AN INVESTIGATION OF THE INTERACTION BETWEEN LANDFILL LEACHATE AND SOILS

MORAG A. CHAFER BSc.

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Department of Civil Engineering
University of Strathclyde
Glasgow

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ABSTRACT

A detailed review of literature reveals that although soil scientists have reported that soil is an excellent stabiliser of land applied waste, there is little evidence to assess the extremely complex reactions that occur when landfill leachate interacts with soil. In order to examine this, studies of mineralogical content, exchangeable cation status and chemical composition of soils were undertaken. Soil-leachate interactions were studied by column and batch techniques.

When dealing with materials as variable and complex as soils, it is difficult to accurately identify the solid phase prior to contact. Owing to the large number and variety of concentrations of leachate constituents, it is considerably more difficult to quantitatively establish the results of interaction and assign alteration values to responsible mechanisms. However, this investigation did reveal the following:-

1. interaction does occur, but this interaction is not unlimited;

2. the degree of interaction is different for different soil types;

3. the relative influence of the mechanisms of interaction;

4. the influence of soil types, soil to leachate ratios and contact times; and

5. soils previously thought to attenuate leachate have been found not to do so.

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CONTENTS

CHAPTER ONE OVERVIEW

1.1 INTRODUCTION

The increase in pollution potential of refuse, coupled with the increase in environmental awareness and consequent statutory legislation, has led to the evolution of the science of landfill technology. Waste disposal today is far removed from the indiscriminate dumping of previous decades.

However, burial of wastes under controlled conditions has yet to reach the state where there is absolute assurance of complete environmental protection. The carefully planned sanitary landfill can still offer serious problems for the environmental quality of surroundings.

Leachate, the polluted water that is produced from a landfill site, is a result of water passing through decomposing refuse and rinsing out or leaching various constituents from the refuse. This leachate may be generally described as having high concentrations of suspended organic matter and organic acids with corresponding high biological oxygen demand (BOD) and chemical oxygen demand (COD) values, high concentrations of dissolved metals, ammonia and inorganic salts. The quality of groundwater and surface water can be degraded by landfill leachate unless precautions are taken to select suitable sites and not overload the capacity of the soil to attenuate (or retain) the potential pollutants.

Historically soils have demonstrated their function as waste utilisation systems. The farmer and home gardener have long made use of waste through application to land of animal manure, compost and other residues. Certain wastes, therefore, have been considered resources to be husbanded for improvement of soil productivity.

In contrast, at the present time there are wastes that must be disposed of without obvious immediate benefit. This includes such disposal options as land treatment of wastewaters, landfills, trenches, encapsulations and other burials. Soils can be used as a lining material for landfill as an attenuation, adsorption and filter barrier for pollutants. An increasing number of landfill sites require to incorporate a leachate collection system in order to carry out treatment processes which can significantly reduce leachate pollution potential. One, or a combination of, the following methods are generally adopted :

a) Spray irrigation where leachate is collected and sprayed either over a section of the site or a selected area adjacent to the site. The hydrogeology and attenuation properties of soils in these selected areas requires to be established to ensure protection of the environment.

b) Leachate recirculation involving the direct pumping of leachate back into the refuse underlain by suitable ground conditions to attenuate the leachate. Again the soil properties will be a vital component in this treatment.

c) Storage of leachate in lagoons before other treatment processes, such as aeration and chemical treatment, or prior to its removal off-site. The local availability of inert, low permeability materials can facilitate the construction of lagoons. Otherwise suitable construction materials will require to be imported.

The prominence of the soil as the last defence against pollution of the environment from solid waste disposal and leachates requires that its behaviour under anticipated management practices be characterised. Site evaluation necessitates a basic understanding of soil components and properties, the treatment mechanisms operating in the soil, and limitations of these mechanisms in terms of pollutant loading rates.

This thesis relates the differences in soil types and properties to their capacity to control movement of waste pollutants. It is these differences in soil type attenuation capacity that make it so essential to understand the reactions and interactions between soils and leachates as an essential function in soil management for waste disposal.

1.2 SCOPE OF THE WORK

A detailed review of the literature was undertaken and revealed that landfill leachate-soil interactions had not been extensively investigated. In particular, the fate of organic pollutants in leachate has not been studied in sufficient depth. Researchers have reported concentration changes in leachate applied to land and in leachate travelling through, beneath and away from landfills. However, no explanation of the mechanisms responsible for these concentration changes have been given.

