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THE SUB-SURFACE DISTRIBUTION OF SOME HEAVY METALS FOLLOWING SEWAGE SLUDGE INJECTION INTO GRASSLAND SOILS

by

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ABSTRACT

The use of suitable sewage sludge in agriculture is currently its cheapest disposal option, both in terms of monetary cost, resource utilisation and environmental impact. Monitoring of the heavy metal content of the soil after sludge application is required by European Council Directive 86/278/EEC, and whilst the behaviour of metals from surface-applied sludge is well documented, the behaviour following other methods of application has received little attention. The most important alternative land application method currently in use is the subsurface injection of sludge.

In this project, field- and laboratory-based experiments were set up to describe the post-injection distribution of Cd, Cu, Ni, Pb and Zn and the effect on this of: tine design (using the straight tine, side-inclined tine and winged tine), rate of injection (225 m^3 ha^{-1} and 300 m^3 ha^{-1}), and soil factors (pH, cation exchange capacity, organic carbon, percentage clay, Fe and Mn concentration, and redox potential). An assessment of the variability of the injection operation was also important, as account needs to be made of metal distribution and variability in order to delimit an appropriate sampling regime.

The results of these experiments indicated that Cu, Pb and Zn are basically immobile, remaining within 120 mm of the centre of the original slot location. Tine design was seen to have a significant influence on the pattern of subsurface metal distribution, but neither this, rate of injection nor soil factors adequately predicted the extent of this distribution. Instead, metal identity and concentration within the sludge were identified as the most influential factors, in that appreciable quantities of Cd and Ni are leached out of the profile to distances exceeding 300 mm from the sludge, and greater metal concentrations (of the remaining metals) in the injected sludge create distinct gradients in the soil and saturates exchange sites, thus promoting mobility via diffusion, over-riding normal metal chemistry. Of those measured variables that had a secondary effect on distribution, pH, Fe oxide concentration and percentage clay were identified as the most important soil factors.The winged tine was seen to promote soil disturbance and hence metal distribution, and the paraplow to restrict both. In practical terms, these conclusions indicate that the current sampling protocol is inadequate. An alternative regime is suggested.

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AUTHOR'S DECLARATION

At no time during the registration for the Degree of Doctor of Philosophy has the author been registered for any other University award.

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The contents of this thesis are identical to the version submitted for examination, except where amendments have been made to meet the requirements of the examiners.

signed: Rachel

date: 3.10.94.

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TERMS AND ABBREVIATIONS

AAS		Atomic Absorption Spectrometer/Spectrometry
C		clay
CEC		cation exchange capacity (expressed as meq 100 g^{-1})
DCP		Direct Current Plasma
DTPA		diethylenetriaminepentaacetic acid
EC		European Council
EDTA		ethylenediaminetetraacetic acid
Eh		redox status (in mV)
enhancement (metals)		maximum minus minimum concentrations
enrichment (metals)		amended concentration minus background concentration
EU		European Union
FYM		Farmyard Manure
ICP		Inductively Coupled Plasma
LDS		liquid digested sludge
LOI		loss on ignition
LUS		liquid undigested sludge
OC		organic carbon
OM		organic matter
p		significance level of statistical statements
PZC		point of zero charge
r		correlation coefficient
RSD		relative standard deviation - i.e. (standard deviation÷mean) x 100
S		sand
stdev / σ / SD		standard deviation
SWW		South West Water
treatments:	HP	Honey Park (Seale-Hayne Farm)
	BM	Broad Meadow (Seale-Hayne Farm)
	CR	Colaton Raleigh
	1	lower rate (225 m^3 ha^{-1}) of injection
	2	higher rate (300 m^3 ha^{-1}) of injection.

Treatments:	S	straight / simple tine
	P	paraplow / side inclined tine
	W	winged tine
WRc		Water Research Centre (Environment)
XRF		X-Ray Fluorescence
Z		silt

1 INTRODUCTION

Each year in the UK, over 30 million wet tonnes of sewage sludge require efficient disposal. This presents difficulties not only due to sheer volume involved but also as a result of the varying concentrations of heavy metals, pathogens and persistent organic compounds that the sludge may contain. The issue has recently become more pressing as the European Union (EU) progresses with its environmental protection strategies, embodied by the enforcement of mandatory European Council (EC) Directives.

The potentially toxic mixture of sewage sludge may equally well contain nutrients in sufficient quantities to render it a valuable organic fertiliser, and for this reason 40 % of the sludge produced in the UK is applied to agricultural land (Hall, 1990). With concern increasing about the odour nuisance, pathogenic availability and loss of nutrients involved in the traditional surface spreading of sludges and slurries, the technique of subsurface injection has been developed over the last two decades (Section 1.4). This process aims to efficiently exploit the beneficial characteristics of sludge whilst negating many of its deleterious aspects (Sections 1.1.1 and 1.1.2). Whatever the mode of application, the use of sludge on agricultural land is regulated by EC Directive 86/278/EEC 'on the protection of the environment, and in particular of the soil, when sewage sludge is used in agriculture', enforced in 1989 and interpreted for the UK by the statutory Sludge (Use in Agriculture) Regulations of 1989 (Section 1.2). In both documents, the use of sludge is limited by volume, heavy metal content (of soil and sludge) and soil pH, with specific sampling and analysis procedures stipulated. However, whilst Directive 86/278/EEC asserts that 'it is necessary to monitor the quality of sludges and of the soil on which they are used', the behaviour of injected metals is unknown and the nominal modifications made to the sampling regimes recommended by the non-mandatory DoE 'Code of Practice for the Agricultural Use of Sewage Sludge' (1989) may therefore be ineffective. This paucity of information forms the basis of this project (Chapter 3), which is based upon the assumptions, explained in the following Sections, that sewage sludge is a resource worth attention and that injection is a potentially significant means of its exploitation.

1.1 SLUDGE CHARACTERISTICS

1.1.1 BENEFICIAL PROPERTIES

It has been estimated that sewage sludge was potentially worth £10.9 million to agriculture in 1981 (Matthews, 1983), principally due to its content of N, P and K, representing (in millions) £4.0, £6.4 and £0.5 fertiliser equivalent respectively, and accounting for 7.3 % of the agricultural needs of the U.K. Whilst sludge may be considered a low grade fertiliser, equivalent to a 4 - 2.5 - 1 (N-P-K) commercial fertiliser (Korentajer, 1991), it is also a low cost option. Additional benefits include the content of lime (if added during treatment), organic matter (OM) and trace elements, especially Mg, Cu, Zn and B (Hall, 1986). Resultant improved soil conditions generally increase crop yields, but may actually reduce short-term yields if the sludge has a high salt content (Randall *et al.*, 1975).

A. NITROGEN CONTENT

During anaerobic digestion of sludge, approximately 40 % of organic matter is decomposed, releasing considerable quantities of plant-available NH_4^+ into solution (Hutchings, 1984). The remaining organic nitrogen is considered resistant to soil decomposition and is only slowly mineralised to ammonium. From this form, N undergoes a two-stage nitrification, firstly to nitrite and finally to nitrate. At any point in this transformation, N is subject to loss either through denitrification to N_2/N_2O, through leaching or through volatilisation (McAllister, 1976; CAST, 1976). As a result, organic-N is described as only 15 % available in the first year (Hall 1986), and considerable research has thus been conducted on the relative efficiency of organic and inorganic fertilisers. Hall (1986) considers the two forms to be comparable whilst other authors are more cautionary about the use of sewage sludge, considering it a less efficient alternative (for example, Bunting, 1963; Tunney, 1980; Coker *et al.*, 1987).

B. PHOSPHORUS AND POTASSIUM CONTENT

Despite the greater potential value of sewage sludge in terms of its combined P and K content, relatively little research has been conducted on either. Potassium tends to be overlooked as it is nearly always deficient in sewage sludge with respect to agricultural needs (Matthews, 1983), especially for root crops (DoE/MAFF, 1981), due to its loss in the early stages of treatment. Animal slurries have proportionately greater K concentrations, but this can lead to a risk of hypomagnesaemia in livestock, since excessive soil K reduces the plant uptake of Mg (MAFF, 1982). The combination of sewage sludge with animal slurries would solve both problems (DoE/MAFF, 1981; Hall, 1986) but is not a popular practice, presumably because of the increase in logistical complexity. In contrast, both the interest in P and the use of sewage sludge as a source is set to increase as P is considered to be the most expensive of agricultural nutrients (Korentajer, 1991) since its supply is limited and non-renewable (Hall, 1986). Coincidentally, the P content of sewage sludge is increasing as the amount discharged in treated water becomes more strictly controlled (Korentajer, 1991).

C. ORGANIC MATTER CONTENT

Digested sludge is 50-60 % organic matter (on a dry matter basis), and whilst this is considerably less than that provided by either raw sludge or farmyard manure (FYM), its humification during treatment renders it more stable (Hall, 1986), decomposing by a maximum of 20 % in 6 months (Miller, 1974). Improving the organic status of the soil potentially increases the water holding capacity of loam, silt (Hamblin and Davies, 1977; Epstein *et al.*, 1976) and sandy soils for up to five years (Spotswood and Raymer, 1973), thus reducing the water stress on plants. Bulk density may be reduced, with an associated increase in porosity (Pagliai *et al.*, 1983) and hydraulic conductivity (Guidi and Hall, 1984), and aggregate stability may also be improved (Evans, 1969). The addition of sludge OM has been observed to reduce erosion and runoff (Korentajer, 1991), but it is likely that this is mainly relevant to surface applications. Along with these physical effects, the addition of organic matter initiates chemical changes such as an improvement in cation exchange capacity (CEC) (Epstein *et al.*, 1976). Sludge as a simultaneous source of nutrients and OM is especially desirable as a control on the reduction of OM caused by, for example, the excessive use of mineral fertilisers (Korentajer, 1991), especially where crop residues are removed.

D. OTHER CHEMICAL EFFECTS

In addition to the fertiliser and organic value of sewage sludge to soil and the attendant effects on CEC, other chemical changes may be instigated, principally to its pH. This usually takes the form of a reduction in pH, regardless of the soil's original acidity (e.g., Epstein *et al.*, 1976; Fresquez *et al.*, 1990; Williams *et al.*, 1987), although experiments have been conducted where no change was observed (Kornegay *et al.*, 1976). The magnitude of change appears to be largely independent of rate of application and is more likely to be related to the characteristics of the sludge used. It has been proposed that the microbial production of CO_2 (Kirkham, 1974), the formation of acids during OM oxidisation (Robertson, *et al.*, 1982) and nitrification reactions (Vlamis *et al.*, 1978) may be important factors in lowering the pH of sludge-amended soil. Conversely, where the Ca content of sludge is relatively high, addition to soil may promote an increase in pH (Guidi and Hall, 1984).

1.1.2 NEGATIVE PROPERTIES

Whilst sewage sludge can be seen from the above Section to be far from merely a waste product, it also has distinct disadvantages associated with its use, not only with reference to the soil environment but also to surface and groundwater bodies receiving runoff and throughflow from these sites. The most environmentally significant drawbacks are the pathogens, toxic metals and organic compounds that are introduced. Other factors include aesthetic problems, and soil Eh and electrical conductivity changes.

A. TOXIC METALS

Since industries such as electroplating and battery manufacture discharge into the sewerage system, it is inevitable that sewage sludge can contain appreciable quantities of heavy metals (Table 2.2). The most toxic of these are generally considered to be Cd and Pb, but Cu and Zn in excess along with Ni and Cr are also problematic. Metal content is currently the only sludge factor that limits its use (Table 2.1). The extent of the problem of heavy metals is considered further in Sections 2.1 and 2.2.

B. TOXIC ORGANIC COMPOUNDS

The most ubiquitous organic compounds present in sewage sludge are persistent organochlorine pesticides (OCPs), especially gamma-HCH (lindane), dieldrin and DDT; polychlorinated biphenyls (PCBs); triazine herbicides and the less persistent organophosphate insecticides (OPs) used extensively in sheep dip. The characteristics for which these pesticides were originally selected, that is, a broad spectrum of activity and long persistence times (White, 1987), also render them as serious pollutants. As a result, many OCPs (e.g. DDT and dieldrin) are now voluntarily banned in the UK. However, new inputs are still made into the sewerage system via, for example, tanneries that obtain their hides from Third World countries where the use of these pesticides is still legal. Other ubiquitous organic products that enter the sewerage system include PCBs from their use in electrical transformers and as capacitors, and polycyclic aromatic hydrocarbons (PAHs) as a by-product of fuel consumption (Alloway, 1992).

The precise 'eco-toxicity' of organic pesticides has not been established and national attitudes vary from the banning of the application of sewage sludge on grazing land in Germany to the conclusion that soil biota, plants and animals are not threatened by organics in sewage sludge in the US (Korentajer, 1991). In the UK, no formal provision is made for either the testing for organic pesticides in sludge or the restriction of its use according to this criteria.

C. PATHOGENS

The pathogen content of sewage sludge largely originates from hospitals, tanneries, meat processing factories and abattoirs (Hall, 1986) and includes Beef Tapeworm (*Taenia saginata*), *Salmonella* sp., *Campylobacter* and *Yersinia* sp. (about which relatively little is known), and plant diseases such as the potato cyst nematode (Bruce *et al.*, 1990). Whilst a significant association has been found between the use of sludge and the incidence of bovine cysticercosis (Bruce *et al.*, 1990), Matthews (1983) argues that the appropriate host is infected via sewage sludge only rarely, and human health has only been compromised in instances where outdated operational practices have been used.

Pathogens are passed up the food chain due to sludge adherence to crops and the direct ingestion of sludge by grazing animals (Korentajer, 1990). Whilst the Sludge (Use in Agriculture) Regulations (1989) and the Code of Practice (1989) do not specify acceptable pathogen levels, the spreading of untreated sludge has been banned by the EC Directive 86/278/EEC, and methods of treatment that are sufficient to reduce pathogen risk have been stipulated (Table 1.2). In addition, a 'no grazing' period of 3 weeks has been enforced and limitations imposed on applications before crop harvest. However, Barbier *et al.* (1990) claim that this time span is insufficient to 'stop all hazards of parasitic disease for cattle or humans'.

D. AESTHETIC PROBLEMS

The main aesthetic problems concerning the agricultural use of sewage sludge relate to odour, sight and tanker routing (Hall *et al.*, 1986; Matthews, 1983). Treatment of sludge, especially composting reduces its odour, and consideration of factors such as wind direction and proximity to residential areas have been suggested in the avoidance of such objections (Matthews, 1983). The subsurface injection of sewage sludge significantly reduces both visual and odour pollution, and is discussed in detail in Section 1.4.

E. ADVERSE EFFECTS ON SOIL CONDITIONS

In Section 1.1.1, the beneficial effects of sludge on soil properties was discussed, but obviously these effects in extreme - such as nitrate or metal pollution, or the poor planning of receiving sites resulting in, for example, the reduction in pH of an already acidic soil - may be deleterious. Additional soil changes that are likely to be negative even in moderation include effects on redox potential (Eh) and electrical conductivity.

Finally, the agricultural use of sewage sludge may incur soil structural damage if not carried out under suitable conditions. Problems such as compaction and wheelslip can be avoided, however, by the use of rain guns (DoE/NWC 1981) or umbilical systems (Hall *et al.*, 1986).

1.2 LEGISLATION

In Section 1.1, reference was made to EC and UK legislation that controls the use of sewage sludge in agriculture. In this country, the immediate precedent to this was the DoE/NWC Guidelines for Sludge Disposal of 1981, which aimed to minimise the effect of the negative characteristics of sludge mentioned above. These Guidelines were directly supplanted by the DoE Code of Practice (1989), which facilitates the implementation of The Sludge (Use in Agriculture) Regulations of 1989. These Regulations in turn represent the UK interpretation of the EC Council Directive of 1986 (86/278/EEC) 'on the protection of the environment, and in particular of the soil, when sewage sludge is used in agriculture'. The Directive was implemented by 1989. The key issues are:

1. the definition of treatment of the sludge via biological, chemical or thermal methods, or long-term storage (Table 1.2; Section 1.3);
2. the prevention of the use of untreated sludge in agriculture, unless it is injected or worked into the soil;
3. the volume of sludge that can be applied is limited by the heavy metal content of the receiving soil and the sludge (Table 2.1);
4. the restriction of receiving sites depending upon their landuse;
5. plant requirements and pH must be considered to reduce the risk of pollution.

Each Member State has some leeway in the enforcing of this Directive, which in the UK represents the removal of non-dedicated land from use if it a) has a pH below 5.0, b) is being used for vegetable or fruit crops, or c) whose soil exceeds the stipulated metal concentrations (Table 1.1). Dedicated sites are used on a sacrificial basis - they are formally defined and can not support crops that are to be offered for sale or for human consumption, and must already have been defined as such by 17th June, 1986, when Directive 86/278/EEC was first published. Sampling and analysis of both sludge and soil for pH, Zn, Cu, Ni, Cd, Pb and Hg has been given strict parameters, and limits provided (Table 1.1). Soil samples are to be taken before sludge application and at least every twentieth year thereafter. For statutory samples, the Sludge Use Regulations (1989) stipulates the preparation of a sample by bulking together 25 separate core samples (per 5 ha) taken to depths of 25 cm, or to the depth of the soil if less. For operational purposes, the Code of Practice (1989) recommends that monitoring samples are to be taken to a depth of 15 cm (arable) or 7.5 cm (grassland). Sludge application by injection is the only exception to this, in which case it is suggested that samples are to be taken 'to the depth of injection', although no reference is made to this deviation in the statutory Regulations (1989) or EC Directive 86/278/EEC. In addition to these quantifiable parameters, the Code of Practice also deals with 'environmental protection', suggesting transport (containing of sludge, size of vehicle, planning of routes), field access (reducing traffic hazards and mud or sludge on public highways), odour control (sludge treatment; injection/incorporation) and minimisation of runoff and water pollution (considering slope, rate, weather) options to attenuate the potentially deleterious factors mentioned in Section 1.1.2.

1.3 TREATMENT AND DISPOSAL OPTIONS

The most basic, raw sludge is obtained from primary settlement tanks, and, besides screening and grit removal, is untreated. As a result, raw sludge disposal is relatively economical, with outlets including agriculture (about 7 % of agricultural sludge is untreated - Hall *et al.*, 1986) and sea disposal (Hall, 1990). However, EC Directive (86/278/EEC) prohibits the agricultural use of untreated sludge unless it is 'injected or worked into the soil', and dumping at sea is set to cease by 1998. Treatment, as defined by the DoE Code of Practice (1989), ranges from storage of untreated sludge for at least 3 months to sludge pasteurisation (Table 1.2) and is largely conducted to 'significantly reduce its fermentability and the health hazards resulting from its use' (DoE Code of Practice, 1989). This has been interpreted as referring to the minimisation of odour and pathogen concentration (Bruce *et al.*, 1990), usually via oxidation and flocculation of OM by micro-organisms (Eden, 1983). In the UK, most sewage treatment works will already comply with the Directive, since most possess facilities for anaerobic digestion and/or dewatering and/or storage (Bruce *et al.*, 1990).

Powlesland (1991) has stated that the cost of disposal accounts for half of the sewage budget - Hill (1991) suggests a total cost of £100 M each year. Bruce *et al.* (1990) conclude that, in general, the greater the degree of treatment, the greater the cost. Present trends are therefore towards reducing the production of sludge, using processes such as wet oxidation and 'LOSLUJ' (Powlesland, 1991). The former has the extreme disadvantage of being very expensive, whilst the latter is a technique still under investigation that produces approximately 40 % fewer solids at 20 % lower costs than conventional treatment (Hall, 1990), but is not expected to have a significant national impact in the near future.

In 1990, 40 % of the sewage sludge produced in the UK was used in agriculture, approximately 34 % to sea, 16 % to landfill, 5 % incinerated and 5 % to other uses (Hall, 1990), such as land reclamation, forestry and composting. Locally, proportions will vary - for example, in the South West in 1988, only 30 % of digested sludge was disposed of on land, with 70 % dumped at sea (SWW, 1988). By 1991, the proportion allocated to offshore disposal had reduced to 60 % (SWW, pers. comm.), and will cease nationally by 1998. For this reason, marine disposal is not considered further in this Section.

1.3.1 AGRICULTURE

Soil has been described as 'a filter, a barrier and a medium for the biotransformation of wastes' (Boyle, 1990), and disposal on land is also relatively simple and cheap (Spotswood and Raymer, 1973). Consequently, agriculture is the single biggest outlet for sludge disposal in the UK, although it is less significant in Europe as a whole, where agriculture accounts for 30 % of sludge disposal (Williams and Hall, 1985). However, its importance is unlikely to increase to compensate for the banning of oceanic dumping, largely due to the constraints identified by Powlesland (1991), such as the limiting of availability of suitable sites by physical features (topography, weather, soil type etc.), environmental considerations (proximity to residential areas or surface/ground water bodies), sludge quality (Section 1.1), farmer acceptability, and future changes in, for example, legislation. Particular problems with the spreading of sludge relate to odour, runoff and disease problems, but these can be minimised or negated by injecting the sludge below the soil surface. This latter approach is discussed in more detail in Section 1.4.

A comparison of agricultural disposal options carried out by Critchley *et al.* (1982) quantified the relative unit costs of applying sludge per cubic metre as: movable rain gun - £0.23; spreading - £0.67-£0.92; subsoil injection - £0.82-£1.35; and spreading cake sludge - £1.60 (where prices vary, tanker size is the determining factor).

1.3.2 LANDFILL

It is envisaged that, at least in the short-term, the surplus of sludge left by the banning of sea dumping will be dealt with in landfill (Hall, 1986). This projection is supported by European examples, where approximately 40 % of sludge goes to landfill sites (Beker and van den Berg, 1991). Sludge improves the quality of landfill leachate (Beker and van den Berg, 1991), and the nutrients contained in sludge may aid the composting of solid waste (Pearson, 1989). The decomposition of sewage sludge also increases methane production (Blakey, 1991) which may be recovered as an energy source (Hall, 1990).

However, disposal in landfill is also very expensive. Sludge must be dewatered to enable its handling as a solid (Eden, 1983), and the paucity of available sites, and the difficulty in creating new ones, inevitably creates high transportation costs (Sterritt and Lester, 1980). The disposal of noxious industrial waste that is unsuitable for agricultural use may contaminate groundwater bodies, especially with persistent organics. The production of greenhouse gases, whilst beneficial if the means exists for their recovery and recycling, can cause at least crop damage and at worst explosions (Lawrie, 1990).

1.3.3 INCINERATION

Whilst incineration accounts for 5 % of UK sludge (Hall, 1990), many other countries employ this method more widely. The European average, for example, is 9 %, whereas in the USA 27 % and in Japan 44 % of sewage sludge is burned (Lowe and Frost, 1990). Incineration in the UK is especially significant in disposing of contaminated industrial effluents (Lowe and Boutwood, 1991) since it destroys carcinogens, many pathological contaminants, biologically active material and some organic compounds (Niessen, 1978), and has additional advantages in volume reduction and energy recovery (Niessen, 1978). Only 6 currently operational plants exist in the UK (Hall, 1990). Despite this, it is likely that this disposal option will, in the long term, account for a significant proportion of that sludge currently dumped at sea (Hall, 1986).

Incineration is a complex and expensive operation, although recent developments such as the use of the calorific value of sludge to provide its own fuel (Lowe and Boutwood, 1991) and the use of ash in concretes (Lowe and Frost, 1990) aim to reduce these drawbacks. Target operating costs for new plants is estimated at £40 - £50 per dry tonne (Lowe and Frost, 1990), a figure considerably higher than for use in agriculture.

As with all disposal options, incineration has disadvantages in addition to cost. To comply with the 1984 EC Directive ‘controlling air pollution from industrial plants’, organic pollutants such as dioxins and furans must be removed from emissions (Lowe and Frost, 1990). These are synthesised at high temperatures when, for example, PVC is incinerated with refuse (Alloway, 1992), but temperatures need to exceed 1200 ^{o}C to destroy stable organic compounds such as PCBs (Alloway, 1992). Other deleterious emissions include metal particles (Alloway and Jackson, 1991), SO_2, CO, N_2O, carcinogenic hydrocarbons, HCl and flyash (Niessen, 1978).

1.4 THE INJECTION PROCESS

Injection, or the direct subsurface application of sludge, was developed in the USA (Reed, 1973) and has been commercially available there since 1976. By 1983, its use was extensive if localised, accounting for 100 % of that sludge produced in some areas (Kirkham, 1983). In the Netherlands, research on slurry injection has been conducted since 1972 (Meer *et al.*, 1987). In the UK, Anglian and Wessex Water were the first to seriously consider injection (Hall *et al.*, 1986), although differing working conditions and priorities limited the use of injection until EC Directive 86/278/EEC precluded any other means of utilising untreated sludge on agricultural land, and the House of Lords Select Committee (1983) recommended injection as the best method of sludge application in the light of its potentially offensive nature.

Whilst injection may represent a solution for official bodies such as Water Companies and the Department of the Environment, it must be demonstrated to the end users - mostly farmers - that injection is logical and beneficial, or the technique will be poorly used. Both advantages (Section 1.4.1) and disadvantages (Section 1.4.2) are therefore often presented from a utilitarian aspect. Whilst environmental impacts have been anticipated, there has apparently been little empirical investigation, especially into the behaviour of heavy metals (Chapter 2), which are the only components of sewage sludge that require monitoring (Section 1.2).

In this Section, the accepted benefits and constraints of injection that justify its use are presented. The conditions and means of operation are also defined to introduce injection and the facets of the process that potentially affect metal behaviour, and complicate its definition.

1.4.1 ADVANTAGES

A. CONTAMINATION MANAGEMENT

In Sections 1.1.2 and 1.2, the heavy metal content of sewage sludge was shown to be the limiting factor of its agricultural use. Whilst injection obviously will not reduce sludge metal content, it has been shown that this technique can reduce the metal content of crops (Kirkham, 1983) and is expected to dilute the metals present by mixture with the soil (Hall, 1985). The burial of slurry is especially beneficial when sheep, which are susceptible to Cu toxicity (MAFF, 1982), are grazing on grassland treated with pig slurry, which is particularly high in Cu. However, some reservations have been expressed with regards to the behaviour of metals within the soil, and these are discussed in Section 2.3.1.

In Section 1.1.2, the principal pathogenic contaminants in sewage sludge were identified as *Salmonella* and the beef tapeworm, which are passed up the foodchain via adherence to crops and/or the direct ingestion of contaminated soil or sludge (Korentajer, 1990). The burial of sludge forms a protective barrier between animals and sludge, and introduces pathogens to an environment in which their numbers rapidly decline (Andrews *et al.*, 1983). Injection thus has the potential to obviate the need for any safety margin between sludge application and a return to normal use, although this would rely on optimum injection performance, a status that would be extremely difficult to monitor.

In addition to rendering pathogens inaccessible to livestock, the injection of sludge can also reduce sludge damage to grassland, which occurs, for example by smothering or scorching (Prins and Snijders, 1987). For example, Pain and Broom (1978) found that cattle grazing on surface spread grassland consumed 30 % less herbage (DM) than those on injected sites, even after a 7 week no-grazing period.

B. ODOUR CONTROL

As rural areas become increasingly populated with 'non-farmers', odour has become an unacceptable facet of sludge and slurry disposal (Noren, 1985). Whilst this may currently have legal implications in terms of private prosecutions, it is anticipated that a draft directive on odour control will be released by the EC in 1996 (Toogood, 1990), and a Code of Good Practice for the Protection of Air was published by MAFF in 1992. Chemical means of reducing or masking odours are available, but are expensive and doubts about their effectiveness have been expressed (McAllister, 1976). The contribution of injection to the reduction of perceived odour is twofold. Firstly, Noren (1985) found that injecting pig slurry reduced its odour to only 1.3 % of that following spreading, compared to 17 % after ploughing in. This opens up more areas for disposal, leading to potential transport savings and the easing of pressure on existing sites (Hall *et al.*, 1986). Secondly, odour and sight have been found to be psychologically connected (Matthews, 1983), and both during and after a properly managed injection operation (Section 2.4), sludge is concealed.

C. NUTRIENT MANAGEMENT

The supply of nutrients is the main feature of sewage sludge that renders it farmer-acceptable and allows a high proportion to be disposed of on agricultural land. However, a significant amount of N can be lost in the volatilisation of NH_3 after spreading, depending upon the season (Klausner and Guest, 1981) and the source of slurry or sludge. In contrast, the delivery of sludge 200 - 500 mm below the surface promotes nutrient conservation through reduced volatilisation (Marriott and Bartlett, 1975) both via burial and increased water content. In the latter case, injection in an aqueous medium has been found to cause clay deflocculation, thereby increasing the water content over and above the amount injected and slowing down the rate of diffusion of ammonia through the soil (Gasser and Ross, 1975; Germon *et al.*, 1979). This reduction in volatilisation has been quantified by Phillips *et al.* (1988) as 95 % for pig slurry, and Thompson *et al.* (1987) state that whilst 20 % of N is lost after spreading, this is reduced to less than 1 % by injecting cattle slurry. Meer *et al.* (1987) reported greater N concentrations in herbage and greater DM yields following injection rather than spreading. Burial of sludge can be assumed to reduce runoff and volatilisation and deliver nutrients more directly to roots.

D. OTHERS

Injection uses hollow tines to deliver the sludge or slurry (Section 1.4.3) so that voids are created to accommodate it, and this soil loosening is beneficial in its own right. Loosening improves water flow and aeration in the soil and can lead to the better development of roots (Warner and Godwin, 1988), and is especially advantageous in breaking up compaction in long-term permanent pastures (Hall *et al.*, 1986). Meer *et al.* (1987) found that dry runs of injection slightly increased crop DM yield and N uptake by promoting the mineralisation of soil organic-N.

When sludges or slurries are surface spread, the increase of both nutrients and OM in runoff has been observed by many authors (e.g. Hewgill and LeGrice, 1976). This is especially evident at application rates in excess of plant requirements or when the soil is wet, and results in the contamination of surface water and problems such as eutrophication and increased suspended solids (SS) and biological oxygen demand (Richardson, 1976). In contrast, Ross *et al.* (1979) observed that the injection (at 153 and 305 mm depth) of slurry ‘essentially eliminates pollution in the runoff’, reducing chemical oxygen demand, N and

SS to levels approaching background concentrations. Similar claims about injection have been made by Warner and Godwin (1988) and Bartlett and Marriott (1971).

Finally, the application of sludge to land has an irrigating potential. Whilst this water would be subject to evaporation if it were surface applied, injection has been shown to increase the soil water content in excess of the amount injected (Gasser and Ross, 1975). After injection operations have ceased, increased water contents have been observed below the depth of injection for at least one month (Stone *et al.*, 1983).

1.4.2 DISADVANTAGES

In a comparison of surface spreading and subsurface injection, there are also many circumstances in which the former has the advantage. The drawbacks of injection include increased operational complexity and associated cost, sward damage and uneven crop response. When the operation is not performed correctly, many of the advantages cited in Section 1.4.1 are nulled, and may even become deleterious.

A. HEAVY METAL CONTAMINATION

The unknown nature of metal behaviour following sludge injection has already been mentioned, and this in itself constitutes a drawback in the technique. Variability is potentially greater than following the surface spreading of sludge, and compliance with EC Directives thus becomes problematic or insufficient. There is also some concern that injection when the soil is excessively dry, or frozen, may create deep fissuring that promotes leaching to drains and groundwater (Hall *et al.*, 1986), although Smith *et al.* (1984) found that the effect on groundwater and deep (1.2 m) percolate was largely negligible. The paucity of knowledge in these three areas forms the basis of this project (Chapter 3).

B. OPERATIONAL COMPLEXITY

It is essential that Water Companies are able to present their product in a favourable light to farmers if they are to use agricultural land as a means of disposal of sewage sludge. To this end, sludge is usually supplied *gratis*, and can be surface spread by the farmer, who will usually own the appropriate equipment already. In contrast, injection equipment is far more specialised and the process is usually conducted by contractors (Hall *et al.*, 1986). Klausner and Guest (1981) found the procedure so complex that they described it as 'tedious'.

In addition, injection may be more complex in terms of appropriate soil and site conditions. Especially on heavier soils, injection during wet soil conditions creates smearing, whilst during dry regimes excessive heave may occur (Hall *et al.*, 1986). The same authors have reservations about the viability of injection on stony soils, which may damage both the injection tines and the surface conditions of grassland soils. The necessary use of heavier equipment than would be used for spreading has implications for the compaction of some soils (Peaty and Kernebone, 1988). For the same reason, and due to the tandem of tractor-tanker-tines, injection downhill has been recommended for stability and to minimise draft requirements (Hall *et al.*, 1986), but the same authors also advocate injection parallel to contours on sloping ground or with less viscous sludge.

C. SURFACE FINISH

A poor surface finish only arises from the inappropriate use of injection, and is only relevant to grassland soils. Conducted poorly, injection can cause wheelslip and rutting, shatter the surface and cause seepage of sludge onto the sward. The traction of tines through the soil necessitates greater draft requirements than are required by spreading operations. If insufficient power is supplied for the operation and/or the sward is wet, wheelslip is likely (Hall *et al.*, 1986). In addition, the wheelruts caused by the weight of injection systems in wet soil conditions has been estimated to reduce grass yield by up to 30 % (Godwin *et al.*, 1990). However, Peaty and Kernebone (1988) defined acceptable wheelslip as 10 % on a firm (not tilled) soil, and measured only 0.9-1.1 % wheelslip after injection under appropriate conditions.

When the soil is dry (moisture deficits > 40 mm), the ground surface can be shattered by the passage of the tines (Warner and Godwin, 1988). Peaty and Kernebone (1988) describe this as 'laterally bending up 100 mm thick slabs of pasture sod'. A similar effect was observed by Graff-Baker (1989), but attributed to moist soil and excessive loosening causing adhesion to the tine.

The seepage of sludge onto the surface is obviously undesirable as it negates many of the benefits of injection. This can arise in a number of ways, the easiest to remedy being the continued pumping of sludge whilst the tines are still above the surface. Warner and Godwin

(1988) found that seepage was likely at gradients greater than 5 degrees and with sludges of less than 6 % DM, and that raw sludge, which is less viscous than digested sludge even at higher DM contents, would be more likely to seep to the surface. Seepage may also result from the formation of insufficient soil voids by the tine to accommodate the sludge (Negi *et al.*, 1978). This is affected by rate of injection and depth (Negi *et al.*, 1978), where depth must be sufficient to provide adequate cover, but not so deep as to cause smearing.

D. CROP RESPONSE AND NUTRIENT MANAGEMENT

Problems that may be associated with crop response and nutrient management following injection include grass dieback, uneven response and a reduction in N efficiency. Uneven crop response can arise in two ways. Firstly, Peaty and Kernebone (1988) calculated a potential reduction in delivery rate of 20 % over a run (measurement not specified) due to a decrease in air pressure and static head, and described an increase in depth of operation as the tanker became lighter. Secondly, the concentration of sludge or slurry in discrete lines along the injector path has been found to cause variations in crop growth, depending upon factors such as soil type and moisture content, and tine design and operating conditions (Warner and Godwin, 1988). The same authors have described crop death above the loosened zone due to excessive surface disturbance when injection is performed on dry soils. This 'die-back' is also caused by the severing of roots when injection depth is insufficient, or the incomplete closure of the injection slot (Warner *et al.*, 1991).

Crop response is also affected by the nutrient status of injected soils. Prins and Snijders (1987) described a gradual decrease in the N and P concentration of herbage with distance from the injector tines, suggesting that this could be remedied by decreasing tine spacing to 300 mm (from 500 mm), but admitting that this would then increase the chances of 'rolling up' the sward, as described earlier in this Section. Hall *et al.* (1986) found a 15 % smaller increase in crop yield following injection rather than surface spreading. Thompson *et al.* (1987) state that denitrification can cause significant losses of N from injected plots, especially if the soil is wet. Comfort *et al.* (1988) similarly considered that injection can lead to reduced availability of N. Meer *et al.* (1987) explained the reduced efficiency of N use following spring injections by the limited reach and activity of roots, and slower recuperation of damaged roots. Section 1.1.1, described the loss of N, P and K from the soil profile through leaching, and there is some concern that this will be exacerbated when injection has been utilised. Smith *et al.* (1984) measured an increase in the nitrate content of deep percolating (1.2 m) water from injected sites (at unspecified depths), whether sludge had been used or not. Bartlett and Mariott (1971) identified elevated concentrations of N and K in soil water at depths of 4 ft (sic) following injection at rates exceeding 15 t acre^{-1} pa (sic). In contrast, the work of Sterritt and Lester (1980) suggests that leaching would not be significant, since they claim that the soil can contain appreciable quantities of P, and that runoff to surface water would therefore be a far greater problem than leaching to groundwater. Similarly, Thompson *et al.* (1987) found that the loss of total N due to leaching was negligible, and Smith *et al.* (1975) found that the presence of a crop will negate any leaching enhancement caused by injection.

D. OTHERS

The soil loosening effect of the tines described in Section 1.4.1 may not be considered advantageous in every case. For example, Twomlow *et al.* (1991) have described a reduction in drainage efficiency following the loosening of a silty clay loam, resulting in higher water contents and a reduction in the load bearing capability of the soil. Spoor (1985) confirms the latter finding and further states that excessively loosened soils are susceptible to poor germination and structural damage due to field traffic. Even with its loosening capability, the weight of fully laden tractor-tanker-tine tandems has been observed to create soil compaction, quantified as a reduction in grass yield by up to 0.7 t ha^{-1} (Godwin *et al.*, 1990).

1.4.3 EQUIPMENT

At its most basic, the injection assembly comprises, in tandem: a means of traction, a supply of sludge or slurry, and a set of tines. There are three types of injector system currently available: field tankers, tractor-drawn tankers and umbilical systems. Self-propelled field tankers are relatively expensive (£50 000-80 000), but have high capacities (typically 9000 l) and high work rates (450 000 l per day) (Hall *et al.*, 1986). On the other hand, tractor drawn tankers are cheaper (£10 000-20 000) and more flexible, since they can be used for other operations such as spreading (Hall *et al.*, 1986), although they require tractors with power capacities in excess of 80 kW (Godwin *et al.*, 1990). Finally, umbilical systems are both cheap and efficient (Hall *et al.*, 1986), and have draft requirements up to 50 % less than mobile tankers, reducing fuel requirements by about 20 % (Godwin *et al.*, 1990). Since tanker weight is kept off the working area, windows for operation are larger, with less than half the number of working days lost if an umbilical system is used in preference to a mobile tanker (Godwin *et al.*, 1990).

The design criteria of the tines stipulates the ability to 'cut, disturb and redeposit a sufficient volume of soil to contain and cover the [sludge] with a stable soil layer' (McKyes *et al.*, 1977). There are three basic tines that can be used to this end, the choice of which is independent of the injector system used. These are illustrated in Figure 4.1 (in which specifications pertain to this project and are not generalisations) as the simple ('straight' or 'narrow') tine, winged tine, and side-inclined tine (or paraplow) (WRc, 1986). The simple tine creates relatively little subsurface disturbance (Figure 4.2), and therefore needs to be operated at depths of 250-350 mm to achieve complete soil cover (Hall *et al.*, 1986). The addition of wings provides greater disturbance (Spoor and Godwin, 1978) and therefore a wider distribution of sludge (Warner and Godwin, 1988), but requires a greater draft force and is therefore operated at 150-200 mm. By inclining what is essentially a simple tine, greater subsurface disturbance is again facilitated, but without the increased draft requirement of the winged tine (Godwin and Spoor, 1977b). Working depths are thus on a par with the simple tine, facilitating loosening to a greater depth than can reasonably be achieved with winged tines (Hall *et al.*, 1986). Tines are set in groups of 2-5 and 0.5-1.0 m apart (Hall *et al.*, 1986). Rate of sludge or slurry delivery through the tines is generally controlled by ground speed, since varying tank pressure has been found to be ineffective (Peaty and Kernebone, 1988). The maximum attainable rate of injection is approximately 300 m^3 ha^{-1} (Hall *et al.*, 1986), although working rates tend to be far less than this, dictated by surface finish, sludge viscosity and field slope.

The depth at which tines work is largely dictated by their draft requirement and the rate of injection. For example, Warner and Godwin (1988) injected 140 m^3 ha^{-1} of sludge through simple and winged tines to assess the depth at which successful injection could be attained, and found that 130 mm was sufficient for the winged tine, whilst the simple tine needed depths of 250 mm, and greater power requirements. However, depth of injection must also be less than the critical depth, described by the WRc (1984) as the depth at which the effect of the tine changes from loosening to compaction.

Since the first injection trials in the early 1970s, a number of refinements have been added that are now in general practice, especially when injecting sludge into grassland soils. For example, disc coulters placed immediately in front of each tine are used to cut the sward to prevent tearing by the tine. Surface heave is minimised by inclining the tines backwards to 105 ° (although this may also increase draft requirements) (Warner and Godwin, 1988), and grass die-back can be reduced by the use of presswheels immediately (> 880 mm) behind the tines (Warner *et al.*, 1991) and/or the subsequent rolling of the sward (Haan *et al.*, 1987). Draft requirements can be reduced by vibration induced by a positively driven crank or a rotating eccentric mass (Warner and Godwin, 1988), although the same authors have reservations about the efficiency of such systems across a range of soil moisture contents. More recent developments have attempted to improve the efficiency of the presswheel (by applying sufficient force) and to further reduce surface heave by adapting the leading tine tip (Warner *et al.*, 1991). In Japan, tine modifications to reduce the draft force requirement by pumping sludge from the tip rather than the rear have been conducted for some time (e.g. Araya, 1985), but this approach has apparently not been emulated by other countries.

A. IDEAL CONDITIONS

Much of the work assessing the optimum conditions for subsurface injection in the UK has been conducted by the WRc (e.g. Hall *et al.*, 1986) and Silsoe College (e.g. Warner and Godwin, 1988) with the aim of limiting the potential disadvantages of injection cited in Section 1.4.2.

In order to reduce problems associated with soil water content, it is recommended that structured soils are injected whilst they are moist friable or plastic, whereas non-structured soils can also be worked in friable conditions, with water contents as low as 8 % (Warner and Godwin, 1988). Optimum tine spacings (to minimise draft requirements and the 'striping' of crop growth) are not as easily defined as this depends upon the tine geometry. The WRc (1984) suggests that the overlap of soil disturbance should be avoided, stipulating 1.5 times the working depth for simple tines, and 300 mm to 450 mm between wing tips (depending upon soil type - a heavier soil in spring requires closer tines) for the winged tine. Warner and Godwin (1988) suggest a spacing of 650 mm for winged tines, a similar measurement to that specified above if the latter authors measured between uprights. Unequivocal agreement is reached with regard to sloping soils, which should be injected at reduced rates, and with sludges of at least 6 % DM. Rates of injection under 'normal' conditions of no more than 140 m^3ha^{-1} are considered satisfactory (Hall *et al.*, 1986). In order to reduce compaction and wheelslip, which is especially problematic when the sludge tanker is mobile, specific tyre design, size and inflation pressures are suggested (Hall *et al.*, 1986) to maintain soil:tyre contact pressures of less than 100 kPa (Soane *et al.*, 1981).

1.4.4 INJECTION VARIABILITY

From the previous Section, it can be seen that one of the principal variables in the injection operation is the effect of tine geometry on both the horizontal and vertical distribution of the injected sludge and the effect that soil type can have on the performance of the tine.

In controlling the rate at which sludge is injected, all contemporary procedures are fraught with problems such as variable viscosity and blockages, and calibration relies on the measurement of engine revolutions and the time taken to fill a known volume. This, whilst simple in theory may be difficult to maintain under field conditions. Thus, the recommended method of monitoring the rate of injection is the comparison of the mass of sludge injected with the area covered (M.J. Haan, pers. comm., 1988), but it is extremely difficult to attain the desired rate of injection, and to maintain this or any rate over time. Other researchers of this subject have found that rate may vary by a potential 20 % due to a reduction in tank pressure as it empties (Peaty and Kernebone, 1988) to 50 % (M.J. Haan, 1988, pers. comm.), influenced by variables such as viscosity, blockages, speed, slope and soil strength. Further complications are introduced by the disparity between an erratic 'window' of ideal injecting conditions and the constant need to dispose of sludge.

The depth at which sludge is injected may be significant if considerable quantities of heavy metals are lost through leaching. Whilst depth is largely dictated by the compromise between tine design and soil conditions, difficulties in control have been noted by Peaty and Kernebone (1988) as the result of the reduced mass of the tanker as it emptied. In addition, Meer *et al.* (1987) have observed a disparity between the depth of injection tines (50 cm) and depth of slurry placement (15-20 cm).

Thus it can be assumed that the variability of injection performance will be significant in any study of the consequences of injection. It is desirable that a measurement of this should therefore form part of the objectives of this project, which are presented in Chapter 3.

TABLE 1.1 SOIL METAL CONCENTRATION LIMITS (mg kg^{-1}) STIPULATED BY THE SLUDGE (USE IN AGRICULTURE) REGULATIONS, 1989

element	limit according to soil pH			
	5.0 < 5.5	5.5 < 6.0	6.0 - 7.0	>7.0
Zinc	200	250	300	450
Copper	80	100	135	200
Nickel	50	60	75	110
	for pH 5.0 and above:			
Lead	300			
Cadmium	3			
Mercury	1			

TABLE 1.2 EFFECTIVE SLUDGE TREATMENT PROCESSES AS DEFINED BY THE CODE OF PRACTICE FOR THE AGRICULTURAL USE OF SEWAGE SLUDGE (1989)

PROCESS	DESCRIPTION
sludge pasteurisation	≥ 30 minutes at 70 °C or ≥ 4 hrs at 55 °C, followed in all cases by primary mesophilic anaerobic digestion.
mesophilic anaerobic digestion	mean retention period of ≥ 12 days primary digestion at 35 °C ± 3 °C or of ≥ 20 days primary digestion at 25 °C ± 3 °C followed in each case by a secondary stage of a mean retention period of ≥ 14 days.
thermophilic aerobic digestion	mean retention period of ≥ 7 days digestion, and at 55 °C for ≥ 4 hrs.
composting	compost maintained at 40 °C for ≥ 5 days and at 55 °C for 4 hrs during this period, followed by sufficient maturation to ensure that the reaction process is substantially complete.
lime stabilisation (liquid sludge)	addition of lime to raise pH to > 12.0 and sufficient to ensure that the pH is not < 12 for ≥ 12 hrs.
liquid storage	for a minimum of 3 months
dewatering and storage	conditioning with lime or other coagulants followed by dewatering and storage of the cake for ≥ 3 months. If the sludge has been subject to mesophilic anaerobic digestion, storage for ≥ 14 days.

2 HEAVY METALS IN SLUDGE-AMENDED SOILS: A REVIEW.

The amount of sludge that can be disposed of by spreading or injection is restricted by the EC Directive (1976) in terms of the heavy metal loading of the sludge and soil (Table 2.1), which are approximate median values of the thresholds cited by the Sludge Use Guidelines of its member states (Webber *et al.*, 1984). These thresholds are in turn based on the extant body of research on metal behaviour, which inevitably forms the basis of any subsequent research. This current knowledge is therefore reviewed here.

2.1 METALS IN SEWAGE SLUDGE

The measured quantity of heavy metals present in sewage sludge depends entirely on the individual metal, the type of extractant used and the source and pretreatment of the sludge (Keefer *et al.*, 1984), whereby an industrial source will contribute more metals than a rural one (although 40-50% of Cd is thought to originate from household waste (Ammann and Koppe, 1984)). Metals enter the sludge via the use of Pb or Cu water pipes, domestic chemicals, road run-off etc, and from industries such as textile, chemical and battery manufacture, which may constitute up to 50% of the total flow (Berrow and Webber, 1972). The manufacture of rayon especially contributes massive amounts of Zn, yielding sludge contents of 1-5% Zn (Berrow and Webber, 1972).

During primary treatment, 70-85% of the total metal content, but only that present in insoluble forms (Lester *et al.*, 1983), is removed from the effluent by precipitation in sedimentary tanks. Secondary treatment removes 70-85% of the total content (40-75% of the dissolved content) of Cr, Cu, Fe and Hg and 30-60% of the total content (<40% of the dissolved content) of Cd, Ni, Pb, Zn and Mn (Newland *et al.*, 1976). The digestion or anaerobic incubation of sludge is thought to decrease the extractability of Cd, Cu and Zn, at least (Bloomfield and McGrath, 1982; Bloomfield and Pruden, 1975), but is expected to increase the total concentration of metals, because the process removes up to 30% of organic colloids, but none of the metals (Leeper, 1978). Conversely, the concentration of metals such as Ni, Pb and Mn, which are thought to enter the sewage works in a mainly dissolved state, is little affected by sedimentation.

Where the activated sludge process is employed, metal removal is achieved through bio-coagulation, bio-flocculation and bio-adsorption (Coker and Matthews, 1983), and depends upon factors such as the availability of free binding sites, the affinity of the metals for these sites (Lester *et al.*, 1983) and the age of the sludge (Sterritt and Lester, 1984). Chemical treatment, however, may further increase the concentration of metals in the sludge due to heavy metal contamination of the treatment chemicals (Ammann and Koppe, 1984). In addition, sewage flow may affect metal concentration in the treated sludge, in that an increase in flow will reduce the efficiency of metal removal. The metal composition of the remaining sewage sludge is thus extremely variable (Table 2.2). Zinc and Cu are usually present in higher concentrations than other heavy metals, although Cr, Ni or Pb may be locally important. Copper, Zn, Cd and Cr are considered to be the most limiting to sludge application (Cottenie, 1981) and Zn, Cu and Ni the most important phyto-toxic metals (MAFF, 1971). EC Directive 86/278/EEC also includes Pb and Hg.

The form of each individual metal in sewage sludge depends very much on source and treatment (Beckett *et al.*, 1979), and it has been proposed that the variability of metal form is greater in sewage sludges than in soils (Sterritt and Lester, 1980). For example, data reported by Kirk *et al.* (1985) showed that the stability constants of Cu and Ni adsorption changed with type of treatment. Similarly, Yeoman *et al.* (1989) found that metal distribution amongst particle size classes is dependent upon treatment (raw, activated or digested), although greater discrepancies were observed within the same sludge type but between treatment works.

Table 2.3 summarises the findings of fractionation procedures employed by a number of authors. In presenting this data, it must be remembered that results depend on the power of the extractants, time of extraction, the type of sample and size of particulates, and that many of the extractants used are not specific to one fraction (Sterritt and Lester, 1980; Harrison, 1987). It is assumed that these studies concern the solid phase, as this contains most of the heavy metals (70-73%, Lester *et al.*, 1979), although metals in the soluble phase are more toxicologically significant, and easier to assess (Yeoman *et al.*, 1989). Bearing these restrictions in mind, it has been shown that the metals are principally in organic (Patterson, 1979; Sposito *et al.*, 1982), carbonate (Stover *et al.*, 1976; Lagerwerff *et al.*, 1976; Unwin, 1977; Emmerich *et al.*, 1982) or oxide (Berrow and Burridge, 1977) form. Copper especially shows a strong tendency for organic combination (Sposito *et al.*, 1982; Emmerich *et al.*, 1982; Cottenie, 1981; Lagerwerff *et al.*, 1976). With reference to only those metals of interest in the present study (i.e. Cd, Cu, Ni, Pb and Zn), the rank of percentage extractability exhibits the expected variability, but is usually cited as: Zn and Ni > Cu (Patterson, 1971; Berrow and Webber, 1972; Lagerwerff *et al.*, 1976; Patterson and Kodukula, 1984). Despite the fact that Ni is widely thought to pass through the sewage works in an almost entirely soluble form (U.S. Dept. Health, Education and Welfare, 1965; Kabata-Pendias and Pendias, 1984), Williams *et al.* (1980) quote Ni as the least extractable in percentage terms. The same authors contradict others in ranking Zn and Cu in an interchangeable position, dependent on the pH of the sludge (where Cu is the more extractable at a higher pH). The similar position of Cu and Zn in the hierarchy is echoed in the work of Bradford *et al.* (1975). The status of Pb especially seems to be dependent on extractant, but is generally one of the least extractable of the metals, in percentage terms. Cadmium is rarely mentioned, but when included has the highest percentage extractability of all the metals (Williams *et al.*, 1980; Bradford *et al.*, 1975). Bojakowska and Kochany (1985) assessed the mobility of metals leached by water through lysimeters containing sewage sludge taken from 19 municipal sources. They cite the series of relative mobility as: Cd > Ni > Cu > Zn > Pb.

Up to 31% of the individual metal may be present in a soluble form (from data presented by Lagerwerff *et al.*, 1976; Patterson, 1979; and Patterson and Kodukula, 1984) but during treatment much of this is co-precipitated with phosphates, hydrous oxides or sulphides of Fe and Al, and with phosphates and carbonates of Ca (CAST, 1980; Logan and Chaney, 1983). Generally, less than 2% of the total heavy metal content of the treated sewage sludge is actually water soluble (Cottenie, 1981; Lagerwerff *et al.*, 1976).

As a result of the domination of organo-metal forms in sewage sludge, metals have been further fractionated to include their distribution among organic fractions. It is assumed that these will be important to trace metal chemistry in sludge (Holtzclaw *et al.*, 1978), determining the transformation of elements into more toxic and available forms (Karapanagiotis *et al.*, 1990). Holtzclaw *et al.* (1978) found that most Cu was in the humic acid fraction (largely insoluble), with Zn in the precipitable (ß-humus) fraction and Cd and Ni mostly in the fulvic acid (soluble) and precipitable fractions (Holtzclaw *et al.*, 1978). The authors propose that Cd, Ni and Zn would be expected to be the more mobile of these elements.

2.2 THE CONCENTRATION OF HEAVY METALS IN SLUDGE-AMENDED SOIL

On a global scale, a maximum of 4% and an average of less than 1% of heavy metals in soil is derived from sewage sludge (Alloway and Jackson, 1991). The addition of sludge to soil will generally only increase the heavy metal content of the mixture if the content of the sludge is greater than that of the untreated soil (Williams *et al.*, 1987). A comparison of Tables 2.2 and 2.4 shows that this situation is usually the case. The concentration of metals in the sludge/soil mixture will also increase with increasing rates of addition and the number of applications used (Le Riche, 1968), and, assuming that the sludge concentration is greater than the soil concentration for all metals, the order of metal contents of the soil will revert to that found in the sludge, regardless of application rate (Sposito *et al.*, 1984). However, the application of a sludge with a metal loading even 50 times greater than that in the soil will not necessarily elevate the resultant soil concentration of all metals (Berrow *et al.*, 1977). A lower-than-expected elevation in contamination has been observed by several authors (e.g. Davis *et al.*, 1988; Chang *et al.*, 1984b; Hinesley *et al.*, 1984; Sposito *et al.*, 1984; Emmerich *et al.*, 1982). Davis *et al.* (1988) and Sposito *et al.* (1984) hypothesised that this was because the sludge may alter the density of the soil away from the assumed 1g cm^{-3}. Davis *et al.* (1988) concluded that this would not account for the difference because the discrepancy was different for all metals and increased with time. In a laboratory experiment, Emmerich *et al.* (1982) tried to prove that movement of metals out of the sludge/soil layer was responsible, but could not detect any increase greater than the variability of the soil. It was concluded that sampling problems must be the cause.

The 'total' (acid-extractable) metal content of the soil does not vary appreciably with time once treatments have ceased, the residence time of heavy metals in soils being of the order of thousands of years (Bowen, 1977). Results that indicate a decrease in metal content with time after sludge treatment have been described as misleading, in that the decrease is not a result of leaching or plant uptake (McGrath, 1987; Giller and McGrath, 1988). Apparent removal of metals from treated plots has instead been attributed to the physical movement of soil away from the plots (McGrath, 1987; McGrath and Lane, 1989). A 'dispersion' model designed by the latter authors describes the extent of lateral movement as 0.24 m^2 and 0.13

m^2 per tillage operation, parallel and perpendicular to the direction of cultivation, respectively. This model follows the diffusion model of Sibbesen and Andersen (1985) that depicts a similar situation, but accounts for movement in only two dimensions, and is qualitatively confirmed by the observations of Stevenson and Welch (1979) and Williams *et al.* (1987). Thus, most of the metal content of sludge-amended soil can be described as chemically 'inactive' (Cottenie, 1981), the 'active' proportion being that which is plant-available.

2.2.1 THE CHANGE IN METAL AVAILABILITY WITH TIME.

Working with acid-zone soils, Sposito *et al.*, (1982 and 1984) concluded that the addition of sewage sludge shifted Ni, Cu, Zn and Pb away from acid-extractable forms to those extractable by weaker solutions, such as dilute NaOH or EDTA. This is supported by Chang *et al.* (1984a) who found that, in addition to these changes, Cu, Ni and Zn in the solid phase would be increasingly associated with carbonates and the organic fraction, whereas the solid phase forms of Cd, Cr and Pb would not be significantly altered. This is contradicted by Keeney and Walsh (1975) Berrow and Burridge (1984) and Bidwell and Dowdy (1987), who report a decrease in availability with time, although not to a point corresponding with background concentrations. Investigating Cu and Zn in soils from pig slurry additions, Unwin (1977) describes a fluctuation with time, with a trend towards a decrease in availability of up to 40%.

Blanket statements are generally avoided, however, with most authors relating a change in availability to the individual metal and soil properties. Keefer and Singh (1986) advocate a change in form of Cu and Zn, but not Pb, with time, and suggest that pH has a significant affect on metal associations. Bloomfield and Pruden (1975) considered the extractability of Cu, Ni, Pb, Cd, Cr and Zn in sewage sludge and soil and observed an increase in solubility, except of Cu, whose solubility was reduced, and Ni and Zn, whose solubility in water and acetic acid decreased. Similarly, Berrow and Burridge (1977) extracted the sludge/soil mixture with EDTA and acetic acid, but with contradictory results. Using the former extractant, Zn, Cu and Ni levels almost doubled in the first 4 years, and then declined slightly. In the same time span acetic acid-extractable Cu concentrations increased sharply, with Zn and Cr showing a slight and Ni a marked decrease. This change in form and concentration of the elements was attributed to changing soil temperatures, pH, Eh, the concentration of other elements, organic matter status and the activity of plants, micro-organisms and man. Using 'spiked' sewage sludge, Adams and Sanders (1984b) found that the concentration of Zn, Cu and Ni in soil solutions depended on soil type, pH and the decomposition of organic matter: a clay soil producing lower and less variable metal concentrations in solution with time, and the decrease in soluble organic matter, and accompanying decrease in pH, with time favouring the release to solution of Ni and Zn particularly. Beckett *et al.*, (1979) suggest that, although metal form in sludge is a function of its source and treatment, once it interacts with the soil the metals revert to a similar form of combination within 12 months (in the same soil), and that availability will change with the progress of this interaction.

Thus, metals originally held in an unavailable form may be released with the microbial degradation of the organic matter - the 'time-bomb' effect. An alternative school of thought expounds the 'reversion' hypothesis, whereby metals released from sludge into soil are occluded into oxides or precipitated as hydroxides, thus reducing their availability (Leeper, 1972; Lewin and Beckett, 1980). Davis and Coker (1980) also found that availability (of Cd) is diminished with time, following only initial release due to the increased microbial activity prompted by sludge addition. Working with a wider range of metals, Kelling *et al.* (1977) found that the extractability and plant uptake of Cd, Cu, Ni and Zn, but not Cr, decreased with time, although these results are confused by a concomitant pH change (McGrath, 1987). Terry *et al.* (1979) support this and directly contradict the idea of the 'time-bomb' effect. In this case, 20-40% of organic matter was found to be decomposed in the first 12-18 months, with the half-life of the remainder being measured in centuries. This and other arguments presented here undermine, at least in the longer term, the assumption made in many Sludge Use Guidelines that treating the soil with small but frequent applications of sewage sludge will cause less damage than one large application (Webber *et al.*, 1984)

2.2.2 FACTORS INFLUENCING ELEMENT FORM

The potential toxicity and mobility of various heavy metals is largely determined by the form in which the metal is present. In sludge-amended soils, metals present in the soil solution are predominantly inorganic and cationic (Alloway and Tills, 1984; Mullins and Sommers, 1986).

A. pH

It is widely acknowledged that pH affects the availability of cationic metals, in an inverse relationship (Sanders *et al.*, 1987; Keefer and Singh, 1986; Coker and Matthews, 1983; Cottenie, 1981; Sterritt and Lester, 1980). This relationship is the result of the increase in the number of negative sites on organic colloids with increasing pH (Leeper, 1978), and the direct competition between cationic H and metal ions as pH drops. It has also been attributed to the increase of Ca^{2+} ions, if a change in pH has been induced by liming (Alloway and Jackson, 1991). Some authors qualify this with the use of threshold values influenced by soil texture (Sanders and Adams, 1987; Adams and Sanders, 1984a). These thresholds are an upper limit, below which availability will increase, and range from pH 5.8-7.0 for Zn, 6.2-7.2 for Ni and 4.5-5.7 for Cu. Kiekens and Cottenie (1983) looked at the percentage of metals mobilised as a function of pH in a sludge amended soil. Sharp increases in mobility were encountered after pH 4 for all metals except Cu, Cr and Pb, which were significantly affected at a pH of 2.8. Similarly, Sanders *et al.* (1986) found that available Cu concentration was not affected by pH changes above 5.5, but Zn and Ni extractability was strongly pH dependent. Therefore a lower proportion of available Cu than Ni was present at pH's between 4.5-6.5, a range that covers most grassland soils. Other authors expound only a change in availability, dependent on the individual metal (Berrow and Burridge, 1977; Williams *et al.*, 1980 and 1984; Sanders *et al.*, 1987). For example, Williams *et al.* (1984) found that the percentage availability of Cu remained constant, as Cu remains as an organic complex over a wide range of pH values (McBride and Blasiak, 1979, Dudley *et al.*, 1987); Zn availability increased in acid soils, as solubility decreases with a pH increase from 5-7 (McBride and Blasiak, 1979); and Pb availability was unaffected by pH. Sanders and Kherbawy (1987) found that the equilibrium between solution and exchangeable Zn was pH dependent, but that the size of the exchange pool was not. Some authors (Sposito *et al.*, 1982; McLaren and Crawford, 1973; Korte *et al.*, 1976) have found that pH has little effect on the forms present, but these results may be attributed to the use of EDTA as an extractant, which is not sensitive to pH changes (Section 4.3.1) or the use of spiked sludge (Section 2.3).

B. THE ADSORPTION OF HEAVY METALS IN SLUDGE-AMENDED SOILS

The mechanism of adsorption of metal ions, and hence their removal from solution, is described by Alloway (1990a) as being conducted through cation exchange (non-specific adsorption), pH-dependent specific adsorption (involving the partial formation of covalent bonds between hydrous oxides of Al, Fe and Mn and the metal cation), the formation of chelation complexes (usually between carboxyl groups in humic and fulvic acids and metal ions), and co-precipitation with clay minerals, hydrous Fe and Mn oxides and calcite. The affinity of each of the soil constituents involved in these reactions for a specific metal ion varies between adsorbents, but Pb and Cu are generally adsorbed in preference to Cd, Ni and Zn (from data presented by Alloway, 1990a), although the amounts involved are dependent on pH (Msaky and Calvet, 1990). Despite the difficulty in determining which of these processes is dominant in a given soil (Alloway, 1990a), it is commonly accepted that cation exchange capacity has a significant effect on the behaviour of heavy metals in sludge-amended soils (Alloway *et al.*, 1988).

(i) CATION EXCHANGE CAPACITY

The cation exchange capacity (CEC) of a soil is a measure of its ability to adsorb cations, which is governed by the density of negative charge sites and is inextricably related to the texture of the soil. Negative sites may be permanent and independent of pH, i.e. those derived from isomorphous substitution within the structure of layer silicates or broken bonds at mineral edges and external surfaces; or pH-dependent charges that are created by the dissociation of hydrous oxides and acidic functional groups in organic compounds (Rhoades, 1982; Alloway, 1990). Each material belonging to the latter group has a pH threshold (point of zero charge) below which exchange reactions will not occur. Thus a rise in pH will increase the CEC (Sterritt and Lester, 1980). The redox status of the soil also affects its CEC, whereby oxidising conditions will tend to favour metal release (Cottenie, 1981).

