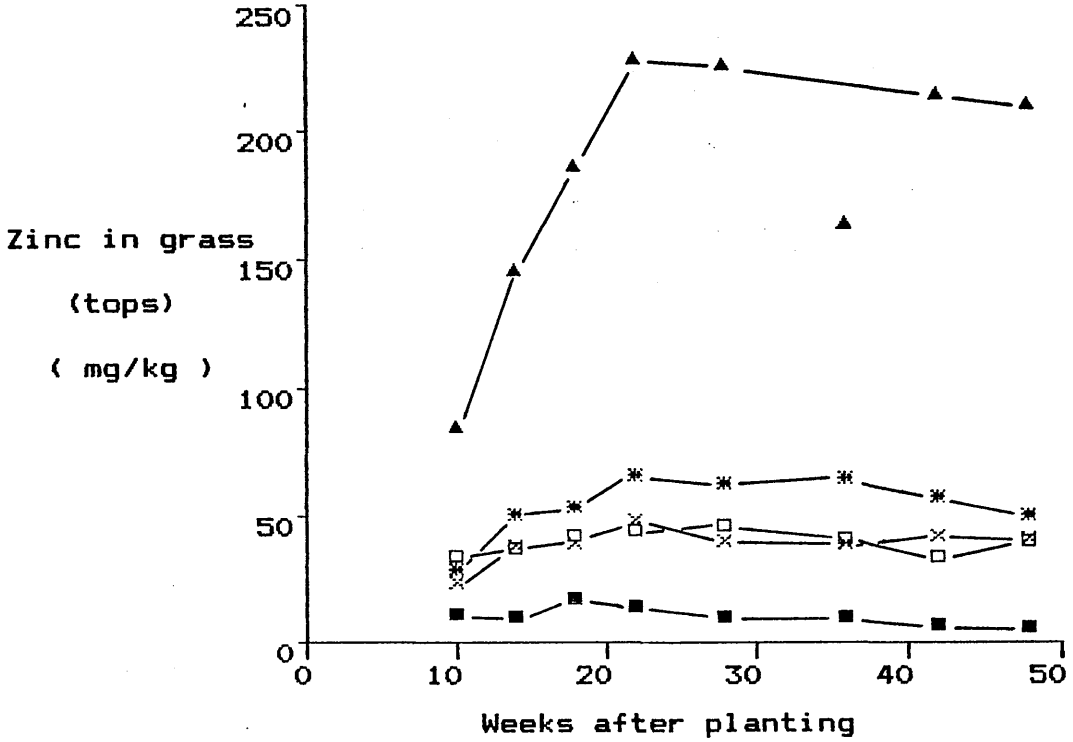


Fig. 3.4 Concentration of zinc in grass (tops).

Dreghorn (Arkleston) (*); Dreghorn (Auchincruive) (x);
Midelney topsoil (□); Midelney subsoil (■);
Zinc contaminated soil (▲).

It is obvious from this studythat total concentration of zinc in the soil is not responsible for plant uptake. Midelney (subsoil) has a higher total amount of zinc than Dreghorn (Arkleston) and Dreghorn (Auchincruive) (Table 2.4 Chapter 2), but the zinc uptake was much lower. The reason why Midelney (subsoil) was lower in uptake of zinc may be due to the high pH levels, which decreased the solubility of Zn^{2+} as reported by Lindsay (1972). The second cause may be due to the lower amount of zinc present in available soil fractions, which are considered immediately bioavailable (LeClair et al. 1984). Soils high in available zinc fractions showed higher zinc concentrations in tops, as well as in other parts of the plant. Lindsay (1972) and Russell (1973) observed that sometimes zinc deficiency can occur due to the unfavourable soil structure which restricts root development. These may be caused due to hardpans, by high water table or by other factors. Loneragan (1975) reported that physical and chemical properties may influence the form and distribution of plant roots in soils in ways which affect the absorption of trace metals.

Cumulative total amount of zinc taken up in tops (mg) is represented by Figure 3.5. All five soils showed two linear portions of the graph showing the difference in rates of zinc taken up by the tops. Zinc contaminated soil showed the higher rate of 100 μg Zn per week taken up in tops up to the 5th harvest at 28 weeks after planting, and declined later to 73 μg Zn per week. The total amount of zinc taken up in tops per week for Dreghorn

(Arkleston), and Midelney (topsoil), Dreghorn (Auchincruive) and Midelney (subsoil) were 27.5, 21.67, 19.17 and 6.67 µg up to the harvest at 22 weeks, which reduced later to 22.31, 16.15, 13.46, and 2.69 µg respectively. It indicates that in the initial growth stages the zinc uptake went up to a certain level and then became in equilibrium with soil zinc with time. Total zinc (mg) taken up by plant material (roots + stubble + tops) is represented in Figure 3.6. Higher amounts of zinc were taken up by plant material from the zinc contaminated soil than the other four soils, indicating a luxury supply of this element in this soil. The rates of total zinc taken up by plant material per week calculated from Figure 3.6 gave higher values for all five soils up to the harvest at the 18th week than the later harvestings. The values of total zinc taken up by plant material per week for zinc contaminated soil, Dreghorn (Arkleston), Dreghorn (Auchincruive), Midelney (topsoil), and Midelney (subsoil) were 273.5, 47.5, 37.5, 28.7, and 6.25 µg up to the harvest at the 18th week after planting, and the rate declined with time to 106.7, 29.7, 16.0, 18.0 and 3.3 µg per week respectively.

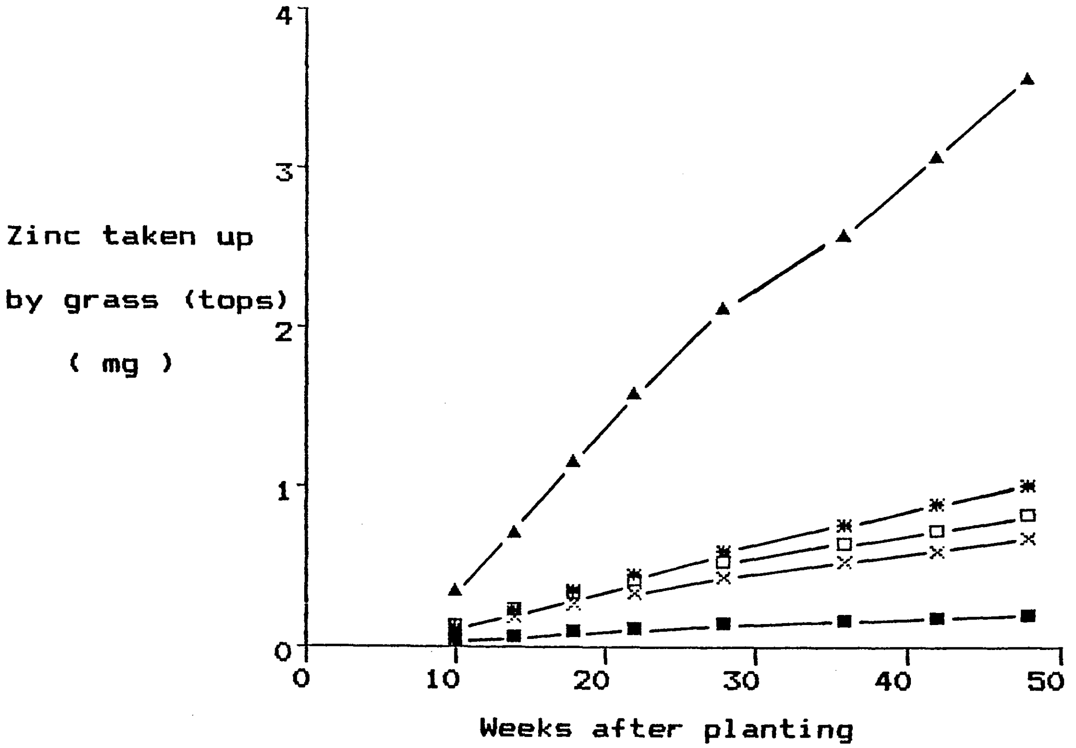


Fig. 3.5 Cumulative amount of Zn taken up by grass (tops).

Dreghorn (Arkleston) (*); Dreghorn (Auchincruive) (x);
Midelney topsoil (□); Midelney subsoil (■);
Zinc contaminated soil (▲).

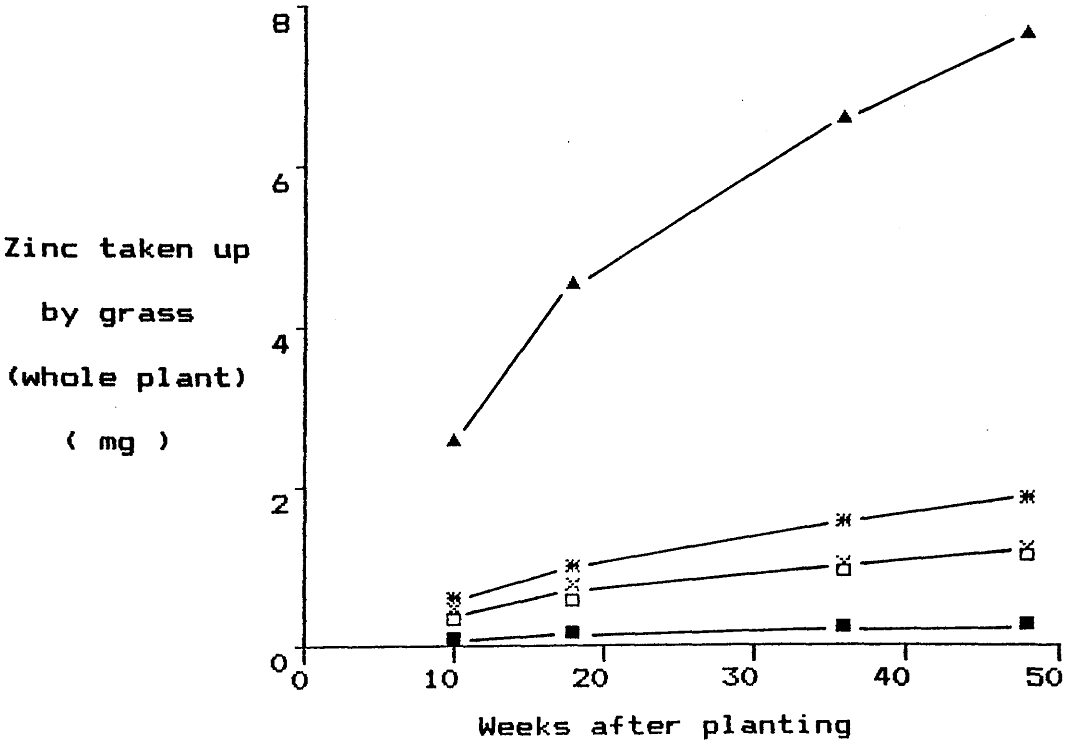


Fig. 3.6 Cumulative amount of Zn taken up by grass (tops + stubble + roots).

Dreghorn (Arkleston) (*); Dreghorn (Auchincruive) (x);
Midelney topsoil (□); Midelney subsoil (■);
Zinc contaminated soil (▲).

It is concluded from this study that the readily available soil pools of zinc are not decreased to any marked extent by plant uptake, but are maintained by other zinc fractions. It is further concluded that total soil zinc is not a good indicator for plant availability, but more available fractions are considered immediately responsible for plant uptake. Having higher amounts of zinc accumulating in roots when there is an adequate supply in soil confirmed the intermediate mobility of this element within the plant.

CHAPTER 4

STUDIES ON ZINC ADSORPTION BY SOIL

4.1 INTRODUCTION

Fundamental to the interpretation of a loss of some substance from an equilibrating solution as an adsorption process is the hypothesis that the phenomenon involved actually occurs on a surface. The loss of material from an aqueous solution phase, implies the concepts of

(i) adsorption, which is defined as a net accumulation at an interface;

or (ii) precipitation, which can be defined as an accumulation of a substance to form a new bulk solid phase (Sposito, 1984).

In soils, the problem of differentiating adsorption from precipitation is made especially severe by the fact that new bulk solid phases can precipitate on to the surfaces of existing solid phases, and that weathering solids may provide host surfaces for the more stable phases into which they transform. When no decision on the process can be made from experimental data, this loss of the material to the solid phases in a soil can be termed simply as "sorption" in order to avoid the implication that either adsorption or precipitation is occurring. It is well known that not only is zinc present in soils in various minerals, but it can also be held by exchange sites, chelated by organic matter and adsorbed on to solid surfaces. Separation of these reactions into precipitation, chelation or adsorption is most difficult, and very few studies permit a clear conclusion on this point. One of the major problems in studying adsorption reactions of zinc has been failure to consider which of the various hydrolysis and complex species of zinc in solution are adsorbed (Lindsay 1972).

The soil is considered as a support to plants and a holder of nutrients, while soil solution is the medium through which plants get nourishment. The composition of the solution phase, as well as soil itself, is most important for plants. Many processes in soil and landscape development are connected with the movement of dissolved substances. The concentration of dissolved nutrients is a characteristic value of the nutrient status of soils. But the processes which determine the concentration of different elements in the soil solution are not yet understood. An understanding of the mechanisms by which the concentrations of trace metals in soil solution are controlled is important regarding their supply to plants. Among these, zinc has been given considerable attention as it is found to be deficient in most wetland rice soils (Murthy 1982, Mandal and Mandal 1986, and Sajwan and Lindsay 1986), as well as in calcareous and alkaline soils (Kuo and Mikkelsen 1979, Shukla and Mittal 1979, Singh and Abrol 1985, and Gupta et al. 1987). It may also be present at toxic levels due to man-made practices such as spreading of sewage sludge (Sposito et al. 1983, and Kiekens et al. 1984).

Adsorption isotherms have been used for many years to investigate the nature of various types of adsorption phenomena. They provide useful models for chemisorption. The Langmuir adsorption isotherm was derived for the adsorption of gases on to solids and has since been used also to describe the relationship between the adsorption of ions by a solid and the concentration of the ions in solution (Shuman 1975). The Langmuir equation is well described in Chapter 1, Section 1.4.3.

In recent years zinc adsorption studies have been carried out on alkaline soils, in which zinc deficiency is very common (Udo et al. 1970, Saeed and Fox 1977, Singh and Sekhon 1977, Trehan and Sekhon 1977, Kuo and Mikkelsen 1979, and Singh and Abrol, 1985); and in acid soils, in which the zinc toxicity can be a greater problem (Saeed and Fox 1977, McBride and Blasiak 1979, Kuo and Baker 1980, and Cavallaro and McBride 1984). The effect of pH on zinc adsorption is very important, and a decrease in zinc solubility has been observed with increasing pH (Shuman 1975, Saeed and Fox 1977, Bar-Yosef 1979, McBride and Blasiak 1979, Harter 1983, Gupta et al. 1987, and Sanders and Elkherbawy 1987). Zinc can be adsorbed on the surfaces of clay minerals (Bingham et al. 1964, Reddy and Perkins 1974, and Wada and Abd-Elfattah 1979) and hydrous oxides, particularly iron and aluminium oxides (Stanton and Burger 1967, Forbes et al. 1976, Kinniburgh et al. 1976, Shuman 1976, 1977, Kalbasi et al. 1978, and Kinniburgh and Jackson 1982).

In spite of these aspects studied by various researchers, there may be other factors which can cause the variability in zinc adsorption by soils, which have not been given much attention. The length of shaking time can be an aspect of variability in zinc adsorption due to equilibration of soil with solution. Air drying of soil from its field moist condition may also alter the adsorption capability of soil, due to changes in the structural arrangement of organic matter. No information is available regarding this aspect of zinc adsorption. Literature shows a great deal of work regarding zinc adsorption by soils in the presence of different background electrolytes at differenmt ionic strengths, and the presence of different anions. The effect of various cations present in equilibrating solution has been studied to a lesser extent. From the work quoted, most of the data was interpreted in terms of adsorption of zinc on solid surfaces and few attempts were made to explain this data in terms of precipitation.

It is important to assess the effects of ionic strength and type of electrolyte when studying adsorption of zinc on soils, because the background salt may complex metals and compete for adsorption sites. Certain anions complex metals to a greater extent than others (Lindsay 1979). There have been several investigations dealing with the effect of anion type on adsorption of zinc in soil. Shuman (1986) used 0.005, 0.01, 0.05 and 0.1M $NaNO_3$ to compare effects of ionic strength on zinc adsorption by soils. He also used 0.01M Na_2SO_4, NaCl and $NaNO_3$ to compare the effect of different anions. Shuman observed that the higher the ionic strength the less zinc was adsorbed by soil. Adsorption of zinc by soil was greater from a SO_4^{2-} background salt that NO_3^- or Cl^-. Adsorption of zinc from the NO_3^- and Cl^- system yielded the same isotherm at pH 6. Kinniburgh and Jackson (1982) used 1M $NaNO_3$ solution as a background electrolyte for zinc adsorption by iron oxides. They observed that zinc adsorption at pH 6.5 was about 10 times greater than at pH 5.5. Sodium salts of chloride, nitrate and sulphate were used at concentration of 0.005, 0.02 and 0.1M for zinc adsorption by soils by Elrashidi and O´Connor (1982). They found that neither ionic strength nor anion complex formation significantly affected zinc sorption. Singh and Abrol (1985) used two soils saturated with 1N NaCl and 1N $CaCl_2$ for a zinc adsorption study, and observed that more zinc was adsorbed by Na-saturated soil than Ca-saturated soil. Pulford (1986) used potassium, sodium and calcium salts in forms of chloride and sulphate as background electrolytes for zinc adsorption by soil. He found that more zinc was adsorbed by the soil in the presence of Na salts as background electrolyte than the other two salts.

Although shaking time can cause variability in adsorption of zinc by soils, various workers have used different times of equilibration of soil with solution. Harter (1983) and Singh and Abrol (1985) used 24 hours shaking time for zinc adsorption by soils. Shuman (1986) used 20 hours, while Kuo and Mikkelsen (1979) used 4 days shaking time for equilibration of soil with solution in zinc adsorption studies. Half an hour shaking time was used for achieving equilibrium by Shukla and Mittal

(1979). Pulford (1986) used 18 hours shaking in his procedure for zinc adsorption by soils. Bar-Yosef (1979) used 16, 48, 168 hours for shaking the samples in his zinc adsorption study. He observed that zinc adsorption by soil was enhanced with time of shaking.

Air-drying field moist soil could provide the possibility of changes in arrangement of organic matter due to the death and decay of micro-organisms. On drying and rewetting unequal swelling and compression of entrapped air could cause aggregates to disintegrate and bring some structural changes within the soil. These changes can cause alteration in the ability of soils to adsorb zinc. No information is available regarding the effect of these observations on zinc adsorption by soils. A few attempts have been made to study this effect for phosphate adsorption by the soil (Olsen and Court, 1982 and Haynes and Swift, 1985). They observed from their studies that phosphate adsorption by soil was increased in air-dried samples compared to moist conditions.

Although precipitation is an important reaction in soil, it is often not considered, because the solid phase species are normally too soluble to exist at pH values found in many soils, (<pH 8). Such zinc species include the oxide, hydroxide, carbonate, phosphate and silicate (Mikkelsen and Kuo, 1977). Shuman (1975) observed that sandy and highly colloidal soils at pH 8 adsorbed similar amounts of zinc, indicating that the zinc was chemically precipitated as $Zn(OH)_2$. The sharp apparent increase in zinc adsorption by iron and aluminium hydrous oxides

reported by Shuman (1977) may also be due to precipitation. Lindsay (1979) suggested that franklinite ($ZnFe_2O_4$) could control the zinc solubility at pH values found in most soils. Bruemmer et al. (1983) considered the mechanisms for the control of zinc in soil solution to be adsorption-desorption in the soils of pH < 7 and precipitation-dissolution in neutral to alkaline pH soils. Pulford (1986) observed that precipitation could be a mechanism for controlling the zinc in soil solution if the presence of iron is not ignored.

The experiment reported here was designed to investigate the amounts of zinc adsorbed by different soils using water as background having no electrolyte, as well as to study the effect of length of shaking time on zinc adsorption by soil. The second objective was to see the effect of field moist condition on zinc adsorption using fresh versus air-dried soils. The third one was to study whether zinc adsorption by soil would be affected by using different salts in forms of chloride and sulphate as background electrolytes.

4.2 METHODS

4.2.1 General procedure for zinc adsorption

1 g air-dried, 2 mm sieved soil was weighed in 4-ounce glass bottles, and 50 cm^3 of solution containing 0, 0.1, 0.2, 0.5, 0.75, 1.0, 2.0, 5.0, 7.5, 10, 20, 30, 40, 50, 60, 70, 80, 90, and 100 mg Zn l^{-1} was added to these bottles. All these zinc solutions were made in 50

cm^3 volumetric flasks from 1000 mg Zn l^{-1} stock solution made up in deionized water. The bottles were tightly sealed and soil-zinc solution suspensions were shaken by end-over-end shaker for 18 hours. The pH of the equilibrium suspension was measured using a combination pH electrode after shaking. The suspensions were filtered through Whatman filter paper no: 42 and filtrates were collected in 100 cm^3 polyethylene bottles. A control set of zinc solutions having the same concentrations (0 - 100 mg Zn l^{-1}) for measuring the initial zinc in solution, was also prepared in 50 cm^3 volumetric flasks. Zinc and iron concentrations in the filtered equilibrium solution, as well as initial zinc concentrations in the control set, were measured by flame atomic absorption spectrophotometry. Zinc and iron were measured at wavelengths of 213.9 nm and 248.3 nm respectively, using the air-acetylene flame. All zinc measurements were made with zinc standards ranging from 0 - 1.5 mg Zn l^{-1} by diluting appropriately the filtrates, as well as the initial zinc solution. The amount of zinc adsorbed was calculated from the difference between the initial and final solution concentrations.

4.2.2 Procedure for water as background for zinc adsorption

Four soils, providing a range of pH, loss on ignition, clay and iron oxide contents (Chapter 2, Section 2.2, Table 2.1) were used for this study. 1 g air-dried, 2 mm sieved soil was taken in 4-ounce glass bottles, and

50 cm^3 of solutions containing all zinc concentrations described in the general procedure (Section 4.2.1) was added. All zinc concentrations were made in 50 cm^3 volumetric flasks from 1000 mg Zn l^{-1} stock solution of $ZnSO_4$ and volume was made with deionized water. A control set of zinc solutions (0 - 100 mg Zn l^{-1}) for measuring initial zinc in solution, was also made in 50 cm^3 volumetric flasks with deionized water. The soil-zinc solution suspensions were treated under the procedure described in Section 4.2.1 to obtain the amount of zinc adsorbed by the soil.

4.2.3 Procedure for examining shaking time for zinc adsorption studies

In the case of shaking time effect, the zinc concentrations used were 10, 20, 30, 40, and 50 mg Zn l^{-1}. These concentrations were made in 50 cm^3 volumetric flasks from a 1000 mg Zn l^{-1} stock solution of $ZnSO_4$, and volume was made with deionized water. A control set of these zinc concentrations was also made in the same way. 1 g air-dried, 2 mm sieved soil taken in 4-ounce glass bottles, and 50 cm^3 of solution having these concentrations was added. The soil-zinc solution suspensions were shaken by end-over-end shaker for one week. All the steps regarding pH, zinc and iron determinations and amount of zinc adsorbed were adopted as described in the procedure 4.2.1.

4.2.4 Procedure for measuring zinc adsorption in air-dried versus fresh soil

To study the effect of field moist conditions on zinc adsorption, the first four soils described in Chapter 2, Section 2.2, Table 2.1 were used. Fresh soils were collected and passed through a 2 mm sieve. Subsamples from each soil were air-dried. 1 g, on oven dry basis, for both fresh and air-dried soil was taken in 4-ounce glass bottles. Zinc solutions ranging from 0 - 100 mg Zn l^{-1} were made up, from a 1000 mg Zn l^{-1} stock solution as $ZnSO_4$, in 50 cm^3 volumetric flasks, and volume made by 0.05M K_2SO_4 were added to these bottles. Zinc solution suspensions were shaken by end-over-end shaker for 18 hours. A control zinc set (0 - 100 mg Zn l^{-1}) was also made in 50 cm^3 volumetric flasks with 0.05M K_2SO_4 for initial zinc in solution. All the measurements of pH, zinc and iron were carried out as described in Section 4.2.1. All the Zn standards and dilution of equilibrium filtered solutions, as well as initial zinc solutions were made with 0.05M K_2SO_4.

4.2.5 Procedure for measuring zinc adsorption in various background electrolytes

Four soils, given in Chapter 2, Section 2.2, Table 2.1, were used to see the effect of background electrolytes on zinc adsorption. 1 g air-dried, 2 mm sieved soil was taken in 4-ounce glass bottles. Zinc solutions ranging from 0 - 100 mg Zn l^{-1} were made from

1000 mg Zn l^{-1} stock solution as $ZnSO_4$ in 50 cm^3 volumetric flasks, and volume made by the appropriate salt solution, was added to these bottles. Salt solutions used were 0.05M K_2SO_4, 0.05M Na_2SO_4, 0.05M $(NH_4)_2SO_4$, 0.05M $MgSO_4$, saturated $CaSO_4$, 0.05M $MgCl_2$, 0.05M $CaCl_2$, 0.1M NaCl, 0.1M KCl and 0.1M NH_4Cl. The salts used were all of analytical reagent grade. The soil-zinc solution suspensions were shaken by end-over-end shaker for 18 hours. A control set of zinc solutions (0 - 100 mg Zn l^{-1}) with each salt was also made for initial zinc in solutions. The procedure for pH, zinc and iron measurements was as adopted before in Section 4.2.1. All the zinc standards and dilutions of filtrates, as well as initial zinc solutions were made up in the appropriate electrolyte, in order to overcome background interferences.

4.3 RESULTS AND DISCUSSION

4.3.1 Zinc adsorption by soils in a water background

This study was carried out for four different soils using different zinc concentrations in deionized water, having no background electrolytes. The observed data will be treated in terms of adsorption-desorption or precipitation-dissolution mechanisms.

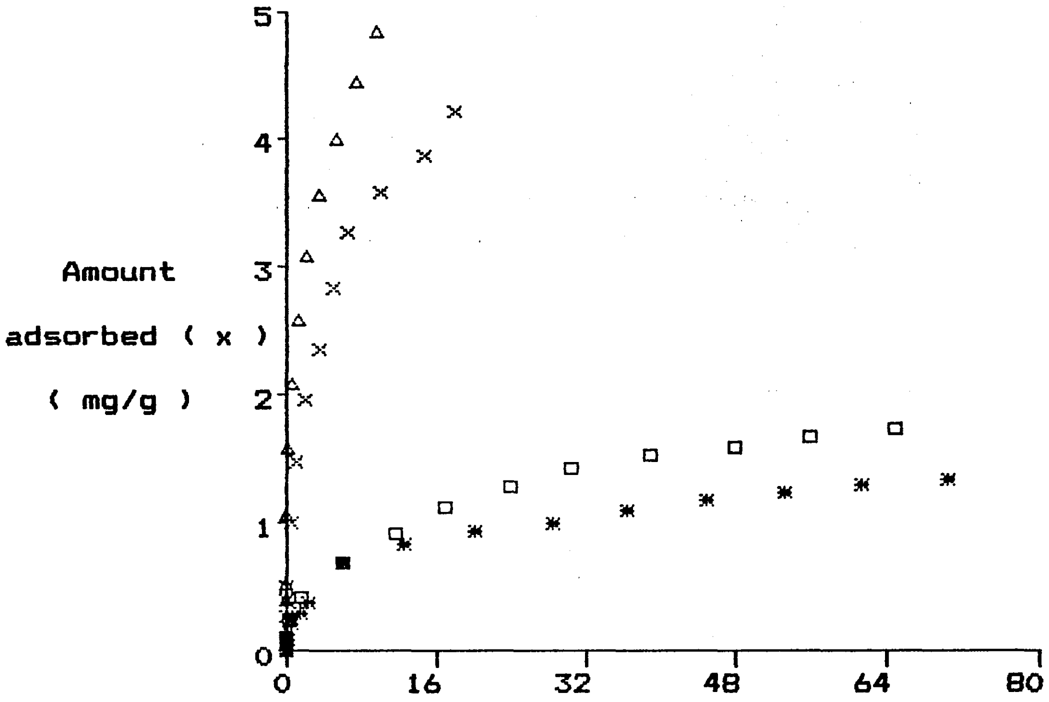


Fig. 4.1a Zinc adsorption isotherm in water background.

Dreghorn (Arkleston) (*); Dreghorn (Auchincruive) (□);
Midelney topsoil (x); Midelney subsoil (△).

4.3.1.1 Adsorption-desorption mechanism

Adsorption isotherms obtained by plotting the amount of zinc adsorbed versus concentration of zinc remaining in solution at equilibrium, were smoothly rising curves (Figure 4.1a). They show the differences in zinc adsorption between the four soils, revealing the order of zinc adsorption as; Midelney (subsoil) > Midelney (topsoil) > Dreghorn (Auchincruive) > Dreghorn (Arkleston). The former two soils are alike in most of their physical and chemical properties, while the latter two are also similar in their properties, but different from the first two (Table 2.1). The latter two soils are highly colloidal soils compared to the other soils, which have high amounts of sand. The observed data show that zinc adsorption was greater in the highly colloidal soils than in the sandy soils, due to greater surface area. Shukla and Mittal (1979) observed that more zinc was adsorbed by a loam soil than sandy soil, showing the effect of the number of adsorption sites. A second reason for retention of more zinc by Midelney (subsoil) and Midelney (topsoil) may be their higher pH, which decreases zinc solubility. Reddy and Perkins (1974) observed a higher fixation of zinc at all levels of zinc application as the pH of a clay suspension was increased from 6.2 to 7.6. They claimed that greater fixation of zinc at higher levels was probably due in part to reduced solubility of Zn. A third reason for higher amounts of zinc adsorption by these soils may be due to the retention of the univalent $Zn(OH)^+$ ion rather than the divalent Zn^{2+} at high pH. Harter (1983) reported that the increase in the ratio of univalent $Zn(OH)^+$ ions to the divalent Zn^{2+} ions from pH 6.0 to 8.0 would predict an approximately 60% increase in metal retention.

Midelney (subsoil) adsorbed more zinc as compared to Midelney (topsoil), although it had lower amounts of organic matter. This increase may be attributed to its greater dispersion at the time of equilibrium with solution, providing more surfaces for adsorption. The observed results are in agreement with Kuo and Baker (1980). They observed that more zinc was sorbed in the subsoil as compared to the surface soil, even though soil samples from the lower depth (60-75 or 75-90 cm) contained lower amounts of organic matter.