It is the purpose of this research to examine the influencing mechanisms individually through a literature review, observe the interaction between soil and landfill leachate experimentally, and identify the mechanisms responsible for the alterations observed in the leachate.

The specific objectives of the research were to: 1 determine if pollutant concentration changes occur in landfill leachate as a result of soil-leachate interaction; 2 identify and quantify the concentration changes; 3 determine if soil type has an effect on these concentration changes; 4 identify and if possible quantify the soil mechanisms responsible for the interactions; 5 establish suitable criteria of soils for landfilling and for land treatment of landfill leachate.

The work performed was experimental in nature and consisted of testing soils and leachate in both column and batch studies. Although predictions based on laboratory data cannot exactly replicate natural field conditions, disposal site preparation often includes mixing the soil to develop homogenous conditions similar to those of soil column experimentation.

The practice of landfilling and the production and management of landfill leachate is reviewed in Chapter 2. A detailed description of the microbiology and biochemistry of landfilled refuse and the various components of leachate is given. This information is directly relevant to the reactions which will occur when leachate is applied to the soil. Chapter 3 brings together and correlates recent information known to have a prominent influence on the rate of movement of pollutants from wastes and their leachates in the soil.

Preliminary experiments were conducted to investigate the variables affecting the efficiency of land treatment of landfill leachate. Factors investigated included leachate strength and application rate, vegetative cover, and soil type. The results from these experiments indicated that soil type has a major effect on the efficiency of removal of pollutants from landfill leachates. Further investigation of soil type was undertaken for the following reasons:

- soil will be the final barrier to pollutant migration from landfill sites and from land treatment areas;

- if the site soil type is inappropriate for pollutant removal, then it would be a major expenditure to import soil to the site;

- little work has been done on soil-leachate interactions and data from other wastewater-soil interaction studies are not directly relevant due to the variability and complexity of landfill leachate.

This investigation of soil-leachate interaction was experimental in nature and consisted of two types of study- soil-leachate interaction using a column technique and an investigation of the mechanisms acting in the soil by means of batch techniques.

Four types of soil were chosen for investigation. Details of their physical and chemical properties are given in Chapter 4. They can be generally defined as topsoil, peat, sandy loam and clay loam. The column experiments (Chapter 4) investigated removal efficiency of pollutants by the bare soil and on soil which had a vegetative cover of perennial ryegrass. The applied leachate was obtained from a domestic refuse site and was characterised by a high concentration of organic matter and ammonia. Leachate was added to the top of the columns and the filtrate was collected and analysed for various constituents. The results and conclusions from the column experiments are given in Chapter 4.

The column experiments had shown that different soils had differing abilities to remove pollutants from landfill leachates. In order to investigate the reason for this a number of small-scale batch experiments were undertaken to investigate the mechanisms acting in the soil. In summary, these experiments involved studies of physical mechanisms acting in soil by means of filtration experiments (Chapter 5), biodegradation rates in the various soils (Chapter 6), and studies of adsorption and exchange reactions by means of soil/leachate shaking experiments (Chapter 7).

The results of this study indicate that soil-leachate interaction is not strictly a removal process in which the soil unilaterally adsorbs organic material and ions, as might be predicted by a mathematical model. Soils will remove some species and release others according to the respective concentrations and preferences in the soil and the leachate. Soils originally thought able to give a high leachate treatment efficiency were found not to do so in the conducted experiments. Mechanisms identified to be most active in interaction were microbial degradation, cation exchange, adsorption, oxidation-precipitation and filtration.

CHAPTER 2 LANDFILLING OF WASTES

2.1 LANDFILL SITE SELECTION AND OPERATION

Proper site selection and investigation are fundamental to the success of any landfill operation. Once a potential site has been selected it is important to carry out a detailed site investigation (British Standard 5930, 1981; Weltman and Head, 1983; DOE, 1984). The investigation should include technical and scientific assessment of hydrological and hydrogeological features, of physical, chemical and biological factors relating to the ability of the site to handle waste, and of the potential impact of the operation on the environment and local community. Many historical leachate problems have been caused by poor initial site selection, lack of investigation or failure to carry out preliminary engineering works (Schwer, 1974; Environmental Institute for Waste Management Studies, 1985; Carter, 1987). The soil and rock strata assume a key position in sanitary landfill site selection, along with the type of waste being considered (e.g. strictly municipal refuse as opposed to hazardous waste). Both determine the site characteristics most desirable for pollutant containment.