In 'normal' soils, an increase in the CEC will decrease the availability of metals, due to stronger chemical binding (Haghiri, 1974). However, Sposito *et al.* (1982) consider this factor irrelevant in determining form in sludge-amended soil, although Sanders *et al.* (1987) argue that the relationship (or lack of it) is strongly influenced by the extractant used: EDTA- and DTPA-extractable metals show no correlation with CEC, whereas $CaCl_2$-extractable metals do. Korte *et al.* (1976) also question the importance of CEC, maintaining instead that it is only some of its constituents that are useful - namely, percentage clay, surface area and percentage free Fe oxide content (only the proportion of clay is important - clay type can be ignored in the UK, with reference to sewage sludge (Sterritt and Lester, 1980)). Other factors that were rejected in this case include electrical conductivity, Mn content, percentage sand and silt, and pH. Keefer and Singh (1986) cite similar controls on metal mobility - that is, soil texture, surface area and free Fe oxide - but, conversely, regard pH and sludge treatment to be significant. McBride and Blasiak (1979) also include specific adsorption on hydrous Al oxides as important. Copper behaves differently than metals such as Zn and Ni (Adams and Sanders, 1984a), in that its solubility is controlled by specific adsorption, which depends primarily on the organic matter and free Mn content of the soil (McLaren and Crawford, 1973; Kiekens and Cottenie, 1985). Clay and free Fe oxide contents only become important to Cu behaviour when abundant (McLaren and Crawford, 1973). If substantial inorganic exchange sites are present, the adsorption by soils of Ni, Pb and Zn may therefore be unresponsive to sludge additions, but Cu can be expected to exhibit a lower percentage availability (Elliott *et al.*, 1986).

Organic matter is an important constituent of the CEC of a soil, with up to 50 % of the total metal content held in this way in mineral soils (Kabata-Pendias and Pendias, 1984) due to its high adsorptive capacity at pHs above 5 (Alloway, 1990). As a result, King and Dunlop (1982) suggest that organic matter can ameliorate the effect on metal release of a decreasing pH. The effect of organic matter on metal solubility depends upon the original form of the metal and the organic fraction involved. For example, fulvic acids are soluble, but less stable than insoluble humic acids (Cottenie, 1981). Fulvic acids are considered to have a greater affinity for heavy metals (Kabata-Pendias and Pendias, 1984), but in sewage sludge, most Cu is found in the humic acid fractions, most Zn in the precipitable fraction and most Ni in the fulvic acid and precipitable fractions (Holtzclaw *et al.*, 1978). The addition of sewage sludge to soil will tend to increase the proportion of metals in fulvate fractions (Mullins and Sommers, 1986), and therefore exacerbate the effect of the metal on plants (Werff *et al.*, 1981). Similarly, but working with metals from an inorganic source, Bolter *et al.* (1975) found that Pb and Cu become strongly complexed, but Zn weakly complexed, with 'water soluble' organic acids in soil. McGrath (1984) suggests that the original type of organic matter added to soil (whether sewage sludge, sludge-straw compost, farmyard manure or vegetable compost) does not affect the percentage of heavy metals that can be extracted with EDTA. It should be noted, however, that his experiments were conducted 20 years after treatments had ceased, and the work of authors such as Mulchi *et al.* (1987) and Christie and Beattie (1989), dealing with shorter term effects, have found that the proportion of DTPA or EDTA extractable metals varies according to the source of the sewage sludge, or type of animal manure.

C. SOIL TEXTURE

Although CEC and soil texture are closely related, one cannot adequately reflect the influence of the other (Adams and Sanders, 1984a; CAST, 1982). Basically, heavier textured soils tend to strongly adsorb metals, and the pH threshold for release is lowered (Adams and Sanders, 1984a), whereas a coarser texture will promote the availability of the metals (Coker and Matthews, 1983). Thus Kiekens and Cottenie (1985) found that the solubilisation of Zn will be at a maximum (up to 43%) at a low pH in light soils, and at a minimum (up to 12%) at a high pH in heavier soils. Dowdy and Volk (1983) concluded that 'a sandy, acid, low organic matter soil' receiving large inputs of draining water would be the most likely to promote metal movement, but Korcak and Fanning (1985) point out that the rank of the extractability of the metals remains unchanged on a variety of textural classes. Unrelated to the CEC is the influence of texture on the soil moisture holding capacity and its hydraulic conductivity (Sterritt and Lester, 1980), in turn affecting the redox potential.

D. REDOX POTENTIAL

The term 'redox potential' refers to the difference in electrical potential in the soil solution caused by the acceptance of electrons by various elements, and the magnitude of the potential is governed by the ratio of oxidised:reduced material (Stolzy and Fluhler, 1978). The redox status of a soil therefore indicates its degree of aeration and is expressed in terms of pE (the negative log of the electron activity) or Eh (the difference in potential between a Pt electrode and a reference H electrode, in millivolts), the two being related in the equation:

$$Eh = 59.2pE \qquad \text{(Lindsay, 1979)} \qquad \text{equation 2.1}$$

In both methods, the greater the positive value, the more aerated the soil, whereas a large negative value indicates extreme anaerobic (reducing) conditions. Redox status is determined by Eh in this research, and will be referred to in these terms hereafter.

The redox potential of a soil generally decreases with increasing pH, although the exact relationship depends upon the soil type (Ponnamperuma, 1972). Reciprocally, the submergence of a soil will tend to cause a convergence of its pH to 6.7-7.2 (Ponnamperuma, 1972). The accumulation of organic matter tends to diminish the Eh, causing a convergence of acid and alkali soils towards neutral (pH 6.7-7.2, Rowell, 1981). Although the forms of the heavy metals of interest here (Cd, Cu, Ni, Pb and Zn) are not directly affected by redox, consequences such as the reduction of Fe(III) and Mn(IV) oxides, the production of organic complexing agents and the formation of sulphides may indirectly affect their availability (Ponnamperuma, 1972). The same author suggests that Cu would thus become more available, but that Zn would be removed from solution and held as a sulphide, in reducing conditions. Bloomfield and Pruden (1975), comparing aerobic and anaerobic incubation of sewage sludge, found that anaerobic conditions and an associated rise in pH decreased the availability of Cu and Zn, increased the availability of Pb, and had an erratic effect on Ni (depending on the extractant). Similar conclusions were obtained by Gambrell and Patrick (1989), who, in a pH-controlled experiment, found that Cu, Zn and Cd became increasingly plant-available with increasing redox potential. However, these results were directly contradicted by Beckett *et al.* (1983), who state that the anaerobic incubation of sludge will increase the extractability of Cu, Ni and Zn. Although these authors used similar extractants to those used by Bloomfield and Pruden (1975), no measurement was made of either the original pH of the sludge, or the effect of Eh on this. Brown *et al.* (1989) found that, although waterlogging increased the availability of Ni and Cd in untreated soils, no effect was observed on sludge-treated soils. Ng and Bloomfield (1962) concluded that the anaerobic incubation of soil in the presence of plant material resulted in the mobilisation of Ni, Pb and Zn but decreases the extractability of Cu (although Cu was mobilised when no plant material was added). The presence of organic matter would therefore appear to offset the mobilising effect of reducing conditions, but it has been suggested that this effect is dependent on the type of organic matter present (Ng and Bloomfield, 1962; Beckwith *et al.*, 1975). Different again, Cottenie (1981) suggests that severe reducing conditions in soil will precipitate most of the heavy metals (including Cu, Zn and Pb) as sulphides. Subsequent aeration of sludge and soil favours the mineralisation of organic matter and therefore the release of metals (Emmerich *et al.*, 1982; Cottenie, 1981). This is confirmed by Bloomfield and Pruden (1975), who observed that Cu, Zn and Ni became more available.

E. TOTAL METAL CONTENT

The total metal content of the soil obviously has some bearing on the availability of those metals, but in percentage terms the relationship is by no means straightforward, and is dependent on the individual metal and the soil and sludge factors discussed in this Section and Section 2.1. For example, Alloway *et al.* (1988) reports that Cd has a larger percentage solubility than Pb and Christie and Beattie (1989) found that the proportion of EDTA-extractable Cu was greater than that for Zn. Mullins and Sommers (1986) cite soil type as being a major determinant of the relative DTPA extractability of Cd and Zn. Kelling *et al.* (1977) found that higher rates of sludge addition, and therefore a greater introduction of heavy metals to the soil, yielded lower percentage availability of metals.

F. THE PRESENCE OF OTHER ELEMENTS

The interactions between elements may also affect metal availability. For example, if the Cd content of sludge is maintained at less than 1% that of Zn, plant uptake of the former can be decreased (Turner, 1973; Chaney, 1973), and Cd adsorption in soil is similarly reduced by the presence of Zn (Christensen, 1987). Nickel and Zn are also antagonistic, an increase in one causing a decrease in the plant availability of the other (Berry, 1976). In addition, other elements may affect those under examination here - for instance, P is known to inversely affect the availability of many of the metals, and Zn in particular (Fleming *et al.*, 1986), although it is argued that the antagonism exists mainly within the plant, rather than the soil (Leeper, 1978).

2.3 METAL MOBILITY

A knowledge of metal form and concentration is of little use in assessing the enhanced metal loading created by sewage sludge unless the mobility of the metals is also taken into account. Many studies have been made of metal mobility, but unless specifically directed at the case of sludge-amended soil they are irrelevant to it, as their salt form represents a simplified system and ignore the potential influence of the chemistry of the sludge (Korcak and Fanning, 1985). For example Mullins *et al.* (1982) found that organically-bound Cu was appreciably more mobile than $CuSO_4$. Conversely, Cottenie *et al.* (1984) found that a salt form of Zn, Cd and Ni was more mobile than the organic form in both clay and sand soils, whereas the mobility of Cu showed little difference between forms. Jenkins and Cooper (1964) observed the translocation of significant quantities of metals from sludge only after inorganic salts were applied. Similarly, Mahler *et al.* (1980) found that metals derived from spiked sludges were more available than those from 'normal' sludges. The difference in behaviour of inorganic salts has been attributed to the resultant decrease in pH that is generally absent from sludge amended soils (Kuntze *et al.*, 1984)

On a silt loam soil, Kornegay *et al.* (1976) observed no movement of Cu and Zn out of the pig slurry/soil zone before ploughing. After this, some movement to 100-200 mm and occasionally 200-300 mm occurred. Under similar conditions, but on grassland, Batey *et al.* (1972) observed no increase in Cu content below 760 mm depth. Holtzclaw *et al.* (1978) concluded that Cd, Ni and Zn would be the more mobile metals (than Cu) in soils amended with sludge. The different behaviour is attributed to the association of Cu with the humic fraction (see Section 2.2). This observation is contradicted by Bittigieg *et al.* (1990), who, after spreading sludge onto uncultivated land, observed significant increases in the concentration of Cu to a depth of 200 mm, but to only 150 mm in the case of Cd and Zn. In a series of experiments, Williams *et al.* (1980, 1984, 1985, 1987) examined the movement of metals out of the zone of incorporation (200 mm) after 2 sludges were applied to a loamy soil at rates up to 225 t ha^{-1}. Cadmium, Cu, Pb and Zn moved 50 mm below the zone, with some Zn moving up to 100 mm away. Rate of addition, time and acidity of the soil had no effect on this mobility. Adsorption or complexation onto organic matter and hydrous oxides of Fe and Mn were suggested as influential factors (Section 2.2.2). Although no downward movement was observed, the authors found enhanced concentrations of metals up to 3' (sic) downhill (laterally). This movement is attributed to the displacement of soil particles during 'rototilling'.

Sterritt and Lester (1980) cite the immobility of metals from surface applications of sludge, as reported by Boswell (1975) for Cu and Pb and Giordano *et al.* (1975) for Cd, Pb and Zn. This behaviour is attributed to waterlogging (Giordano *et al.*, 1975), the precipitation of Pb as phosphates from phosphatic fertiliser (Zindahl and Foster, 1976), redox effects (Bloomfield and Pruden, 1975), pH (Bolton, 1975) and adsorption mechanisms (Ellis and Knezek, 1972). More significantly, Sterritt and Lester (1980) subscribe to the view that appreciable movement of organic matter and associated elements will only occur after bases (Ca and Mg) are washed out of it. This process is largely dependent on seasonal factors, especially rainfall (Surorov, 1974).

Following relatively low rates of application and subsequent incorporation of pig slurry on fine sandy loam, silt loam and a loam/clay complex, Mullins *et al.* (1982) observed movement of Cu into the B horizon (no depth given) in the fine sandy loam only. The authors considered that enhanced leaching, allowed by a low CEC relative to the other soils, was responsible. Davis *et al.* (1988) also spread sludge on calcareous loam and sandy loam soils supporting grassland. In all cases, over 70% of the metal remained in the upper 50 mm, but orders of mobility were established as:

sandy loam: Cu > Zn > Cd > Ni > Pb
calcareous loam: Cd > Cu = Pb > Ni = Zn.

Despite this, it was concluded that mobility was independent of soil type. Differences in rainfall also had no effect. Instead, movement was attributed to the infiltration of sludge particles in soil water and pedoturbation by earthworms. Similarly, Fuller *et al.* (1976) observed no significant movement of metals from landfill leachate (compared to pure water), regardless of soil type.

Metal mobility may be enhanced, however, under extreme conditions. For example, Campbell and Beckett (1988) report an increase in the concentration of Cu and Zn at 600 mm (the maximum depth sampled) after heavy dressings of sludge were applied to a freely draining loam. It is proposed that the metals moved to this depth in solution, and were later precipitated out by the higher pH. Dowdy *et al.* (1991) report movement of Cd and Zn, but not Cu, to 500 mm depth in a silt loam soil prone to dessication cracking. The former metals were preferentially adsorbed in cutans coating ped faces and the authors suggest that non-matrix water flow around and between the peds was therefore responsible for translocation of metals. Lund *et al.* (1976) found elevated concentrations of Cr, Cu and Zn at 2 m, and levels of Cd and Ni three times higher than the background concentration at 3-3.5 m in permeable sands and coarse loam soils below drying ponds. In a similar situation, Kirkham (1975) observed movement of Cd, Cu, Ni and Zn to 610 mm. The difference between the two studies is likely to be the time factor involved - the pond used by Lund *et al.* (1976) had been in use for 20 years, compared to 3 years in the Kirkham (1975) case. The influence of time does not seem to extend to less severe applications of sewage sludge, however. For example, 20 years after sludge treatments ceased, McGrath (1984) found that an average of 85% of the metals Zn, Cu, Ni, Pb, Cd and Cr that had been applied could be recovered from the top 230 mm of the soil. Physical movement of the soil was dismissed as the proportion was not constant between metals, but the shortfall can probably be accounted for by extractant inefficiency, as McGrath (1987) later established that a maximum of 0.57% of metals were removed by crops harvested over 20 years, and, in leaching columns, found no evidence of enhanced metal levels in lower horizons or the leachate.

Very little information exists on the movement of trace elements from applications made by injection. Kirkham (1983) injected sludge, on a weekly basis, to a total of 32 t ha^{-1} yr^{-1} and found enhanced concentrations of Cu, Fe, Mn and Zn at a maximum depth of 300-450 mm. The majority of the metals was found in the upper 150 mm. Nickel concentrations were elevated between 200-450 mm only. Control and sludge-treated soil had similar Pb concentrations. The soil was a fine silt loam, but the depth of injection was not specified.

2.4 THE TOXICITY PROBLEM

It was not until the late 1950s that the toxic potential of sewage sludge was realised (Le Riche, 1968). It then took until the 1970s for any proposals limiting the accumulation of heavy metals to be made (Long, 1989). These culminated in EC Directive 86/278/EEC, interpreted for the British case by the Department of the Environment's Code of Practice (1989). However, ranges of metals specified in the EC Directive may be exceeded by even background levels in some soils in the UK (Berrow and Reaves, 1984) and toxic effects may occur in the soil at concentrations close to the EC limits (Giller and McGrath, 1988). In addition, no account is made of the form in which the metal is present - for example, CdO is considered to be more toxic than $CdSO_4$ (Webber, 1973). However, Alloway and Tills (1984) point out that metals in sludge, such as Cd, are not absorbed by plants to the same extent as metals from other pollution sources, and Kiekens *et al.* (1984) and Korcak and Fanning (1985) found that Zn, Cu, Cd and Ni in an inorganic salt form are taken up by plants to a greater extent than those derived from sludge. The literature abounds with information regarding the plant uptake of metals from soils (e.g.Sterritt and Lester, 1980; Kirkham, 1974; Coker and Matthews, 1983; Berrow and Burridge, 1977; Giller and McGrath, 1988; Beckett *et al.*, 1979; Baxter *et al.*, 1983; Newland *et al.*, 1976; CAST, 1976; Bradford *et al.*, 1975), which will not be repeated here. It is sufficient to realise that the critical soil solution concentration does not necessarily create a critical tissue concentration, beyond which yield would decrease (Beckett and Davis, 1982), depending upon the efficiency of the 'soil-plant barrier' (Webber *et al.*, 1984). Emphasis has shifted recently onto the investigation of the additive nature of this uptake in plants. Interest began with the assumption of UK Guidelines (MAFF, 1971) that the toxic effects were additive, the extent of which was later challenged by Beckett and Davis (1982). In defining the scope of the problem toxic elements, Beckett *et al.* (1979) describe the combined effect of toxic metals as 'no more than additive' - that is, they are not synergistic. The degree of uptake, accumulation and tolerance of heavy metals varies according to the individual element, plant species and cultivar (Sterritt and Lester, 1980; Alloway and Jackson, 1991), time of year (Alloway *et al.*, 1988) and, to a lesser extent, soil type (Hue *et al.*, 1988) (whereby uptake will be enhanced from a sandy soil and restricted from a clay soil - Kiekens *et al.*, 1984), and soil cultivation (Buttigieg *et al.*, 1990, found that the herbage concentration of Cu, Ni and Zn was significantly enhanced on soils that were cultivated before of after sludge addition). For example, Cd and Ni have been found to accumulate in leaves (Alloway *et al.*, 1990; Davis 1984, respectively); Cu in potatoes, the seed of soya beans, but the leaves of maize (Mondy *et al.*, 1984; Reddy *et al.*, 1987); and Zn in the grain of cereal crops and in potato tubers (Gebhardt *et al.*, 1988; Mondy *et al.*, 1984). Plant uptake of Pb is not necessarily enhanced by the addition of sewage sludge (Chaney, 1988).

Moore (1988) suggests that the accumulation of metals by plants could be minimised by the use of fungal mycelium of mycorrhiza that may accumulate heavy metals and therefore act as a barrier between soils and higher plants (Bradley *et al.*, 1982). Giller and McGrath (1988) quickly dismiss this, as some crops are non-mycorrhizal. Instead, they argue that the only way to reduce uptake is to reduce the heavy metal content at source. As an alternative to this solution, which would inevitably require a substantial input of both time and money, Leeper (1978) postulates the initial use of an inedible crop to remove the heavy metals. However, this apparently simple solution incorrectly assumes that all available heavy metals are removed by the plant, and that no further metals are later mobilised.

Toxic effects of metal overloading include the suppression of symbiotic nitrogen fixation, a yield decrease (of clover) of 40 % (McGrath *et al.*, 1988), a halving of the microbial biomass (Brookes and McGrath, 1984), prevention of the growth and N-fixation by blue-green algae (Brookes *et al.*, 1986), the inhibition of enzyme activity (Reddy *et al.*, 1987) and the disruption of protein structures and functions, causing enzymatic and metabolic disorders in fauna living both in and on the soil (Vallee and Ulmer, 1972). In animals and man, toxicity is usually a chronic effect (i.e. biological build-up) resulting from bio-accumulation and bio-magnification up the food chain (Sterritt and Lester, 1980). The accumulation of metals is governed by both the individual metal and the species of animal. For example, metals such as Cd, Cu, Pb and Zn tend to be concentrated in offal, whereas the metal content of muscle and animal products are generally unaffected (Alloway *et al.*, 1988). In analysing the metal content of organs of small mammals living in sewage-treated areas, Hegstrom and West (1989) found that only Cd was universally accumulated in the liver and kidney. Whether Pb, Zn and Cu concentrations were increased in these organs depended upon animal species. Conversely, Levine *et al.* (1989) found that small mammals concentrated Cu but not Cd in their liver. This is likely to be a reflection of plant uptake, as both Cd and Cu were found in earthworms at concentrations greater than that in the soil. However, plant tissue is not the only food chain pathway for heavy metals For example, Khan (1980) reports the ingestion of 140-1400 g soil each day by cattle, whilst Davis *et al.* (1985) point out that intake of heavy metal through human lungs is 3-10 times greater than absorption through the gut. Goodman and Roberts (1971) found that the two factors were related, with 27% of the variability of Pb in house dust being explained by soil Pb.

Toxicity may be manifested as brain and liver damage and death (Batey *et al.*, 1972), although these symptoms have not been observed in the case of sewage sludge. Some metals have been linked with cancers (Sunderman, 1977; Hernberg, 1977), although the case is by no means conclusive.

TABLE 2.1 EC LIMITS FOR THE HEAVY METAL CONTENT OF SEWAGE SLUDGE AND SOILS.

metal	content in sludge (mg kg^{-1} dry matter)	content in soil (mg kg^{-1} dry matter)
Cd	20 - 40	1 - 3
Cu	1000 - 1750	50 - 140
Ni	300 - 400	30 - 75
Pb	750 - 1200	50 - 300
Zn	2500 - 4000	150 - 300
Hg	16 - 25	1 - 1.5
Cr	-	-

TABLE 2.2 TOTAL HEAVY METAL LOADING OF SEWAGE SLUDGE IN THE U.K. (mg kg^{-1}).

element		author*				
		1	2	3	4§	5§
Cd	range	2-1500	0-300	3-3000	0.1-158	1.5-12#
	average	20	20	16	16.3	5
	difference**					- 69 %
Cr	range	40-14000	10-5000	40-8800	1-11743	27-489#
	average	400	500	250	434	208
	difference**					- 52 %
Cu	range	200-8000	1-3000	200-8000	20-2900	215-974#
	average	650	250		519	574
	difference**					+ 11 %
Hg	range	0.2-18	0-5	0.1-50	0.2-22.0	1.1-6.1#
	average	5	2	5	3.3	3.5
	difference**					+ 6 %
Ni	range	20-5000	10-1300	20-5300	5-615	15-225#
	average	100	150	80	101	65
	difference**					- 36 %
Pb	range	50-3600	50-5000	120-3000	25-3106	70-585#
	average	400	700	700	329	201
	difference**					- 39 %
Zn	range	600-20000	500-20000	700-49000	143-4920	454-1471#
	average	1500	3000	3000	1123	922
	difference**					- 18 %

* 1 = Moss *et al*, 1984; 2 = Cottenie, 1981; 3 = Davis and Lewis, 1978; 4 = DoE/NWC, 1983; 5 = CES, 1993.

§ References 4 and 5 refer to only that sewage sludge used in agriculture

'Range' cited by reference 5 refers to the 10 %ile - 90 %ile

** 'difference' refers to the change over 10 years between 2 DoE-initiated sewage sludge surveys, and percentage change is relative to the earlier data.

TABLE 2.3 THE FRACTIONATION OF METALS IN SEWAGE SLUDGE

author*	Cd	Cu	Pb	Ni	Zn
1	organic	organic / CO_3	-	organic / CO_3	-CO_3
2	-CO_3 (49%)	-S (35%)	-CO_3 (61%)	-CO_3(32%) 22% exch.	organic (50%)
3	-CO_3	organic	-	-CO_3	CO_3
4	exch./ads.	CO_3/S	CO_3/organic	exch./Ads/ organic/CO_3	organic/CO_3

* 1 = Sposito *et al.*, 1982; 2 = Stover *et al.*, 1976; 3 = Emmerich *et al.*, 1982b; 4 = Lo and Chen, 1990.

TABLE 2.4 BACKGROUND CONCENTRATIONS OF METALS IN UK SOILS (mg kg^{-1}).

		author*					
		1	2	3	4&5	6	7
Cd	range	<.1-10.5	.01-1	.01-2.4	.01-.7	-	<.2-40.9
	average	0.5	0.5	1.0	.06	0.4	0.8
Cr	range	4-160	5-1000	5-1000	5-3000	-	.2-838
	average	54	100	100	100	50	412
Cu	range	1.8-215	2-100	2-100	2-100	-	1.2-1508
	average	18.4	20	20	20	12	23.1
Hg	range	.01-2.12	<.01-.5	.01-.3	.01-.3	-	-
	average	.09	.1	.03	.03	.06	-
Ni	range	2-98	5-500	10-1000	1-1000	-	.8-440
	average	24	50	50	40	25	24.5
Pb	range	4.5-2900	2-200	2-200	2-200	-	3-16338
	average	36.8	20	20	10	15	74
Zn	range	3.9-975	10-300	10-300	10-300	-	5-3648
	average	80	50	50	50	40	97.1

* 1 = Archer and Hodgeson, 1987; 2 = Berrow and Burridge, 1977; 3 = Moss *et al.*, 1984; 4 = Bowen, 1966; 5 = Davis and Lewis, 1978; 6 = Berrow and Reaves, 1984; 7 = McGrath and Loveland, 1992.

3. AIMS AND OBJECTIVES

Sludge has many useful characteristics, principal amongst which are its nutrient and organic matter content that have beneficial effects both on soil and crops (Chapter 1). Whilst sludge also contains deleterious elements such as heavy metals, pathogens and organic components, treatment and/or monitoring practices routinely identify that sludge whose pollutant loading overrides its usefulness. This being the case, the use of suitable sewage sludge in agriculture is currently its cheapest disposal option, both in terms of monetary cost, resource utilisation and environmental impact. However, monitoring the heavy metal content of the soil after sludge application is also required by the 1986 EC Directive, and whilst the behaviour of metals from surface-applied sludge is well documented (Chapter 2), the behaviour following other methods of application has received little attention.

The most important alternative land application method currently in use is the subsurface injection of sludge, which is free from many of the constraints imposed on the spreading of sludge. This process is described both in the 1986 EC Directive 86/278/EEC and the Sludge (Use in Agriculture) Regulations (1989). The House of Lords Select Committee on the European Communities (1983) considered that injection represents the least offensive current method of sludge application, whose use should therefore be encouraged. However, sampling practices modified for injection are only nominally mentioned in the Code of Practice (DoE, 1989), and not at all in either the Sludge Regulations (1989) or EC Directive 86/278/EEC. In addition, it is known that the design of injector tine affects the subsurface distribution of sewage sludge, but the effect that this has on metal distribution has apparently not been investigated, and no proviso has been made for this potential variant in any sampling regimes. The House of Lords Select Committee on Science and Technology (1984) has identified a need for research into 'techniques of disposal to minimise resultant air and water-borne pollution'. Thus it is of both academic and practical interest to define the post-injection distribution of the metals that control its use and the factors that might affect this, and this essentially constitutes the aim of this project. In order to achieve this aim, a number of objectives can be identified that need to be satisfied. These are:

(1) To describe the post-injection behaviour of those 'total' heavy metals stipulated in EC Directive 86/278/EEC. It is necessary to ascertain whether these metals can be considered mobile, and whether the metals behave in a similar manner;

(2) To assess the variability of metal behaviour both under the same set of conditions and under a variety of treatments, thereby assessing both the efficiency of the injection operation and the usefulness of generalisations that can be made;

(3) To identify those soil and injection factors that influence both (1) and (2);

(4) Thus establish whether the Code of Practice sampling regime can be expected to successfully and consistently define metal concentrations.

In addition, but of secondary importance to the aim of this project, the effect of time and the relative availability of the metals will be considered, since these factors may influence the larger issue of plant uptake and hence passage through the food chain.

It is intended that these objectives will be met using an empirical approach. To this end, Chapter 4 describes two phases of field trials, incorporating injector, soil and rate variables that could reasonably be anticipated to have some effect on the subsequent metal distribution and to be a realistic representation of the circumstances under which injection is routinely performed. Soil columns were used to supplement these sites, and to allow greater control over the measured parameters. Soils were sampled extensively and in detail after injection, with replicated sampling points clustered around individual tines. Chemical, and some key physical, properties were defined in the laboratory, using techniques that will also be cited in Chapter 4. Results are presented in terms of injector performance, particularly the loosening effect of the tines and the deposition of the sludge mass (Chapter 5); soil characterisation (Chapter 6); and metal behaviour, particularly the extent and form of distribution (Chapter 7). Discussion of these results, both in isolation and collectively, are presented in Chapter 8, along with inferences that can be made about metal distribution (specifically, can distribution be described as the result of movement, or are patterns observed 6 months after injection created during the injection process, and which factors are therefore important in defining the extent of this distribution) and therefore the sampling protocol currently in use. The implication of these conclusions are presented in Chapter 9.

4. METHODS AND MATERIALS

4.1 EXPERIMENTAL DESIGN

4.1.1 FIELD VARIABLES

In assessing the behaviour of trace elements in soil, it has been established (Section 2.3) that laboratory experiments or additions of inorganic forms of metals do not accurately reflect the distribution and movement of metals introduced into the soil in sewage sludge. Field experiments are therefore essential in satisfying the aims of this research.

There are many field variables that may influence the behaviour of heavy metals that are introduced into the soil via the injection of sewage sludge. These can be classified as: type of injection tine; rate of injection; soil type; landuse and climate. Grassland was selected for study on the basis that it is in this situation that injection is at its most advantageous.

A. TYPE OF INJECTION TINE

There are three basic designs of injection the currently available in the UK (WRc, 1986), *viz* : narrow (simple) tines, winged tines and side-inclined tines (paraplow) (Figure 4.1), each creating a distinctive pattern of sub-soil disturbance (Figure 4.2) and sludge placement (Section 6.2), which potentially yield different patterns of metal distribution. The effects of each on soil disturbance may be modified by, e.g. rake angle, depth of work and induced vibration (WRc, 1986). It would be impractical to address each of the possible permutations, although it is essential that each of the basic designs should be considered.

The most preferred tines are those incorporating wings as these result in a more uniform distribution of sludge, greater soil disturbance, and, consequently, increase the volume of sludge that can be injected (Warner and Godwin, 1988). However, whilst the initial financial outlay for injection equipment remains relatively large and whilst the system is both relatively novel and still undergoing improvement, the bulk of injection procedures are conducted by contractors, who inevitably dictate the selection of tine design. Thus, initial experiments were conducted commercially employing straight tines and paraplows, whilst winged tines were used for the more restricted second phase (Section 4.2). The geometry of these tines is indicated by Figure 4.1.

For the purposes of this research, all types of tine worked in groups of 4 and at a spacing of 600 mm. It was intended that depth should be maintained at a constant 250 mm, representing the minimum depth required for all three tines in terms of draught force and complete coverage of the sludge (WRc, 1986). However, due to the inherent heterogeneity of surface conditions, soil and the process itself, the depth of injection varied considerably (from approximately 200-300 mm), but consistently, within each replicate (Section 6.4).

B. RATE OF INJECTION

There is little existing research to indicate whether there is a relationship between the rate of sludge injection and the sub-surface distribution of both soil disturbance and heavy metals from that sludge. Instead, investigations have focused on the depth/rate relationship that aim to maximise the amount of sludge that can be injected whilst minimising surface disturbance and draught force. Whilst it is possible to inject greater quantities of sludge than would normally be spread, too high a rate of injection will create seepage onto the surface. As a result, the WRc (1986) stipulates a maximum rate of 140 m^3 ha^{-1}. This is significantly lower than the maximum capability of the injection equipment, which may be as high as 300 m^3 ha^{-1}. Since problems may be encountered in detecting the effect of a low rate of injection on soil metal concentrations following a single application, a 'medium' (140 m^3 ha^{-1}) and 'high' (300 m^3 ha^{-1}) rate were deemed the most practical for this experiment.

C. SOIL TYPE

It has already been established that many soil parameters affect the behaviour of metals in sludge amended soils (Section 2.2.2), and that a quantification of the relative importance of these is a primary objective of this research. As such, it is essential that experiments should be conducted on soils with significantly different chemical properties. The most cited influential factor is pH, and this is the only measurement required by EC Directive 86/278/EEC. However, pH is a relatively variable entity, and may be modified by management practices and by the addition of sewage sludge. Furthermore, the identification of suitable sites with significantly different pH values, or any other chemical property, would be unfeasible in terms of the time requirement. In contrast, soil texture remains relatively constant with time and also exerts an influence over many of the soil factors that are considered to affect metal behaviour (Section 5.4). In addition, it has the advantage of being classified in soil maps. The sites were therefore selected as texturally contrasting, with significantly different pHs as a secondary prerequisite. Similarity of extrinsic characteristics and landuse history were also considered important.

The sites on which these experiments were conducted were a clay loam at Seale-Hayne Farm (Newton Abbot) and sandy loam at Clinton Devon Estates (Colaton Raleigh), located in East and South Devon, respectively (Figure 4.3). Under the criteria stipulated by the WRc (1986), both sites are suitable for injection in terms of soil type and slope angle. The pH at Colaton Raleigh (4.94) is significantly lower ($p<0.01$) than that at Seale-Hayne (average pH = 5.84). Under the Sludge (Use in Agriculture) Regulations of 1989 (Statutory Instruments), Colaton Raleigh, selected as an experimental site in 1988, would now be considered unsuitable for sludge amendment as it has a pH of < 5. Both sites are proximal to water courses and that at Colaton Raleigh overlies a large aquifer (Section 4.1.2). In view of the unknown quantity of NO_3-N leaching and in (retrospective) compliance with the Nitrate Sensitive Area scheme, the sites were therefore cleared for use with ADAS before injection commenced.

4.1.2 SITE DESCRIPTION

The sites used for field experiments are described according to criteria specified by Hodgson (1976). Five soil profiles were described at each site from pits used to sample soil (Section 4.2) for laboratory analysis.

A. SEALE-HAYNE FARM (Honey Park and Broad Meadow, Grid Ref.SX826273)

Seale-Hayne Farm lies approximately 3 km north-west of Newton Abbot at an elevation of 45-176 m above sea level. Underlying geology is complex as the farm straddles both slate and igneous rock, a situation typical of the Newton Abbot area (Durrance and Laming, 1982; Selwood, 1984). Within Seale-Hayne Farm, two adjacent and intrinsically similar fields (Honey Park and Broad Meadow on Figure 4.3) were selected as suitable for injection. Both sites are located in a valley floor, and are underlain by Gurrington Slate of Upper Devonian age (Durrance and Laming, 1982). The slates are of unknown depth, and may be purple/green or grey in colour (Selwood, 1984), the latter being present at Seale Hayne. At Broad Meadow, the slate is overlain by alluvium of recent origin (Clayden, 1971). Honey Park slopes gently through a maximum of 2 degrees, with an aspect ranging through 180 degrees from north to east to south. The plots located at Broad Meadow are level. No bedrock was exposed at either site. The landuse at both Broad Meadow and Honey Park is permanent pasture, the latter since 1966.

Climatological data is useful in any study of soil chemistry, through its effect on both soil water status and soil temperature, which in turn affect chemical and microbiological reactions. Seale-Hayne has its own meteorological station. Measured variables (rainfall and soil temperature) are summarised in Figure 4.4, for the experimental period of April-November, 1988 and September-April, 1990 and the 3 months immediately preceding it. Potential evapotranspiration figures quoted are mean values taken over 30 years by MAFF (1976) for area 43S. During the first experimental period, potential transpiration (taken as indicative of evapotranspiration in the absence of more appropriate data) exceeded rainfall during April, May, June and August. Thus soil was at its driest immediately following injection in April, 1988, but had wetted up again before sampling. Conversely, soil was wetting up by the time the second injection was performed, and drying during the second sampling stage (compare Figure 4.4 and Table 4.1).

(i) SOIL DESCRIPTION

The soils of Seale Hayne are of the Denbigh Association (Findlay *et al.*, 1984), formerly mapped as the Highweek Series by Clayden (1971). The soils of Honey Park have been mapped as belonging to the Denbigh 1 Association (Findlay *et al.*, 1984), and as such are highly variable within the field in terms of depth, texture, and colour (Table 4.2).

Denbigh soils are described as fine loamy typical brown earths, with a maximum depth of 800 mm. Colour, as determined by Munsell Soil Colour Charts, grades down the profile from dark brown to brown to yellowish brown, accompanied by an increase in stone content with depth (Findlay *et al.*, 1984). At Honey Park, the soils demonstrate many of the departures from this standard description that were noted by Clayden (1971). Depth ranges from 350-700 mm, and is most commonly 500 mm deep. Despite displaying the typical brown-dark brown (7.5YR 3-4/2 to 10 YR 3-4/3) colouration in surface horizons, this frequently grades to dark reddish grey or greyish brown (5YR 4/2 or 10YR 3-4/2, respectively). No further colour change is apparent in most profiles, but when present, the adjustment is to the typical yellowish brown (10YR 4/4). Texture, as determined by particle size analysis, is usually the typical clay loam throughout the profile, with silt becoming increasingly conspicuous with depth in some cases. In terms of colour and, less frequently, texture, the dominant series of the Denbigh Association therefore appears to intergrade with the Barton Series, as described by Palmer (1976), in this field.

The soil conforms to the norm as stated by Findlay *et al.* (1984) in terms of stoniness, root abundance and structure. Stone content (i.e.that retained on a 2 mm aperture sieve) increases from a maximum of 14% in the Ap horizon to a maximum of 42% at the base of the profile, and there is a corresponding increase in stone size, from fine gravel and very small (5 mm diameter) slate particles to stones and slate particles with a diameter of up to 50 mm. Structural differences between horizons are difficult to identify, especially between the Ap and B horizons, both of which vary between medium granular or fine subangular blocky with low packing density and strength. The B/Cu horizon merges from this to a large subangular structure, occasionally with a very firm soil strength. The C horizon has not been investigated in detail by the present author as it is considered to be away from the sphere of influence of injected heavy metals, but is described by Twomlow (1989) as a dark reddish grey weathered slate matrix overlying unweathered *insitu* slate.

The soil of Broad Meadow is mapped by Clayden (1971) as 'mixed bottomlands', a classification often assigned to soils overlying riverine alluvium. This influence is manifested in the more silty nature of the profile (usually silty clay throughout) compared with that of Honey Park, although in other respects the soil conforms with the description of the Denbigh Association, as detailed above. The variability of soils at the Broad Meadow site is illustrated by Table 4.2. There are small inclusions of clay soil (10YR 5/2, greyish brown) with extensive mottling (10YR 6/8, brownish yellow) at a depth of 300-500 mm. As a result, these soils are more reminiscent of the Conway Series (Thompson, 1982), a relatively minor component of the Denbigh 2 Association (Findlay *et al.*, 1984). The soil is a typical alluvial gley, usually with a fine silty texture, although particle size class is variable (Thompson, 1982). The soil of the Conway Series at Broad Meadow deviates from the reference description given by Thompson (1982) in profile depth and colour of the A horizon. Soil depth is much shallower than the norm (approximately 500 mm as opposed to 1.5 m), probably reflecting the influence of the Denbigh Association to which it belongs, and colour is browner (10YR 3/3, dark brown) than the cited greyish brown, as the water table is lower than in the average case (Findlay *et al.*, 1984).

B. COLATON RALEIGH (Pophams Field, Grid Ref. SY 075876)

Colaton Raleigh is located approximately 15 km south east of Exeter in the Otter Valley, with an elevation of less than 61 m above sea level. The area is underlain by Triassic Otter Sandstone (Durrance and Laming, 1982; Selwood, 1984), originally termed New Red Sandstone (Ussher, 1913). This in turn is underlain by the Budleigh Salterton Pebble Beds, originating from the Lower Trias (Durrance and Laming, 1982). The pebbles are predominately quartzite and lie in a sand and silt matrix (Durrance and Laming, 1982). Together, the Sandstone and Pebble Beds constitute the largest aquifer in the county, and boreholes exist in the Colaton Raleigh area to access the water (Durrance and Laming, 1982). Identifying the extent of movement of heavy metals is therefore of particular importance in this region.

The site at Colaton Raleigh was selected for its extrinsic similarities to the Seale Hayne sites. Its location is illustrated by Figure 4.3. The field has a slope of 2^{0} and faces north east. No bedrock is exposed. As with Honey Park, the field has been used as permanent pasture since 1966. A summary of meteorological data for the area, taken from the nearby Bicton College of Agriculture's weather station (rainfall) and from the MAFF (1976) description of area 45W (potential transpiration) is presented in Figure 4.4. Soil temperature data is not available, but can be inferred from that for Seale-Hayne, since soil temperature broadly reflects potential transpiration, with a delay of approximately 1 month and a temperature oscillation of 15 ^{O}C. From a comparison of the rainfall data from the two locations, it is apparent that, whilst Colaton Raleigh was appreciably drier immediately prior to injection, differences are far smaller after injection.

(i) SOIL DESCRIPTION

The soils of the Colaton Raleigh site are of the Bridgnorth Association (Findlay *et al.*, 1984), formerly the Bridgnorth Series (Clayden, 1971). These are typical brown sands, permeable, and have a depth of approximately 800 mm (Findlay *et al.*, 1984). The soils at this site have a fine band (50-70 mm thick) of pebbles, often in a single layer, at 350-600 mm depth (depth decreasing downslope and towards the watercourse). The pebbles are rounded or sub-rounded and 50-100 mm in diameter. This feature is probably derived from the Budleigh Salterton Pebble Beds, reworked and deposited on terraces of the River Otter (Selwood, 1984). Accordingly, the pebbles are underlain by silty material, greyish brown (10YR 5/2) in colour and containing occasional dark yellowish brown (10YR 4/6) sand lenses. In all subsequent descriptions, this pebble layer is taken as the base of the profile.

The variability of soils at this site are summarised in Table 4.2. The soils are browner (10YR 4/3-4 to 7.5YR 4/3 or 6, with depth) and have a higher content of small, subangular stones than the standard description of the Bridgnorth Series given by Jones (1983), and in addition show some translocation of organic matter into the Bh horizon. Most profiles have the standard sandy loam texture, but silt becomes more evident in some cases, yielding a sandy silty loam texture. Textural class is generally unchanged with depth. Structure, however, is typical, with fine subangular blocky peds in the surface horizon deteriorating to single grain and structureless down the profile. Worm channels are abundant throughout the profile, and there is evidence of mole activity in many A and Bh horizons.

4.2 FIELD METHODS

In order to design a statistically sound experiment, the treatments described above must be replicated and randomised (Clarke, 1980). In so doing, results can be shown as 'real', rather than chance observations, and the effect of experimental errors or natural variation can be minimised by insuring that they are mutually independent. Natural variation is of particular importance in studies of this type, due to the heterogeneity and spatial variability of soil (Cameron *et al.*, 1971).

Two field trials were set up to determine the distribution of metals after injection, their variability and the soil factors that influence that distribution. The sewage sludge was obtained from the Countess Wear Sewage Treatment Works in Exeter and transported to the experimental site by road tanker. Increments of this sludge were transferred to the field tanker for injection, and samples taken for laboratory analysis. In Phase I, extending from

April to November, 1988 (Table 4.1), plots of 2.4 m x 20 m were injected with sewage sludge at the Honey Park and Colaton Raleigh sites, employing a simple and side inclined tine (paraplow). Plots were injected at an actual rate of 225 m^3 ha^{-1} and 300 m^3 ha^{-1}. With each combination of the 3 variables, this gives 4 plots and 1 control on each soil type. The plots were arranged randomly within a block, according to random number tables, and each block replicated four times to identify any systematic variation in soil depth (Figure 4.3). A separate random arrangement of plots was used in each block. Each plot was 2.4 m from the next, and a further buffer zone of 5 m was left between blocks. The water content of the soil at injection was 39 % and 30 % at Seale-Hayne and Colaton Raleigh respectively.

Two weeks after injection, the resultant disturbance of soil was assessed using a hand-held shear vane. Measurements were made vertically on a grid pattern between two injection slots at 50 mm depth and distance increments, to a depth of 450 mm or the depth of the soil, whichever was the shallower. After 1 and 3 months, Dutch auger samples were taken at 150 mm increments to a depth of 450 mm, and 100 mm increments away from the point of entry of the tine into the soil (Figure 4.5). The point of entry of the injector tine thus forms the first sampling position. Samples were collected to one side of the tine only, under the assumption that, with the exception of the paraplow (whose entire influence is offset from the point of entry) metal distribution should be reasonably symmetrical about this point. This assumption is made following the work of, for example, Hall *et al.* (1986), whose expectations of soil disturbance is illustrated by Figure 4.2. Two sets of soil samples were taken from each plot. After 7 months, soils were sampled from a pit face in order to generate a more detailed picture of metal distribution. Due to the destructive nature of shear vane measurements, these pits were located approximately 1 m from original sampling points. The pits were excavated to a depth of 420 mm (approximately 1.5 times the depth of injection, which, from the work of other authors (Chapter 2) should be sufficient to encompass any downwards translocation of the metals), or the maximum depth of the soil, whichever was the shallowest. Samples were taken in 60 mm increments, as shown in Figure 4.5b. This somewhat unusual sampling interval was determined by the diameter of the sampling cans, with which it was originally intended to take undisturbed soil samples. The soil was ultimately collected with an unpainted, stainless steel blade and stored in sealed, food-grade polyethylene bags during transport to the laboratory. Samples from the same site were collected within 1 week.

The results obtained from this field trial indicated the importance of completing the suite of injection tine designs, and assessing the role of redox potential in metal distribution. Phase II thus comprised of a second injection, conducted at Broad Meadow (Figure 4.3), there being insufficient space at Honey Park. The lack of variation in metal distribution between soil types indicated by preliminary results from Phase I precluded the necessity for a second soil type in Phase II, especially since variability was seen to be as great within as between soils. The winged tine was employed here, and sewage sludge was injected at a rate of 300 m^3 ha^{-1} into three plots, each 2.4 x 50 m, separated from each other by 2.4 m. The water content at injection was 26 %. Immediately following injection, a) soil disturbance was assessed, as above, and b) field redox experiments were initiated (detailed below). Soils were sampled from a pit face, as above, after seven months. Four replicates were taken.

Results from Phase I and II field trials left some of the metals unaccounted for, and in order to ascertain the mass balance of the metals in sludge-injected soil, a laboratory simulation involving undisturbed soil columns was devised (Figure 4.6). Four columns of rigid plastic piping, with internal dimensions of 192 mm x 300 mm and with their lower edges sharpened were used. The inside of each column was generously smeared with axle grease to facilitate (i) ease of soil extraction from the field, and (ii) quality of the soil:column contact. Columns were filled from Broad Meadow whilst the soil itself was relatively dry, thus minimising the potential for subsequent soil shrinkage away from the column sides. Soil was excavated to the depth of the base of disturbance created by the passage of the tine and the columns placed on this surface. Soil was then removed from around the column to within 10 mm of it. At regular intervals, a uniform pressure was exerted around the rim of the column, gradually filling it with soil. The excess soil is thus shaved away by the column, whilst maintaining good contact between its inner edge and the enclosed soil. After removal from the field, 200 mm-diameter filter funnels containing acid-washed coarse sand, held in place with a glass wool bung, were sealed to the base of the column and the entire ensemble placed on a stand enclosing a collection vessel. It is more usual to contain the soil within the column with a nylon disc, but it has been found that this causes smearing and hence the sealing of conducting channels (Twomlow, 1989). A 20 mm (200 m^3 ha^{-1}) layer of sewage sludge was added to half the columns, and was covered with a 50 mm layer of <2 mm soil, in an attempt to mimic the effect of a greater depth of 'normal' soil. The columns were sheltered from rainfall, but exposed to other field conditions, such as temperature. Every 4 days, 400 ml of rainwater, collected in a stainless steel container, was added to each column, and a sample of the known volume of percolate and of the rainwater (thus allowing the percolate to be corrected for any metal contamination of the rainwater) were analysed for metal content using DCP techniques (Section 4.3.2). It is unnecessary to extract the metals from the solution, but 3 drops HNO_3 and the relevant quantity of $LiNO_3$ were added prior to analysis (Section 4.3.1). The columns were dismantled after 4 months and in increments of 25 mm. Each depth increment was sampled in two concentric rings to check that the soil:column contact had not been compromised, and that no contamination had been caused by the axle grease, which is apparently a source of Mo only (Gomez *et al.*, 1986). Samples were treated according to the criteria laid out in Section 4.3.

4.2.1 SOURCES OF ERROR: 1. FIELD ERRORS

Problems such as uneven rate and depth of application are unavoidable with the injection of sewage sludge (Section 1.4.4). The description of this variability by detailed sampling of plot replicates forms part of the objective of this research, thus no attempt has been made to nullify this effect. However, at Honey Park, excessive wheelslip due to damp surface conditions caused appreciable surface damage and soil disruption on plot 4 (Figure 4.3), forcing an immediate redistribution of sludge away from the tine leg slot, leaving only three replicates of each plot.

In attempting to quantify the variability of the injection process and the subsequent distribution of heavy metals, it is essential that all other variability is minimised. Sampling errors are by far the largest source of inaccuracy, analytical errors being negligible by comparison (Robinson and Lloyd, 1915; Gomez *et al.*, 1986). The use of a blade as a soil sampling implement is generally considered superior to augers or corers in minimising contamination and bias (Cline, 1944). Contamination of the samples can be further reduced in a number of ways. Plots were located as far from roads as was possible, since these are a known source of Pb contamination (Jackson *et al.*, 1987). Self-sealing polyethylene bags were used to eliminate contamination from metal staples, from B and Zn (in paper bags) and between samples by water or dust (Berrow, 1988).

The use of pot and column experiments in heavy metal analysis is a fairly common procedure, and the inherent inaccuracies of using pot experiments to assess the plant uptake of heavy metals has been well documented by authors such as Kuntze *et al.* (1984) and Alloway and Morgan (1987). However, little information exists with reference to the design and accuracy of soil column experiments, although it is known that many authors use PVC columns and grind soil to < 2 mm prior to use in such experiments (e.g. Emmerich *et al.*, 1982; Fuller *et al.*, 1976; Korte *et al.*, 1976). As surface area has been cited as a controlling factor in heavy metal adsorption (Korte *et al.*, 1976; Keefer and Singh, 1986), and since this procedure alters the pore size distribution and continuity, to which soil water movement is directly related (Anderson and Bouma, 1977) and which will therefore affect physical movement mechanisms, this was not emulated here. In addition to the problems that have been anticipated in the design of column experiments in this research (e.g. the washing of water down the inside edge of the column), inaccuracies could arise from the creation of artificial conditions. Kuntze *et al.* (1984), for example, point out that the impedance of runoff may reduce the sideways movement of metals. Although the effect of surface runoff can be assumed to have little effect on injected heavy metals, the washing of metals along the injection slot under field conditions can not be discounted, and results are reported with this limitation in mind.

4.3 LABORATORY METHODS

A variety of laboratory methods are available to assess the metal content of a soil and to characterise that soil in terms of factors that might be expected to influence metal mobility. In order to be of use in this research, however, each method should satisfy the following criteria:

1. Results must be at least representative of the aim of each method. For example, in assessing 'total' metal content, only a pseudo-total result is necessary, as long as there is a constant and known relationship between the result and absolute total concentration, and/or between results.
2. The method must be cheap, accessible and reproducible.
3. As far as possible, methods should comply with EC Directive 86/278/EEC and procedures used by the water industry.
4. For the results to be useful in a wider context, practices should be comparable with those of other analysts within the subject area.

4.3.1. SAMPLE PRETREATMENT

The first essential step in pretreating soil is immediate drying, to reduce the rate of chemical and biological reactions (Wright, 1939; Cline, 1944; Piper 1950). However, it has been suggested that drying soils increases surface acidity and Mn, Al and Fe solubility (Bartlett and James, 1980), although air drying is a lesser culprit than oven drying (Smith, 1990). However, since the disruption caused by drying soil samples in the laboratory can not be distinguished from the corresponding situation in the field (Bartlett and James, 1980), soil samples were air dried at <30 ^{o}C in polyethylene-lined aluminium trays. The percentage difference in water content between an air dried and oven dried (at 105 ^{o}C) subsample was measured as 3 % (Honey Park and Broad Meadow) and 2 % (Colaton Raleigh). Once dry, a subsample was set aside for particle size determinations and the remainder was ground to <2 mm using a mechanical grinder. Stones were removed prior to grinding, as their disintegration may bias the results by adding material not weathered to soil (Hamilton, 1980). Further contamination may be introduced by the grinder itself, but no difference in metal concentration was observed between subsamples that had been ground in this manner and using a ceramic mortar and pestle.

To obtain the sample size needed for analysis, further mixing of the soil was ensured by riffling. This mixing is essential as it reduces the error caused by the heterogeneity of the sludge/soil components (Emmerich *et al.*, 1982).

4.3.2 HEAVY METAL ANALYSIS

A EXTRACTION OF HEAVY METALS

(i) EXTRACTION OF 'TOTAL' HEAVY METALS

EC Directive 86/278/EEC stipulates the use of 'strong acid digestion' to determine the total metal concentration in sludge treated soils. The most popular of these acids are HNO_3, $HNO_3/HClO_4$, HNO_3/HCl (aqua regia), HF/H_2SO_4, HCl or $HClO_4$. Sulphuric acid is unsuitable as it causes precipitation of Pb as $PbSO_4$ or coprecipitation with other sulphates (Balraadjsing, 1974; Seeley *et al.*, 1972). Hydrofluoric acid /$HClO_4$ is the strongest extractant and HF/HNO_3 has been found to consistently extract more Pb than other techniques (Harrison and Laxen, 1977), but both methods are time-consuming due to the extreme care necessary. Similarly, $HNO_3/HClO_4$ acid mixtures may explode when used with high organic matter content soils (Ure, 1990) or sewage sludge, although pretreatment with HNO_3 (Lim and Jackson, 1982) or dry-ashing (Ure, 1991) to remove the organic matter reduces the risk. However, it is unnecessary to use such a strong reagent in the case of heavy metals introduced in sewage sludge as they are seldom bound in silicate forms that require dissolution (Ure, 1983).

Aqua regia is now the most popular of these methods (Ure, 1983), although Berrow and Stein (1983) found little difference in the efficiency of HCl, concentrated (16 M) HNO_3 and aqua regia in extracting elements of interest here (Cd, Cu, Ni, Pb and Zn) while Singh and Narwal (1984) report that HNO_3 is more efficient than aqua regia in extracting Cd, Ni, Pb, Co and Ni. The WRc usually uses XRF (X-Ray Fluorescence) on solid samples, but uses HNO_3 as an extractant or for comparative purposes, where necessary (e.g. Davis and Stark, 1981; Powlesland, 1986; Hall and Powlesland, 1986). Similarly, SWW, who provided the sludge for these experiments, use HNO_3 for sludge and soil analysis (K. Boult, pers. comm., 1991) and HMSO (1982) recommends the use of HNO_3 for the Cd, Cr, Cu, Pb, Ni, and Zn assay of sewage sludge. Bradford *et al.* (1975) found a favourable comparison with results from the complete acid decomposition of soil with those from HNO_3 digestion. Williams *et al.* (1985) have compared HNO_3 with the 'par bomb' method of extraction and found only slight differences with metals such as Zn and Cu. John (1972) extracted 90 % of soil Pb with HNO_3 and Burau (1982) considered that this method could extract '80 % or more' of the total Pb in most soil samples. Concentrated HNO_3 is the preferred method with sediments because it is associated with minimum problems of precipitation (Forstner, 1984). Emmerich *et al.* (1982) recorded an 87-99 % recovery of Cd, Cu, Ni and Zn, explaining the shortfall in terms of sampling error, rather than analytical error. Deficiencies are, however, consistent and are considered acceptable when used in conjunction with atomic absorption spectrometry (AAS) due to advantages over other extractants, such as minimised matrix effects and adaptability to routine analysis (Cao *et al.*, 1984).

The present author has found that the digestion of soils with 16 M HNO_3 at 135 ^{o}C in a TURBOSOG acid digestion system extracts between 70 % and 80 % of Cu, Ni, and Zn (depending upon the organic content of the soil) and between 110 % and 120 % of Cd and Pb (but 77 % of Pb when the soil is organic) (Table 4.4, Section 4.3.4). The recently popular method of microwave digestion was neither available or considered necessary, especially in view of its limited capability in terms of sample numbers. Concentrated (16 M) HNO_3 thus satisfies all the selection criteria and was chosen as a method of identifying total metal concentrations in soil and sludge in this study. A ratio of 2 g soil:30 ml acid was used, heated at 135 ^{o}C for 2 hours. The selection of this procedure is detailed in Appendix A1.1. The volume of solution obtained after filtration was determined from its mass, assuming a density of 1.42 g cm^{-1}. This is not affected by heating (Figure A1.1).

(ii) EXTRACTION OF PLANT-AVAILABLE HEAVY METALS

A measurement of 'available' metal concentrations is useful as an indicator of their mobility and effect on plants. The term is used here only loosely, as elements sampled by an extracting solution may be chemically unavailable to plants, and because trace elements may be stored within the plant or rendered unavailable by external factors such as drought (Atkinson, 1988). A range of extractants can be used, including dilute HCl or HNO_3, acetic acid, $CaCl_2$, EDTA and DTPA, of which EDTA and DTPA are the most popular. Calcium chloride is frequently used when pH is an important consideration, as it has less effect on the natural soil pH (McLaren and Crawford, 1973). In experiments comparing the use of ammonium acetate, EDTA, $NaNO_3$ and $CaCl_2$ to identify Cd and Zn availability, Sauerbeck and Styperek (1985) found that EDTA vastly overestimated 'availability' of metals, yielding results only slightly less than those from aqua regia extractions. Inversely, $NaNO_3$ extracted Cd in quantities too small to be detected. Instead, they advocate the use of either 0.5 M or 0.1 M $CaCl_2$ as it reflects the differences created by soil type, metal source and pH changes 'very well'. Similarly, Sanders and Adams (1987) report that CEC and pH will alter $CaCl_2$-extractable Zn, Cu and Ni. Comparing $CaCl_2$ to EDTA and DTPA, Sanders and Kherbawy (1987) and Sanders *et al.* (1987) describe DTPA and EDTA as extracting 'ill defined fractions' and being independent of pH and CEC. The preferred method was 0.1 M $CaCl_2$. Similarly, Singh and Narwal (1984), investigating the use of HCl, NH_4OAc and DTPA to indicate plant availability, found that none of the extractants gave a reliable prediction, whereas $CaCl_2$ extractability has been reported as 'remarkably' proportional to plant uptake rates (Sauerbeck and Styperek 1984). This is reiterated by Alloway and Morgan (1987), who cite 0.05 M $CaCl_2$ as one of 'the most suitable' indicators of bioavailable Cd in polluted soils.

The soil : $CaCl_2$ ratio, if it is specified, is usually 1:2.5 (e.g. Sauerbeck and Styperek, 1985, and the WRc), and this ratio was used in the present work. Extraction time and solution concentration (0.05 M or 0.1 M) are not, however, unanimously agreed. The extraction procedure selected used 20 g soil:50 ml 0.1 M $CaCl_2$, shaken for 2 hours in polypropylene conical flasks (the rationale for which is presented in Appendix A1.2). After filtration, the solution was observed to be compromised by the growth of septate mycelium (even at 4 ^{o}C) and adsorption of metals to the side of the container. This problem was obviated by the addition of a few drops of HNO_3 after filtration. The volume of the filtrate was determined by mass, assuming a density of 1 g cm^{-1}.

B INSTRUMENTATION

(i) ATOMIC ABSORPTION SPECTROMETRY

EC Directive 86/278/EEC on the disposal of sewage sludge to agricultural land stipulates the use of Atomic Absorption Spectrometry (AAS) in 'total' heavy metal analysis, and this procedure is considered sensitive enough to determine 'available' (acetic acid- and/or EDTA-extractable) Cd, Cu, Ni, Pb and Zn without pre-concentration (Ure,1991). AAS was therefore selected for use. Operating instructions and the principles of operation have been detailed many times (e.g.Ure, 1990 and 1991; Hamilton, 1980; HMSO, 1979; Isaac and Kerber, 1971; Kahn, 1968; Robinson, 1966) and are therefore only briefly outlined in Appendix A1.3.1. Interference problems and sources of inaccuracy are similarly ubiquitous and are investigated in Appendix A1.3.2 and A1.3.3. The AAS used was the Baird Alpha 4. An air/acetylene flame was used in all cases.

(a) PRECISION AND ACCURACY

Statements of precision, accuracy and detection limits are often omitted in the reporting of results, and when included, often refer to the best case. For example, Baker and Suhr (1982) cite a precision of better than ± 1 %, but qualify this as being 'in favourable circumstances'. Routh (1987) quotes a precision of ± 0.5-1 %, but points out that this is only attainable at solution concentrations at least 50 times greater than the detection limit. The same author states that long-term precision (i.e. over the course of a days analysis) is considerably degraded to a range of ± 1-3 %. As no other workers have made this distinction, it is likely that the less representative short-term precision has been used.

HMSO (1979) state that AAS precision should be ±1-5 %, but in a later work, present figures as high as ±4.9-6.9 % for Cd, Cu, Pb, Ni and Zn (HMSO, 1987). Similarly, Paveley *et al.* (1988) obtained a precision of only ±9.6 % and ±9.3 % for Pb and Zn, respectively. The present author has encountered long-term precision ranging from ±1-50 %. Any results with a precision of >5 % were discarded.

The range of stated detection limits is again large, varying from an order of 10^{-3} (Routh, 1987; Baker and Suhr, 1982; Isaac and Kerber, 1971) to 10^{1} (HMSO, 1987), although it is generally agreed that Pb has the highest detection limit and Zn and/or Cd the lowest. Since the detection limit is frequently calculated as 2 times the standard deviation of the concentration of the lowest standard (Baker and Suhr, 1982), the same problems as those encountered in reporting precision are likely to arise. Some of the quoted detection limits are so low as to render them useless, as metal concentrations in the blank solution exceed the apparent detection limit (Baker and Suhr, 1982). In addition, the presence of interference effects and the use of optimisation procedures that are not viable for routine work may increase the practical detection limit by a factor of 5 or 10 (Ure, 1991). The worst case detection limits included in this research were (in mg kg^{-1}): Cd: 0.1, Cu: 0.05, Ni: 0.02, Pb: 0.4, Zn: 0.02.

Accuracy is calculated as the percentage deviation from the known concentration of a standard. It depends on the extent to which interference effects and sources of inaccuracy can be overcome and is therefore unique to each analyses and is not mentioned by the above authors. Accuracy is cited as being as low as ±20 % (HMSO, 1982), but is taken as a worst case of ± 5% in this research, lower figures being discarded.

(ii) DIRECT CURRENT PLASMA ATOMIC EMISSION

Despite the many advantages cited for AAS (e.g. Paveley *et al.*, 1988), the method was found to be too problematic and not sufficiently sensitive for use in this research, so an alternative was sought. With reference to relevant literature, the obvious option is ICP (inductively coupled plasma) or XRF techniques, but neither were available for the analysis of the existing volume of samples.

Direct Current Plasma (DCP) is a less well known method of analysing metal concentration, but has been accepted as a valid test procedure by organisations such as the USEPA, who describe it as 'substantially equivalent in both precision and accuracy to the techniques [ICP, AAS, colorimetry] already approved' (EPA Federal Register, 1990). In addition, the DCP has advantages over flame AAS such as a multi-element capability better than that of some ICPs (Broekaert, 1987), reduced interference problems, long linear working ranges (Sparkes and Ebdon, 1986b), a sample throughput rate of 1000 determinations per hour (at maximum multi-element capability) compared to 250-350 AAS determinations per hour (Routh, 1987) and is especially useful for samples with a high concentration of dissolved solids (Broekaert, 1987), whilst having a similar capacity as ICP MS (Routh, 1987; Keliher *et al.*, 1988). An explanation of DCP instrumentation used in this research is given in Appendix A1.4.1. Two DCPs were used in this research - a SpectraSpan III and a SpectraSpan VB ARL (both made by SpectraMetrics Incorporated).

(a) PRECISION AND ACCURACY

The DCP has had only limited use for soil samples digested by acid, so there is a paucity of information regarding precision in these cases, but for a range of unspecified liquid samples, Routh (1987) suggests a short term precision of 0.5-1 % and a long term precision of 2-5 %. For a geological samples, Feigenson and Carr (1985) attained a precision better than 2 % for most metals. The present author has achieved a long term precision and accuracy better than 5 %, despite the claim of Broekaert (1987) that the compromise conditions necessary for the multi-element mode of the DCP may affect its performance.