Dreghorn (Auchincruive) and Dreghorn (Arkleston) adsorbed less zinc compared to the other two soils. This may be attributed to their sandy, coarse textured nature. These soils have low amounts of clay and may provide less adsorption sites for zinc. These results have an agreement with Sidhu, Randhawa, and Sinha (1977). They claimed that zinc adsorption isotherms for soils had slopes that increased as the texture of the soils became coarser. The other reason for less adsorption of zinc by these soils may be due to their lower pH levels, which may keep this element in solution. Shuman (1975) observed that low pH reduced zinc adsorption more for the sandy soils than for those high in colloidal-size material.

Adsorption data was analysed according to the

Langmuir adsorption equation, which in its linear form is:

$$\frac{c}{x/m} = \frac{1}{kb} + \frac{c}{b}$$

This equation is discussed in Section 1.4.3. The values of c/x versus c were plotted (Figures 4.1b,c) to fit the data to the Langmuir isotherm. Figures 4.1b and c show an excellent fit when the curves were resolved into two linear portions. Shuman (1975), Shukla and Mittal (1979), and Pulford (1986) used this approach to their data of zinc adsorption by soils, which did not conform to the simple Langmuir equation as it did not fit a single straight line. They described their data by resolving the curves into two straight lines, as split isotherms. The existence of two linear portions in the curves might indicate two types of adsorption sites or adsorption reactions as reported by Shuman (1975) and Shukla and Mittal (1979).

The most common way of resolving this deviation from a straight line is to split the isotherm. The data in Figures 4.1b and c lie on two straight lines, but there is no reason to suppose that adsorption occurs at only two surfaces, as suggested by Pulford (1986). A large number of surfaces, covering a range of bonding energies, are more likely to be found in soil. Two straight lines may only show the distribution of experimental data. If there had been more points, more evenly distributed, then a curve could have a better description than two straight lines.

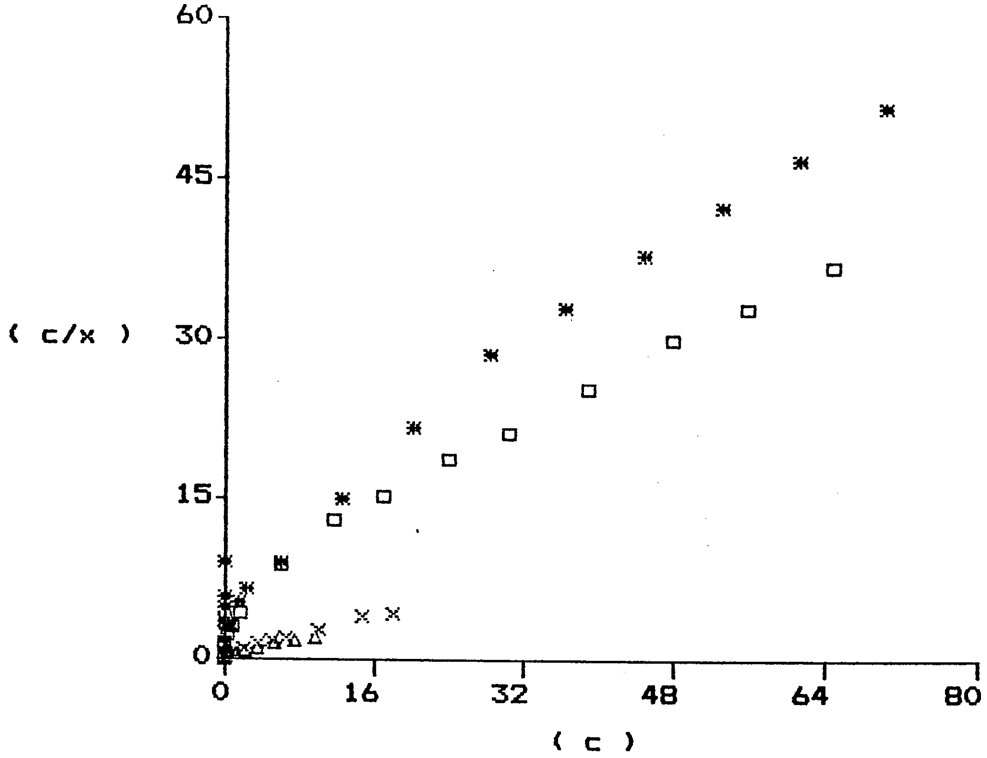


Fig. 4.1b Langmuir adsorption isotherm in water background.

Dreghorn (Arkleston) (*); Dreghorn (Auchincruive) (□);
Midelney topsoil (x); Midelney subsoil (Δ).

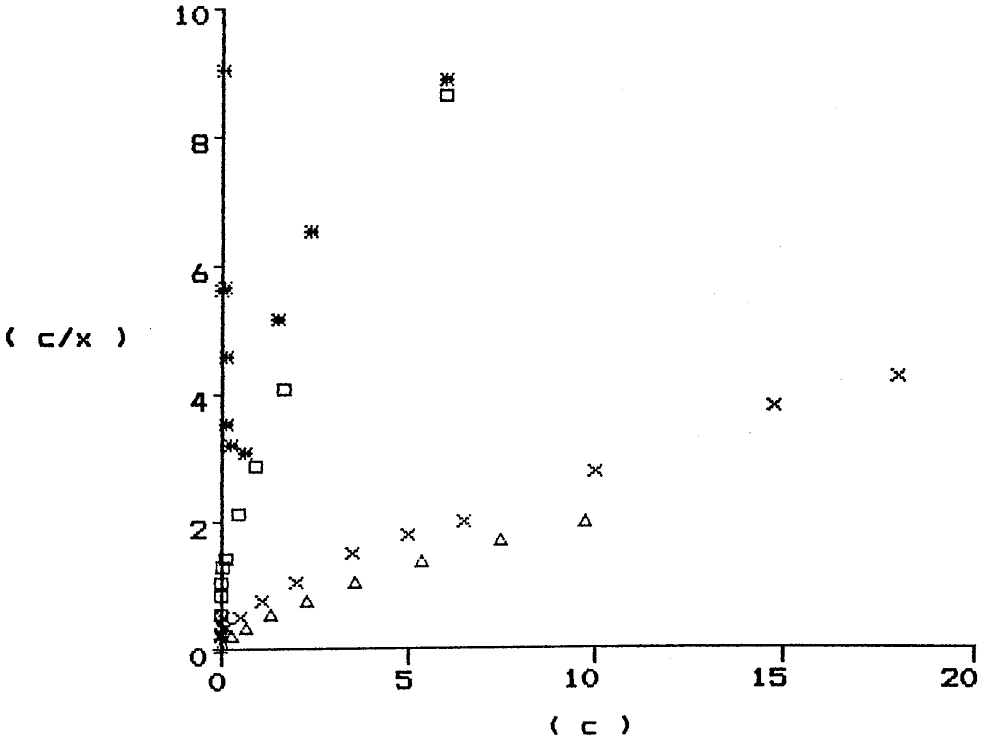


Fig. 4.1c Langmuir adsorption isotherm in water background.

Dreghorn (Arkleston) (*); Dreghorn (Auchincruive) (□);
Midelney topsoil (x); Midelney subsoil (Δ).

When the use of the Langmuir equation was critically examined by Harter and Baker (1977), they gave evidence that the equation soil scientists have been using is in the wrong form. This error is of no great importance when the equation is used to calculate the adsorption maximum, but becomes important to understand adsorption dynamics and bonding strengths.

Veith and Sposito (1977) observed that precipitation and adsorption reactions give straight line plots when fitted to the Langmuir equation under certain experimental conditions. They also suggested that if the measurements are made at very low equilibrium solution concentrations, the line for precipitation reactions bends upwards and approaches infinite values. This type of behaviour is clearly seen in Figure 4.1c from the experimental data for Dreghorn (Arkleston). The same behaviour was also reported by Pulford (1986).

If data fail to conform to the Langmuir equation, a less demanding equation can be used. Bohn et al. (1985) presented the linear form of the Freundlich equation as below (see also Section 1.4.3):

$$\log \frac{x}{m} = \frac{1}{n} \log c + \log k$$

Experimental data was replotted according to this linear form of the equation, and all the soils conform to the Freundlich equation above initial zinc concentrations of 7.5 mg l^{-1} (Figure 4.1d), where the Langmuir equation was giving two straight lines (Figures 4.1b and c).

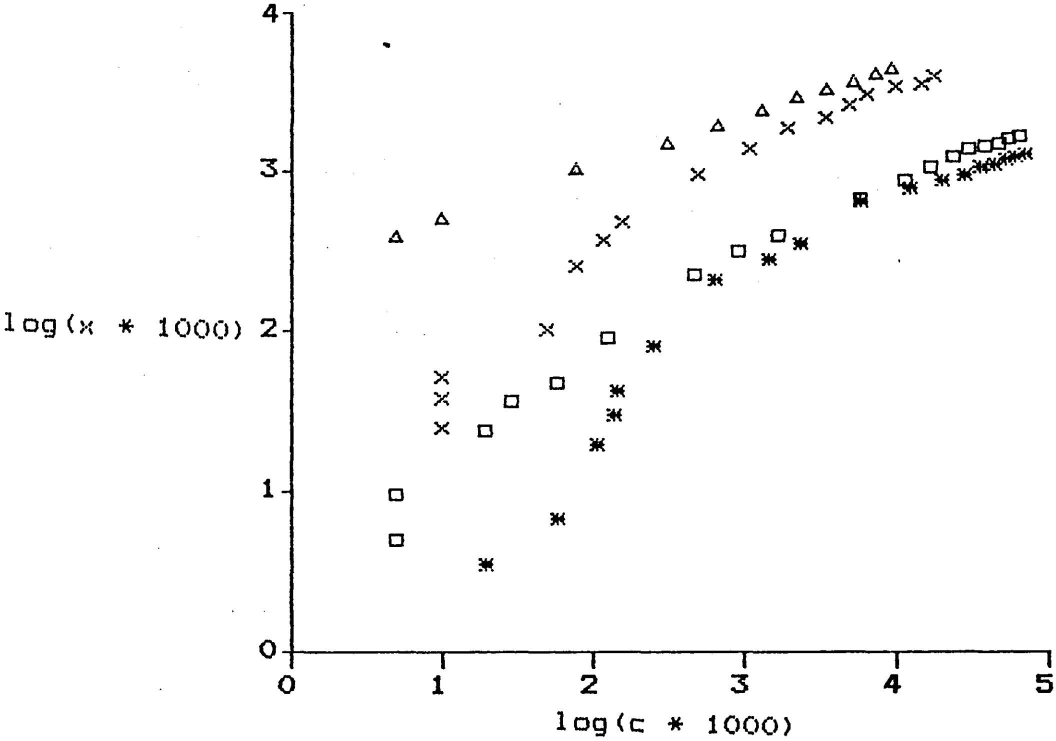


Fig. 4.1d Freundlich adsorption isotherm in water background.

Dreghorn (Arkleston) (*); Dreghorn (Auchincruive) (□);
Midelney topsoil (x); Midelney subsoil (△).

This suggests that the energy of adsorption decreases logarithmically as the fraction of covered surface increases. Kurdi and Doner (1983) observed that zinc or copper ion sorption by different soil types, conformed to a Freundlich equation but not to a Langmuir equation. When all zinc concentrations from 0.1 - 100 mg l^{-1} were taken into account for Freundlich plots (Figure 4.1d), two straight lines were drawn as a split isotherm. It indicates that this could be due in part to a different adsorption mechanism occurring at high zinc concentrations, with increasing surface heterogeneity that affects the adsorption at higher surface coverage. Kuo and Mikkelsen (1979) also observed in their zinc adsorption study by two alkaline soils, that the Freundlich plot could be drawn as two linear portions. While Shukla and Mittal (1979) reported the resolving of Freundlich isotherms into three distinct portions having different k and n values. They suggested that different adsorption patterns at different concentrations indicated differential bonding energies for adsorbed Zn, and occurrence of precipitation reactions along with adsorption in the soils used.

Zinc adsorption constants for the four soils were calculated from Langmuir as well as Freundlich plots and are given in Table 4.1. This shows that adsorption maxima were in the same order when both the full Langmuir plots and the upper linear part of the plots were considered (Figure 4.1b and c). Adsorption maximum values, indicating the adsorption capability of soils, were much higher in the two soils having more clay than the two sandy soils. The adsorption maximum values for the upper linear part of the plots were higher than the full Langmuir plots for each soil. For the bonding energies (k), a lower value was obtained when calculated from the upper linear part of the plot, compared with that obtained from the full isotherm. The overall order of bonding energies increases with increasing adsorption maximum. It indicates that bonding energy for zinc decreases with the increase of surface coverage by adsorption at higher zinc concentrations. Initially high energy sites are filled, which have a high bonding energy, after that the low energy sites are occupied and bonding energy is reduced. The soils high in clay content had higher bonding energies for zinc than sandy soils, as reported by Shuman (1975). The R^2 values remain mostly the same or slightly different when calculated for the whole or upper part only of the Langmuir plots.

The slope, intercept and R^2 values for each soil calculated from the Freundlich plots are also represented in Table 4.1. There is no meaning of constants, as compared to the Langmuir, but these changes indicate the heterogeneity of adsorption surfaces or different adsorption sites.

Table 4.1 Zinc adsorption constants for four soils calculated from Langmuir and Freundlich Plots in water background

Soil		Langmuir Plot			Freundlich Plot		
		Adsorption maximum b mg g^{-1}	Bonding energy k l mg^{-1}	R^2	Slope	Intercept	R^2
Dreghorn (Arkleston)	(Full)	1.42	0.13	0.99	0.68	0.01	0.93
"	(Top)	1.79	0.04	1.00	0.39	1.25	0.98
Dreghorn (Auchincruive)	(Full)	1.75	0.22	0.98	0.57	0.64	0.98
"	(Top)	2.17	0.06	1.00	0.40	1.32	0.99
Midelney (Topsoil)	(Full)	4.38	0.56	0.99	0.65	1.06	0.96
"	(Top)	4.92	0.28	0.99	0.40	1.95	0.99
Midelney (Subsoil)	(Full)	4.85	1.43	0.98	0.33	2.39	1.00
"	(Top)	5.67	0.51	0.99	0.33	2.39	1.00

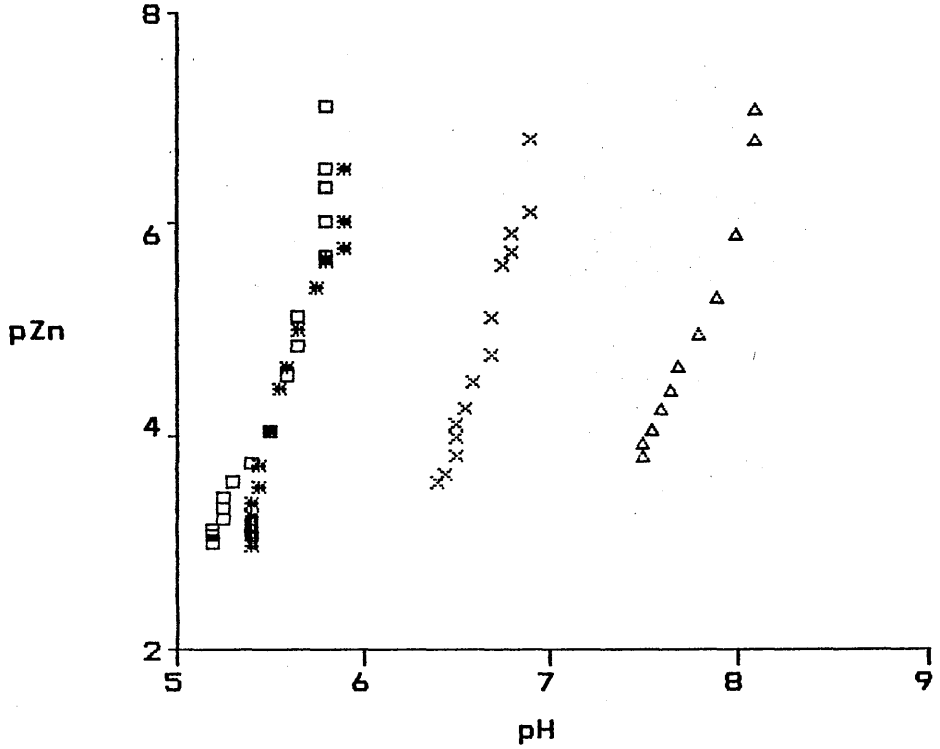


Fig. 4.1e Equilibrium pZn versus pH in water background.

Dreghorn (Arkleston) (*) $pZn = -25.88 + 5.43pH$
Dreghorn (Auchincruive) (□) $pZn = -21.34 + 4.68pH$
Midelney (topsoil) (x) $pZn = -32.71 + 5.65pH$
Midelney (subsoil) (Δ) $pZn = -25.04 + 3.85pH$

4.3.1.2 Precipitation-dissolution mechanism

Zinc solubility, as influenced by suspension pH for different soils is presented in Figure 4.1e by plotting the negative log of Zn remaining in solution (pZn) versus pH. Experimental data showed a relationship between pH and zinc solubility in different soils. Figure 4.1e indicates two linear parts of the graphs for each soil at different equilibrium zinc concentrations. At low zinc concentrations, the upper part of the graph indicates that no H^+ ions were replaced and pH of the suspension remained unchanged. While at higher zinc concentrations, the corresponding decrease in pH was observed as a result of H^+ ions released. It suggests that there are two mechanisms involved in controlling zinc concentration, but that H^+ ions are released only by one of these mechanisms. The slopes of the lower linear part of the graphs (Figure 4.1e) for each soil are given, indicating the variability in H^+ ions released from the soil surface. Two soils, Dreghorn (Arkleston) and Dreghorn (Auchincruive), having $pH < 6$, released more H^+ ions per Zn^{2+} ion adsorbed than Midelney subsoil ($pH > 8$), but less than Midelney topsoil ($pH > 7$). Zinc removal from solution was highest in Midelney subsoil. It may be that the Midelney subsoil has a high base saturation, and so exchange of zinc on to the surface releases few H^+ ions. In Midelney topsoil the release of more H^+ ions compared to the other soils may be due to the role of organic matter.

The uptake of zinc from solution increased in soils with increasing pH. The possibility of precipitation of

Zn as $Zn(OH)_2$ at relatively high pH could not be dismissed, as reported by Bingham, Page and Sims (1964). Bruemmer et al. (1983) also suggested the possibility of precipitation in the B horizon (subsoil) at pH 7 - 8. Barrow (1986) observed that zinc retention by soils was increased as pH increased, suggesting that this effect could be described by assuming that $ZnOH^+$ ion was retained, and the effect of pH was due to the increased proportion of this ion in solution. The observed data for Midelney subsoil may also suggest the retention of this form of zinc.

4.3.2 Effect of shaking time on zinc adsorption

The experimental data obtained from this study will be explained in terms of adsorption-desorption or a precipitation-dissolution mechanism.

4.3.2.1 Adsorption-desorption mechanism

Figures 4.2a, 4.2b, 4.2c, and 4.2d represent the zinc adsorption isotherms for 18 hours and 7 days shaking time of Dreghorn (Auchincruive), Dreghorn (Arkleston), Midelney (topsoil), and Midelney (subsoil) respectively. The amounts of zinc adsorbed at 7 days shaking were slightly higher than at 18 hours shaking in three soils, but a much greater increase was observed in Midelney (subsoil) (Figure 4.2d). It indicates that the length of shaking time enhanced the zinc adsorption due to better equilibration of soil with zinc solution.

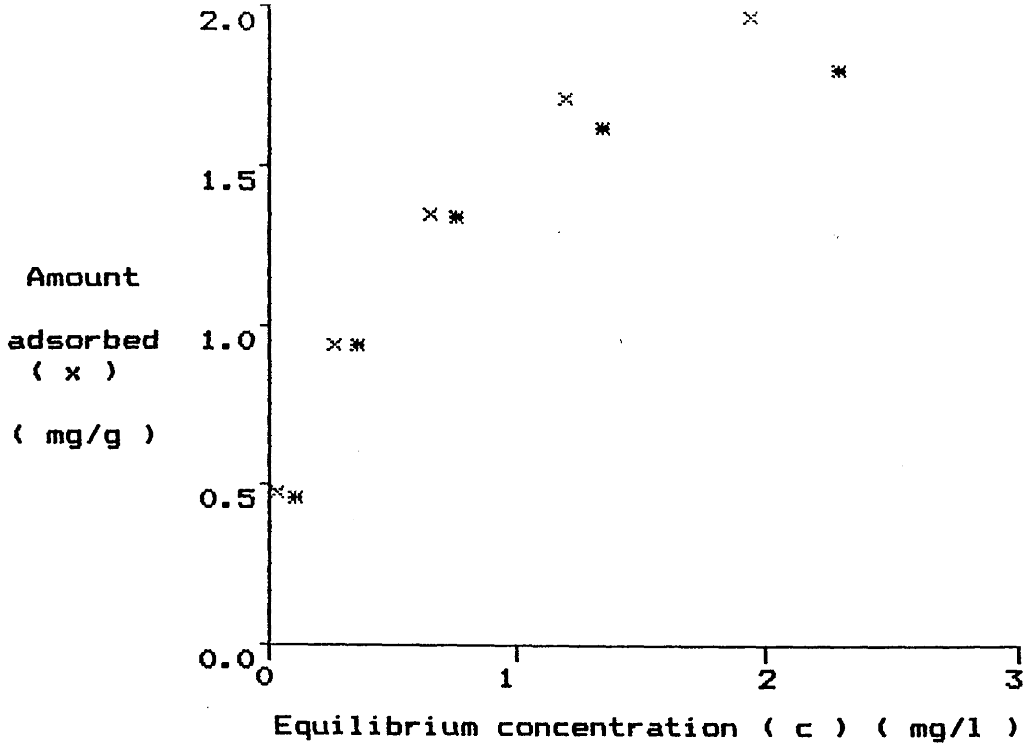


Fig. 4.2a Dreghorn (Auchincruive) zinc adsorption isotherm after 18h (*) and 7d (x) shaking.

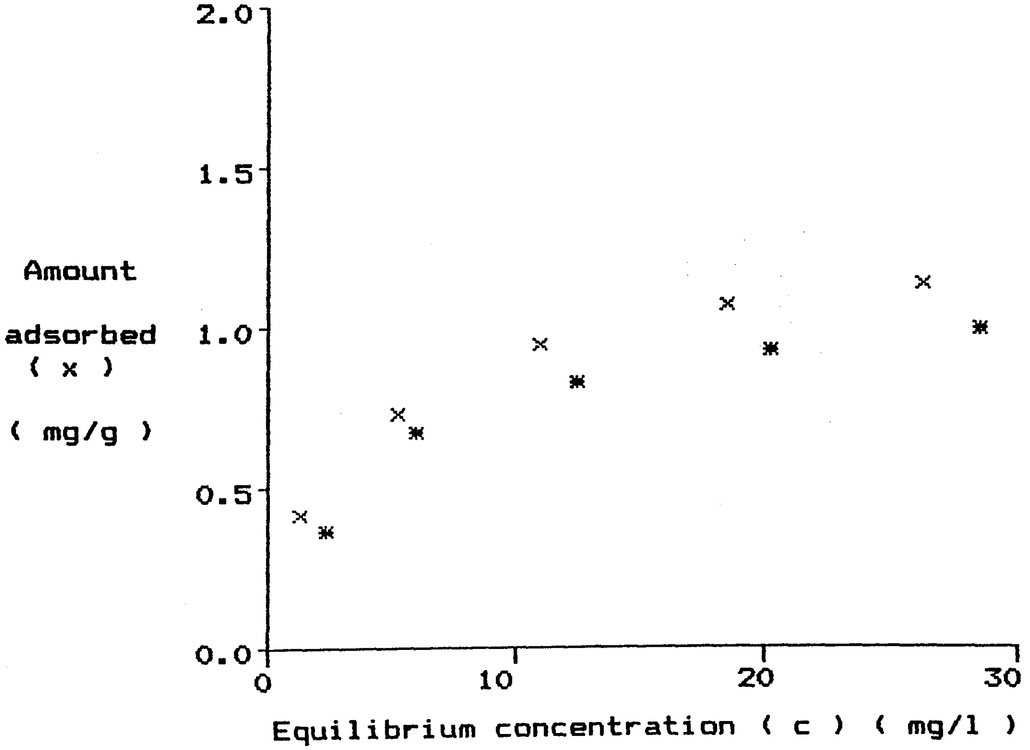


Fig. 4.2b Dreghorn (Arkleston) zinc adsorption isotherm after 18h (*) and 7d (x) shaking.

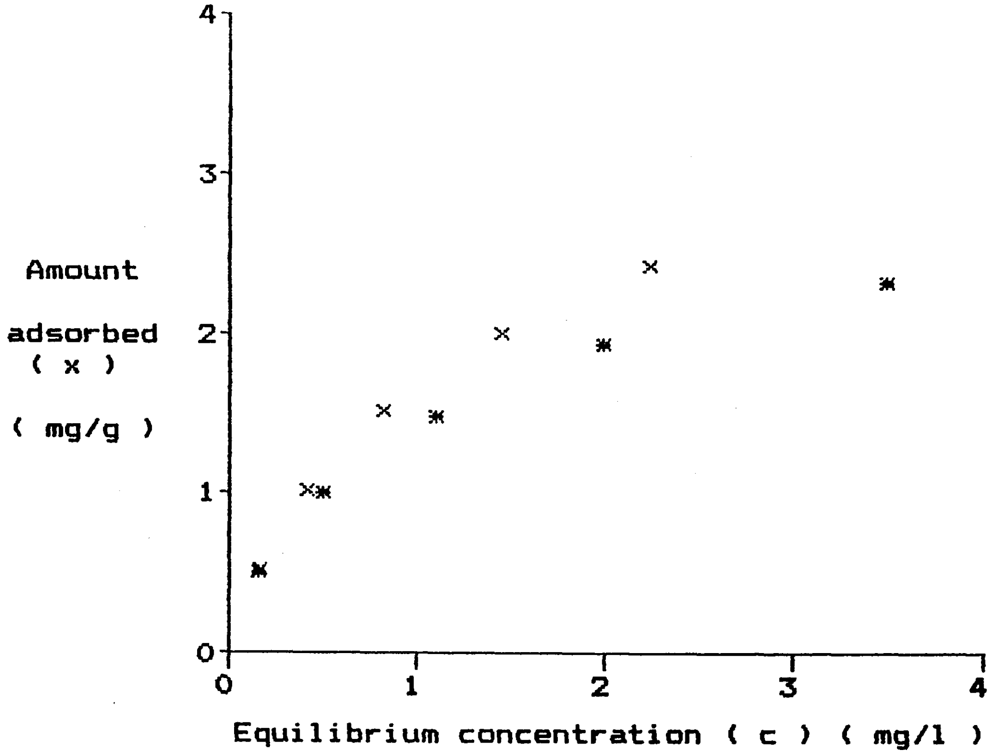


Fig. 4.2c Midelney (topsoil) zinc adsorption isotherm after 18h (*) and 7d (x) shaking.

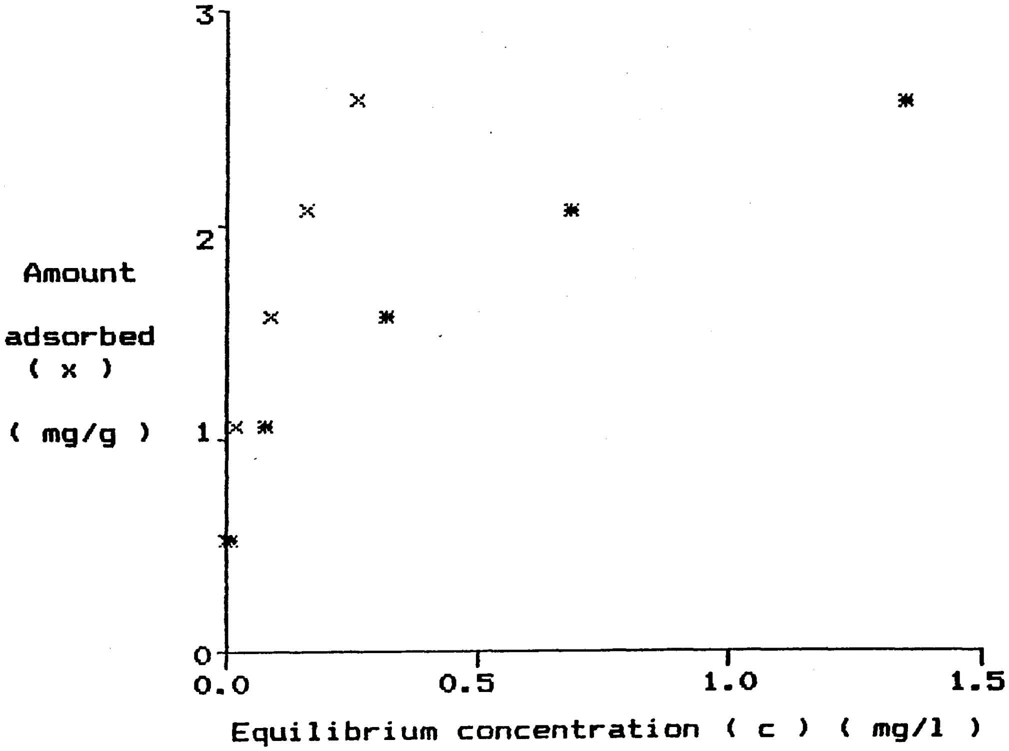


Fig. 4.2d Midelney (subsoil) zinc adsorption isotherm after 18h (*) and 7d (x) shaking.

Similar results were reported by Bar-Yosef (1979), who used 16, 48, and 168 hours shaking times in his zinc adsorption study on various soils. Zinc adsorption by synthetic goethite increased with increasing shaking time from 2 hours to 42 days at 20°C by about 33% (Bruemmer, Gerth and Tiller 1988).

Experimental data were plotted according to the Langmuir equation and represented in Figures 4.3a, 4.3b, 4.3c, and 4.3d. Although in some cases the Langmuir isotherms appeared to be split into two parts, a single line was used in all cases to calculate the Langmuir constants.

When experimental data was plotted according to the Freundlich equation (Figures 4.4a, 4.4b, 4.4c, and 4.4d), all the soils showed no difference between the 7 days and 18 hours shaking, except Midelney (subsoil), where two lines were seen (Figure 4.4d). Deviation from a straight line at higher zinc concentrations, suggests the presence of more than one type of site or mechanism for zinc adsorption in soils. It may be that at low zinc concentrations, only the most specific sites would be occupied by the metal (lower part of isotherm). At high zinc concentrations, sorption on sites of lower specificity could be expected since Zn^{2+} ion activity in solution would become high enough to compete effectively for the relatively nonspecific sites. The availability of high specificity sites might be expected to be correlated with clay or organic matter content, as reported by Elrashidi and O´Connor (1982).