Landfill sites fall into a spectrum in terms of the extent to which leachate is contained within the landfill. It is convenient to distinguish two broad categories, that is, "attenuate and disperse sites" and "containment" sites. These designations correspond to two different approaches to the protection of water resources.

The aim of a containment site is to isolate leachate from the environment by taking advantage of low permeability strata (slates, shales, mudstones, soft clays and marls) which prevent significant leachate movement through the base and sides of the landfill. If suitable strata are not available the same effect can be achieved by use of a liner. This might be imported or reworked clay or shale, bentonite with polymer additives or a synthetic liner such as high density polyethylene or butyl rubber. However, failure of synthetic liners has been reported (Haxo, 1983; Swinnerton, 1984; Haxo and Nelson, 1984). In the selection of sites, it should be appreciated that high secondary permeability conditions can result in a rapid rate of leachate transport along discrete pathways with little dilution or dispersive effects to reduce leachate concentrations. Clay becomes muddy when wet and cracks when dry. This can lead to fissures which will allow direct flow of leachate to groundwater (Daniel, 1984; Day and Daniel; 1985). There is also evidence in the literature of landfill leachate producing an increase in hydraulic conductivity of clay (Michaels and Lin, 1954; Hardcastle and Mitchell, 1974; Anderson et al, 1982; Fernandez and Quigley, 1985).

Attenuate and disperse sites allow the slow release of leachate from the landfill and rely on various attenuation mechanisms (Chapter 3) operating within the body of the waste and the underlying strata to ameliorate the polluting characteristics of the leachate (DOE, 1978; Water Research Centre, 1981; Williams, 1982). All soils are not equally effective in attenuating or retaining pollutants (Chapter 3). In general, the finer the texture in mineral soils, the greater is the capacity to retain ionic pollutants. However, soils high in clay have the distinct disadvantage of unusually slow drainage, allowing water to collect in the disposal excavation and accumulate leachates. Sandy soils characteristically allow unrestricted flow of leachate. Obviously these two extreme soil textures are least suited for burial of solid wastes. Medium textured soils (e.g.loams of 50% sand, and a 50% mixture of silt and clay with about equal proportions of each) are most desirable (U.S Department of Agriculture, 1972).

In order to evaluate the potential leachate generation at a landfill site it is necessary to define the hydrological regime, including an appraisal of meteorological data (Meteorological Office, 1981). Prospective sites require to be engineered to ensure that ground and surface waters have minimal impact on the site operations and leachate generation. In order to minimise leachate generation, water entering the site should be intercepted and removed by a suitable drainage system. The position of perched and regional water tables needs to be established, together with surface water run-off and groundwater inflows.

For most sites in the UK, precipitation infiltrating the waste is the major water source. During filling operations low permeability intermediate cover materials are required to minimise rainfall percolation (Holmes, 1984). The operation of the landfill by placing waste into cells (i.e. small contained areas) can minimise the surface of waste exposed to rainfall (DOE, 1986). Upon completion, the accepted restoration design is to minimise long term rainfall percolation and post-operational leachate generation by final capping and contouring. Formation of cover/capping layers can involve significant quantities of selected cohesive materials and the identification of suitable soils within the site or its vicinity can result in considerable cost savings.

An increasing number of landfill sites require to incorporate a leachate collection system in order to carry out treatment processes which can significantly reduce leachate concentrations. Domestic waste can take several decades to decompose to an essentially inert material (Stanforth et al., 1979) and leachate control systems may require to function for a considerable amount of time after landfilling operations have ceased. The control system should include for the provision of ground and surface water quality monitoring by means of suitably located boreholes and selected sampling of watercourses.

In summary, a landfill site must provide long-term protection of the quality of surface and groundwaters by minimising surface and groundwater flow into the site, control of leachate generation and a means for collecting and disposing of any leachate formed.

2.2 LANDFILL COMPOSITION

Municipal solid waste is the familiar household, industrial and commercial garbage generated in every community and is composed mainly of waste food, paper, plastic, rubber, metals and glass (DOE, 1976; Pocock and Rufford, 1984).

The demise of the coal fire and the rise of an affluent society with a large packaging industry has meant the proportion of paper and putrescible material in refuse has approximately doubled since 1935. Plastic in domestic waste has become significant (Bickerstaffe, 1984) and is likely to increase (Table 2.1). It is clear that the potential strength of crude domestic waste leachate is much greater than in previous decades.