(iii) A COMPARISON OF AAS AND DCP-AE PERFORMANCE

The vast majority of the heavy metal analysis in this research was conducted using DCP, but some early work was accomplished with AAS. For this reason, and to facilitate comparison with contemporary research, it is desirable to compare the performance and output of the two instruments. Overall, the literature (e.g. Routh, 1987) considers that whilst the DCP is a 'better' method of analysis than AAS, results obtained by either method are comparable. These statements need to be validated by a specific comparison of the instruments used. Copper and Zn are used as examples, as Cd concentration in samples was frequently less than the detection limit of the AAS; the use of background correction increased the detection limit of Pb with AAS to greater than the soil concentration; and excessive problems were encountered with the Ni lamp. Zinc is of particular interest as this is among the group of metals (Hg, Zn, Cd, Pb, As) that are better determined using AAS (Baker and Suhr, 1982). The same authors consider that both AAS and plasma emission spectrometry are equally efficient in analysing Cu concentration.

Performance, in terms of detection limits, precision and accuracy of standard solutions, is very similar for both instruments. Performance in terms of sample analysis is a more significant appraisal, as more problems are experienced in this case. Analysis of a complete set of subsamples from a pit face (n=50) was conducted using both AAS and DCP techniques. The average concentration for Zn in the samples was considerably greater (29 %) when measured using DCP, with a similar discrepancy in the range of Zn results (32 %). These discrepancies are caused by a few individual results, as reflected by a difference in RSD of 25 %. Therefore the error may lie with subsampling or extraction techniques. Conversely, a maximum discrepancy of 6 %, representing only 0.5 mg kg^{-1}, was observed between the results obtained for Cu concentration, which are therefore considered so similar as to be directly comparable. Both sets of results are therefore considered acceptable, as long as relative, rather than absolute, Zn concentration is used.

4.3.3 SOIL CHARACTERISATION

A. SOIL pH

The pH of disturbed soil samples can be measured electrometrically with 1 : 2.5 w/v suspensions in either distilled water, 0.01 M $CaCl_2$ (White, 1969; Avery and Bascomb, 1974; Alloway, 1990) or 1 N KCl (McLean, 1982). However, the dilution of the soil solution by water causes the expansion of the diffuse double layer of cations, and yields an apparent pH higher than the actual pH (Alloway, 1990), illustrated by White (1969), who, after increasing the soil:solution ratio to 1: 10, observed a pH increase of 0.35 units when measured in water, compared to an increase of only 0.01 units measured in 0.01 M $CaCl_2$. This concentration of Ca^{2+}, safely assumed to be the most abundant cation in a soil solution, approximates that of the soil solution, and therefore prevents its dilution and maintains equilibrium. A more effective masking of soil solution differences is performed by KCl, but this method also displaces more exchangeable

H^+ and Al^{3+} into solution, lowering its pH (McLean, 1982). In addition, the use of dilute salt solutions, rather than water, obviates errors introduced by extraneous electromotive forces (McLean, 1982), and suspending the soil in 0.01 M $CaCl_2$ minimises the 'suspension effect' (Graham, 1959; Grewling and Peech, 1960; Woodruff, 1967). Briefly, this effect refers to the measured pH difference between the sediment and supernatant, and has been ascribed to differences in H^+ concentration with distances from soil particles (McLean, 1982), or liquid junction potential effects (Coleman and Thomas, 1967). Since pH is such an important factor in heavy metal mobility (Section 2.2.2), these differences in accuracy are considered significant. Consequently, the $CaCl_2$ method was selected for use.

B. CATION EXCHANGE CAPACITY

There are a variety of methods available to identify the cation exchange capacity (CEC) of a soil, most of which involve forcing the cation exchange reaction to completion by saturating exchange sites with an index cation (Bohn *et al.*, 1979), usually ammonium ions (Talibudeen, 1981). However, these methods are often time consuming and unsuitable for soils rich in organic matter (Bascomb, 1964), and errors may be introduced in rinsing excess cations from the soil (Okazaki *et al.*, 1963). In selecting the most appropriate method of determination for CEC, it was considered significant that the Soil Survey and Land Resource Centre has adopted Bascomb's method (1964) using Ba^{2+} as the index ion. This procedure employs the principle that the amount of Ba^{2+} displaced from the soil after saturation is indicative of the CEC of the soil, and has been favourably compared with techniques using NH_4^+ (Bascomb, 1964). The method also removes the potential for error presented by: (a) $CaCO_3$ solubility (by maintaining an alkaline pH), (b) hydrolysis during removal of the index solution (by eliminating exhaustive washing), (c) the presence of slightly soluble zeolite minerals, which provide exchange sites for monovalent cations (such as index ions NH_4^+, K^+) but not divalent or trivalent ions, such as Ba^{2+} (Bascomb, 1964), and d) the inefficient exchange of exchangeable Al, and its hydroxy forms, by monovalent cations (Rhoades, 1982). This method was selected for use (after experimentation described in Appendix A1.5), but it is recognised that this procedure is sometimes considered as being related to the 'potential', rather than existing, CEC (Thomas, 1982).

C. ORGANIC MATTER CONTENT

A measurement of the organic matter (OM) content is essential in characterising a soil, as it has a major influence on the chemical properties of soil (Alloway, 1990). Typical values quoted for the OM content of British soils are variable, ranging from 0.5-5 % by weight (Bohn *et al.*, 1979) to 7.9-9.5 % (Simpson, 1983). A great deal of research has been devoted to fractionating organic matter and assessing its effects on heavy metal behaviour in soil (e.g. Sposito *et al.*, 1984; Dudley *et al.*, 1987; Holtzclaw *et al.*, 1978; Karapanagiotis *et al.*, 1990; Castetbon *et al.*, 1986; DeNobilli *et al.*, 1985; Newland *et al.*, 1976), but as an instrument in differentiating soil type, a measure of total OM content is sufficient.

Traditionally, an expression of total OM content of a soil is assessed by either loss in weight after ignition or by dichromate acid digestion followed by titration of excess dichromate (Alloway, 1990). Loss on ignition intrinsically overestimates OM contents, whereas organic carbon, assumed to account for anything between 58-60 % (Alloway, 1990) and 48-58 % (Nelson and Sommers, 1982) of OM, underestimates the total organic content of the soil. Research undertaken to delimit the relationship between OM and OC has eventually concluded that, although constants exist, they are different for each soil and soil horizon (Broadbent, 1965). Despite these limitations, a constant and linear relationship might be expected between the results from the two methods, and an identification of any association would serve as both a measure of quality control and a basis for comparison. Figure 4.6 plots LOI against OC results from the Seale-Hayne site. The linear relationship between the two is described as:

$$LOI = 4.7 + 0.8(OC) \qquad r^2=0.976 \qquad \text{equation 4.1}$$

Both methods have been employed here, to satisfy different aims. Neither purport to assess actual OM content, it being 'not an appropriate or an accurately measurable entity' (Nelson and Sommers, 1982). They are used instead as an index.

(i) LOSS ON IGNITION

In an attempt to identify the presence of sewage sludge in selected soils, loss on ignition (LOI) was used to gain a 'thumbnail' sketch. The method can only be used as an index of

OM content because: a small amount of ash always remains, there are other sources of weight loss on ignition (volatilisation of sulphides, loss of structural water in some clays at 450-600 ^{o}C, and loss of CO_2 from calcareous soils at very high temperatures) and because no distinction is made between elemental and organic carbon. Maintaining furnace temperatures at 400 ^{o}C and igniting soils for a relatively short period of time (<24 hours) somewhat reduces these errors, although some inorganic weight loss is inevitable. Despite this, temperatures such as 850 ^{o}C (Avery and Bascomb, 1974) are often used. A more substantial reduction of error can be achieved by pretreating the soil with HCl/HF to remove hydrated mineral matter (Rather, 1917), but besides being time-consuming, this step also introduces errors of its own (Nelson and Sommers, 1982). Since a rapid estimate of relative OM content, rather than an absolute determination of OM, was a priority in this case, the procedure adopted is similar to that cited by Alloway (1990), although the time period has been reduced for convenience to 4 hours. Repeated ignition of the same soil samples produced a variability of <0.01 %.

(ii) ORGANIC CARBON

The Organic Carbon (OC) content of soil can be determined by gravimetric techniques (wet or dry combustion), or by titrimetric procedures based on Schollenberger's method (1927) using dichromate and sulphuric acid. The latter practice has elicited popularity with its relative rapidity and a number of variants are available. Of these, the Tinsley III method (Kalembasa and Jenkinson, 1973) was selected for use in this study, due to its precision and rapidity. A justification of this choice is made in Appendix A1.6.

D. PARTICLE SIZE ANALYSIS

Particle size analysis is usually conducted using the pipette or hydrometer methods (B.S.I. BS1377, 1975). The former is the more popular as the hydrometer method is not suitable if less than 10 % of the material passes the 63 µm test sieve, and is fraught with inaccuracy. The pipette method was therefore selected, using test sieves with 2 mm, 500 µm, 250 µm and 63 µm apertures.

Initial analyses revealed that there was little variation in textural class with depth for each soil type, as described by Clayden (1971) and Findlay *et al.*. (1984). Therefore analysis was restricted to those samples taken at the surface, at injection depth and at the base of the sampled profile.

E. SOIL IRON AND MANGANESE CONTENT.

A measurement of the content of Fe and Mn available for reaction is often used in characterising soils, and especially soil horizons (Kabata-Pendias and Pendias, 1984). Much of this is in the form of oxides, either in discrete particles, as coatings on soil minerals or as cement between mineral particles (Olson and Ellis, 1982). The measurement of Fe and Mn oxides can provide a secondary indication of redox status, in that gleying decreases their soil concentration (Alloway, 1990b). Generally, dithionite, oxalate or pyrophosphate solutions are used as extractants, each identifying different forms of the two metals (McKeague and Day, 1966). Criticisms have been levelled against all methods, as their extraction ability is influenced by soil characteristics, especially in the B horizon (Page and De Kimpe, 1989). Specifically, sodium dithionite has been observed to overestimate the free Fe oxide content of soil (Deb, 1949; Gorbunov *et al.*, 1961; Lundblad, 1934), whereas oxalate has been shown to underestimate soil contents of available Fe and Mn (Schwertmann, 1964). Conversely, pyrophosphate determinations are especially suitable for the purpose of this research, predominantly extracting those metals associated with organic matter (McLaren and Crawford, 1973; Stover *et al.*, 1976; Alloway *et al.*, 1979), or 'available' metals in inorganic compounds (Page and De Kimpe, 1989). The version of this method adopted by the Soil Survey (Avery and Bascomb, 1974) was selected for use in this study.

F. REDOX POTENTIAL

The quantification of anaerobiosis in soils can be accomplished via measurements of air-filled porosity, respiration rate, gaseous diffusion, the composition of soil gases, the identification of reduced soil constituents, or the electrochemical measurement of redox potential (Glinski and Stepniewski, 1985; Stolzy and Fluhler, 1978). Redox potential is considered to be 'one of the most important characteristics of soil aeration status' (Glinski, 1985). Electrochemical assessments of redox relationships are generally expressed in terms of Eh or pE (Section 2.2.2), but despite the compatibility of pE with units of mole l^{-1} and its attendant ability to be treated as other reactants, Eh is often the preferred unit of measurement (Lindsay, 1979). Techniques of redox assessment have been called into question by many authors, whilst others claim that accurate and consistent measurement can be easily achieved. Bohn (1971) suggests that the disparity is created by the treatment of redox and equilibrium potentials as synonymous. As a result of the low concentration of redox couples in oxidised environments (Stolzy and Fluhler, 1978), Lindsay (1979) warns that Pt electrodes are somewhat unreliable in highly oxidised soils (i.e. where $pH + pE \geq 18$), and Bohn (1971) concurs, with the statement that 'redox potential measurements would appear to be most useful in reducing conditions'. Since these are the circumstances under which redox measurements are intended to be made in this research, this criticism of Pt electrodes can be rejected. Mueller *et al.* (1985) have found that Pt electrodes perform uniformly, even under 'dissimilar' soil conditions and in pot experiments. Comparing three different methods of measuring aeration (redox potential, oxygen flux and the concentrations of dissolved and gaseous oxygen), Blackwell (1983) found that Pt electrodes were more indicative of the general (rather than large pore) situation than methods involving destructive sampling. Still, technical problems such as poor contact between the electrode and the soil, the slow reaction between redox couples and Pt electrodes, and the heterogeneity of the medium need to be addressed in the design of a redox experiment.

Platinum is selected for the electrode as an inert electrical conductor that theoretically responds only to the potential of the electrodes (Bohn, 1971). Although this statement applies to other materials (e.g. gold, graphite and tungsten), most have been found to be unresponsive to redox changes (Bohn, 1968). Ideally, the potential of each redox couple should be measured by an electrode responsive to that couple only, but the disadvantages of time, expense and potential error outweigh those inherent in the use of Pt electrodes as a measurement of all the redox couples together (Bohn, 1971). It should be noted, however, that the possible errors mentioned above, and the unmeasured influence of the activity of micro-organisms on redox potential (Bohn, 1971; Lindsay, 1979), reduce the results yielded by Pt electrodes to 'mere indications' of the tendency of the soil to be oxidised or reduced (Leiros and Guitian Ojea, 1985). In addition, redox can only be measured as a ratio of oxidised:reduced material, with no indication of the total quantities involved (Stolzy and Fluhler, 1978) and is thus only semi-quantitative (Ponnamperuma, 1972).

Platinum electrodes were constructed according to the scheme set out by Vepraskas and Bouma (1976) and Mueller *et al.* (1985). The probes were standardised in a standard ferrous-ferric solution (Light, 1972). This solution has an Eh of +675 mV at 20 °C (Vepraskas and Bouma, 1976), and any deviation from this value can be almost entirely attributed to the electrodes as the solution is not sensitive to minor concentration errors or temperature changes (Light, 1972). Any electrode differing from this value, and/or the average reading obtained in water, by >± 10 mV was discarded. This cut-off value is selected as the mixed potentials that comprise the overall redox potential render any greater degree of precision insignificant (Mueller *et al.*, 1985). The output of the redox probes were monitored continuously with a Grant 1200 Series 'Squirrel' data logger, using a BDH calomel reference electrode. Observed redox measurements were adjusted to Eh by adding +245 mV, the standard potential of the calomel half cell (Zobell, 1946).

To assess the impact of redox potential, it was intended that selected portions of the injection run should be maintained in a waterlogged state. However, it proved impossible to maintain a constant anaerobic state, both spatially and temporally. In addition, the volume of sludge injected proved to be significantly different in one of the three plots. The experiment therefore can not be considered adequately replicated and was discontinued. Instead, a laboratory-based trial was devised.

The laboratory trial consisted of three treatments (control, sludge amended/freely draining and sludge amended/waterlogged), replicated three times. Experiments were conducted within soil columns similar to those described in Section 4.2, with an inner radius of 192 mm and 300 mm in length. Holes with a diameter of 10 mm were drilled into the sides of the column at depths of 100 mm (corresponding to the sludge layer) and 200 mm to accommodate the redox probes, which were inserted through the column sides and sealed in place with silicone rubber sealant (Figure 4.7). The columns were filled with disturbed soil from Broad Meadow only, since it is anticipated that differences far greater than those resulting from the use of different soil types under such conditions would be required to modify metal behaviour. The soil was extracted from the field dry to ensure that there would be no subsequent shrinkage of the soil away from the sides of the column. Earthworms were removed to eliminate the effect of pedoturbation on metal movement, and the soil thoroughly mixed, as recommended by Patrick and Mahapatra (1968) as a means of reducing variation among replicate readings. Finally, soil was tightly re-packed into the columns.

In the laboratory, 200 mm diameter filter funnels were sealed onto the base of the columns. The funnels were filled with acid-washed sand, held in place with a glass wool plug. The output from the funnels of the sludge-amended/waterlogged treatments was controlled by creating a manometer from the column and a length of 15 mm-diameter rubber tubing (Figure 4.7). Sewage sludge was placed on the soil surface at a rate of 300 m^3 ha^{-1} (i.e. to a depth of 30 mm) and covered with soil to a depth of 50 mm. Prior to emplacement, the soil cap was ground to <2 mm in an attempt to emulate the effect of a greater depth of 'normal' soil on the oxidation status of the lower horizons. Redox potential was recorded every hour by the data-logger. Due to the inter-relationship of pH and Eh, simultaneous, *in situ* pH measurements were made, but no adjustment of redox to pH has been conducted, due to the difficulty in obtaining representative values. The Eh value of the soil is usually adjusted to pH 7 by -0.060 V per unit pH (Zobell, 1946), although this practice has been criticised as having little theoretical or experimental justification (Bohn, 1968). Twice weekly, distilled water was added to the columns in an amount approximately equal to twice the long-term monthly rainfall average (i.e. 600 ml), as recorded by the Seale-Hayne weather station. The control and sludge amended/freely draining treatments were allowed to drain, and the percolate was collected and both a 30 ml aliquot of the measured volume and a 30 ml sample of the input water were analysed for metal content using DCP techniques. The sample was analysed without any further treatment, except for the addition of 3 drops HNO_3 and the relevant quantity of $LiNO_3$ (Section 4.3.2). The sludge amended/waterlogged treatment was saturated from the base, to prevent entrapment of air, and prevented from draining. Water was added only as required to maintain a waterlogged state. Throughout the experiment, the laboratory air temperature was a constant 25 °C. After 4 weeks, all columns were allowed to drain and 500 ml of a methylene blue solution was added to the columns to ascertain the quality of the soil:column contact and of the packing of the soil. No percolation beyond a depth of approximately 100 mm was detected. The columns were dismantled in 25 mm increments and the soil treated as per the method laid out in Section 4.3.1.

Although inaccuracies occurring within individual redox probes may be identified by comparison with its replicate, some errors may be ubiquitous. For example, leaving probes *in situ* for the duration of the experiment has been identified as potentially problematic (Blackwell, 1983). However, the removal, cleaning and reinsertion of probes would create additional problems, such as the drainage of saturated columns and the oxidation of the surrounding soil, in this experiment. In addition, McIntyre (1970) and Bailey and

Beauchamp (1971) argue that few 'poisoning effects' occur in mineral soils. Rickman *et al.* (1968) and Blackwell (1983) report no appreciable difference in the performance of probes left *in situ* for periods in excess of four weeks. The performance of redox probes may also be affected by the movement of water through a soil profile (Swartzendruber and Gairon, 1975), but this can be identified by the continuous monitoring of the meter readings. Erratic results are considered to be indicative of this problem (Blackwell, 1983), but no such effect was observed. The quality of the soil saturation that can be achieved with this method is somewhat questionable - more established procedures employ vacuum saturation (Stibbe *et al.*, 1970), but this is impractical for the relatively large columns employed here. Instead, the redox probes are used to both monitor the quality of, and conduct, the experiment.

4.3.4 ANALYTICAL ERROR AND QUALITY CONTROL

Some degree of analytical error is inevitable with any procedure, arising from both intrinsic inaccuracies in the method itself (which have been dealt within the relevant section of this chapter) and from transgressions in the handling of materials and execution of the method. The use of quality control procedures described in this Section identifies the extent of these problems as they arise. The maximum extent of these errors, above which results were rejected, are presented in Table 4.4.

A. CONTAMINATION

Contamination of soils and solutions is one of the largest sources of error encountered in analysing soils (HMSO, 1984). Day-to-day contamination is minimised by thorough cleaning of all plastic- and glass-ware, followed by soaking in 2 % HNO_3, at least overnight. Sub-samples were obtained by riffling, and no excess soil or chemical was returned to the bulk sample or solution. Soils and soil extracts were kept in sealed containers to reduce contamination from gases (Cline, 1944) and dusts. All chemicals used were at least 'AnalaR' grade, and all water was distilled at least once. Contamination may also arise from laboratory tissues, disposable dispenser tips and filter paper (Hamilton, 1980), and is almost impossible to avoid. In order to minimise the effect on results in these cases, identical materials were used for all analyses, and since the chemical assay may alter from batch to batch (Ure, 1990), a record was kept of batch numbers and corresponding soil analysis. No significant deviations attributable to this factor were observed.

B. QUALITY CONTROL

Inherent, unavoidable or unknown errors were monitored by the implementation of quality control procedures, such as standard addition and the use of standards and blanks randomly dispersed throughout the run. Error can be further minimised by standardising the procedure for all samples - for example, using the same balance for all measurements of mass. The maximum standard error accepted for analytical procedures are presented in Table 4.4.

Heating blocks and muffle furnaces are notorious for introducing inaccuracy through the presence of 'hot-spots' (Hamilton, 1980). With heating blocks, this can be minimised by the use of insulating shields around the perimeter, and a bias in results can be avoided in both cases by randomly allocating the position of the sample. Variability was monitored by the use of internal standards - a bulk sample made up of a variety of subsamples from samples from both soil types, and including both sludge-treated and control soils. The standard soil was ground *en masse,* sieved to <500 µm and thoroughly mixed before use. Standard soils were analysed both in batches and randomly in 'normal' batches for each method.

The efficiency of heavy metal analysis is checked on a short-term (consecutive) and long-term (throughout the day) basis with element standards, the results of which are reported in Section 4.3.1. Randomly selected samples were retained from each days work to check both sample deterioration and daily variation. If any sample deterioration was discovered, the remaining analysis was conducted on new samples. Day-to-day variation is not reported as results were adjusted accordingly and the error thus eliminated. The percentage metal recovery of the method was analysed using standard soils. The results encompass both the efficiency of HNO_3 in extracting the metals and errors encountered in the method. The soils used were Community Bureau of Reference (BCR) certified reference material 142 (trace elements in a light sandy soil) and 143 (trace elements in a sewage sludge amended soil). A comparison of the absolute total (reference) metal content and the pseudo-total metal content found by the method of analysis used in this research is provided by Table 4.3. All results are substantially, but consistently, biased. This is to be expected, as the HNO_3 method does not purport to extract all the metal present (Section 4.3.1). The percentage recovery from BCR 143 is generally better than that from BCR 142, which is again the anticipated result as metals in sewage sludge are presumably more available to HNO_3 than those in soil. The concentration of Cd in the soil extracts was greater than the detection limit of the equipment, but was so close to it that subsequent calculations produced anomalously high results. As such, these are not presented here, and all discussion regarding Cd concentrations will treat them as relative, rather than absolute, values, as standard addition techniques indicate that these, at least, are correct.

South West Water (SWW) has analysed all sewage sludge samples used in this research, so it is appropriate that any comparison should include their laboratories. Usefully, SWW is a participant in WRc's 'aquacheck' programme (comparing the heavy metal content of soil, sludge and water) and apparently achieves results within 10 % of the average of all participating laboratories for the metals of interest here. From a duplicate analysis of SWW samples, this author obtained results within 14 % (± 13 %) of those from SWW. No information is available regarding the standard deviation of the SWW analysis.

Finally, blanks were used where appropriate, and the result considered the 'base line' of subsequent analysis. It is insufficient to use the chemical straight from its container as it may be modified in use (Hamilton, 1980). Instead, the reagent was treated in exactly the same way as if it were being used in analysis - for example, a HNO_3 blank was heated and filtered in batches with acid digestions of soil.

4.4 STATISTICAL ANALYSIS

Statistical analysis of soil factor data is complicated by the fact that data may or may not be normally distributed: for example, CEC and OC data is normally distributed at all sites, but whilst Fe concentration is normally distributed at Honey Park and Colaton Raleigh, it is slightly negatively skewed at Broad Meadow. Whilst non-parametric statistics overcome this situation, they are less powerful. Analysis of variance (the *F*-test) and the related *t* test are, however, relatively insensitive to the violation of their assumptions (robust), although in extreme cases the conclusions that they infer will be somewhat conservative (Donaldson, 1968). These tests are therefore suitable for use for analysis of all soil factors, thus allowing inferences to be made about the relationship between factors and between sites. Multiple and step-wise regression analysis, used to describe the relationship between soil factors and metal behaviour in Chapter 8, is also a parametric test, but is again very robust if it is used only for descriptive purposes (Norcliffe, 1982).

Where possible, statistical analysis was conducted using MINITAB software.

TABLE 4.1 TIMING OF INJECTION AND SAMPLING OPERATIONS

OPERATION	PHASE I		PHASE II
	HONEY PARK	COLATON RALEIGH	BROAD MEADOW
INJECTION:	13.4.88	14.4.88	21.9.89
tine*	S, P	S, P	W
rate*	M, H	M, H	H
SAMPLING:			
shear strength	9.5.88	11.5.88	11.10.89
		21.4.90	
soil (auger)	8.5.88	10.5.88	-
	11.7.88	18.7.88	-
soil (pit)	28.10.88	3.11.88	10.4.90

* where: S = straight tine, P = paraplow, W = winged tine

M = 220 m^3 ha^{-1}, H = c. 300 m^3 ha^{-1}

TABLE 4.2 SOIL VARIABILITY 1: HONEY PARK

horizon	Ap	B	BC
depth (cm)	8-25	15-25	12-20
colour*	br./dk.br./gr.br.	dk.r.gr./dk.gr.br.	gr.br./dk.gr.br.
roots (fibrous)	abundant	abundant	few
boundary	diffuse	diffuse	diffuse
stones (%)	9-14	15-23	17-42
sand (%)	11-31	13-25	13-22
silt (%)	39-47	44-48	43-66
clay (%)	22-45	17-44	21-35
OC (%)	10-12	7-9	4-6
pH ($CaCl_2$)	5.4-5.5	5.8-6.1	6.0-6.3

*Colour determined with Munsell Soil Colour Charts: dk.=dark, br.=brown, gr.=grey, r.=red.

TABLE 4.2 contd SOIL VARIABILITY 2: BROAD MEADOW

horizon	Ap	B	BC
depth (cm)	8-18	15-22	15-20
colour*	dk.br.	br./dk br or gr.br.	dk.gr.br./gr.br.
mottles	none	none/common	none/many
roots (fibrous)	abundant	abundant/few	few
boundary	diffuse	diffuse/clear	gradual/clear
stones (%)	0.1-1.0	2.5-3.4	1.0-3.0
sand (%)	6-13	11-15	7-16
silt (%)	45-55	50-63	44-54
clay (%)	39-47	22-43	28-48
OC (%)	8-9	4-5	2.5-3.0
pH ($CaCl_2$)	4.9-5.8	6.1-6.3	6.3-6.4

*Colour determined with Munsell Soil Colour Charts: dk.=dark, br.=brown, gr.=grey, y.=yellow.

TABLE 4.2 contd SOIL VARIABILITY 3: COLATON RALEIGH

horizon	Ap	Bh	B2
depth (cm)	17-30	20-30	7-20
colour*	br.dk.br./dk.y.br.	dk.br./br.dk.br.	stg.br./br.dk.br.
roots (fibrous)	abundant	abundant/few	none
boundary	diffuse	gradual	sharp
stones (%)	0-4	0-1	0.5-2.0
sand (%)	40-60	40-55	50
silt (%)	33-41	32-40	35
clay (%)	10-15	12-20	15-17
OC (%)	5.5-6.7	2-3	<2
pH ($CaCl_2$)	4.5-5.1	4.4-5.5	4.4-5.5

*Colour determined with Munsell Soil Colour Charts: dk.=dark, br.=brown, y.=yellow, stg.=strong.

TABLE 4.3 A COMPARISON OF ELEMENTAL CONTENT OF REFERENCE AND SAMPLE SOILS (mg kg^{-1})

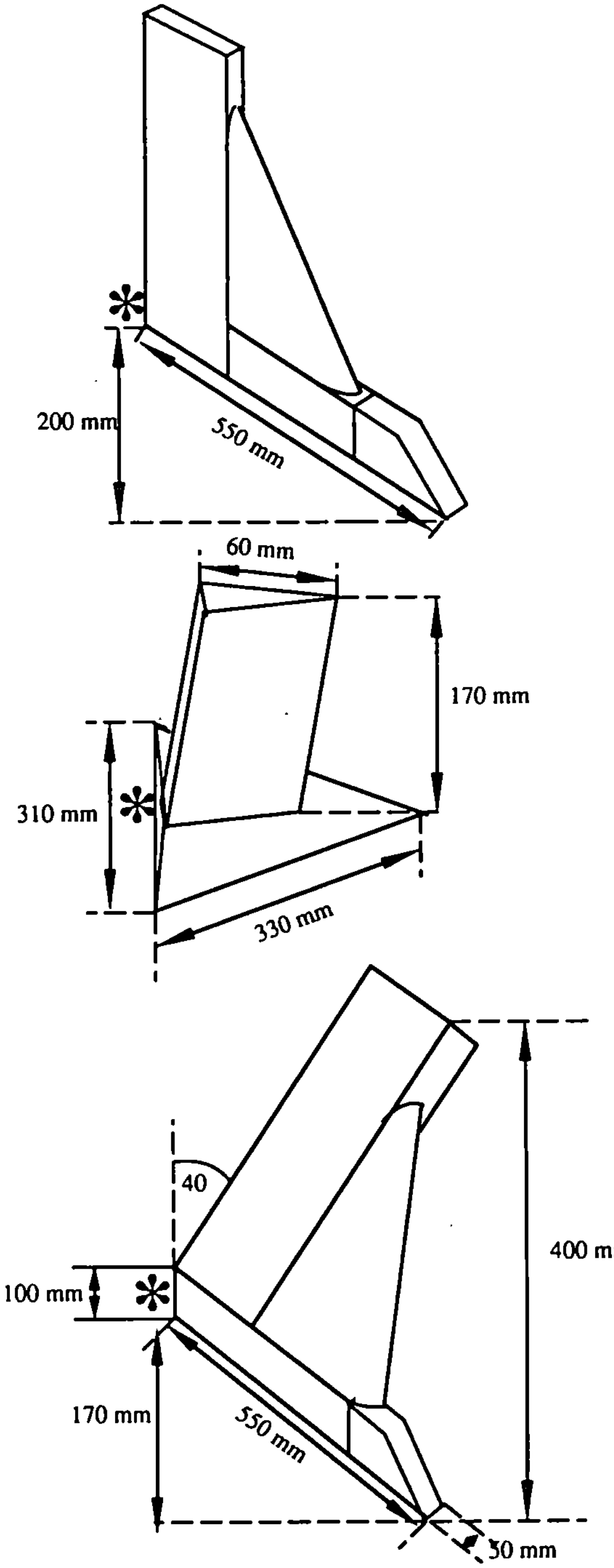
		BCR 142				BCR 143				
		Cu	Ni	Pb	Zn	Cd	Cu	Ni	Pb	Zn
certificated:	average	27.5	29.2	37.8	92.4	31.1	236.5	99.5	1333	1272
	±	0.6	2.5	1.9	4.4	1.2	8.2	5.5	39	30
analysis:	average	19.3	19.8	44.7	64.5	34.6	186.8	78.4	1031	997
	±	0.3	0.63	3.8	3.9	2.3	7.1	4.9	21.6	28.9
percentage:	average	70	68	118	70	111	80	79	77	78
	±	2	3	8	6	7	4	6	2	3

TABLE 4.4 'WORST CASE' STANDARD ERRORS ACCEPTED FOR ANALYTICAL PROCEDURES.

procedure	error
digestion of soils	+/- 5% *
AAS	+/- 5%
DCP	+/- 3%
CEC	+/- 3% *
LOI	+/- 3% *
OC	+/- 10% *
particle size	+/- 10% *
pH	+/- 0.2% *

* error includes sample variability and methodological inaccuracy

FIGURE 4.1 TINE CONFIGURATION



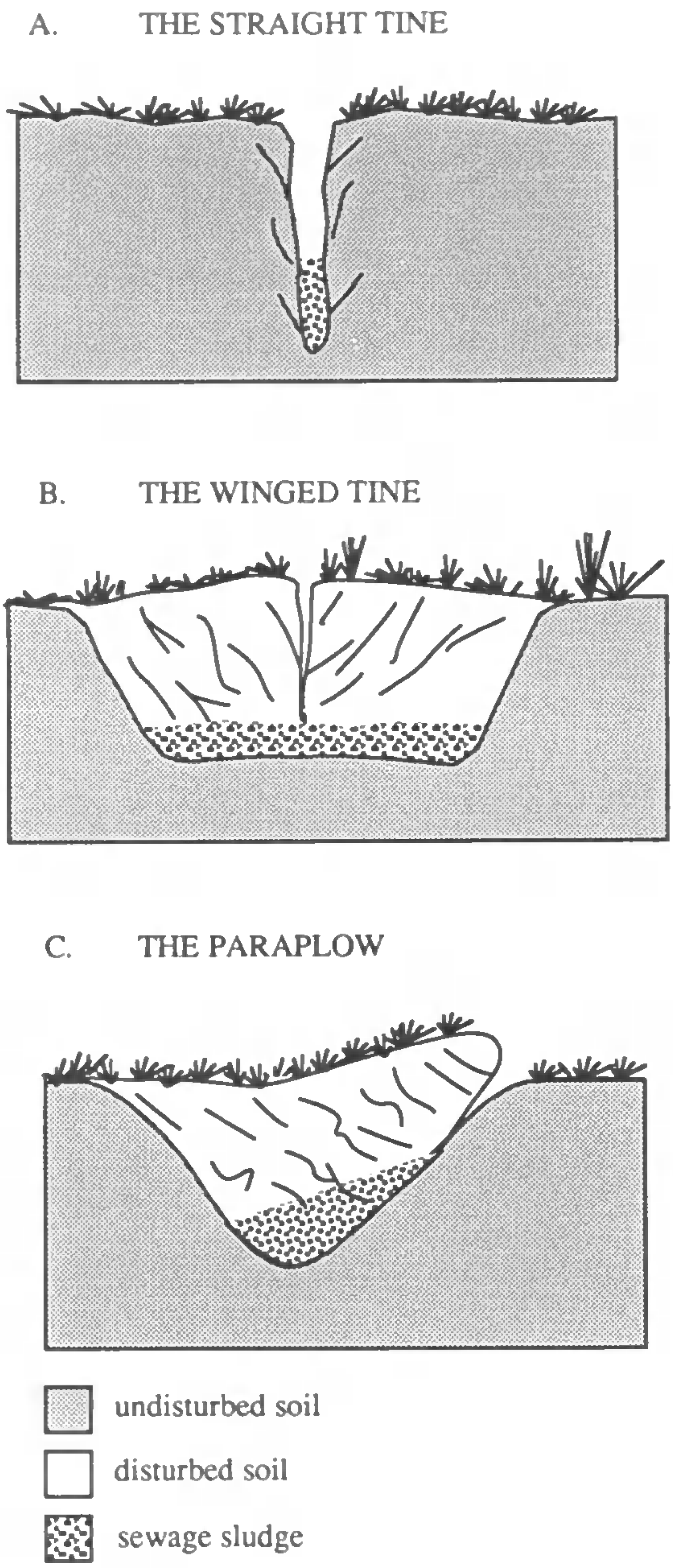
(a) STRAIGHT TINE

(b) WINGED TINE

(c) PARAPLOW

✻ Point of sludge exit from tine

FIGURE 4.2 SOIL DISTURBANCE CREATED BY THE PASSAGE OF TINES



* taken from Hall *et al.*, 1986. Tine passage is out of the page.

FIGURE 4.3 LOCATION OF FIELD SITES AND PLOT LAYOUT WITHIN SITES

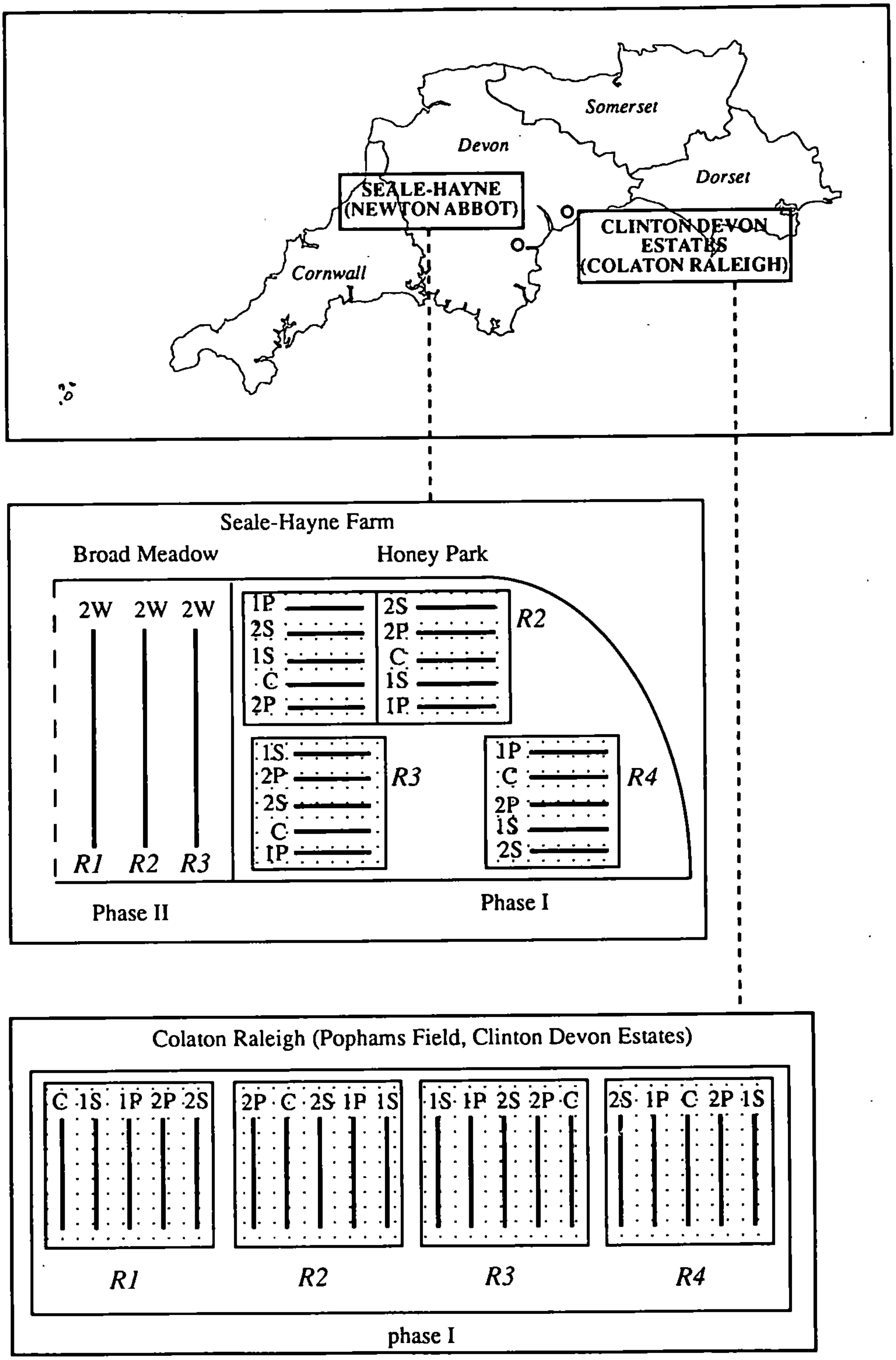
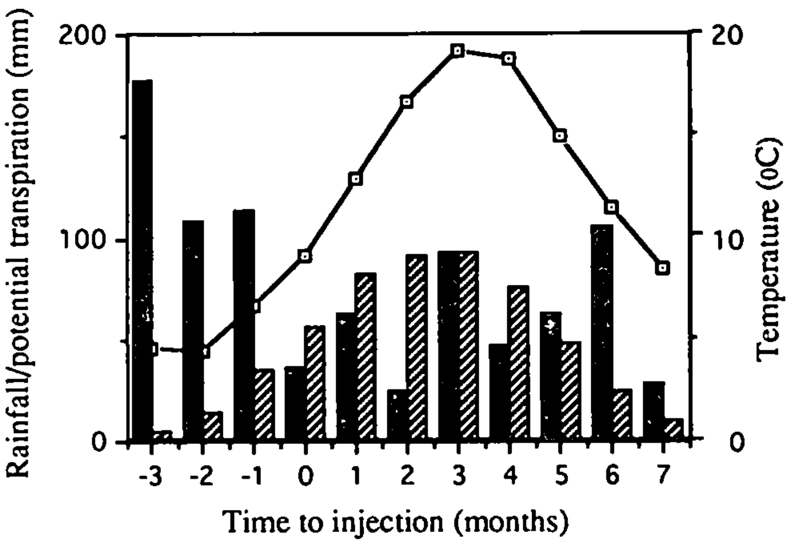
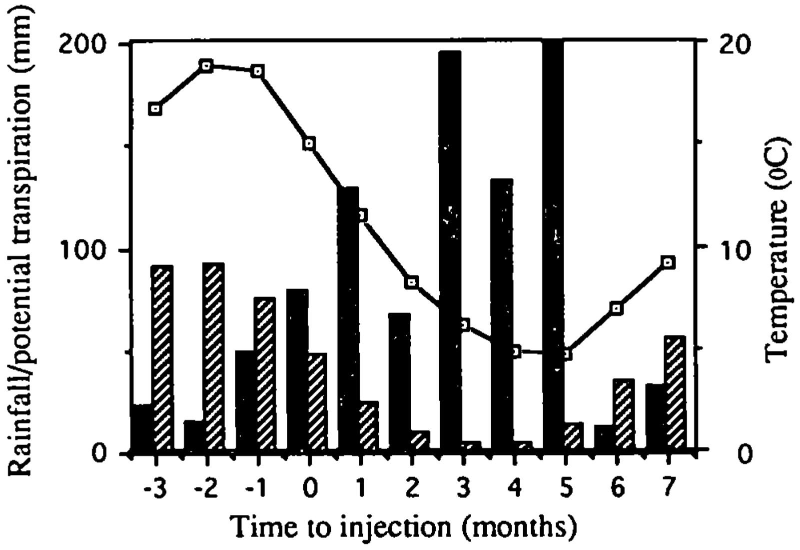


FIGURE 4.4 METEOROLOGICAL DATA FOR THE THREE FIELD SITES

A. SEALE-HAYNE: FIRST INJECTION (14.4.88)



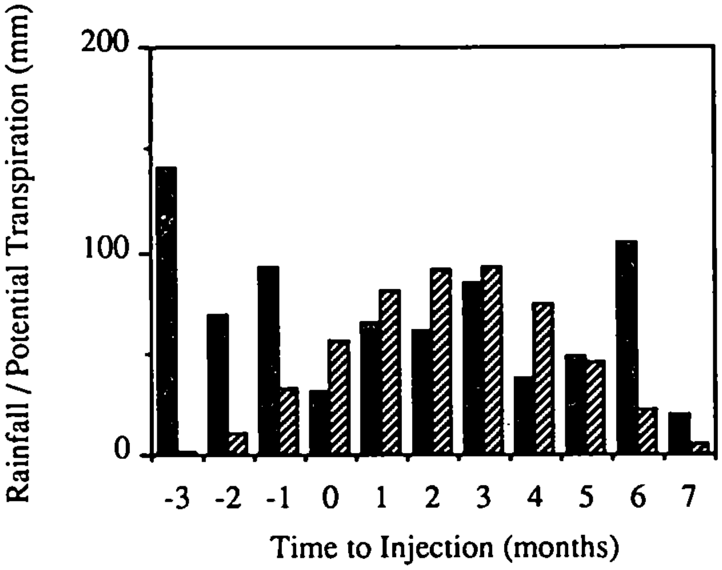
B. SEALE-HAYNE: SECOND INJECTION (21.9.89)



—□— Soil temperature at 20 cm (oC)
■ Rainfall (mm)
▨ Potential Transpiration (mm)

FIGURE 4.4 (continued) METEOROLOGICAL DATA* FOR THE THREE FIELD SITES

C. COLATON RALEIGH



■ Rainfall (mm)
▨ Potential Transpiration (mm)

* soil temperature data is not available for Colaton Raleigh

FIGURE 4.5.1 SAMPLING PROTOCOL FOR AUGER SAMPLES

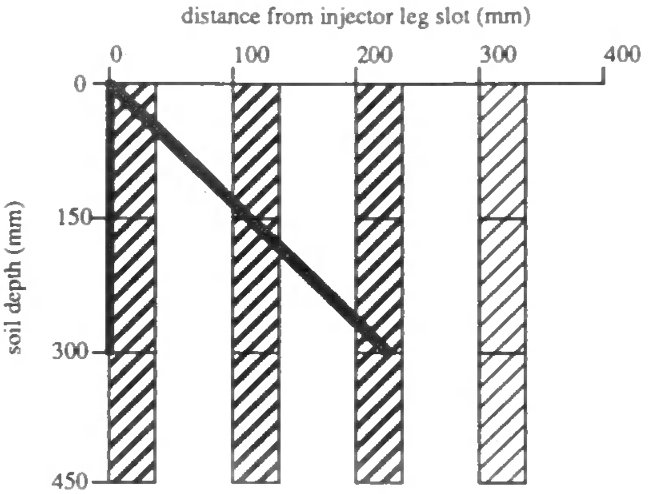


FIGURE 4.5.2 SAMPLING PROTOCOL FOR PIT SAMPLES.

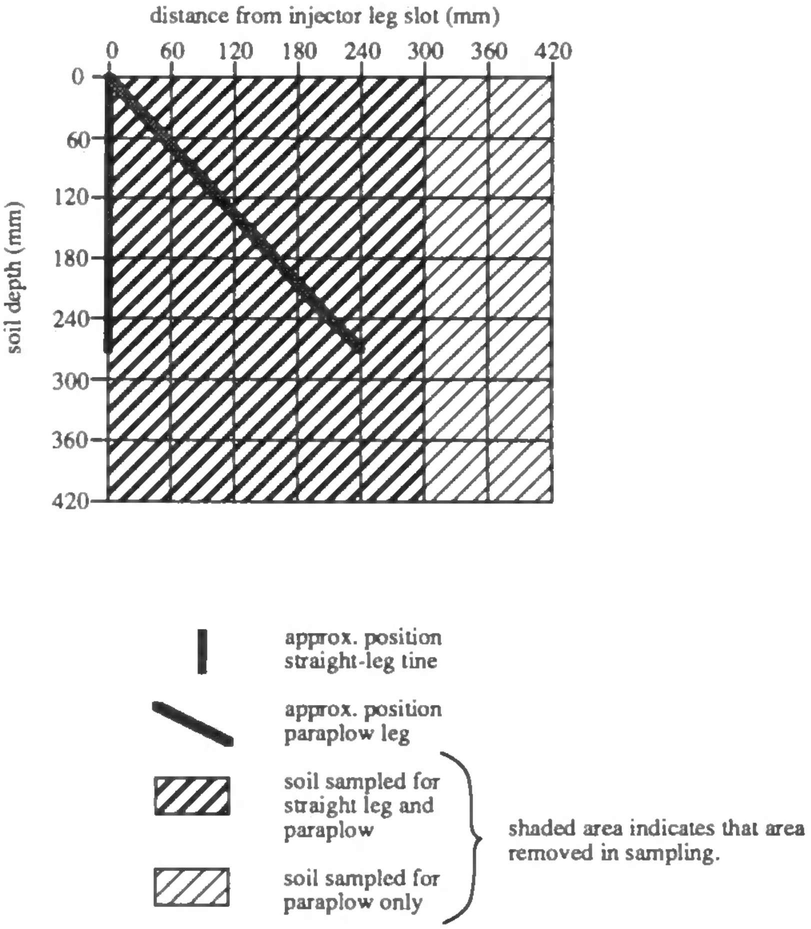


FIGURE 4.6 SOIL COLUMN APPARATUS.

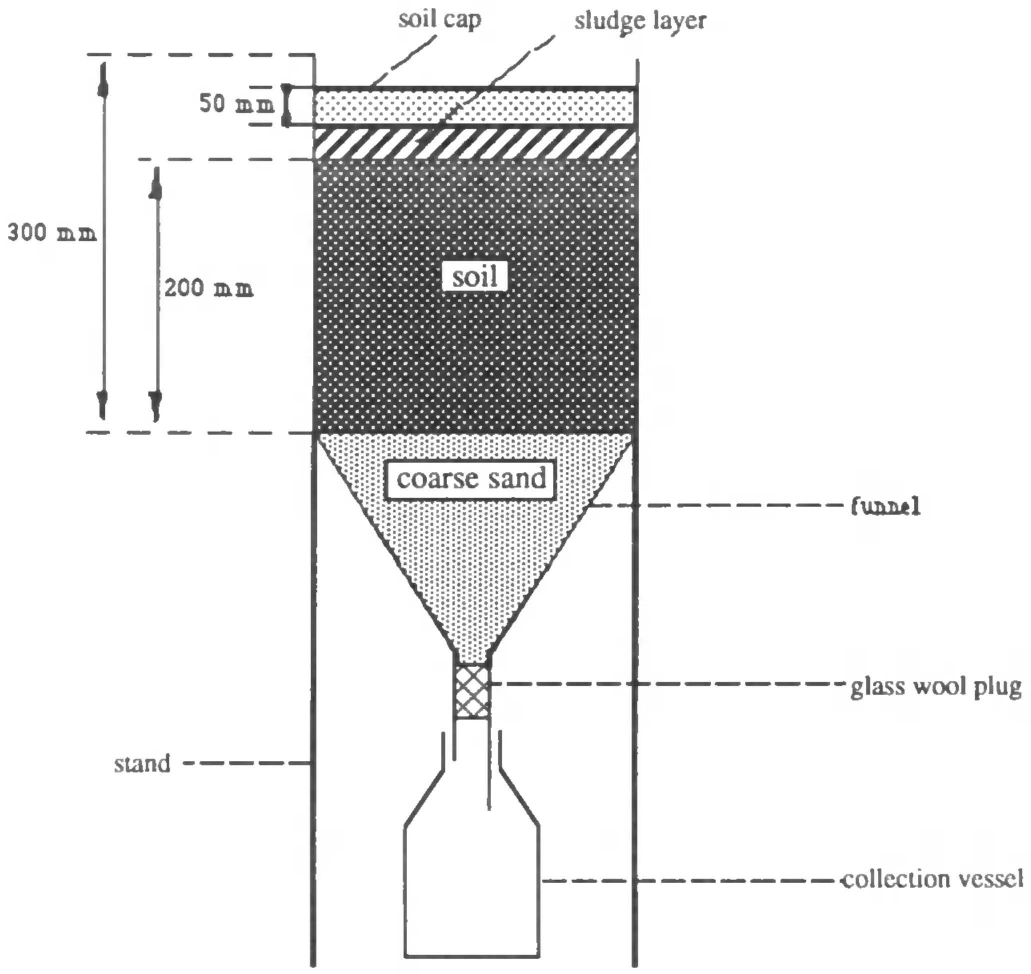


FIGURE 4.7 THE RELATIONSHIP BETWEEN LOI AND OC

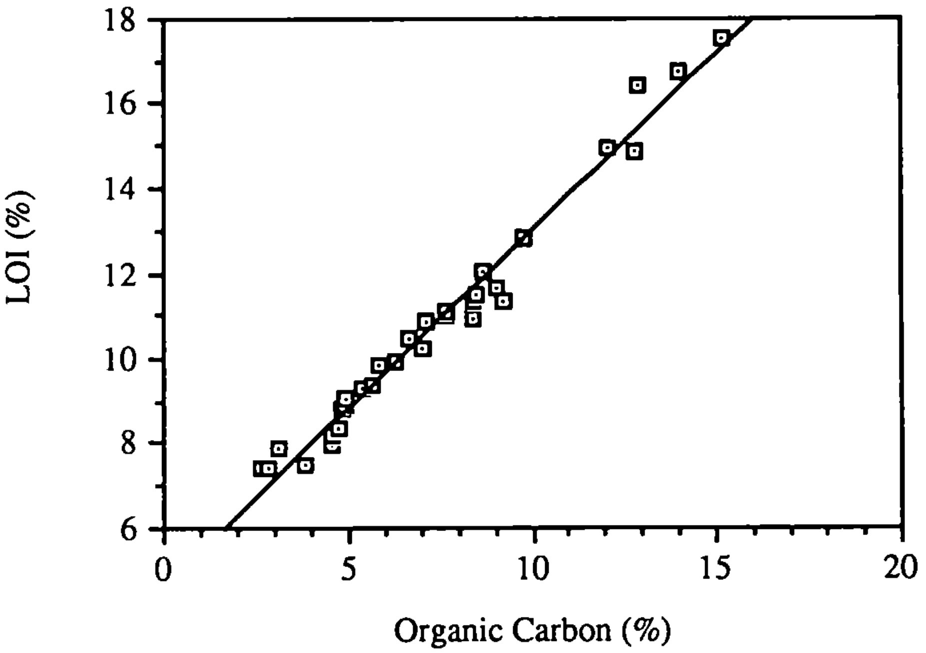
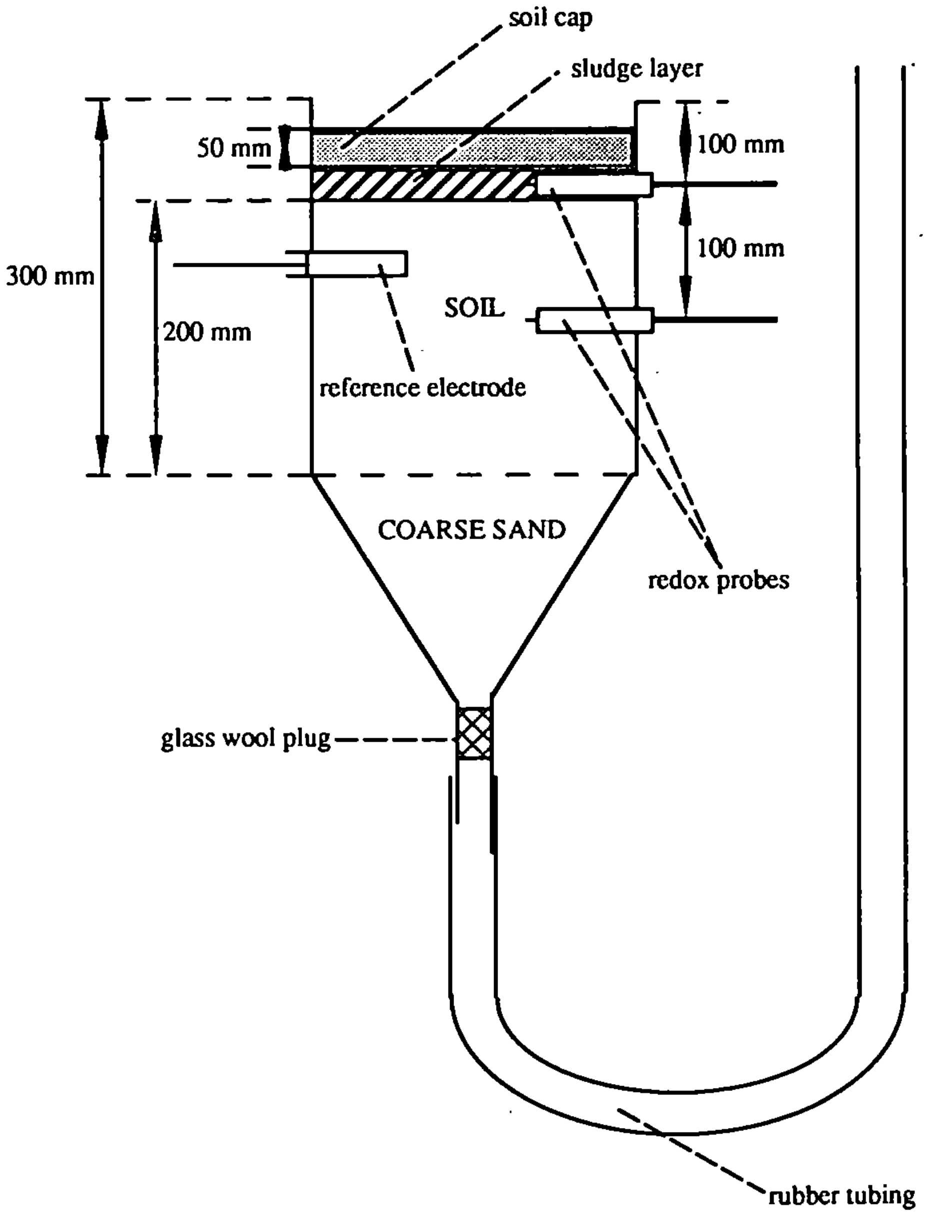


FIGURE 4.8 APPARATUS FOR SLUDGE-AMENDED / WATERLOGGED REDOX COLUMNS.



5. RESULTS 1: SOIL CHARACTERISATION

In assessing the relative distribution of metals introduced into the soil via the injection of sewage sludge, and the effect on this of soil type, it is necessary to gauge those soil factors that can be expected to affect metal distribution, and identify which soil type parameters can be described as significantly different between sites. To reiterate Section 4.3, the soil is to be described in terms of pH, cation exchange capacity (CEC), organic carbon content (OC), texture, available Fe and Mn and redox potential. The potential effect of each parameter and its possible interaction with others is discussed here, but the actual effects and interactions are dealt with in Chapter 8.

In quantifying the characteristics of the soil, it is also important to consider the within-site variability of these factors, as their impact on the consistency of the subsequent distribution of metals may have serious implications on the viability of injection as a means of disposing of sewage sludge in a manner which can be routinely checked from a standardised sampling regime. The variability of each soil factor with depth is also of significance, as the difference between surface values and those at the depth of injection also has sampling connotations, and the depth at which any appreciable changes occur may well affect the behaviour of heavy metals introduced into the soil at that depth. Thus three expressions of variability are used in this Chapter: that within a replicate, i.e. with depth (diagrammatic evidence and significance testing); that between replicates of the same soil type (using the same tools but also correlation analysis); and that between soil types, which will also involve all three available methods.

5.1 pH

A summary of the distribution of pH values (in $CaCl_2$) with soil depth is illustrated by Figure 5.1. Each data point for each soil type is the mean value of three replicates, with the variability associated with this mean expressed as error bars. Despite this variability, the use of averages can be considered legitimate, as each replicate is strongly correlated with the mean at Honey Park ($p<0.01$), Broad Meadow ($p<0.05$) and all except replicate 1 at Colaton

Raleigh ($p<0.01$). The RSD of the mean pH increases with depth at Colaton Raleigh and Honey Park. At the latter site, this takes the form of an abrupt change at a depth of 180 mm, after which mean pH remains an almost invariable 6.1, with an RSD at each depth of between 4 and 5 %. Conversely, the disparity between replicates at Broad Meadow decreases with depth, especially around 240 mm, after which pH changes little.

Statistical analysis of pH data reveal that there is no significant difference between either i) replicates of the same soil type at Honey Park and Colaton Raleigh or ii) Honey Park and Broad Meadow soils, but that iii) the pH of both Seale-Hayne soils are significantly ($p<0.05$) higher than that of Colaton Raleigh soils at depths greater than 60 mm, and iv) the replicates of the Broad Meadow soil are significantly ($p<0.05$) different from one another.

The pH of the soil at all three sites exhibits the classic increase in pH with depth caused by the removal of H^+ by interaction with soil minerals. This distribution exhibits a strong positive correlation ($p<0.01$) between each site, and the range of values indicated by Figure 5.1 fall within that specified for its relevant soil association by Findlay *et al.* (1984) and Clayden (1971).

Besides metal concentrations, a measurement of pH to a depth of 250 mm is the only soil factor required by the Sludge (Use in Agriculture) Regulations (1989) and the Code of Practice for Agricultural Use of Sewage Sludge (1989). According to this criteria, the pH at Honey Park = 5.68, Broad Meadow = 5.52 and Colaton Raleigh = 4.87. These regulations would therefore prohibit the application of sewage sludge to Colaton Raleigh, but permit a relatively high metal loading at the Seale-Hayne sites (Table 1.1). A comparison of metal behaviour at the two localities should therefore afford a good indication of the applicability of the Guidelines. To assess the potential effect of pH on the behaviour of metals located at an unknown or variable depth, an index (average) pH of 4.9, 5.9 and 5.8 is taken for Colaton Raleigh, Broad Meadow and Honey Park respectively, with an associated RSD[1] of 8.3 %, 10.9 % and 6.6 % respectively (Table 5.1). According to the scheme proposed by Sanders and Adams (1984), the availability of Cu, Ni and Zn would therefore be enhanced at Colaton Raleigh, whereas the less acidic soil at Honey Park and Broad Meadow would affect only Ni and Zn. Conversely, the work of Kiekens and Cottenie (1983) suggests that only Cd and Zn would be significantly mobilised in either soil, with Cu, Ni and Pb little

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[1] It should be noted that these error terms, and those cited for each soil factor index (Table 5.1), encompass both variability with depth and between replicates, and will be integrated into all statistics involving the index itself.

affected by the existing pH.

The difference in pH between the Seale-Hayne and Colaton Raleigh sites may further, indirectly, affect metal behaviour via its influence on factors such as the pH-dependent charge component of CEC and on redox potential. In general, an increase in pH will favour negative charges on oxide surfaces and clay mineral edge faces (White, 1987), thus increasing the potential retention of metals. However, the point of zero charge (PZC) range of these groups is large, with each value depending upon the nature of the oxide or clay. For example, the PZC of gibbsite is approximately pH 9, whereas that for silica is around pH 2 (Mott, 1981). The effect of pH on the contribution of organic matter to the CEC is appreciable over the ranges encountered in these soils, as the dissociation of the carboxyl and phenolic groups, on which the charge depends, occurs at pHs between 3 and 5. Thus the contribution of organic matter to the CEC of the soil is only substantial above pH 5 (Alloway, 1990), that is, at the Seale-Hayne sites. This is of importance in this experiment as the metals are introduced into the soil with organic matter of an approximately neutral pH. The release of metals may therefore depend almost entirely on the acidification of this organic matter upon contact with the soil (although the significance of this effect relies upon the organic fraction involved: Section 2.2.2), and the extent of subsequent lateral movement may thus be dictated by the variability of pH with depth at the Seale-Hayne sites.

5.2 CATION EXCHANGE CAPACITY.

The CEC of the soil at each site, its variability and its relationship with depth, is summarised in Figure 5.2. As with pH, each data point represents the mean value of three replicates. Overall variability (i.e. when depth is included) is ranked as Honey Park > Colaton Raleigh > Broad Meadow. Accordingly, although all replicates exhibit a similar change with depth as that represented by the mean for each site, replicates of the same soil do not necessarily correlate with each other. There is no significant difference (at $p<0.05$) between replicates within the Broad Meadow and Colaton Raleigh sites, whilst replicates 1 and 3 at Honey Park are significantly different ($p<0.01$), although values converge with depth. There is no apparent pattern in the variability of replicates at other sites, although the greatest variability is found at each extreme of depth at Broad Meadow, whilst the reverse is true at Colaton Raleigh. Despite these marked differences, there is no significant reduction (at $p<0.05$) in CEC with depth at the latter site. Similarly, the CEC of the other soils decreases only gradually with depth: generally, the CEC at a given depth is not significantly different (at

$p<0.05$) from its three nearest neighbours, despite the marked change at 180 mm and 120 mm at Broad Meadow and Honey Park respectively (Figure 5.2).

The measured components of CEC used in this work are organic matter, which has a CEC of up to 400 meq per 100 g (Leeper, 1972); clay, which, depending upon type, has a CEC of < 100 meq per 100 g, and (potentially) hydrous Fe oxide, with a lesser potential CEC of 10 meq per 100 g. Correlation analysis conducted between these parameters and CEC indicates a strong association between CEC and OC ($p<0.01$) at all sites, with a similar ($p<0.01$) relationship between Fe and CEC at Broad Meadow and Colaton Raleigh, whilst percentage clay is of secondary importance ($p<0.05$) at all sites. Whilst correlation analysis can not define causal relationships, these results infer that, as anticipated in Section 5.1, OC is the most important component of CEC at the more acidic Honey Park, whilst it is of equal importance to Fe at Broad Meadow and the sandy soil at Colaton Raleigh.

A survey of the literature reveals that there is no direct or universally accepted relationship between CEC and soil depth, as the former is controlled by the presence or absence of its component parts, which may have conflicting relationships with depth. For example, OC content tends to decrease with depth (Section 5.3), whilst clay is dependent upon soil type in defining this relationship. The overall effect may therefore be expected to be erratic, as observed in this case, where each soil type is significantly different ($p<0.01$), in terms of both absolute values and pattern of variation. Despite this, there is a similar gradual reduction in CEC with increasing soil depth at all sites, due to their resemblance in pH characteristics, the relationship between OC and CEC, and land use and climate.

The CEC index and associated RSD of each site is indicated on Table 5.1. That for Colaton Raleigh conforms to the reference description of the Bridgnorth Series (Clayden, 1971) as possessing a low CEC, but no reference is made to the CEC of soils of the Denbigh (Highweek) Series (Clayden, 1971; Findlay *et al*., 1984). Broad Meadow and Honey Park indices are significantly different at the $p<0.05$ level, and both have significantly larger CECs than Colaton Raleigh ($p<0.01$). It would therefore be expected that the metals would have a greater percentage availability at Colaton Raleigh than at either of the Seale-Hayne sites. This can be translated into the amount of metal that could be held in the cation exchange complexes by converting metal concentrations into meq l^{-1} using the equation:

$$\text{meq } l^{-1} = \frac{\text{mass } (\text{mg } l^{-1})}{\text{equivalent weight}}$$

$$\text{equivalent weight} = \frac{\text{Relative Atomic Mass}}{\text{ion charge}} \qquad \text{equation 5.1}$$

Further inferences are only valid in the context of other soil factors and the properties of individual metals (Chapter 8).