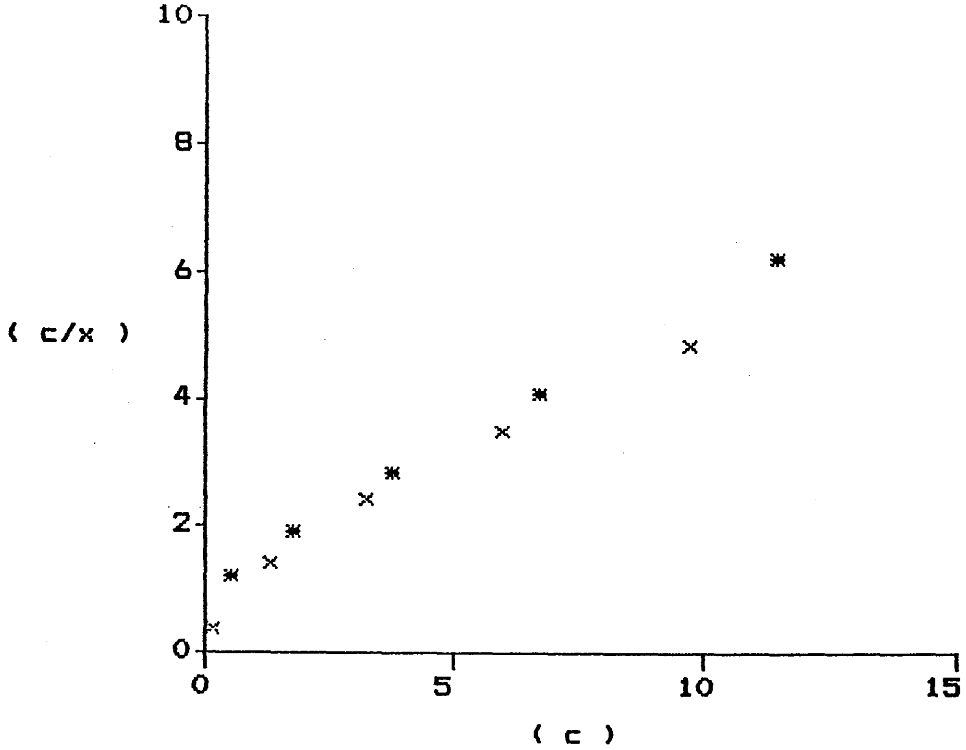


Fig. 4.3a Langmuir zinc adsorption isotherm for Dreghorn (Auchincruive) after 18h (*) and 7d (x) shaking.

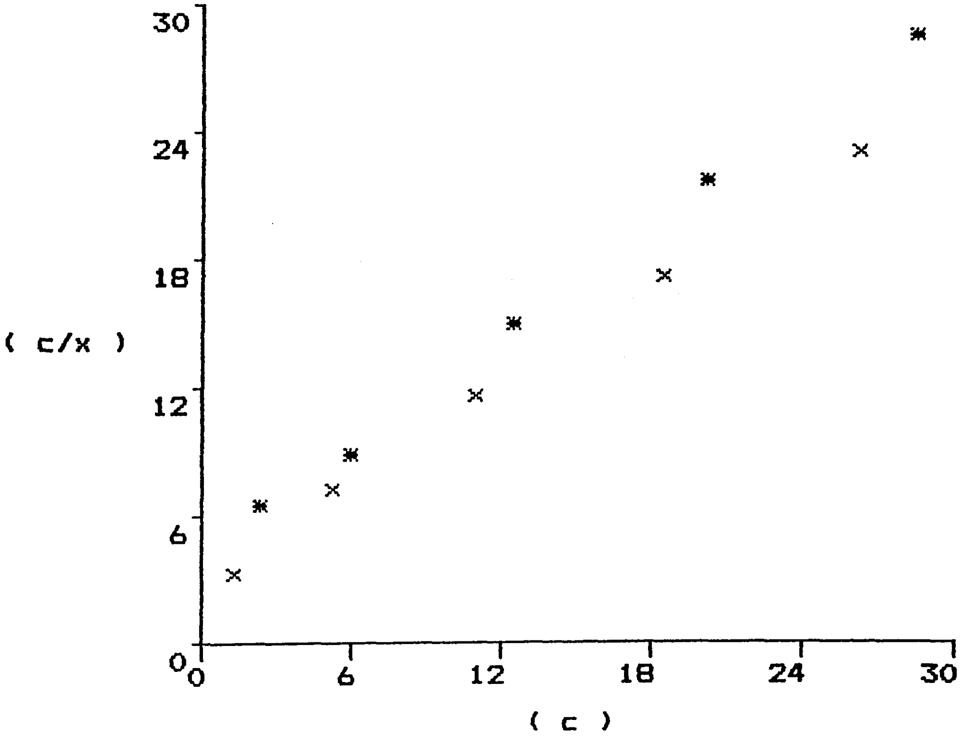


Fig. 4.3b Langmuir zinc adsorption isotherm for Dreghorn (Arkleston) after 18h (*) and 7d (x) shaking.

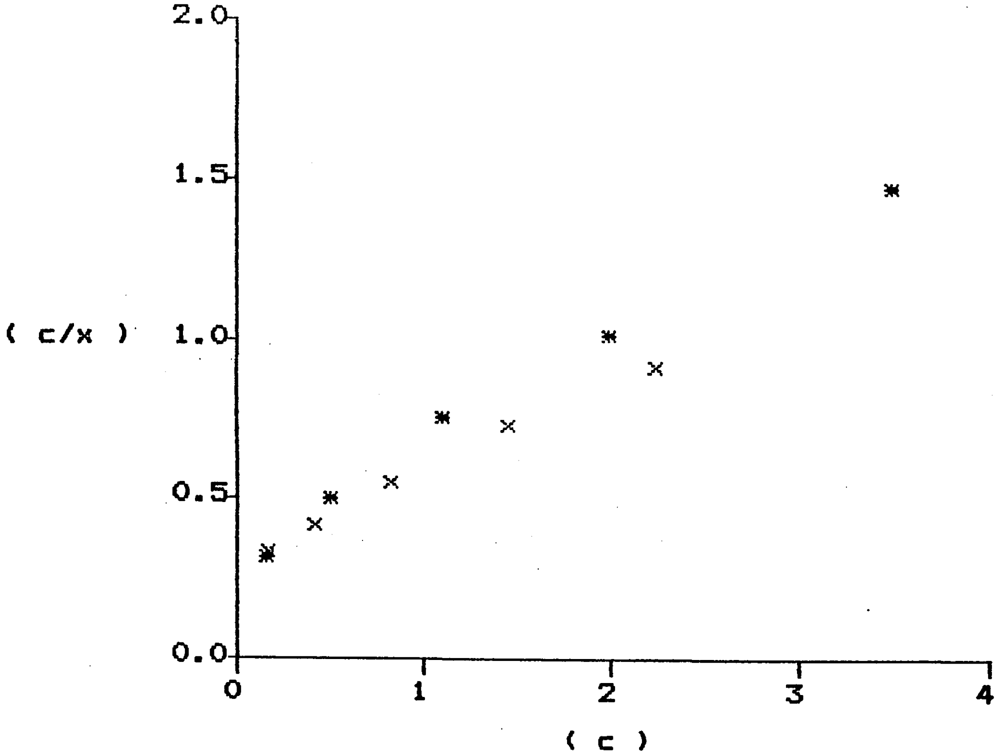


Fig. 4.3c Langmuir zinc adsorption isotherm for Midelney (topsoil) after 18h (*) and 7d (x) shaking.

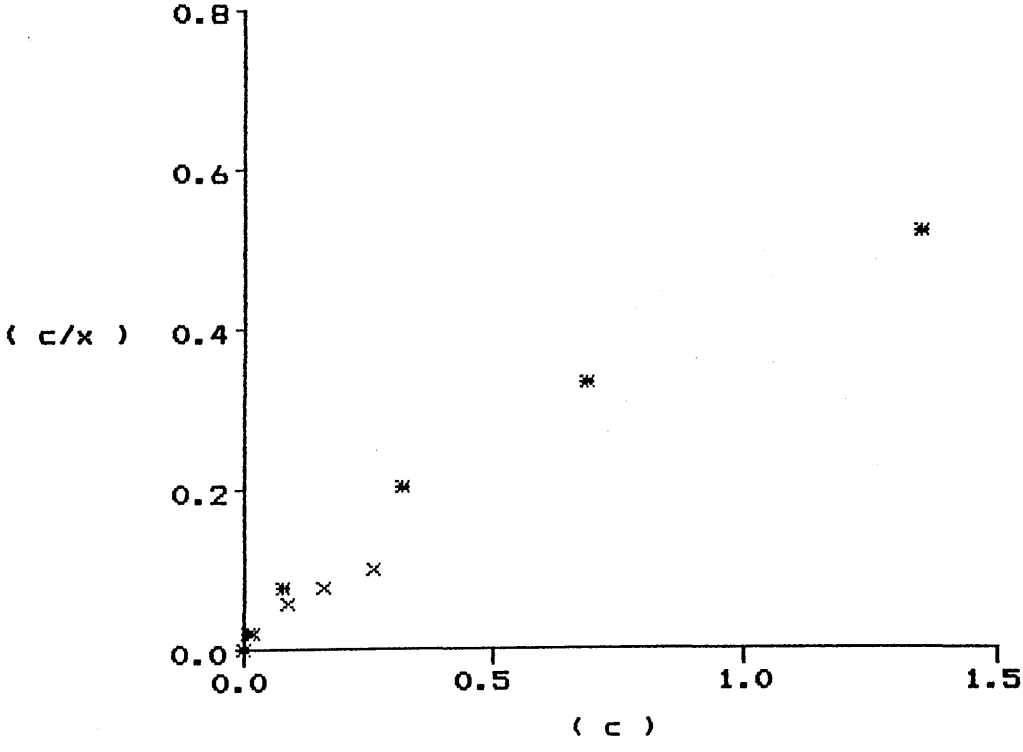


Fig. 4.3d Langmuir zinc adsorption isotherm for Midelney (subsoil) after 18h (*) and 7d (x) shaking.

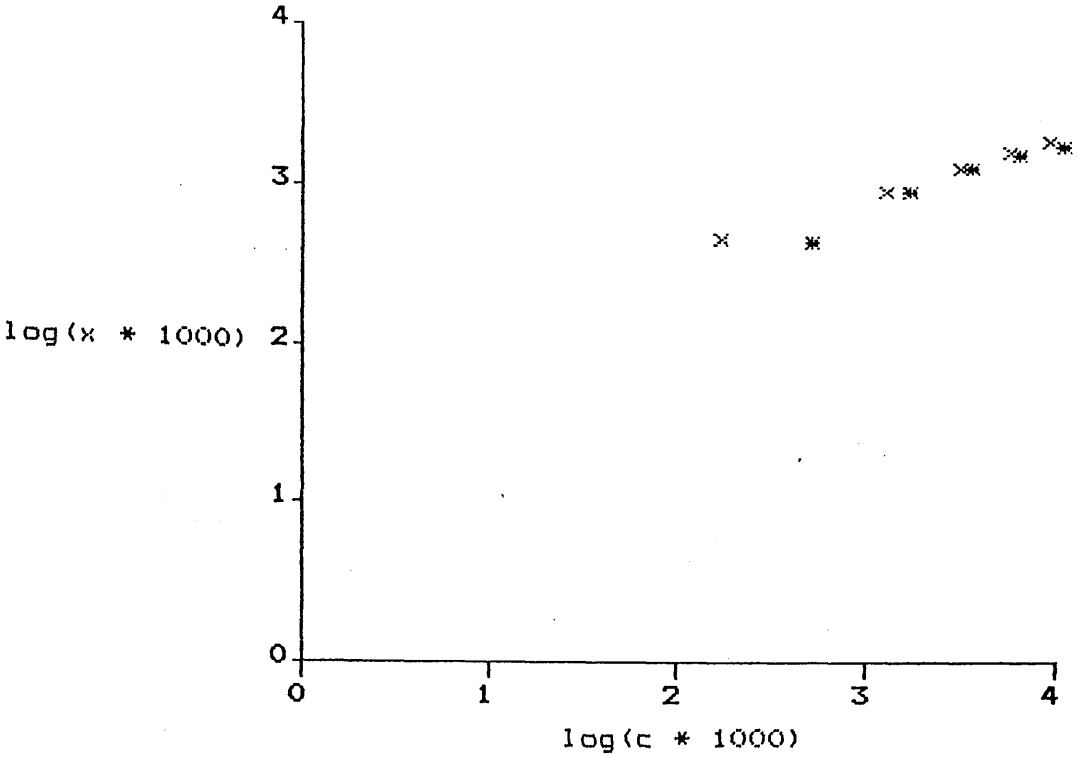


Fig. 4.4a Freundlich zinc adsorption isotherm for Dreghorn (Auchincruive) after 18h (*) and 7d (x) shaking.

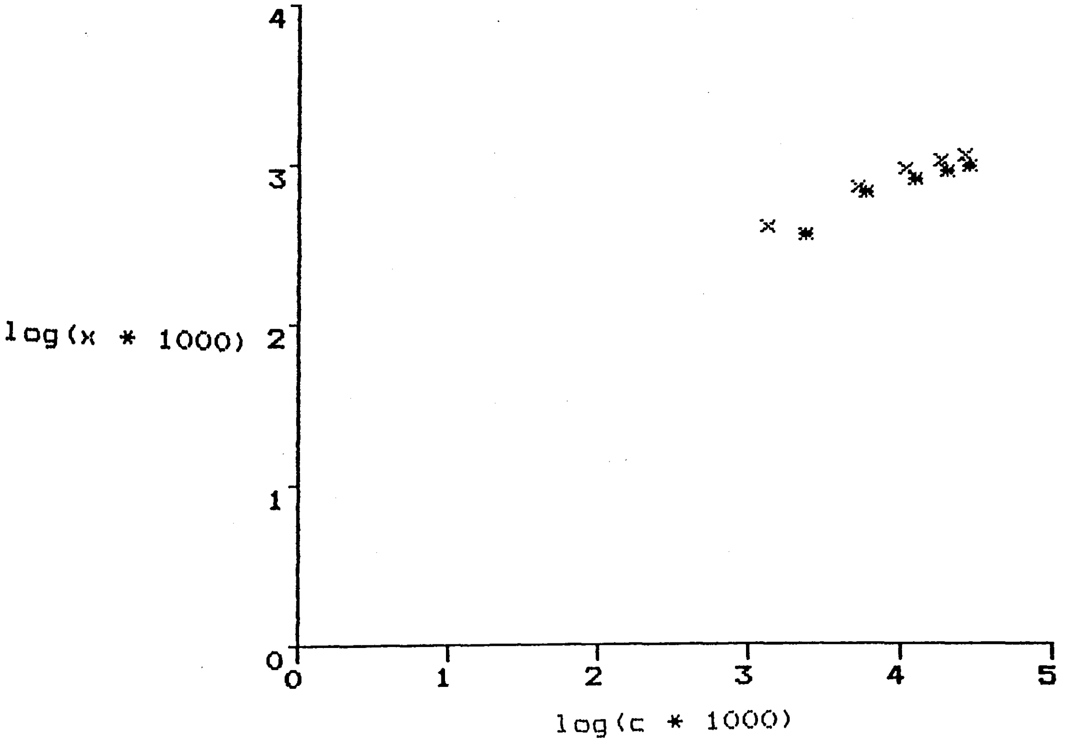


Fig. 4.4b Freundlich zinc adsorption isotherm for Dreghorn (Arkleston) after 18h (*) and 7d (x) shaking.

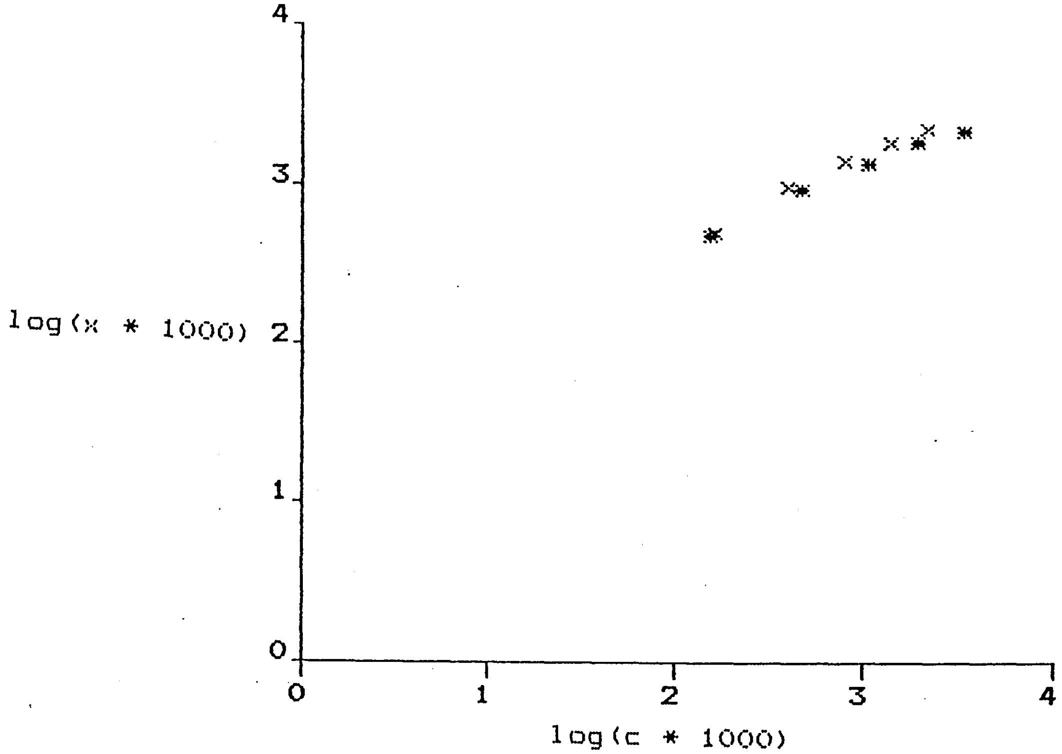


Fig. 4.4c Freundlich zinc adsorption isotherm for Midelney (topsoil) after 18h (*) and 7d (x) shaking.

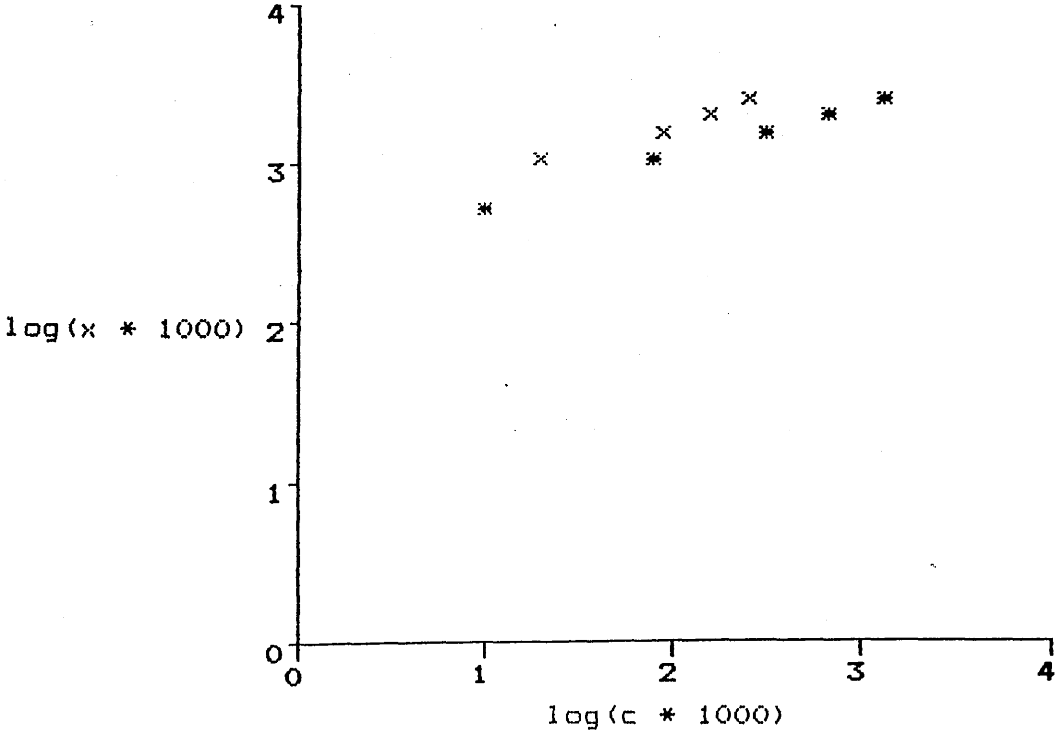


Fig. 4.4d Freundlich zinc adsorption isotherm for Midelney (subsoil) after 18h (*) and 7d (x) shaking.

The constants obtained from the Langmuir and Freundlich equations for both shaking times of each soil are given in Table 4.2. This indicates that adsorption maximum was slightly higher in the case of 7 days shaking than 18 hours shaking, except for Midelney (subsoil). Slopes of the two lines from Langmuir plots were compared by calculating a t statistic from a pooled residual mean square. It has been observed that all the soils showed no significant difference within the soil for the two shaking times, except Dreghorn (Arkleston) where these slopes were significantly different. Bonding energies for zinc were higher in 7 days shaking for three soils, but not Midelney (topsoil). The slopes of the Freundlich plots for 7 days shaking were the same as those for 18 hours for all soils except Midelney (subsoil) which showed significant difference between shaking times. Results in Table 4.2 suggest that zinc adsorption was slightly enhanced with time of shaking, possibly as a result of dispersion of soils providing more surfaces for retention of this metal.

Table 4.2 Zinc adsorption constants for four soils, for two shaking times calculated from Langmuir and Freundlich Plots

Soil		Langmuir Plot			Freundlich Plot		
		Adsorption maximum b mg g^{-1}	Bonding energy k l mg^{-1}	R^2	Slope	Intercept	R^2
Dreghorn (Arkleston)	7 days	1.27a	0.29	1.00	0.35a	1.55	0.98
" "	18 hours	1.16b	0.21	1.00	0.39a	1.29	0.94
Dreghorn (Auchincruive)	7 days	2.21a	0.68	0.98	0.36a	1.85	1.00
" "	18 hours	2.18a	0.44	1.00	0.46a	1.42	0.97
Midelney (Topsoil)	7 days	3.53a	0.95	1.00	0.60a	1.39	0.99
" "	18 hours	2.92a	1.07	0.99	0.50a	1.61	0.99
Midelney (Subsoil)	7 days	2.66a	34.50	0.94	0.11a	3.02	0.86
" "	18 hours	2.73a	7.09	0.98	0.32b	2.40	1.00

Values for comparison of shaking times for each soil having the same letter following are not significantly different at the 5% level.

4.3.2.2 Precipitation-dissolution mechanism

Although precipitation-dissolution reactions can influence the composition of both the solid material and the composition of soil solution, they are ususally not considered a mechanism for controlling zinc, as the solubilities of the common solid phase zinc compounds are too high at the pH values of most soils (Pulford, 1986). Lindsay (1979) proposed a solubility diagram of several zinc minerals and reported that all of the $Zn(OH)_2$ minerals, ZnO (zincite) and $ZnCO_3$ (smithsonite) are too soluble to persist in soils. They are 10^5 times more soluble than soil-Zn. The mineral Zn_2SiO_4 (willemite) is of intermediate solubility, but it is too soluble to account for the soil-Zn found in most soils. He also claimed that the predominant zinc species in solution below pH 7.7 is Zn^{2+}, although $ZnOH^+$ is more prevalent above this pH. Hodgson (1963) reported that precipitation could occur at high concentrations of ions, but it is unlikely in acid soils with copper, cobalt, and zinc at least. The possibility of precipitation as $Zn(OH)_2$ at relatively high pH could not be discounted (Bingham, Page, and Sims, 1964). Udo et al. (1970), and Trehan and Sekhon (1977) observed that when the added Zn^{2+} exceeded the adsorption maximum, the solid phase of zinc controlling its concentration in solution was either zinc hydroxide or carbonate so long as soil carbonates were present. They also suggested that soils retain Zn^{2+} more strongly than $Zn(OH)_2$ or $ZnCO_3$. Bruemmer et al. (1983) also observed in their study that B horizon samples (subsoils) were consistent with the possibility of precipitation in the pH range 7 - 8. Lindsay (1979) suggested that franklinite ($ZnFe_2O_4$) in equilibrium with Fe(III) oxides could possibly control Zn^{2+} ions in soil solution. The solubility of franklinite shifts depending on the activity of Fe^{3+}. For example, $Fe(OH)_3$ (amorphous) associated with higher levels of ferric ion in solution, depresses the solubility of franklinite, whereas crystalline Fe(III) oxides such as goethite lower Fe^{3+} and permit higher equilibrium levels of Zn^{2+}. Hence the amorphous iron oxides at a given pH will result in the formation of franklinite at a lower zinc concentration than will a well-crystallized iron oxide, such as goethite.

The pZn versus pH lines for both shaking times of each soil lie within the area bounded by the lines for franklinite in equilibrium with amorphous iron oxide and goethite (Figures 4.5a, b, c, and d). It has been observed from the experimental data, by plotting pZn versus pH, that shaking time was related to zinc solubility in three soils, but not in Dreghorn (Auchincruive) where the same amounts of zinc in solution at the same pH were observed at both shaking times. While in the case of the other three soils, slightly more zinc in solution was observed at 18 hours shaking than 7 days shaking time.

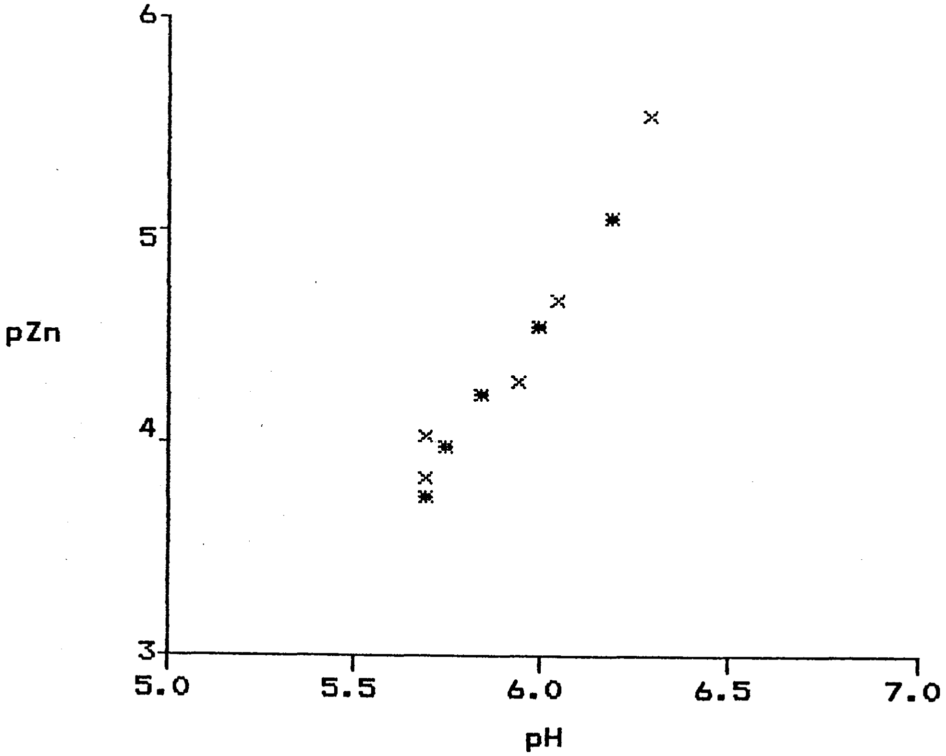


Fig. 4.5a Equilibrium pZn versus pH for Dreghorn (Auchincruive) at two different shaking time.

18h (*) pZn = − 10.57 + 2.52pH
7d (x) pZn = − 11.04 + 2.61pH

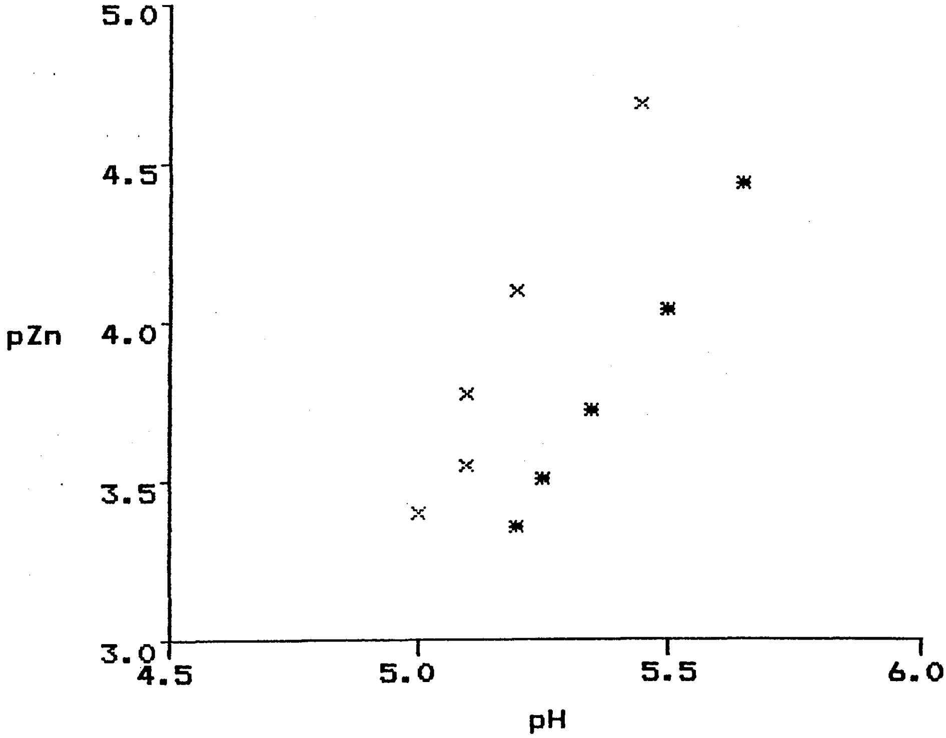


Fig. 4.5b Equilibrium pZn versus pH for Dreghorn (Arkleston) at two different shaking time.