The sum of paper, putrescibles and fines generally amount to 70-75% of refuse by weight and these fractions constitute the most readily biodegradable portion (Kasali, 1986). Although the fine screenings consist of approximately 30% organic matter (Kaiser, 1975) the carbon is probably more readily available than that of paper, for example, and so contribute significantly to early landfill metabolism. The putrescible fraction contributes significantly to the overall water content of 20-25%. Much water may be adsorbed by the paper during transit to the landfill. In the early stages of decomposition, microbiological activity will be concentrated in these areas of high water content (Eliasson, 1972; Rees, 1980).

About 80% of the plastic waste in refuse is discarded packaging and represents about 30% of all the plastic consumption in the UK (Rees, 1980). Compositional analysis of refuse plastics showed polyethylene and polypropylene to contribute 50-60% by weight with polystyrene and polyvinylchloride contributing 16% and 8%, respectively. The residual 20% consisted of an aggregate of a number of minor constituents. The plastic component of household refuse comprises about 5% by weight but

TABLE 2.1 - COMPOSITION OF DOMESTIC WASTE (%)

(Ministry of Housing and Local Government. 1961; DOE. 1971; Gulley. 1984)

CLASSIFICATION	1935	1967	1980
Cinder and Dust	57	31	10
Paper	14	29	41
Vegetable and Putrescible	14	15	20
Metal	4	8	7
Glass	3	8	10
Textile	2	2	4
Plastic	-	1	5
Unclassified	6	6	3

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the total weight of synthetic polymeric material could approach 10% if the contribution of synthetic textiles, rubber and unclassified components such as carpets, other floor coverings and foam cushions were taken into account (White and Plaskett, 1981).

The chemical composition of refuse, which will be a direct reflection of the various components given in Table 2.1, has been reported by a number of workers (Rees et. al., 1972; Pfeffer, 1978). Comparison of the chemical composition of refuse with that of sewage sludge is given in Table 2.2. The elemental analysis of refuse is given in Table 2.3. Carbohydrates are the main components of refuse, as protein and lipids together account for only 8% of refuse dry weight. One important element that is not detailed is phosphorus. It has been reported (Pfeffer, 1978) that the concentration of phosphorus is essentially zero. However, conflicting evidence (Robinson and Maris, 1979) has indicated concentrations in excess of 0.025 g/m^3. Trace elements such as nickel, iron, cobalt , molybdenum and copper, together with sulphur, also play major roles in landfill bacterial metabolism.

2.3 LANDFILL BIOCHEMISTRY

Various reactions occur when water comes into contact with refuse. The simplest reaction is the direct dissolution of the refuse constituents which are present in water soluble form. These are mainly inorganic ions such as sodium, potassium, calcium, magnesium, chloride, sulphates and phosphates. Some of the more soluble organics, such as humic acid, will also be leached out. However, only about 5% of refuse (dry weight basis) is soluble in water (Schoenberger, 1970). It is therefore obvious that mechanisms other than the low velocity flow that carries off the fine-size particles initially present are responsible for the high concentrations of dissolved and suspended organic and inorganic solids

TABLE 2.2 CHEMICAL COMPOSITION OF REFUSE AND DOMESTIC SEWAGE SLUDGE

COMPONENT	% DRY WEIGHT
Domestic Sewage Sludge (Dry)	
Hemicellulose	6.15
Cellulose	34.48
Lipids	14.01
Protein	18.98
Ash	34.88
Municipal Waste (21% Moisture)	
Cellulose, Sugar, Starch	58.8
Lipids	5.7
Protein	2.6
Plastics	1.5
Ashes, Metal, Glass	31.4

TABLE 2.3 ELEMENTAL ANALYSIS OF REFUSE (Kaiser, 1975)

ANALYSES (% BY WEIGHT)							
H_2O	C	H	O	N	Cl	S	INORGANICS
25.2	25.5	3.4	20.3	0.5	0.5	0.2	24.4

found in sanitary landfill leachate. Solid wastes placed in a landfill undergo a number of simultaneous biological, physical and chemical changes.