5.3 ORGANIC CARBON CONTENT

The organic carbon (OC) content of all three sites again shows a typical decrease with increasing depth, as illustrated by Figure 5.3, with each site displaying a positive correlation ($p<0.01$) with the others. Statistically, the change with depth at each site is abrupt, with each depth being significantly different ($p<0.01$) than all but its two nearest neighbours. However, these differences become less marked down the profile. Variability, as indicated by error bars, increases appreciably with depth at all sites. Despite this, the indicated averages are positively correlated ($p<0.01$) with their component replicates. Index OC concentration are cited on Table 5.1, and each site is significantly different ($p<0.01$). The difference between Honey Park and Broad Meadow is somewhat incongruous, but can be explained by the more recent, alluvial derivation of Broad Meadow soil and different landuse histories, as soil under permanent pasture (Honey Park) is known to have a greater OC content than more recently cultivated (Broad Meadow) soil (e.g. Jenkinson, 1981). Nevertheless, the OC content of both soils is appreciably higher than the reference values given by Findlay *et al.* (1984) and the range cited for South West soils (3-5 %) by McGrath and Loveland, 1992). The OC status of Bridgnorth soils (Colaton Raleigh) is described as 'low' (Clayden, 1971), but this is not quantified. Within the same field, there is no significant difference ($p<0.05$) between replicates at Broad Meadow, but replicate 2 has a significantly higher ($p<0.01$) OC concentration than replicate 1 at Honey Park. At Colaton Raleigh, OC content increases across the field: thus replicate one has a significantly lower ($p<0.01$) OC content than replicate three.

The organic matter content of the soil is influenced by water content (Jenkinson, 1981), pH (Jenkinson, 1977), soil texture (Jenny, 1941) and the type and accessibility of the organic debris (Jenkinson, 1981), whereby decomposition will be limited in extremes of water content, at low pHs, in heavy soils and when organic debris has a small relative surface area. Reciprocally, the organic matter content affects pH, CEC and the water holding capacity of the soil (Bohn *et al.*, 1979). It thus has a range of direct and indirect effects on metal availability and mobility, via ion exchange, surface sorption, chelation and coagulation (Kabata-Pendias and Pendias, 1984), rendering generalisations of its prospective effect on metal behaviour meaningless in isolation. The situation is further complicated by the disparate response of the metals to organic matter and the different properties of organic matter fractions (Section 2.2.2). Discussion will therefore be continued in Chapter 8.

5.4 SOIL TEXTURE

In any assessment of soil texture, discussion is inevitably focused on the percentage clay content, as the most influential factor in terms of metal movement (Section 2.2.2). Percentage sand and silt will be used for descriptive purposes only. Thus, soil at Honey Park can be described as a clay loam (with an increasing silt content with depth), at Broad Meadow as a silty clay, and at Colaton Raleigh as a sandy loam with some tendency towards a sandy silty loam (Section 4.1.2). Figure 5.4 illustrates the variability of particle size analysis of each of the three soils, represented by samples extracted from depths of 0-60 mm, 180-240 mm and 360-420 mm (Section 4.3.2). As with previous Sections, each data point represents the mean of three replicates. The variability of these replicates with depth, in terms of percentage clay, can be ranked as Honey Park > Broad Meadow > Colaton Raleigh. The pattern of change in variability is erratic at both Seale-Hayne sites, but is greatest at about 240 mm, and exhibits a reduction with depth at Colaton Raleigh. Each mean has a positive correlation ($p<0.05$) with most of its component replicates, with the exception of one replicate on each soil type. In-site percentage clay content at any given depth is therefore considered to be the most variable of the soil factors considered here. However, whilst exhibiting appreciable differences (especially at Broad Meadow) the average (index) percentage clay content of each replicate within the same soil type is statistically no different from the next ($p<0.05$).

Mechanical analysis in the laboratory supports the field descriptions cited in Section 4.1.2, in that the percentage clay content varies little (non-significantly) with depth at each site. Only Honey Park displays a steady reduction in the clay content with depth, whereas the remaining sites are characterised by an erratic, minor change. Thus, there is a significant positive correlation ($p<0.01$) between Honey Park and the other sites, but none between Broad Meadow and Colaton Raleigh. The sand content at all sites remains largely unchanged with depth. Colaton Raleigh has a significantly ($p<0.01$) lower index percentage clay content (Table 5.1) than either Honey Park or Broad Meadow, which are themselves significantly different ($p<0.05$). These differences are consistent with the soil descriptions given by Clayden (1971) and Findlay *et al.* (1984), and the more clayey nature of Broad Meadow reflects the difference in parent material between this site and Honey Park. For the same reasons, percentage silt follows the same trend (i.e. Broad Meadow > Honey Park > Colaton Raleigh), although the differences are less marked. The relative sand contents of the soil therefore follows the reverse trend.

Section 2.2.2 previously outlined the potential influence of soil texture on the behaviour of metals. Extrapolation to the specific cases here suggests that the expected positive effect of the greater clay content of the Seale-Hayne soils on their CEC should immobilise metals. This may be tempered by the apparently greater effect of OC on CEC (Section 5.2), although the two components of CEC may be related - percentage sand has been significantly negatively correlated with percentage organic matter (Pitty, 1978). A restriction of metal movement may be further exacerbated by the potential influence of a heavier soil in limiting the extent of soil disturbance created by the passage of the tine (Chapter 6), thereby confining the sewage sludge within a smaller volume of soil.

In addition to the effect of soil texture on the CEC of a soil, it may further exert an indirect influence via its effect on the soil's water holding capacity, and the attendant effects on diffusion coefficients (whereby a drier soil has a lower diffusion coefficient as a result of the increasing tortuosity of pathways - Wild, 1981) and redox potential. Mass flow may also be affected by soil texture, but this factor can not be considered further due to the complications caused by, e.g., the activity of soil fauna and the effect of cracking (Wild, 1981). It would be expected that the heavier soils of Seale-Hayne would have a greater water holding capacity, and this would tend to be confirmed by the standard descriptions of these soils (Clayden, 1971) and the greater water content of samples taken from these sites both during injection and during sampling operations. Seale-Hayne soils are more susceptible to waterlogging, but may be expected to have a greater diffusion coefficient. The water holding capacity of a soil in turn affects the temperature of the soil, in that a heavier soil will tend to respond more slowly to changes in air temperature (White, 1987), and therefore the rate of chemical reactions. In an experimental period extending from April-November, the soil at Honey Park would thus be cooler than that at Colaton Raleigh during injection (April), but warmer during the final sampling phase.

5.5 AVAILABLE IRON AND MANGANESE CONTENT

5.5.1 IRON

The decrease in the 'available' Fe concentration with depth at each site is illustrated in Figure 5.5.1, in which the magnitude of this change is seen to be greatest for Broad Meadow soils, which have the highest 'available' Fe content in surface layers, but the lowest concentration at the base of the sampled profile. The reverse is true at Colaton Raleigh, where changes with depth are more gradual and the Fe concentration at the base of the sampled profile (360-420 mm) is significantly ($p<0.01$) less than that at the top of the profile. The variability between the replicates that constitute the mean is substantial, but generally insignificant ($p<0.05$) and increases in the order: Broad Meadow > Honey Park > Colaton Raleigh. The change in Fe concentration with depth of each replicate is strongly positively correlated ($p<0.01$) with the relevant average.

The index of Fe concentrations at each site are given by Table 5.1, ranking as: Colaton Raleigh > Honey Park > Broad Meadow. Colaton Raleigh has a significantly greater ($p<0.01$) 'available' Fe concentration than that at either of the Seale-Hayne sites, which are statistically no different from one another. The pattern of Fe variability with depth is positively correlated between all sites ($p\leq0.05$).

5.5.2 MANGANESE

As with the pyrophosphate-extractable Fe concentration, the corresponding Mn content of these soils decreases with depth (Figure 5.5.2). The replicates that contribute to the represented average concentration vary from each other in an inverse relationship with concentration, indicated by error bars. However, the total variability (i.e. taking account of the variability of replicates at each depth) can be ranked as: Honey Park > Colaton Raleigh ≥ Broad Meadow. This is reflected statistically, in that replicate 1, Honey Park has a significantly ($p<0.01$) greater Mn concentration than replicates 2 and 3. Replicates within the remaining sites are statistically similar, but are increasingly variable with depth at Colaton Raleigh and at depths greater than 300 mm at Broad Meadow. Despite the substantial disparity in absolute Mn concentration, the change in concentration with depth of each replicates correlates significantly ($p<0.01$) with the site average in all cases except replicate 1, Colaton Raleigh. In terms of significance testing, the surface soil layer (60-120 mm) at the Seale-Hayne sites have significantly ($p<0.01$) greater contents of Mn than those lower in the profile. At Colaton Raleigh, a gradual change is observed, with significant differences occurring only between depth extremes.

Figure 5.5.2 also illustrates the marked similarity in Mn concentration of both Seale-Hayne sites. Accordingly, these sites are strongly correlated ($r<0.997$; $p<0.01$). In a less close but significant ($p<0.01$) relationship, the Mn concentration of these sites is also positively correlated with that at Colaton Raleigh. However, the index Mn concentrations (Table 5.1) of the two Seale-Hayne sites are significantly different from each other ($p<0.05$). Similarly, the average Mn content of Broad Meadow soils is significantly ($p<0.05$) less than that at Colaton Raleigh.

5.5.3 DISCUSSION

The use of pyrophosphate as extracting solution for Mn and Fe is generally used by authors investigating podzolisation (e.g. Page and De Kimpe, 1989; Xie and MacKenzie, 1989) and it would therefore erroneous to compare the amount of Fe and Mn contained within these soils with that reported by others. The potential effect of pyrophosphate-extractable Fe and Mn, rather than the more general 'free (hydrous) Fe/Mn oxide', on the behaviour of heavy metals is similarly uncertain - the measurement of these factors was made largely as a descriptive tool. It is known, however, that these metal concentrations are closely linked with the OC status of the soil, which controls the relationship of metal concentration with depth. Fe and Mn oxides are also known to contribute to the CEC of the soil (Sections 2.2.2 and 5.2) and may affect the uptake of other metals by plants. However, it has also been suggested that Fe may only affect the specific adsorption of some metals when Fe is present in considerable quantities (e.g. McLaren and Crawford, 1973). This should be prominent at Colaton Raleigh rather than the Seale-Hayne sites, although it has been seen to be equally important at both Broad Meadow and Colaton Raleigh (Section 5.2). Conversely, the pH and redox status of the soil is important in the chemistry of Fe and Mn (Knezek and Ellis, 1980), and the absence of their oxides may be indicative of reducing conditions in the soil (Alloway, 1990b). Since the concentration of Fe oxides especially is anomalously low at Honey Park and Broad Meadow (considering their relatively large 'total' loading of other metals - see Section 7.1.2), and since it is known that these soils are prone to flooding, this will be taken as a secondary redox indicator in the absence of superior results from redox probes.

5.6 REDOX POTENTIAL

The soils of the Seale-Hayne site are known to be substantially less well drained than those of Colaton Raleigh (Findlay *et al.*, 1984; Clayden, 1971), and were observed to be prone to waterlogging during the experimental period. In chemical terms, the effect of this is manifested as a reduction of redox potential. However, due to the difficulties encountered in collecting representative redox potential data in the field (Section 4.3.3), redox potential was investigated in a different manner than the remaining soil properties, in that its effect is monitored by the use of soil columns containing soil from Broad Meadow (Section 4.3.3).

Redox potential was monitored continuously (hourly), and Figure 5.6 summarises this data to one reading every three days. Such a long sampling interval inevitably masks the period required for stabilisation, but this in any case was observed to be immediate (i.e. within an hour). Figure 5.6 clearly shows that those probes in the sludge treated / waterlogged columns are an exception to this observation, but this can be attributed to the changing redox potential of the soil, rather than the response time of the probes. Similarly, the sludge layer of the freely draining columns took three days to reach its stable, oxidised state, during which time the anaerobic sewage sludge drained. It can be seen that, at least in the upper half of the column, this soil took six days of waterlogging to achieve a stable, reducing state.

Immediately after each data point, 600 mls of distilled water was added to each of the draining columns. Previous authors (e.g. Blackwell, 1983) have suggested that such additions of water would give rise to somewhat erratic readings, usually in the form of negative peaks when the water is passing through initially air-dry media (Swartzendruber and Gairon, 1975). The same authors found that Pt electrodes responded almost immediately to the passage of the 'wet front', although some time lag developed as the front progressed. This effect was negligible in the work conducted by the present author (negative changes of <0.01 V). Interestingly, the situation is reversed in the control treatments. Here, the addition of water is marked by an abrupt positive peak in redox potential at the upper probe (changing from approximately 0.08 V to 0.13 V) and a far smaller increase (of less than 0.01 V) at 175 mm. The return to the original reading is gradual, and is only attained immediately prior to the next water addition, i.e. a three day cycle. Both the direction of change and the length of recovery time are incongruous - the data set, replications and preinstalment checks (Section 4.3.3) dismiss the obvious explanations that a) leads were incorrectly connected (yielding positive instead of negative results, and vice versa), or that b) the movement of water, which was introduced to the columns in a single addition, trapped air which was initially pushed in advance of the 'wet front' but had largely dissipated by 175 mm.

Unlike the other Figures in this Chapter, Figure 5.6 uses one replicate to represent each treatment. Mean values have not been used as redox potentials measured in this way are known to be only semi-quantitative (Ponnamperuma, 1972) and thus only give an indication of the degree of aeration without assigning it an absolute value. In addition, the time taken for the soil to reach a stable, reducing state was variable, although the resultant redox potential was similar in all cases. If it is erroneous to use mean values with this data, it follows that significance testing is meaningless, and even correlation analysis is impossible with data sets that are somewhat out of phase. Table 5.2 qualitatively compares replicates and treatments, and indicates an acceptable similarity between replicates of the same treatment. The trend in redox changes is correspondingly similar between replicates, albeit somewhat out of step. Both Table 5.2 and Figure 5.6 illustrate the greater degree of aeration that is found at depth in each column. Since this is regardless of treatment, and since each column is water-tight, this would seem to be a result of factors other than the effect of a greater organic matter content on the more rapid attainment of stable reducing conditions (above, and Ponnamperuma, 1972), or the enhanced drainage afforded by the sand at the base of each column. Nor can it be the interaction of both factors, as the disparity between probes would thus be expected to be greatest in sludge treated / freely draining columns, but this is not the case. Since the soil was thoroughly mixed before filling the columns (Section 4.3.3), and should therefore be of reasonably uniform pH, this disparity is too great to be negated by an adjustment of -0.060 V/unit pH (according to the scheme of Zobell, 1946). Similarly, the effect of microbial activity and the soil content of Fe, Mn, N and S compounds on the redox potential of the soil should be uniform throughout the columns. It is interesting to note that under a variety of water conditions in the field, the incidence of higher redox potentials at 300 mm was approximately 50 % greater than the occurrence of similar conditions at 10 mm. It should be noted at this point that although the use of the field redox experiment has been rejected, this is not because of a lack of confidence in the data (Section 4.3.3).

Figure 5.6 also introduces the additional complication of a redox potential at depth that gradually decreases, only to become increasingly aerated about halfway through the experiment, whilst soils are still waterlogged. A similar phenomena was observed by IRRI (1964) and Blackwell (1983), although the experimental duration was longer than 1 month in both cases. This feature was not discussed, but data presented by the latter author suggests that there is no relationship between this negative peak and oxygen concentration (either gaseous or dissolved) or oxygen flux.

In assessing the potential effect on metal movement, any attendant change in pH must be considered, especially because 'these parameters acting together have a much greater effect than either one acting alone' (Stolzy and Fluhler, 1978). In these cases, the final pH of the columns ranged from 5.8 (sludge treated / freely draining) to 6.0 (control) and 6.5 (sludge treated / waterlogged). Of these, only the sludge treated / waterlogged treatment is significantly different ($p<0.01$). Between replicate variability is minimal, with associated RSDs of 3.0 %, 1.9 % and 1.5 %, respectively. This change in pH with the onset of anaerobic conditions is common for initially acidic soils (Rowell, 1981; Ponnamperuma, 1972), where the decrease in pH caused by CO_2 accumulation is minor, and more than offset by the increase in pH induced by the use by redox couples of more protons than electrons.

The potential effect of Eh/pH changes on the extractability of Cu and Zn, the only metals considered in this sub-experiment, has already been identified as indirect and variable (Section 2.2.2), although the consensus is, when considering soils of similar characteristics to those at Broad Meadow, that extractability would be increased under anaerobic conditions (Beckett *et al.*, 1983; Beckwith, 1975; Bloomfield and Pruden, 1975; Ng and Bloomfield, 1962). However, although some of this research purports to investigate the changing mobility of the metals, all in fact refer only to extractability with weak extractants. None investigate the changing areal distribution of metals. Ng and Bloomfield (1962) and Bloomfield and Pruden (1975) include water as one of their extractants, which may be used as an indicator of final metal distribution, but results directly contradict each other. It can therefore be taken that there is no directly relevant precedent that can be used to anticipate the results of the present authors work.

5.7 SUMMARY

In selecting Honey Park, Broad Meadow and Colaton Raleigh as sites for the investigation of metal movement following the injection of sewage sludge, it was assumed that: a) Honey Park and Colaton Raleigh soils would be significantly different in terms of soil characteristics; and that b) Broad Meadow would have similar characteristics as Honey Park and be significantly different from Colaton Raleigh. In terms of pH, CEC, OC, texture and pyrophosphate-extractable Fe, Honey Park and Colaton Raleigh have been shown to be significantly ($p<0.01$) different. A substantial difference in physical properties, such as water content and drainage, has also been observed, in that Honey Park was consistently wetter than Colaton Raleigh throughout the experimental period. Such properties are beyond the scope of this research and have therefore not been quantified, although their effect in chemical terms was investigated in the stylised redox experiment.

Statistical differences have also been observed with depth within the same soil type and property. This is a potential source of error when inferring causal effects using the mean value only. However, the use of mean values is unavoidable when dealing with metals at a variable depth, although inaccuracy can be offset by the use of a variability index (RSD) and a knowledge of the depth at which these changes are most marked. At Honey Park, this depth is between 120 and 180 mm, at Broad Meadow between 120 and 240, depending on the parameter in question, and at Colaton Raleigh there is rarely any such inflection point. These changes can not be uniquely attributed to land use history, as that of Colaton Raleigh and Honey Park is identical (i.e. permanent pasture since 1966), and different from Broad Meadow, but may be considered to be the result of soil type ameliorating the effect of historical cultivations.

A significant difference between the soil properties of two sites does not, however, inexorably lead to significantly different effects on metal behaviour. Firstly, the limitations of the statistical test itself yields results that can only state that given these mean conditions, Honey Park and Colaton Raleigh are significantly different. The test can not indicate whether the two soils would be considered significantly different if all the soil types that would be suitable for injection were taken into account. Since nothing short of a national survey could rectify this situation, the error is considered inherent to any experiment of this scale, and therefore must be accepted. Secondly, the significant differences observed between soil types will only exert different controls over metal behaviour if they cross thresholds. For example, if each soil was strongly alkaline, the effect on the behaviour of the metals investigated in this research would be minimal, whether the difference between soils was significant or not. The soils of Seale-Hayne and Colaton Raleigh can be classed as 'different' in terms of such thresholds where they exist and are widely subscribed to - for example, in the case of pH and redox potential.

Table 5.1 summarises the soil factor indices assigned to each soil type. Bearing the aforementioned limitations in mind, a 'rule of thumb' can be established from these results that, if soil factors have an overriding control over metal movement and subsequent distribution, metals would be more mobile at Colaton Raleigh than at the Seale-Hayne sites. The in-site variability of each soil parameter is considered to be an important sub-control on metal results and has also been included on Table 5.1. 'Variability' in this case refers to between replicate differences, including a depth term. Ranking each site in terms of the variability of each soil factor clearly shows that Broad Meadow is the most variable of the sites. This is congruent with field observations, but may also be influenced by the smaller size of experimental plot here. Colaton Raleigh and Honey Park are essentially similar in these terms.

TABLE 5.1 SOIL FACTOR INDICES: A SUMMARY

soil factor	Honey Park		Broad Meadow		Colaton Raleigh	
	x	RSD	x	RSD	x	RSD
pH	5.8	7 %	5.9	11 %	4.9	8 %
CEC (meq 100 g^{-1})	26.1	23 %	20.5	30 %	15.6	27%
OC (%)	8.5	35 %	5.8	59 %	4.6	45%
clay (%)	33	29 %	39	20 %	15	18%
silt (%)	48	-	51	-	36	-
sand (%)	19	-	10	-	49	-
Fe (mg kg^{-1})	1318	42 %	1242	88 %	2544	18%
Mn (mg kg^{-1})	158	77 %	118	97 %	146	37%

TABLE 5.2 THE EFFECT OF TREATMENT ON REDOX POTENTIAL (V)

treatment	range (V)*	
	75 mm	175 mm
control	0.10 - 0.30	0.45 - 0.50
sludge treated/ freely draining	0.05 - 0.20	0.30 - 0.45
sludge treated/ waterlogged	-0.45 - -0.30	-0.25 - 0.25§

* 'range' refers to between-replicate differences

§ range includes within-replicate trends

FIGURE 5.1 SOIL pH WITH DEPTH

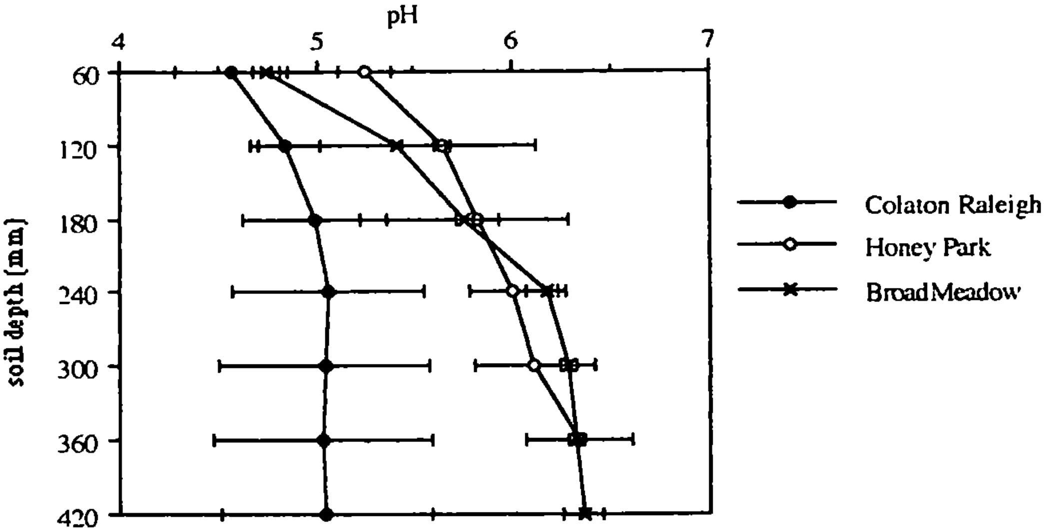


FIGURE 5.2 SOIL CATION EXCHANGE CAPACITY WITH DEPTH

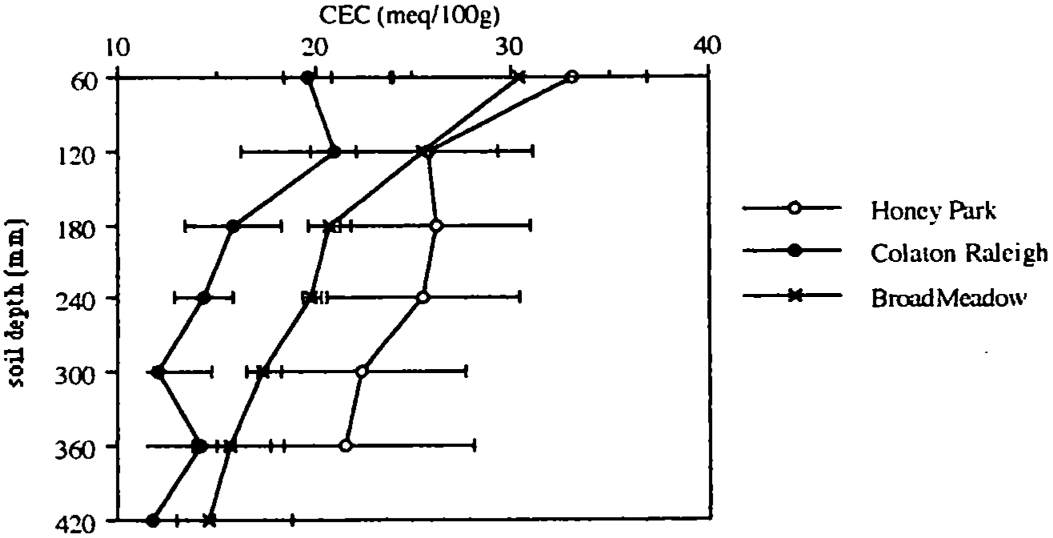
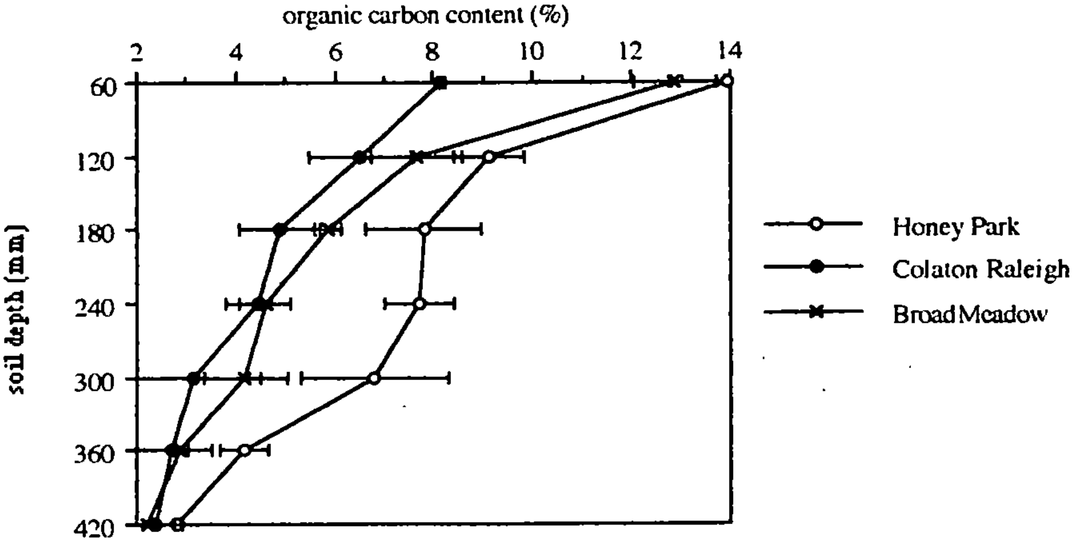
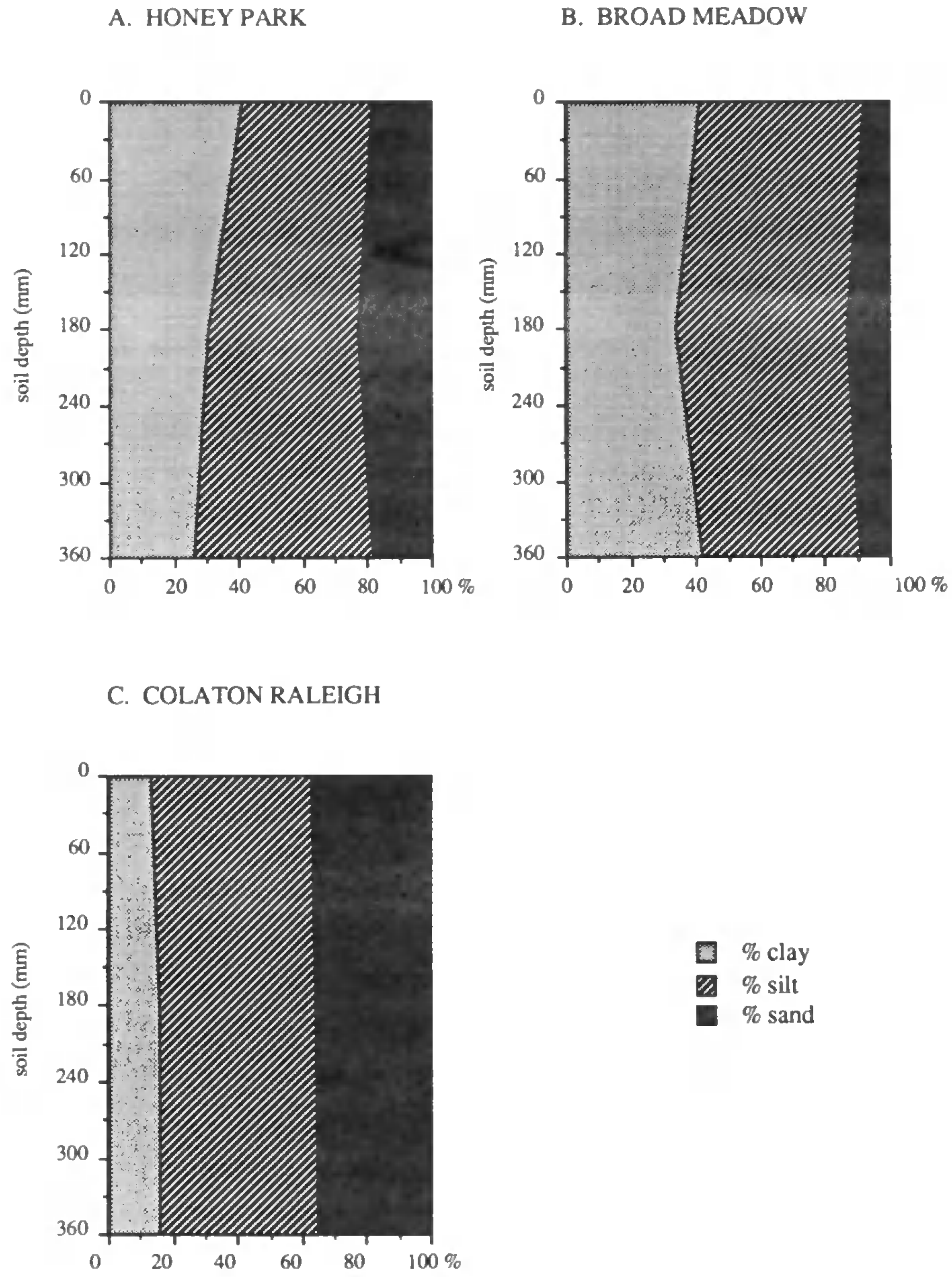


FIGURE 5.3 PERCENTAGE ORGANIC CARBON CONTENT WITH DEPTH



All points are the mean of 3 replicates, with variability represented by error bars.

FIGURE 5.4 PARTICLE SIZE ANALYSIS (< 2 mm) OF EXPERIMENTAL SOILS


A. HONEY PARK

B. BROAD MEADOW

C. COLATON RALEIGH

FIGURE 5.5.1 Fe CONTENT WITH DEPTH

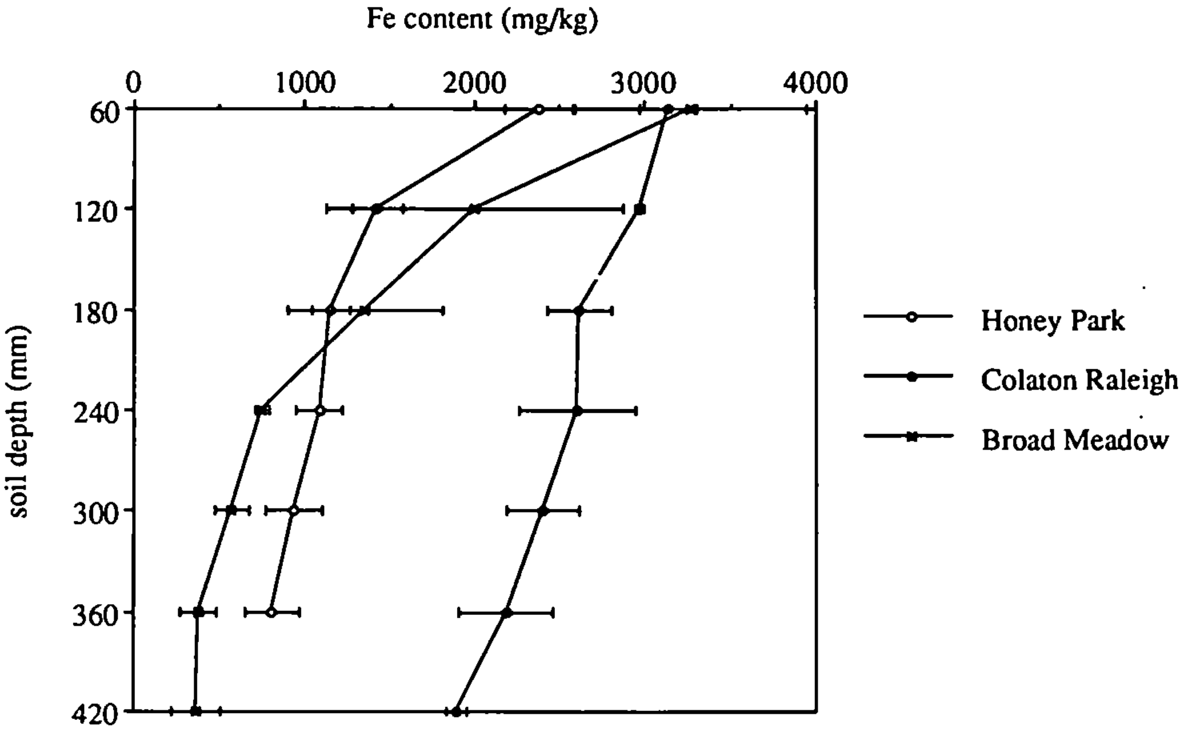
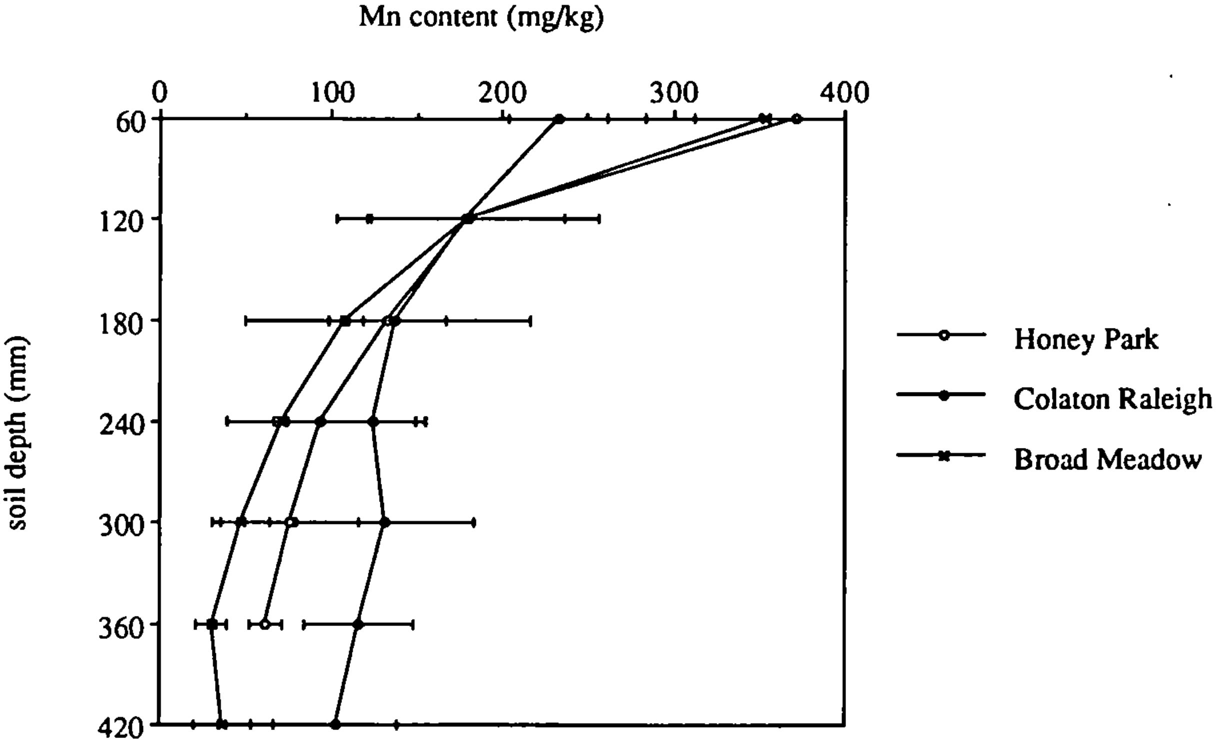
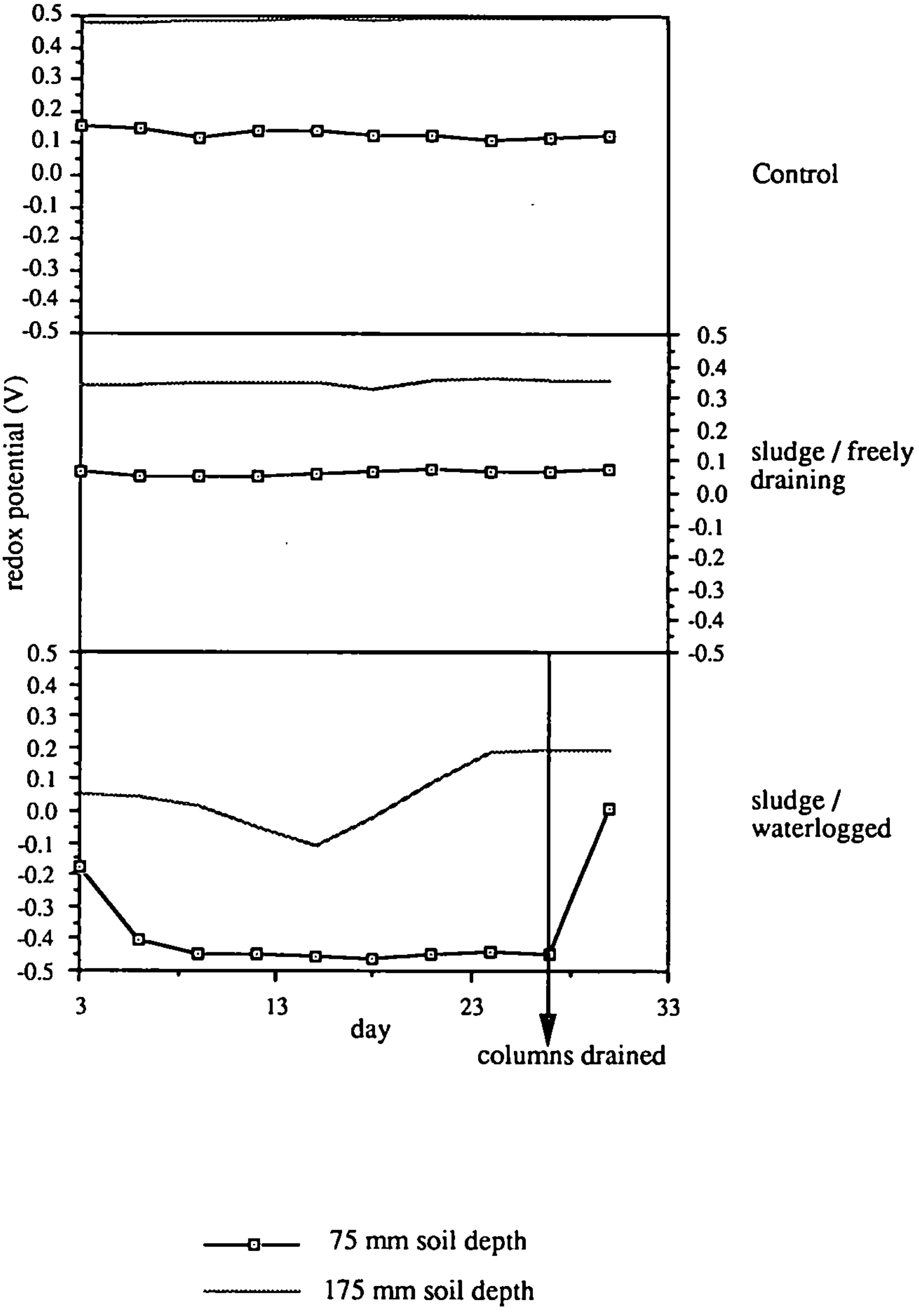


FIGURE 5.5.2 Mn CONTENT WITH DEPTH



All points are the mean of 3 replicates, with variability represented by error bars.

FIGURE 5.6 CHANGING REDOX POTENTIAL (V) IN SOIL COLUMNS



6 RESULTS 2: SLUDGE PLACEMENT

6.1 INTRODUCTION

In Chapter 1, the work of other authors, notably those associated with the WRc or Silsoe College, was used to indicate the potential difference in the soil loosening capabilities of different types of tine. However, such research is often conducted in homogeneous soil or sand bins. In contrast, the current author has employed the three main categories of tine design - namely, the straight (simple) tine, the side-inclined tine (paraplow), and the winged tine - in field situations. The resultant soil disturbance is therefore of interest both in its own right and in the context of this research, since the effect of tine design on sludge placement and the concomitant soil loosening is likely to be an important control on the ultimate location of metals.

To reiterate the methodology discussed in Chapter 4, the extent of soil loosening was identified for each replicate using shear vanes normal to the injection run on a similar grid to that used for sampling soils for their metal content. These vanes measure the shear strength of the soil, comprising cohesion, stress normal to the shear plane and the tangent of the coefficient of internal friction (Marshall and Holmes, 1988). Cohesion is closely related to clay content, whilst the coefficient of internal friction is defined by the size and shape of the particles or aggregates of which the soil is composed. In using shear strength data, it must be noted that since shear vanes themselves disturb the soil, samples for metal analysis must be taken from a different position along the injection run, and thus the two sets of results can only be expected to coincide exactly if the process of injection is constant, a factor that will be discussed in Sections 6.3 and 6.5.

6.2 SOIL LOOSENING

6.2.1 UNTREATED SOIL STRENGTH

Figure 6.1 illustrates the mean change in soil strength (kPa) with depth at each of the three sites. Broad Meadow and Honey Park display similar characteristics, in that there is an overall increase in soil strength with depth, as bulk density increases and aggregation decreases. This trend is enhanced after a depth of 120 mm, which can be considered the residual depth of past cultivations. The high clay content of these soils accounts for much of their strength, although other factors can not be ignored (Findlay *et al.*, 1984). Between-replicate lateral variability at Broad Meadow and Honey Park is reasonably depth-consistent (15 % and 8 %, respectively, values that are statistically indistinguishable from within-replicate variability). Conversely, soil strength decreases with depth at Colaton Raleigh, with the greatest change occurring between depths of 0 and 120 mm, representing a compacted layer. Structural development declines with depth to a single grain / structureless character (Jones, 1983) which exhibits few of the components of strength. Between-replicate variability increases from 5 % at the top to 23 % at the base of the profile (although it must be stated that these values are only just significantly greater than within-replicate variability). The differences between sites reflect factors such as soil texture, soil structure, and water content, in that strength will be compromised at either extreme: very dry soils become brittle, whereas a high water content may cause smearing. Water content can be assumed to have an inverse relationship with soil strength - i.e. Broad Meadow, injected at the end of summer, would have the greatest strength, *ceteris paribus* (Marshall and Holmes, 1988). With mean water contents at injection of 26 % (BM), 30% (CR) and 39 % (HP), none of the soils reach these extremes for their relevant textures (Baver, 1972), although Honey Park (which, at injection, was just beginning to dry after Winter) will have been close to its upper plastic limit, as defined by Baver (1972), whereas Broad Meadow at injection was probably close to its yearly driest. Despite the statistically proven chemical similarities between Honey Park and Broad Meadow, soil strength is thus significantly ($p<0.01$) lower at the former site. The same relationship also exists between Broad Meadow and Colaton Raleigh. This behaviour conforms to that predicted from other soil characteristics.

6.2.2 TREATED SOIL STRENGTH

Isoline diagrams of soil strength two weeks after injection (to allow for the drying of sewage sludge, which may otherwise reduce apparent strength) were generated without bias from shear vane measurements using a 'Diasurf' Fortran package. This utilises numerical algorithms and is based upon the work of Heap and Pink (1969). Contour intervals are 2 times the standard deviation of the mean, or multiples thereof. Diagrams representative of each treatment are presented by Figures 6.2, 6.3 and 6.4, which should be compared with Figures 4.1 and 4.2 for reference. In order to statistically assess the relative effect of the tines both in terms of soil type and alternative tine designs, quantitative descriptions in terms of the area covered that is less than background values (namely, 50 kPa at Colaton Raleigh and 70 kPa at Honey Park and Broad Meadow), and the range of soil strength found in untreated and treated soils can be employed. These background values, below which strength can be assumed to have been affected by injection, are taken from the lower critical value (2 standard deviations from the mean) of the distribution curve of untreated soil strength, since any value less than this can be said with 95 % confidence to be significantly different from control values. Similarly, any values greater than the upper critical value can, in association with a knowledge of the loosening patterns created, be used to identify any zones of compaction that the proximity of the tine legs to each other or to more resistant horizons causes. It must also be noted that the maximum reading on the shear vanes employed is 130 kPa, a value that was frequently exceeded at Broad Meadow and occasionally at Honey Park. The following Sections deal with the dimensions and variability of the shape and extent of soil disturbance. The relationship between field observations and expected performance of the tines in terms of depth and rate of injection is discussed in Section 6.5.

A THE STRAIGHT (SIMPLE) TINE

It has been shown in Section 4.1.1 that the straight tine is widely held to produce less soil disturbance than tines incorporating modifications such as wings, vibration and so on (e.g. Godwin *et al.*, 1976), that the soil disturbance created by the simple tine would be restricted to within a few centimetres of the leg, and that there would be no means of redepositing disturbed soil over the injected slurry or sludge (e.g. Hall *et al.*, 1986).

Figure 6.2 illustrates the subsurface soil strength (indicative of disturbance) of soils of both Honey Park and Colaton Raleigh that have been treated with simple tine injections. Each diagram represents the disturbance on one side of the injector only (it is assumed that the pattern will be approximately symmetrical) and for one replicate only, as the variability between replicates is as important as the pattern of disturbance itself. It can be seen that the basic configuration of disturbance takes the form of an elongated oval (long axis vertical), with a slightly enlarged base, that represents the passage of the leg itself. This holds both within and between the different soil types. The traction of the forward movement of the tine is manifested by the horizontal extent of secondary isolines that extend to merge with those of the adjacent tine in an approximate 'dumbbell' shape (long axis horizontal) as the tine 'tears' the soil. Soil strength at every point within this configuration is less than that found in untreated soil, thus contradicting previous observations regarding the limited effect of the straight tine. However, in the area surrounding this dumbbell, there is some evidence of compaction, especially at Honey Park. This compaction is caused not only by the weight of the implements, but more importantly by the compression of the soil. Thus, in a shallow soil with a high untreated soil strength this effect is more prominent. At Honey Park, all replicates exhibit significant ($p < 0.05$) compaction under the the tine leg at a depth of approximately 330 - 400 mm (see Figure 6.2). Further compaction, equally significant but not evident from the illustration, is located under the 'waist' of the dumbbell at both sites. The injection of a normal volume of sewage sludge (200 m^3 ha^{-1}) using a straight tine, followed by rolling, was observed to create an adequate soil covering. This is borne out by the lack of grass die-back experienced (anticipated in Section 1.4.2) and the fact that minimum soil strengths, illustrated in Figure 6.2, do not extend to the surface.

In quantitative terms, the area affected by simple tine injections is 40 ± 2 % (Honey Park) and 69 ± 6 % (Colaton Raleigh) of the sampled section (see Section 4.2.1). The significantly ($p<0.01$) greater disturbance at Colaton Raleigh outweighs the proportional difference in untreated strength between the two soils, demonstrating the effect of the components of shear strength on the manner in which the soil deforms. Thus, with a clay content of less than 15 %, the soil at Colaton Raleigh will possess little of the plasticity of Seale-Hayne soils (Baver, 1972) at their relevant water contents, tending to fracture instead. The data above also indicates, somewhat unexpectedly, that the process of injection, in terms of soil loosening only, is extremely consistent, especially at Honey Park. The range of soil strengths encountered at both sites is similar (not significantly different) to their respective background ranges (c.100 kPa and c. 80 kPa, for Honey Park and Colaton Raleigh, respectively), but these figures mask the downward transposition of the data by at least 10 kPa and 25 kPa (respectively) at each site. Thus, although many points remain greater than the average background soil strength, the entire sampled profile of 420 mm x 600 mm has been affected by the passage of an injector tine at approximately half this depth (Section 6.5) and with a width of only 50 mm.

Interestingly, the volume of sewage sludge injected also has an effect on the area disturbed by the passage of the tine. This is most pronounced at Colaton Raleigh, where the mean area of soil that has a post-injection strength less than that of untreated plots is significantly ($p<0.01$) smaller following a rate of injection of 200 m^3 ha^{-1} than after 300 m^3 ha^{-1} of sludge is added (52 % and 69 % of the sampled area, respectively). The basic oval configuration of soil loosening illustrated by Figure 6.2, whilst covering a smaller area, is not affected. The decrease in soil strength may partially reflect increasing water contents, but it is unlikely that this is the principal cause, since (a) water content should have a greater effect on clay soils, which are less well drained and are more subject to plastic failure; (b) monitoring the water content of a similar range of injected soils over a similar field season, Jury (1993, pers. comm.) observed that substantial (summer) drying of soils commenced 6 days after injection; and (c) the sludge mass was observed to be at incipient dryness when shear strength reading were taken. In addition, Stevens *et al.* (1988), studying the effect of spread pig slurry, found that a total of 2000 m^3 ha^{-1} would need to be applied to create significant strength decreases. Rather, the force of the injection of sludge under pressure (Section 1.4), which will obviously be affected by volume, may contribute to the deformation of the soil, flowing relatively easily through the disturbed soil and widening the affected area. This is supported by a reduction of the soil compaction found between the tines, but not underneath them, when a lower rate of injection is employed. Thus Araya (1985) observed that a low rate of injection (160 g/s (*sic*)) had ‘little disruptive effect on the soil with most of the sludge flowing out to the subsoiler path’, whereas a larger rate of injection increased soil failure. This effect would be enhanced by an increase in viscosity, but investigations related to the position of organic matter from the injected sludge (Section 6.3) suggest that the only the liquid fraction is actively involved in this process, with the majority of the solid material being filtered by the soil.

A third and unexpected form of soil loosening promoted by the injection of sewage sludge is that of the attraction of the sludge to earthworms, an important generator of macropores in undisturbed soils (Beven and Germann, 1982). Thus, a marked increase in the population density of earthworms was observed within the residual sludge mass during sampling, an effect that, whilst in evidence under other treatments, was at its most significant in the case of the straight tine. At Colaton Raleigh, this effect was taken one stage further by the presence of moles, presumably attracted by the number of earthworms and/or the ease of movement afforded by a loosened soil. These unerringly followed the line of minimum resistance and would presumably be responsible for a wider distribution of metals (N.B. areas affected in this manner were avoided during sampling as the effect is difficult to quantify and adds an unwanted variable to the investigation).

B. THE SIDE-INCLINED TINE (PARAPLOW)

Compared to the simple tine, the side-inclined tine is expected to increase the area of soil disturbed, and therefore the volume of sludge that can be injected. In this case, a wedge of soil is lifted and broken, and the sludge deposited beneath it. The efficiency of this mechanism compared to the simple tine was demonstrated in the field by a reduction in the volume of sludge present on the surface immediately following injection at a rate of 300 m^3 ha^{-1}. It is therefore anticipated that larger patterns of disturbance and/or greater areas of soil less than the background strength would be observed for the paraplow relative to the straight tine, and at Colaton Raleigh rather than Honey Park.

Figure 6.3 illustrates the effect of the paraplow on soil strength (in kPa) at both experimental sites, and shows the entire sampled slice between leg slots as, unlike either of the straight tines, its effect can not be assumed to be symmetrical. These isoline patterns are substantially different to those relevant to the straight tine, with configurations ranging from a distorted 'V' (e.g. the example shown for Colaton Raleigh) to a simple diagonal line (a distortion of which is illustrated by the Honey Park example). It must be noted, however, that each pattern is equally likely to occur at either site, although those at Colaton Raleigh are again more expansive. In accordance with this observation, the mean area of soil that is weaker than untreated soil is significantly ($p<0.05$) larger at Colaton Raleigh than at Honey Park (50 ± 18 % and 30 ± 4 %, respectively). Again, injection at Colaton Raleigh is significantly ($p<0.01$) more variable than at Honey Park, which again shows a remarkable consistency in area affected, if not configuration.

A comparison between this data and that pertaining to the straight tine (S) leads to the unexpected conclusion that the simple tine creates a greater area of disturbance within the sampled slice than does the paraplow (P). It is possible that the occurrence of more disturbance (greater area), but of a lesser magnitude within that area, is being masked by the generation of data in terms of 'less than background'. Accordingly, the maximum extent of disturbance is considerably less pronounced when the paraplow is employed (mean minimum values: 5 kPa (S) and 13 kPa (P); 2 kPa (S) and 8 kPa (P) for Honey Park and Colaton Raleigh, respectively), and distribution curves generated from paraplow data are flatter than those relevant to either the straight tine or untreated data. However, most paraplow data from Honey Park lies in the region principally occupied by untreated values, with its flatter nature largely attributable to an elongated lower tail (negatively skewed) which can therefore be considered unaffected by injection. In contrast, all distribution curves generated from Colaton Raleigh are distinctly normal, with paraplow data lying midway between straight tine and untreated data. It can therefore be taken that a similar area of soil at Colaton Raleigh is affected by both modes of injection, although the magnitude of disturbance within that area is decreased by the use of the paraplow.

In accordance with the statement that 100 % of the sampled soil slice is loosened by the passage of the paraplow, there is no area which is significantly more compacted in treated than untreated soil at either site. There is, however, an area of greater strength located 'under' the leg, where 'under' is defined by the extrapolation of the area of greatest disturbance downwards. This is not evident in all replicates.

In contrast to the indistinct difference between tines in terms of area of soil loosened, the simple tine has a distinct advantage over the paraplow in terms of both quantitative and qualitative variability, a result of the introduction of leg angle (with the concomitant complications of depth, draft requirements etc.) as an additional variable, and the different mechanism of disruption employed, in that a wedge of soil is lifted as well as 'torn', as with the straight tine.

It was noted previously that the rate at which sludge is injected may influence the extent of soil disturbance caused by the straight tine. When a lower rate of sludge is introduced through a side-inclined tine, a similar reduction in configuration of disturbance is observed, but in this case the effect is non-significant. Interestingly, if the effects of soil loosening by the tine and disturbance as a result of pressurised liquid introduction are considered to be cumulative and mutually exclusive, the removal of the effect of rate of injection from the total effect of the straight tine brings the loosening effect of the two tines into approximate equilibrium - that is, the paraplow loosens approximately the same area of soil as the straight tine at a lower rate of injection.

C. THE WINGED TINE

Most recent research on the physical dynamics of soil injection concentrates on the winged tine, as this method is considered to create the most soil disturbance (e.g., Hall *et al.*, 1986), allowing a greater quantity of sludge to be disposed of at a more even loading and a more suitable (shallow) depth for plant utilisation (Section 1.4). This type of injection was performed at Seale-Hayne only (Section 4.2.1) and at the higher rate of injection (Table 4.1).

Figure 6.4.1 describes the soil disturbance generated by the winged tine, illustrating a distinctive inverted 'T' configuration that mirrors the shape of the tine itself, although the dimensions of the wings especially are exaggerated (compare to Figure 4.1 and 4.2). This basic pattern is found at all replicates, although the dimensions are variable. This can be quantitatively described in terms of background concentrations. A mean 46 % of the sampled area has been disturbed by injection, but this value may vary by up to 18 %, making the winged tine the most variable of the tines investigated according to this criterion, an observation compounded by the identification of Broad Meadow as the least variable untreated soil in strength terms (Section 6.2.1).

From a comparison of the above description and that pertaining to the straight tine and the paraplow, it can be seen that the soil fails in a similar manner for the two straight tines. This is further reflected in the compaction characteristics of the two - most compaction created by the winged tine is located between the two tine uprights but at a depth less than that of the crosspieces of the 'T'. There is also some, but non-significant, compaction directly under the feet of the tines. This is likely to be the result of the deeper soil at Broad Meadow, but may be further relieved by the spreading of the downward force acting on the soil over a larger area. After six months, the central area of compaction is still evident and to a similar extent, but the gradient of change between loosened and compacted areas is lessened (compare Figures 6.4.1 and 6.4.2)

In assessing the relative effect of each of the tines, some compensation must be made for relative untreated soil strengths and thus the statistics employed in other parts of this Chapter cannot be used. It has been shown that a lower untreated soil strength (i.e. Colaton Raleigh) will fail to a greater extent when treated, regardless of tine design. Since Broad Meadow has significantly greater shear strength than either Honey Park or Colaton Raleigh (Section 6.2.1), it can therefore be assumed that a failure rate of 46 % at Broad Meadow is actually significantly greater than a failure of 40 % at Honey Park, despite the fact that the inherent variability in the former mean prevents the difference between the two sites being described as statistically significantly different. As with other treatments, winged tine injection appears to affect a greater area than is indicated by the above mathematical expression - soil strength does not return to values found at corresponding depths in untreated soil at any point in the treated profile other than where the passage of the tines have created compaction. This hypothesis is supported by field observations in the form of large vertical cracks extending from the base of the (horizontal) injection plane, highlighted by the addition of methylene blue to the injection slot. The relative effect of the tines in terms of area of soil disturbed can therefore be ranked as: winged tine > straight tine > side-inclined tine. This holds regardless of soil type, rate of injection or time of year (see Section 6.2.1).

D. DETERIORATION OVER TIME

Honey Park and Colaton Raleigh were injected in the field season preceding Broad Meadow treatments (Table 4.1), and preliminary results from these experiments indicated that the mechanics of slot closure may play an important role in metal distribution. These sites had subsequently been cultivated and therefore could not be re-sampled, but the strength of Broad Meadow soils was measured both two weeks after injection and immediately prior to sampling for heavy metal analysis (i.e. six months after injection). This new pattern of soil disturbance is illustrated by Figure 6.4.2. It is immediately apparent that the area of maximum disturbance (less than 70 kPa) has diminished, with the complete loss of the cross pieces of the 'T', a constricting of the area corresponding to the tine upright and the loss of disturbance in the zone between adjacent tines, to such an extent that the configurations become more reminiscent of the straight tine. This difference with time is appreciable - after 6 months, the average area affected is only 34 % of the sampled area, compared to the original 46 %. Peripheral weakening is eliminated altogether, with values returning to those corresponding with untreated values at equivalent depths within a few centimetres of the 70 kPa boundary. Interestingly, there is a concomitant reduction in between-replicate variability to 4 %. Unfortunately, it is not possible to accurately extrapolate these observations to include other tine designs, due to the different tine geometries, different soil types and different field seasons. However, this rapid consolidation has been observed by many authors (e.g. Carter, 1988; Ide *et al.*, 1987; Hipps and Hodgson, 1988; and Soane *et al.*, 1988) working with a variety of tines, soil types and field conditions, and Twomlow *et al.* (1994), working with similar soils. Most subscribe to the view that loosening remains for 3 years (or 3 field seasons). Recompaction has been related to traffic, cultivation and harvesting (Soane *et al.*, 1988) and wetting/drying processes in conjunction with plant root growth (Koolen and Kuipers, 1983). The latter will be the most significant process in the case of this study because a) traffic/cultivation/harvesting was kept to a minimum and involved only the harvesting of the grass on two occasions, and b) the injection of Broad Meadow was conducted at the beginning of the wetting-up season. Under these circumstances, Honey Park and Colaton Raleigh are likely to recompact at a slower rate.

6.3 LOCATION OF ORGANIC MATTER

Section 6.2 has shown that the soil loosening conducted by the tine, and influenced by the introduction of sewage sludge under pressure, falls into distinct and predictable patterns that are unique to each tine. However, it is important to identify how accurately this reflects the distribution of the sewage sludge itself, as this is the source of the added heavy metals. To this end, soils sampled for heavy metal analysis were ignited to estimate their organic matter content (Section 4.3.3), which is related to organic carbon as described by equation 4.1.

Of all treatments analysed by LOI, only the high rate straight tine yielded any definite pattern of organic matter distribution, illustrated by Figure 6.5. In using these patterns as the basis of the following discussion, it must be noted that at no point is treated LOI significantly greater than background LOI in statistical terms, and observations can therefore only be of a qualitative nature. Despite this constraint, LOI distribution can be seen to closely follow those configurations observed for soil disturbance - that is, an oval form with a vertical long axis. The centre of concentration is discrete, covering only one sampling point. Vertically, the location of the tine, as defined by soil loosening, is reflected by LOI results that exceed background values, but horizontally only those positions immediately adjacent to the centre of concentration are affected. Thus soil disturbance is indicative of organic matter location, provided that only the zone of maximum effect is considered - that is, the greatest depth of OM location will be less than that for disturbance. However, since the numerical definition of this zone varies for each replicate and soil type, it is only possible to delimit this correlation qualitatively.

With a limited distribution, an absolute maximum of 18 % (low rate treatments), 25 % (high rate treatments) and 17 % (winged tine treatments) extra organic matter would be expected within the sampled slice. This assumes no dispersion of the sewage mass, a soil bulk density of 1.3 g cm^{-3} and that all the dry matter constituent of the sludge is organic. The percentages quoted above are therefore overestimates, but nevertheless indicate some movement and/or degradation of the sludge since a maximum enrichment of about 15 % (high rate treatment) is observed. This statement also gives some insight as to why amended organic matter content can not be distinguished from untreated soil in the case of the side-inclined and winged tines - the side-inclined tine does not produce such extremes of soil disturbance, whilst the winged tine produces a larger area of maximum disturbance. Both these factors will tend to promote a wider distribution of sludge which will not be differentiated by LOI, by virtue of the low mass of organic matter compared to an equivalent volume of soil.

A less statistically sound, but nevertheless valuable, tool for identifying the relationship between soil disturbance and sludge location is that of visual observation. During sampling, residual dry sludge was very much in evidence from both straight tine and paraplow treatments. This was arranged in a discrete mass (straight tine), or a 'V', diagonal or horizontal configuration (paraplow), illustrated by Plate 6.1. These distributions reflect the range of patterns observed for soil loosening.

As a result of the evidence presented in this Section, it can be taken that extreme soil loosening is indicative of sludge location, and since soil strength was measured immediately after injection but sludge location was identified six months after injection, it seems that the bulk of the sludge dry matter remains *in situ*, at least over this time period, and that much of the shortfall in actual organic volumes can be attributed to degradation and imprecise measurement. The observed inertia of the organic matter confirms the supposition stated in Section 6.2.2 that the solid fraction of the sludge would be filtered by the soil and therefore remain essentially stationary, whilst any movement of the sludge mass was confined to the liquid fraction. As a result, the organic matter itself may impede its own progress in the soil and thus only minimal differences would be observed between the distributions of the two rates of sludge addition. In support of the argument of Section 6.2.2, the role of the solid fraction in enhancing soil disturbance, whether through its effect on water content, recompaction or some other process, is thus further eroded. This is not to say, however, that the liquid fraction has no role in this process.