18h (*) pZn = − 8.78 + 2.34pH
7d (x) pZn = − 11.25 + 2.93pH

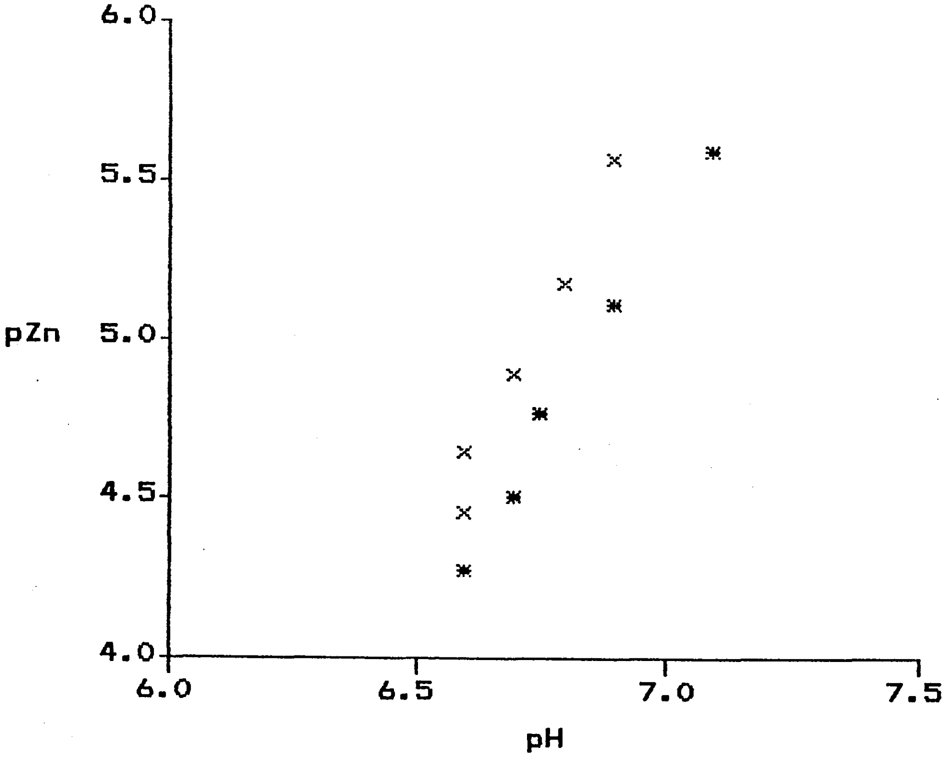


Fig. 4.5c Equilibrium pZn versus pH for Midelney (topsoil) at two different shaking time.

18h (*) pZn = − 13.45 + 2.69pH
7d (x) pZn = − 17.62 + 3.36pH

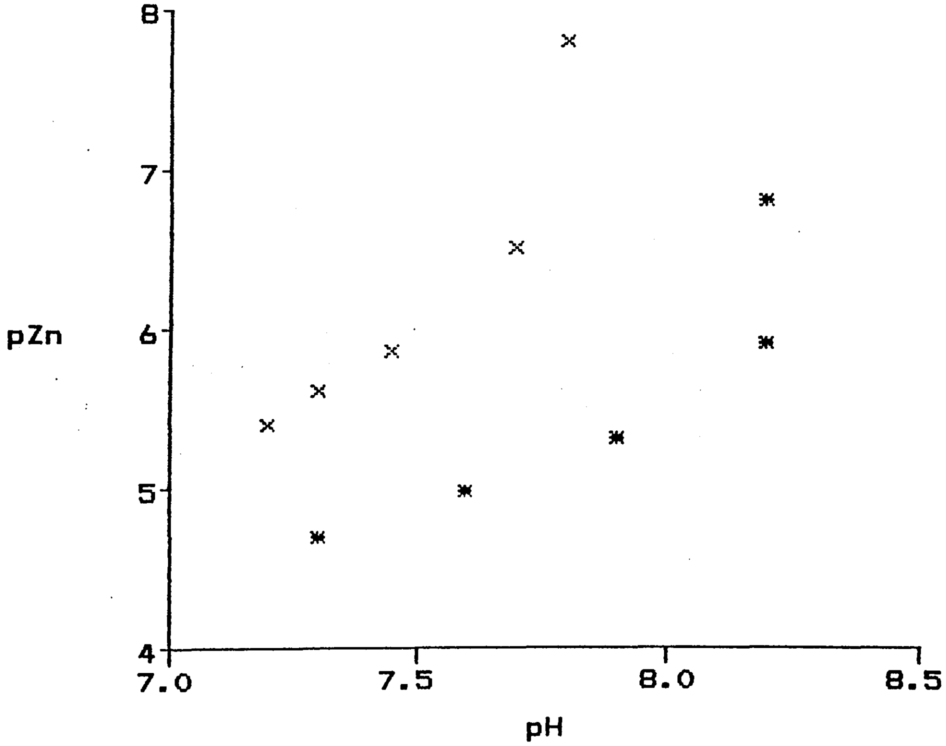


Fig. 4.5d Equilibrium pZn versus pH for Midelney (subsoil) at two different shaking time.

18h (*) pZn = − 5.09 + 1.33pH
7d (x) pZn = − 10.50 + 2.20pH

The reaction between Zn^{2+} and Fe^{3+} to form franklinite can be written (Lindsay, 1979),

$$Zn^{2+} + 2Fe^{3+} + 4H_2O \rightleftharpoons ZnFe_2O_4 + 8H^+ \qquad (1)$$

Ferric concentration is controlled by an equilibrium with the various forms of iron oxide,

$$2Fe(OH)_3 + 6H^+ \rightleftharpoons 2Fe^{3+} + 6H_2O \qquad (2)$$

Thus overall

$$2Fe(OH)_3 + Zn^{2+} \rightleftharpoons ZnFe_2O_4 + 2H_2O + 2H^+ \qquad (3)$$

From this equation the relationship between Zn^{2+} concentration and pH can be derived as

$$pZn = 2pH - constant.$$

The constant depends on which form of iron oxide controls the ferric concentration. The experimental data in Figures 4.5a, b, c, and d do not lie along lines giving the exact slope of +2, suggesting that franklinite does not control the zinc concentration in solution. The slopes of the pZn v pH lines all lay between 2 and 3, except for Midelney (topsoil) 7 days and Midelney (subsoil) 18 hours. The slopes of the two lines were compared by calculating a t statistic from a pooled residual mean square. All soils showed the same slope at both shaking times except Midelney (subsoil), where these slopes were significantly different.

From equation (1), the ion product pZn + 2pFe - 8pH should be a constant. Table 4.3 shows that for these soils this ion product is similar at both shaking times for each soil, but is different for different soils. This would imply that a process involving H^+ ions (equations 1 to 3) is not involved. While the pZn + 2pFe ion product is more constant, it is still significantly different between soils. Analysis of variance showed that the values of both constants were significantly different over all soils and shaking times, and over all soils for each individual shaking time. There is some evidence that a mechanism is operating that involves zinc and iron. The decrease observed in iron concentration in solution with increasing zinc concentration is supporting evidence for some interaction between zinc and iron. The experimental data plotted as pZn versus pFe is presented in Figures 4.6a, b, c, and d for each soil. All soils showed the same pattern of decreasing iron concentration with increasing zinc concentration for both shaking times.

Table 4.3 Ionic products pZn + 2pFe and pZn + 2pFe - 8pH in water for two shaking times and (standard deviation)

Soil and shaking time		pZn + 2pFe (sd)	pZn + 2pFe - 8pH (sd)
Dreghorn (Arkleston)	7 days	14.12 (0.17)	-27.24 (1.53)
" "	18 hours	13.69 (0.23)	-29.43 (1.31)
Dreghorn (Auchincruive)	7 days	13.53 (0.43)	-33.90 (1.45)
" "	18 hours	12.71 (0.33)	-34.49 (1.30)
Midelney (Topsoil)	7 days	14.38 (0.31)	-39.38 (1.10)
" "	18 hours	15.16 (0.26)	-39.32 (1.31)
Midelney (Subsoil)	7 days	16.31 (0.19)	-43.55 (1.42)
" "	18 hours	15.02 (0.38)	-47.70 (2.84)

Analysis of variance showed that the values of both constants were significantly different over all soils and shaking times, and over all soils for each individual shaking time.

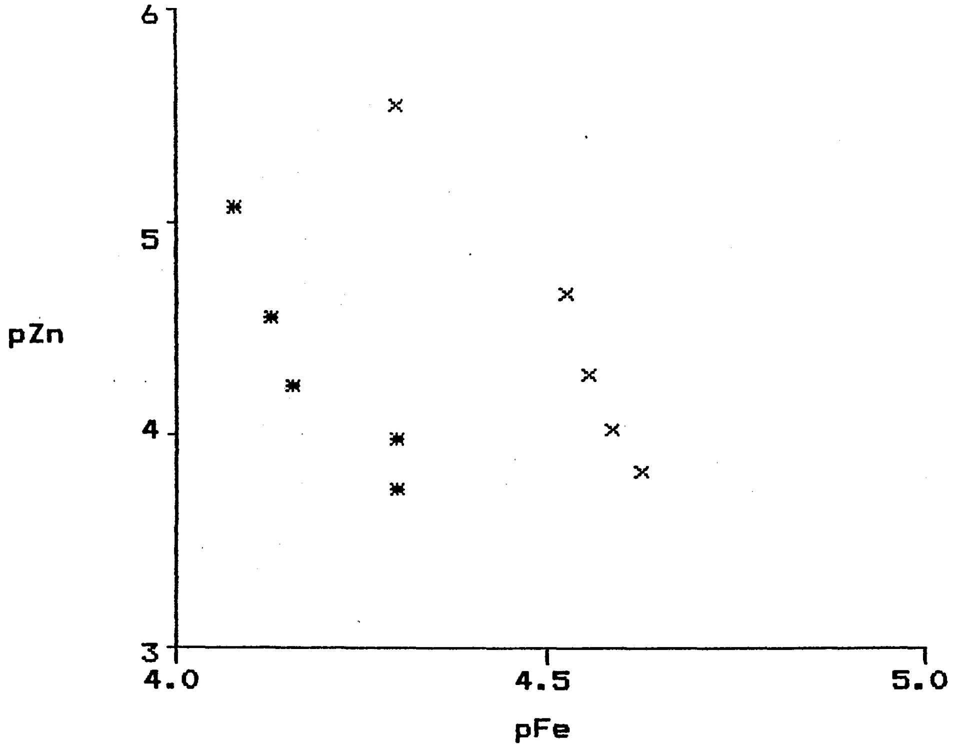


Fig. 4.6a Equilibrium pZn versus pFe for Dreghorn (Auchincruive) after 18h (*) and 7d (x) shaking.

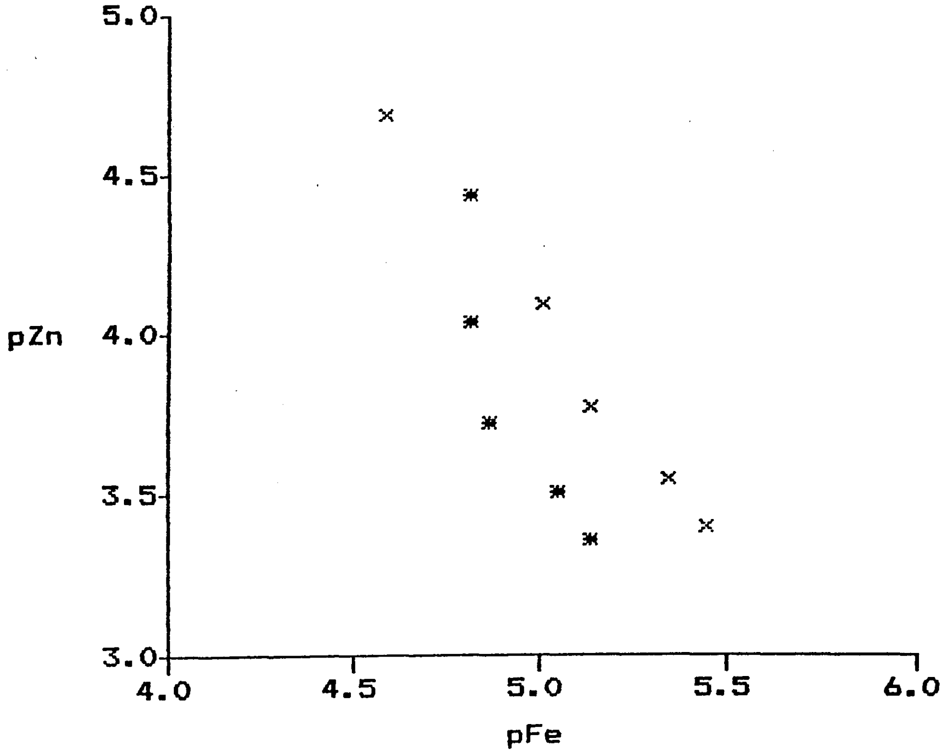


Fig. 4.6b Equilibrium pZn versus pFe for Dreghorn (Arkleston) after 18h (*) and 7d (x) shaking.

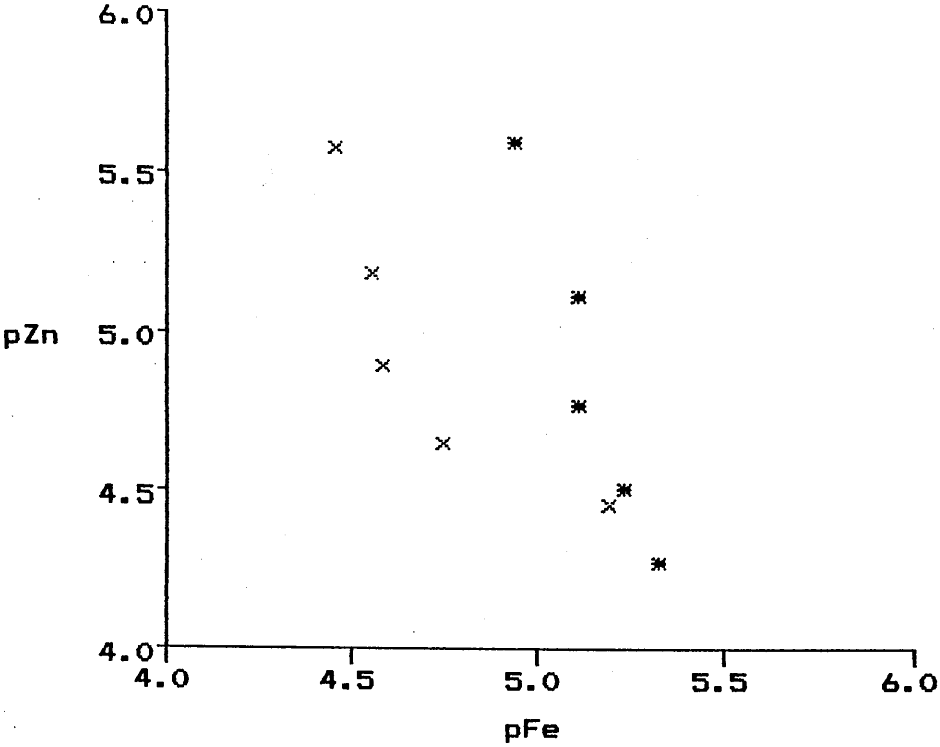


Fig. 4.6c Equilibrium pZn versus pFe for Midelney (topsoil) after 18h (*) and 7d (x) shaking.

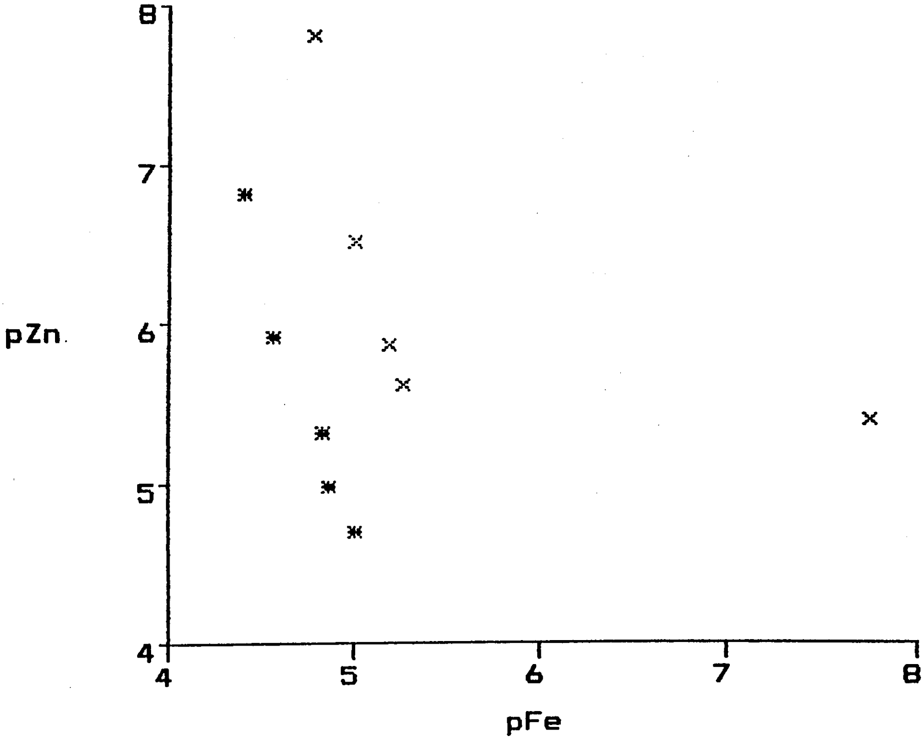


Fig. 4.6d Equilibrium pZn versus pFe for Midelney (subsoil) after 18h (*) and 7d (x) shaking.

4.3.3 Effect of air-drying on the adsorption of zinc by different soils

The adsorption isotherm curves of air-dried soil were the same as that of a fresh sample (Figures 4.7a and b). This was a general pattern for all four soils, but the figures given represent a sandy and a clayey soil respectively. No information is available for zinc adsorption regarding this aspect. In the past most of the work has been done regarding this aspect in phosphate adsorption by soils. The observed results for zinc have no agreement with reported ones by Olsen and Court (1982), and Haynes and Swift (1985) for phosphate adsorption by soils. Phosphate adsorption was enhanced by air-drying the soil, but the reason was not clear (Haynes and Swift, 1985). They suggested that changes in the structural arrangement of organic matter/Fe and Al associations caused by drying may in some way be responsible for the increased adsorption capacity of the soils. An increase in the number of adsorption sites due to the drying of samples is likely (Olsen and Court, 1982). Birch (1960) suggested that the cracking of organic colloids on drying could expose a greater surface to equilibrating solution. The effect of drying could also be due to decreasing the time required to reach adsorption equilibrium as suggested by Haynes and Swift (1985). They observed that with prolonged adsorption the moist and air-dried soils could adsorb similar quantities of added phosphate, which indicated that this may be the case.

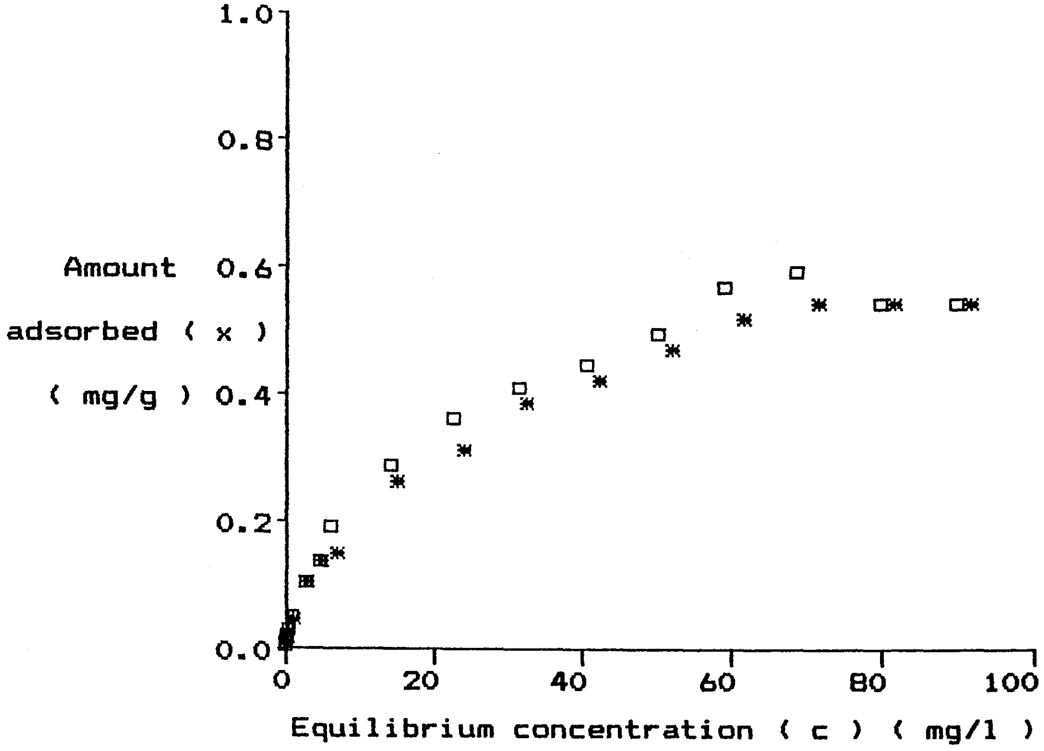


Fig. 4.7a Dreghorn (Arkleston) zinc adsorption isotherm for air-dried (□) and fresh (*) condition.

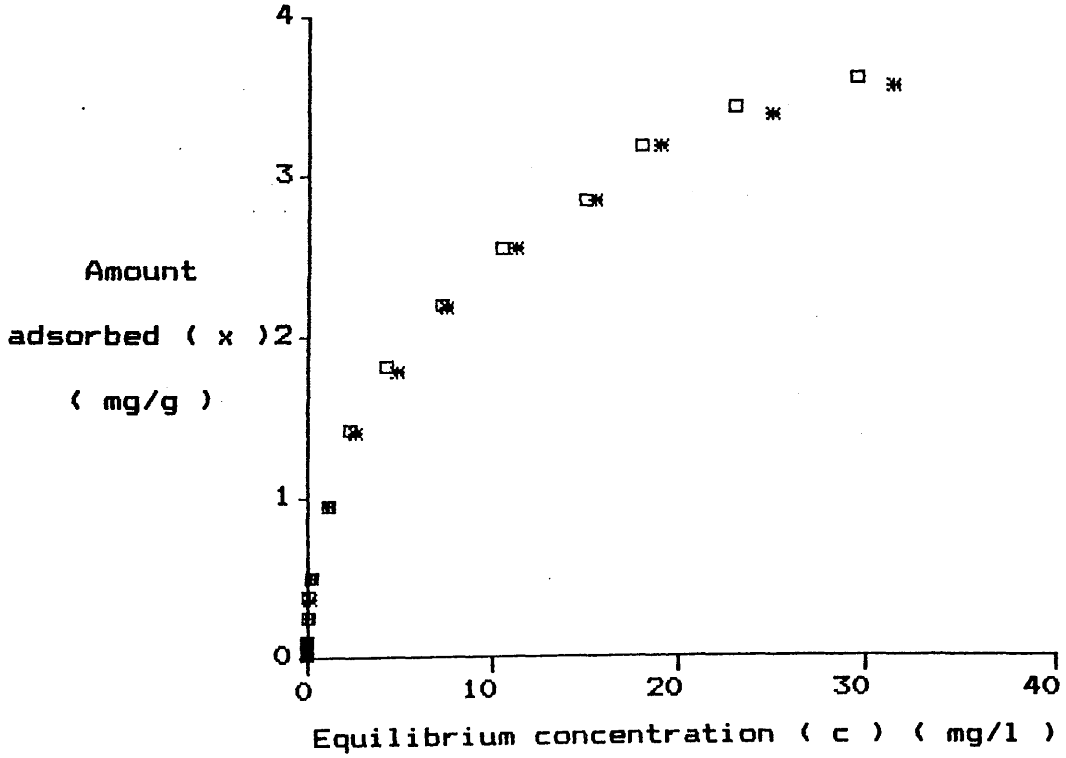


Fig. 4.7b Midelney (topsoil) zinc adsorption isotherm for air-dried (□) and fresh (*) condition.

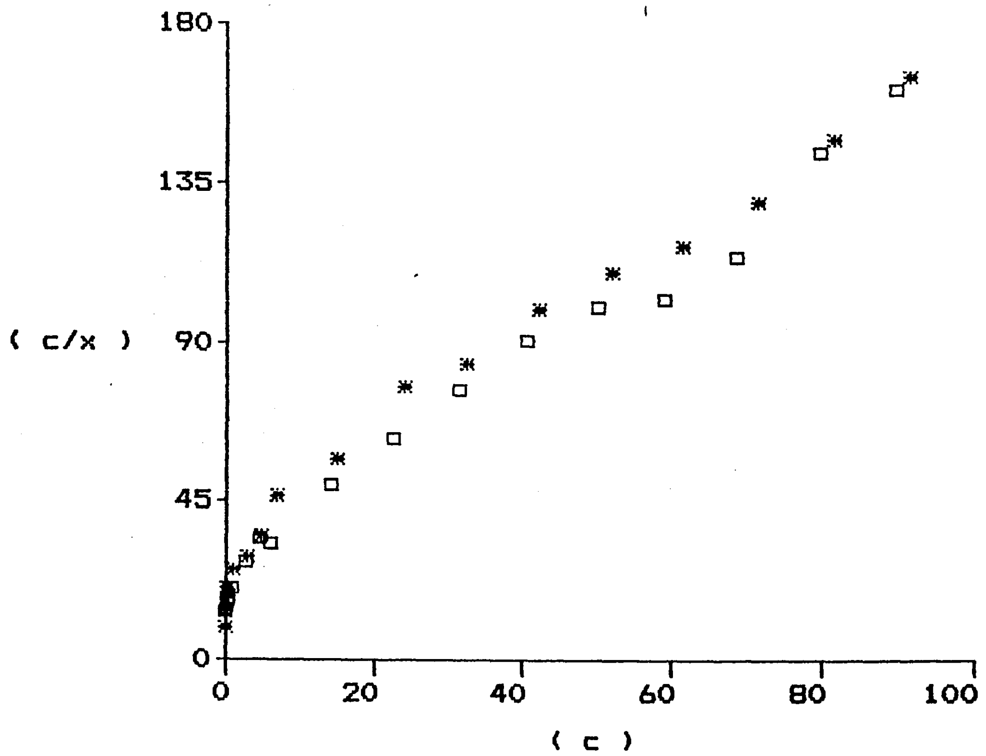


Fig. 4.7c Dreghorn (Arkleston) Langmuir zinc adsorption isotherm for air-dried (□) and fresh (*) condition.

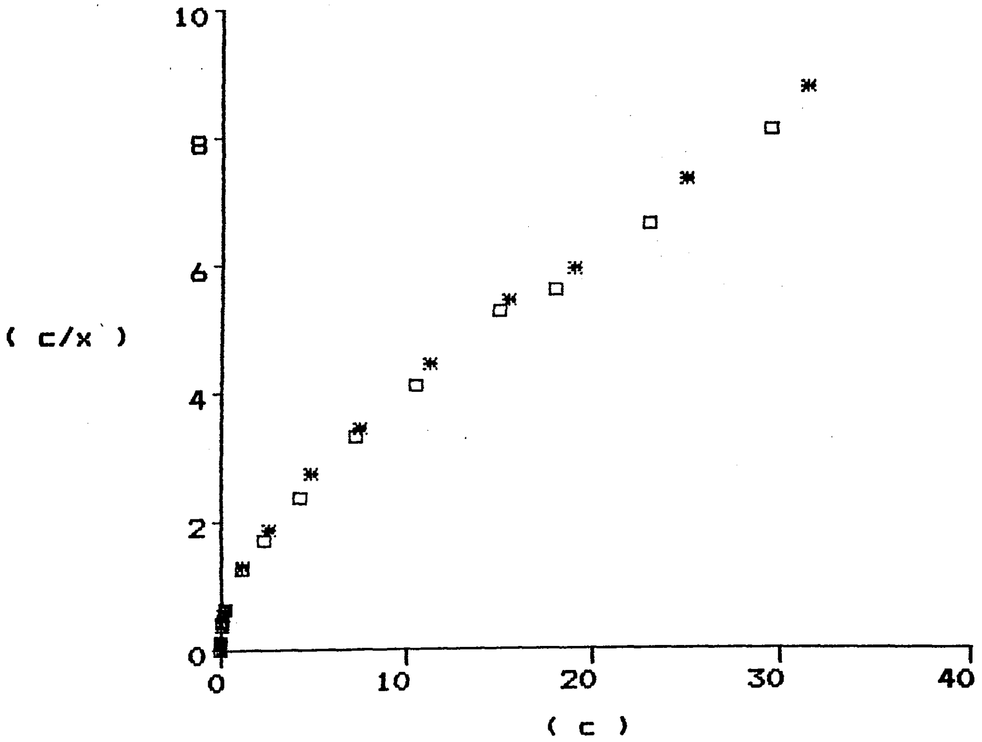


Fig. 4.7d Midelney (topsoil) Langmuir zinc adsorption isotherm for air-dried (□) and fresh (*) condition.

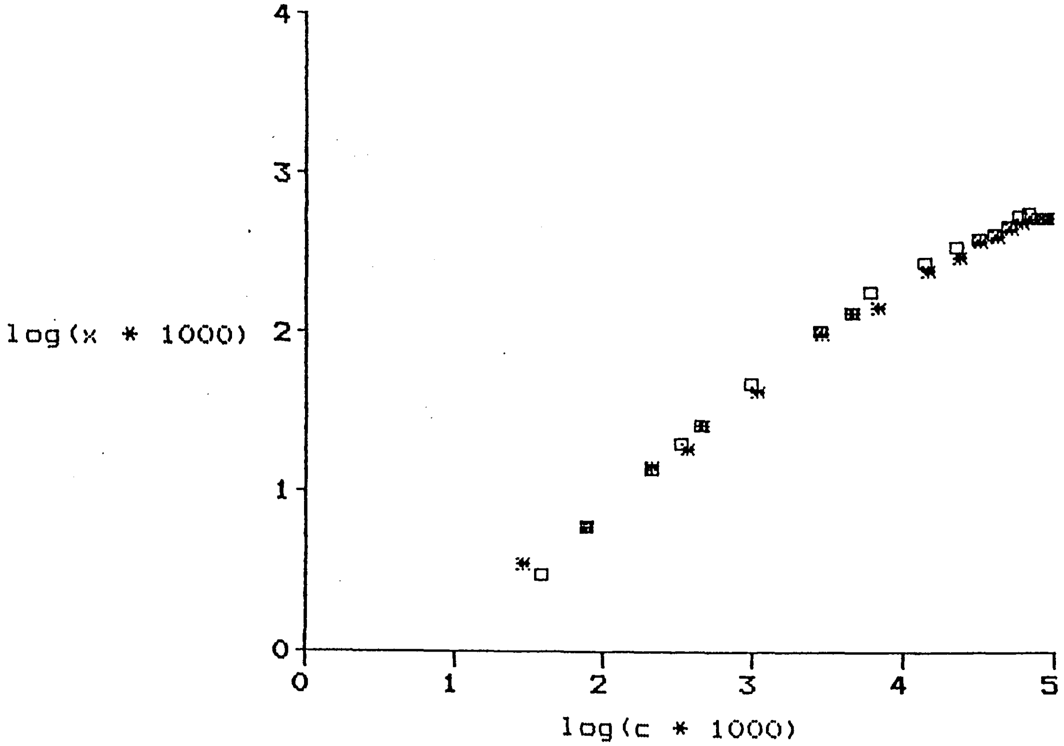


Fig. 4.7e Dreghorn (Arkleston) Freundlich zinc adsorption isotherm for air-dried (□) and fresh (*) condition.