The chemical composition (Table 2.2) of refuse has shown it to be a multicomponent substrate which will be subject to biodegradation by a wide range of organisms (Dobson, 1964; Filip and Kuster, 1979; Rees, 1980; Rees and Grainger, 1982; Donelly, 1983). An outline of the degradation pathways of the major constituents of refuse is given in Figure 2.1. Biodegradation within a landfill passes through a series of stages:

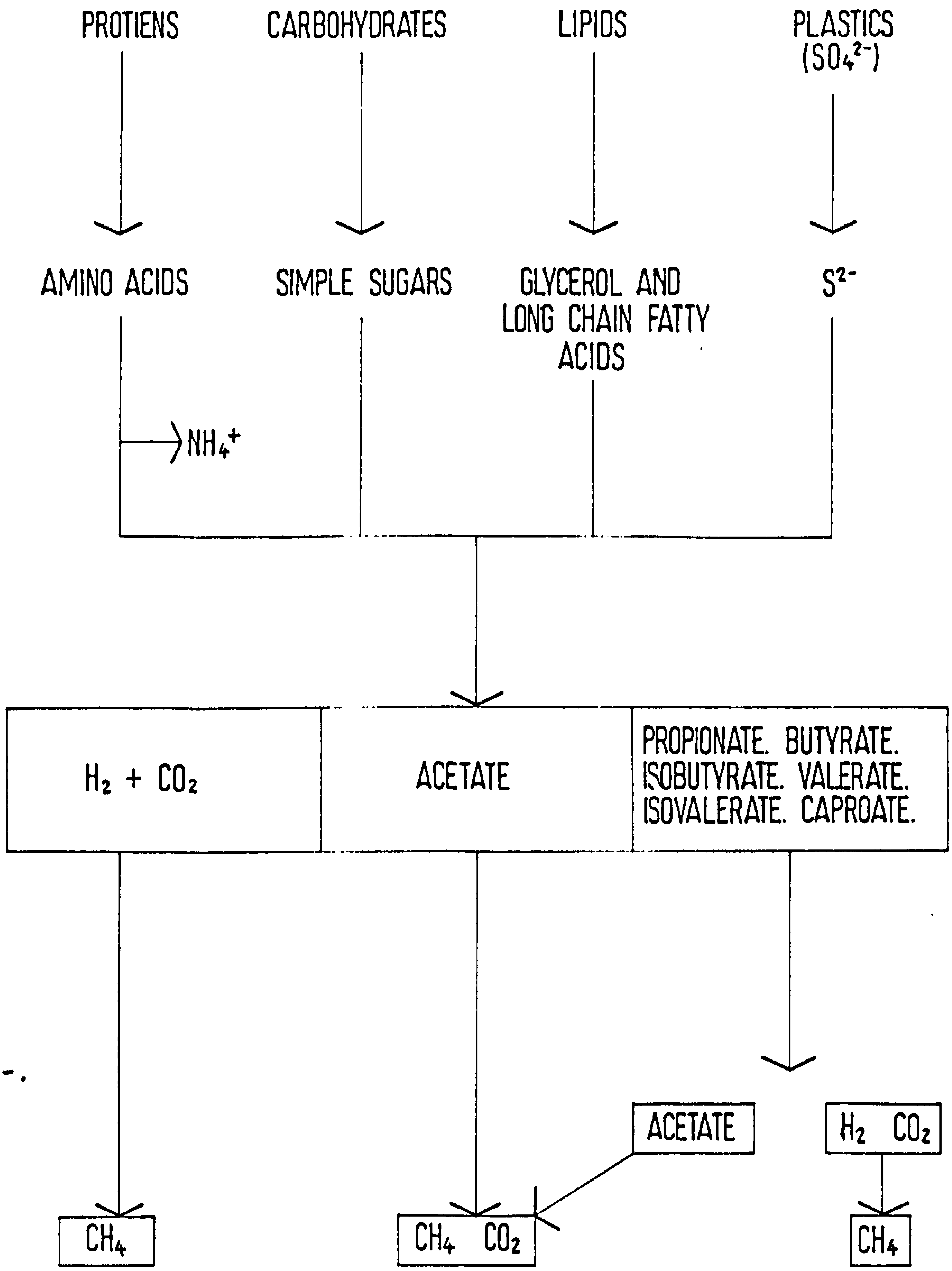
- aerobic stage; often of short duration because oxygen is rapidly consumed and replenishment from the atmosphere is slow;

- acidification stage; complex organic compounds are fermented anaerobically, forming soluble organic acids (free volatile fatty acids), amino acids and other low molecular compounds such as H_2 and CO_2;

- CH_4 fermentation stage; free volatile acids are fermented, yielding CH_4 and CO_2 gas as end products.