In contrast to straight tine and paraplow injections, there was little evidence of residual sludge when the soil was sampled after winged tine treatments (not photographically distinct). There are three likely causes of this disappearance which may have acted singly or in accord. Firstly, the winged tine creates a larger area of disturbance and there are presumably more pathways of movement as a result - it has already been indicated, for example, that there was considerable vertical cracking extending out of the sampled profile. The winged tine is purported to create substantial mixing of the soil and sludge (Hall *et al.*, 1986), thus discrete residues of sludge would not be expected. Secondly, the sludge used in Phase II was considerably less viscous and of lower dry matter than that used in Phase I (4.0 % and 6.3 % dry matter, respectively - see Table 7.1) and would therefore encounter less resistance to flow, be more difficult to identify once dry, and/or create fewer blockages. Finally, the far greater incidence of rainfall between injection and sampling at Broad Meadow (Figure 4.4) may have encouraged the down-profile movement of the sludge both in suspension and solution, since organic matter only moves once bases such as Ca and Mg have been washed out (Sterrit and Lester, 1980). Of these, additional soil loosening is the least likely scenario, at least individually, since actual loosening is considerably less than that observed at Colaton Raleigh, where residual sludge was easily identified; since the sludge showed no inclination towards downwards movement immediately after injection (when the sludge was at its most liquid); and since little of the anticipated mixing was actually observed. Without additional evidence, such as heavy metal distribution (Chapter 7), any further discussion is conjecture. This subject will be revisited in Chapter 8.

6.4 IMPLICATIONS FOR WATER MOVEMENT

It has already been noted that the process of injection loosens the entire sampled area of soil, generating both macro- and micro pores of substantial continuity. In addition, the main position of soil loosening frequently remains as a definite 'tunnel' in the soil, indicated on Figures 6.2, 6.3 and 6.4 by a concentration of isolines. These factors would be expected to increase the hydraulic conductivity of the soil, although the effect of this on infiltration rates is likely to be minimal as the surface is left virtually intact. These processes are likely to be influential in the movement of metals away from the zone of placement. On the other hand, it has been suggested that such operations may disrupt existing macropores (Beven and Germann, 1982), especially if (a) plastic deformation is involved in the failure of the Seale-Hayne soils (Marshall and Holmes, 1988), and (b) there is clogging of fissures as a result of the filtration of larger (> 250 μm) suspended solids by the soil (Lea *et al.*, 1982), microbial growth or chemical precipitation (Vecchioli *et al.*, 1980, working on the recharging of aquifers with sewage sludge). However, the magnitude of loosening described in this

Chapter far exceeds untreated disturbance and can be considered to more than offset damage to existing networks, at least on the small scale. In addition, Oberdorfer and Peterson (1985) have found that the clogging of pores is at worst a short term problem, and there is no evidence in the literature to suggest that these effects, observed for aquifers, extend to topsoil.

The straight tine, with its discrete 'tunnel' of maximum soil loosening and surrounding secondary disturbance, can be assumed to behave in a similar manner to a mole drain, especially in the heavier Honey Park soil where plastic deformation is favoured. In this way, soil loosening will provide a direct and rapid vertical and lateral route for subsequent precipitation to the 'drain' and would then be conducted away (Leeds-Harrison *et al.*, 1982), thus increasing water movement above and beyond that anticipated from loosening alone. The winged and side-inclined tines do not yield such a distinctive 'drain', but loosening will still promote increased water movement due to the resultant macropores (Bouma, 1981; Beven and Germann, 1982), presumably in proportion to the relative amount of disturbance created (i.e. winged > paraplow). Thus, Stone and Kirkham (1983) found that, whilst the water content of the top 900 mm of soil was not affected by injection, it was significantly increased below this depth. This argument is by no means straightforward, however. For example, working on similar soils to those used by the present author, Twomlow (1989) found that loosening a silty clay loam enhanced the water content of the soil due to the improved storage capacity generated, which would presumably be further bolstered by the presence of the added organic matter, whilst S. Jury (pers. comm., 1992) confirms the work of Stone and Kirkham (1983) in the observation of greater water contents below the depth of injection only. Therefore, if water is to be cited as a mechanism for metal movement after injection, and assuming that injection improves the movement of water through the soil, metals in a soluble form would be largely absent from the sampled profile, moved either vertically in the case of paraplow and winged tine treatments, or laterally in the straight tine example. If, on the other hand, water has no role in the movement of metals, or if the metals were immobile after injection, the increased surface area of the subsoil created by its loosening would be expected to exaggerate the intrinsic inertia of the metals.

6.5 EXPECTED VERSUS ACTUAL TINE PERFORMANCE

In Chapter 4, the desired parameters of injection were stated as: a rate of injection of 300 m^3 ha^{-1} for all 'high' rate injections (including Broad Meadow) and a lower rate of 140 m^3 ha^{-1} (paraplow and straight tine injections, only). It was intended that the depth of injection be a constant 250 mm for all tines in order to facilitate direct comparison. It is important that the working depth of the straight tine and paraplow should not exceed this by more than 50 mm, since Godwin and Spoor (1977b) have found that a depth:width ratio of more than 6 will minimise the extent of soil disturbance. The paraplow and straight tine used had a width of only 50 mm.

In practice, it is extremely difficult to attain the desired rate of injection, and to maintain this or any rate over time. Other researchers of this subject have found that rate may vary by 20 %, due to a reduction in tank pressure as it empties (Peaty and Kernebone, 1988), to 50 % (M.J. Haan, 1988, pers. comm.), influenced by variables such as viscosity, blockages, speed, slope and soil strength. Such variations have been encountered by the current author, to such an extent that sections of runs or individual tine slots may be left completely devoid of sludge in some places. It is impossible to accurately measure this variability, since the constant interruption of injection that this would require would destroy the run. Instead, obviously anomalous areas were marked and avoided. Still, the resultant distribution of sewage sludge, as measured by LOI data, was found to vary by 20 % within the same field. Actual rates of injection were measured as 300 m^3 ha^{-1} and 225 m^3 ha^{-1} for the high and medium rate of injection, respectively, at Honey Park and Colaton Raleigh, and 324 m^3 ha^{-1} at Broad Meadow. These figures varied by less than 5 % between plots, thus inferring that whilst the delivery of sludge may be variable in the short run, overall it is a relatively constant process. The contribution of this factor to the overall variability of the injection process, and the importance of this variability in the acceptance of injection by its targeted users - the water and agricultural industry - is discussed in Chapter 8.

From isolines generated by shear vane data and field measurements, the depths at which each tine operated was found to be approximately 300 mm, 250 mm and 200 mm for the straight, side-inclined and winged tines, respectively, regardless of rate of injection. Site, however, was influential, with injections at Colaton Raleigh (both tines) being slightly (non-significant) shallower than at Honey Park. The role of soil type in this relationship is, however, questionable, as depth is largely controlled by the operator, with variability affected by factors such as stoniness and surface conditions. According to this criteria, Honey Park should contain the most variable injection depths, but the reverse is true - Honey Park is less variable (0 % and 28 % for simple and paraplow treatments, respectively) than either Colaton Raleigh (8 % and 35 %, respectively) or Broad Meadow (35 % for winged tine treatments). Small variations (not quantified) in depth have been noted by Peaty and Kernebone (1988) as the result of the reduced mass of the tanker as it emptied (with greater tyre deflection when the tank was full resulting in shallower depths of operation). However, if this was significant in this experiment, Broad Meadow should be the least variable as the sludge was supplied from a remote source using an umbilical tube, and variation would be systematic, rather than the observed random pattern. Instead, this may be the result of the greater 'stickiness' of Honey Park soils effectively holding the tine in place, or due to the greater exerted force at Honey Park than at Colaton Raleigh, rather than direct soil type influences: due to the heavier soil and wetter surface conditions, the straight tine required the power of two tractors for a successful injection. The paraplow has a smaller draft requirement under any set conditions (Hall *et al.*, 1986) and did not encounter this problem. Having less force of its own, the straight tine with single tractor would be more easily offset by soil and site inconsistency at Colaton Raleigh. Regardless of site, the paraplow has a greater percentage depth variability than the straight tine, even when adjusted for its shallower depth of operation. Presumably, this increased variability is a result of tine angle and the attendant differences in loosening methods (Section 6.2.2), as this is the only major difference between this and the straight tine. It is not possible to conclusively place the winged tine in this ranking due to soil type differences, but it is likely from a comparison with the similar Honey Park that it is more variable than the straight tine and at least as variable as the paraplow. These figures have implications for the sampling of sludge-amended fields (further discussed in Chapter 8) since the only modification made to the existing sampling protocol (DoE, 1989) to encompass injection is the inclusion of a proviso that soils should be sampled 'to the depth of injection', whilst no mention of the case of injection is made in the actual Regulations (1989). Since this depth is somewhat variable in the case of the paraplow and winged tines, a disadvantage compounded by the less extreme nature of soil disturbance and the location of this zone away from the surficial slot (thus, even immediately after injection, the sampler is not able to easily 'feel' the depth of injection), the efficiency of this sampling regime is called into question even before the distribution of the metals is considered.

6.6 SUMMARY

To summarise, this Chapter has shown that the process of injection effectively loosens the soil, both through the action of the tine and of the pressurised flow of sewage sludge into the soil. The pattern of soil disturbance caused by three different tines on three soils that have significantly different soil strengths is distinctive for each tine, but consistent both between and within soils. For the straight tine, this configuration takes the form of a vertically elongated oval, which does not vary with site. The paraplow creates a distinctive 'V' configuration, although this may be present in one diagonal only. This variability is not governed by soil type. The winged tine gives rise to an inverted 'T' configuration, with variability introduced in the extent to which the cross-pieces are present. In terms of actual area disturbed, the efficiency of the tines can be ranked in the order:

winged tine > straight tine > paraplow

- although it is possible that the straight tine and paraplow performances are equivalent, with the apparent result affected by (a) paraplow disturbance that is present but statistically undistinguishable; and/or (b) the greater effect of sludge volume on increasing the area loosened by the straight tine. Within the above ranking, relative loosening is of the order:

Colaton Raleigh > Honey Park and Broad Meadow

In terms of variability of area disturbed, the rank is modified (with the most variable first) to:

winged tine > paraplow > straight tine

and

Colaton Raleigh > Honey Park

Whilst it is difficult to separate the variability of the effect of soil type at Broad Meadow from that created by the winged tine, the similarity between Honey Park and Broad Meadow implicates the tine design at this stage.

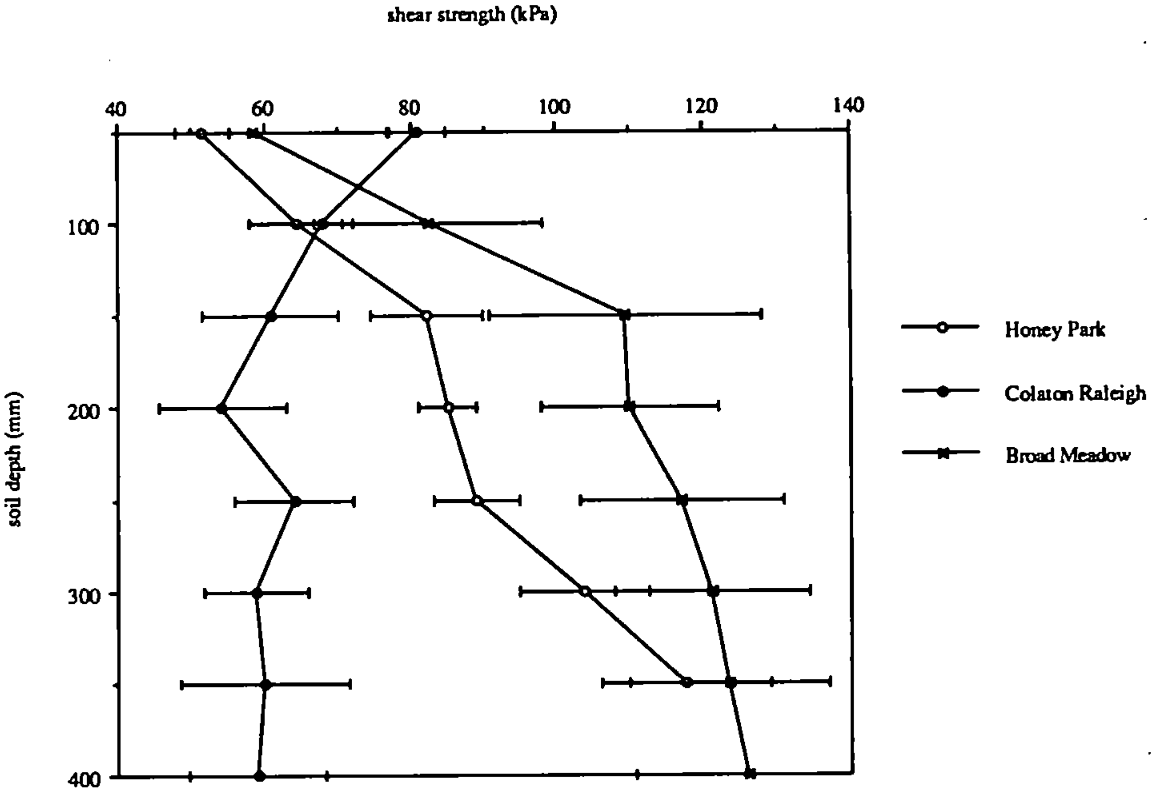
Whilst these parameters are extremely important in identifying the three-dimensional distribution of metals, only a measure of depth of injection is relevant to current guidelines (DoE Code of Practice, 1989). This depth varies with injector, as is anticipated in the aforementioned guidelines, but also between and within soil types. Furthermore, the variability of actual delivery of sewage sludge is approximately 20 % within the same field. Taking all these factors into consideration (namely, depth of injection, variability of sludge delivery, and treated soil strength), maximum average percentage variability of each treatment can be ranked, with values for each in brackets:

winged tine	>	paraplow	>	straight tine
(31 %)		CR (30 %) > HP (20 %)		CR (12 %) > HP (8 %)

In addition, high rate treatments are more variable than medium rate treatments, an effect largely generated by the more consistent area of loosening in the latter case.

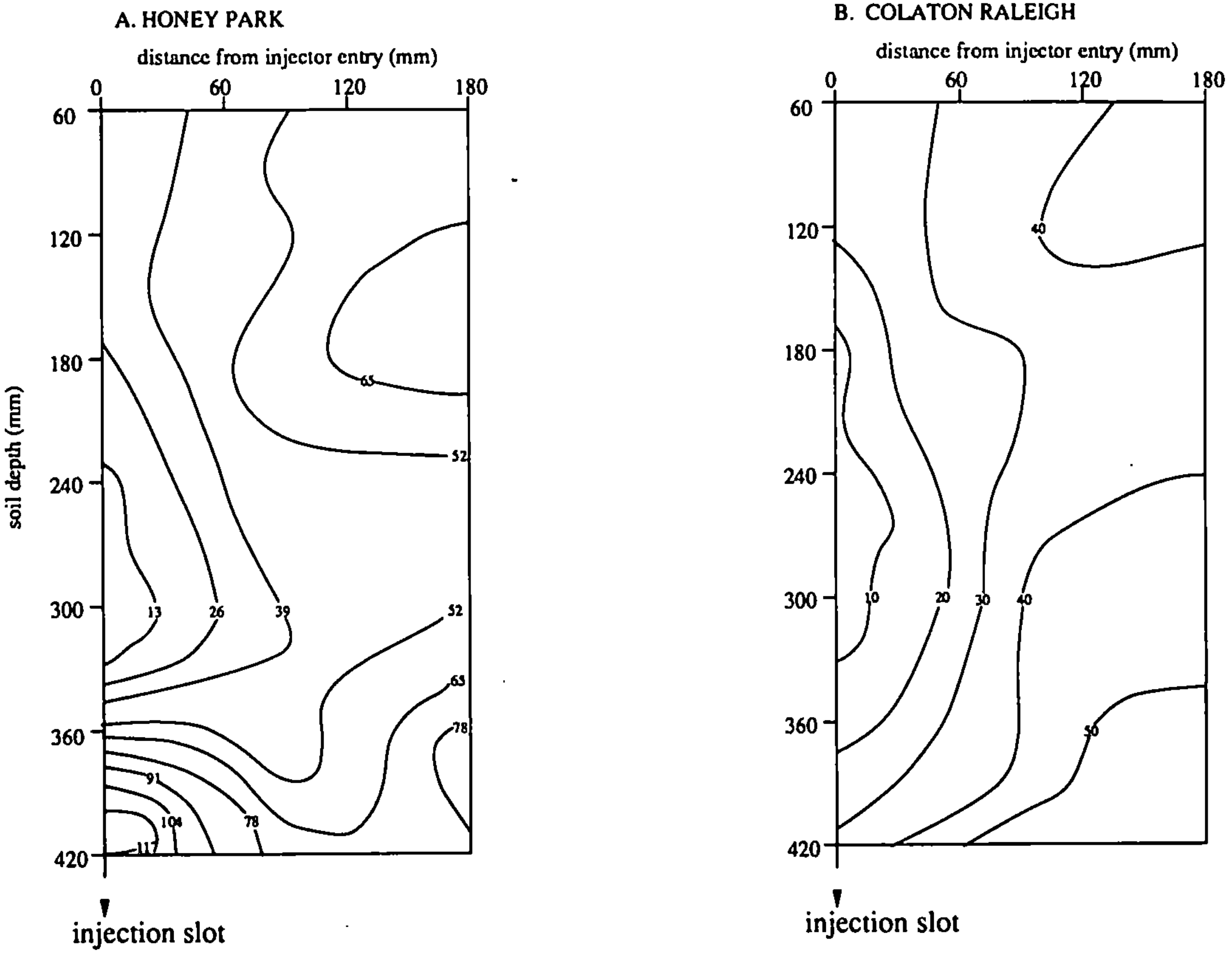
FIGURE 6.1 UNTREATED SOIL SHEAR STRENGTH (kPa)

- CONTROL PLOTS 2 WEEKS AFTER INJECTION



NB. Each point represents the mean of 3 replicates. Variability is represented by error bars

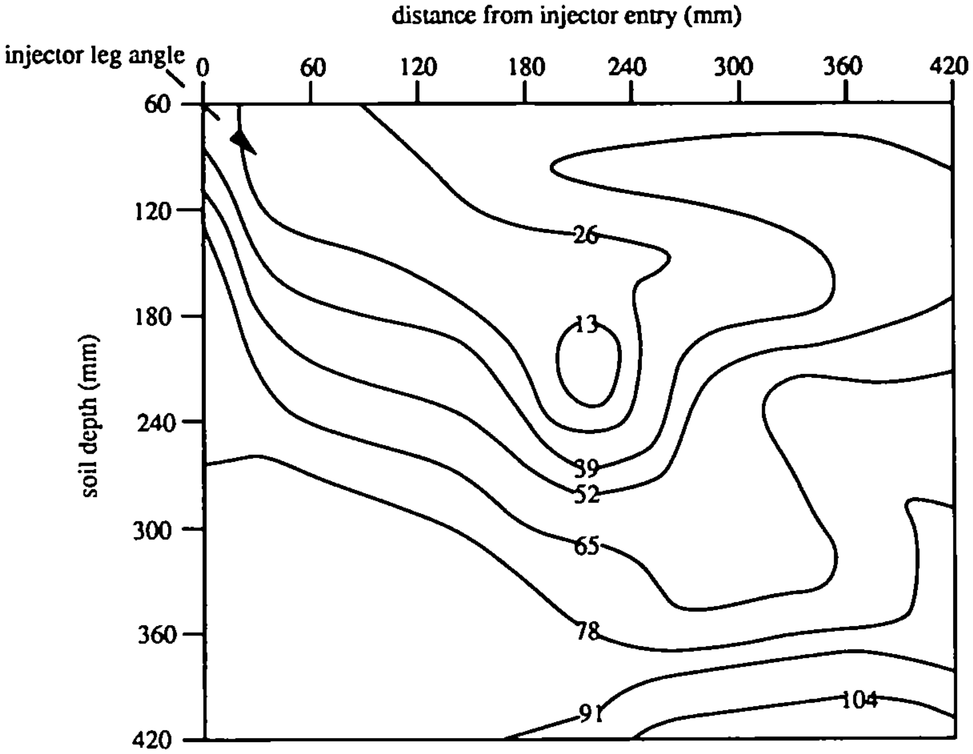
FIGURE 6.2 SUBSOIL SHEAR STRENGTH (KPa) 2 WEEKS AFTER INJECTION WITH THE STRAIGHT (SIMPLE) TINE


A. HONEY PARK

B. COLATON RALEIGH

FIGURE 6.3 SOIL SHEAR STRENGTH (kPa) 2 WEEKS AFTER INJECTION WITH THE SIDE-INCLINED TINE (PARAPLOW)

A. HONEY PARK



B. COLATON RALEIGH

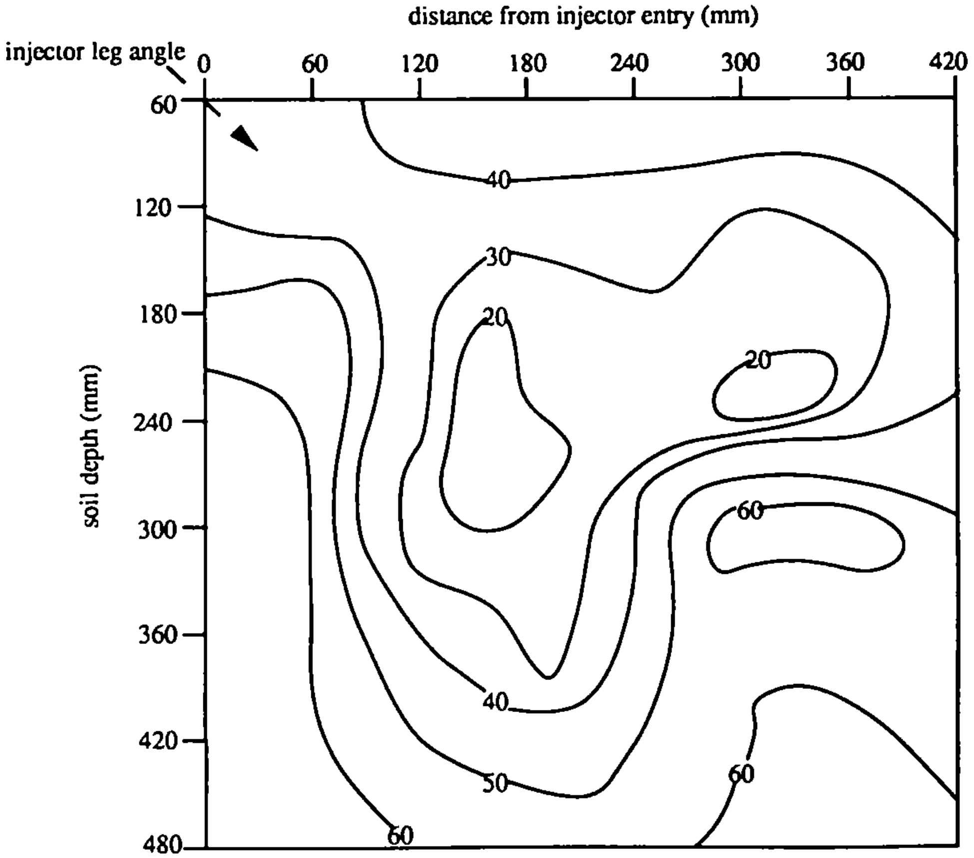
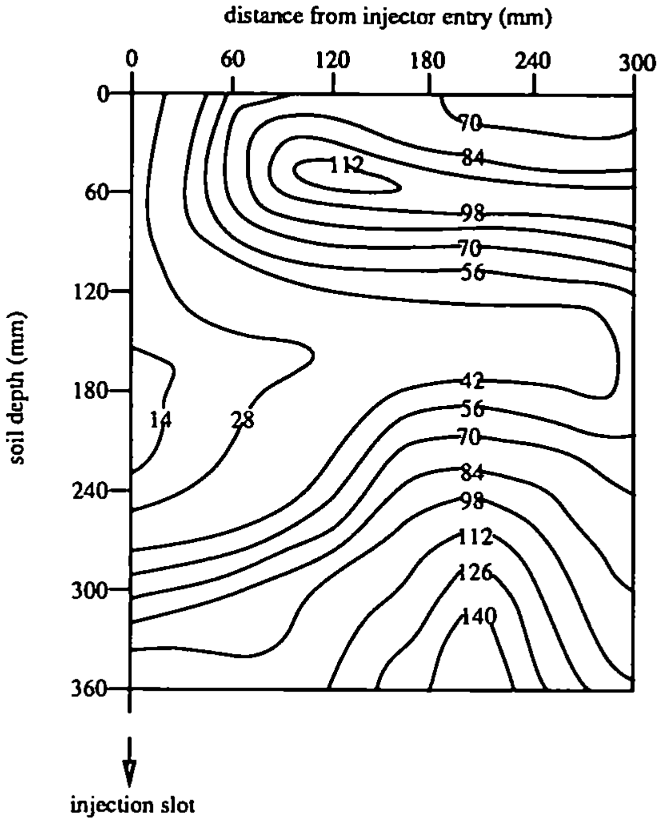


FIGURE 6.4 SOIL SHEAR STRENGTH (kPa) FOLLOWING INJECTION WITH THE WINGED TINE

6.4.1 TWO WEEKS AFTER INJECTION



6.4.2 SIX MONTHS AFTER INJECTION

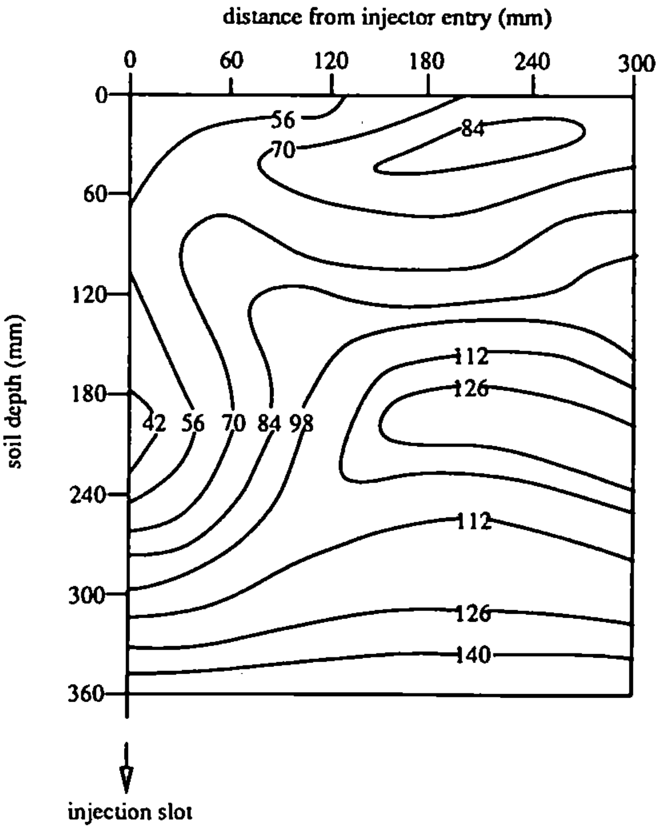
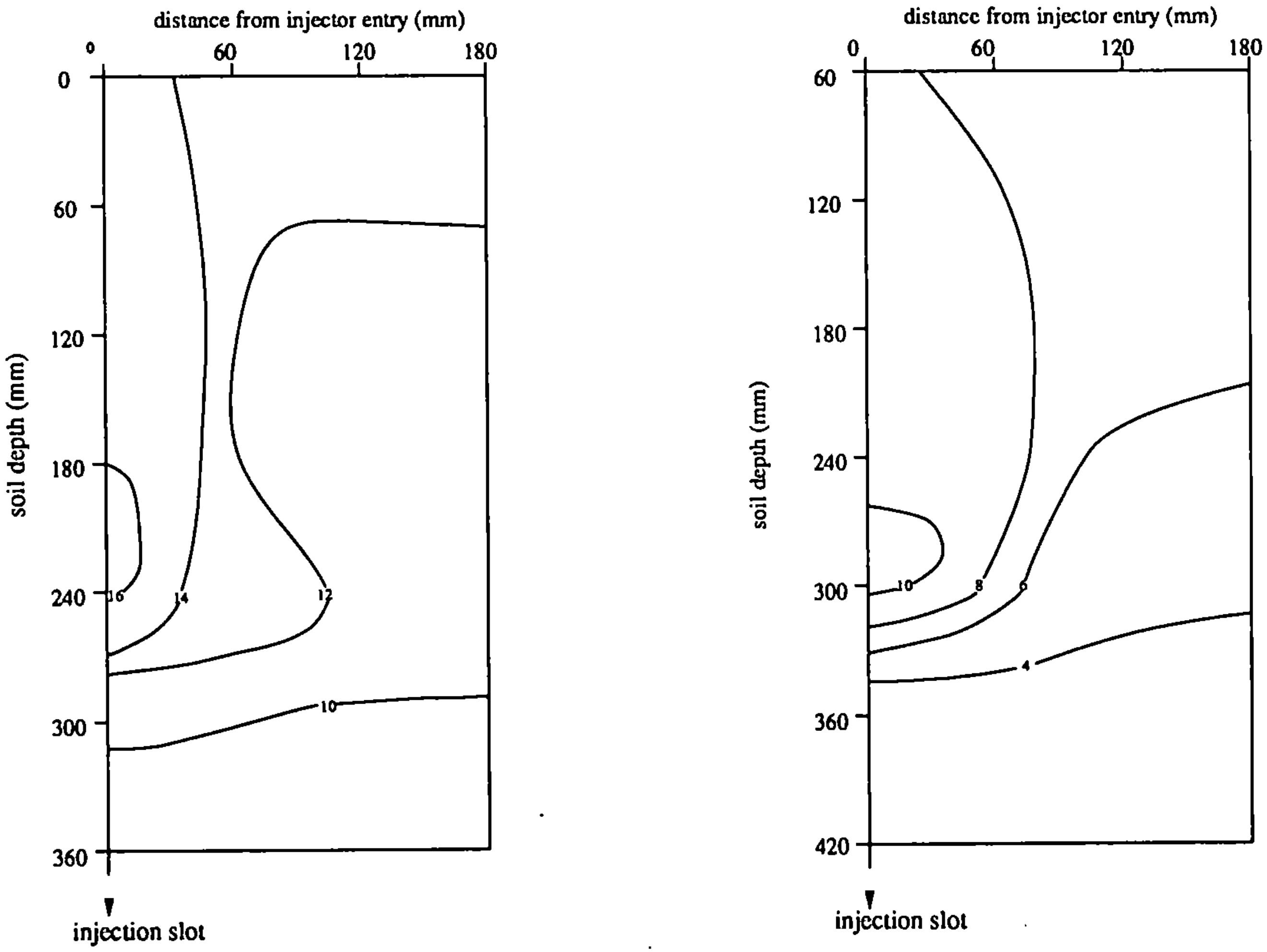


FIGURE 6.5 SUBSOIL ORGANIC MATTER CONTENT FOLLOWING INJECTION WITH THE STRAIGHT TINE (% BY MASS)


A. HONEY PARK

B. COLATON RALEIGH

PLATE 6.1 SUB-SURFACE DISTRIBUTION OF SEWAGE SLUDGE - 6 MONTHS AFTER INJECTION

1. THE STRAIGHT TINE

2. THE SIDE-INCLINED TINE

7. RESULTS 3: HEAVY METALS

In Chapter 2, current knowledge pertaining to the concentration, distribution and mobility of metals was reviewed. It was shown that, whilst a substantial body of research into movement from spread sludge exists, the behaviour of metals from injected sludge remains largely unknown. In this Chapter, the post-injection concentration and distribution of heavy metals is described, and the effect of time and tine design on this is considered. The distribution of metals is represented by isoline diagrams, generated without bias using the same 'diasurf' Fortran package that was employed for Section 6.2. It is impossible to have a consistent contour interval for all the metals at each site due to the differences in scale, and the necessity of having sufficient contours to reduce the probability of 'accidents of geometry' obscuring important features (Robinson *et al.*, 1984). Originally, each diagram has been drawn with a contour interval of two times the standard deviation of the control, as this statistic inherently contains a 95% confidence interval. Where this interval masks trends (for example, it is generally too small for Zn, which has a wide range of concentrations, and too large for Cd), multiples of the original value are used.

7.1. ANTECEDENT HEAVY METAL CONCENTRATIONS

7.1.1 HEAVY METALS IN SEWAGE SLUDGE

Analysis for total (HNO_3-extractable) Cd, Cu, Ni, Pb and Zn was conducted on Phase I sludge (1) (Table 4.1), and for Cu and Zn on Phase II (2) and soil column sludge (3):

sludge 1	sludge 2	sludge 3
Honey Park	Broad Meadow	redox-controlled columns
Colaton Raleigh	(injection 1989)	
(both injections 1988)	mass balance columns	

The heavy metal concentrations are reported in Table 7.1. Whilst making no adjustment for percentage dry matter, a comparison with Table 2.2 shows that the metal content of sludges 1 and 3 are similar to the averages stated by Moss *et al.* (1985) and within the ranges stated by other authors. The exception is Ni, whose content falls short of the range stated by each of the considered authors. Sludge 2 is exceptional in its high content of Cu (greater than each of the stated averages, but still within each range) and extremely low Zn content (not even falling within the range stated by most authors). It can also be seen that sludge 2 is more variable than sludge 1 for the selected elements, largely because of their different origins - sludge 2 originates from Crediton and is transported by tanker to Countess Wear for treatment, whilst sludges 1 and 3 are collected at Countess Wear and remain there for treatment. Crediton has a greater incidence of minor pollution events, exacerbated by a lower flow rate (SWW, 1991, pers. comm.).

The difference between the two sludge types (i.e. Countess Wear or Crediton) is further emphasised by the proportion of the metal concentration that exists in the liquid phase (Table 7.1). Within the same sludge, this percentage varies for each metal by up to 20 % and 50 % for sludges 1 and 2, respectively. However, these figures represent less than 20 mg kg^{-1}, so the differences in liquid-phase variability can not account for the different variability of total metal concentrations. Despite the 'in-sludge' disparities, the partitioning of metal concentrations between solid and liquid fractions is significantly ($p<0.05$) different between sludges. Taking Cu and Zn for example, 0.7 % of Cu and 0.3 % of the Zn concentration is found in the liquid phase of experimental sludge 2 (Crediton), but only 0.2 % and 0.1 % (respectively) of the metal concentration is accounted for by the liquid fraction in experimental sludge 1 (Countess Wear). Nickel, as may be expected (Section 2.2.2), is present in the liquid phase in a significantly ($p<0.01$) greater proportion than any other metal.

7.1.2 HEAVY METALS IN SOILS.

A. PHASE I: HONEY PARK AND COLATON RALEIGH.

The average background concentration of individual metals at Honey Park and Colaton Raleigh are compared in Table 7.2. Each metal is present in significantly greater ($p<0.01$) concentrations at Honey Park, but the relationship between metal pairs is not constant, that is, each metal is not present at Colaton Raleigh at a constant x % of that at Honey Park. However, Cu, Ni and Zn at Colaton Raleigh are a relatively similar 24-37 % of those at Honey Park, and only the Pb concentration at Colaton Raleigh is more than 50 % of that at Honey Park. This is reflected in the different position of Pb in the rank of metal concentrations at each site, which is of the order:

Zn > Ni > Pb > Cu > Cd Honey Park
Zn > Pb > Ni > Cu > Cd Colaton Raleigh

The latter ranking is identical to that of the national average concentration of metals that can be formulated from the data cited by Archer and Hodgson (1987) and Berrow and Reaves (1984). The concentration of Cd at the experimental sites is anomalously high in comparison to the means expressed by other authors (compare Tables 7.2 and 2.4), but the apparent Cd concentration of the experimental sites are known to be exaggerated, and are presented under the proviso that they are considered in relative terms only (Section 4.3.2). All other metal concentrations fall well within the ranges observed by other authors, although particularly those at Colaton Raleigh and Zn at Honey Park are present in considerably lower concentrations than would be expected from a survey of the literature, possibly affected by the sampling of soil here to a greater depth than the norm. It is important that any decrease in metal concentration with depth is identified, in order to assess the impact on metal concentrations of sludge addition at a relatively uncertain depth. However, Figure 7.1 shows that there is no statistically significant change with depth for any metal at any site. Correlation analysis (Table 7.3) shows that metals within the same site have similar depth characteristics. Only Pb maintains this similarity between sites.

In order to facilitate the identification of factors that influence any variability in the behaviour of sludge-borne metals, it is also desirable to identify the variability of background metal concentrations between replicates. Each data point on Figures 7.1 represents the mean of three replicates. The RSD of this mean varies with depth, as indicated by error bars, although not necessarily in a constant manner. At Honey Park, the maximum RSD at any given depth varies between 23 and 30 % for all elements. The average (in depth terms) percentage variability between replicates at Honey Park is correspondingly similar for each metal, and RSDs are strongly correlated. Variability can be roughly ranked as:

Zn > Pb ≥ Ni > Cd ≥ Cu

Percentage variability between replicates is generally considerably lower at Colaton Raleigh for Cu, Ni and Zn. The metals in this case are ranked in the order:

Cd > Pb > Zn > Cu > Ni

There is an overall increase in variability with depth with respect to Cd, Cu, Ni and Pb, whilst that for Zn is erratic. However, there is little correlation between the variability of each metal with depth. It can therefore be concluded that Honey Park and Colaton Raleigh are significantly different soils in terms of metal loading and the variability of that loading both vertically and laterally (Honey Park is significantly greater in both respects).

B PHASE II: BROAD MEADOW

Phase II, conducted at Broad Meadow, Seale-Hayne Farm (Figure 4.3), investigates the behaviour of Cu and Zn only, consequently the background concentrations of these metals only are presented in Table 7.2. As would be expected both from a review of the literature (Table 2.4) and from the similarity with the Honey Park site, Zn is present in significantly greater ($p<0.01$) quantities than Cu at Broad Meadow. Both metals are present in significantly greater ($p<0.01$) concentrations than at Colaton Raleigh, but in concentrations that are statistically no different from those at Honey Park. This supports the treatment of Honey Park and Broad Meadow as the same soil, in terms of metal content, and the feasibility of using Zn and Cu to represent the larger group of metals. Similarly, the absolute variability (including both depth and replicate variations) of the metals is broadly comparable to that at Honey Park, although between-replicate variability for Cu is greater than at the other sites, whereas the reverse is true for Zn, in a significant relationship ($p<0.01$). As with Phase I sites, neither Cu or Zn exhibits any consistent change in concentration with depth at Broad Meadow (Figure 7.1), and there is no significant change in variability with depth.

7.2 THE HEAVY METAL CONCENTRATION OF SLUDGE-INJECTED SOILS. 1: THE DIFFERENCE BETWEEN SOIL TYPES

Whilst this research focuses mainly on the sub-surface distribution of metals after injection, it is only the concentration that is of direct relevance to Directive 86/278/EEC. The effect of injection on this is best illustrated using the straight tine, which is relatively free of complications in terms of soil disturbance and the final location of the bulk of the sewage sludge. Similarly, the variability incurred by averaging the results of each replicate favours their use individually. To minimise bias, one replicate from both Honey Park and Colaton

Raleigh has been randomly selected to represent the site as a whole. Deviation from this case is discussed below.

An illustration of the change in metal concentration in a slice of soil taken directly down the leg slot, and therefore including the sewage sludge mass itself, is provided by Figure 7.2, about which it must be noted that all values represent amended concentration minus background concentration, and that all data refers to that collected from high rate treatments. At both sites, the maximum increase in concentration is of the order:

Zn > Cu > Pb > Ni > Cd,

although this relationship is somewhat confused by the fact that most, if not all, sampling points contain Ni and Cd in concentrations less than that found in the control samples. Interestingly, this rank of concentration reflects neither that found in the sewage sludge alone (Zn > Pb = Cu > Ni > Cd, Section 7.1.1), nor that contained in the untreated soil (where Pb > Cu in both cases), probably because Cu is strongly associated with the organic fractions included within the sampled section.

Figure 7.2 also clearly illustrates the difference between soil types with respect to the location of elevated metal concentrations. At Colaton Raleigh, there is a distinct 'peak' in all metal concentrations at 300 mm, with a secondary maxima at 240 mm observed in cases where amended metal concentrations exceed background concentrations. In conspicuous contrast, the metals at Honey Park reach a maximum concentration at depths shallower than 240 mm, although the specific depth involved is somewhat metal-dependent, and therefore rules out complete control by depth of injection (Section 6.5 discusses the variability of the injection process). Thus, Cu and Pb concentrations have a relatively broad peak around 240 mm, whereas Zn and Ni peak sharply at 180 mm. There is some, but by no means unequivocal, evidence in the literature to suggest a similarity in the behaviour of these metal pairs. For example, Baker (1990) states that Cu and Pb are both specifically adsorbed in soils, and therefore have similar soil chemistry. In contrast, Zn and Ni are known to be strongly pH-dependent (Sanders *et al.*, 1987) and have similar pH thresholds (Sanders and Adams, 1987 and 1984a). In addition, it has been proposed that Zn and Ni are present in similar fractions in sewage sludge (Holtzclaw *et al.*, 1978), and are the more mobile of the heavy metals (Holtzclaw *et al.*, 1978). The concentration of Cd is less than its background concentration at all depths.

Unexpectedly, because the disparity between sludge and background soil metal concentrations is far greater at Colaton Raleigh than Honey Park (compare Tables 7.1 and 7.2), there are more sampling points that contain Zn or Pb in excess of background concentrations at the latter site, and only in the case of Ni is the expected relationship evident. These observations may be the result of either the interaction of the antecedent soil chemistry, or of the differential movement of metals out of the sampled profile. Both these points are discussed in detail in Section 7.4, where the entire sampled slice is considered, and in Chapter 8.

Figure 7.3 illustrates the in-site variability of replicates in terms of metal concentration. It must be noted that, in order to assess the concentration of Ni and Cd throughout the entire profile depth, no account of background concentration has been made in this diagram. Only two replicates are represented for Cd at each site as soil concentrations were less than the detection limit of the AAS used for the analysis of the missing replicate (Section 4.3.2).

At Colaton Raleigh, percentage variation (RSD) is seen to be at its lowest where metal concentrations are greatest, in the order:

Pb > Zn > Cu > Ni > Cd RSD at Colaton Raleigh

At Honey Park, replicates are most similar at the base of the profile (with the exception of Ni). The rank of variability here is:

Pb > Cu ≥ Zn > Ni > Cd RSD at Honey Park

Honey Park is generally more inconsistent than Colaton Raleigh. The exception is Pb, which is also significantly more variable than any other metal, due largely to the inclusion of one replicate at each site that can be considered a statistical outlier.

When the between-replicate variability of the background metal results are subtracted from the variability of the sludge-amended soil (Table 7.4 compares the two sets of figures) - that is, producing that variability that is solely the result of injection treatments - an interesting pattern emerges. At Colaton Raleigh, the change in variability with depth is strongly metal-dependent, except for a ubiquitous minimum at 300 mm - the depth at which sludge-amended metal concentrations reach their maximum. In the case of Zn, Ni and Cd this constitutes a negative value - that is, at a depth of 300 mm between replicate variability is reduced by the addition of sewage sludge. Except for Zn and Pb, which show extremely erratic variation with depth, the concentration of metals is most inconsistent between depths of 120 - 300 mm (exclusive). At Honey Park, however, there is a very definite pattern of between-replicate variability with depth that holds for all metals. In this case, percentage RSD peaks at the focus of metal concentration: 240 mm, with a secondary maxima at 180 mm. The results from each replicate are most consistent at 120 mm.

The results pertaining to the concentration of metals after sewage sludge has been injected through a straight, simple tine thus imply that the process is more uniform on a sandy soil in terms of depth of placement and the subsequent elevation in metal concentrations. On a more clayey soil, the process of injection has far less reproducible effects on vertical metal distribution, and is especially erratic at depths close to that of sludge placement. The effect of soil disturbance on the concentration of metals away from this area appears to be minimal at this point, but will be discussed in more detail in Section 7.4.

By comparing the point concentrations of each treatment replicate, it is possible to define the relative variability of each tine, as well as each site. Maximum variability is large, ranging from approximately 50 % at Honey Park to 75 % at Broad Meadow and c.80 % at Colaton Raleigh. This is regardless of tine design. However, the rank variability of tines is not consistent throughout all treatments, but it would appear that injection in a drier soil using a winged tine and less viscous sludge (i.e. Broad Meadow) increases variability, as it has been shown that the soils of Broad Meadow and Honey Park are essentially similar. Section 7.1 has previously described the inherent variability of metal concentrations at Colaton Raleigh as falling considerably short of that at Honey Park, but it has also been shown in this Section that injection in a sandy soil is more consistent in terms of sludge placement. Thus at Honey Park and Broad Meadow, variability of each metal is maximised (although not necessarily at its absolute maximum) in the zone of sludge placement, whereas the reverse is true at Colaton Raleigh. It would appear that whilst the depth of operation is more difficult to control on a heavier soil, the concomitant loosening, and its subsequent effect on metal distribution, is the more difficult to predict on a sandy one, an hypothesis that would support the observations made in Chapter 6.

The increase in metal concentration down the leg slot created by injection at a lower rate (approximately 200 m^3 ha^{-1} compared to approximately 300 m^3 ha^{-1}) is described by Figure 7.4. Data is available for two replicates only, and it is clearly evident that the difference between replicates is at least as great as it is for the higher rate of injection. Variability is especially marked at Colaton Raleigh, where replicate 1 shows no definite increase in metal concentration at any one depth. It would be easy to point to sampling error as the cause of this apparent anomaly, except that a) a deposit of sludge was observed during sampling, and b) all values are substantially in excess of background concentrations, excepting Cd, whose amended concentrations can not be distinguished from background concentrations at either replicate. Replicate 2, on the other hand, exhibits a similar change in metal concentration with depth as that observed for higher rate treatments, that is, distinct peaks in the soil metal content occur at a depth of 300 mm. Reducing the rate of injection does not necessarily, therefore, reduce the variability of subsequent metal concentrations.

At Honey Park, definite concentration peaks are evident for all metals at most replicates, the exceptions being Zn and Cd in replicate 1. The vertical location of each metal peak is variable, irrespective of rate. It is interesting to note that, whilst the extent of this deviation is similar for both rates of injection, there is no variation with replicate or metal that holds for both rates of injection. This would tend to suggest that the variability is created by the injection process rather than by soil factors, and that whilst individual metal behaviour may modify this effect, it is not of primary importance. This hypothesis is further implicated in a comparison of the extent of metal enrichment (amended concentration minus background concentration) in high and low rate treatments. Since the low rate of injection is approximately two thirds of the high rate, and since the same sludge, throughout which the metals are reasonably well distributed, was used, two thirds of the metal enrichment would therefore be expected in soils injected at the lower rate. This is rarely the case, with Honey Park soils generally containing less than 60% and Colaton Raleigh more than 100% of the metals found after high rate treatments. It therefore appears that the rate of injection can not be controlled even within these crude boundaries, although it is impossible to dismiss other factors, such as the effect of soil type on metal or sludge movement (see Chapters 6 and Section 8.2) since only one slice of soil is being investigated at this stage.

7.3 THE HEAVY METAL CONCENTRATION OF SLUDGE-INJECTED SOILS. 2: THE CHANGE WITH TIME.

Up to this point, results have described the effect of sludge injection on soil metal concentrations six months after the event. However, it is also desirable to ascertain whether there is any substantial change in the metal concentration in the zone of sludge placement with time, which may clarify the distinction between the distribution of metals created by the injection of sludge and the movement of metals away from this area. To this end, auger samples were taken one and three months after injection and compared to six month grid samples by downscaling the latter to comparable detail (Figure 4.5 illustrates the different sampling regimes). The change in the HNO_3-extractable concentration of selected metals at Honey Park is illustrated by Figure 7.5. Several points need to be noted: a) the location of these samples corresponds with those discussed in Section 7.2 - that is, taken down the leg slot of soils amended with 300 m^3 ha^{-1} of sewage sludge injected through a straight tine; b) each data point represents the sum of three replicates due to the anticipated variability of the replicates and the obvious inability to take all sets of samples from exactly the same point; and c) all samples were taken by the present author, but those for 1 and 3 months were analysed by another (Williams, 1990), using contemporary instrumentation (a Pye SP-9 AAS) and the same methods of extraction. To minimise the error incurred by the use of different times of sampling, different instrumentation and different operators, all results presented in Figure 7.5 take account of their relevant control values.

Figure 7.5 illustrates a surprising increase in Zn concentration with time. The most appreciable change takes place between 3 and 6 months, representing in all but the basal layer a significant increase at $p<0.01$. Since no additions of metal were made in this time scale, the increase may reflect a shifting in metal form to one more readily extractable with HNO_3, or may not be a real result. The former theory supports the 'time-bomb' hypothesis investigated in Section 2.2.1, which states that metals may become increasingly available with time, although this seems unlikely over the timescale involved here. The alternative explanation is favoured by the involvement of 2 analysts (but an increase with time still exists if only that data from 1 and 3 months (i.e. one analyst) is considered) and the degree of variability that has previously been observed.

In contrast to the increase in concentration observed for Zn, the change in concentration of Cu and Pb is erratic and shows no significant increase when the whole timescale is considered. This lack of change tends to rule out any contribution that increasing transpiration (Figure 4.4) may make to the focusing of metal concentration, although this effect is anticipated to be negligible even at best. In all cases, there is a decrease in metal concentration between 3 and 6 months, indicating a change in extractability with time or movement of metals away from the sampled area. The latter hypothesis is favoured by significantly ($p<0.01$) greater relative change in Pb concentration, the greater affinity of Cu for organic matter (Section 2.2), and previous evidence of the enhanced movement of Pb (Section 7.2). However, concentrations of both Cu and Pb 150 mm and 300 mm from the leg slot show no concomitant increase in concentration with time, being statistically undistinguishable from background contents.

7.4 THE DISTRIBUTION OF HEAVY METALS IN SLUDGE-INJECTED SOILS

Thus far, the movement of metals has been considered in one dimension only, which is the standard framework of investigation when considering the translocation of metals out of a surficial sewage layer (e.g. Williams *et al.*, 1980, 1984, 1985, 1987; Campbell and Beckett, 1988; Dowdy *et al.*, 1991. See Chapter 2). The study of the lateral movement of metals has similarly been restricted to the surface of the soil and has been attributed to physical mechanisms (McGrath, 1987; Giller and McGrath, 1988). However, when metals are introduced below the surface of the soil, these approaches are insufficient. The distribution of metals is represented in this Section by isoline diagrams with a contour interval for each metal of twice the standard deviation of its control, or multiples thereof. This being the case, it is meaningless to superimpose any diagrams but those for the same metal at the same site and the same treatment. However, it has already been shown (Section 7.2) that the centre of metal concentration is replicate-dependent at Honey Park, and it is assumed at this stage that the same observation will hold for other treatments. Thus, each metal, replicate, treatment and site must be considered separately. The same approach used in Section 7.2 is adopted here - namely, that one replicate will be used to represent the situation as a whole, with data from each replicate presented in tabular form (Table 7.5). Interpretation of these Tables is facilitated by the use of shape definitions that are explained in the final Section of Table 7.5. These are used as readily accessible descriptions and in the absence of any established qualitative conventions.

7.4.1 THE EFFECT OF SOIL TYPE

A THE SIMPLE (STRAIGHT) TINE

The basic pattern of distribution of the metals following the subsurface injection of sewage sludge using a simple tine and at the higher rate is illustrated for one replicate by Figure 7.6 and on the field scale by Table 7.5.1. At both sites, metal concentration is centred around one sampling point only, the variable depth of which is discussed in Section 7.2. Soil metal concentration then decreases away from this point in a manner that is site-dependent, and somewhat metal-dependent, only on the small scale (that is, in terms of centimetres). Thus at Honey Park, an approximately bell-shaped configuration is formed, with a greater enhancement in metal concentration towards the base of the profile. At Colaton Raleigh, the reverse is apparent. Here, the influence of the sludge addition reaches its greatest lateral extent towards the surface of the profile. This same basic pattern holds for all replicates and at both sites. Thus it becomes impossible to describe differences as site-controlled without investigating the precise differences in soil properties between replicates (see Chapter 8), as the patterns are as different between replicates as they are between sites.

Table 7.5.1 indicates the percentage area of the sampled soil profile in which metal concentrations are greater than the relevant background concentrations. This data is simply generated by comparison with the mean background concentration (since there is no significant deviation with depth - see Section 7.1.2) plus 2σ. This can be used as an indication of the effect of soil type on metal distribution, although it must be reiterated in presenting these figures that no distinction is made at this point between metal movement and the original distribution created by the injection of sewage sludge. The relationship between soil type and metal distribution is seen to be unclear, since replicate variability is great. However, when outliers are removed from the data, Zn and Cu (marginally) are seen to be more mobile at Honey Park than Colaton Raleigh. In contrast, Ni has a wider distribution at the latter site.

Whilst distribution patterns of metals and the volume of soil affected by sludge injection are important descriptive tools, the range of absolute metal concentrations is more useful in quantitatively comparing the effect of soil type. Concentration ranges are presented in Table

7.5.1 by metal, replicate and site. As stated in Section 7.2, metal concentrations are generally greater at Honey Park than at Colaton Raleigh. However, the extent of average concentration enhancement (that is, maximum concentration minus minimum concentration) of each metal is remarkably similar between soil types. This consistency reflects the identical sewage addition to each treatment, regardless of soil type, but is surprising when these soils have been shown to be inherently variable, and have been subjected to a treatment which is difficult to standardise (Chapter 6). The magnitude of concentration enhancement does not necessarily correspond with that expected from the addition of metal laden sewage sludge (Section 7.6), but in all cases except Cd at Colaton Raleigh, concentration ranges are significantly ($p<0.01$) greater than those for unamended soils. This holds even where amended concentrations do not exceed background contents, indicating a loss of these metals (Cd and Ni) from the sampled soil as a result of the introduction of sewage sludge, thereby yielding lower minimum values. Within the average enhancement there is considerable metal-dependent variability, with Colaton Raleigh (33-66 % at the range minimum; 15-54 % at the upper end of the range) tending to exhibit larger between-replicate RSDs for each metal than Honey Park (1-21 % and 9-27 %, respectively). The relative extent of these ranges may be important, in that greater variability at the lower end of the range would tend to indicate variation induced by the actual process of injection and/or the variability of background metal concentrations (i.e. at Colaton Raleigh). In contrast, a more variable maximum (than minimum), as at Honey Park, implicates the addition of sewage sludge. Both scenarios confirm the hypothesis laid out in Section 7.2.

Using the same tine configuration but a lower rate of sludge injection (225 m^3 ha^{-1}), patterns of metal distribution remain essentially the same as that for the higher rate of injection. The soil area affected (Table 7.5.1) may be expected to be less than or equal to that area influenced by a higher rate of injection, depending on whether sludge volume or injector configuration is of overriding importance. However, replicates are so variable that both rates appear equivalent except in the case of Ni, which has a wider distribution after a higher rate of sludge application. This is further discussed in Section 7.8 and 8.4.

The range of metal concentrations resulting from a lower rate of sewage sludge application is significantly ($p<0.01$) greater than that measured in untreated soils, but not necessarily significantly smaller than that arising from injection at the rate of 300 m^3 ha^{-1}. This begins to quantify the variability of the injection process and the difficulty in regulating it that is further discussed in Chapter 8 and Sections 6.5 and 7.6. As with all results presented thus far, there is considerable variability in the range of metal concentrations between replicates. At both sites, this variability is generally less than that found after injection at a higher rate, but at Honey Park, low rate concentration ranges are less variable than background concentration ranges. This is reversed at Colaton Raleigh.

B THE SIDE-INCLINED TINE (PARAPLOW)

The side-inclined tine is regarded as creating greater soil disturbance, and presumably therefore a greater spread of metals, than the simple tine discussed above (e.g. Hall *et al.*, 1986). Thus it would be anticipated that, (a) following sludge injection, a greater proportion of the soil profile would contain metal concentrations exceeding background contents, and (b) the range of concentrations would therefore be smaller.

Table 7.5.2 describes the parameters of metal behaviour pertinent to soils injected with sewage sludge through a side-inclined tine. The distribution patterns thus created are further illustrated by Figure 7.7, from which it is immediately apparent that appreciable differences exist between the distribution of metals injected using simple and side-inclined tines, although the difference between metals, replicates and soil types is similarly minimal within treatments. However, the available means of describing these distributions masks the greater between-replicate variability at Colaton Raleigh than Honey Park. Metals tend to hold an approximate 'V' configuration corresponding to the passage of the injector leg and a second arm normal to it. This may be distorted to a greater or lesser extent, or be represented by one arm only, the greatest departure from this being the 'keyhole' configuration. These deviations are dictated by which 'arm' the main concentration of metals is found in, or whether it is located at the base of the 'V'. Each metal has a centre of concentration, which, unlike the simple tine, may encompass more than one sampling point and it is thus more likely that there will be at least one secondary focus when the side-inclined tine is employed. Despite this, the area of soil that subsequently has metal concentrations greater than those in untreated soil is no greater, and frequently less than, that pertaining to the straight tine. This corresponds with observations made in Section 6.2.2, although Pb is a notable exception to this. Similarly, every metal within each replicate will not necessarily possess the same locus of maximum concentration (Section 7.4.2). The depth of this maximum, described in Section 7.2 for the simple tine, varies from 180-420 mm (with Honey Park concentrations the more shallow) and is thus more variable for the side inclined tine than the simple tine.

The percentage soil area that contains metal concentrations in excess of background contents is, on average, greater at Honey Park than Colaton Raleigh. However, if each site is split into its component replicates and all are considered together, they can not be statistically differentiated from each other in all cases. According to this criteria, Colaton Raleigh is more variable than Honey Park, irrespective of injector tine design. It therefore appears that the role of soil type in controlling the extent of 'movement' of the metals is only secondary to the importance of injector configuration.

As would be expected, the range of concentrations is significantly greater in soils treated with paraplow-injected sewage sludge than in untreated soils. Metals except Cd and Ni are present in significantly ($p<0.01$) greater quantities, but the aforementioned metals are frequently present in concentrations less than that found in untreated soil. Concentration ranges are generally greater with the simple tine than the paraplow. Maximum concentrations attained at Honey Park significantly ($p<0.01$) exceed those at Colaton Raleigh, with the exception of Pb, but, as with the straight tine, there is little difference in the mean extent of metal enhancement when the different soils are injected through a side-inclined tine. Greater disparities are observed in the variability (RSD) of these averages: Colaton Raleigh is generally, but not universally, more variable than Honey Park, although the source of this variability is metal-dependent. Similarly, an assessment of the variability created by the paraplow compared to the simple tine depends upon which metal is being investigated.

The final treatment of Phase I was the injection of sewage sludge at a rate of 225 m^3 ha^{-1} through the side-inclined tine. The basic configurations of metal concentration thus created are little different from those associated with a higher rate of injection (Table 7.5.2), although the discrete shapes are generally smaller following the lower rate, regardless of the area of soil that possesses metal concentrations in excess of background contents. The effect of volume of sludge addition on the loosening of soil has been discussed in Section 6.2.2, and, along with the effect that rate has on metal distribution (see next paragraph), this factor can be further associated with these observations. Within-replicate consistency of these shapes is better than for any other treatment, but, whilst this applies to both soil types, Colaton Raleigh again tends to be more variable than Honey Park. When the position of the main focus of concentration is considered, which may again encompass more than one sampling point, Honey Park is seen to be the more variable. These foci are located between

120 mm and 300 mm (again, the deeper locations are at Colaton Raleigh), and are as such more variable than those created by the simple tine, but less variable than those associated with a higher rate of injection.

Despite the fact that distinct patterns of concentration are smaller when a lower volume of sludge is injected through a paraplow, the area that is subsequently affected by an increase in metal concentration is frequently wider than that for either the higher rate or simple tine treatments (Table 7.5, sections 1 and 2). Since an enhanced distribution was expected for the side-inclined tine (Chapter 6), it therefore appears that there is some barrier to metal distribution when a high rate of sludge is introduced into the soil in this manner, possibly created by the sludge itself (Section 6.3). However, there is no significant difference in the concentration range of most metals between the rates of injection to suggest the immobility of metals at the higher rate.

C THE WINGED TINE

In any discussion on the effect of the winged tine on soil metal distribution, it must be remembered that this injection was conducted at a different site (albeit basically no different from Honey Park), unavoidably using a sewage sludge of a different composition, at a different time of year and at one rate (Table 4.1).

Table 7.5.3 summarises the effect of a winged tine injection on metal characteristics at Broad Meadow, and the configuration of metal distribution is further illustrated by Figure 7.8. A third basic configuration is introduced by this tine, consisting in its simplest form as an inverted 'T'. This is remarkably consistent between replicates, at least for Cu, although the extent to which the passage of the upright strut of the tine is mirrored by metal concentration varies. Similarly, the centre of metal concentration may be located at the axis of the 'T', or in the crosspieces. The depth of this focus is more uniform than in any other treatment, varying between 180 mm and 300 mm, depending upon the metal involved (Zn is always deeper than Cu). However, the configurations are not always distinctly different from those created by the simple tine. In addition, Zn does not always exhibit any definite pattern at all (largely the result of amended concentrations that are rarely significantly higher than background concentrations), thus only centres of concentration are evident. This contrasts with the situation observed for Cd and Ni under similar conditions - namely that a pattern of distribution is evident for these metals, regardless of whether concentrations exceed those of

background soils. The reasons behind this are discussed in Section 7.6.
In accordance with the relatively small volume of Zn introduced into the soil by the process of injection, less than 20 % of the sampled area has subsequent concentrations greater than those already in the soil. This contrasts sharply with Cu, where the entire sampled area contains concentrations in excess of background contents. At this point, it is impossible to say whether the apparently greater movement of Cu is the result of the use of a different tine, or of a sludge with greater metal loading. The lesser distribution of Zn than has been observed elsewhere favours the latter explanation - it is unlikely that the introduction of such a small amount of Zn would attain a broad distribution under any circumstances.

As a result of the relatively small introduction of Zn, the range of concentrations is somewhat greater after the soil has been treated with sewage sludge, but this difference is not significant. Contrarily, Cu is present at concentrations far exceeding background levels, a position inevitably reflected in significantly greater ($p<0.01$) concentration ranges. These ranges are far more constant between replicates (for both metals) than is evident after any other treatment. As anticipated, a comparison of the various sections of Table 7.5 show that the increase in Zn concentration is significantly less than that observed elsewhere. There is little difference between Cu enhancement (ranges) at this site and at other sites receiving different treatments, despite the addition of almost three times the amount of Cu. This restriction may indicate a wider distribution of metals than other types of tine. This will be further discussed in Chapter 8, after the situation is investigated in a 'mass balance' approach (Section 7.6).

7.4.2 DIFFERENTIAL METAL BEHAVIOUR

In this assessment of the distribution of metals following different rates and modes of injection into different soil types, the term 'metal-dependent' has been used extensively. This Section aims to clarify this statement, but parameters such as the different shapes of metal distribution following different types of injection will be largely ignored, being basically metal-independent. Furthermore, all types of tine will be considered together, as universal metal similarities and differences are of interest here.

A. COPPER AND ZINC

Section 7.2, dealing with the concentration of metals in sludge-amended soil, introduced the concept of metal 'pairs' (Zn:Ni; Cu:Pb), associated by their behavioural similarity. There is also some parity between Zn and Cu, but this can be attributed to the large relative addition of these metals. This is supported by Broad Meadow treatments, where the disparity between sludge Zn and Cu relative to soil background concentration is greater, and little association between the metals is evident. However, the argument that the pattern of metal distribution is affected by metal concentration is apparently only true at such extremes - the case of Ni illustrates this point, where amended metal concentrations do not exceed background contents, but distinct distribution patterns are nevertheless evident. This apparent anomaly is considered further in Section 7.6.

B. NICKEL AND CADMIUM

Both Ni and Cd in treated soils are present in quantities less than or equal to background contents, but whilst Ni normally displays definite evidence of sludge amendment (in terms of distribution configuration) as mentioned above, Cd rarely does. This is interesting, because although Ni is introduced in significantly greater concentrations, neither metal is present in the sewage sludge in quantities greater than that found in untreated soils, at either site. The irrelevance of the relative loading of the sludge is further confirmed by a comparison of the two sites: Cd / Ni patterns are no more distinct at Colaton Raleigh, which has a far smaller ambient metal loading.

Whilst Ni shows no great departure from the basic distribution found for other metals within the same replicate, it often has a wider centre of concentration, especially at Honey Park. Where the simple tine has been used, this takes a vertically elongated form, starting at a shallower depth than that for other metals, but extending to the same depth. In the case of the side-inclined tine, Ni is more likely than other metals to have a secondary and more prominent concentration point, usually at a greater depth.

C. LEAD

In contrast to what can be considered as modifications of Ni distribution within the same broad parameters as exist for other metals, Pb is the metal most likely (but not inevitably) to deviate from this configuration. This is most often seen in replicate 3, Honey Park (all treatments) and can therefore not be entirely attributed to the fact that Pb was analysed separately from other metals in the laboratory (Section 4.3.1), and unlike other metals, is more efficiently extracted with HNO_3 from 'normal' than high organic-matter soils (Table 4.4). The variability of these concentrations is generally greater than for any other metal.