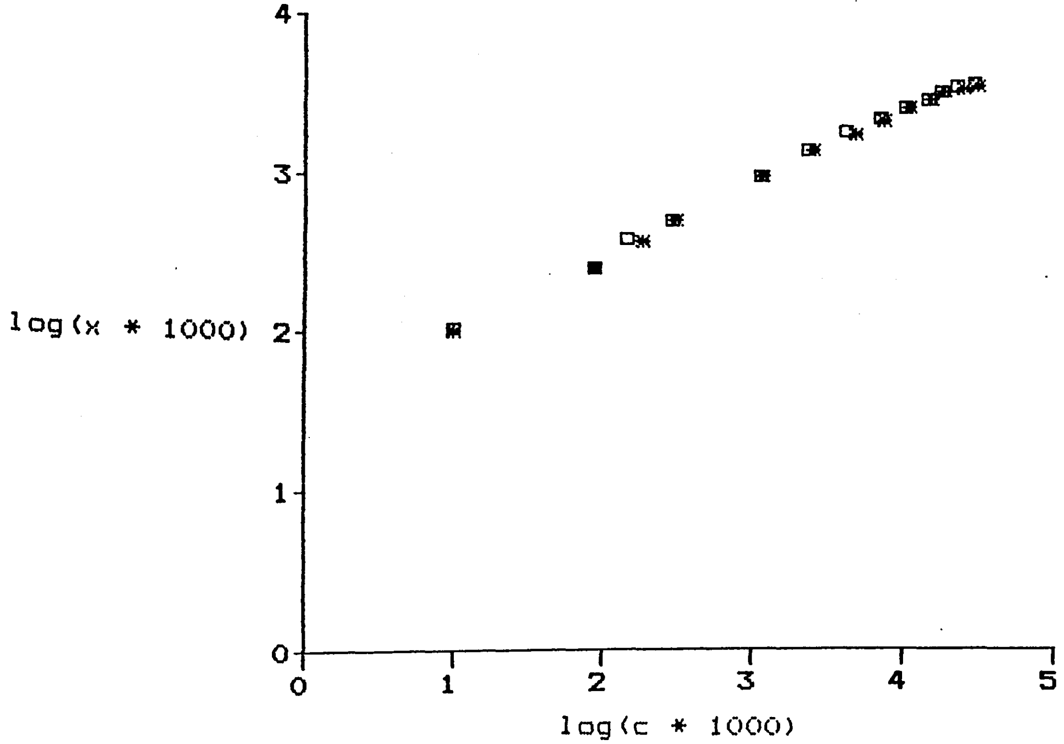


Fig. 4.7f Midelney (topsoil) Freundlich zinc adsorption isotherm for air-dried (□) and fresh (*) condition.

Table 4.4 Zinc adsorption constant for four soils calculated from Langmuir and Freundlich Plots in air-dried and fresh samples

Soil			Langmuir Plot			Freundlich Plot		
			Adsorption maximum b mg g^{-1}	Bonding energy k l mg^{-1}	R^2	Slope	Intercept	R^2
Dreghorn (Arkleston)	Full	F	0.63a	0.07	0.973	0.64a	0.35	0.992
" "	Top	F	0.76	0.03	0.988	-	-	-
" "	Full	AD	0.64a	0.08	0.983	0.67a	0.41	0.983
" "	Top	AD	0.71	0.05	0.970	-	-	-
" (Auchincruive)	Full	F	0.65a	0.05	0.949	0.66a	0.46	0.996
" "	Top	F	0.85	0.02	0.974	-	-	-
" "	Full	AD	0.65a	0.06	0.946	0.65a	0.39	0.995
" "	Top	AD	0.91	0.02	0.960	-	-	-

F = Fresh sample AD = Air-dried sample

Values for comparison of fresh versus air-dried samples for each soil having the same letter following are not significantly different at the 5% level.

Table 4.4 (continued) Zinc adsorption constant for four soils calculated from Langmuir and Freundlich Plots in air-dried and fresh samples

Soil			Langmuir Plot			Freundlich Plot		
			Adsorption maximum b mg g^{-1}	Bonding energy k 1 mg^{-1}	R^2	Slope	Intercept	R^2
Midelney	(Topsoil)	Full F	3.72a	0.32	0.973	0.46a	1.54	0.997
"	"	Top F	4.47	0.12	0.997	-	-	-
"	"	Full AD	3.75a	0.34	0.972	0.46a	1.55	0.997
"	"	Full AD	4.52	0.13	0.993	-	-	-
"	(Subsoil)	Full F	4.49a	1.11	0.983	0.40a	2.06	0.990
"	"	Top F	5.13	0.42	0.995	-	-	-
"	"	Full AD	4.55a	1.07	0.984	0.35a	2.25	0.990
"	"	Top AD	5.11	0.46	0.996	-	-	-

F = Fresh sample AD = Air-dried sample
Values for comparison of fresh versus air-dried samples for each soil having the same letter following are not significantly different at the 5% level.

Adsorption data was plotted according to the linear form of Langmuir equation and represented by Figures 4.7c and d. The data shows a good fit when the curves were resolved into two linear portions, suggesting different adsorption sites as described in Section 4.3.1.1. All soils yielded the split isotherm but both sample conditions lie on a single line indicating no real differences. The observed data was also used to calculate the Langmuir constants and are represented in Table 4.4. The t statistic calculated from a pooled residual mean square showed that there is no significant difference in the adsorption maxima of fresh and air-dried sample.

Replotting the data according to the Freundlich equation produced linear graphs (Figures 4.7e and f) for all soils irrespective of their sample condition. Freundlich isotherms lie on the same line, like Langmuir plots, for air-dried and fresh samples in each soil and reveal no effect of drying the sample on zinc adsorption. The constants calculated from Freundlich plots are also represented in Table 4.4. The statistical analysis to compare the slope of two lines by calculating the t value from a pooled residual mean square, showed no significant difference at 5% level, indicating no difference in zinc adsorption by air-dried and fresh soil samples.

It is concluded from this study that drying has no enhancing effect on zinc adsorption by soils unlike phosphate adsorption reported by Haynes and Swift (1985). It suggests that for some surfaces the sites involved in zinc adsorption may be different from the sites involved for phosphate adsorption.

4.3.4 Effect of various electrolytes as background on the adsorption of zinc by different soils

In previous experiments, the removal of zinc from solution by soil, or soil components has been conducted both in water and salt solution. It is important to assess the effects of type of cation and anion on adsorption of metal by soil and soil components because the background salts may complex zinc or compete for adsorption sites. Supporting electrolytes used have added Na^+, K^+, NH_4^+, Mg^{2+} or Ca^{2+} as cation as well as SO_4^{2-} or Cl^- as the anions. The data will be treated in terms of both adsorption-desorption or a precipitation-dissolution mechanisms.

4.3.4.1 Adsorption-desorption mechanism

The observed data have been arranged into two figures for each soil as the sulphate and chloride system, showing graphically the amount of zinc sorbed with increased zinc concentration. The five lines in each figure are for five different cations used as background electrolytes for zinc adsorption by soil. Experimental data was plotted as the amount of zinc adsorbed against equilibrium zinc concentration in solution giving the adsorption isotherm as the rising curve for each salt and soil.

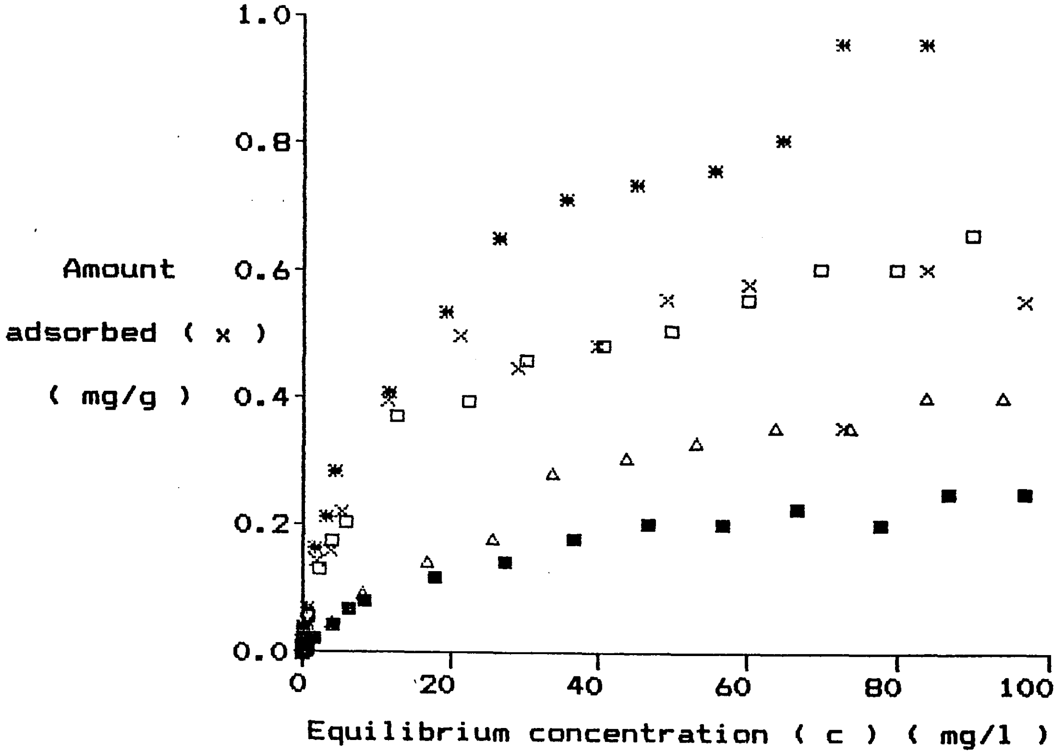


Fig. 4.8a Zinc adsorption isotherm in sulphate system for Dreghorn (Arkleston) soil.

Sodium (*) ; Potassium (x) ;
Ammonium (□) ; Magnesium (Δ) ;
Calcium (■) .

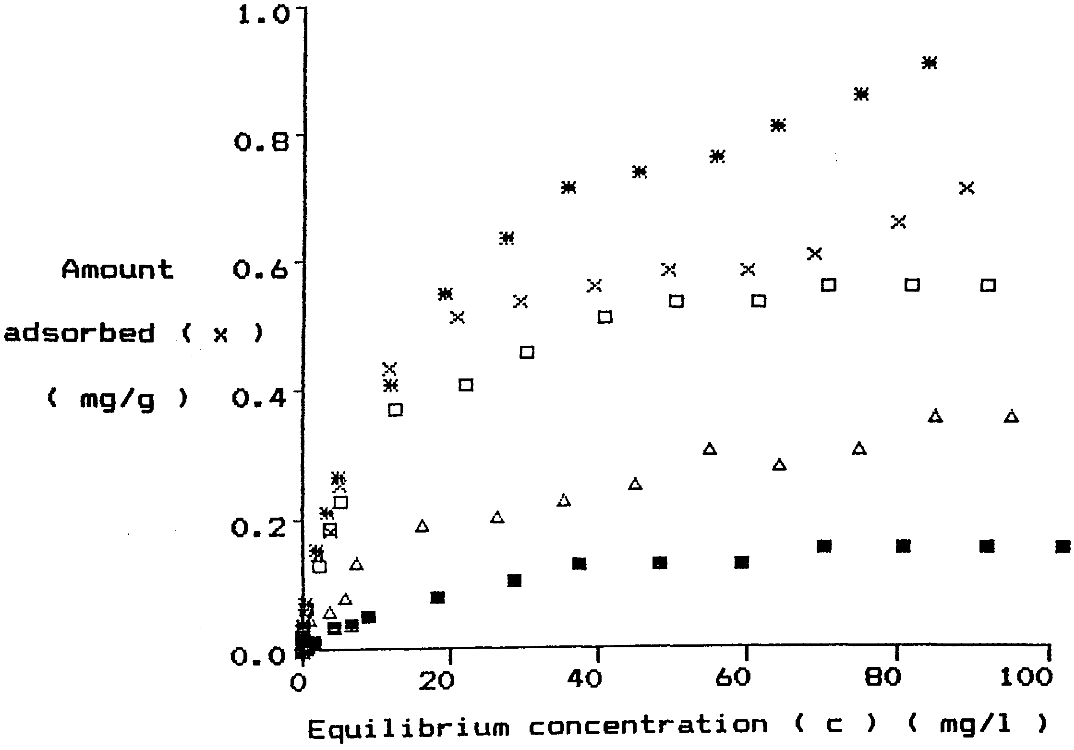


Fig. 4.8b Zinc adsorption isotherm in chloride system for Dreghorn (Arkleston) soil.

Sodium (*) ; Potassium (x) ;
Ammonium (□) ; Magnesium (Δ) ;
Calcium (■) .

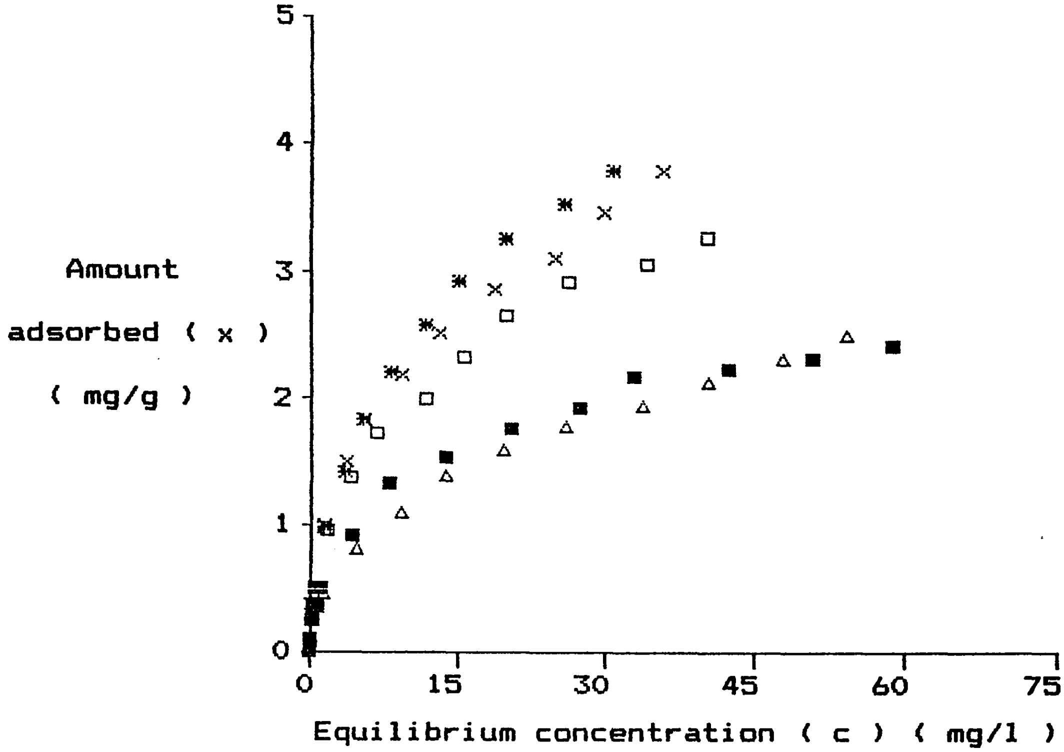


Fig. 4.9a Zinc adsorption isotherm in sulphate system for Midelney (topsoil).

Sodium (*) ; Potassium (x) ;
Ammonium (□) ; Magnesium (△) ;
Calcium (■) .

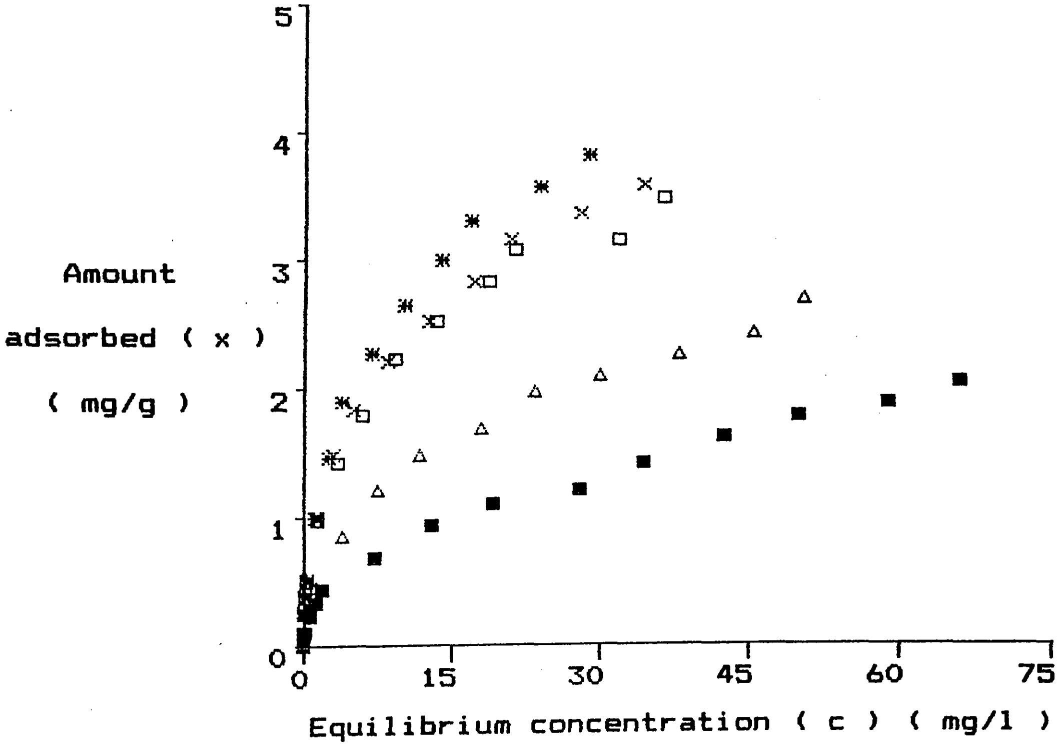


Fig. 4.9b Zinc adsorption isotherm in chloride system for Midelney (topsoil).

Sodium (*) ; Potassium (x) ;
Ammonium (□) ; Magnesium (△) ;
Calcium (■) .

Figures 4.8 and 4.9 (as a and b) show the zinc adsorption isotherm with five supporting electrolytes as sulphate and chloride salts for Dreghorn (Arkleston) and Midelney (topsoil) respectively, representing the sandy and clayey soils. It has been observed that all the soils responded in the same way to the effect of different cations. All the monovalent cations gave an isotherm above the divalent cations in all soils. It could be that Ca^{2+} and Mg^{2+},being alike in charge to the zinc ion, can easily compete for adsorption sites compared to the monovalent cations. Soil prefers to hold the divalent cations as compared to the monovalent cations, hence more zinc was adsorbed in the case of monovalent cations. Zinc adsorption in all soils was in the order: sodium > potassium $\geq$ ammonium > magnesium $\geq$ calcium using sulphate or chloride form of the salts. These observations are similar to those of Shukla et al. (1980) and Pulford (1986).

The results indicated that the form of the supporting electrolyte is an important factor when measuring zinc adsorption by soil. It is not only the case of the cation of the electrolyte saturating cation exchange sites and preventing the physisorption (ion exchange) but also causing the effect through changes in surface area for adsorption. Sodium has a dispersive effect causing an increase in surface area for adsorption, hence more zinc was adsorbed. As K^+ and NH_4^+ ions have lesser dispersive effects on soil, zinc adsorbed was lower than in a sodium background but higher than the divalent cations. Calcium has a flocculating effect, and so reduced the surface area hence zinc adsorption was depressed in all soils by calcium salts irrespective of anion type. In chloride systems, where the anion would not be held on the soil, except by ion exchange at positive sites, the different behaviour of the five salts suggests that surface area was an important factor for zinc adsorption. In sulphate systems the nature of the hydrous oxide type surfaces may be altered by adsorption of sulphate. This will tend to lower the point of zero charge, making it easier for Zn^{2+} ions to approach the surface (Pulford, 1986). There is also the possibility that zinc ions could be bonded to the surface via sulphate.

To see the effect of anion type on the adsorption of zinc, the adsorption isotherms were drawn separately for the same cation in the form of sulphate and chloride for each soil. Figures 4.10 and 4.11 (as a, b, c, d, and e) represent the adsorption isotherm for sodium, potassium, ammonium, magnesium and calcium salts as sulphate and chloride for Dreghorn (Arkleston), and Midelney (topsoil) respectively. The results showed no clear difference due to anion type, except for the calcium salts, where sulphate yielded an isotherm above the chloride in each soil. This increase in the amount of zinc sorbed may be attributed to the lower ionic strength of calcium sulphate than calcium chloride in solution due to its lower solubility.

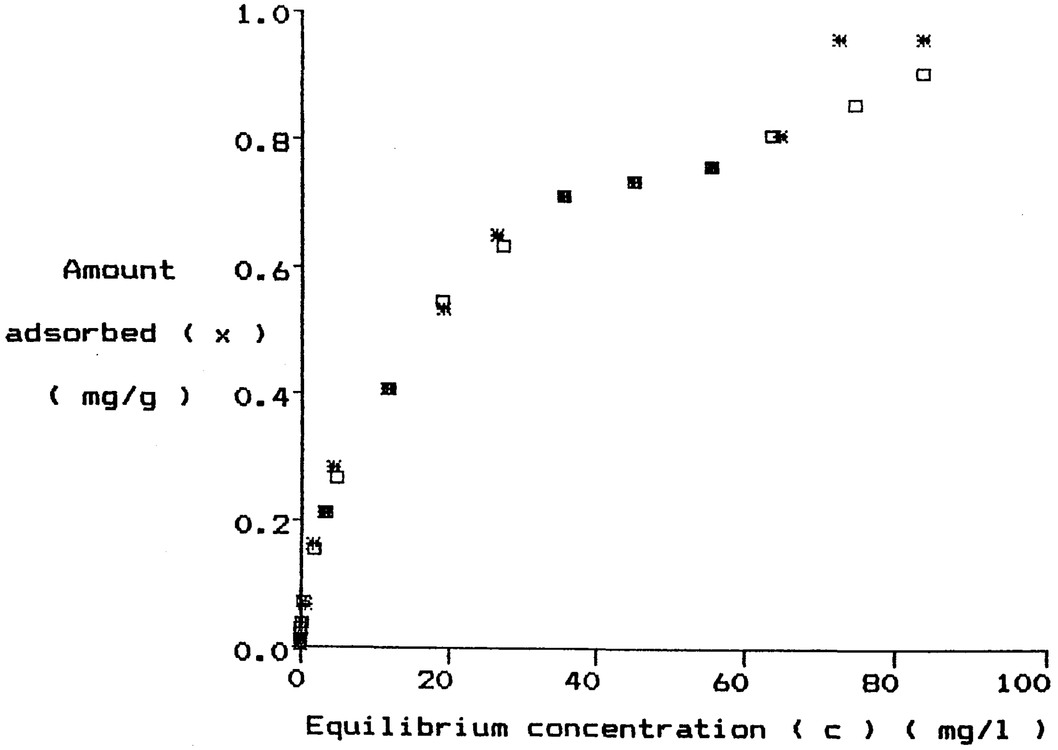


Fig. 4.10a Zinc adsorption isotherm for Dreghorn (Arkleston) soil in sodium sulphate (*) and sodium chloride (□) as background.

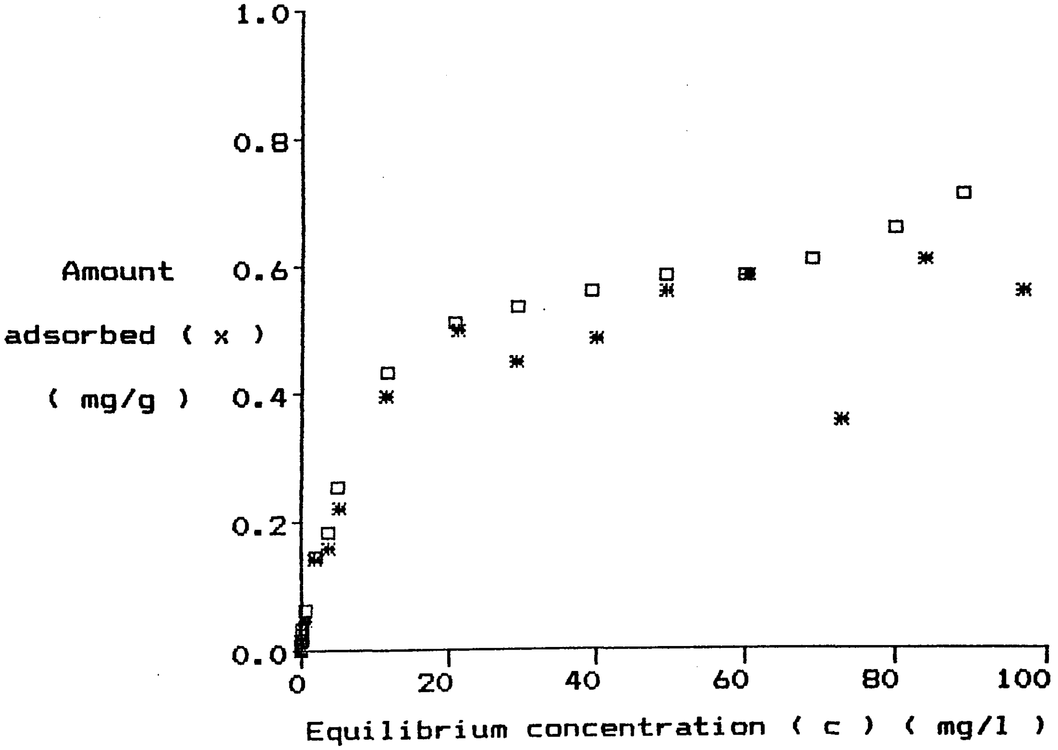


Fig. 4.10b Zinc adsorption isotherm for Dreghorn (Arkleston) soil in potassium sulphate (*) and potassium chloride (□) as background.

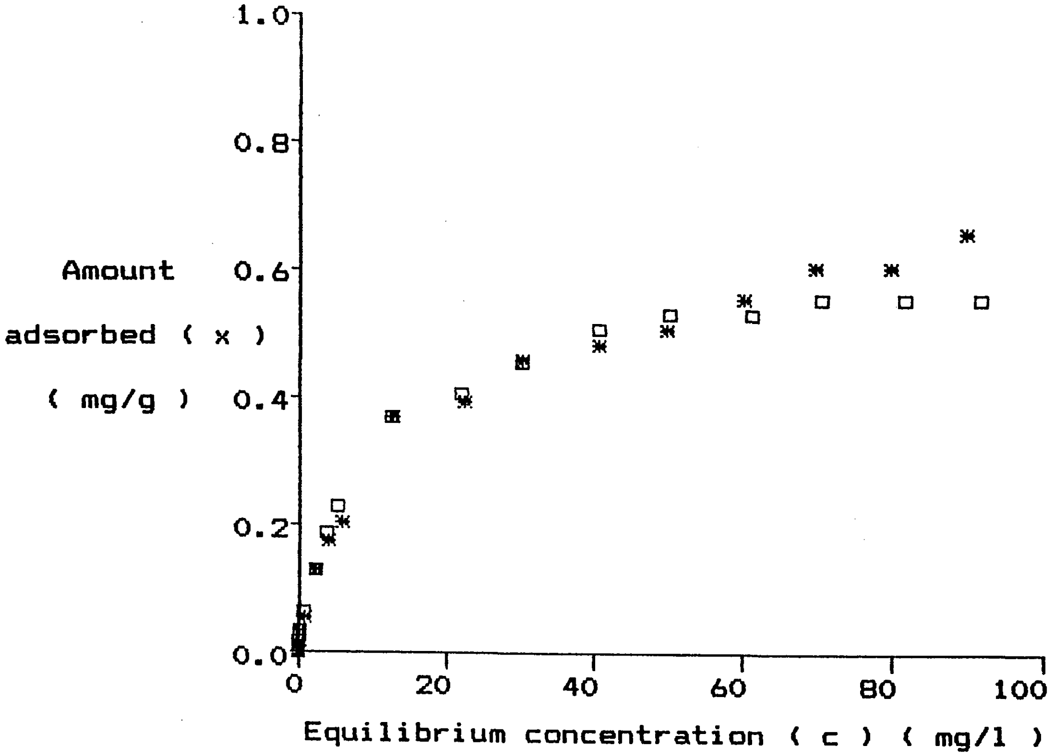


Fig. 4.10c Zinc adsorption isotherm for Dreghorn (Arkleston) soil in ammonium sulphate (*) and ammonium chloride (□) as background.

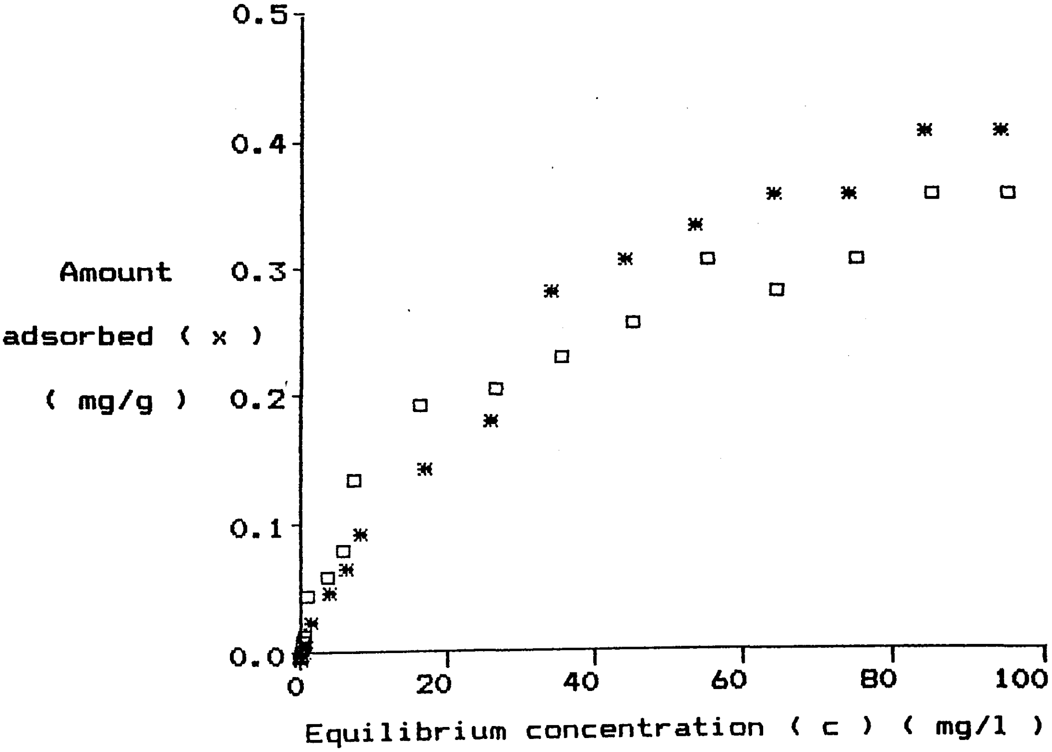


Fig. 4.10d Zinc adsorption isotherm for Dreghorn (Arkleston) soil in magnesium sulphate (*) and magnesium chloride (□) as background.