Initially, aerobic decomposition predominates. The duration of the aerobic phase will inevitably vary from site to site depending on particular landfill characteristics (e.g. moisture content and degree of compaction of refuse). The major contribution of aerobic catabolism to the overall landfill metabolism lies in the ability of aerobic microorganisms to degrade lignin, which is commonly believed not to be digested and fermented under anaerobic conditions (Hungate, 1982). The net effects of aerobic metabolism are that the temperature is raised above ambient, the moisture content of the refuse increases and the redox potential decreases (Satriana, 1974; Loehr, 1984). These effects

Figure 2.1 General Scheme of Landfill Reactions



are a result of the fact that aerobic microbial activity is characterised by the consumption of oxygen, the production of carbon dioxide and water, and the liberation of heat.

As the oxygen becomes depleted, microaerophilic conditions develop which promotes the enrichment of facultative anaerobic bacteria. However, anoxic conditions soon become established and obligate anaerobes become dominant (Kasali, 1986). The major anaerobes and their functions are listed in Table 2.4.

During the acidification stage, large amounts of volatile fatty acids and carbon dioxide are produced. These acids reduce the pH to between 4 and 5. The low pH helps to solubilise inorganic materials, which along with the high concentration of low molecular weight organics, produce a high ionic strength. Ionic strength may affect the leaching of materials in three ways: by increasing the solubility through lowered activity coefficients; by ion-exchange processes replacing an ion bound to an ion exchange site with one or more predominant ions in solution; and by decreasing the size of the double layer around colloidal particles and promoting coagulation (Stanforth et al, 1979). The high volatile acid concentrations contribute to the high chemical oxygen demand (COD) often found during this phase (Ehrig, 1983). The redox potential is reduced to below 0 mV. The thermodynamically predicted sequence of reactions for redox-sensitive elements is given in Table 2.5.

The second stage of anaerobic decomposition occurs when methane-producing microorganisms (methanogens) complement the facultative anaerobes (Hoeks and Borst, 1982). Methanogens are strict anaerobes and require a neutral pH i.e. 6.6 to 7.3 (Alexander, 1964). Thus the volatile acid concentration must be reduced to less than 2000 mg/l (Eckenfelder and O'Conner, 1961; Farquhar and Rovers, 1973; Lettinga, 1977). Volatile acids, produced by facultative anaerobes, and other organic matter are converted to methane and carbon dioxide (Farquhar and Rovers, 1973; Hobson et al.,

TABLE 2.4. MAJOR ANAEROBES AND THEIR FUNCTIONS

ORGANISM	FUNCTION
HYDROLYTIC BACTERIA	Ferment complex multicarbon compounds eg. saccharides, lipids and proteins to a variety of end products including acids (lactate, acetate butyrate and propionate) neutral compounds (ethanol and methanol) and hydrogen, carbon dioxide.
HYDROGEN - PRODUCING ACETOGENS	Ferment alcohols larger than methanol and organic acids larger than acetate, to hydrogen and acetate
HOMO - ACETOGENS	Ferment multicarbon compounds, hydrogen/CO_2 or one - carbon compound into organic acids.
METHANOGENS	Ferment hydrogen/CO_2, one - C compounds and acetate to methane and carbon dioxide.

TABLE 2.5 SEQUENCE OF REDOX REACTIONS

	ΔG^{o} (W) Kcal
1. AEROBIC RESPIRATION	
$CH_2O + O_2 \longrightarrow CO_2 + H_2O$	-120.0
2. DENITRIFICATION	
$CH_2O+4/5NO_3+4/5H^+ \longrightarrow CO_2+2/5N_2+7/5H_2O$	-113.9
3. Mn (IV) REDUCTION	
$CH_2O+2MnO_2+4H^+ \longrightarrow 2Mn^{2+}+3H_2O+CO_2$	- 81.3
4. NITRATE REDUCTION	
$CH_2O+\frac{1}{2}NO_3^-+H^+ \longrightarrow CO_2+\frac{1}{2}NH_4^++\frac{1}{2}H_2O$	- 78.2
5. Fe (III) reduction	
$CH_2O+8H^++4Fe(OH)_3 \longrightarrow 4Fe^{2+}+11\ H_2O+CO_2$	- 27.7
6. SULPHATE REDUCTION	
$CH_2O+\frac{1}{2}SO_4^{2-}+\frac{1}{2}H^+ \longrightarrow \frac{1}{2}HS^-+H_2O+CO_2$	- 25.0
7. METHANOGENESIS	
$CH_2O + \frac{1}{2}CO_2 \longrightarrow \frac{1}{2}\ CH_4 + CO_2$	- 22.0

$\Delta G^{o}(W)$ = FREE ENERGY AT pH 7.