D. RELATIVE METAL BEHAVIOUR

The area of the soil that has metal concentrations greater than background contents plus 2σ has been used to indicate the extent of the distribution of metals, whether created by the original injection or by subsequent metal movement. Taken as an average for all injection treatments, the metals can be ranked according to this criteria in the order:

	Zn > Pb / Cu > Ni > Cd	at Honey Park and Colaton Raleigh
and	Cu > Zn	at Broad Meadow

The position of Cd and Ni in this order is interchangeable at Honey Park, or they may be equivalent. Where this rank does not hold, it is distorted by one metal in an incongruous position and these deviations are generally the result of an 'outlying' replicate distorting the mean result.

The ranks above bear little resemblance to those inherent to the soil. To reiterate:

Zn > Ni > Pb ≥ Cu > Cd	Honey Park
Zn > Pb > Ni > Cu > Cd	Colaton Raleigh
Zn > Cu	Broad Meadow.

Instead, the amended concentration ranks are similar to that found in the sludge:

Zn > Pb = Cu > Ni > Cd	HP and CR sewage sludge
Cu > Zn	BM sewage sludge.

The rank of relative sludge metal loading (i.e. sludge concentration minus background concentration) is identical to this. Thus, whilst sludge metal concentration has no effect on the configuration of metal distribution, it appears to be important in determining the extent of the discernible effect of metal addition, in that the rank of metal distribution correlates with the rank of metal concentration in sludge. This holds even when sludge concentration is substantially less than soil concentration, as with Cd and Ni, where patterns of distribution are evident despite there being few, if any, points greater than background concentrations. The exception to this correlation is Cu, which generally has a tighter distribution than Pb, confirming the hypothesis and observations made in Section 7.2.

7.5 THE AVAILABILITY OF HEAVY METALS

In addition to the 'total' metal content of soil treated with sewage sludge, it is also desirable to assess the potential impact of these levels on plant uptake, and thus the results can be considered in a practical context. Table 7.6 summarises the $CaCl_2$-extractable Cu, Ni and Zn content of treated soil. Results are presented only if there is complete confidence in them, and this represents selected metals only. Not unexpectedly, $CaCl_2$-extractable soil metal concentrations are frequently less than the detection limit of the instrument used to measure them. Since this inevitably represents a convergence to background concentrations and a minimal agricultural impact, it was considered unnecessary to further pursue results through the use of pre-concentration techniques. It is therefore not possible to present a comprehensive or statistically tested argument - instead, only general conclusions can be drawn.

From Table 7.6, it is evident that the mean available metal concentration of soils treated with sewage sludge is minimal, but somewhat greater than the concentrations found in untreated soil, confirming the results of authors such as Mulchi *et al.* (1987). Besides this generalisation, it is difficult to relate these results to those of other authors, due to the great disparity that arises from the use of alternative extractants (Section 4.3.2), but as a 'rule of thumb' the WRc suggests the following ranges for 'contaminated' soils (J. Hall, 1988, pers. comm.): Cd <0.25-2.00 mg kg^{-1}; Cu 0.9-4.5 mg kg^{-1}; Ni <1-5 mg kg^{-1}; Pb $\leq$2.5 mg kg^{-1}; Zn 4-24.5 mg kg^{-1}. In all cases and under all treatments, the 'available' metal content of these experimental soils is less than the figures quoted above, under these criteria would therefore not be statistically distinguishable as 'contaminated' soils in a comparison of national averages.

Table 7.6 also shows that the mean $CaCl_2$-extractable metal concentration in treated soils is greater at Colaton Raleigh than Honey Park, but is little affected by the mode of injection. However, the use of the straight tine considerably reduces the variability of 'available' metal concentrations, suggesting that a more uniform distribution is produced. Highest 'available' concentrations generally conform to the position of highest 'total' concentrations where the straight tine has been used. If the sludge has been injected through a paraplow, the same situation exists for Cu, whilst the main concentrations of $CaCl_2$-extractable Zn and Ni tend to be located together, but away from the relevant 'total' maxima, perhaps because Zn and Ni are both complexed on soluble organic matter (Sanders and Adams, 1987) and may therefore have moved further during injection. Correlation coefficients between 'total' and 'available' concentrations are therefore usually poor (approximately 0.3), with Cu as the only exception to this rule, with correlation coefficients of approximately 0.6. Thus Cu can be considered relatively immobile, with the bulk of 'available' Cu located at the centre of the 'total' concentrations, and corresponding with organic matter concentrations (Section 7.2), whereas the mobility of Zn and Ni is influenced by injector tine design.

The most consequential information that can be gleaned from results pertaining to the $CaCl_2$-extractability of these metals is their relative and percentage availability, as this illuminates the different behaviour of the metals, which is somewhat masked in the case of 'total' concentrations by the disparity between the concentration of different metals in sludge. From Table 7.7 it can be seen that percentage 'availability' of metals can be ranked as:

Ni > Cu ≥ Zn	Honey Park
Ni > Zn > Cu	Colaton Raleigh

The placement of Cd and Pb in these orders is conditionally given as:

Cd > Ni > Pb > Cu ≥ Zn	Honey Park
Ni > Cd > Pb > Zn > Cu	Colaton Raleigh

From these results, it is apparent that Ni is the most relatively 'available' of all the studied metals, but that the identity of the least relatively 'available' metal depends upon soil type. Thus, Cu is the least 'available' at Colaton Raleigh, but Zn and Cu are similarly unavailable at Honey Park. These general conclusions fit well with the work of other authors (such as Williams *et al.*, 1980), but can not be directly compared with many due to the different extractants used. In conjunction with Section 7.4, which described Cu and Zn as having the widest distribution, this clearly shows that the relative extent of metal distribution depends more upon the quantity of the individual metal introduced into the soil than on the metals' availability. However, when similar concentrations of two metals are added to a soil also containing similar concentrations (the case of Cu and Pb mentioned in Section 7.4.2), the difference in availability becomes important - thus Pb often has a wider distribution than Cu.

A significant increase ($p<0.01$) in the percentage availability of Zn is observed in the zone of maximum metal concentration, and therefore presumably the area of sludge location. This implies that: a) there has been little translocation of $CaCl_2$-extractable Zn away from the 'pool' of 'total' Zn (which is not to say that the 'pool' can not have a wide distribution of its own) and is therefore probably water-insoluble; or b) Zn from the 'pool' is constantly becoming available and replacing any which may have already moved (i.e. that there is an equilibrium reaction proceeding, especially at the Colaton Raleigh site where pH is lower). In contrast, there is no corresponding significant change in the percentage availability of Ni and Cu, although it is highly likely that this is the result of different mechanisms. Thus Cu, which has a slight, but non-significant, decrease in percentage availability in the region of sludge location, is likely to be present in tightly-bound organic (humic acid) forms, whilst it is probable that much of the potentially $CaCl_2$-extractable Ni has already moved away from the main area of sludge location, since it is present in sewage sludge in a highly mobile form (Kabata-Pendias and Pendias, 1984).

In terms of soil type, Colaton Raleigh inevitably has a greater percentage metal availability than Honey Park, with figures of less than 8% and less than 2%, respectively. By far the greatest disparity between values occurs in the case of Zn, which is less 'available' at Honey Park than would be expected from Colaton Raleigh results.

7.6 THE MASS BALANCE OF METALS

Throughout this Chapter, reference has been made to the 'mass balance' of metals, without which it is impossible to assess the relative movement of those metals as some may have moved to such an extent that they are no longer within the sampled profile. This 'mass balance' can be calculated from field results, or measured in soil columns, and both approaches have been used in this study.

When the heavy metal content of sewage sludge and untreated soil is known, along with the relevant volumes of each, the amount of metal (in mg) that should be present is simply calculated from the following equation:

$$\text{expected metal concentration} = \frac{(\text{untreated conc. x soil mass}) + (\text{sludge conc. x sludge mass})}{\text{soil mass}}$$

This can be compared with the average metal concentration that is known to be in treated soil, and any shortfall can be considered to be the result of metal movement out of the sampled profile. Any conclusions thus drawn will, however, rely heavily on the assumptions that (i) metals are uniformly distributed throughout the sludge volume (NB account has already been made of the sludge solid:liquid partition); (ii) the calculated rate of injection is constant throughout the injection run; and (iii) the addition of sewage sludge, once dry, adds little to the soil volume. No assumptions have been made about the bulk density of the soil and sewage sludge, but since expected metal concentration and actual metal concentration calculations ignore this factor, results should be relatively correct. In support of this approach, McGrath and Lane (1989) found that the change in bulk density was significantly related to organic carbon content. Since little change in organic matter content was observed (Section 6.3), little change in bulk density is expected. The main source of inaccuracy is likely to arise from the consideration of injection rate as uniform. It has already been stated that this factor may vary by up to 50 %, but it is impossible to accurately quantify this at this stage, as it represents one of the aims of this project. Thus any within-metal inconsistency in mass balance results must be considered to reflect the inconsistency of injection as well as that of metal movement.

Figure 7.9 summarises the results of these calculations, expressed as a proportion of 'expected' concentrations (i.e.expected ÷ actual concentration). Thus, any values greater than 100 indicate that actual concentrations fall short of those calculated, and movement out of the sampled profile is implicated. This data infers that a higher rate of injection thus increases the movement of Cd, Ni and Pb, but only Cd and Ni show movement out of the profile. Due largely to the low concentration of Cd in added sewage sludge, none was identified in column leachate (discussed later in this Section), but the increased mobility of Cd has been advocated by other authors. For example, Schmitt and Sticher (1986a) postulated that Cd will eventually be leached out of the amended horizon since it is out-competed by other metals for exchange sites.

Most other authors that have expressed their results in terms of a mass balance of metals have observed metals in concentrations less than would be expected, which they have attributed to metal movement or sampling/analytical errors (e.g. Chang *et al.*, 1984b). In this case, however, Cu, Pb and Zn are present in quantities in excess of their calculated concentrations. This is likely to indicate that the sampling regime used at some point favours the collection of sewage sludge rather than soil, and therefore that Cd and Ni are no longer present in the sewage sludge. This being the case, it is still feasible to use these results to determine the extent of movement of each of the metals. If a decreasing volume of soil is factored into the above equation, the point at which expected concentration equals actual concentration indicates the furthest extent of movement of that metal. This value inevitably correlates with the data presented in Figure 7.9, in that the lower the data point is below 100, the less that metal has moved. Ranks of movement are inevitably unclear, potentially confused by factors such as soil type, injector tine design and rate of injection as well as the characteristics of the individual metal. The most mobile elements are Cd and Ni, although the relative position of the two in any ranking is interchangeable. In terms of actual distances, this represents more than 300 mm (ie. half the distance between injector leg slots) in the case of Ni and Cd, but generally less than 180 mm, and frequently less than 120 mm for Cu, Pb and Zn. At Colaton Raleigh, Ni moves further than at Honey Park, whilst Zn is more mobile at Honey Park than Colaton Raleigh. The movement of Cu, Pb and Cd after a high rate of injection is approximately equal at both sites, variability between replicates being so great.

When a winged tine is used as the injection instrument, both elements under investigation (i.e. Cu and Zn) move to a considerably greater extent than under any other treatment (Figure 7.9). Both metals are equally mobile, and the zone of influence extends beyond the sampled area (neither metal, however, is more mobile than either Cd or Ni at other sites). This increase in mobility is unlikely to be primarily affected by soil type, as it has been shown (Chapter 5) that the soils of Honey Park and Broad Meadow are not significantly different under most criteria. In addition, enhanced metal movement is somewhat preempted by observations in the field of considerable downward movement of the sludge itself, compared to the discrete sludge mass that was uncovered even six months after injection with a straight tine or paraplow. However, whether the enhanced movement observed is the result of a different type of tine or of a sludge with a lower dry matter content (4.0 % compared to 6.3 %) is questionable. The use of the same sludge in undisturbed soil columns containing untreated soil (see below) and an investigation of the loosening effect of the different tines (Chapter 6) will clarify the situation (Chapter 8).

The second phase of mass balance experiments took the form of soil columns sampled from Broad Meadow. A known and constant amount of sewage sludge was applied, so there can be no error from this source. The Cd, Cu, Ni, Pb and Zn content of the leachate was analysed, but due to a change in DCP used, only Cu and Zn were analysed from soil samples. Figure 7.11 summarises the metal content (in mg) of the soil columns with depth. From this analysis, an extra 23 mg of Zn and 38 mg of Cu is calculated as present after treatment with sludge. However, 16 mg of Zn and 56 mg of Cu were added in the sludge. There was less than 2 mg loss of either Cu or Zn in leachate (Figure 7.11). Despite this disparity, these columns can be used to assess the extent of metal movement through loosened soil without the complications of variable injector performance, and to investigate the extent of metal leaching out of the soil profile after sludge addition.

Figure 7.11 also illustrates the metal content of this leachate and its change with time. Each data point is the mean of two readings, and takes account of both the metal content of leachate from untreated columns and the metal loading of the rainwater added to the columns. Note that, in order to take account of the different volume of leachate collected at each sampling point, data is presented in terms of mg. Cadmium has not been included as all values are less than the detection limit of the equipment. It is instantly recognisable that, excepting Ni, the leaching of metals occurs almost immediately after the sludge is added to the soil. The quantity of metal involved can be ranked as a proportion of the metal loading of the sludge in the order :

Ni (135±40%) > Zn (9±3%) > Pb (5±2%) > Cu (1±0.8%)

It would therefore seem that the major proportion of metal (except Ni) in sludge is immobile, and probably moves through the soil with the sludge, whilst its soluble constituent will move through the soil with ease. Since this soluble component is tiny compared with the soil metal content, it would not necessarily be identifiable within that medium. To support this hypothesis, it would be expected that the percentage of the sludge metal content present in its liquid fraction and/or its percentage availability in sludge-amended soil would follow a similar rank. These ranks are:

% in liquid fraction:

Ni [> Cd] > Pb > Zn > Cu
(6.8±3.9%) (5.2±3.2%) (5.0±1.3%) (3.0±1.5%) (1.0±0.4%)

% availability (Section 7.5): [Cd] ≥ Ni [> Pb] > Cu ≥ Zn

Two important points are evident from the above ranks. Firstly, Zn is higher in the 'leachate rank' than the 'sludge rank', and secondly, the percentage metal content in the leachate of all metals except Cu and Pb is higher than the corresponding sludge content. When these facts are considered in conjunction with the pattern of metal release illustrated by Figure 7.11, it would seem that only that Cu and Pb that is already present in the liquid fraction of sludge is mobile in the short term, and is therefore immediately flushed through the system. In contrast, a greater proportion of Zn and especially Ni than is present in the sludge liquid appears to be mobile, and this may be released over a slightly longer time period. This mechanism seems to progress even further with Ni, to the extent that soil Ni is mobilised by the addition of sewage sludge and thus the quantity of Ni found in soil leachate exceeds that originally introduced in the form of sewage sludge (although this is not to say that 100% of the sludge Ni is necessarily present in this fraction). This hypothesis not only conforms to the appreciable movement of Ni postulated from field mass balance calculations, but also explains the presence of Ni in treated soil in quantities less than in untreated soil, whilst still exhibiting definite distribution patterns (Section 7.4). Similar phenomena have been described by McGrath and Smith (1990) who suggest that the dissolution of precipitates (carbonates, hydroxides, phosphates) is responsible, triggered by pH and soil gaseous changes as a result of microbial activity.

Finally, it was hoped that the use of a relatively less viscous sewage sludge in these columns would identify whether the sludge, injection tine design or increased rainfall was responsible for the enhanced movement of Cu and Zn at Broad Meadow compared to Honey Park. The immobility of the bulk of these metals in the soil columns despite high volumes of addition of a thin sludge indicated that the tine design is responsible. In the same vein, the variability of metal concentration in these columns can be compared to that in the field in order to further clarify the relative roles of soil, sludge and injection variability on the disparity of between-replicate results observed in the field (Section 7.4). When soil columns are treated with sludge, the between-replicate variability of both metals at any given depth is less than 5%, a value considerably less than that encountered in both control and field situations, but similar to that pertaining to the sewage sludge used (see Tables 7.1 and 7.2). It would seem, therefore, that for Broad Meadow at least, the process of injection is responsible for much of the variability in field metal concentrations and distributions.

7.7 THE EFFECT OF REDOX POTENTIAL ON METAL BEHAVIOUR

In assessing the impact of redox potential on the movement of heavy metals, soil columns were again employed, but containing disturbed soil (Section 4.3.3). Again, a known quantity of sludge with a known heavy metal loading was used, and the concentration of metals in any percolating water was analysed. Quantification of redox changes were presented in Section 5.6, and final pHs of 6.0 (control), 5.8 (draining) and 6.5 (waterlogged) were measured, indicating the reduction of, for example, Fe (Alloway, 1990a) and/or sulphate (Bloomfield, 1981). Figure 7.12 illustrates the soil Cu and Zn content of the columns. These metals were selected under the assumption that redox would have a different effect on each - Cu is anticipated to be more susceptible than Zn (Alloway, 1990a), with the latter being more likely to display an increase in mobility, and vice versa (Rowell, 1981). The metal content (ie amount in mg rather than concentration) of the percolating water was minimal, comprising less than 0.5 mg Cu and less than 1.0 mg Zn, there being significantly more metal in the water from sludge treated columns, and slightly less (non-significant) in the leachate from redox than oxidised columns. From Figure 7.12, it is apparent that the depth of movement of Cu and Zn is no different between redox or oxidised columns - metal movement in freely draining soil can not, therefore, be unequivocally ascribed to water movement, or permanently released into solution upon the reduction of associated Fe oxides. However, there is a significant shortfall in the recovery of metals from the redox columns, especially in the sludge layer (75 mm) and, in the case of Zn, at 175 mm, where reducing conditions are less severe than at the top of the column (Figure 5.6). This loss can not be attributed to loss in water, uneven sludge distribution or inefficient sampling techniques, nor to the increase in pH observed in the waterlogged treatment. It can only be assumed, therefore, that the metal has been converted to a form not easily extracted by concentrated HNO_3, the most obvious contender being metal (especially Zn) precipitation as sulphides (Cottenie, 1981; Ponnamperuma, 1972). However, there have been no reports known to the present author that suggest HNO_3 would be incapable of extracting these forms, and Brown *et al*. (1989) observed that waterlogging had no effect on the availability of heavy metals in sludge-amended soils. Reducing conditions thus appear to have no effect on the mobility of acid-extractable metals under these circumstances, probably because of the ameliorating influence of organic matter (Section 2.2.2).

7.8 SUMMARY

A large number of results have been presented in this Chapter, but these can be summarised into the following overall trends:

The injection of sewage sludge will increase the soil loading of heavy metals only if the background concentration is exceeded by the sludge. This is regardless of soil type, injector tine design or rate of injection. However, even when background concentrations are not exceeded, patterns of Ni distribution as a result of injection are still discernible. There appears to be no relationship between background concentrations and subsequent sludge-amended concentrations beyond this, in that the concentration enhancement of metals (range magnitude) caused by the addition of sewage sludge is comparable for each metal between sites, regardless of tine design. However, where a pattern exists, the area of soil with metal contents substantially exceeding background concentrations is greater at Honey Park than Colaton Raleigh.

The patterns of metal distribution in treated soil depend upon injector tine design - a straight tine produces an approximate flask shape, a paraplow results in a 'V' configuration, whilst the winged tine creates an inverted 'T'. These configurations override soil type, rate of injection and individual metal characteristics. In terms of area covered by these patterns, the tines can be ranked in the order:

winged > straight ≥ paraplow	high rate injections
paraplow > straight	low rate injections

-and concentration ranges can be ranked in the order:

straight > paraplow (> winged)

Considering all 3 rankings together, this suggests that mobility is enhanced by a winged tine and suppressed by use of the straight tine, although this is not necessarily statistically distinguishable. Increasing the rate of injection has little statistical effect on the distribution of metals, being just as likely to reduce as increase the reach of the metals.

Soil type and metal characteristics affect the distribution patterns in terms of their size, focus of concentration, and variability. Thus, the results of injection are generally more variable at Colaton Raleigh than Honey Park, despite Colaton Raleigh being more consistent in terms of background metal concentration. The area of treated soil that contains metal concentrations in excess of background concentrations is frequently greater at Honey Park than Colaton Raleigh, except in the case of Ni injected through a straight tine. There is a greater percentage availability of the metals at Colaton Raleigh, regardless of treatment. Centres of sludge concentration are generally more shallow and variable at Honey Park than Colaton Raleigh. The relative size of the distribution patterns of different metals appears to reflect the relative loading of the sludge rather than any characteristics of the metal, although reducing the rate of injection does not necessarily produce a proportional change in the parameters of metal distribution.

A measurement of the relative availability of the metals, used in conjunction with leachate studies and the change in metal concentration with time can be used to make some tentative statements about the behaviour of the metals. It has already been stated that Ni is one of the most mobile of the metals, and it is likely that this is the result of the addition of sewage sludge increasing not only the overall availability of Ni, but also the availability of soil Ni, which is then released into solution over a relatively long period of time. In conspicuous contrast, the addition of sludge will increase the short-term availability of Cu, but this metal becomes increasingly well held in the soil, to such an extent that it is rendered immobile. Zinc behaves in a similar manner, although more is initially released and its subsequent immobility is somewhat soil type-dependent. The behaviour of Pb seems to be more closely governed by soil factors. Thus, the rank of metal movement that is apparent from considering the volume of soil that has metal concentrations greater than background concentrations is known to mask the fact that Ni and Cd have moved out of the sampled profile in quantities sufficient to render remaining concentrations less than those found in untreated soil. Furthermore, it is postulated that the addition of organic matter mobilises some inherent Ni and Cd (as organic leachate), possibly as a result of pH changes. Thus, patterns of distribution are evident in a soil that, in terms of metal loading, appears unaffected by sewage injection. The revised rank of mobility can therefore be stated as:

Ni and Cd > Zn > Cu and Pb.

This holds, with a few exceptions, at both Colaton Raleigh and Honey Park. Similarly, the order of affected soil at Broad Meadow:

Cu > Zn

masks the movement of approximately 10 % of each metal out of the samples profile. Thus, although most Cu has a wider distribution than most Zn, the furthest distance that either reaches can be considered equivalent.

An important aim of this research is to identify how great a role the process of injection plays on the subsequent variability of the metal loading of the soil. At this point, injection seems to exacerbate the innate variability of the soil, most noticeably at Colaton Raleigh. However, the physical presence of sewage sludge seems to decrease the disparity of metal concentration when the uniformity of its application is assured. Further conclusions will be deferred until Chapter 8, when the variability of soil disturbance and sludge placement will be considered in conjunction with the results of this Chapter.

TABLE 7.1 THE HEAVY METAL CONCENTRATION OF EXPERIMENTAL SEWAGE SLUDGE (mg kg^{-1}).

(a) SLUDGE 1 (Phase I)

element	average total concentration	RSD	% RSD	concentration in liquid phase	% metals in liquid phase
Cd	17.1	0.9	5.3	<	-
Cu	409.7	10.0	2.4	0.9	0.2
Ni	66.7	6.9	10.3	1.0	1.5
Pb	410.3	20.5	5.0	<	-
Zn	1414.3	68.1	4.8	1.6	0.1
pH	7.1	0.3	4.2		
dry matter (%)	6.3	0.3	4.8		

(b) SLUDGE 2. (Phase II and Mass Balance Columns)

element	average total concentration	RSD	% RSD	concentration in liquid phase	% metals in liquid phase
Cu	2220.0	131.0	5.9	14.5	0.7
Zn	626.0	41.9	6.7	1.9	0.3
pH	7.2	0.1	1.4		
dry matter (%)	4.0	0.1	2.5		

where: < = less than detection limit of instrumentation.

TABLE 7.1contd THE HEAVY METAL CONCENTRATION OF EXPERIMENTAL SEWAGE SLUDGE (mg kg^{-1}).

(c) SLUDGE 3 (Redox Columns).

element	average total concentration	RSD	% RSD
Cu	243.5	7.1	2.9
Zn	1152.4	93.7	8.1
pH	7.1	0.2	2.8
dry matter (%)	1.8	0.0	2.2

TABLE 7.2 BACKGROUND METAL CONCENTRATIONS (mg/kg) AT SEALE-HAYNE FARM AND COLATON RALEIGH

		Cd	Cu	Ni	Pb	Zn
Honey Park	mean	8.28	14.97	36.40	17.69	65.41
	* stdev	1.36	2.24	5.73	2.78	11.73
	* RSD(%)	16.40	14.96	15.74	15.70	17.94
Colaton Raleigh	mean	2.74	5.69	8.41	10.59	22.12
	* stdev	1.10	0.70	0.77	3.72	3.22
	* RSD(%)	40.08	12.22	9.11	35.08	14.55
Broad Meadow	mean	-	14.87	-	-	66.22
	* stdev	-	2.49	-	-	8.01
	* RSD(%)	-	16.75	-	-	12.09

* Error terms include both lateral (between replicate) and vertical variation

TABLE 7.3 WITHIN-SITE CORRELATION COEFFICIENTS OF THE PATTERN OF METAL CONCENTRATION WITH DEPTH IN UNTREATED SOIL

A. HONEY PARK

	Cu	Zn	Ni	Pb	Cd	Cu$_v$	Zn$_v$	Ni$_v$	Pb$_v$
Zn	$\underline{0.817}$								
Ni	0.613	0.710							
Pb	$\underline{0.798}$	0.708	0.124						
Cd	0.705	$\underline{0.758}$	$\underline{\underline{0.989}}$	0.241					
Cu$_v$	$\underline{\underline{0.883}}$	$\underline{0.864}$	$\underline{\underline{0.972}}$	-0.066	$\underline{\underline{0.978}}$				
Zn$_v$	$\underline{0.865}$	$\underline{0.788}$	$\underline{0.827}$	0.172	$\underline{\underline{0.873}}$	$\underline{0.911}$			
Ni$_v$	0.718	$\underline{\underline{0.915}}$	0.579	0.124	0.596	$\underline{0.745}$	$\underline{0.773}$		
Pb$_v$	-0.234	-0.487	-0.239	-0.072	0.601	-0.268	0.028	-0.239	
Cd$_v$	$\underline{\underline{0.901}}$	0.658	$\underline{0.793}$	0.081	$\underline{0.848}$	$\underline{0.859}$	$\underline{\underline{0.977}}$	$\underline{0.793}$	0.121

B. COLATON RALEIGH

	Cu	Zn	Ni	Pb	Cd	Cu$_v$	Zn$_v$	Ni$_v$	Pb$_v$
Zn	$\underline{\underline{0.970}}$								
Ni	$\underline{\underline{-0.873}}$	$\underline{-0.856}$							
Pb	$\underline{\underline{0.961}}$	$\underline{\underline{0.958}}$	$\underline{\underline{-0.882}}$						
Cd	-0.723	-0.673	0.488	0.361					
Cu$_v$	-0.437	-0.453	0.665	-0.330	-0.008				
Zn$_v$	0.122	0.166	0.060	0.092	-0.530	0.220			
Ni$_v$	-0.418	-0.525	0.356	-0.305	-0.176	0.530	0.220		
Pb$_v$	-0.581	-0.484	0.400	-0.537	0.494	0.150	0.287	0.243	
Cd$_v$	0.447	0.449	-0.625	0.361	0.282	-0.661	-0.591	-0.736	-0.244

C. BROAD MEADOW

	Cu	Zn	Cu$_v$
Zn	$\underline{0.752}$		
Cu$_v$	$\underline{\underline{-0.877}}$	$\underline{\underline{-0.922}}$	
Zn$_v$	0.600	0.470	-0.410

$\underline{\underline{0.883}}$ = significant at $p<0.01$; $\underline{0.817}$ = significant at $p<0.05$.

The suffix v indicates RSD values.

TABLE 7.4 BETWEEN-REPLICATE VARIABILITY (%) OF METAL CONCENTRATION WITH DEPTH: THE EFFECT OF SLUDGE INJECTION

A. HONEY PARK

depth (mm)	Cd		Cu		Ni		Pb		Zn	
	bg	am	bg	am	bg	am	bg	am	bg	am
60	11	6	27	4	8	13	27	17	23	8
120	14	24	25	26	5	28	32	8	36	30
180	9	9	21	12	11	15	37	4	18	10
240	30	9	60	3	17	1	62	4	58	12
300	13	20	21	17	6	12	19	23	14	21
360	4	3	9	6	19	7	13	20	11	5

B. COLATON RALEIGH

depth (mm)	Cd		Cu		Ni		Pb		Zn	
	bg	am	bg	am	bg	am	bg	am	bg	am
60	11	13	21	4	43	4	44	4	23	6
120	14	14	22	10	55	4	50	18	33	9
180	34	19	68	7	48	11	62	17	31	21
240	24	17	49	10	38	8	32	10	30	8
300	0	3	15	11	3	12	75	34	21	24
360	69	55	15	8	57	8	91	40	27	15

bg = background; am = amended

TABLE 7.5.1 THE EXTENT OF METAL MOVEMENT: 1. THE STRAIGHT TINE

A. HIGH RATE INJECTION

	R1			R2			R3		
element	range mg kg^{-1}	% area >bg	shape*	range mg kg^{-1}	% area >bg	shape*	range mg kg^{-1}	% area >bg	shape*
(i) HONEY PARK									
Cd	4-7	0	oval	5-8	0	bell	-	-	-
Cu	18-51	100	oval	20-72	87	bell	13-33	93	oval(a)
Ni	21-32	0	oval	23-37	0	bell	23-32	0	oval(a)
Pb	11-30	12	oval	12-50	62	bell	10-38	61	oval(a)
Zn	83-223	100	oval	76-348	100	bell	92-226	100	oval(a)
(ii) COLATON RALEIGH									
Cd	1-4	4	oval	1-4	3	oval	-	-	-
Cu	6-45	94	pear	5-60	87	flask	7-49	100	oval(a)
Ni	3-13	3	flask(f)	2-13	4	flask	7-14	44	oval(a)
Pb	11-30	24	pear	3-29	19	flask	16-70	100	oval(a)
Zn	19-192	96	flask(f)	19-232	87	flask	15-150	30	oval(a)

where:

oval(a)	oval, long axis vertical and with extending 'arms' or other distortion
flask(f)	flattened flask configuration

*Descriptions of shapes are intended as an indication only, and are diagrammatically illustrated by Table 7.5.4. In addition, it should be noted that shapes are not necessarily mutually exclusive.

B. LOW RATE INJECTION

	R1			R2		
element	range mg kg^{-1}	% area >bg	shape*	range mg kg^{-1}	% area >bg	shape*
(i) HONEY PARK						
Cd	6-11	38	oval(v)	5-7	0	oval(v)
Cu	11-28	24	oval	13-48	80	flask
Ni	25-36	0	flask	27-38	14	flask(f)
Pb	17-33	95	flask(f)	22-38	93	flask(f)
Zn	57-132	100	oval(v)	19-138	100	flask(f)
(ii) COLATON RALEIGH						
Cd	2-4	5	oval(v)	3-4	20	oval(v)
Cu	4-5	48	oval(v)	5-24	93	oval(v)
Ni	7-15	33	flask(i)	9-13	100	oval(v)
Pb	7-56	19	flask	14-34	100	oval(v)
Zn	16-146	62	pear	23-78	93	oval(v)

where:

oval(v)	oval, long axis vertical
flask(f)	flattened flask configuration
flask(i)	inverted flask configuration

*Descriptions of shapes are intended as an indication only, and are diagrammatically illustrated by Table 7.5.4. In addition, it should be noted that shapes are not necessarily mutually exclusive.

TABLE 7.5.2 THE EXTENT OF METAL MOVEMENT: 2. THE SIDE-INCLINED TINE

A. HIGH RATE INJECTION

element	R1			R2			R3		
	range mg kg^{-1}	% area >bg	shape*	range mg kg^{-1}	% area >bg	shape*	range mg kg^{-1}	% area >bg	shape*
(i) HONEY PARK									
Cd	3-8	0	diag	4-6	0	none	2.4	0	diag
Cu	12-41	99	diag(v)	12-35	71	V	13-35	87	diag
Ni	14-33	0	diag	13-20	0	none	12-20	0	diag(v)
Pb	10-41	87	diag(v)	19-48	100	elbow(v)	17-47	100	diag(v)
Zn	48-151	100	diag(v)	68-172	100	V	63-146	100	diag(e)
(ii) COLATON RALEIGH									
Cd	1-2	0	V	0-2	0	V	2-4	0	none
Cu	4-39	57	elbow	3-19	79	elbow	5-22	94	key
Ni	2-5	0	elbow	2-8	0	diag	5-14	9	diag
Pb	7-37	86	elbow	18-40	100	diag	6-33	74	diag
Zn	17-105	74	elbow	16-68	85	elbow	18-92	78	diag(k)

where:

diag	diagonal; (d) = tending towards diagonal
(v)	tending towards a 'V' configuration
(e)	tending towards an 'elbow' congiguration
(k)	tending towards a 'keyhole' configuration

*Descriptions of shapes are intended as an indication only, and are diagrammatically illustrated by Table 7.5.4. In addition, it should be noted that shapes are not necessarily mutually exclusive.

TABLE 7.5contd THE EXTENT OF METAL MOVEMENT: 2. THE SIDE-INCLINED TINE

B. LOW RATE INJECTION

	R1			R2		
element	range mg kg^{-1}	% area >bg	shape*	range mg kg^{-1}	% area >bg	shape*
(i) HONEY PARK						
Cd	5-11	6	diag	7-8	0	keyhole
Cu	11-28	100	diag	17-32	100	keyhole
Ni	19-38	6	diag	32-38	72	none
Pb	8-44	55	diag	30-42	100	keyhole(d)
Zn	56-166	100	diag	82-134	100	keyhole(d)
(ii) COLATON RALEIGH						
Cd	1-3	0	diag	2-5	35	none
Cu	6-30	100	diag	4-21	65	elbow
Ni	9-14	100	diag	7-20	29	elbow(s)
Pb	13-36	100	diag	6-24	76	elbow
Zn	6-30	9	diag	4-21	0	elbow(s)

where:

keyhole(d)	keyhole configuration with some form of distortion
elbow(s)	elbow-shaped, but distinguishable configuration covers a limited area only

*Descriptions of shapes are intended as an indication only, and are diagrammatically illustrated by Table 7.5.4. In addition, it should be noted that shapes are not necessarily mutually exclusive.

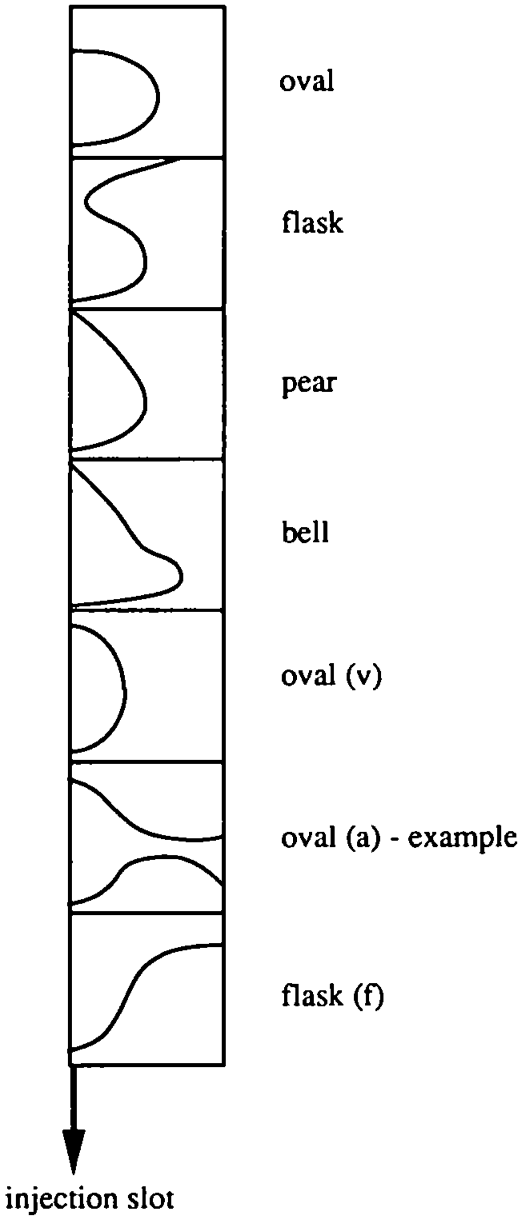
TABLE 7.5.3 THE EXTENT OF METAL MOVEMENT: 3. THE WINGED TINE

element	R1			R2			R3		
	range mg kg^{-1}	% area >bg	shape*	range mg kg^{-1}	% area >bg	shape*	range mg kg^{-1}	% area >bg	shape*
Cu	20-92	100	'U'	17-41	100	⊥	22-63	100	⊥
Zn	48-80	20	none	51-81	52	none	50-72	11	⊥

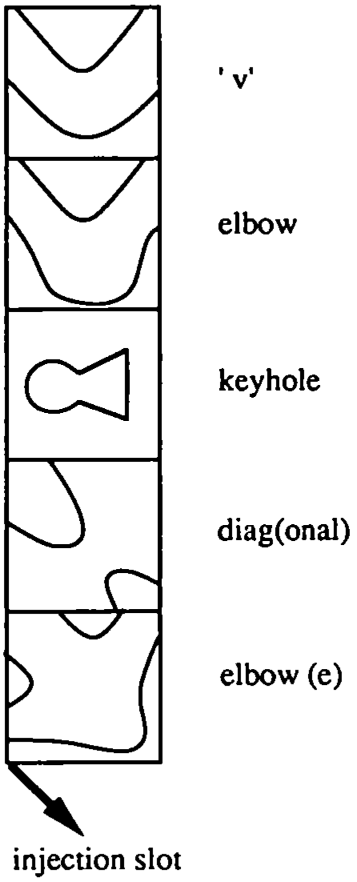
*Descriptions of shapes are intended as an indication only, and are diagrammatically illustrated by Table 7.5.4. In addition, it should be noted that shapes are not necessarily mutually exclusive.

TABLE 7.5.4 EXPLANATION OF DESCRIPTIONS USED IN TABLE 7.5 TEXT

A. THE STRAIGHT TINE



B. THE SIDE-INCLINED TINE



C. THE WINGED TINE

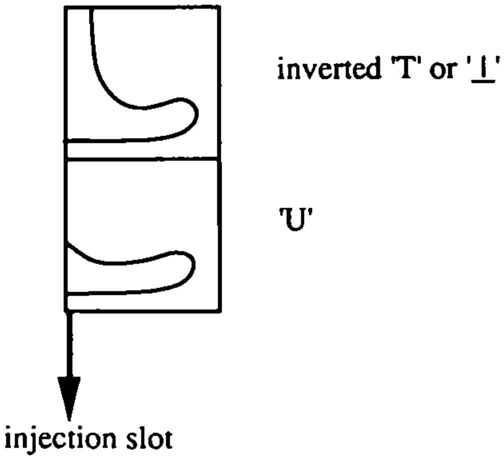


TABLE 7.6 $CaCl_2$-EXTRACTABILITY OF SELECTED METALS

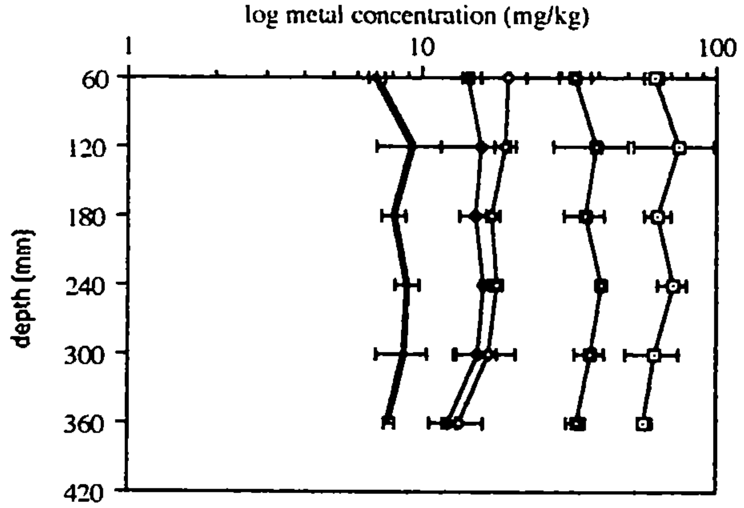
	2S		2P		WRc
element	av.(mg/kg)	RSD	av.(mg/kg)	RSD	av.(mg/kg)
A. HONEY PARK					
Cu	0.08	38	0.05	136	0.9-4.5
Ni	0.29	10	0.27	107	<1-4.5
Zn	0.28	87	0.25	121	4-24.5
B. COLATON RALEIGH					
Cu	0.12	28	0.01	147	0.9-4.5
Ni	0.64	16	0.48	68	<1-4.5
Zn	1.48	136	1.04	143	4-24.5

TABLE 7.7 PERCENTAGE AVAILABILITY OF SELECTED METALS

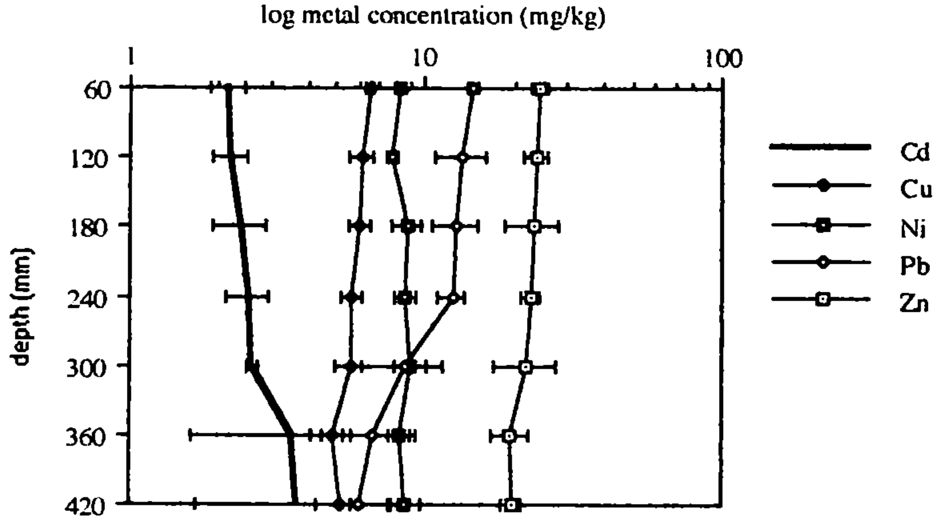
	2S		2P	
element	av. (%)	RSD	av. (%)	RSD
A. HONEY PARK				
Cu	0.44	36	0.24	145
Ni	1.06	10	1.30	118
Zn	0.22	64	0.25	105
B. COLATON RALEIGH				
Cu	1.12	35	1.39	170
Ni	7.63	15	6.87	64
Zn	4.6	73	2.94	93

FIGURE 7.1 BACKGROUND SOIL METAL CONCENTRATION (mg/kg)

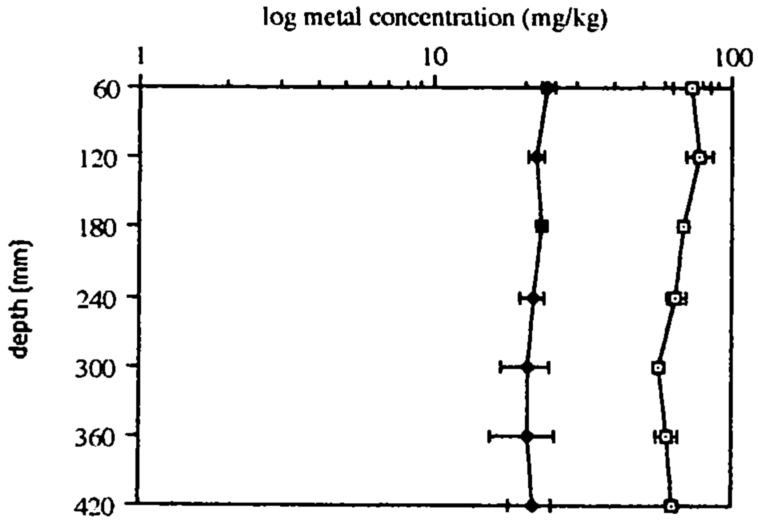
1. HONEY PARK



2. COLATON RALEIGH



3. BROAD MEADOW



Each point represents the mean of 3 replicates.
Error bars indicate the associated variability.

FIGURE 7.2 ENRICHMENT* OF METAL CONCENTRATIONS (mg/kg).
1: HONEY PARK

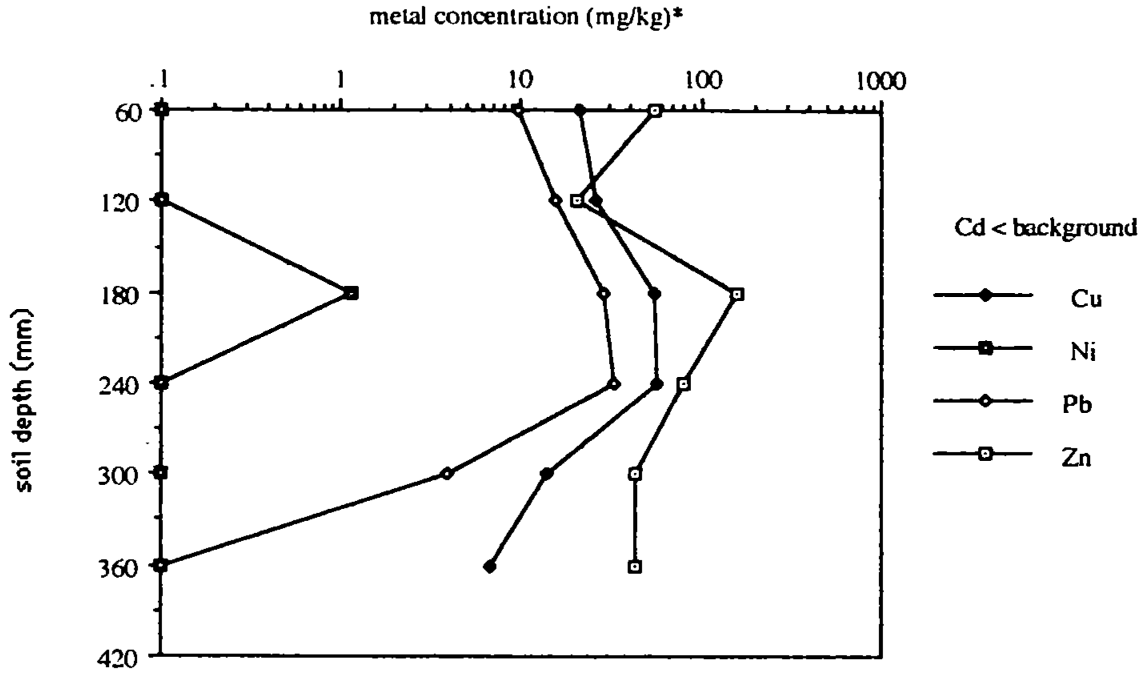
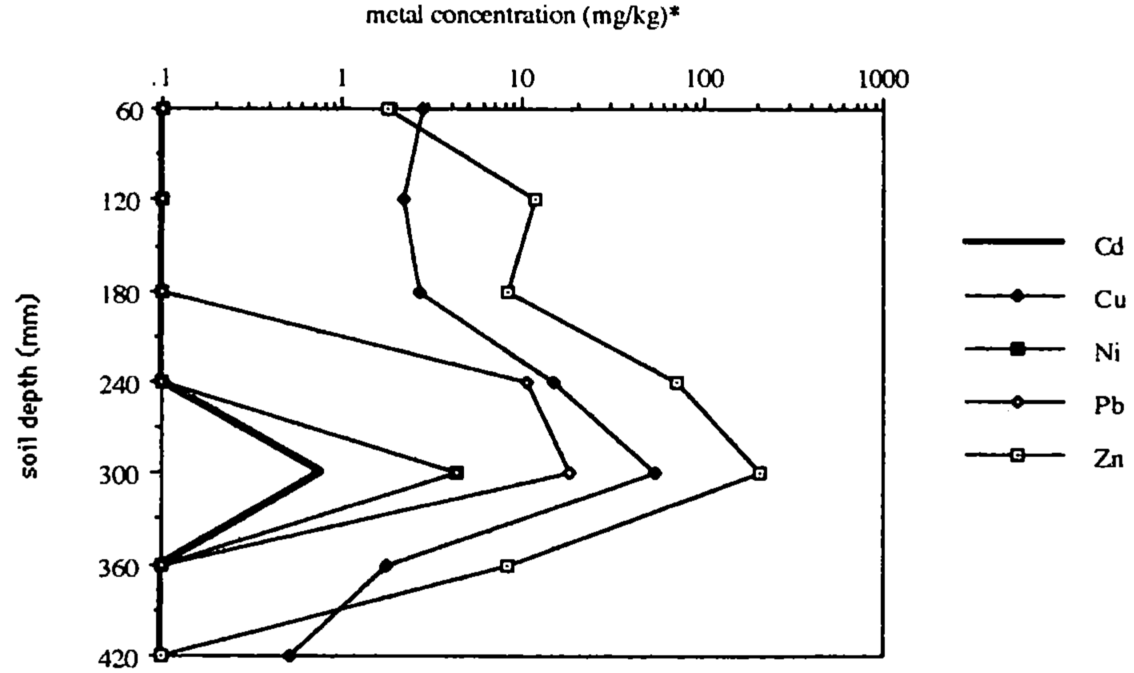
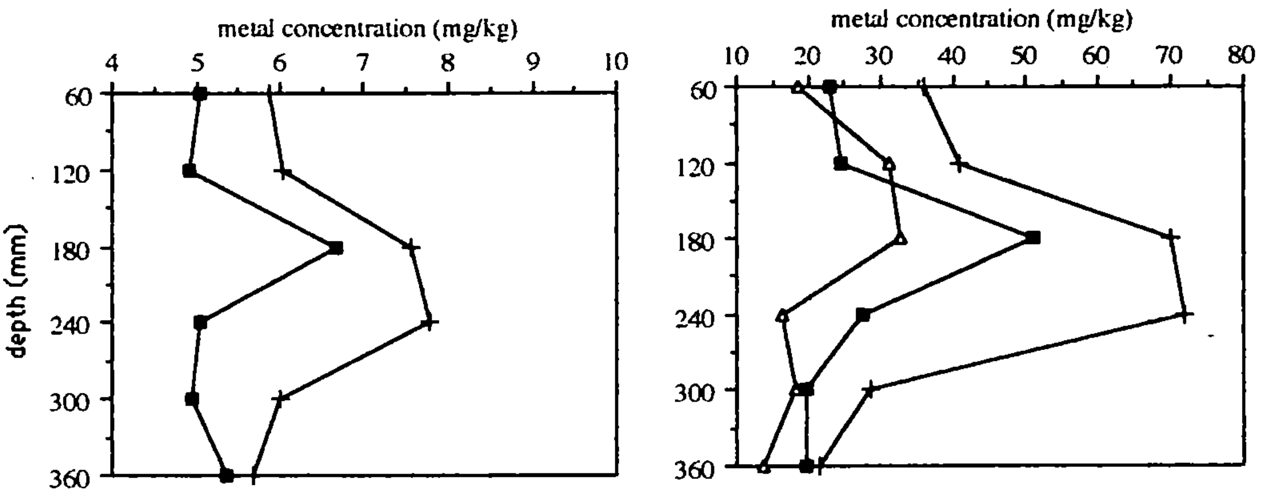


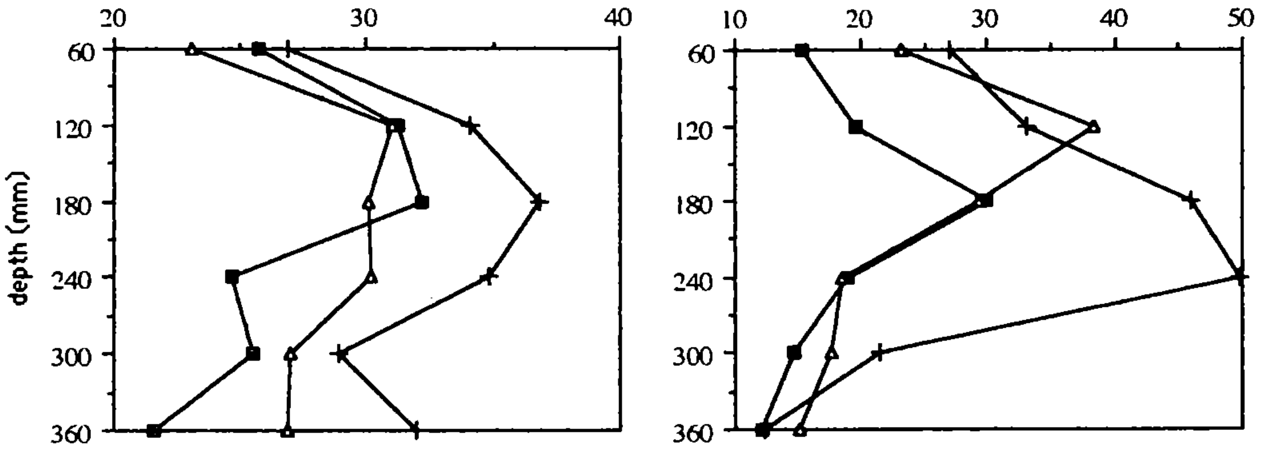
FIGURE 7.2 ENRICHMENT* OF METAL CONCENTRATION (mg/kg).
2: COLATON RALEIGH



* The term 'enrichment' and all metal concentrations cited here refer to the amended concentration - average background concentration. Negative values are therefore inevitable, but to facilitate clarity of presentation, these have been assigned a value of 0.1. These values should therefore be ignored.

FIGURE 7.3 THE IN-SITE VARIABILITY OF SLUDGE-AMENDED METAL CONCENTRATION - HIGH RATE INJECTIONS.
A: HONEY PARK


(i) Cd (ii) Cu


(iii) Ni (iv) Pb

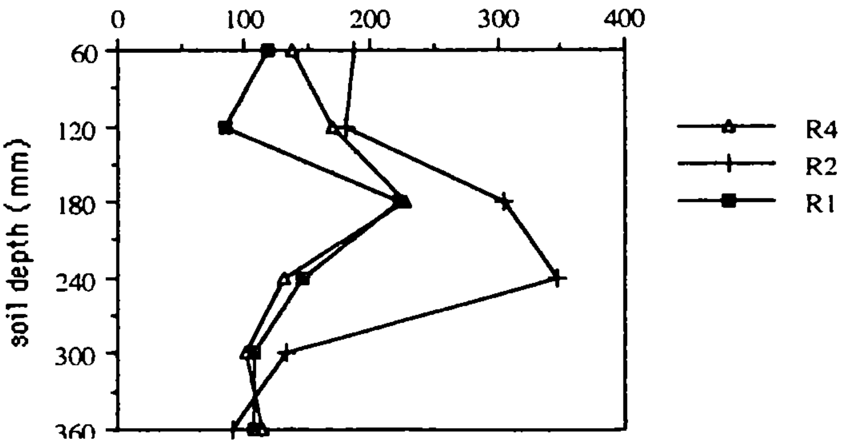
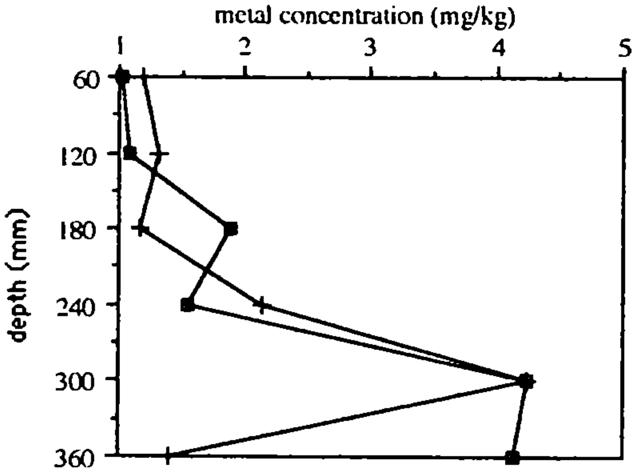
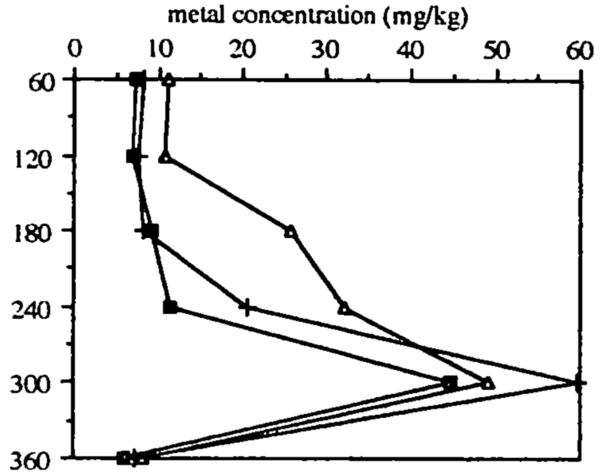

(v) Zn

FIGURE 7.3 contd THE IN-SITE VARIABILITY OF SLUDGE-AMENDED
METAL CONCENTRATION - HIGH RATE INJECTIONS
B: COLATON RALEIGH

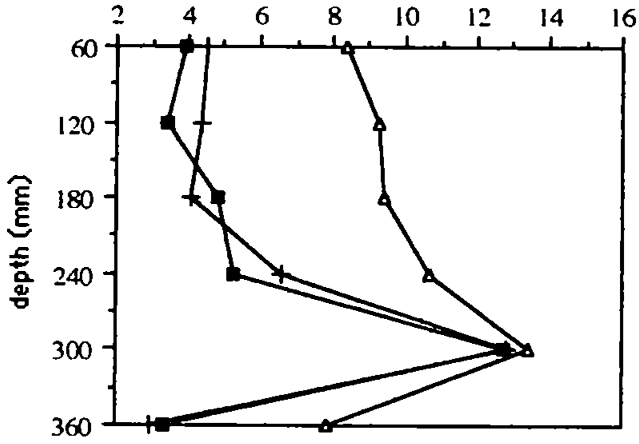
(i) Cd



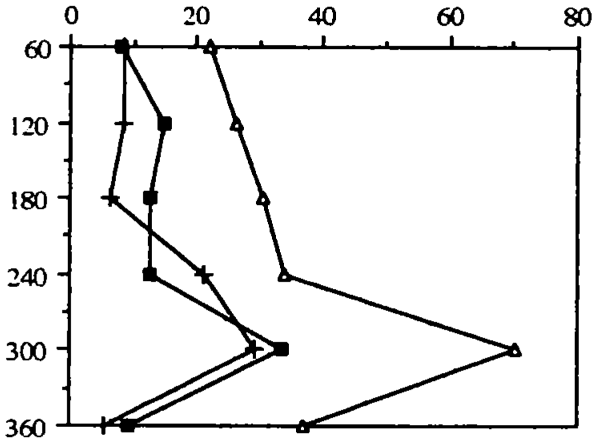
(ii) Cu



(iii) Ni



(iv) Pb



(v) Zn

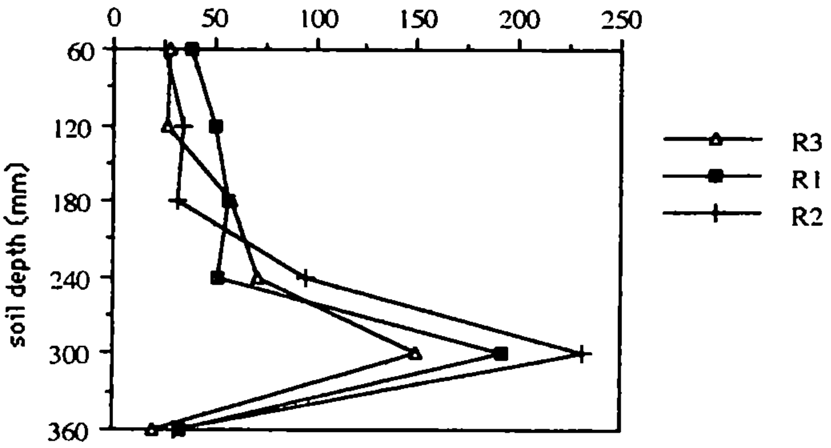
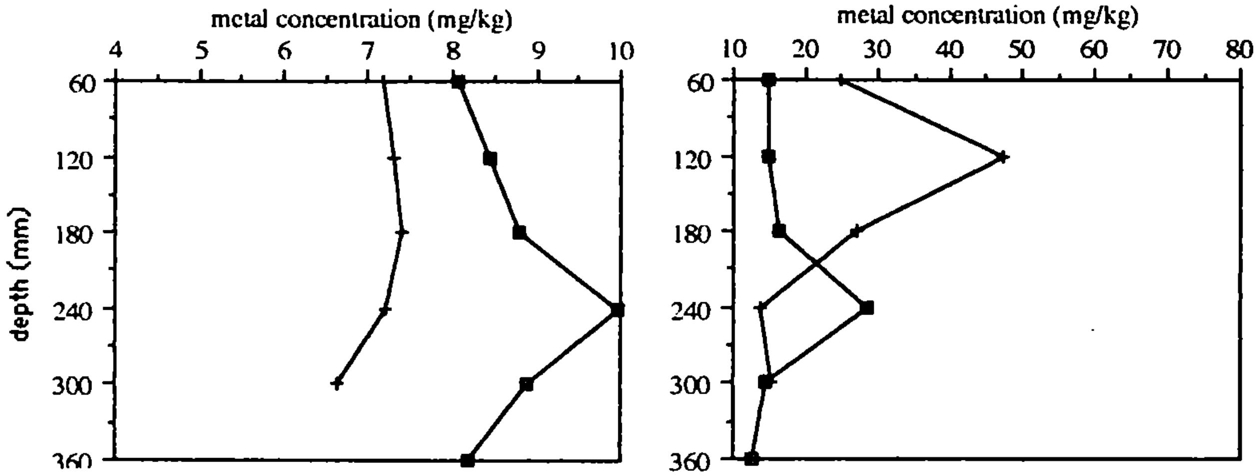
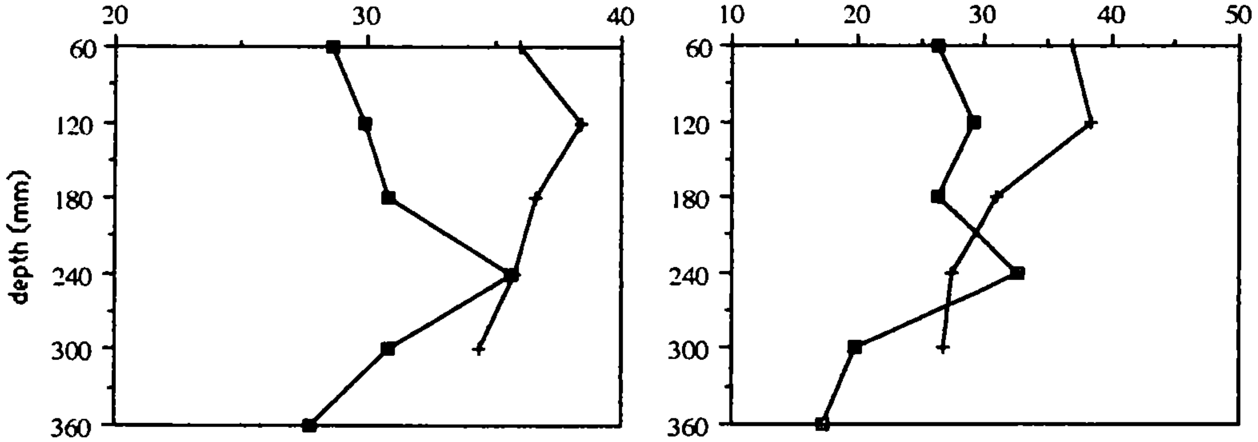