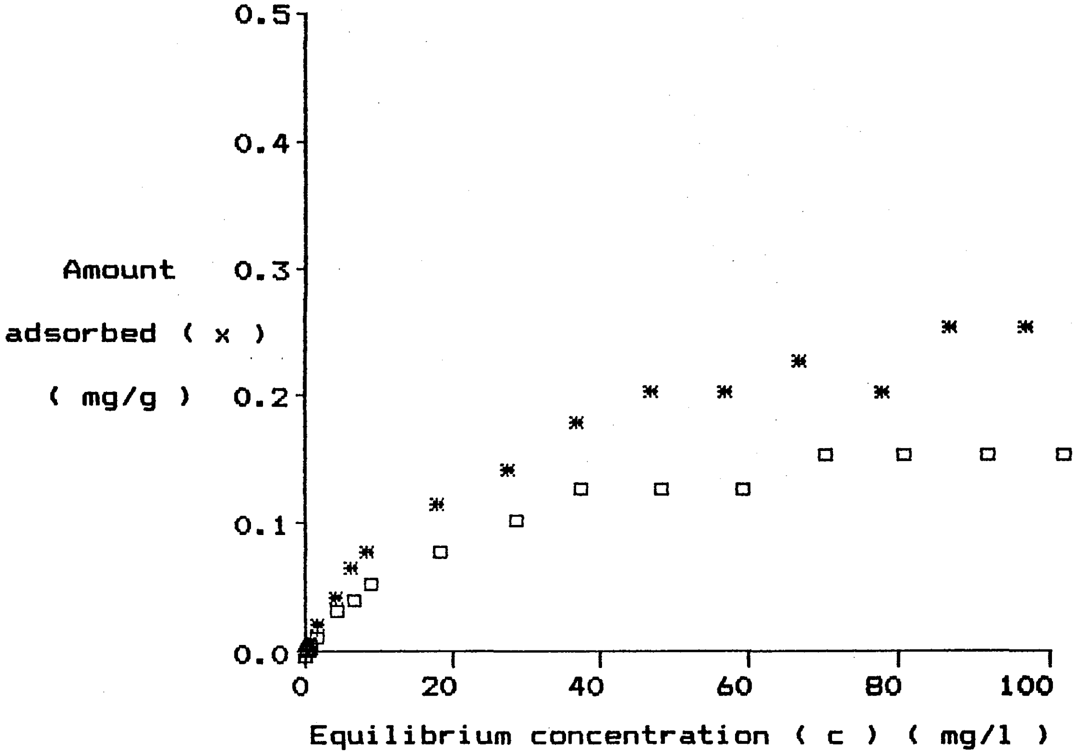


Fig. 4.10e Zinc adsorption isotherm for Dreghorn (Arkleston) soil in calcium sulphate (*) and calcium chloride (□) as background.

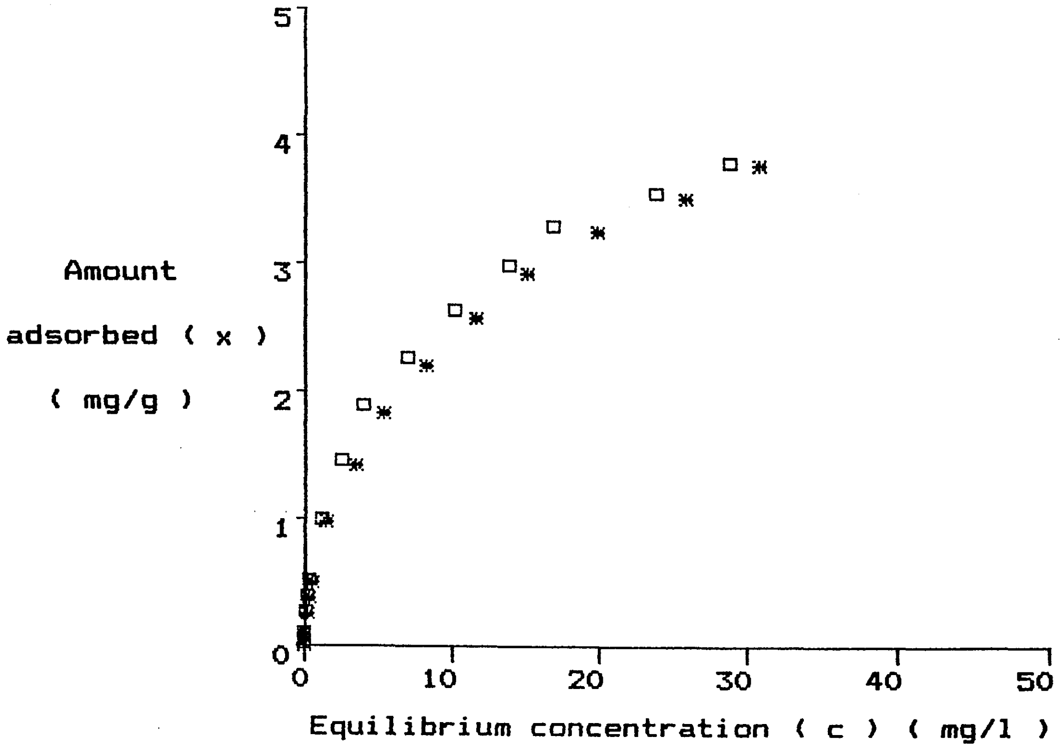


Fig. 4.11a Zinc adsorption isotherm for Midelney (topsoil) in sodium sulphate (*) and sodium chloride (□) as background.

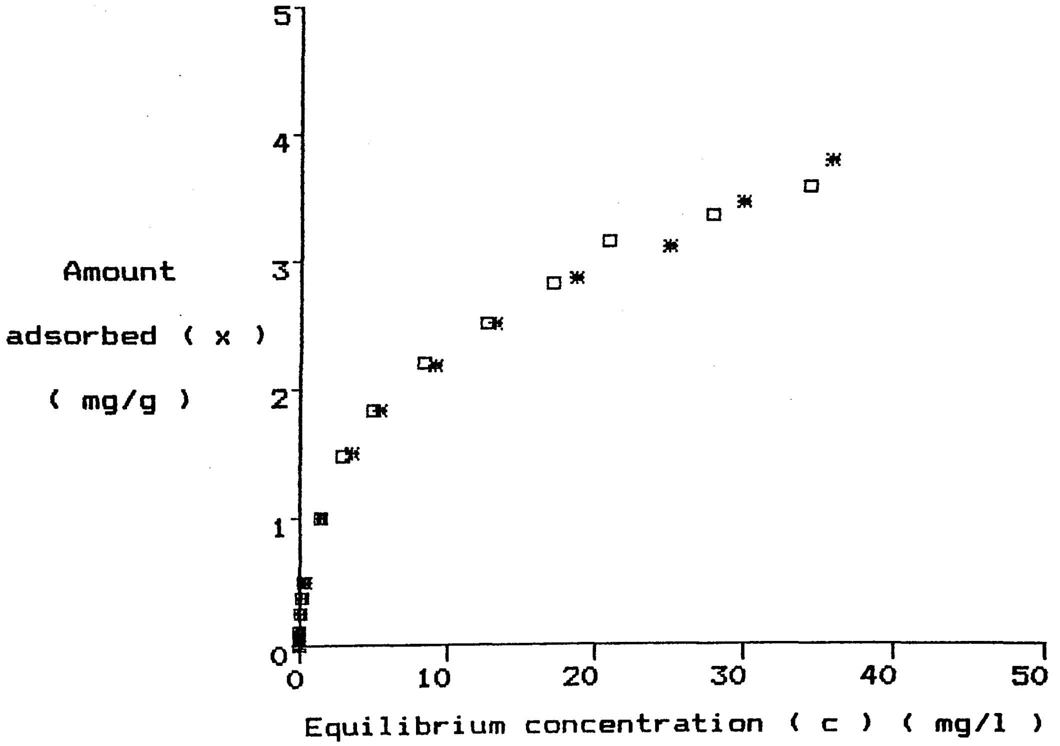


Fig. 4.11b Zinc adsorption isotherm for Midelney (topsoil) in potassium sulphate (*) and potassium chloride (□) as background.

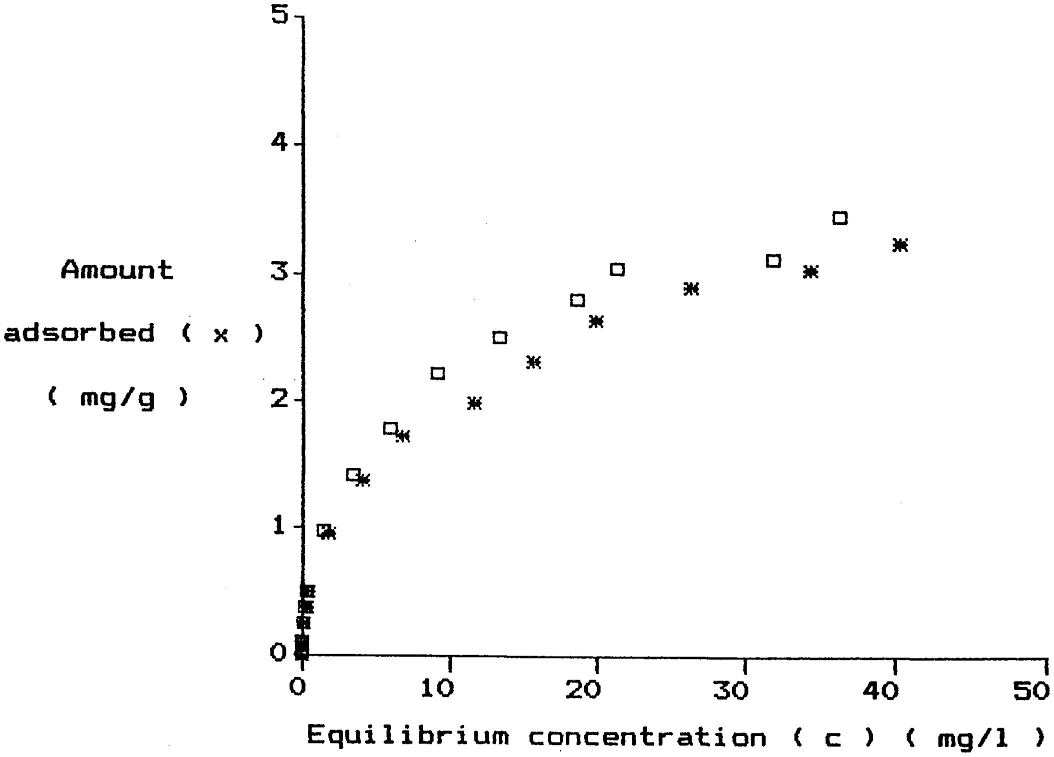


Fig. 4.11c Zinc adsorption isotherm for Midelney (topsoil) in ammonium sulphate (*) and ammonium chloride (□) as background.

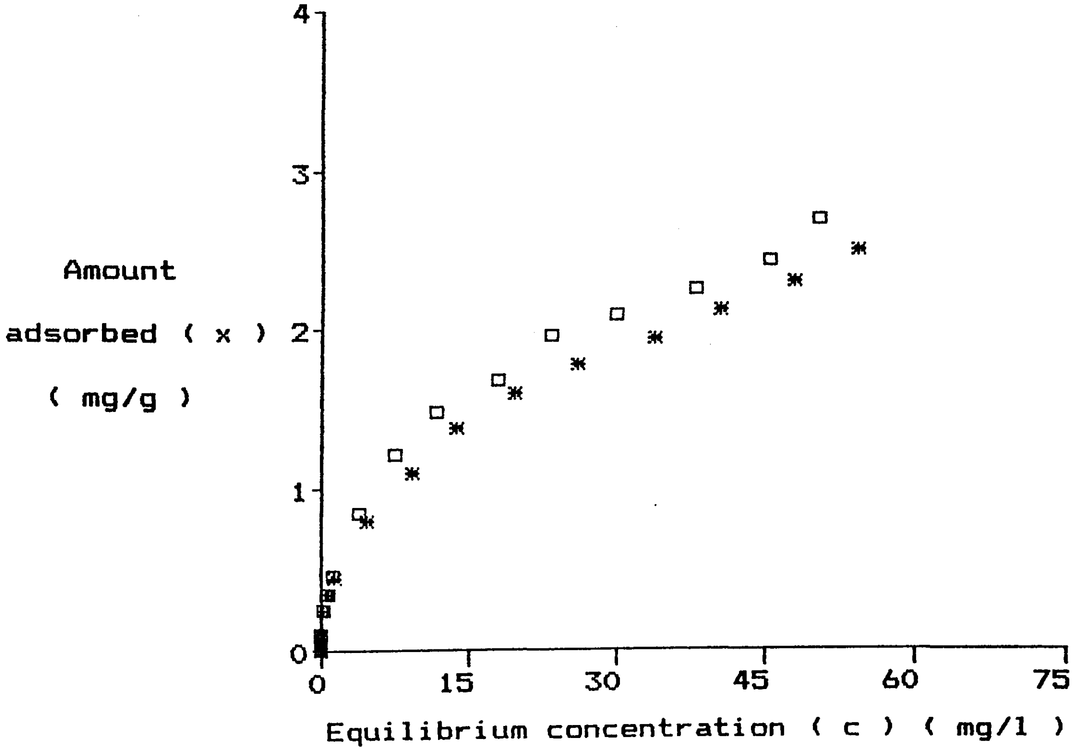


Fig. 4.11d Zinc adsorption isotherm for Midelney (topsoil) in magnesium sulphate (*) and magnesium chloride (□) as background.

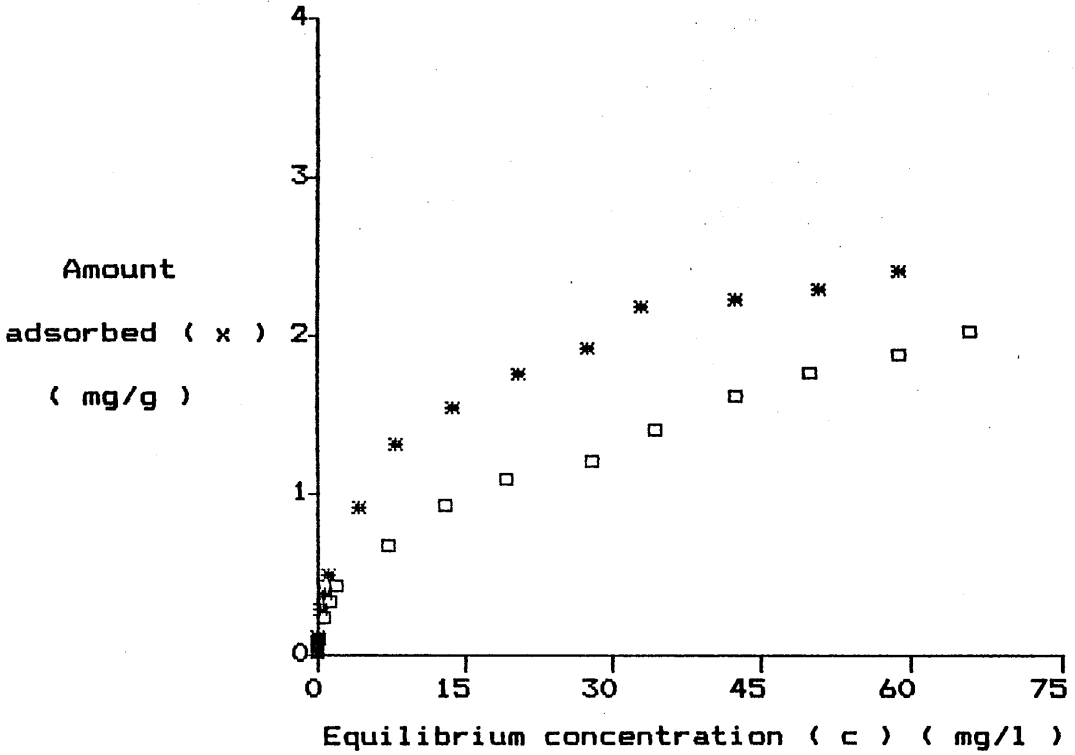


Fig. 4.11e Zinc adsorption isotherm for Midelney (topsoil) in calcium sulphate (*) and calcium chloride (□) as background.

Shuman (1986) reported that the lower the ionic strength, the more zinc was adsorbed. At the higher ionic strength of the calcium chloride system, the Ca^{2+} offers more competition for adsorption sites due to mass action. The molarity (0.0145M) of the saturated calcium sulphate was approximately 3.5 times lower than calcium chloride. To some extent these observations have agreement with the reported ones of Elrashidi and O´Connor (1982). They found no differences in zinc adsorption on a sandy loam soil at pH 7.6 using sodium salts of Cl^-, NO_3^- and SO_4^{2-}. However, Bowman and O´Connor (1982) found that SO_4^{2-} decreased adsorption of Ni^{2+} and Sr^{2+} by clay and soil compared to Cl^- using sodium and calcium salts. In contrast Shuman (1986) observed that SO_4^{2-} ion produced higher adsorption than NO_3^- or Cl^- ions which yielded the same isotherm at pH 6. It has been observed that SO_4^{2-} showed a slight increase in the zinc adsorption in all soils except Midelney (topsoil) but the differences are very small. The increased zinc adsorption in the SO_4^{2-} system could be due to changes in the surface potential due to SO_4^{2-} adsorption as reported by Shuman (1986).

The values of c/x versus c were plotted to fit the observed data to the Langmuir isotherm and to obtain the adsorption maximum. The Figures 4.12 and 4.13 (as a and b) represent the Langmuir isotherms for the sulphate and the chloride systems of Dreghorn (Arkleston) and Midelney (topsoil) respectively.

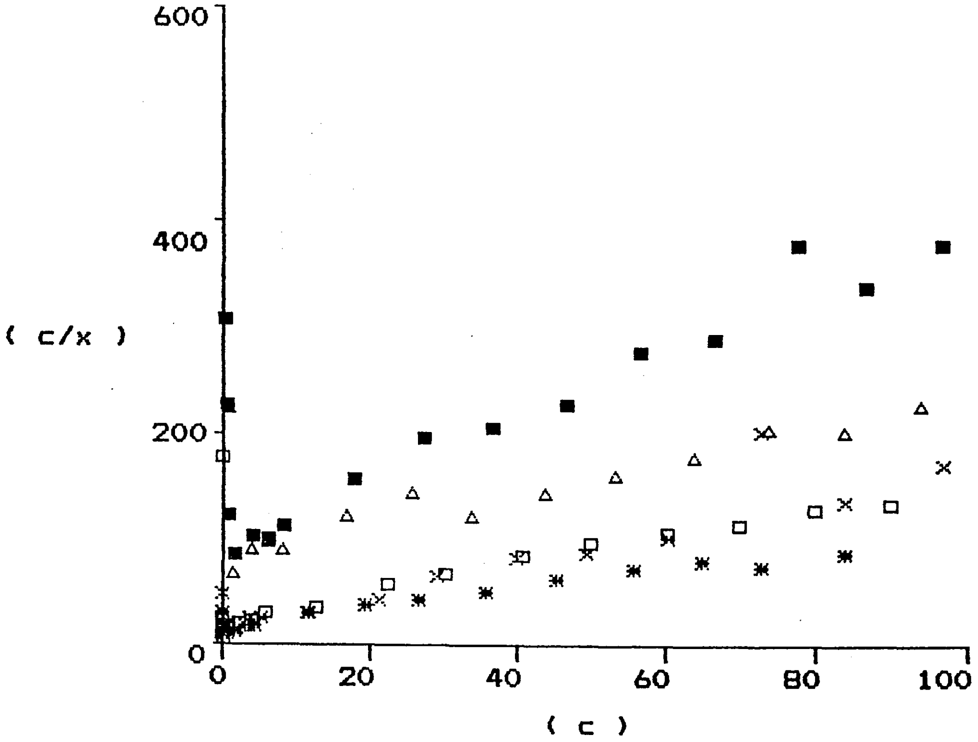


Fig. 4.12a Langmuir zinc adsorption isotherm in sulphate system for Dreghorn (Arkleston) soil.

Sodium (*) ; Potassium (x) ;
Ammonium (□) ; Magnesium (Δ) ;
Calcium (■) .

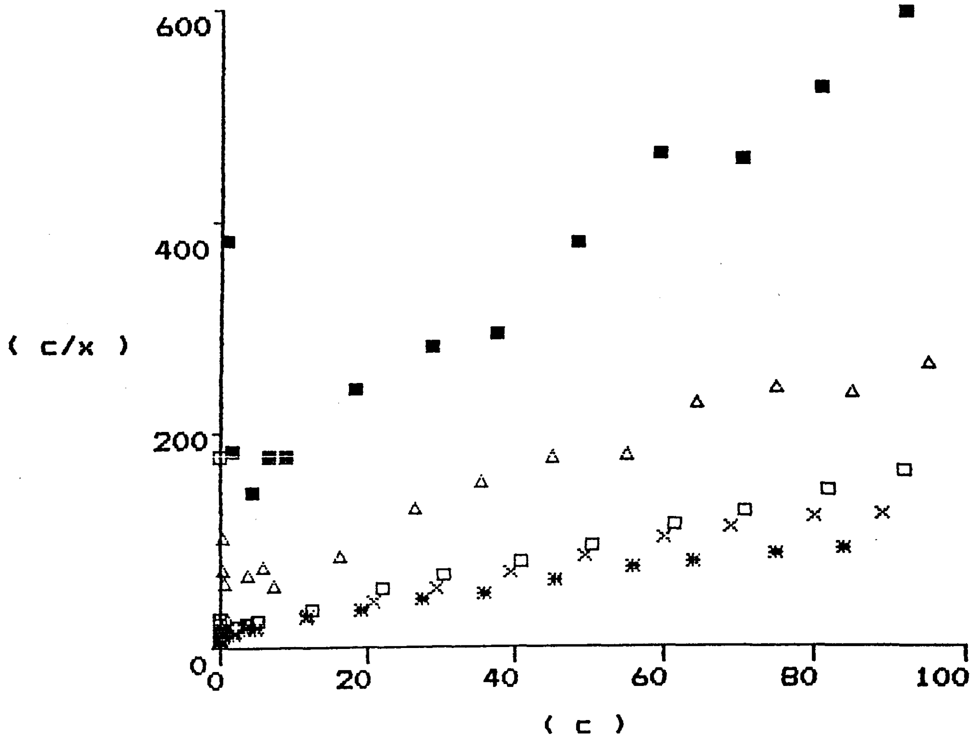


Fig. 4.12b Langmuir zinc adsorption isotherm in chloride system for Dreghorn (Arkleston) soil.

Sodium (*) ; Potassium (x) ;
Ammonium (□) ; Magnesium (Δ) ;
Calcium (■) .

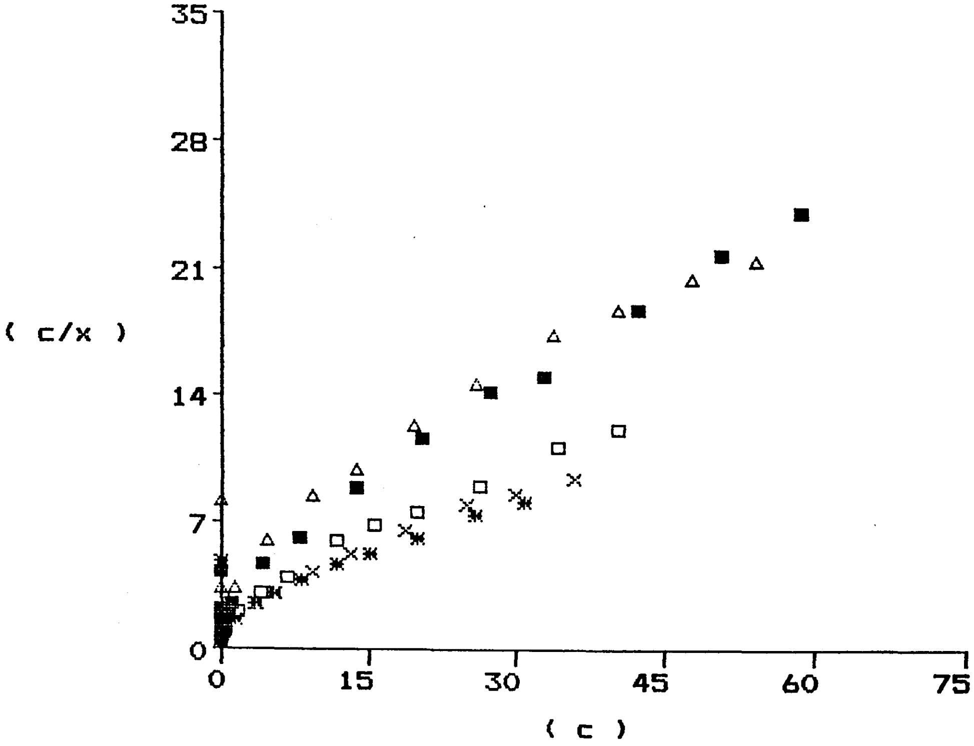


Fig. 4.13a Langmuir zinc adsorption isotherm in sulphate system for Midelney (topsoil).

Sodium (*) ; Potassium (x) ;
Ammonium (□) ; Magnesium (Δ) ;
Calcium (■) .

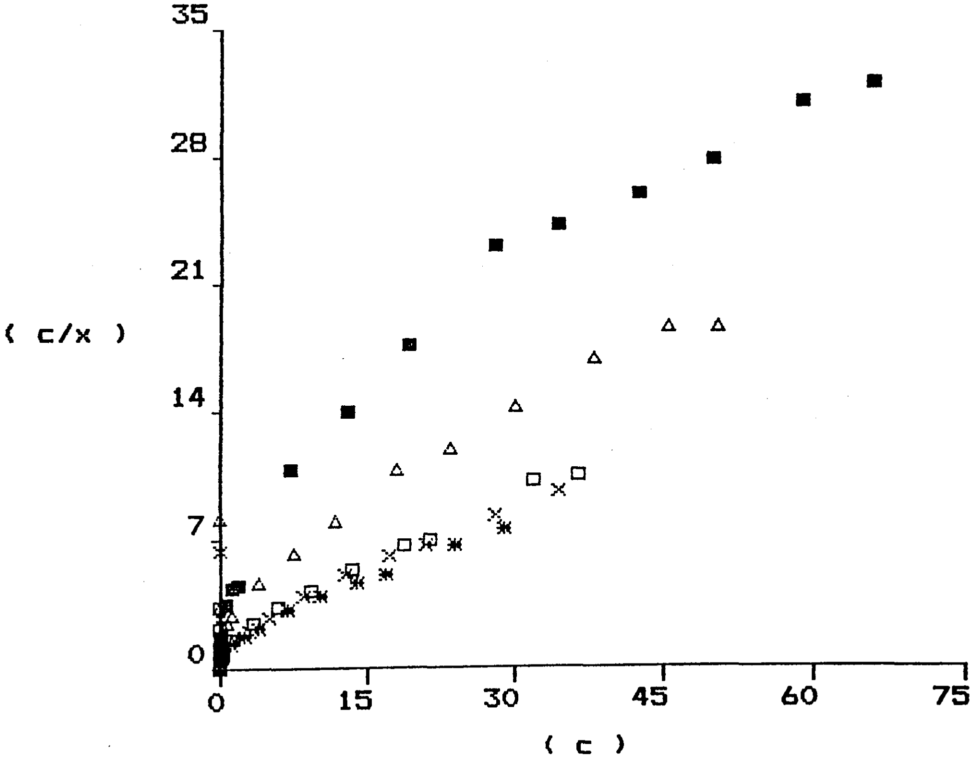


Fig. 4.13b Langmuir zinc adsorption isotherm in chloride system for Midelney (topsoil).

Sodium (*) ; Potassium (x) ;
Ammonium (□) ; Magnesium (Δ) ;
Calcium (■) .

It has been observed that the data did not obey the Langmuir equation and they did not lie on a single straight line, but curves were resolved into two linear portions as split isotherm. In all cases they could be described by a split isotherm in the same way as Shuman (1975), Shukla and Mittal (1979) and Pulford (1986) observed from their data. The equilibrium concentration at which the change of slope occurred was not always the same for any one soil in the various background electrolytes. The same pattern was followed in all soils irrespective of the anion system. This split isotherm may suggest the presence of different adsorption sites or reactions, or be associated with possible heterogeneity in the surface energy, as suggested by various workers, described in Section 4.3.1.1. The data in Figures 4.12 and 4.13 (a and b) appear to lie on two straight lines, fitted by eye. There is, however, no reason to suppose that adsorption occurs at only two surfaces as described in Section 4.3.1.1.

Experimental data for the Dreghorn (Arkleston) and Midelney (topsoil) at low equilibrium solution concentrations, represented in Figures 4.14 and 4.15 (a and b) respectively, show the lines bending upward as reported by Veith and Sposito (1977) and Pulford (1986). Although there are variations depending upon background solution, all systems studied show this upturn at low concentration, except for both soils in sodium chloride and Midelney (topsoil) in calcium chloride.