FIGURE 7.4 IN-SITE VARIABILITY OF SLUDGE-AMENDED METAL CONCENTRATION - LOW RATE INJECTIONS
A: HONEY PARK



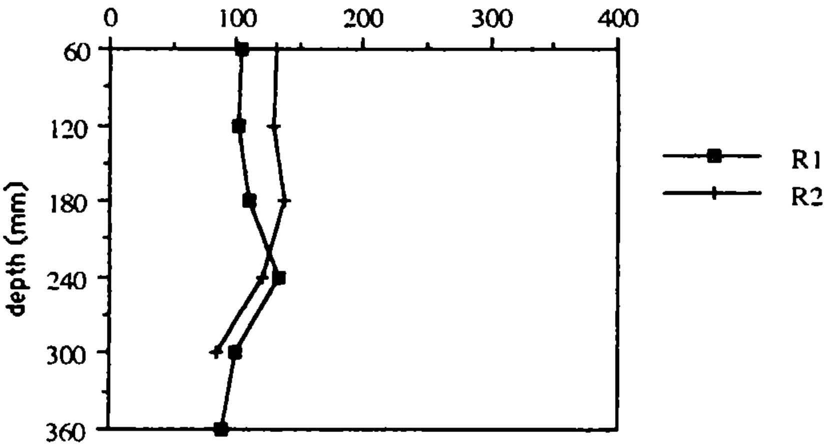
(i) Cd

(ii) Cu



(iii) Ni

(iv) Pb



(v) Zn

FIGURE 7.4 contd IN-SITE VARIABILITY OF SLUDGE-AMENDED METAL CONCENTRATION - LOW RATE INJECTIONS
B: COLATON RALEIGH

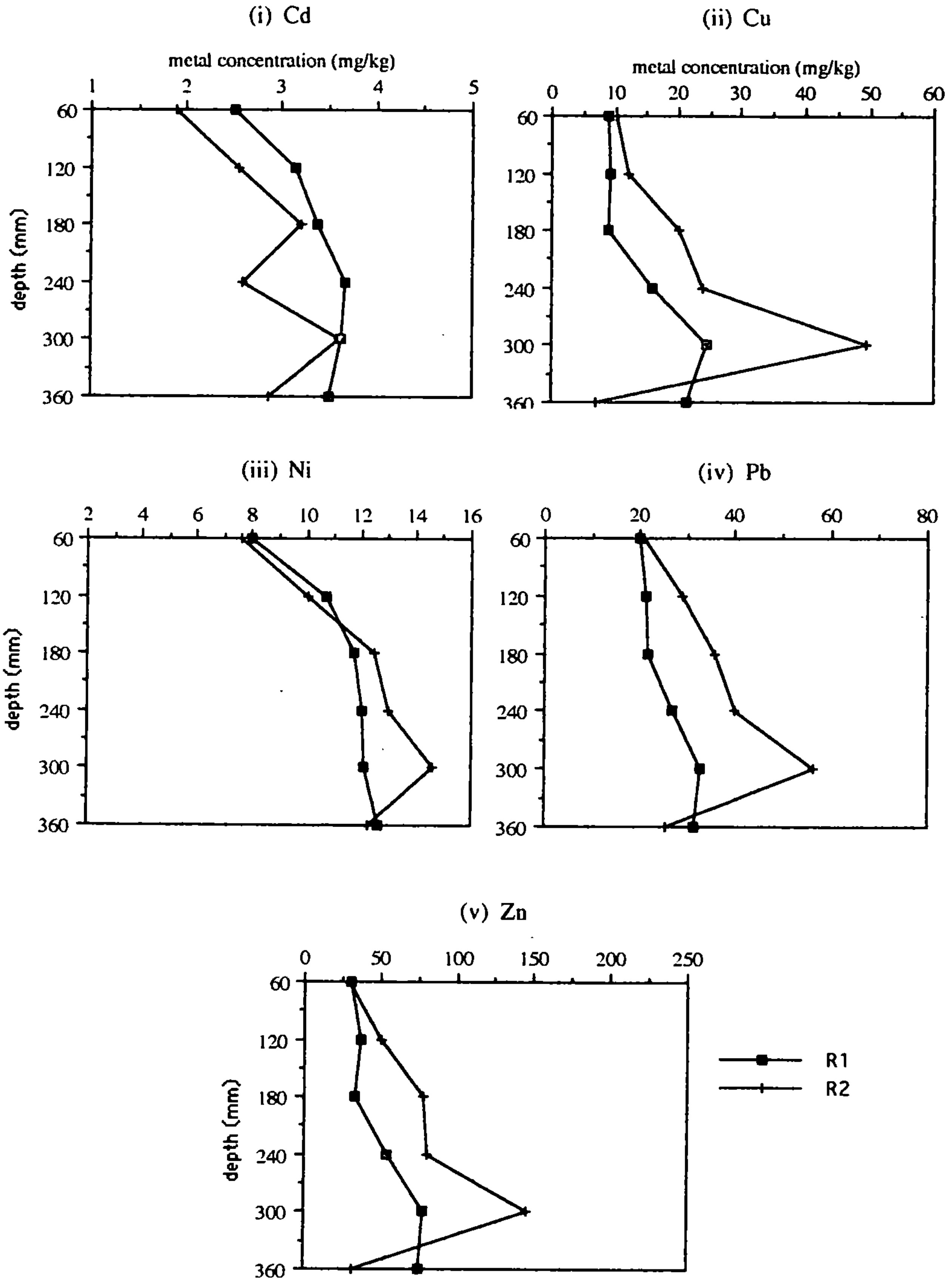


FIGURE 7.5 THE CHANGE IN SELECTED METAL CONCENTRATIONS (mg/kg) WITH TIME

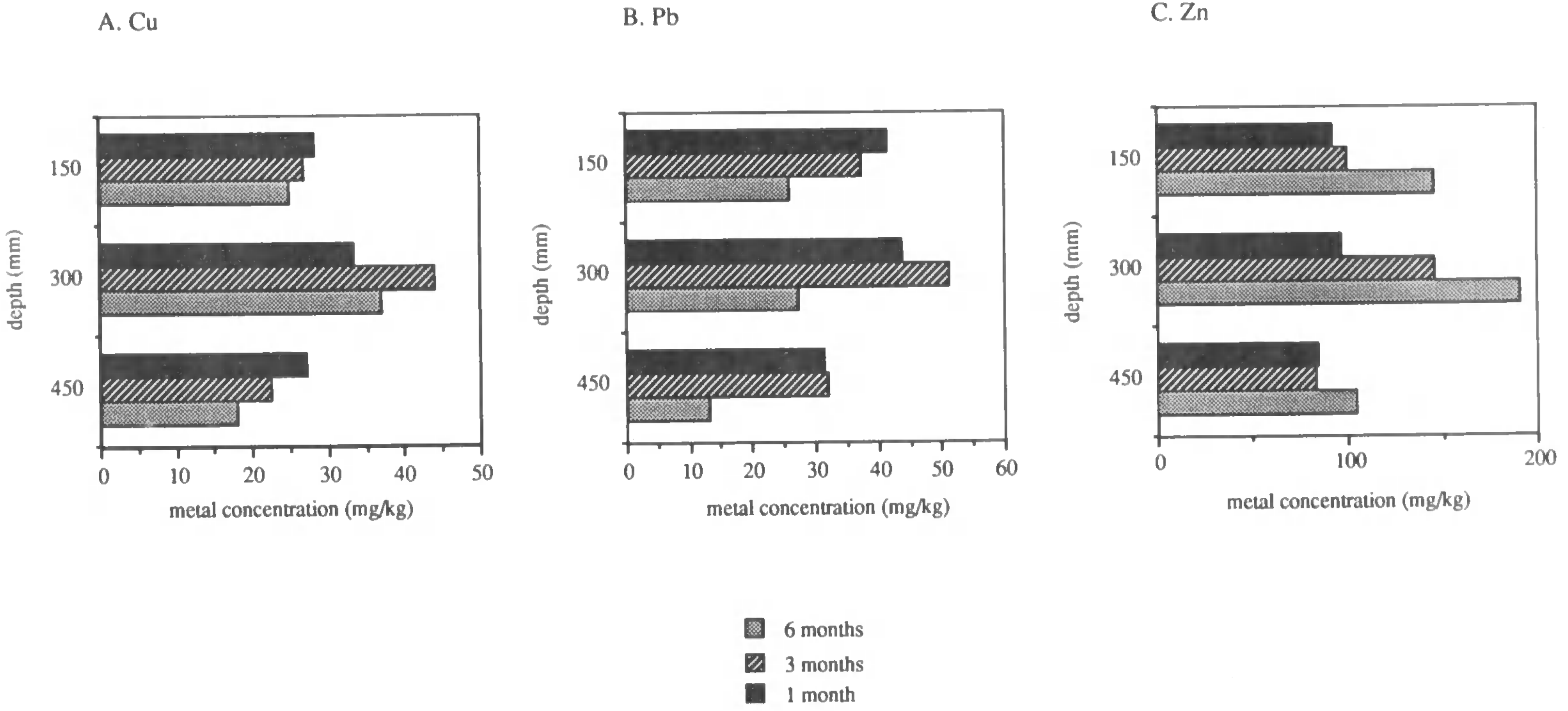
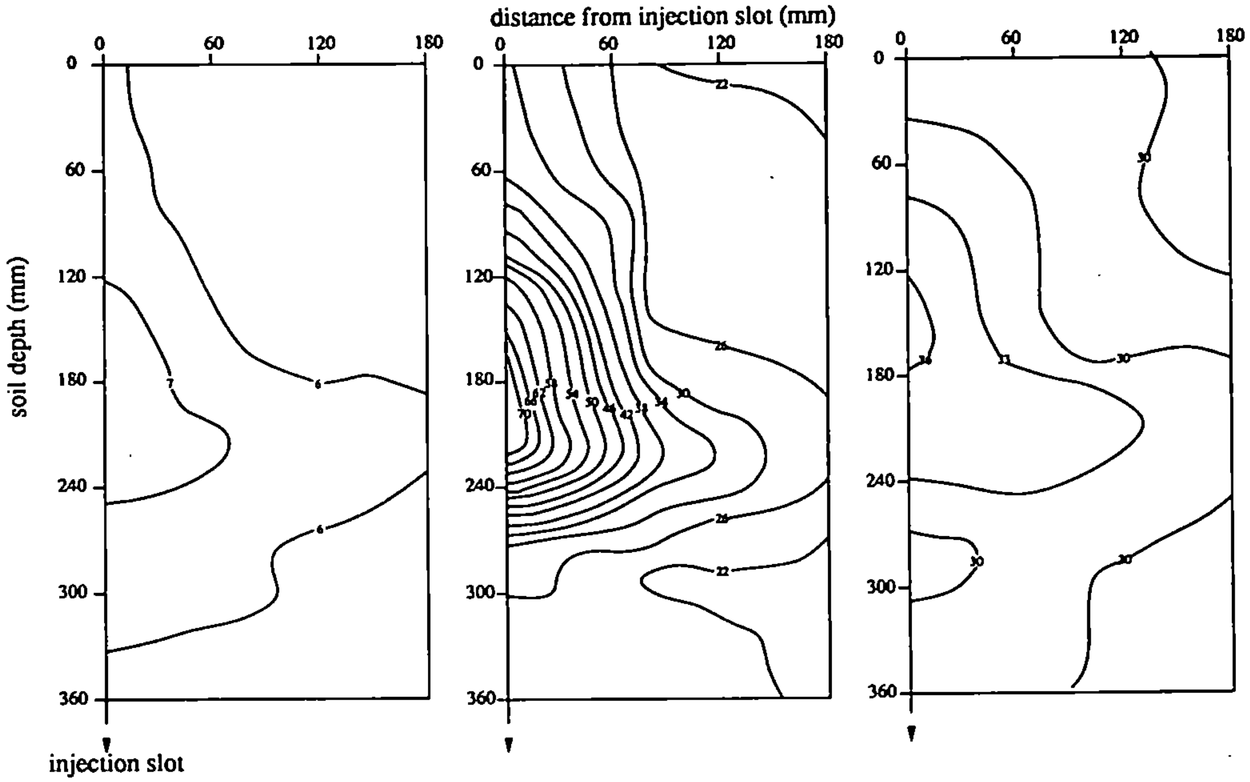


FIGURE 7.6 METAL DISTRIBUTION FOLLOWING A HIGH RATE OF INJECTION THROUGH A STRAIGHT TINE:

A. HONEY PARK

i) Cd ii) Cu iii) Ni



iv) Pb v) Zn

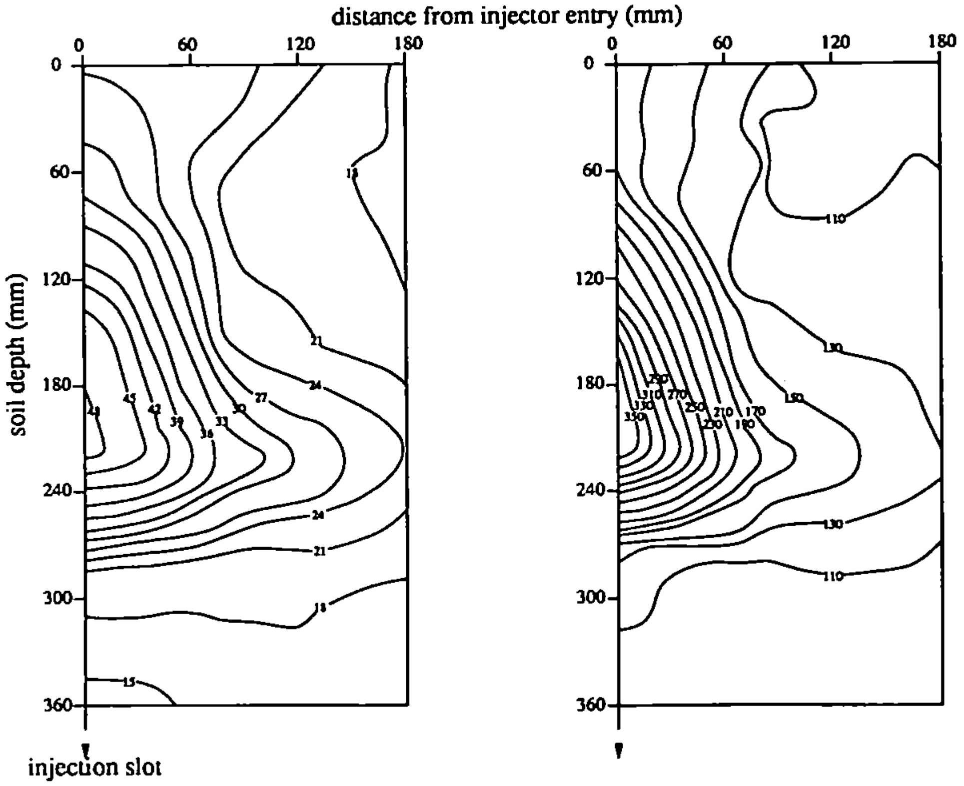
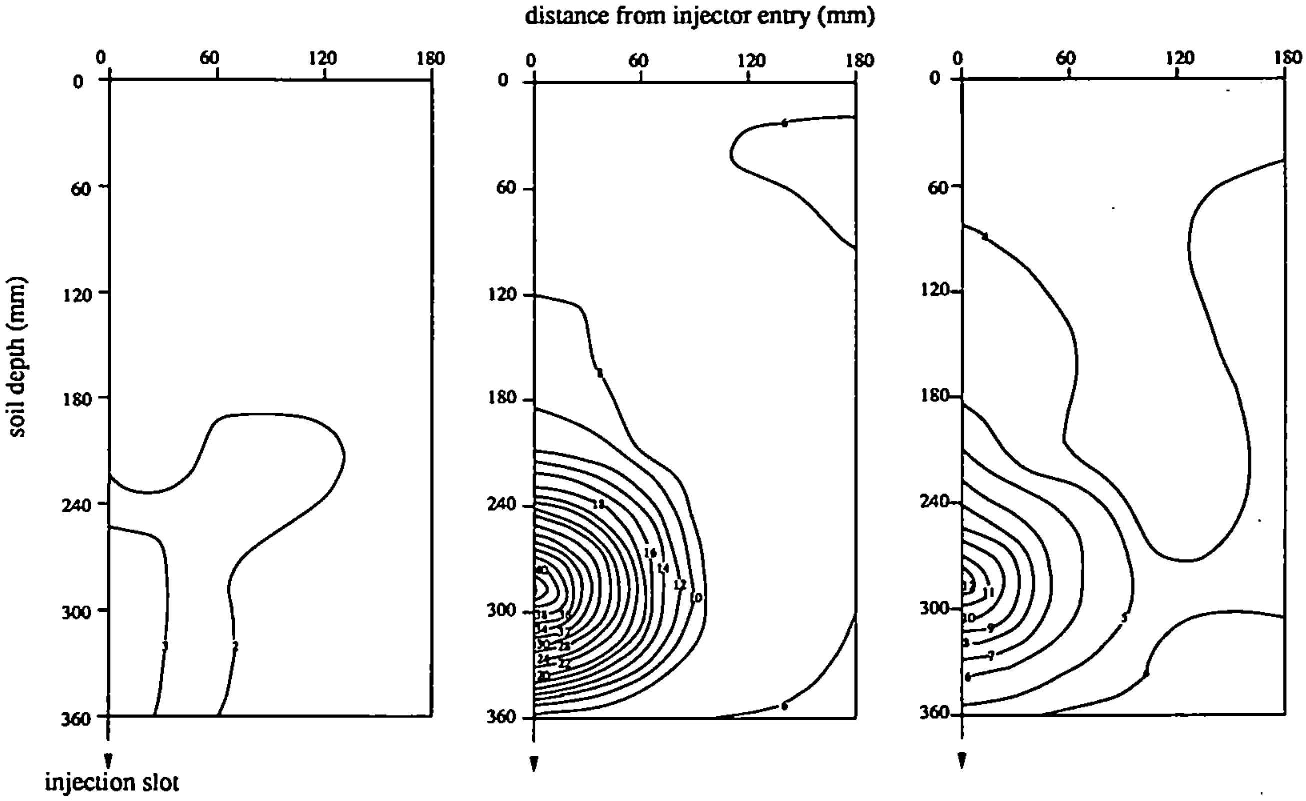


FIGURE 7.6 contd METAL DISTRIBUTION FOLLOWING A HIGH RATE OF INJECTION THROUGH A STRAIGHT TINE:

B. COLATON RALEIGH

i) Cd ii) Cu iii) Ni



iv) Pb v) Zn

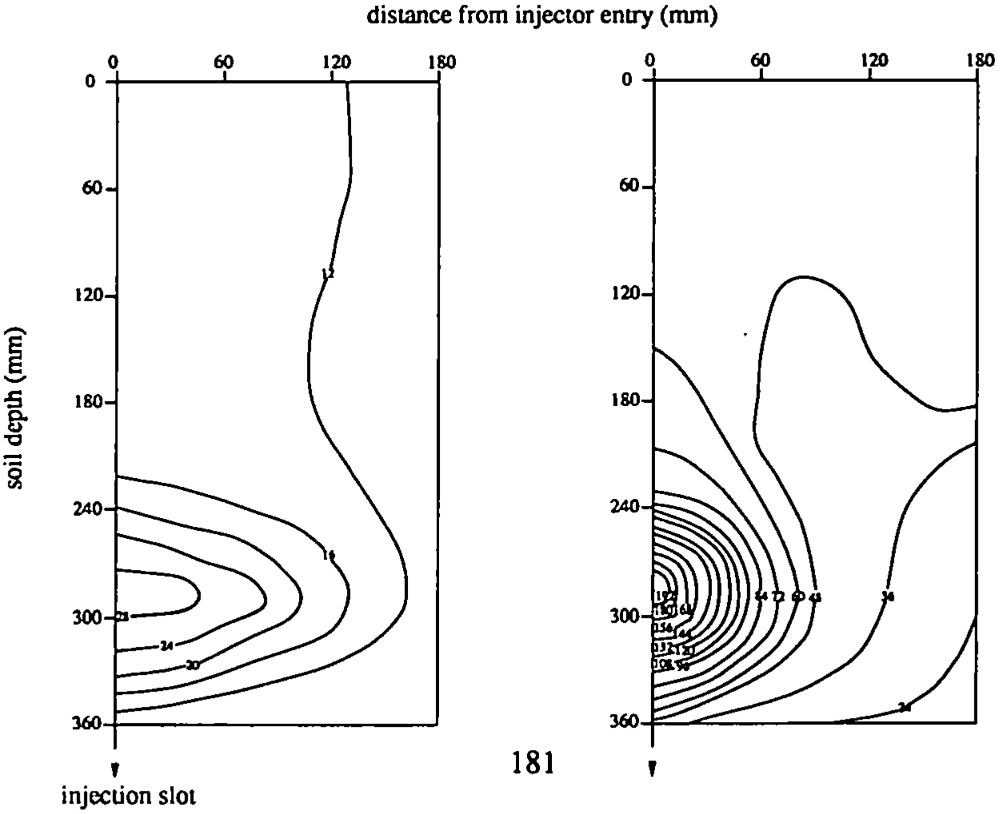


FIGURE 7.7 METAL DISTRIBUTION FOLLOWING A HIGH RATE OF INJECTION THROUGH THE SIDE-INCLINED TINE: A. HONEY PARK

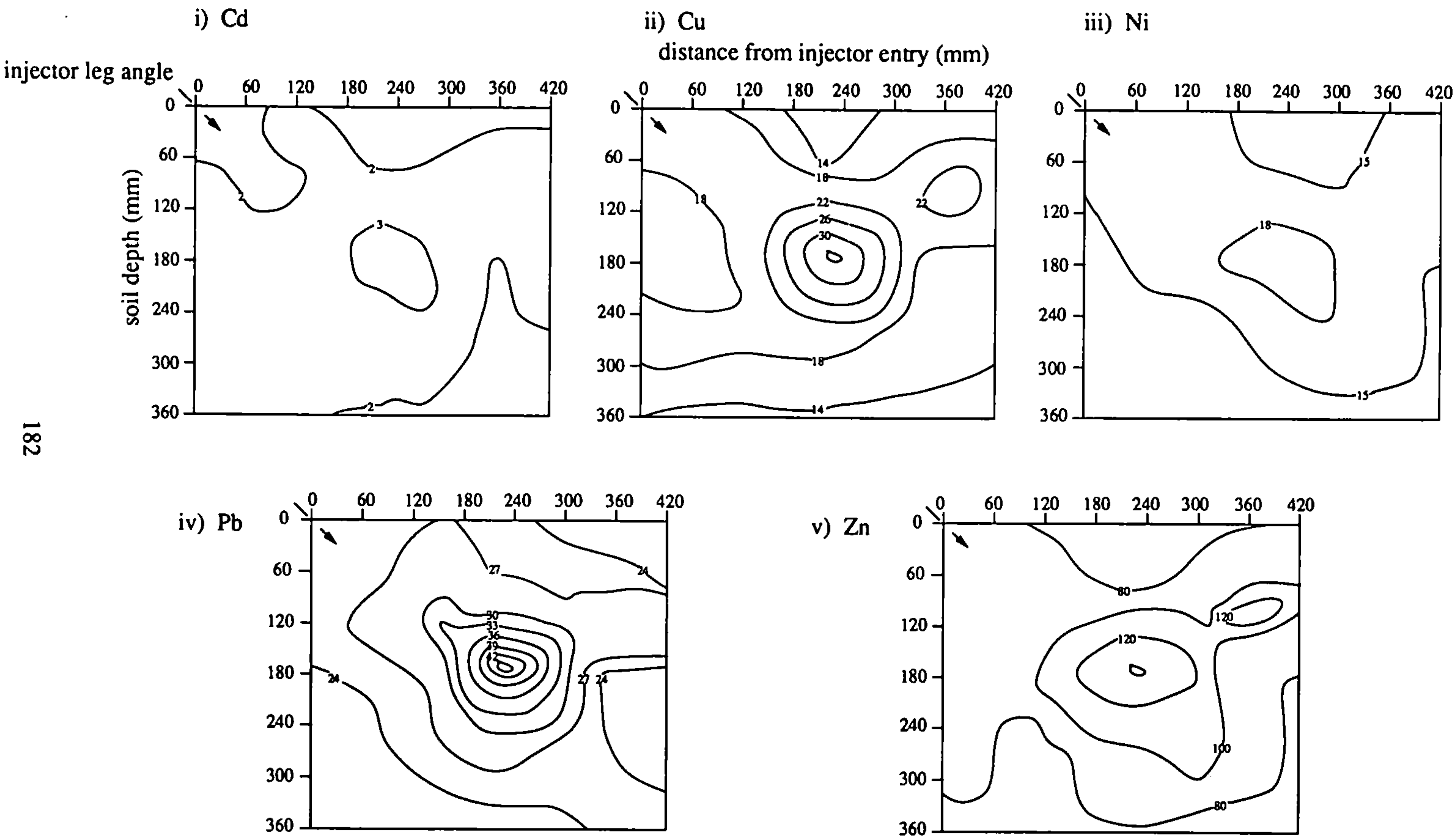


FIGURE 7.7 METAL DISTRIBUTION FOLLOWING A HIGH RATE OF INJECTION THROUGH A SIDE-INCLINED TINE: B. COLATON RALEIGH

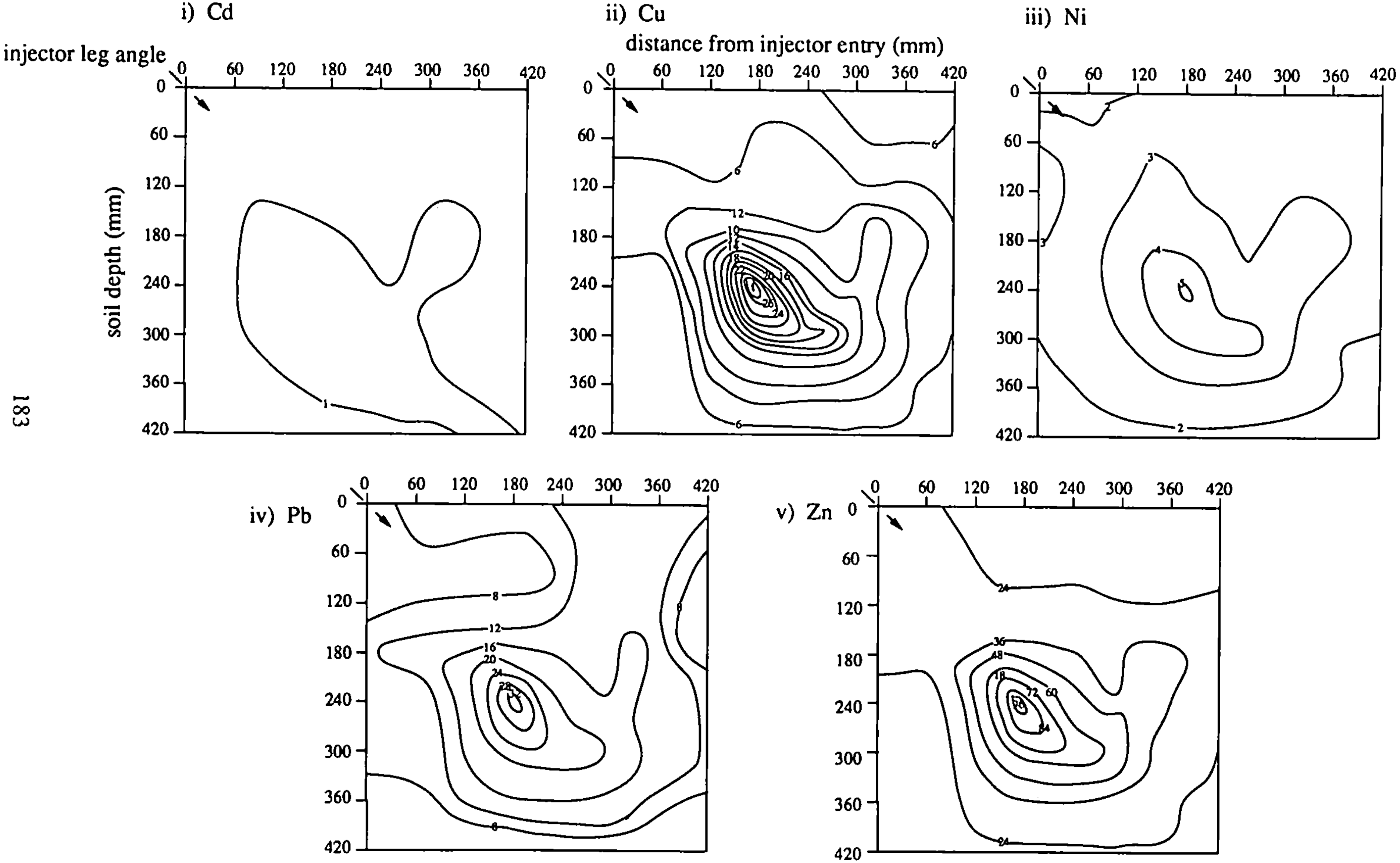
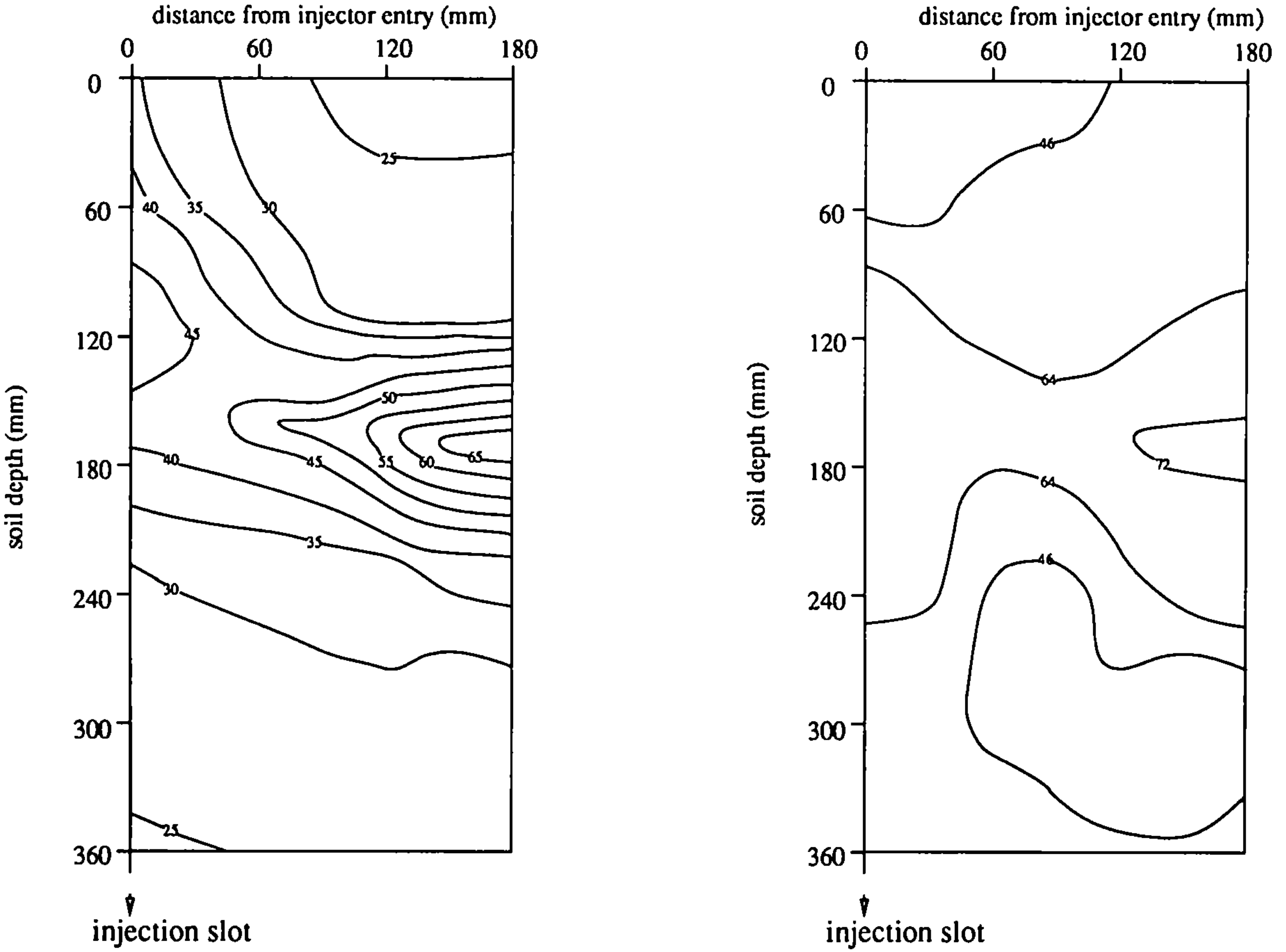


FIGURE 7.8 METAL DISTRIBUTION FOLLOWING INJECTION THROUGH A WINGED TINE


i) Cu

ii) Zn

FIGURE 7.9 FIELD MASS BALANCE OF METALS

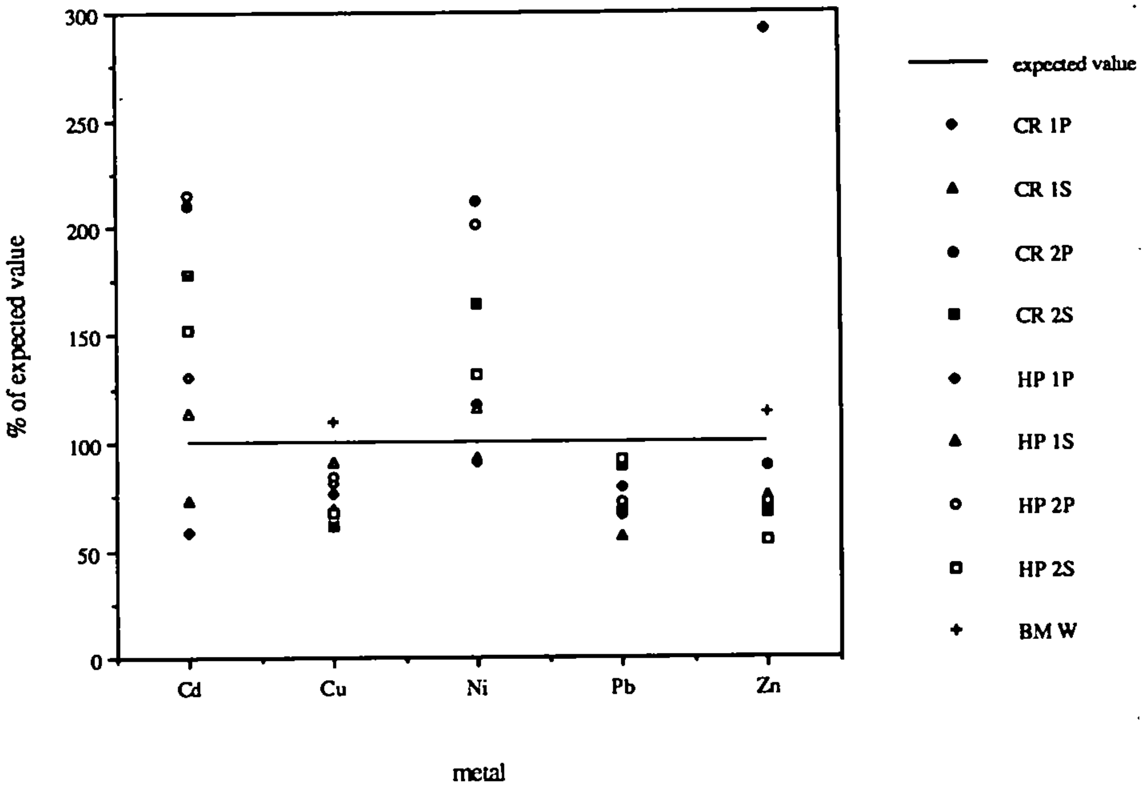
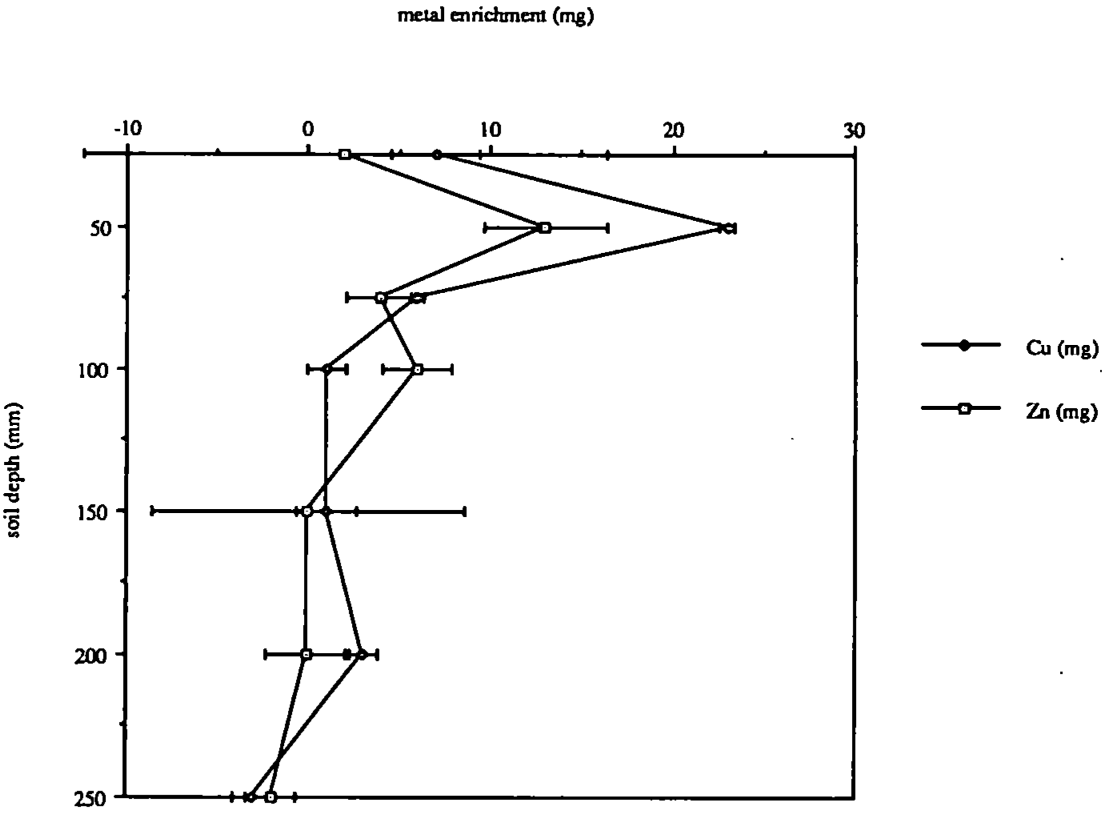


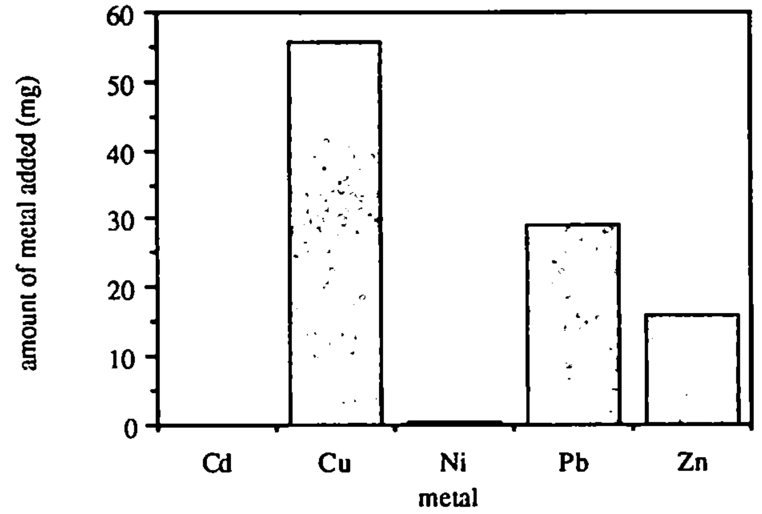
FIGURE 7.10 SOIL METAL CONTENT OF MASS-BALANCE COLUMNS

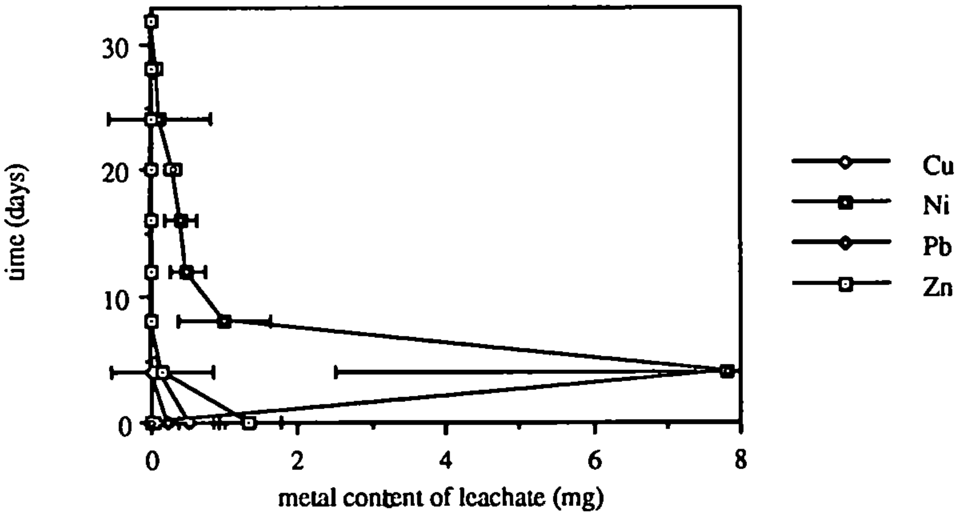


N.B. data refers to soil metal content in excess of background concentrations

Each data point represents the mean of 3 replicates. Associated variability is indicated by error bars.

FIGURE 7.11 METAL CONTENT OF MASS BALANCE COLUMN LEACHATE (mg)

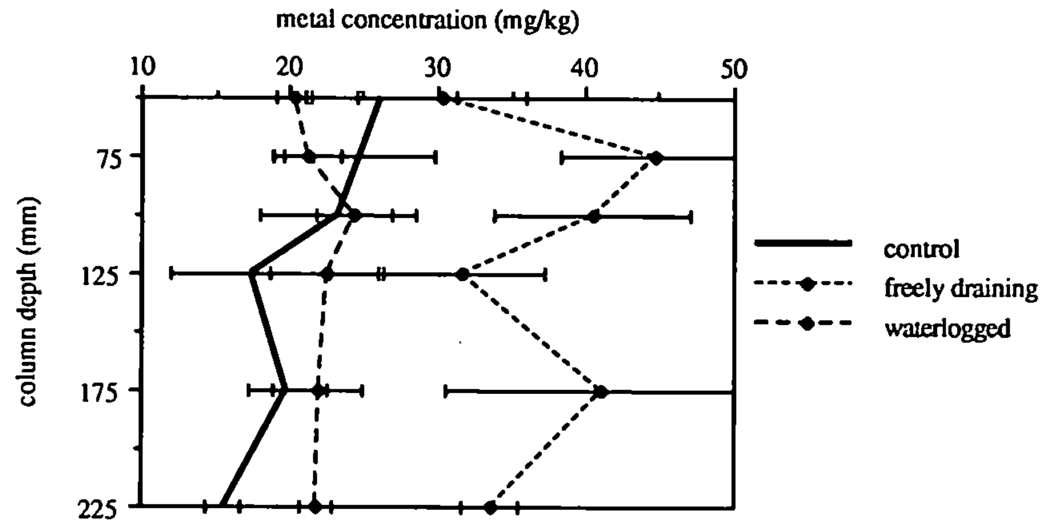




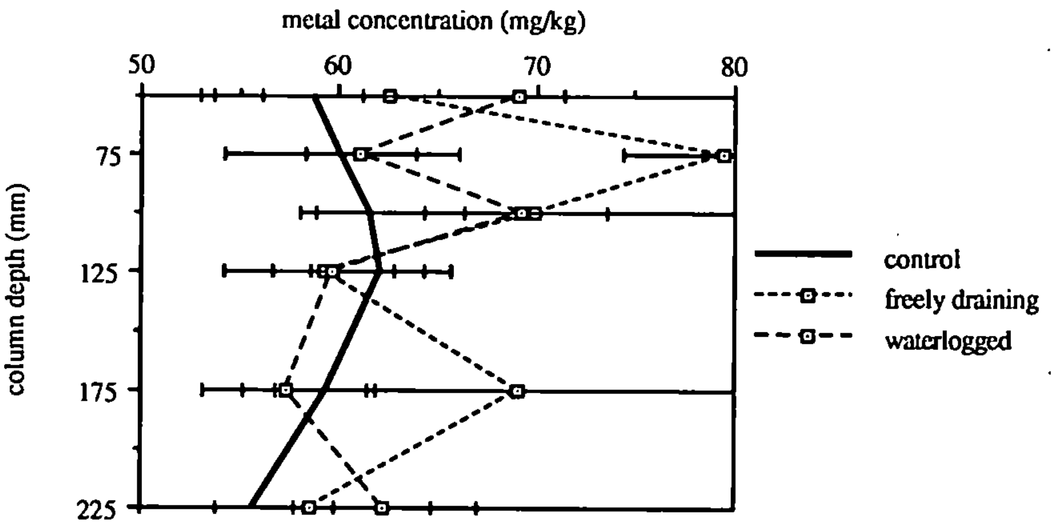
N.B. Results presented take account of the metal loading of the added water
Each data point represents the mean of 3 replicates.
Associated variability of leachate metal content is indicated by error bars.

FIGURE 7.12 SOIL METAL CONTENT UNDER DIFFERING WATER REGIMES

1: Cu



2: Zn



Each data point represents the mean of 3 replicates. Associated variability is indicated by error bars.

8. DISCUSSION

8.1 INTRODUCTION

In previous Chapters (Chapters 5, 6 and 7), field and laboratory results from experiments intended to ascertain the extent and pattern of heavy metal movement from injected sewage sludge have been presented, along with the quantification of those factors that might be expected to affect this. The question remains: is the extent and pattern of metal movement predictable? And, which of the measured factors is influential, and what influences the substantial variability in metal movement that has been observed? Within these larger issues, each Chapter has raised individual points for discussion that will be dealt with here.

In attempting to predict metal movement from a knowledge of potentially influential factors, the use of correlation and regression analysis is employed in the discussion of soil factor:metal movement interactions. These tools are also used for the assessment of the effect of soil disturbance on metal movement, but in this case the tests are not so robust because 1) the measurement of one or both factors may exceed 100 % (that is, the extent of metal movement and/or soil disturbance may be greater than the area of soil sampled), 2) much of the significant information is of a qualitative nature (i.e the importance of the shape of movement/disturbance on ascertaining a relationship between the two) and 3) the fact that the number of observations is too small, due to the unavoidable use of mean values since sampling for both factors could not be conducted at exactly the same position (Section 6.1) and both have been seen to vary as much within as between replicates (Sections 6.2 and 7.4). Thus, limits are inherently placed on the mathematical expression of relationships and it must be remembered that the following discussion holds only within this framework.

8.2 THE EFFECT OF SOIL PROPERTIES ON METAL DISTRIBUTION

In Chapter 7, the hypothesis that the soil types studied had little influence on the distribution of metals after their injection into soils was introduced. This was based on the finding that the basic pattern of distribution was entirely dictated by tine design (Section 7.4), and that the extent of this distribution was little different between soil types (Section 7.4). By correlating soil factors against metal distribution and using the same factors to predict distribution through regression analysis, it is now appropriate to statistically test this.

8.2.1 BACKGROUND CONCENTRATIONS

Correlation analysis of background metal concentration against soil factors, summarised by Table 8.1, indicates that only percentage clay is significantly ($p<0.05$) related to the background concentration of all metals at Honey Park, in a negative relationship except with Pb. The unique position of Pb is further highlighted by its interaction with pH (negative), organic carbon and cation exchange capacity (both positive), which is found for no other metal. The soil content of Fe and Mn apparently is not related to background metal concentration (although correlation analysis can not pin-point causal relationships). In contrast, each of the measured soil factors at Colaton Raleigh correlate significantly ($p<0.05$) with the background concentration of each metal except Cd; and Pb and Ni in the case of percentage clay. Nickel is further isolated by its negative relationship (the reverse of the general case) with organic carbon, Fe and Mn, but its positive association with pH. Surprisingly, the relationship between metal content and measured soil factors at Broad Meadow is similar to that at Colaton Raleigh rather than Honey Park, in that both Zn and Cu have a significant ($p<0.05$), positive correlation with all factors but pH (significant, negative association) and percentage clay (no significant relationship). Thus, only clay content has any bearing on the ambient metal concentration at Honey Park, whilst at Colaton Raleigh and Broad Meadow all factors but percentage clay are related to the background metal concentration.

8.2.2 AMENDED CONCENTRATION

When soils have been amended by the addition of metal-laden sewage sludge, correlation analysis between concentration and soil factors becomes meaningless (no significant interactions) as the ranking of metal concentration has been upset by an external and independent source. This lack of correlation between parameters that are related in untreated soil is also found between soil factors and the extent of metal movement (Table 8.2), where the 'extent of movement' is defined by the proportion of the soil that has metal concentrations in excess of background contents plus 2σ (Section 7.4). Together, these observations begin to suggest that another control is now in place, or that insufficient time has elapsed to allow equilibration between the added metals and soil factors. Applying multiple regression analysis across all treatments (including soil type) shows that metal movement is significantly predicted by soil factors only for Zn ($p < 0.05$), since Zn alone always has a wider distribution at Honey Park than Colaton Raleigh (Section 7.4.1):

$$\text{Zn movement} = 152 - 3.4\ \text{pH} + 4.69\ \text{CEC} + 0.027\ \text{Fe} + 0.44\ \text{Mn} + 1.37\ \%\text{C}$$

In the case of Zn, pH and Fe content are cited by the regression equations as being the most influential factors. This behaviour is the reverse of expectations (that metals would be more mobile at Colaton Raleigh), and can not logically be attributed to pH because movement is enhanced at the less acidic Honey Park site. Msaky and Calvet (1990) and Korte *et al.* (1976) state that Fe oxide is largely responsible for the adsorption Zn (and Cu), especially in acid, clay soils. As shown in Section 5.5, Fe oxide concentrations at Honey Park and Broad Meadow are significantly less than those at Colaton Raleigh, and Section 5.2 demonstrated that Fe oxide was significantly correlated with CEC at Broad Meadow and Colaton Raleigh, but not at Honey Park. Therefore, if this is controlling Zn activity, distribution would indeed be greater at the latter site.

The effect of soil factors on the distribution of the remaining metals is minimal (non-significant). For this reason, it is unnecessary to present the equations themselves, but rather to use this analysis to indicate which, if any, of the soil factors is more important. For Cd and Cu, pH is identified as the most influential factor, whereas cation exchange capacity is of greater importance to the movement of Ni. No one soil factor can be distinguished for Pb. As a secondary influence, Fe is cited for Ni and Cd, and cation exchange capacity for Cu (N.B. organic carbon content is not present in any regression equation as it is highly correlated with other soil factors). On the whole, the identification of these controls differs little from that cited in the literature. For example, pH is almost unanimously considered to be the single most important factor in the mobilisation of heavy metals (Section 2.2.2). However, this factor is seen here to have little influence over Ni mobility, probably because the pH of each soil is well below the threshold for Ni cited in Section 2.2.2. Thus, Ni would be expected to be mobilised at each site. Many authors (e.g. McGrath and Smith, 1990) consider CEC to be the secondary control over Ni mobilisation, and in the absence of the influence of pH it seems reasonable to expect that this factor would assume a primary role. Similarly, percentage Fe oxide has been considered to be as important to Ni behaviour by others (Korte *et al.*, 1976); and Alloway and Jackson (1991) consider that hydrous Fe and Mn oxides have a significant role in the adsorption of metals (see also above). No one soil factor can be isolated as influential on the distribution of Pb, and it seems likely that this can be attributed to the fact that the pH threshold for Pb is below that found at any of the sites (e.g., Davies, 1990, states that the pH has to be reduced to 2.5 - 3.0 before significant quantities of Pb will be mobilised). It is also known that Pb is associated mainly with clay minerals, Mn oxides, Fe and Al hydroxides and organic matter (Kabata-Pendias and Pendias, 1984). Of these, only percentage clay and Mn oxide content are included in the regression equations.

In addition to suggesting a causal relationship between metal movement and soil type, regression equations can also indicate how much variability of the dependent (in this case movement) is caused by the independents (soil factors). This can be ranked in terms of r^2 (which values are presented in brackets) as:

Zn (44 %) > Ni (22 %) $\geq$ Cd (21 %) > Pb (11 %) > Cu (8 %)

Soil factors thus account for less than 25 % of the variability of the distribution of all metals except Zn, upon which these factors have significantly more influence, as described above.

The above arguments have used multiple regression analysis as their basis and have dealt with individual metals. In order to assess the precise controls over metal movement and to assess the importance of soil type to metal movement as a whole, all treatments have been grouped together and individual soil factors regressed against them. No one factor was shown to be significant in predicting general metal movement, and a total r^2 of only 6.4 % was yielded in this way, with the importance of various soil factors ranked in the order:

%C > pH and Fe > CEC > OC > WC > Mn
(1.5 %) (1.3 %) (1.0 %) (0.9 %) (0.4 %) (0.0 %)

(where WC = soil water content at injection)

The importance of both percentage clay and pH is initially misleading since enhanced mobility was observed in clayey soils of a relatively high pH. However, it has already been shown that clay contributes relatively little to the CEC of these soils (Section 5.2), and it will be shown (Section 8.5.3) that clay content has other important effects on metal mobility.

Crudely introducing site characteristics as a whole (i.e. as 1, 2 or 3) did little to enhance the performance of soil type in predicting the extent of movement, largely because of the confusing interaction of tines (since more movement is observed at Honey Park after the paraplow is used, but movement of most metals is approximately equivalent between sites for the straight tine) and metal identity (accounting for 22 % of the variability of movement). The effect of injection factors is considered in Section 8.3, but this regression analysis can be used to infer that:

1) soil factors are less important than other factors (see Sections 8.3 and 8.5)

and that 2) the effect of soil factors on movement is metal-dependent.

Although it has been shown that soil type has only a secondary role in affecting the variability in the recognisable distribution of metals, it is desirable to ascertain the controls over percentage availability as this may clarify which, if any, metal has moved by chemical means rather than been physically transported in suspension either during or after injection (although it is noted that Alloway and Jackson (1991) report increases in availability without any corresponding increases in mobility). In Section 7.2 it has already been shown that availability is increased for all metals by the addition of sewage sludge, since a greater proportion of each metal is found in soluble organic chelates in sludge than in soil (e.g. Alloway, 1990b [Cd]; Kabata-Pendias and Pendias, 1984 [Cu, Ni, Zn]; McGrath and Smith, 1990 [Ni] and Stevenson and Welch, 1979 [Pb]), and that percentage availabilities are significantly greater at Colaton Raleigh than Honey Park. However, it is not appropriate to statistically differentiate the contribution of the individual measured soil factors because of the intra-site variability in 'available' metal concentration of up to 170 %, rendering replicates of the same soil type statistically different. There are no corresponding between-replicate anomalies for soil factors. In addition, there is far greater (an order of magnitude) disparity between replicates receiving paraplow injections, although the site mean variability is similar for both paraplow and straight tine treatments. It has also been postulated that the paraplow creates soil disturbance that is more variable than that created by the straight tine (Section 6.2.2). It is therefore likely that aeration (greater in the lighter soil of Colaton Raleigh) is significant in controlling percentage availability. Other factors that are known to increase metal extractability, and conform to the observations made in this experiment are a reduction in pH (especially in the case of Cd, Cu and Zn, whose pH threshold of availability lie between the pHs of the experimental sites) and the sorptive capacity of the soil.

Whilst soil factors appear to have only a secondary effect on determining the extent of distribution of injected heavy metals, this may be the result of omissions from the regression equation. For example, Korte *et al.* (1976) found surface area to be important in the behaviour of inorganic Ni and Zn. Keefer and Singh (1986) similarly related mobility to surface area, as well as texture, free Fe oxide concentration and pH. Alloway *et al.* (1988) state that calcium carbonate may directly remove Cd via precipitation and substitution processes. Welch and Lund (1987) found that only the final pH of amended soils is significant in determining metal chemistry, and since the pH of the sludge was approximately neutral, this may have had a substantial effect especially on Colaton Raleigh soils. Such an effect was not observed, however, in soil column studies (Broad Meadow soils), where the effect of sludge addition on pH was seen to be insignificant when acting alone (Section 5.6). Authors such as Alloway (1990b) and Baker (1990) have stated that CEC (non-specific adsorption) is not the best measure of potential Cd and Cu adsorption, since specific adsorption plays a substantial role in their activities. Some indication of potential specific adsorption can be inferred from the measured concentration of Fe and Mn, since their hydrous oxides are important constituents of specific adsorption (Alloway, 1990a). Fe (but not Mn) concentration has been shown above to correlate well with the distribution of Cd, Ni and Zn and is one of the most important of the soil factors in defining overall metal movement. Specific adsorption may therefore explain the increase in mobility at Honey Park, as Fe concentrations are low there.

However, it must be remembered that the extent and pattern of distribution of each metal is remarkably similar, regardless of soil type and that including 'soil type' as a variable did not improve the fit of the regression equations above. It is therefore unlikely that any missing soil factor is implicated, although the effect of injection on soil physics may be important (Sections 1.4 and 8.5.3). It is also possible that the same result (i.e. distribution patterns and extent) is created by different means. For example, Colaton Raleigh has a significantly lower CEC than either of the Seale-Hayne soils where, in addition, organic matter will have a greater influence on CEC because of the higher pH (Sterritt and Lester, 1980), and metals would therefore be expected to be more mobile at the former site, *ceteris paribus*. However, when CEC is considered in terms of the amount of metals present (background and amended) and using Equation 5.1, it is apparent that there are twice as many metals as could be held in cation exchange sites at Honey Park, whereas most metals at Broad Meadow and Colaton Raleigh could be adsorbed (these statements are only made to indicate the relative capacity of the soils - obviously no firm statement can be made without knowing the concentration of competing cations and the identity and relative affinities of each of the exchange complexes for each ion. Also, the effect of the sludge mass itself in sorbing metals is ignored). Thus, Bruemmer *et al.* (1988) state that an increase in metal concentration may saturate bonding sites and cause a decrease in relative adsorption. On the other hand, the significantly lower pH of the soil at Colaton Raleigh is lower than the mobility threshold of all metals except Pb and may offset the effect of the CEC as H ions displace metal cations.

Alternatively, soil factors may indeed have little effect. Russell (1973) stated that pH has no precise agricultural significance, largely because of the greater changes that agricultural practices induce (Sterritt and Lester, 1980) and Sposito *et al.* (1982) also found that soil parameters had little effect. Korte *et al.* (1976) state that soil properties had no effect on the behaviour of Pb or Cu (added as chlorides) and Webber and Corneau (1975) suggest that the extractability of Cd ($CaCl_2$ and DTPA) is independent of soil properties. Campbell and Beckett (1988) suggest that metals may be present in an anionic or neutral form that would not necessarily be affected by the soil properties measured in this project. Korcak and Fanning (1985) consider that the chemistry of the sludge may override soil properties in defining the chemistry of metals. Instead, there may be a constant factor overriding soil type, such as injector tine or the volume of sludge (and associated metals) added.

8.3 DISTURBANCE CONTROLS: SOIL TYPE AND TINE DESIGN

In previous Chapters, it has been suggested that the pattern of metal distribution is primarily related to tine design, and that soil type plays a secondary role, via its effect on metal chemistry (discussed in Section 8.2), and its effect on the loosening capabilities of the injector tine. Before metal distribution can be described as largely soil type-independent, therefore, the effect of soil parameters on disturbance relative to the effect of tine design will be discussed.

A. TINE DESIGN

In Chapter 6, the effect of tine design on soil loosening was described and the relative capabilities of each, adjusted for factors such as time, sludge characteristics and soil factors, were summarised as:

winged tine > straight tine > paraplow

It is obvious that the amount, pattern and extent of disturbance is primarily dictated by tine design, and regression analysis shows a significant ($p < 0.05$) causal relationship between design (quantified by assigning numbers to each) and disturbance. However, the same analysis states that only 7.5 % of the variability of this disturbance can be accounted for in this way, in the equation:

$$\text{disturbance} = 55.2 - 6.35 \text{ tine design}$$

In Section 6.2.2, it was shown that rate of injection positively affected subsequent disturbance, but that this was only significant for the straight tine, where the same pressurised flow was acting on a smaller area. By elimination, the variability of tine performance must therefore be predominantly dictated by soil factors.

B. SOIL TYPE

In Chapter 6, it was shown how each tine created more loosening at Colaton Raleigh than Honey Park, and that the variability of the injection operation was also greater at the former site. In Section 6.2.2, it was shown from the literature that this would be a result of the disparate clay content of the different soils. The following regression equations were obtained relating soil factors to the amount of disturbance created by the straight tine and paraplow (the winged tine is not included in this discussion as it was only used on one soil type):

1) The Straight Tine

$$158 + 25.9 \text{ pH} - 1.38 \text{ CEC} - 3.71 \text{ \%C} - 7.94 \text{ OC} - 0.18 \text{ Mn} - 0.04 \text{ Fe} + 0.94 \text{ WC}$$

$$r^2 = 95.1\%$$

2) The Side-Inclined Tine (paraplow)

$$228 + 22.2 \text{ pH} + 3.32 \text{ CEC} + 1.35 \text{ \%C} + 5.13 \text{ OC} + 0.25 \text{ Mn} + 0.06 \text{ Fe} - 4.45 \text{ WC}$$

$$r^2 = 56.9\%$$

These relationships are not significant, but more important than the equations themselves is the difference between them, the difference in fit, and which of the factors is shown to be the more important. The observation that the loosening performance variability of the straight tine can be almost entirely predicted by soil factors, whereas other factors are almost equally important in controlling the irregularity of the paraplow, is particularly interesting and begins to explain the greater variability of the latter. It was suggested in Section 6.2.2 that the performance of the paraplow was more erratic because of the additional variable of leg angle creating complications of depth, draft requirements and, most importantly, soil failure mechanisms. Since these are the only major differences between the two tines, and the variability of the straight tine is largely attributed to soil type, rather than other potentially influential factors (that in this case remained almost constant) - such as operator, sludge characteristics (degree of treatment, viscosity), momentum, method of sludge delivery (i.e., under pressure or by gravity) and so on - this explanation is confirmed by statistical analysis. This being the case, it can be inferred that a similar explanation would be relevant to the even greater variability of the winged tine, with its similarly more complex design (than the straight tine), although it is anticipated that the 'potentially influential factors' mentioned above would also come into play.

Of those factors considered in the above regression equation, stepwise regression predictably highlights percentage clay, water content and Fe content as being the most influential over straight tine variability, but only water content is an outstanding factor for the paraplow, probably because of the different and more disruptive manner in which the soil is disturbed.

The differential effect of soil type on loosening variability can also be related to the relative positions of the soil factor inflection points mentioned in Sections 6.1-6.5 and the different depths at which injectors are deployed. At Honey Park, inflection points are at 120-180 mm, after which the variability of each soil factor remains constant or decreases. At Colaton Raleigh, there are no marked inflection points, but variability increases with depth, especially after 180-240 mm. Thus, soil variability would have a greater effect on deeper injections (the straight tine) at Colaton Raleigh. Those factors that change at 240 mm, and therefore may be expected to have a different (greater) effect on straight tine (300 mm depth) and paraplow (250 mm depth) injections are percentage clay and percentage Fe contents. Similarly, these inflection points have some bearing on the anomalously high degree of disturbance created by the straight tine, in that the decrease in clay content with depth, although non-significant (Section 5.4), may favour an increase in disturbance with depth and therefore an apparently greater loosening potential. This is exacerbated by the difficulty in statistically distinguishing much of the loosening action of the paraplow (Section 6.2.2).

8.4 THE EFFECT OF INJECTION ON THE DISTRIBUTION OF METALS

The effect of injection on the subsequent distribution of metals can be seen as two-fold: firstly, the type of tine that is used has already been seen (Chapter 6) to create distinct void patterns which the sewage sludge is expected to fill. Secondly, the effect of the location of the sewage mass, its metal loading and the rate at which it is injected may be important. These two factors are not, of course, mutually exclusive. To review Chapter 6, these void patterns take the form of a vertically elongated oval when the straight tine is employed, a 'V' configuration with the paraplow, and an inverted 'T' configuration after the winged tine has been used. There is relatively little variation in these patterns, and that which does exist can not be attributed to soil type. The relative efficiency of the tines in terms of the area disturbed can be ranked as:

winged > straight tine > paraplow

-although specific values within this ranking depend upon soil type. Similarly, depth of injection depends both on tine configuration (where the straight tine injected deepest and the winged tine the shallowest) and soil type. The relationship between soil type and injection depth is theoretically random as the operator has control over the latter factor.

The unique characteristics of each tine have distinct effects on metal distribution. These effects are difficult to quantify statistically (Section 8.1), but a comparison of Figures 6.2, 6.3 and 6.4 with Figures 7.6, 7.6 and 7.7 shows that the pattern of metal distribution, regardless of which metal is discussed or of soil type, directly reflects the soil disturbance created by the passage of the tine, and can be ranked in the same order. The conclusion that injector design and efficiency directly controls metal distribution is unavoidable. The rank of metal movement (in a comparison of tines) also follows that of injection depth (in an inverse relationship) because of the connection between tine design and depth of injection. However, there appears to be no causal relationship between depth of injection and the movement of 'total' metals, as variation within the same treatment does not produce a proportional change in metal distribution, and vice versa. The possibility of extremes of depth affecting metal movement can not, however, be rejected - were the critical depth to be exceeded, for example, the restrictive effect that this would have on soil disturbance can reasonably be expected to similarly inhibit the movement of metals, especially if the smearing effect mentioned above was active.

Tine design, via its disturbance patterns, clearly determines metal configuration, but statistical analysis shows that not only is tine design and loosening extent not related to metal distribution, but neither can one predict the other to a significant extent, nor can tine design be used to accurately predict the variability of metal movement. This can be partially attributed to the unavoidable sampling for metals and disturbance at slightly different locations (Section 4.2.1) within an injection run that has been shown to be highly variable (Section 6.5).

Of all the soil and injection factors that have been quantified in this experiment, only two - the easiest to measure - have a significant ($p < 0.01$) relationship with extent of distribution and have any appreciable ability to account for the variability of distribution observed. These have been postulated in Chapter 7 and are metal type and metal loading of the sewage sludge. Both these points will be further discussed in Section 8.5.

Injection at a higher rate has been shown to affect the disturbed area, but it was shown in Sections 7.4, 7.6 and 7.8 that this would not necessarily increase the distribution of metals, despite the significant and positive causal relationship between metal loading (which inherently contains some indication of rate when the same sewage sludge is used) and metal distribution:

$$\text{distribution} = 36.6 + 0.553 \text{ loading}$$

The 'goodness of fit' of this equation is affected by the differential response of the metals, and also of different treatments. Thus it was seen in Section 7.8 that the distribution of Zn, Pb (paraplow) and Cu (paraplow) was little affected by rate of injection, but that the amount of Ni and Cd that moved out of the profile was increased by increasing the rate of injection (and, by association, the metal loading), an effect that is exacerbated by using the straight tine (since the distribution of organic matter is subsequently far more discrete than that after a paraplow or winged tine injection, and therefore the effect of increasing the rate of injection has a greater effect on the metal loading of that small area). Obviously, the metals behave differently because of their differing chemistry, but this is likely to be in response to sewage sludge rather than soil factors, since it has been shown in Section 8.2 that soil properties have little (statistical) effect on the distribution of any metal except Zn.

The observation that increasing the rate of injection will not necessarily create greater metal distribution is corroborated to some extent by the work of other authors. For example, Hooda and Alloway (1993, 1994) found that Cd and Pb plant uptake was reduced and soil retention enhanced by the elevated pH and organic matter concentration caused by sludge addition. Similarly, Bell *et al.* (1991) state that 'sludge Fe addition to the soil may be substantial and more reactive than soil Fe' and that there is a tendency for hydrous Fe oxides to be formed.

It has also been stated that metal movement may be inhibited by soil pore blockage with sludge organic matter (Section 6.3 and 7.4.1). However, this hypothesis is confounded by the work of Yeoman *et al.* (1989) and Lea *et al.* (1982). The former authors state that the majority of metals present in sewage sludge are associated with the 2.5-20.0 μm sludge fraction, and the latter authors suggest that the soil filters particles greater than 250 μm. Whilst the soils' ability to filter a given particle size must depend on factors such as its own particle size distribution and bulk density, the disparity between these two sets of figures is so great that it must be assumed that the soil is not capable of substantially physically blocking the movement of metals still associated with the sludge fraction.

8.5 MOVEMENT VS DISTRIBUTION - POTENTIAL MECHANISMS

In Section 8.4, it was stated that final metal distribution (i.e. after 6 months) was primarily related to metal type and the metal loading of the sludge. This tends to infer which potential mechanisms are likely to be significant, and therefore demonstrate whether this final distribution is obtained during injection or subsequent to it. Redistribution of metals (i.e. after injection) will largely occur through mass flow (convective flow) or through diffusion (Sommers *et al.*, 1987), although, especially at Colaton Raleigh, the role of soil fauna (especially moles) can not be overlooked. As long as metals can be supplied to the soil solution, there is potential for continuing redistribution. If the distribution characteristics of these metals and their variation with treatment do not follow that which would be expected from such mechanisms, it is likely that the final distribution of metals was instantaneous - i.e. occurred during injection - in which case, further movement has not occurred.

8.5.1 MASS FLOW

The mass flow of water through soils is related to the hydraulic conductivity of the soil, the water potential (the sum of matric, gravity and osmotic potentials), precipitation, surface run-off, evapo-transpiration, and the soil's storage capacity. This will also be affected by dispersion (largely defined by pore space and fluid velocity). The movement of solutes within this flux will be determined by adsorption-desorption reactions, but metals may also move in suspension - for example, in association with clay particles (Sterritt and Lester, 1980) or sludge organic matter. Metal movement in this manner may be instantaneous (i.e. carried with the liquid fraction of the sludge) or ongoing - flushed through the soil with rainfall or rising towards the surface, for example, as a result of capillary movement induced by evapo-transpiration. In support of this hypothesis, metal movement was enhanced at Broad Meadow where rainfall was higher - and evapo-transpiration lower - than during the Honey Park and Colaton Raleigh experiments. Accordingly, apparent metal movement was greater, to the extent that a larger proportion of both Cu and Zn was absent from the sampled slice (Section 7.6) than in previous treatments. Gerritse *et al.* (1982) found that mobility of metals was increased by complexation with dissolved organic compounds and related this to rainfall, soil moisture, soil density and sludge loading. Scotter *et al.* (1991) successfully predicted the leaching of an inorganic solute to mole drains using 2 models, one of which was based on precipitation and evaporation, experiencing very little loss of solute unless the water table was perched. However, in Section 7.6 it was shown that the increase in movement with rainfall was more likely to be the result of a different tine design than of either increased precipitation or decreased sludge viscosity, and in Section 7.7 it was shown that reducing the flow of water through the soil (i.e. by water-logging the soil in a closed system) did not necessarily reduce the extent of metal distribution. The movement of metals away from the centre of loosening rather than towards it, as above, also tends to suggest that metal movement within the sampled slice is not related to percolating rainwater.

Despite these considerations, it is possible that mass flow has a role to play in the removal of Cd and Ni from the sampled profile - since their association with water-soluble organic ligands is thought to reduce their adsorption onto clays (Dowdy *et al.*, 1991) - or (since soil columns used a heavier soil and are therefore relevant only to it) of metals from the more sandy soil of Colaton Raleigh, with its potentially greater pore sizes and weaker electrostatic forces. Under unsaturated conditions, such as those experienced during the field season, mass flow of the liquid fraction of the sludge may pass dissolved or suspended metals out of the treated zone, and would then tend upwards, possibly aided by the mechanics of slot closure (Section 6.2.2), after the initial addition of liquid (i.e. injection) had passed. Since mass flow processes do not require a concentration gradient (Wild, 1981), a lower rate or metal loading of injected sludge would not necessarily reduce the extent of metal distribution.

However, mass flow has been observed in injected soils at Seale-Hayne (Parkinson *et al.*, 1994) and the dispersion of this flow would explain the flask-shaped secondary metal distribution observed for straight tine, Colaton Raleigh treatments (Section 7.4.1). Upward movement would not necessarily be observed after paraplow treatments because of the more diffuse location of sludge (thus, whilst this movement may occur, its wider lateral distribution may be statistically indistinguishable from antecedent concentrations) and the less extreme loosening that in addition creates a less direct path to the surface (i.e. since unpressurised water is highly unlikely to travel from low to high density soil, direct ascent of metals is precluded). In Section 7.4.1, it was seen that straight tine treatments conformed to a bell configuration at Honey Park. This corresponded with cracking patterns observed in Section 6.2.2, and it is assumed that the two are linked. In this case, mass flow would be downwards and lateral, following the path of least resistance and exacerbated by a compacted layer at 300 - 400 mm (Section 6.2.2). Once removed from the vertical zone of maximum loosening, significant upward movement would again meet substantial resistance.

8.5.2 DIFFUSION

In addition to the movement of Cd and Ni within the sampled soil with percolating rainwater, slower water-based movement via diffusion is highly plausible. Since a concentration gradient is involved, bulk diffusion is likely, the expression of which is based on Fick's First Law of Diffusion (Wild, 1981). In this case, solute flux varies with the diffusion coefficient, water content, tortuosity of the pathway and the distances involved, but ignores adsorption-desorption reactions which may alter the concentration gradient. To account for such reactions, a modified model was presented by Nye and Tinker (1977):

$$D_e = D_l \theta f (\delta C1 / \delta C)$$

where: D_e = diffusion coefficient for metals in soil
D_l = diffusion coefficient in pure water
θ = volumetric water content
f = tortuosity impedance factor
$C1$ = concentration of the ion in solution
C = concentration of diffusible or labile ion in soil, with $\delta C1 / \delta C$ accounting for buffering capacity

Thus, the rate of diffusion increases with water content and metal concentration and decreases with tortuosity, and considerable diffusion may be expected in lightly cultivated or cracked soils where macropore drainage is substantial (Burns, 1978). Since all the factors of the above equation were not measured for the soils under investigation here, it is not possible to numerically fit this to the present situation, but the difference in behaviour attributed to various treatments can be inferred.

It is already known that loosening and injection increases the water content and the water storage capacity of the treated soil initially (Parkinson *et al.*, 1994; Twomlow, 1989), but may affect only that soil immediately beneath the treated area ultimately (Stone and Kirkham, 1983; S. Jury, pers. comm., 1992), and that injection increases the mean pore size of the soil at least locally (Section 6.4), thus reducing tortuosity. The addition of metal-laden sludge into a small area (Section 6.3) inevitably generates a considerable concentration gradient, especially for Cu, Pb and Zn at Honey Park and Colaton Raleigh and for Cu at Broad Meadow. From the equation above, injection would therefore be expected to favour diffusion of metals away from the sludge mass. To relate this to specific soil and tine characteristics, heavy metal concentrations were greatest at Honey Park, although the enrichment at both Honey Park and Colaton Raleigh is comparable on a range and mass balance basis (Section 7.4, Figure 7.9), and the immediate concentration gradient will be equivalent at both sites. Figure 7.2 indicates that the concentration gradient after 6 months is less steep at Honey Park than Colaton Raleigh, and this is echoed in Section 7.4 where paraplow-injected soils are seen to have a wider distribution of metals at the former site. If diffusion is responsible for the distribution of the metals, this decrease in gradient may be indicative of desorption reactions (Wild, 1981), which tends to favour the saturation of exchange sites, mentioned in Section 8.2.

From the equation above and the controls over mass flow identified in Section 8.5.1, it is apparent that the injection of sewage sludge and its concomitant loosening effects (i.e. increased water storage capability, increased water content, decreased tortuosity) and introduced concentration gradients will favour the increase of both diffusion and mass flow processes, in a manner largely independent of the soil parameters defined in this research.

8.5.3 SOIL PHYSICS VS SOIL CHEMISTRY

Figure 7.9 shows that, within each treatment the mass balances of Cd and Ni are similar, as are those of Cu, Pb and Zn. This also tends to hold, with occasional outlying exceptions, between treatments (including soil type). These differences represent a considerable loss of Ni and Cd that may be accounted for by movement out of the profile. Percolating rainfall is the most likely agent for transporting metals out of the sampled profile, if a greater solubility of Cd and Ni can be demonstrated. Bojakowska and Kochany (1985) cited the 'removal coefficients' (amount removed ÷ total amount) of metals from sludge-treated lysimeters as:

Cd > Ni > Zn > Cu > Pb

- a rank almost identical to that found in this research. The high mobility of Cd and Ni was attributed by the above authors to water solubility. Williams *et al.* (1980) state that Cd remains active in solution as it is not easily chelated. Similarly, many authors state that Cd is less preferentially adsorbed than the other metals under investigation (e.g. Bloomfield and Sanders, 1977 - Cu, Pb and Zn; Schmitt and Sticher, 1986b - Pb). McGrath and Cegarra (1992) concluded that Cd was more than 4 times more available ($CaCl_2$-extractable) than Ni, Pb or Zn. The case for a highly soluble form of Ni is more controversial, if not directly contradictory, but the observations here of a highly mobile form (Section 7.6) tend to support those of Korte *et al.* (1976) who found that (inorganic) Ni moved rapidly through all soils but heavy clays, and of Kabata-Pendias and Pendias (1984) and Newland *et al.* (1976) that Ni in sewage sludge is in a mainly soluble form. Welch and Lund (1987) found that most added Ni remains in the sludge layer, but went on to say that moisture content accounts for 62% of the variability of leached Ni, and that the solubility of Ni is controlled by inorganic rather than organic reactions (see Korte *et al.* above). Williams *et al.* (1980) state that most Ni is strongly bound in organo-metal complexes, but do not state whether these are soluble or insoluble. From the evidence of Section 7.6 and from that found in the literature, it thus appears feasible that a proportion of Ni and Cd added to the soils' subsurface can be leached to a depth exceeding 420 mm. However, Figure 7.11 shows that this process is not necessarily initiated by rainwater - for example, Cd leaching from columns was only discernible in the leachate from the initial sludge application, despite the subsequent addition of considerable quantities of water. There was no significant rainfall in the week immediately following the spring field injections, and Section 7.6 illustrated that the percolation of substantial volumes of water did not encourage the leaching of most metals. In similar field experiments, deep drainage of water was observed only within the first 6 days after injection (Parkinson *et al.*, 1994). Together, these results suggest that the downward translocation of Cd is independent of rainfall. Accordingly, a similar amount of Cd is lost for each injector tine (same amount of soluble Cd added), although the proportion of Cd lost is greater at a higher rate of injection and at Honey Park. On the other hand, Ni leaching reaches a peak after the initial throughflow of sludge liquor, and continues to be apparent for nearly a month afterwards. If this is water-borne (which is inevitable since Ni is the only metal displaying these characteristics and therefore rotovation by whatever means is unlikely), rainfall must be responsible. As with Cd, but with no other metal, a greater proportion of Ni is unaccounted for after a high rate of injection. The distribution of Cd and Ni out of the sampled profile can therefore be considered as true movement, and therefore the location of the concentration maxima can not be considered indicative of the presence of sewage sludge.

Section 7.4.2.2 ranked the mobility of the remaining metals as:

Zn > Pb and Cu

From the literature (Table 2.3) it has already been seen that metals in sewage sludge tend to be in organic or carbonate forms, with Cu most likely to also exist as a sulphide and Ni and Cd most likely to be exchangeable. Whether organic forms are soluble (such as fulvates) or insoluble (e.g. humins) is rarely stated. Sanders and Adams (1987) found that the equilibrium between solid and solution forms of metals was determined by adsorption-desorption reactions rather than precipitation-dissolution reactions, therefore any metals held in forms such as sulphides, carbonates and hydroxides can be considered permanently unavailable on the timescale used here, although this does not preclude metals in insoluble organic forms especially being redistributed in suspension. Karapanagiotis *et al.* (1990) considered that Cu binding occurred to a greater degree than the nominal complexation capacity of sludges (indicating the formation of new complexes). Keefer and Singh (1986) found that metals moved as metal-organic complexes, and that Cu was most likely to be strongly associated with insoluble complexes. Knezek and Ellis (1980) state that Cu forms strong covalent bonds with organic matter, and Sanders and Adams (1987) stated that Cu was strongly adsorbed to soil surfaces and that the strength of this bond was greater than those found in sewage sludge. In addition, Cu readily precipitates with anions such as sulphides (Kabata-Pendias and Pendias, 1984), which may be common in sewage sludge. Thus Cu added as sewage sludge may remain immobile even if the sludge mass itself moves. In contrast, McGrath and Cegarra (1992) identified a greater proportion of Cu in organic forms than other metals studied (> 30 % compared to < 10 % of Zn, Ni and Pb). This confirms the work of authors such as Williams *et al.* (1980) and Keefer and Singh (1986), who explain the low mobility of Cu in this way. The consensus seems to be that Cu is strongly bound by organic matter, but even if this is the case, mobility is debatable - for example, Mullins *et al.* (1982) found that organic Cu was relatively mobile, probably because of downward movement in chelates. The behaviour of Pb is similarly debated - most authors advocate strong adsorption onto organic matter (e.g. Miller *et al.*, 1983 observed higher stability constants than for Zn / Cd and organic matter), whilst Cao *et al.* (1984) argue that Pb in sludged soil occurs and stays in a mineral form. Similarly, McGrath and Cegarra (1992) observed no association with organic matter and found availability after sludge treatment to be extremely low. Considering exchange sites as a whole, Schmitt and Sticher (1986b) agreed that Pb out-competes Cd for exchange sites, but is itself out-competed by Cu. In contrast, the case for Zn is relatively straightforward, with most authors agreeing that Zn in a sludge-amended soil is in a relatively soluble form (Williams *et al.*, 1980; Webber and Corneau, 1975), complexed by soluble organic matter at pH greater than 6.0 - 6.5, and as free ions in more acidic environments (Sanders and Adams, 1987; McBride and Blasiak, 1979). Zinc (similarly, Pb) is also strongly adsorbed onto organic matter, but the stability constant is much lower than for Cu (Kabata-Pendias and Pendias, 1984), and it tends to be precipitated with carbonates (Lo and Chen, 1990) rather than sulphides. After fractionating sewage sludge, Holtzclaw *et al.* (1978) concluded that Zn (along with Cd and Ni) would be more mobile than Cu.

The above literature substantiates the general rank of mobility described in Section 7.4.2, but refers more to the solubility of the metals than to their movement. It has already been stated (Section 7.5) that the percentage availability of Cu, Pb and Zn is extremely low, although higher at Colaton Raleigh and following paraplow injections. Therefore their mobility, if dictated entirely by solubility, whilst being almost undetectable would be higher under these conditions. Similarly, the rank of metal movement at Broad Meadow of Cu > Zn demonstrates that the rank according to metal chemistry may fit the actual rank at Colaton Raleigh and Honey Park only coincidentally - that is, because it also reflects the concentration of the sewage sludge. In addition, the comparable distribution of metals (other than Ni and Zn) at Honey Park and Colaton Raleigh contradicts predictions that would be made from metal chemistry. However, Levy and Francis (1976) found that the adsorption capacity of clay-humic acid complexes is considerably less than the sum of the two components separately, thus any component that is associated with organic complexes may be more mobile than would be expected in a clay soil rather than a sandy one. In addition, if a sampling regime favoured the collection of sewage sludge in an amended soil, as was suggested in Section 7.6, then it is likely that this bias would be exacerbated on a sandy soil, where non-cohesive particles are less likely to be intimately associated with added organic matter. Thus movement, as defined by mass balance, would seem more limited in such a soil.

Confusing the issue is the difference in the rank of metal movement when 2-dimensional patterns are considered than when movement downwards is being investigated. Thus, the size of the pattern of movement appears to be dictated by the amount of metal in the sewage sludge (Section 7.4.2), whereas the extent of vertical movement out of the sampled profile is related more to the individual metal - Cd, Ni and Zn are all likely to be mobilised, in the order: Cd and Ni > Zn. These metals are all relatively easy to extract from sewage sludge (Lo and Chen, 1990), and mass balance experiments (Section 7.6) showed that substantial quantities of Ni especially, but also Zn (Cd being present in quantities too small to measure) was released through the column.

From the above discussion, it can therefore be assumed that the movement of heavy metals is based on physical rather than chemical parameters, with soil and metal chemistry only contributing to part of the equation. Thus, Ni and Cd move out of the sampled profile by mass flow and soil type determines how well that can proceed. On the other hand, Pb and Cu are bound strongly with organic matter and tend to be equally immobile, although where particularly large concentrations of sewage sludge are present (high rate, straight tine), Pb may be relatively immobilised. Similar observations were made by Williams *et al.* (1984). Where particularly high concentration gradients exist (Zn at Honey Park and Colaton

Raleigh; Cu at Broad Meadow), the saturation of exchange sites and the effect on diffusion processes promotes a greater degree of movement than would otherwise be anticipated, and soil type assumes a more dominant role (Section 8.2). Factors such as reduced sludge viscosity and increased soil loosening exacerbate metal movement, as observed at Broad Meadow.

8.6 SAMPLING IMPLICATIONS

The above discussion has dealt with the controls over the maximum extent of metal movement, but it has been stated that there is little movement of substantial amounts of most metals away from the injection zone (Section 7.6), and therefore the enhancement of metal concentration within that zone, and the location of such concentration maxima, becomes vital to the efficiency of subsequent sampling regimes. The effect of measured factors on the enhancement of metal concentrations and the position of concentration maxima within the affected zone is ignored by regression equations such as those used above. Sections 6.5 and 7.2 have dealt with the the position of these maxima and the depth at which injection was conducted. Supplemented by Section 6.3 (organic matter location) and visual observation in the field, the following conclusions can be drawn with reference to the effect of soil type and the relative behaviour of the metals.

To recap, sewage sludge was injected at an average depth of 300 mm (straight-legged tine), 280 mm (side-inclined tine) and 250 mm (winged, straight-legged tine). At Colaton Raleigh, the bulk of the sewage sludge remained at the depth of injection, with some upward movement (to a depth of approximately 220 mm - just outside the limits of injection depth variability) following side-inclined tine treatments. In contrast, the sludge mass at Honey Park was most concentrated at 180 - 240 mm for both types of tine. This can be assigned to movement as these values exceed the variability of the injection process. Rate of injection has no effect on this behaviour at either site and for either tine.

It can be surmised that soil type affects the movement of sewage sludge via its effect on injection characteristics, and that this movement is likely to occur during the injection process itself. The greater untreated soil strength and finer soil texture of Honey Park confirms this explanation, in that the greater confining effect of the soil would tend to promote movement upwards, along the path of least resistance. Thus metal concentrations would be more shallow at Honey Park than Colaton Raleigh, despite a greater depth of injection at the former. There is no mechanism relevant to these conditions that could be responsible for the movement of the sludge *en masse* after injection - alternatives such as different mechanisms by which different tine slots seal on different soil types can be rejected because some, if not all, the sewage mass would remain *in situ* unless the process was instantaneous. In addition, it has been shown in Section 6.2 that slot closure, at least at Broad Meadow, tends to take the form of a loss of peripheral weakness and an increase in soil strength in the central zone, although the size of that zone remains relatively unaffected.

The location of Cu, Pb and Zn concentration maxima (Figure 7.2, 7.6 and 7.7) accurately reflect the differing depth of the sludge mass for all treatments, and the tendency for deviation from this is replicate- rather than site- or metal-dependent. Thus, the stipulation by the DoE in their 1989 Code of Practice that 'sampling should be carried out to the depth of injection' initially appears sufficient, in depth terms, to locate most of the metals injected into the soil using a simple or side-inclined tine only, providing that sludge viscosity and metal content, rainfall and soil texture characteristics are not likely to promote the rapid translocation of not only dissolved metals but also of the sludge mass itself. Even within these limits, sampling according to the DoE Code of Practice (1989) for statutory and especially monitoring purposes is likely to underestimate the soil metal content following injection rather than surface spreading due to the diluting effect of unaffected soil. For example, data provided by the WRc (J. Hall, pers. comm., 1990) suggests that sampling a (surface) sludge-amended soil to 250 mm yields significantly lower results for the less mobile and more concentrated elements (Cu, Pb, Zn) than sampling to 75 mm. Thus, samples taken to the stipulated 25 cm (or 75 mm for the purpose of monitoring grassland) can be expected to contain all the added metal plus, according to the literature (Section 2.3), up to 100 mm depth of unaffected soil. In contrast, an injection carried out at, say, Colaton Raleigh with a straight tine would require sampling to a depth of 300 mm. Assuming that, as an example, Cu is being monitored and Figures 7.3, 7.6 and 7.7 represent its subsurface distribution, it can be seen that whilst concentration undoubtedly peaks at 300 mm, soil in the adjacent sampling block - i.e. to a depth of 360 mm - inevitably contains significant quantities of Cu. Perhaps more importantly, soil to a depth of approximately 180 mm contains Cu concentrations that are not appreciably greater than the background concentration and therefore represents a considerable dilution. The greater proportion of Cu, Pb and Zn is located within 120 mm of the centre of the sludge mass (Section 7.6) and therefore sampling within 120 mm of the depth of injection (i.e. to the depth of injection plus and minus 120 mm - in this case from 180 - 420 mm) provides a sample of comparative size to that required after surface spreading and reduces the dilution effect. This is by no means a perfect solution, since the location of sewage sludge at Honey Park above the depth of injection may reverse the above case to some extent and since both Ni and the more toxic Cd will still be underestimated, but constitutes the most practical compromise.

At Broad Meadow, where injection was carried out using a winged, straight tine at a depth of 250 mm, the focus of Zn concentration is found at 250 - 300 mm and Cu at 200 - 250 mm. The less viscous sewage sludge injected here was observed to remain at the depth of injection, within the leg slot, or move downwards. This behaviour can be attributed to, for example, the consistency of the sludge or the greater loosening effect created by the winged tine along with the physical blocking effect to upward movement afforded by the larger surface area of the base of the tine during injection (see Figure 4.1) - that is, due to the lack of substantial chemical differences between Broad Meadow and Honey Park, the differing direction of movement of the sludge mass between the two sites can not be assigned to soil types. Unfortunately, it can not be unequivocally attributed to injector design, either. Large concentrations of both Cu and Zn again appear to remain with the sewage sludge, and this more mobile sludge introduces the possibility of different metals being associated with different fractions of sludge. Thus, whilst Cu distribution patterns are greater due to the greater concentration of that metal in the sludge, the bulk of Cu is apparently associated with the less mobile fraction which remains in the leg slot or the voids created by the passage of the wings, whilst Zn is more likely to be found in the wing slots or with that sludge that has moved downwards (Figure 7.8). Thus the existing sampling regime would be inefficient. In a sub-experiment, soil samples were taken in an ADAS 'W' both from injected and control plots in Broad Meadow and were analysed with the samples taken from more detailed pits. Results for both types of sample were comparable, with no extra Zn detected and only slightly less Cu detected using auger rather than pit collection methods. Since an auger sample is far easier to collect than one from a pit face, it seems that the former method is preferable. However, it must be remembered that much of the added metal was missing from both types of sample, and this parity between methods may not be found in a situation where the difference between amended and background concentrations was more distinct.

The definition of an effective sampling regime, both for injected and surface treated soils is further complicated by the lack of stipulation regarding the method of sampling to be employed. For example, Powlesland and Ellis (1986) found that metal concentrations determined with cheese auger samples were consistently higher (by 64 %) compared to those taken with a tube auger. The difference was accounted for by the loss of 'a substantial portion of the lower part of the sample' - that is, that portion that is likely to contain the greatest concentrations of heavy metals in injected soils. More recent data from WRc trials (J. Hall, pers. comm., 1990) comparing various manual and automatic corers and augers suggests that there is no significant difference between sampling devices, and this is confirmed by Berrow (1988).

The suitability of the ADAS 'W' as a sampling guide has been questioned in some instances by the WRc (Powlesland and Ellis, 1986), since it is particularly susceptible to bias and often involves re-sampling following the same pattern as had been previously used.The same authors found that a random sampling regime is more accurate but less precise than an ADAS 'W', but that increasing the number of random sub-samples taken to 50 would bring precision in line with that of systematic sampling.

In the case of injection, this project has shown that field variability caused by both soil and injection factors can be substantial and systematic, and infers the following recommendations: 1. Sampling should be orientated perpendicular to the injection runs, and should have an equal number of sampling points at each extreme. 2. The number of sampling points should depend upon the device used, aiming for at least three replicates of each point between the leg slots (ignoring overlap, for the sake of practicality):

$$\frac{\text{tine spacing}}{\text{width of sampling instrument}} \times 3$$

Because the distance between the location of maximum metal concentration is fixed when sludge is injected, then the distance between sampling points should also be fixed, in a manner that varies the sampling position relative to the sludge position. For example, multiples of:

$$\frac{\text{tine spacing}}{\text{width of sampling instrument}} + \text{width of sampling device}$$

should ensure representative results.

Ideally then, samples should be taken with a suitable and specified instrument and according to a suitable and specified protocol. Further complications are introduced by the bulking of subsamples, which is likely to mask the actual field situation. It has been shown throughout this and the preceding Chapter that metals are essentially immobile, and especially when the straight tine is used, will remain in the discrete sewage mass at considerable concentrations. It will thus be necessary to ascertain whether only the average metal intake via crop consumption is significant, or whether isolated doses of high concentrations may be damaging, a factor that will inevitably depend on the crop itself (i.e. whether the plant is consumed as an individual or bulked with others - a lettuce compared to wheat, for example).

Of all the soil factors measured, only pH is required by Directive 76/278/EEC, but it has been shown that, whilst a low pH inevitably affects metal behaviour, other soil factors may be more important at pH levels approaching 'acceptable'. It is postulated instead that other factors should be considered, including tine design, sludge viscosity, and soil physical parameters (Section 9.5), as these have all been shown to contribute more to the distribution of injected, sludge-borne metals.

TABLE 8.1 CORRELATION BETWEEN UNTREATED METAL CONCENTRATION AND SOIL FACTORS

		pH	CEC	OC	%C	Fe	Mn
HP	Cd	.265	-.479	-.332	-.999	-.479	-.506
	Cu	-.357	.169	.295	-.976	.095	.075
	Ni	.363	-.567	-.436	-.999	-.569	-.594
	Pb	-.827	.719	.808	.978	.664	.641
	Zn	-.384	.153	.286	-.596	.147	.120
CR	Cd	.301	-.0456	-.601	.212	-.739	-.473
	Cu	-.797	.905	.957	-.787	.941	.877
	Ni	.696	-.967	-.866	.672	-.838	-.741
	Pb	-.671	-.889	.917	-.483	.950	-.786
	Zn	-.794	-.927	.942	-.737	.961	.891
BM	Cu	-.882	.816	.847	.410	.874	.860
	Zn	-.820	.812	.719	.150	.796	.730

TABLE 8.2 CORRELATION BETWEEN METAL MOVEMENT AND SOIL FACTORS (ALL SITES).

	pH	CEC	OC	%C	Fe	Mn
Cd	.003	-.205	-.095	.018	.033	.364
Cu	.075	.147	.124	.040	-.077	-.209
Ni	-.315	-.295	-.291	-.390	.382	-.208
Pb	.204	.268	.271	.184	-.220	-.079
Zn	.500	.564	.563	.576	-.619	.176

where: .820 = significant at 5% level; .882 = significant at 1% level.

9. CONCLUSIONS

At the outset, the objectives of this work were established as:

1. the description of heavy metal distribution following injection with sewage sludge
2. the identification of influential factors
3. the description of associated variability
4. the assessment of current sampling regimes.

Results were presented and summarised in Chapters 5-7, and the relationship between these was discussed in Chapter 8. From these, and considering research that predates this work, several conclusions can now be drawn and placed in context.

9.1 THE DISTRIBUTION OF HEAVY METALS AND THE EFFECT OF INJECTOR VARIABLES

Several authors have described the process of injection, most notably those from the WRc and Silsoe College (Chapter 1). This work has dealt largely with injection logistics and as an ongoing concern is continuing to improve the process. There is also a plethora of information concerning the movement of sludge-borne heavy metals in soils (Chapter 2) that generally concludes that enhancement would be restricted to within 200 mm of the sludge and that metals would move out of this layer to varying degrees, dictated by metal-, soil-, and in some cases, sludge chemistry. Determining the relative movement of metals thus depends upon the experimental conditions employed by each author, but it is widely considered that Cd will be more mobile than Zn, with Cu remaining relatively immobile.

Despite the extant body of research concerning a) injection and b) metal behaviour, there is apparently very little that combines the two, and none that considers the problem on a scale smaller than the field scale. The work of the current author has demonstrated these variables will be significant in practical terms. For example, tine design was found to be the most significant determinant of the pattern of metal distribution, overriding the influence of other measured variables such as soil type and metal chemistry. Each tine thus generates distinct and individual metal configurations that are largely related to its loosening capabilities (compare Chapters 6 and 7). The disturbance/distribution created, with the relevant configurations in parenthesis, was summarised in these Chapters as:

winged (⊥) > straight (0) > paraplow (V)

These patterns are discrete, and whilst 100 % of the sampled area may contain enhanced metal concentrations in some cases (Table 7.5), the bulk of the added metals stays within 100 mm of the injection slot (Figures 7.6, 7.7 and 7.8), with the exception of Cd and Ni, which move out of the sampled profile (i.e. > 420 mm).

Accurate prediction of the precise extent of distribution relies upon the metal loading of the sludge, the individual metal being assessed, tine design, soil factors and the rate of injection, in descending order of importance. By far the most significant factors were shown in Section 8.4 to be metal loading and identity, which are fortunately also the easiest to assess since Water Companies are required to routinely analyse sludge metal concentrations to comply with EC Directive 86/278/EEC. In a simple relationship, the greater the loading of heavy metals, the wider their subsequent soil distribution, due to saturation of exchange sites and consequent diffusion and mass flow processes. As a result, those metals that are present in sufficient quantities in the sludge to establish a concentration gradient in the soil such that the extent of distribution is associated with the loading of the sludge (e.g. Zn at Honey Park and Broad Meadow) - and in addition are behaving in a manner that is not predictable from their chemistry (e.g. Cu at Broad Meadow) - can be considered truly mobile. The numerical definition of such a concentration gradient is beyond the scope of this research, but would be a useful objective in further studies.

Whilst increased loading has been shown to increase distribution of the same metal, it does not necessarily follow that this will be reflected in the ranking of mobility. For example, mass balance studies that included the analysis of percolating water (Section 7.6) indicated that both Cd and Ni are prone to leaching, Cd immediately and Ni with percolating rainwater and in concentrations exceeding that in the sludge - that is, indigenous soil metals may be mobilised. Again, this obviously represents movement rather than distribution according to sludge location immediately after injection, and Cd and Ni are considered to be the most mobile of the selected metals in the conditions measured in this study. Thus, if the concentration gradient is not adequate and sorption sites are not saturated, the spread of metals may be affected by their chemistry. Similarly, Cu in Phase I experiments is associated with the sludge mass and is therefore apparently immobile, owing its distribution entirely to injection processes. However, this latter influence of metal chemistry can apparently be over-ridden by increasing metal loading (and therefore concentration gradients and soil saturation), as demonstrated by a comparison of Cu behaviour at Honey Park (Phase I) and Broad Meadow (Phase II). Thus it can be seen that each metal behaves in a distinct but not entirely predictable manner, and that therefore no one metal could be selected to represent the rest.

9.2 THE INFLUENCE OF SOIL FACTORS

Of the soil factors that influence mobility, Section 8.2 cited free Fe oxide content, pH, and percentage clay as the most important, in that movement would be enhanced in soils where each of these factors was low. However, no one factor influenced all the metals or was significant in defining metal behaviour.

The addition of sewage sludge was seen to increase the availability ($CaCl_2$-extractable) of metals and soil factors had a distinct effect on this, with greater availability observed on lighter soils. This, however, was not quantifiable due to variabilities of up to 170 %, and apparently also had little effect on mobility.

Instead, the main role of soil type was shown to be in its effect on the performance of the tines in terms of their loosening capability, working depth and depth of final sludge placement (Section 8.3). Thus it was shown that injection variables (tine design, rate of injection, sludge characteristics), rather than those pertaining to metal/soil chemistry, have the greatest control over the behaviour of Cu, Pb and Zn in injected soils, and that some consideration of these factors should be made in the definition of 'suitable injection conditions'.

9.3 VARIABILITY

Whilst it has been possible to define the determinants of metal behaviour, and to anticipate the extent of movement from their measurement, the extreme variability encountered precludes the construction of precise models, and this in itself threatens the integrity of practical monitoring practices. In Chapter 6, it was shown that sludge delivery at best varies by approximately 20 %, and at worst can fluctuate to the extent that portions of the run may be dry. The depth of injection varies by 0 - 33 %, dependent primarily upon soil type, but also affected by tine design. Comparatively, the metal content of sewage sludge is constant, varying by 4 - 6 %. This depends entirely upon source and treatment, and therefore has a potential variability far greater than that observed in this study. The variability of metal concentration and distribution between replicates of the same soil type is huge - point-to-point concentration comparisons (Section 7.2) yielded RSDs of 50 % (Honey Park), 75 % (Broad Meadow) and 80 % (Colaton Raleigh). Despite this, the addition of sewage sludge to a sandy soil reduces the between-replicate variability of metal concentrations where the concentration of organic matter is greatest. This is reversed at Honey Park (Section 7.2). The extent of metal distribution is generally less variable, with maximum RSDs (representing the average variability of all 5 metals) of 14 % (Honey Park), 39 % (Broad Meadow) and 62 % (Colaton Raleigh). In Chapters 7 and 8, this variability was shown to vary with soil type (Colaton Raleigh being the more disparate), tine design (with the paraplow causing greatest variability), rate of injection (with lower rates generally yielding more variable performances) and metal type, although this variability was not systematic. However, statistically expressing this causality was disappointing, with all factors together only able to account for just over half the variability observed. It is hypothesised that this is due to the inadequacy of statistical analysis in situations of this type, since each case is so individual and can not be considered suitably replicated.

9.4 PRACTICAL IMPLICATIONS

In Section 1.4, it was shown that for an injection operation to be considered successful, sufficient subsurface disturbance must be created to deposit the selected volume of sludge without seepage onto the surface. It has been shown in Chapters 6 and 7 and from field observations that this criteria can be achieved at volumes of 140 m^3 ha^{-1}, suggested by the WRc in their Code of Practice (1984). However, it has also been stated (Section 1.4) that the method must also be farmer-acceptable, in that a good distribution of sludge and its attendant essential elements should be attainable. To this end it is desirable that the 'best' option should be identified. The winged tine is currently popular, as it represents a balance between minimum power requirements and maximum disturbance. In Section 6.3, this was confirmed, as the winged tine disturbed a greater area than the other tines, and this was reflected by a greater distribution of metals (Section 7.8). This would presumably be echoed by the distribution of N, P, and K, thus negating the uneven crop response that has been cited as a constraint of injection (Section 1.4.2). However, in Sections 6.2.2 and 7.2 it was shown that both the disturbance generated by the winged tine and subsequent metal concentrations are more variable than with other tines. This inevitably exacerbates the already extant sampling problems (see below). More importantly, the greater disturbance initiated by the winged tine may encourage metal movement out of the sampled area (Section 7.6), but it is unknown how far these metals may disperse. Thus, the winged tine may be the 'best' option in terms of sludge disposal capacity, but not necessarily for farmers or the environment. On the other hand, the straight tine caused greater statistically distinguishable metal distribution than the side-inclined tine (although the majority of Cu, Ni and Zn remained associated with the sludge mass and within 120 mm of the injection slot) and furthermore was the least variable of all the tines. However, the best visually observed crop response followed paraplow injections, which also yielded a good distribution of sludge within the sampled profile (rather than out of it, as with the winged tine) and therefore did not encourage steep concentration gradients and resultant metal movement (Section 8.5.2). This must therefore be considered the best compromise between sludge disposal and agricultural and environmental requirements.

It has been shown in the preceding Section that the pattern of metal distribution can be predicted, and that certain metals (Ni and Cd) will move to a greater extent than others. Both measurements are influenced primarily by injection factors which are in turn affected by soil type. It has also been shown that there are so many variables within these apparently simple measurements that an accurate, mathematical prediction is impossible at this stage. However, from a practical, rather than academic, point of view, it is necessary only to be able to monitor metal concentration to enable compliance with EC Directive 86/278/EEC. Section 8.6 illustrated that the sampling protocol stipulated in the DoE Code of Practice (1989) was insufficient to monitor amended metal concentrations following sludge injection. Instead, it was suggested that a better approximation of metal build-up in the soil could be made by systematic sampling perpendicular to the injection run to the depth of injection plus and minus 120 mm, and with the frequency of and distance between samples dictated by the injection conditions and sampling device used. This scheme would tend to increase the spatial sampling frequency, which may seem an impractical proposition - Harkness (1986), for example, considers that it would take a sampler a day to complete 5 25-sample ADAS 'W's. However, mechanised devices designed specifically for this function are becoming increasingly available, and have been reviewed by Sneath *et al.* (1989). From mass balance experiments described in Section 7.6, it is apparent that up to 10 % of Zn, Pb and Cu may be lost, even when the entire population is considered as opposed to merely sampled. This is not an isolated incidence, having been reported by many previous authors, and therefore must be taken into consideration when soil metal concentrations are approaching maximum permissible levels.

9.5 RECOMMENDATIONS FOR FURTHER WORK

From the above Sections, it seems inevitable that appreciable quantities of Cd and Ni, both indigenous and amended, will be lost from that area encompassed by current sampling practices, and thus the impact of these elements may be seriously underestimated. In Section 1.4, it was shown that existing research indicates that deep leaching of metals is insignificant, but since it has been shown here that distribution is directly affected by metal loading of the sludge, it is necessary to establish whether this holds through a range of sludge concentrations and soil conditions. It was not originally thought that the volume of sludge addition used in this work would significantly affect soil properties, and this was apparently confirmed by low LOI results (Section 6.3). However, it since appears that sludge factors may be more important than soil chemistry. The role of hydrous Fe oxides and sludge chemistry in these circumstances therefore need delimiting, and the metal concentration thresholds above which distribution is enhanced should be defined. Furthermore, reducing the viscosity of sludge and/or increasing the disturbance created by the tines has been shown to enhance distribution even of those metals such as Cu, that are conventionally considered immobile, and it is desirable that both these factors be investigated further and recommendations amended accordingly.

The recommendations cited above relate mainly to the refining of those observations made in this study. However, in Section 8.5, it was postulated that much of the movement of Cu, Pb and Zn was dictated by soil physical rather than chemical properties, relating to the movement of the sludge mass either during or immediately after injection. This hypothesis has been partially substantiated in this work in anticipating the mechanisms of slot closure, but is important that the physics of sludge movement should be empirically established in order to present a complete picture. Such work is currently being undertaken using equivalent equipment and field sites to those used in the present study.

APPENDIX. LABORATORY METHODS

A1.1 PROCEDURAL SELECTION OF THE ACID DIGESTION OF SOILS

The length of extraction time and the soil:acid ratio used in the extraction of soils with 16 M HNO_3 varies between authors, so experiments were set up to establish the best method. The first test (soils 1 and 2, Table A1.1) compares ratios of soil:acid of 1:15 and 1:10 (1:15 being recommended) on the 2 soil types. This shows that an extraction ratio of 2 g soil:30 ml of acid gives consistently higher results than other combinations. Using 2 g of soil, ratios of 1:15 and 1:5 were then compared (Table A1.1, soil 3), 1:10 having been rejected. Improved results were achieved for the ratio of 1:5. However, the coefficient of variation of these results is considerably higher than those for the 1:15 results - for Cu 21 % and 7 % and for Zn 10 % and 3 % respectively. Finally, a ratio of 1:15 soil:acid was extracted for varying periods of time (Table A1.2). Times of over 4 hours were considered impractical in view of the number of samples to be processed. The results are erratic, but generally show an increase in Cu and Zn extracted with time, with the largest discrepancies occurring between 1 and 4 hours. These were not, however, considered sufficient to outweigh the important difference in time required, so a compromise of 2 hours was set.

A1.2 PROCEDURAL SELECTION OF THE $CaCl_2$ EXTRACTION OF SOILS

An experiment was set up to find the most suitable conditions for $CaCl_2$ extraction, with 0.1 M and 0.05 M $CaCl_2$ shaken with soils for 2 and 4 hours. The results (Table A1.3) are erratic, but either 0.1 M for 4 hours or 0.1 M for 2 hours consistently give the highest and least variable results, with 0.05 M for 2 hours always yielding the lowest. In half the cases, 0.1 M for 4 hours extracts more metal than 0.1 M for 2 hours, but this difference is not appreciable.

A1.3 ATOMIC ABSORPTION SPECTROMETRY

Atomic Absorption Spectrometry is one of the most popular methods of trace element analysis (Hamilton, 1980), accounting for up to 90 % of environmental heavy metal determinations (Willis, 1975), but problems of operation are not comprehensively dealt with in the literature, and in some cases are almost impossible to correct (Baker and Suhr, 1982). In the experience of the present author, this method of analysis is by no means straightforward when dealing with low levels (but above detection limit) of analyte in concentrated nitric acid. Problems have been identified through personal experience; literature surveys and communication with the manufacturers.

A1.3.1 INTERFERENCES (Ure, 1983, 1991; Isaac and Kerber, 1971)

Any phenomenon that affects the apparent absorption at the specific wavelength of interest will interfere with the reading obtained. Chemical interferences may enhance or (usually) suppress the formation of atoms in the flame. This can be counteracted by the addition of releasing agents such as EDTA or lanthanum/strontium chlorides. Alternatively, the heat of the flame can be increased (usually by the use of the nitrous oxide/acetylene) to break down the compounds formed. However, if sufficient energy is present, the ionisation potential of the element may be exceeded and ions will be generated instead of atoms, resulting in a decrease in absorption signal. If an air/acetylene flame is used, ionisation effects are not usually a problem with heavy metals due to their high ionisation potentials.

Matrix, or physical, interferences may occur with samples containing a high dissolved solid content or high acid concentrations which have different viscosities than the aqueous standard. As a result, different amounts reach the flame per unit of time. This is an important consideration in the analysis of both 'total' (HNO_3) and 'available' ($CaCl_2$) metals. The problem can be rectified by dilution if metal levels are high in the concentrate. Alternatively, the standard matrix and sample matrix can be matched, but this is difficult to do except generally. Standard addition is a more popular method (Hall *et al.*,1980) and can also identify interference effects (Ure, 1991). Aliquots of an increasingly strong standard are added to the sample solution, from which the sample concentration and the relationship between sample and standard plots can be evaluated. Any deviation denotes an interference effect. It is important that the plot is linear, and that the ratio of standard to sample is at least 1:4. A higher proportion of standard will dilute the matrix effects, a factor often neglected in the use of standard addition techniques (Berman and Desaulniers, 1975). This test was performed for each of the metals under investigation. A maximum error of 5 % was observed for Cd, Cu, Ni and Zn. Only Pb showed any appreciable matrix effects (a deviation of 21 %) that need to be accounted for.

Dried salt particles of Al, Ca, Mg and Na may scatter the light from the element lamp, producing artificially high readings. This is a background, or spectral, effect, but only happens at high salt concentrations and low wavelengths. With a wavelength of 324.7 nm, Cu is rarely affected. Background effects are corrected by the use of a D_2 lamp, which is incorporated into most modern AAS instruments. This measures the scattering through molecular absorption light loss and subtracts it from the original, unamended reading. The lamp has a maximum absorption at 350 nm and is therefore not suitable for elements with specific wavelengths greater than this. It was ascertained that background correction should be used for Zn, Pb and Cd in HNO_3 extracts and Zn, Ni, Pb and Cd in $CaCl_2$ extracts.

A1.3.2 SOURCES OF INACCURACY

Ubiquitous problems of AAS operation are adequately covered by instruction manuals, but those specific to this type of research are seldom included. For example, the use of concentrated HNO_3 samples frequently creates a steady downward drift in readings, and damage to the nebulizer and capillary. Dilution is not feasible because of the low levels of metals in the samples. An alternative is the use of the peak height or peak area mode. In this way, results can be achieved from a 0.2 ml sample (Thompson and Godden, 1976). However, the method is relatively time-consuming and sacrifices the advantage of the interfaced computer. Instead, by manually overriding the computers' sampling interval, and thoroughly flushing the system with water after each sample, reproducible results can be obtained from 0.7 ml of sample.

Dilution is also cited as a means to maintain absorbance readings within the linear portion of the calibration curve. However, even a relatively small dilution (1/2) was observed to produce substantial changes in results (Table A1.4), and is therefore not suitable. There are three main alternatives to dilution: the use of a less sensitive wavelength, the reduction of sensitivity by rotating the burner head at an angle to the element light path, or the use of supplementary air. To maintain sensitivity and minimise inaccuracy, the latter option was adopted, which increased the linear range of calibration curves by an order of magnitude.

Deposits, especially from $CaCl_2$, build up rapidly on the burner head and reduce the reproducibility of the results. A high solids head helps minimise this effect, but daily cleaning is also necessary. Some authors use only warm water, but this is insufficient for HNO_3 and $CaCl_2$ samples. A cleaning regime using dilute H_2SO_4, rinsed with distilled water and finally acetone, to promote rapid and thorough drying, is preferable. The high solids content of samples may also cause blockage of the capillary or nebulizer, in turn causing a reduction of sample delivery rate to the flame. For the Baird Alpha 4, this should be maintained at 0.5 ml / min. In more modern equipment, nebulizers such as the Babington or Conespray type may be used in order to offset the effects of viscosity or a high salt content (Ure, 1991).

The use of element lamps is usually straightforward, but Ni especially is prone to wavelength drift, which needs frequent correcting. Under intensive use, the Ni lamp will only give reproducible results for the first 1.5 hours. The lamp has been checked by the manufacturers, who now confirm the finding with other Ni lamps. No explanation has been found. Distinct from this, wavelength drift may also arise as the monochromator gets too hot under intensive use. The situation is quickly corrected by pumping air only.

A1.4 DIRECT CURRENT PLASMA ATOMIC EMISSION

A1.4.1 INTERFERENCES

DCP techniques are generally fairly free of interference due to the high accessible energy available in the plasma (with an apparent temperature of 6000-7000 K), but some enhancement of the reading may be induced by easily ionised elements such as Al, Ca, Fe, Li, and Mg. This influence is suppressed by the addition of 12.5 ml of 40 $g\ l^{-1}$ $LiNO_3$ per 100 ml of sample or standard (Sparkes and Ebdon, 1986b). To minimise potential matrix effects, standards are made up in $CaCl_2$ or HNO_3, where relevant.

Background effects are often more substantial with DCP than AAS (Routh, 1987), but can be similarly counteracted by the use of background correction. This was employed for all elements as the DCP was used in a multi-element mode, thus individual elements could not be isolated for special treatment.

A1.4.2 SOURCES OF INACCURACY

Direct Current Plasma operation is not, of course, trouble free, and the literature abounds with reviews and the confrontation of problems such as optimising sample introduction (Ebdon and Sparkes, 1985; Keliher *et al.*, 1986; Sparkes and Ebdon, 1986a and b; Ebdon *et al.*, 1989). However, as with AAS, little attention has been focused on day-to-day operational considerations.

Daily optimisation procedures involve computer - aided manual peaking onto the desired wavelength (usually Cu if a combination of metals is to be determined), and varying the horizontal and vertical viewing positions of the plasma, the nebulizer gas flow and sleeve gas flow. The position of the observation region is generally considered to be independent of electrode erosion (Decker, 1980) and therefore small differences are insignificant in optimisation, although problems in forming the initial plasma may be encountered as a result. The electrodes should, however, be replaced on a daily basis. In addition, ceramic sleeves and pump tubing need replacing daily, to maintain the structure of the plasma and check the suction exerted on the sample by the plasma, respectively.

It is a relatively easy matter to maintain the cleanliness of the equipment, but, for stable operation, the manufacturers also recommend a temperature of 18-27 ^{o}C controlled to ± 5 ^{o}C, a relative humidity of <55 % and the exclusion of draughts or heating elements. Without the use of a controlled unit, this is extremely difficult to maintain. Figure A1.2 illustrates the effect of an increasing ambient temperature on the variability of standard readings, caused simply by the operation of other instruments in the same room. The effect of draughts and temperature change was eventually curtailed by placing an insulating jacket in close contact with the DCP.

Following the analysis of each sample, there is a recovery period during which residual material is flushed from the pump tube, nebulizer, chimney and electrodes. If further analysis is conducted during this time, an apparent enhancement of the results is observed. This is a 'memory effect', illustrated by Figure A1.3. It is especially evident with HNO_3 samples containing a high concentration of metals, and may also be affected by the precise matrix, as standards solutions in HNO_3 do not exhibit the effect to the same extent as samples, even of a lower metal concentration. The influence of this phenomenon is eliminated by rinsing the system through with 10 % HNO_3 to remove those metals attracted to plastic surfaces such as the pump tubing or nebulizer chamber. Allowing air to be pumped into the plasma is a more effective remedy, although it is unclear why.

A1.5 CATION EXCHANGE CAPACITY

Whilst the method for determining CEC described by Bascomb (1964) enjoys considerable popularity, the number of samples that can be analysed per day in this way is limited by repeated use of a centrifuge and mechanical shaker. In contrast, Soon's method (1988), employing methylene blue adsorption, requires only 2.5 hours for completion, is suitable for large batches and was found to yield results similar to those using NH_4^+ (Soon, 1988), and was therefore an attractive alternative for use in this research. In this case, the exchange sites are saturated with a known concentration of methylene blue, and the concentration of the supernatant solution analysed in comparison to a methylene blue blank, assuming that CEC is proportional to the difference between the two.

A1.5.1 SELECTION OF TEST PROCEDURE

To test the validity of these procedures, each method was conducted on 5 subsamples of the same clay and sandy soil. Identical results from the two procedures are not expected, as CEC is somewhat dependent upon the conditions under which it is measured (Rhoades, 1982). Bascomb's method (1964) was slightly modified from the original due to the difficulty in obtaining and using the indicator, omega black. The modifications are those used by the Soil Survey (pers. comm., 1990). After shaking with $MgSO_4$, 2 mls of buffer solution (142 mls conc. ammonia and 17.5 mls ammonium chloride, diluted to 250 mls) are added to a 5 ml aliquot of the centrifuged solution to stabilise the pH at 10 for the titration. The indicators used are sodachrome black 6B (0.5 g in 100 ml ethanol) and tartrazine (0.5 g in 100 ml distilled water), and the colour change is from orange / red to apple green.

The results from Soon's method (1988) were found to be several orders of magnitude lower than those obtained from Bascomb's method (1964), and included a standard error of more than 100 %. The problem seemed to focus around the relatively high concentration of the methylene blue solution used, and the minuscule difference between sample and control transmittance. This situation is exacerbated by clay soils, apparently because 2 hours is insufficient time to allow the soil to completely settle, thus transmittance is a function of methylene blue and clay particle concentration. It is likely that the situation would be amended by thorough filtering or centrifuging, but this negates the appeal of the method - i.e. its speed. This routine was therefore rejected without further investigation.

Results obtained from Bascomb's method (1964) had an acceptable standard error of <3% for both soils (Table 4.5), and were within the expected range of up to 60 meq 100 g^{-1} for the surface horizons of mineral soils (Wiklander, 1964), or more specifically, 15-45 meq 100 g^{-1} for agricultural soils (Bohn *et al.*, 1979). The results presented are towards the lower end of this range as they are taken from a depth of 180-240 mm. This method was therefore selected for use.

A1.6 ORGANIC CARBON TEST SELECTION

The most popular methods of establishing the organic carbon (OC) involve a version of that established by Schollenberger (1927). Seven of these versions (Tinsley I and II (1950), Anne (1945), Mebius (1960), Walkley-Black (1934), Tyurin (Kononova, 1966) and a new version, Tinsley III) were compared for accuracy, precision and speed of determination, and against gravimetric techniques, by Kalembasa and Jenkinson (1973). Of the titrimetric methods, their version of the Tinsley method (Tinsley III) was the most precise and recovered the greatest proportion of OC, compared to gravimetric techniques. Contrary to these results, the Walkley-Black (1934) method is very popular, due largely to its simplicity and rapidity. However, other authors propose that results from this procedure can not be considered quantitative as extended heating (omitted by Walkley-Black) is necessary to achieve satisfactory oxidation of OM (Anne, 1945; Tinsley, 1950; Mebius, 1960; Kalembasa and Jenkinson, 1973). The method has been further criticised as being so variable (extracting between 63 and 86 % OC) as to preclude the implementation of correction factors (Allison, 1960), unnecessary in procedures such as Tinsley III that involve the complete oxidation of OC.

The results of Kalembasa and Jenkinson (1973) were externally validated in their report, but before the method was accepted for use in the present research, a brief experimental comparison using subsamples of the same soil was made between the Tinsley I procedure, adopted by the Soil Survey (Avery and Bascomb, 1974), and the Tinsley III method. Both methods were found to extract similar percentages of OC, although Tinsley III was marginally more successful. This reflects the findings of Kalembasa and Jenkinson (1973). The relative standard deviation of the results of both methods was high (although tiny in terms of percentage OC) and may be the result of interference by soil constituents such as Cl^-, Fe^{2+} and MnO_2, which are readily oxidised/reduced by dichromate (Walkley, 1947). Although unlikely to be significant in this research, other possible sources of error include the use of unconfirmed assumptions with reference to the oxidation state of OC in soil (Nelson and Sommers, 1982) and the unsuitability of this method when carbonised materials are present (Bremner and Jenkinson, 1960). However, these are problems inherent to any dichromate technique, and as Tinsley III was considerably more precise and rapid, this technique was therefore selected for use.

TABLE A1.1 OPTIMUM RATIOS OF SOIL MASS:VOLUME OF 16 M HNO_3 IN DETERMINING 'TOTAL' METAL CONCENTRATIONS

	average concentration (mg kg^{-1})					
soil:acid	Cu soil 1	Cu soil 2	Cu soil 3	Zn soil 1	Zn soil 2	Zn soil 3
1:15	15	20	-	44	72	-
2:30	23	34	11	61	112	34
5:75	20	31	-	60	111	-
10:100	18	29	-	60	109	
2:10	-	-	14	-	-	38

TABLE A1.2 OPTIMUM EXTRACTION TIMES FOR 16 M HNO_3 DIGESTS

	average concentration (mg kg^{-1})					
soil	Cu 0.5 hr	Cu 1 hr	Cu 4 hr	Zn 0.5 hr	Zn 1 hr	Zn 4 hr
1	14	18	14	55	61	75
2	13	16	27	46	52	66
3	16	21	24	48	52	67
4	11	11	16	54	58	60
5	6	7	8	16	12	12
6	4	5	5	16	17	20
7	6	7	9	12	15	16
8	3	5	7	18	19	23

TABLE A1.3 OPTIMUM EXTRACTION TIMES AND MOLARITY OF $CaCl_2$ SOLUTIONS

	treatment		average concentration (mg kg^{-1})			
soil	M $CaCl_2$	hr	Cd	Cu	Ni	Zn
1	0.1	4	3	5	8	15
1	0.05	4	2	3	6	13
1	0.1	2	4	4	11	13
1	0.05	2	2	2	3	10
2	0.1	4	2	3	10	3
2	0.05	4	2	3	8	3
2	0.1	2	2	3	9	4
2	0.05	2	1	2	6	3

TABLE A1.4 THE NON-LINEARITY OF HNO_3 DIGEST SOLUTIONS

dilution factor (A)	Cu (mg kg^{-1})		Zn (mg kg^{-1})	
	av conc (B)	A x B	av conc (C)	A x C
1	1.82	1.82	5.8	5.8
2	1.07	2.14	3.05	6.1
4	0.61	2.44	1.55	6.2
8	0.34	2.72	1.06	8.48
16	0.21	3.36	0.61	9.76
32	0.13	4.16	0.06	1.92

FIGURE A1.1 SPECIFIC GRAVITY OF CONCENTRATED NITRIC ACID FOLLOWING HEATING AT 135 C FOR VARYING LENGTHS OF TIME.

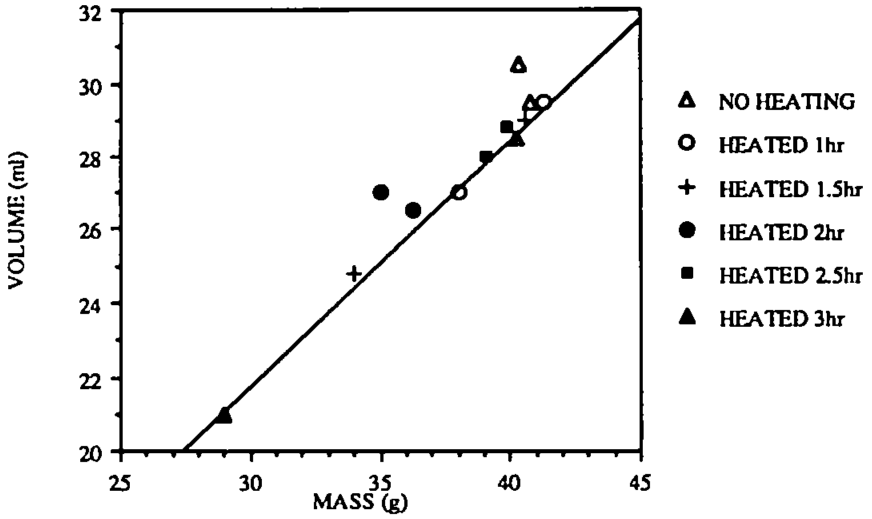


FIGURE A1.2 VARIATION IN DCP READING CAUSED BY CHANGING AMBIENT TEMPERATURE

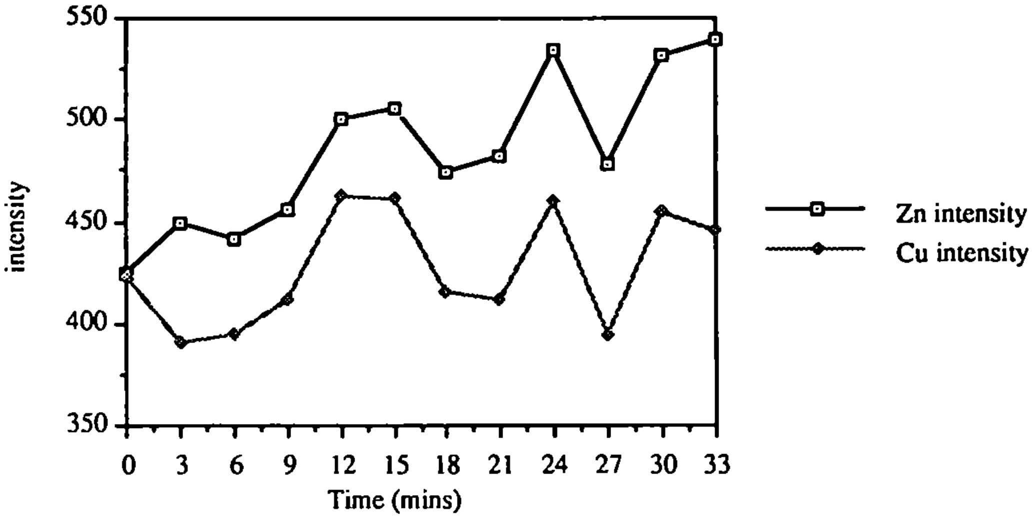
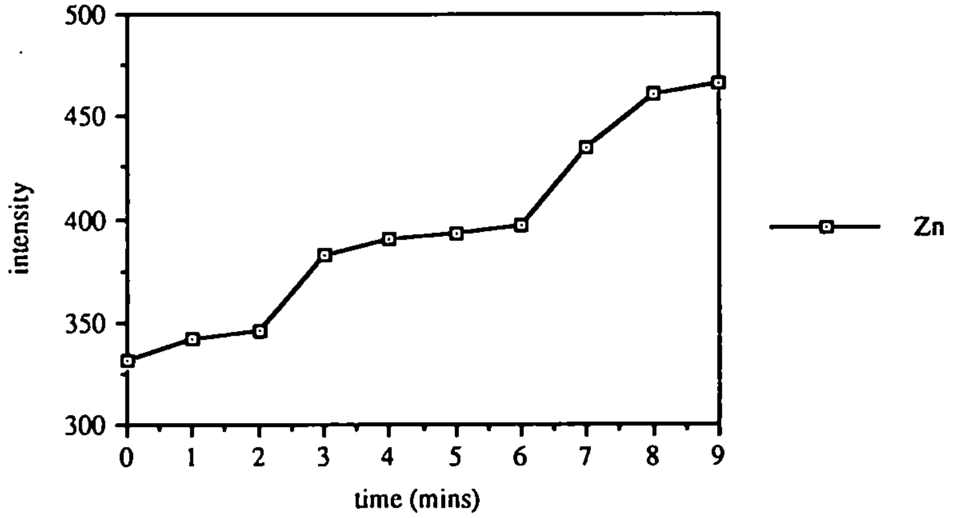


FIGURE A1.3 MANIFESTATION OF THE MEMORY EFFECT ON A 10 mg/l Zn STANDARD.



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