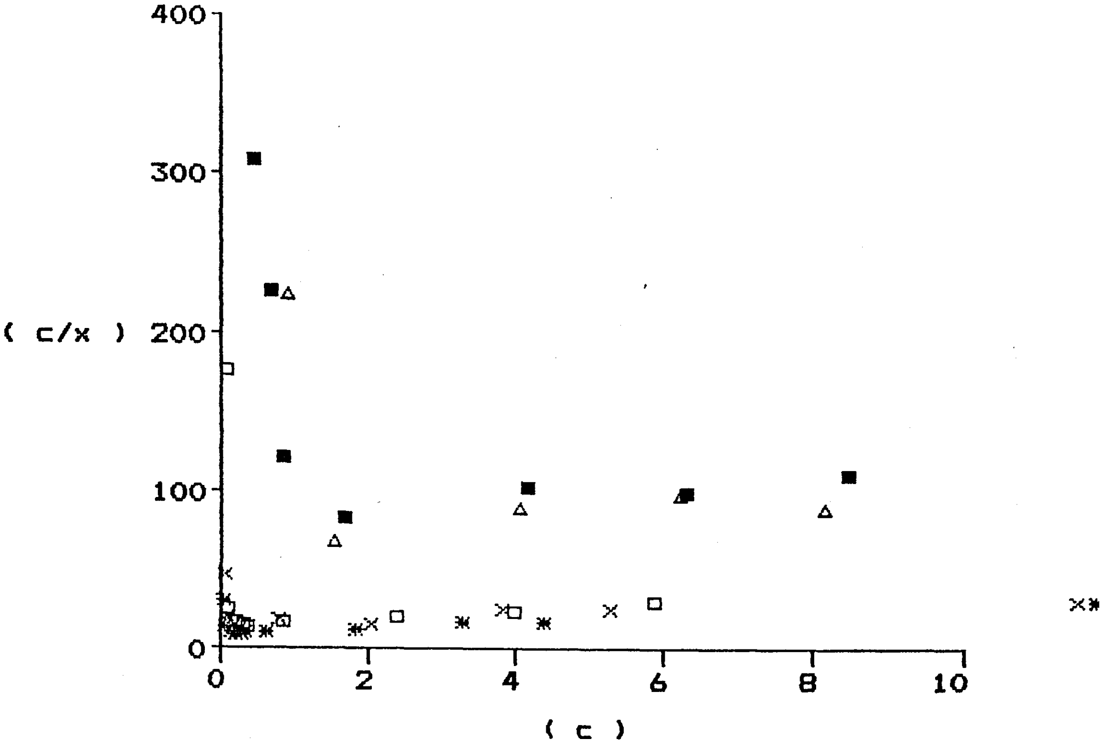


Fig. 4.14a Low Langmuir zinc adsorption isotherm in sulphate system for Dreghorn (Arkleston) soil.

Sodium (*) ; Potassium (x) ;
Ammonium (□) ; Magnesium (Δ) ;
Calcium (■) .

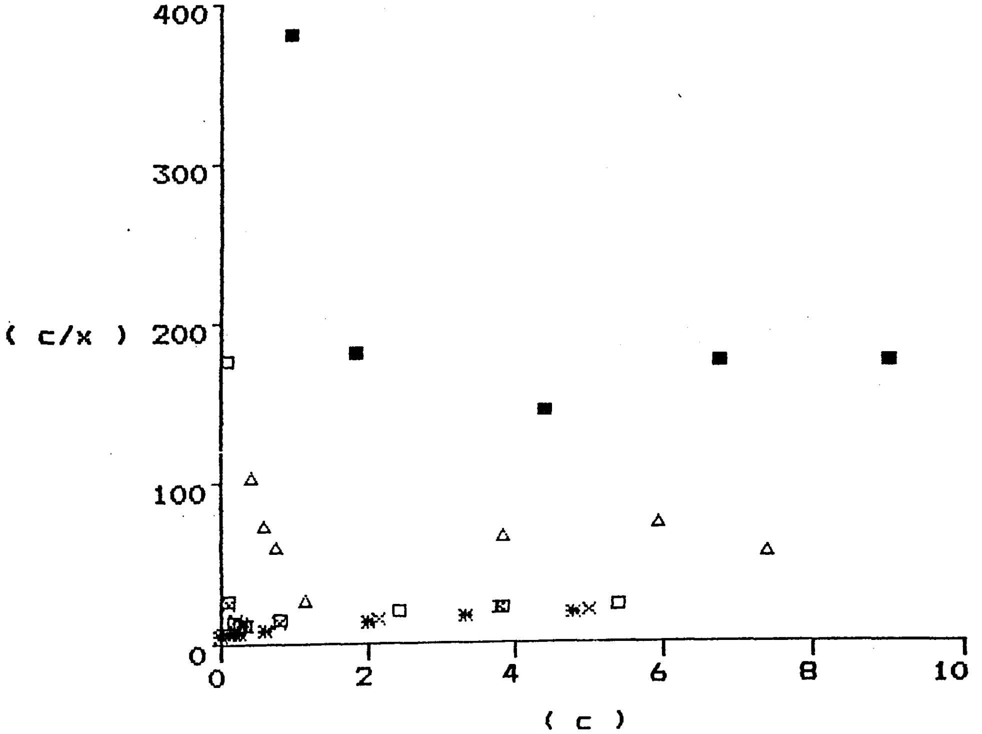


Fig. 4.14b Low Langmuir zinc adsorption isotherm in chloride system for Dreghorn (Arkleston) soil.

Sodium (*) ; Potassium (x) ;
Ammonium (□) ; Magnesium (Δ) ;
Calcium (■) .

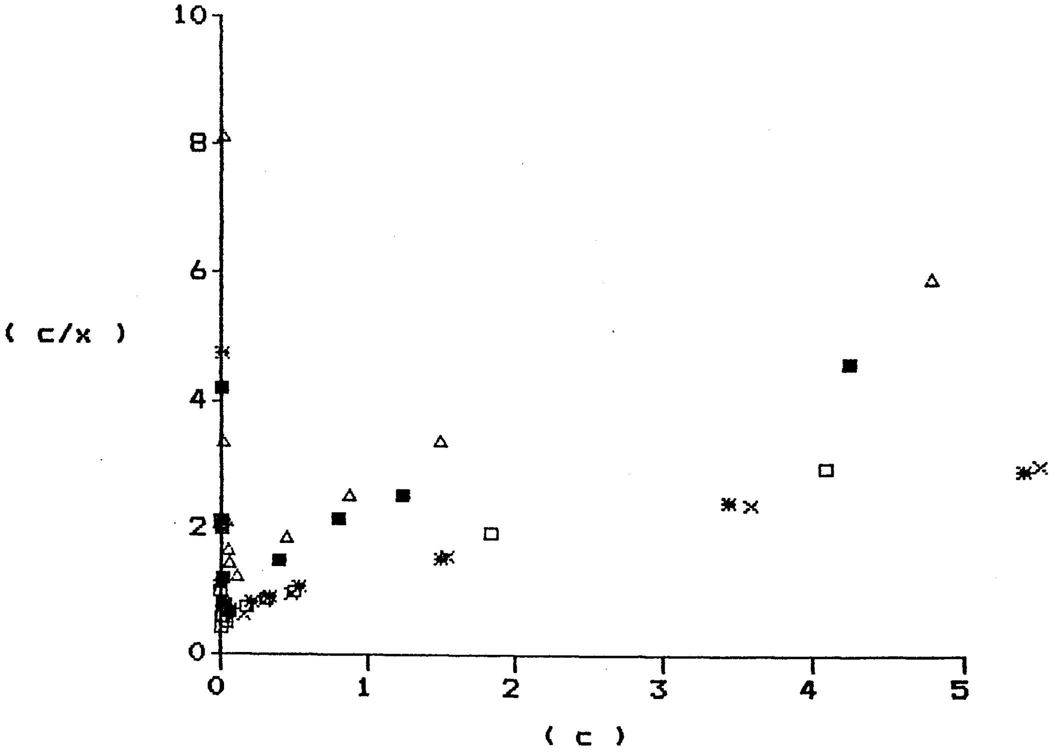


Fig. 4.15a Low Langmuir zinc adsorption isotherm in sulphate system for Midelney (topsoil).

Sodium (*) ; Potassium (x) ;
Ammonium (□) ; Magnesium (Δ) ;
Calcium (■) .

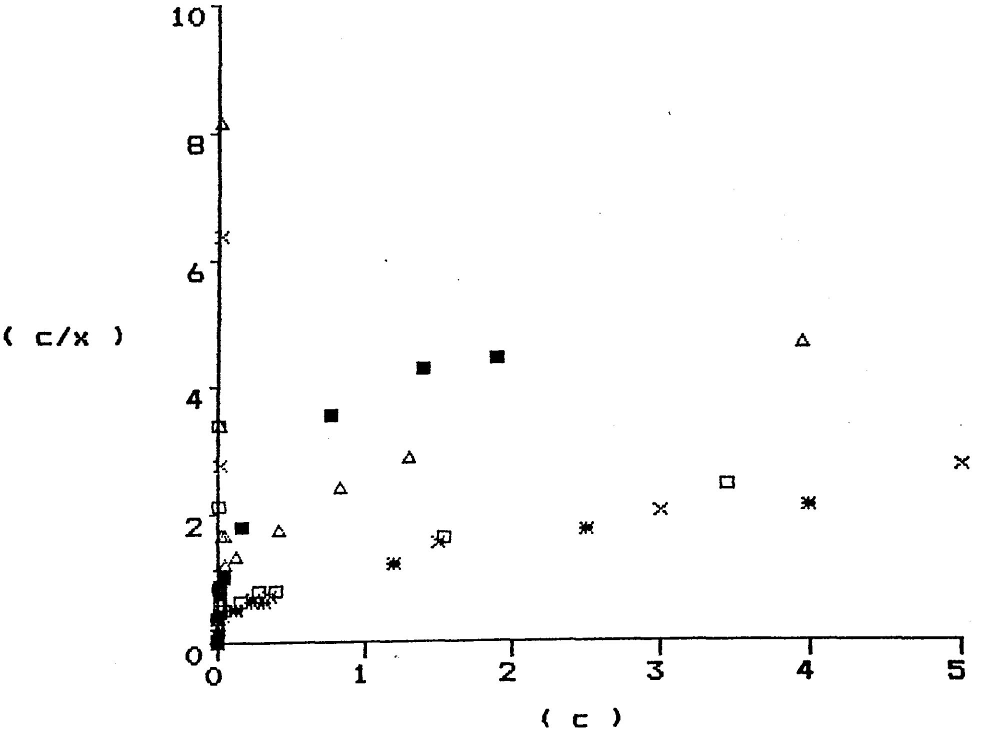


Fig. 4.15b Low Langmuir zinc adsorption isotherm in chloride system for Midelney (topsoil).

Sodium (*) ; Potassium (x) ;
Ammonium (□) ; Magnesium (Δ) ;
Calcium (■) .

The explanation for this is given in Section 4.3.1.1 from work by Veith and Sposito (1977), that the line for precipitation reactions bends upward and approaches infinity. This observed behaviour implies a mechanism that maintains zinc in solution with no apparent adsorption, a condition which could be met by precipitation as suggested by Pulford (1986).

The data plotted according to the Freundlich equation is represented by Figures 4.16 and 4.17 (a and b) for sulphate and chloride salt systems, for Dreghorn (Arkleston) and Midelney (topsoil) respectively. It has been observed that the data fits the Freundlich equation when curves are split into three linear portions for the sulphate salts in the case of Dreghorn (Arkleston). These observations are similar to ones reported by Shukla and Mittal (1979). They found three distinct portions of the isotherm having different k and n values for zinc adsorption in loamy and sandy soils. In most cases the isotherm showed two linear portions, which is most obvious in both salt systems for Midelney (topsoil). These results agree with the findings of Kuo and Mikkelsen (1979). Deviation from a single straight line may be due to the increasing surface heterogeneity at higher zinc concentration or different adsorption mechanisms in soil, as reported in Section 4.3.1.1. Elrashidi and O´Connor (1982) also observed deviation from a straight line using this equation and suggested the presence of more than one type of site or mechanism for zinc adsorption in soils.

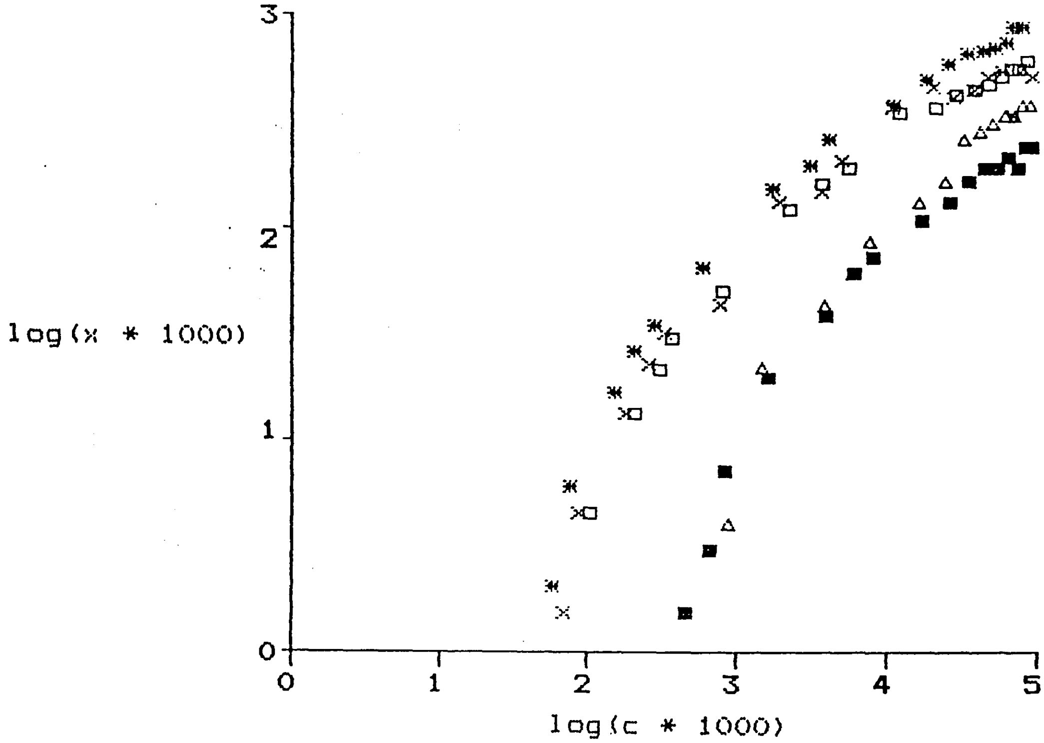


Fig. 4.16a Freundlich zinc adsorption isotherm in sulphate system for Dreghorn (Arkleston) soil.

Sodium	(*) ;	Potassium	(x) ;
Ammonium	(□) ;	Magnesium	(△) ;
Calcium	(■) .		

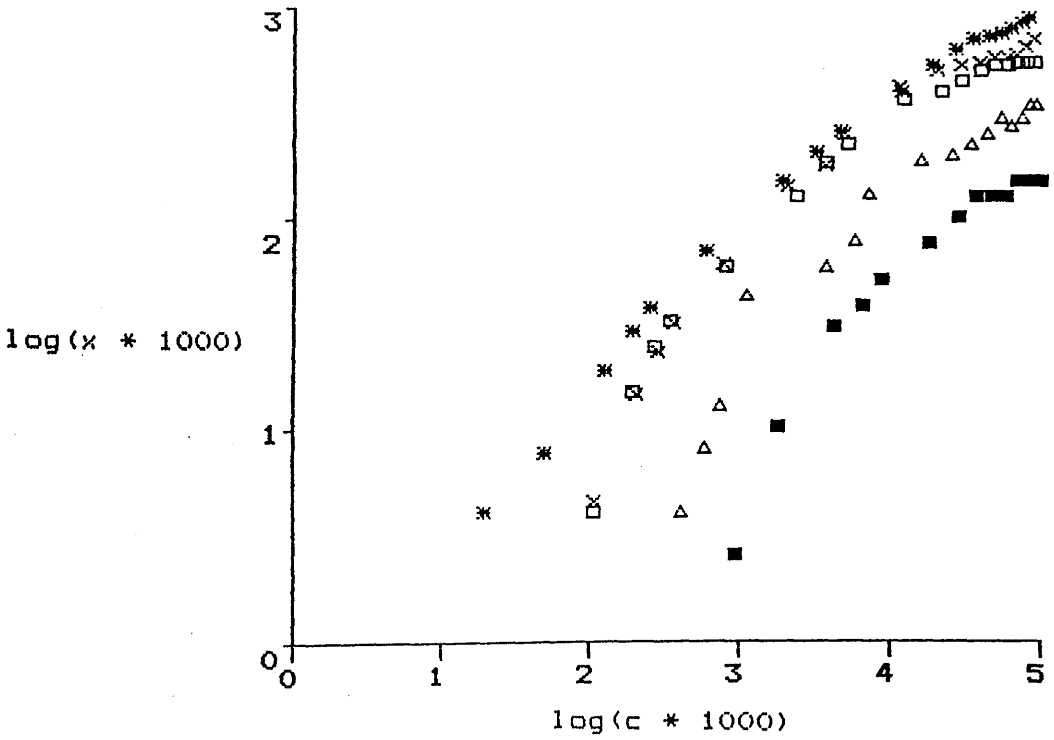


Fig. 4.16b Freundlich zinc adsorption isotherm in chloride system for Dreghorn (Arkleston) soil.

Sodium	(*) ;	Potassium	(x) ;
Ammonium	(□) ;	Magnesium	(△) ;
Calcium	(■) .		

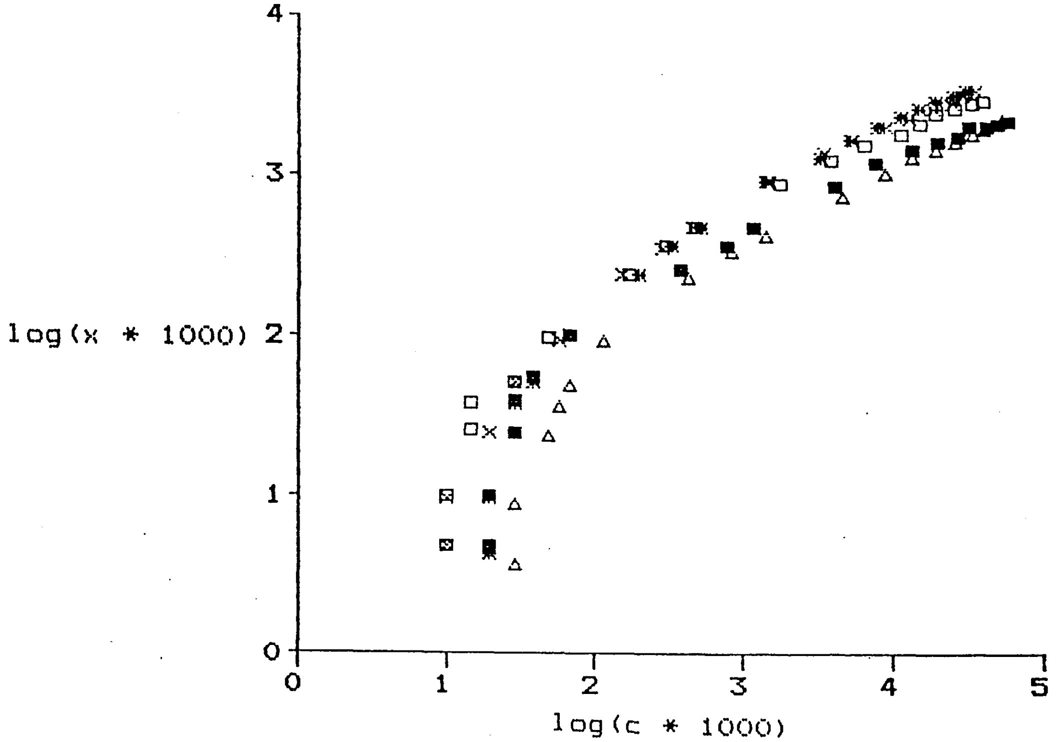


Fig. 4.17a Freundlich zinc adsorption isotherm in sulphate system for Midelney (topsoil).

Sodium	(*) ;	Potassium	(x) ;
Ammonium	(□) ;	Magnesium	(△) ;
Calcium	(■) .		

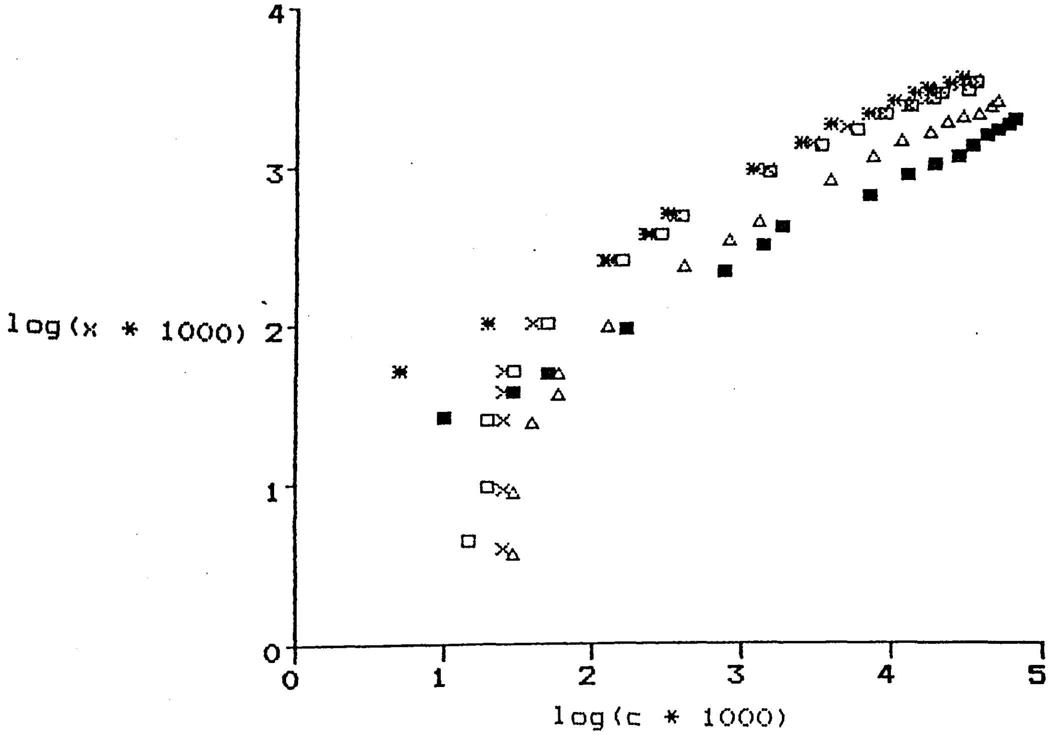


Fig. 4.17b Freundlich zinc adsorption isotherm in chloride system for Midelney (topsoil).

Sodium	(*) ;	Potassium	(x) ;
Ammonium	(□) ;	Magnesium	(△) ;
Calcium	(■) .		

The different parts of the curve also indicated that the nature of zinc adsorption differed at different initial zinc concentrations. The first part, at low zinc concentrations, indicated predominantly adsorption reactions. The second part showed the possibility of both adsorption and precipitation reactions. Any third portion, where the amount of zinc adsorbed rose steeply, may be due only to precipitation as suggested by Shukla and Mittal (1979).

The constants calculated from both the full and the linear top part of Langmuir and Freundlich isotherms are represented in Table 4.5. It reveals that the values of adsorption maxima were higher for all monovalent salts compared to the divalent salts irrespective of anion form in all soils. Sodium systems showed the highest values of adsorption maximum, while calcium the lowest values in all soils, suggesting again the lesser ability to compete for zinc adsorption of monovalent cations. The soils high in colloidal material and with higher pH showed higher values for adsorption maxima as well as bonding energies, compared to the soils low in colloidal material and pH. As reported by Shuman (1975) higher values are found in soils high in clay or organic matter than sandy soils low in organic matter. In most cases the values of adsorption maxima for sulphate systems are slightly higher compared to chloride systems, showing no real anion effect because the differences are very small.

Table 4.5 Zinc adsorption constants for four soils calculated from Langmuir and Freundlich plots for different salts used as background electrolytes. (SS = Na_2SO_4, SC = NaCl, KS = K_2SO_4, KC = KCl, AS = $(NH_4)_2SO_4$, AC = NH_4Cl, MS = $MgSO_4$, MC = $MgCl_2$, CS = $CaSO_4$, CC = $CaCl_2$)

Soil	Langmuir Plot			Freundlich Plot		
	Adsorption maximum b mg g^{-1}	Bonding energy k 1 mg^{-1}	R^2	Slope	Intercept	R^2
Dreghorn (Arkleston) SS (full)	1.06	0.07	0.954	0.72	-1.24	0.939
" " " (top)	1.22	0.04	0.964	0.42	-0.82	0.983
" " SC (full)	0.95	0.10	0.983	0.63	-1.14	0.982
" " " (top)	1.11	0.05	0.992	0.32	-0.67	0.980
" " KS (full)	0.64	0.11	0.991	0.69	-1.39	0.907
" " " (top)	0.65	0.10	0.988	0.32	-0.81	0.925
" " KC (full)	0.74	0.09	0.989	0.66	-1.28	0.936
" " " (top)	0.75	0.09	0.987	0.19	-0.56	0.965
" " AS (full)	0.71	0.08	0.985	0.66	-1.34	0.953
" " " (top)	0.75	0.06	0.983	0.35	-0.88	0.980
" " AC (full)	0.61	0.12	0.998	0.63	-1.31	0.930
" " " (top)	0.62	0.10	0.999	0.23	-0.68	0.956
" " MS (full)	0.64	0.02	0.954	0.86	-1.97	0.941
" " " (top)	0.67	0.02	0.949	0.38	-1.13	0.967
" " MC (full)	0.44	0.04	0.942	0.72	-1.76	0.925
" " " (top)	0.51	0.02	0.943	0.50	-1.42	0.963
" " CS (full)	0.32	0.03	0.969	0.86	-2.14	0.931
" " " (top)	0.34	0.03	0.988	0.54	-1.62	0.994
" " CC (full)	0.20	0.04	0.987	0.77	-2.20	0.913
" " " (top)	0.20	0.03	0.986	0.39	-1.57	0.902

Table 4.5 (continued)

Soil	Langmuir Plot			Freundlich Plot		
	Adsoprtion maximum b mg g^{-1}	Bonding energy k 1 mg^{-1}	R^2	Slope	Intercept	R^2
Dreghorn (Auchin) SS (full)	1.05	0.12	0.984	0.62	-1.06	0.982
" " " (top)	1.12	0.08	0.997	0.18	-0.36	0.978
" " SC (full)	0.98	0.14	0.987	0.58	-1.02	0.987
" " " (top)	1.08	0.08	0.996	0.16	-0.34	0.969
" " KS (full)	0.86	0.08	0.962	0.66	-1.24	0.925
" " " (top)	1.09	0.03	0.975	0.42	-0.90	0.990
" " KC (full)	0.81	0.08	0.937	0.66	-1.27	0.901
" " " (top)	0.97	0.03	0.986	0.42	-0.93	0.965
" " AS (full)	0.81	0.07	0.955	0.68	-1.31	0.940
" " " (top)	1.02	0.03	0.979	0.46	-1.00	0.998
" " AC (full)	0.90	0.07	0.954	0.68	-1.28	0.958
" " " (top)	1.00	0.04	0.965	0.49	-1.02	0.993
" " MS (full)	0.60	0.03	0.906	0.79	-1.75	0.950
" " " (top)	0.64	0.03	0.963	0.43	-1.18	0.969
" " MC (full)	0.51	0.05	0.919	0.75	-1.69	0.929
" " " (top)	0.54	0.04	0.890	0.23	-0.88	0.958
" " CS (full)	0.46	0.03	0.935	0.77	-1.85	0.952
" " " (top)	0.49	0.02	0.974	0.45	-1.34	0.990
" " CC (full)	0.39	0.04	0.935	0.69	-1.78	0.975
" " " (top)	0.50	0.02	0.991	0.61	-1.66	0.995

Table 4.5 (continued)

Soil	Langmuir Plot			Freundlich Plot		
	Adsorption maximum b mg g^{-1}	Bonding energy k l mg^{-1}	R^2	Slope	Intercept	R^2
Midelney topsoil SS (full)	4.40	0.15	0.855	0.77	-0.36	0.928
" " " (top)	4.84	0.11	0.995	0.45	-0.08	0.997
" " SC (full)	3.93	0.35	0.972	0.51	-0.09	0.995
" " " (top)	4.93	0.11	0.998	0.37	-0.05	0.994
" " KS (full)	3.88	0.23	0.968	0.71	-0.34	0.946
" " " (top)	4.18	0.13	0.987	0.41	-0.07	0.996
" " KC (full)	4.08	0.16	0.793	0.72	-0.34	0.879
" " " (top)	4.12	0.16	0.989	0.47	-0.11	0.992
" " AS (full)	3.36	0.27	0.971	0.66	-0.37	0.939
" " " (top)	4.16	0.09	0.992	0.40	-0.12	0.994
" " AC (full)	3.70	0.21	0.950	0.72	-0.36	0.915
" " " (top)	3.82	0.16	0.996	0.43	-0.10	0.991
" " MS (full)	2.64	0.11	0.937	0.70	-0.68	0.930
" " " (top)	3.09	0.06	0.990	0.48	-0.43	0.999
" " MC (full)	2.87	0.12	0.928	0.72	-0.64	0.930
" " " (top)	2.97	0.09	0.992	0.39	-0.25	0.994
" " CS (full)	2.52	0.19	0.981	0.64	-0.57	0.927
" " " (top)	2.80	0.10	0.996	0.48	-0.38	0.993
" " CC (full)	2.01	0.13	0.934	0.50	-0.60	0.997
" " " (top)	3.79	0.02	0.988	0.50	-0.60	0.997

Table 4.5 (continued)

Soil	Langmuir Plot			Freundlich Plot		
	Adsorption maximum b mg g^{-1}	Bonding energy k 1 mg^{-1}	R^2	Slope	Intercept	R^2
Midelney subsoil SS (full)	5.25	0.70	0.898	0.73	0.22	0.865
" " " (top)	5.46	0.55	0.996	0.32	0.36	0.994
" " SC (full)	4.74	1.33	0.981	0.39	0.31	0.985
" " " (top)	5.46	0.49	0.996	0.34	0.33	0.996
" " KS (full)	5.04	0.64	0.931	0.67	0.13	0.863
" " " (top)	5.43	0.40	0.981	0.35	0.29	0.994
" " KC (full)	4.69	0.67	0.966	0.63	0.11	0.835
" " " (top)	4.95	0.45	0.992	0.32	0.28	0.994
" " AS (full)	4.11	0.50	0.959	0.65	-0.08	0.901
" " " (top)	4.79	0.18	0.978	0.42	0.06	0.998
" " AC (full)	4.21	0.38	0.923	0.61	-0.08	0.902
" " " (top)	4.56	0.20	0.990	0.41	0.07	0.998
" " MS (full)	4.15	0.32	0.949	0.68	-0.16	0.905
" " " (top)	4.57	0.19	0.997	0.42	0.03	0.990
" " MC (full)	4.08	0.33	0.952	0.67	-0.17	0.901
" " " (top)	4.52	0.19	0.997	0.43	0.01	0.992
" " CS (full)	3.30	0.34	0.968	0.46	-0.15	0.961
" " " (top)	4.44	0.07	0.991	0.38	-0.08	0.997
" " CC (full)	2.75	0.18	0.960	0.39	-0.25	0.998
" " " (top)	3.99	0.04	0.989	0.41	-0.26	0.999

The values of adsorption maxima calculated from full Langmuir plots were lower than from the top linear parts for all electrolytes in all soils. In contrast values for bonding energies decreased in the upper linear parts compared to the full Langmuir isotherm, also suggesting the different type of adsorption sites with differing bonding energies. The higher bonding energies in full Langmuir isotherms suggest that the exchange sites for zinc had appreciably greater affinity due to their specificity below the top linear part than the sites responsible for upper portion. At low levels of zinc application, sorption of zinc seemed to be a chemisorption whereas at high zinc concentrations, zinc could be held by a combination of both physisorption and chemisorption, as was reported by Singh and Abrol (1985). The R^2 values of Langmuir plots were mostly higher than 0.9 in all soils for the full isotherm as well as the top linear portion. The constants for Freundlich plots are also given in Table 4.5, but have no meanings compared to these for Langmuir constants.

A calculation was made to determine whether consideration of the activity of free Zn^{2+} would result in differences in the adsorption data compared to use of zinc concentration. It has been suggested that although Zn^{2+} is the dominant zinc species below pH 7.7, activity coefficients and the presence of other zinc species may be important (Lindsay, 1979, Bowman and O´Connor, 1982 and Shuman, 1986). Activity of free Zn^{2+} ion in the equilibrium solution was calculated using the Davis equation from the concentration of Zn and the ionic strength of the solution for monovalent and divalent cations in both sulphate and chloride systems. In the experimental systems used here some zinc ion pair species may be important. In the sulphate background, $ZnSO_4^0$ may be significant, while in chloride systems $ZnCl^+$ and $ZnCl_2^0$ may be present (Lindsay, 1979). Consideration should also be given to hydrolysed zinc species, depending upon the pH of the system. Under the conditions in some of the soils used here $ZnOH^+$ may be present in significant amounts (Lindsay, 1979). Free Zn^{2+} in solution was calculated by:

$$[\text{Zn inorg}] = [Zn^{2+}] + [\text{Zn ion pairs}] + [\text{Zn hydrolysed species}]$$

Using the equilibrium constants for the ion pairs and hydrolysed species given by Lindsay (1979), the following equations were derived to calculate (Zn^{2+}).

1. Sulphate system

$$[\text{Zn inorg}] = [Zn^{2+}] + [ZnSO_4^0] + [ZnOH^+]$$

$$Zn^{2+} + SO_4^{2-} \rightleftharpoons ZnSO_4^0 \qquad \log k^0 = 2.33$$

$$Zn^{2+} + H_2O \rightleftharpoons ZnOH^+ + H^+ \qquad \log k^0 = -7.69$$

$$\frac{(ZnSO_4^0)}{(Zn^{2+})(SO_4^{2-})} = 10^{2.33}$$

$$(ZnSO_4^0) = 10^{2.33}(Zn^{2+})(SO_4^{2-})$$

$$\frac{(ZnOH^+)(H^+)}{(Zn^{2+})} = 10^{-7.69}$$

$$(ZnOH^+) = \frac{10^{-7.69}(Zn^{2+})}{(H^+)}$$

$$[Zn\ inorg] = \frac{(Zn^{2+})}{\gamma Zn^{2+}} + 10^{2.33}(Zn^{2+})\overset{(SO_4^{2-})}{\wedge} + \frac{10^{-7.69}(Zn^{2+})}{(H^+)\gamma ZnOH^+}$$

$$[Zn\ inorg] = (Zn^{2+})\left(\frac{1}{\gamma Zn^{2+}} + 10^{2.33}(SO_4^{2-}) + \frac{10^{-7.69}}{(H^+)\gamma ZnOH^+}\right)$$

$$(Zn^{2+}) = \frac{[Zn\ inorg]}{\frac{1}{\gamma Zn^{2+}} + 10^{2.33}(SO_4^{2-}) + \frac{10^{-7.69}}{(H^+)\gamma ZnOH^+}}$$

So the simplest form of equation derived for different cations,

(a) Divalent cations: $$\frac{c}{13.920 + \frac{10^{-7.69}}{0.75 \times (H^+)}}$$

(b) Monovalent cations: $$\frac{c}{13.720 + \frac{10^{-7.69}}{0.76 \times (H^+)}}$$

2. Chloride system

$$[Zn\ inorg] = [Zn^{2+}] + [ZnCl^+] + [ZnCl_2^0] + [ZnOH^+]$$

$Zn^{2+} + Cl^- \rightleftharpoons ZnCl^+$ log $k^0 = 0.43$

$Zn^{2+} + 2Cl^- \rightleftharpoons ZnCl_2^0$ log $k^0 = 0.00$

$Zn^{2+} + H_2O \rightleftharpoons ZnOH^+ + H^+$ log $k^0 = -7.69$

$$\frac{(ZnCl^+)}{(Zn^{2+})(Cl^-)} = 10^{0.43}$$

$$(ZnCl^+) = 10^{0.43}(Zn^{2+})(Cl^-)$$

$$\frac{(ZnCl_2^{\,0})}{(Zn^{2+})(Cl^-)^2} = 10^{0.00}$$

$$(ZnCl_2^{\,0}) = 10^{0.00}(Zn^{2+})(Cl^-)^2$$

$$\frac{(ZnOH^+)(H^+)}{(Zn^{2+})} = 10^{-7.69}$$

$$(ZnOH^+) = \frac{10^{-7.69}(Zn^{2+})}{(H^+)}$$

$$[Zn\ inorg] = \frac{(Zn^{2+})}{\gamma Zn^{2+}} + \frac{10^{0.43}(Zn^{2+})(Cl^-)}{\gamma ZnCl^+} + 10^{0.00}(Zn^{2+})(Cl^-)^2 + \frac{10^{-7.69}(Zn^{2+})}{(H^+)\gamma ZnOH^+}$$

$$[Zn\ inorg] = (Zn^{2+})\left(\frac{1}{\gamma Zn^{2+}} + \frac{10^{0.43}(Cl^-) +}{\gamma ZnCl^+} + 10^{0.00}(Cl^-)^2 + \frac{10^{-7.69}(Zn^{2+})}{(H^+)\gamma ZnOH^+}\right)$$

$$(Zn^{2+}) = \frac{[Zn\ inorg]}{\dfrac{1}{\gamma Zn^{2+}} + \dfrac{10^{0.43}(Cl^-)}{\gamma ZnCl^+} + 10^{0.00}(Cl^-)^2 + \dfrac{10^{-7.69}}{(H^+)\gamma ZnOH^+}}$$

So the simplest forms for different cations are:

(a) Divalent cations $= \dfrac{c}{3.484 + \dfrac{10^{-7.69}}{0.76 \times (H^+)}}$

(b) Mononvalent cations $= \dfrac{c}{3.058 + \dfrac{10^{-7.69}}{0.76 \times (H^+)}}$

Table 4.6 Zinc adsorption constants calculated from activity and concentration Langmuir plots (top) for different salts as background electrolytes

Soil				Sulphate salts			Chloride salts		
				Adsorption maximum b mg g^{-1}	Bonding energy k 1 mg^{-1}	R^2	Adsorption maximum b mg g^{-1}	Bonding energy k 1 mg^{-1}	R^2
Dreghorn	(Arkleston)	Na^+	(conc)	1.22	0.04	0.964	1.11	0.05	0.992
"	"	"	(act)	1.22	0.53	0.964	1.11	0.15	0.992
"	"	K^+	(conc)	0.65	0.10	0.988	0.70	0.11	0.995
"	"	"	(act)	0.65	1.40	0.988	0.70	0.35	0.995
"	"	NH_4^+	(conc)	0.70	0.07	0.988	0.62	0.10	0.999
"	"	"	(act)	0.70	0.98	0.988	0.62	0.32	0.999
"	"	Mg^{++}	(conc)	0.64	0.02	0.982	0.51	0.02	0.943
"	"	"	(act)	0.64	0.28	0.982	0.51	0.08	0.943
"	"	Ca^{++}	(conc)	0.33	0.03	0.987	0.20	0.04	0.989
"	"	"	(act)	0.33	0.18	0.987	0.20	0.13	0.989
"	(Auchincruive)	Na^+	(conc)	1.12	0.08	0.997	1.08	0.08	0.996
"	"	"	(act)	1.12	1.08	0.997	1.08	0.23	0.996
"	"	K^+	(conc)	1.09	0.03	0.975	0.97	0.03	0.986
"	"	"	(act)	1.09	0.42	0.975	0.97	0.11	0.986
"	"	NH_4^+	(conc)	1.02	0.03	0.979	1.00	0.04	0.965
"	"	"	(act)	1.02	0.37	0.979	1.00	0.12	0.965
"	"	Mg^{++}	(conc)	0.64	0.03	0.963	0.40	0.08	0.992
"	"	"	(act)	0.64	0.38	0.963	0.40	0.27	0.992
"	"	Ca^{++}	(conc)	0.49	0.02	0.974	0.50	0.02	0.991
"	"	"	(act)	0.49	0.14	0.974	0.50	0.07	0.991

Table 4.6 continued

Soil				Sulphate salts			Chloride salts		
				Adsorption maximum b mg g^{-1}	Bonding energy k l mg^{-1}	R^2	Adsorption maximum b mg g^{-1}	Bonding energy k l mg^{-1}	R^2
Midelney	(topsoil)	Na^+	(conc)	4.84	0.11	0.995	4.93	0.11	0.998
"	"	"	(act)	4.83	1.49	0.995	4.91	0.37	0.998
"	"	K^+	(conc)	4.18	0.13	0.987	4.12	0.16	0.989
"	"	"	(act)	4.18	1.79	0.987	4.10	0.50	0.989
"	"	NH_4^+	(conc)	4.16	0.09	0.992	3.82	0.16	0.996
"	"	"	(act)	4.15	1.22	0.992	3.80	0.50	0.996
"	"	Mg^{++}	(conc)	3.09	0.06	0.990	2.97	0.09	0.992
"	"	"	(act)	3.09	0.78	0.990	2.96	0.31	0.992
"	"	Ca^{++}	(conc)	2.80	0.10	0.995	3.79	0.02	0.988
"	"	"	(act)	2.79	0.53	0.995	3.78	0.06	0.989
"	(subsoil)	Na^+	(conc)	5.46	0.55	0.996	5.46	0.49	0.996
"	"	"	(act)	5.35	9.45	0.996	5.40	1.99	0.995
"	"	K^+	(conc)	4.92	0.53	0.989	4.95	0.45	0.992
"	"	"	(act)	4.84	8.78	0.988	4.86	1.85	0.992
"	"	NH_4^+	(conc)	4.79	0.18	0.978	4.87	0.16	0.994
"	"	"	(act)	4.77	2.72	0.979	4.78	0.67	0.996
"	"	Mg^{++}	(conc)	4.57	0.19	0.997	4.52	0.19	0.997
"	"	"	(act)	4.51	3.08	0.997	4.40	0.89	0.997
"	"	Ca^{++}	(conc)	4.44	0.07	0.991	3.99	0.04	0.989
"	"	"	(act)	4.41	0.43	0.991	3.96	0.16	0.998

Results in Table 4.6 represent the Langmuir constants calculated from the upper linear part of the isotherm, including the same points for both concentration as well as activity in sulphate and chloride systems. It has been observed that the adsorption maxima for the activity data are the same as those for the concentration data for the same cation in all soils except Midelney (subsoil), where these values for activity data were slightly lower than for concentration. Shuman (1986) has also reported no differences in adsorption maxima for the activity and concentration data, since only the Zn^{2+} in solution is affected by activity coefficients. He only observed that the isotherm curves were more compressed for the activity data compared to concentration. Bonding energy values increased using activity compared to concentration Langmuir plots for both anion systems in all soils. At higher zinc concentration the Zn^{2+} ion activity in solution would become high enough compared to the complex ions to compete effectively for relatively nonspecific adsorption sites. As the ability of clays to hold calcium more tightly than sodium is reported by Russell (1973). This may be due to the size of ion that in soil they tend to be bound more tightly than small ones. For concentration, the bonding energy constant considers retention on adsorption sites of Zn^{2+} and its complexes, while activity gives only the free Zn^{2+} ion retention. It suggests that Zn^{2+} is retained more tightly on the surface than its complexes. The R^2 values of Langmuir plots were above 0.9 in all cases for all soils, but were similar for both concentration and activity.

The effect of anion on free Zn^{2+} adsorption is not clear because the values for adsorption maxima do not vary in the same order. Shuman (1986) observed that both soils exhibit higher Zn^{2+} adsorption with SO_4^{2-} counter ion than Cl^- and NO_3^-. In contrast Bowman and O´Connor (1982) found that activity calculations for the free metal brought the sulphate and chloride curves together, as the activity curves were plotted on the same axes as the concentration curves.

Table 4.7 represents the constants calculated from concentration and activity Freundlich upper linear part for sulphate as well as chloride systems. The intercept decreased when activity was used compared to concentration, while the slope and R^2 values remained unchanged. These constants have no meanings compared to Langmuir constants.

Table 4.7 Zinc adsorption constants calculated from activity and concentration Freundlich plots (top) for different salts as background electrolytes

Soil	Sulphate salts			Chloride salts		
	Slope	Intercept	R^2	Slope	Intercept	R^2
Dreghorn (Arkleston) Na^+ (conc)	0.42	-0.82	0.983	0.32	-0.67	0.980
" " " (act)	0.42	-0.34	0.983	0.32	-0.51	0.980
" " K^+ (conc)	0.32	-0.81	0.925	0.19	-0.56	0.965
" " " (act)	0.32	-0.45	0.925	0.19	-0.47	0.965
" " NH_4^+ (conc)	0.35	-0.88	0.980	0.23	-0.68	0.956
" " " (act)	0.35	-0.48	0.980	0.23	-0.57	0.956
" " Mg^{++} (conc)	0.38	-1.13	0.967	0.50	-1.42	0.963
" " " (act)	0.38	-0.70	0.967	0.50	-1.15	0.963
" " Ca^{++} (conc)	0.54	-1.62	0.994	0.39	-1.57	0.902
" " " (act)	0.54	-1.22	0.994	0.39	-1.36	0.902
" (Auchincruive) Na^+ (conc)	0.18	-0.36	0.978	0.16	-0.34	0.969
" " " (act)	0.18	-0.15	0.978	0.16	-0.26	0.969
" " K^+ (conc)	0.42	-0.90	0.990	0.42	-0.93	0.977
" " " (act)	0.42	-0.42	0.990	0.41	-0.71	0.989
" " NH_4^+ (conc)	0.46	-1.00	0.998	0.49	-1.02	0.993
" " " (act)	0.46	-0.49	0.998	0.49	-0.78	0.993
" " Mg^{++} (conc)	0.43	-1.18	0.969	0.23	-0.88	0.958
" " " (act)	0.43	-0.69	0.969	0.23	-0.76	0.958
" " Ca^{++} (conc)	0.45	-1.34	0.990	0.61	-1.66	0.995
" " " (act)	0.45	-1.01	0.990	0.61	-1.33	0.994

Table 4.7 continued

Soil	Sulphate salts			Chloride salts		
	Slope	Intercept	R^2	Slope	Intercept	R^2
Midelney topsoil Na^+ (conc)	0.45	-0.08	0.997	0.37	0.05	0.994
" " " (act)	0.45	0.44	0.997	0.36	0.24	0.994
" " K^+ (conc)	0.41	-0.07	0.996	0.47	-0.11	0.992
" " " (act)	0.41	0.40	0.996	0.46	0.12	0.992
" " NH_4^+ (conc)	0.40	-0.12	0.994	0.43	-0.10	0.991
" " " (act)	0.40	0.34	0.994	0.42	0.12	0.991
" " Mg^{++} (conc)	0.48	-0.43	0.999	0.39	-0.25	0.994
" " " (act)	0.48	0.12	0.999	0.38	-0.04	0.994
" " Ca^{++} (conc)	0.48	-0.38	0.993	0.50	-0.60	0.997
" " " (act)	0.48	-0.02	0.993	0.50	-0.33	0.997
" subsoil Na^+ (conc)	0.32	0.36	0.994	0.34	0.33	0.996
" " " (act)	0.30	0.73	0.995	0.31	0.54	0.998
" " K^+ (conc)	0.35	0.29	0.994	0.32	0.28	0.994
" " " (act)	0.32	0.69	0.995	0.29	0.47	0.997
" " NH_4^+ (conc)	0.42	0.06	0.998	0.41	0.07	0.998
" " " (act)	0.41	0.55	0.998	0.40	0.31	0.998
" " Mg^{++} (conc)	0.42	0.03	0.990	0.43	0.01	0.992
" " " (act)	0.40	0.52	0.991	0.40	0.29	0.993
" " Ca^{++} (conc)	0.38	-0.08	0.997	0.41	-0.26	0.999
" " " (act)	0.37	0.21	0.996	0.40	-0.02	0.999

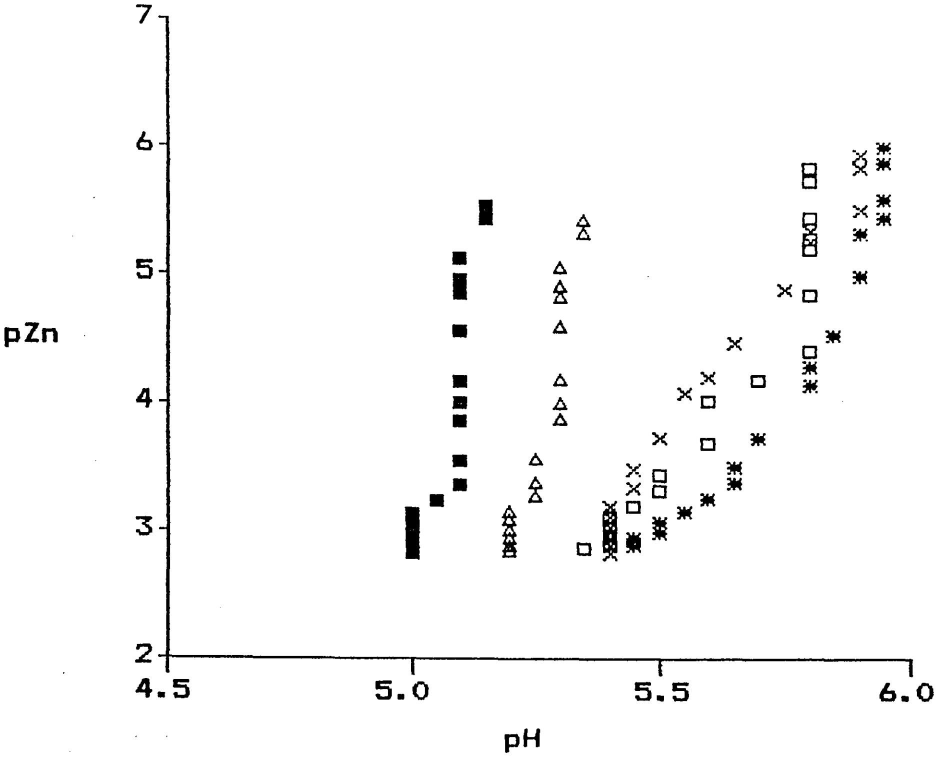


Fig. 4.18a Equilibrium pZn versus pH in sulphate system for Dreghorn (Arkleston) soil.

Sodium (*) pZn = − 20.87 + 4.34pH
Potassium (×) pZn = − 26.15 + 5.41pH
Ammonium (□) pZn = − 19.09 + 4.09pH
Magnesium (△) pZn = − 50.63 +10.31pH
Calcium (■) pZn = − 22.33 + 5.06pH

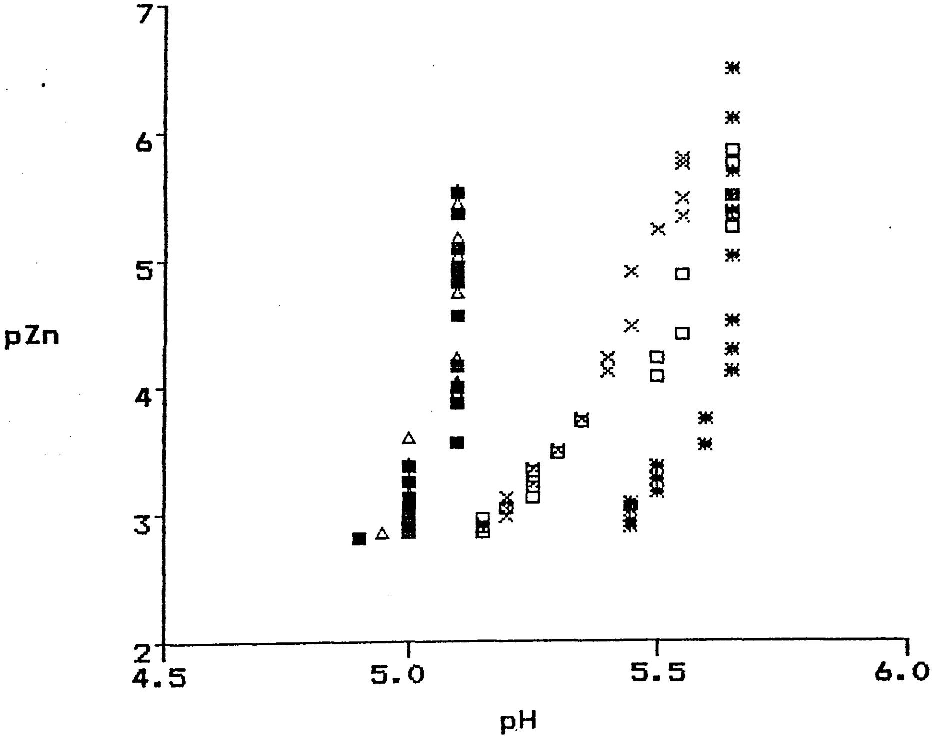


Fig. 4.18b Equilibrium pZn versus pH in chloride system for Dreghorn (Arkleston) soil.

Sodium (*) pZn = − 24.60 + 5.06pH
Potassium (×) pZn = − 30.42 + 6.43pH
Ammonium (□) pZn = − 16.41 + 3.74pH
Magnesium (△) pZn = − 34.60 + 7.55pH
Calcium (■) pZn = − 15.40 + 3.70pH

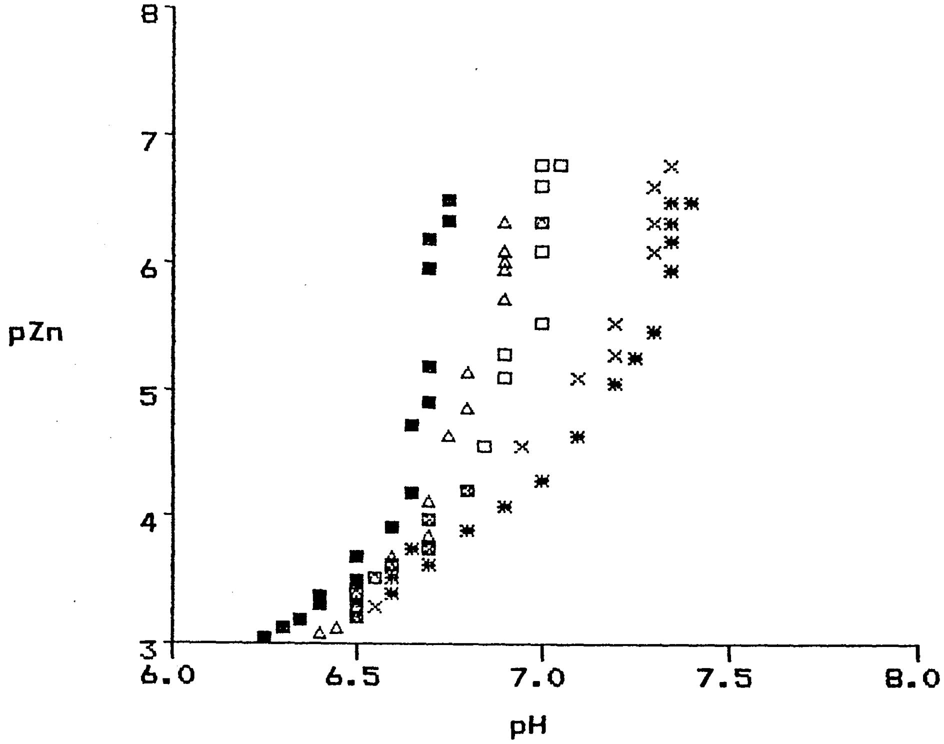


Fig. 4.19a Equilibrium pZn versus pH in sulphate system for Midelney (topsoil).

Sodium (*) $pZn = -15.50 + 2.87pH$
Potassium (x) $pZn = -20.02 + 3.56pH$
Ammonium (△) $pZn = -25.80 + 4.46pH$
Magnesium (□) $pZn = -31.15 + 5.30pH$
Calcium (■) $pZn = -21.65 + 3.91pH$

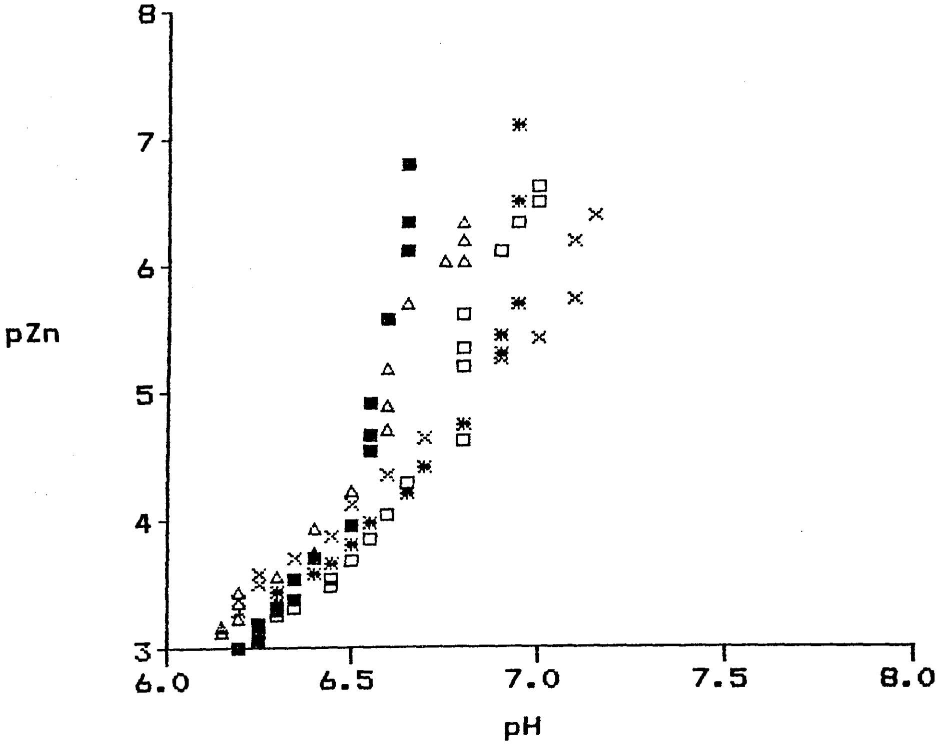


Fig. 4.19b Equilibrium pZn versus pH in chloride system for Midelney (topsoil).

Sodium (*) $pZn = -18.43 + 3.43pH$
Potassium (x) $pZn = -13.11 + 2.65pH$
Ammonium (△) $pZn = -15.41 + 2.94pH$
Magnesium (□) $pZn = -16.53 + 3.20pH$
Calcium (■) $pZn = -18.08 + 3.39pH$

4.3.4.2 Precipitation - dissolution mechanism

Figures 4.18 and 4.19 (a and b) represent the plots of negative log of Zn remaining in solution (pZn) versus pH in both sulphate and chloride salt systems for Dreghorn (Arkleston) and Midelney topsoil respectively. It has been observed that the soils behaved differently due to differences in colloidal material and pH. The plots of pZn v pH for both soils in each salt solution gave two straight lines irrespective of anion type. At low zinc concentrations (upper linear part) no release of H^+ ions was observed, and the pH remained unchanged. The lower part, at increasing solution concentration of zinc, revealed that pH of the suspension decreased due to the release of H^+ ions. It suggests that there are two mechanisms involved to remove Zn from solution, with or without releasing H^+ ions as described in Section 4.3.1.2. The slopes from the lower linear part at high zinc concentrations were calculated, and showed a greater variability in the two different soils. In Dreghorn (Arkleston) soil, the release of H^+ ions was greater compared to the Midelney topsoil due to the difference in the nature of ion present at different pH levels. However, more zinc was taken up from the solution by Midelney topsoil than by Dreghorn (Arkleston). The presence of background electrolytes may also suggest these differential effects on the release of H^+ ion in the two different soils. The release of more H^+ ions in the case of Dreghorn (Arkleston) soil may be due to the exchange of competing cation with H^+ ion. While Midelney topsoil due to its higher pH, may have high base saturation and so Zn^{2+} or the competing cation may exchange with other cations already present on the surface, hence less H^+ ions were released.

No regular pattern in slopes was observed in Dreghorn (Arkleston) soil (Figures 4.18a,b) in different background solutions as well as in different anion systems. Midelney topsoil showed coinciding lines to some extent at the lower part, for higher solution concentrations in all background electrolytes irrespective of anion form, which were gradually separated from each other at the upper part with decreasing solution concentrations. Although the adsorption maximum values calculated from the upper linear Langmuir plot varied within a soil in the presence of different background salt solutions (eg. about 3 to 5 in calcium to sodium salt), the slopes of the lower linear parts in Figure 4.19b were all about 3, and seem to be constant for different background electrolytes. It suggests the possibility of a precipitation mechanism. McBride and Blasiak (1979) observed that at pH 5.4 and 7.2 the pH - pZn slopes were essentially constant, and the solubility of zinc in this part was very similar for 20, 40 and 70 ppm levels of added Zn, suggesting that a precipitation reaction was operative.

4.4 CONCLUSION

It has been observed from the adsorption of zinc by various soils in water as background that soil texture plays a dominant role in the adsorption capability of soil. The soils high in clay content adsorbed more zinc than sandy soils due to providing more surface area for adsorption. Although a slight increase in zinc adsorption by soil was observed with the length of shaking time, this was not significant, suggesting that one week shaking time has no effect on adsorption of metal. Moreover, slightly more zinc was adsorbed in air-dried than fresh samples but no significant difference was seen. It is concluded that air-drying has no effects on zinc adsorption by soil.

Zinc adsorption by soil in the presence of different salts as background electrolytes suggested that the form of supporting electrolyte is an important factor. All soils adsorbed more zinc in the presence of monovalent compared to divalent salts. It is suggested that soil prefers divalent cations to be adsorbed, hence monovalent salts offered less competition for adsorption sites. The nature of the anion has no serious influence on zinc adsorption by soil.

It has been concluded from the data treated for precipitation-dissolution mechanism that pH plays a dominant role for controlling the zinc in solution. More H^+ ions were released for one unit zinc adsorbed from soils having pH < 6 compared to the soils pH > 7. Decrease in iron concentration in solution with increasing zinc concentration is evidence for some interaction between zinc and iron.

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