1981). The volatile acid concentration is reduced to low levels, with a consequent reduction in the BOD and COD values and an increase in pH. With the neutral pH, fewer inorganic materials will be solubilised and conductivity will fall. However, some materials will still be solubilised by decomposition processes, so the fall in conductivity will not be as drastic as the fall in volatile acid concentration. Eventually bacterial action decreases as the substrate is depleted.

Environmental conditions may alter this degradation pattern considerably. The composition of refuse, the moisture content, landfilling practices and seasonal variations in temperature will effect the rate of degradation. To complicate matters further, different microenvironments in the landfill may undergo different stages of decomposition at the same time (Emcon Associates, 1976).

2.4 LANDFILL LEACHATE QUANTITY AND QUALITY

One of the difficulties of studies of landfill leachates is the characterization of leachate composition. A large number of factors interact to produce a variable quality and quantity of leachate from a single site. These factors include composition and compaction of waste (Marian, 1982), landfill microbiology (Section 2.3), seasonal variation in infiltration (Holmes, 1980; Blakey and Croft, 1986), absorptive capacity of refuse (Blakey, 1982; Campbell, 1982; Stegman, 1982) and age of landfill (Cameron and Koch, 1980).

Predictions of the volume of leachate which can be generated from domestic wastes has been variously described by Lu, 1985; Holmes, 1984; Ehrig, 1983; Campbell, 1982; Blakey, 1982; and the Department of the Environment, 1978. These predictions are basically derived from the following water balance equation :-

$$L = P - R - S_s - E - S_r$$

where L - leachate generation
P - precipitation
R - run-off
S_s - change in soil moisture storage
E - evaporation losses from soil and vegetated surface
S_r - change in moisture absorption of the refuse components.

Additional factors which may have to be taken into account include liquid discharged to the site and any subsurface inflow to the disposal area.

Experimental investigation of leachate characteristics has been reported by many workers (Robinson and Maris, 1979; Rovers and Farquhar, 1972; Chian et al., 1977; Qasim and Burchinal, 1970; Ham and Anderson, 1975; Chen and Bowerman, 1974). The composition of leachate samples from different landfills as reported in the literature show a large variation for the reasons mentioned. However, a general trend in leachate composition can be identified as landfill ages. The comparitive composition of leachate from fresh (less than 5 years) and aged wastes (greater than 5 years) with domestic sewage is given in Table 2.6. It is important to note that the strength of leachate from fresh wastes is some 35 times stronger than domestic sewage.

Landfill leachates are typically dark green or brown in colour, turbid and have the tendency to turn darker or even black in colour (Qasim and Burchinal, 1970). The smell is often offensive, somewhat like ammonia, hydrogen sulphide, and merceptan, but the typical faecal odour of domestic sewage is absent (Clark and Piskin, 1977; Parker, 1983).

Leachates from young landfill sites contain high concentrations of organic matter. This consists mainly of low molecular weight fatty acids (e.g. acetic acid) and a small concentration of fulvic or other more complex organic acids. As the refuse ages and stabilises much of the

TABLE 2.6 COMPARISON OF LEACHATE COMPOSITION BETWEEN FRESH AND AGED WASTES AND DOMESTIC SEWAGE. (ROBINSON AND MARIS 1985).

DETERMINANDS	FRESH WASTES	AGED WASTES	DOMESTIC SEWAGE
pH	6.2	7.5	7.5
COD	24,000	700	700
BOD	13,600	70	400
TOC	8,000	400	240
VOLATILE FATTY ACID	6,000	<5	<40
AMMONIACAL N	600	260	46
OXIDISED N	<0.5	7.5	<0.5
ORTHOPHOSPHATE	0.7	0.5	14
CHLORIDE	1,300	1,400	120
SODIUM	960	880	100
MAGNESIUM	250	130	4.5
POTASSIUM	780	340	20
CALCIUM	1,820	200	110
CHROMIUM	0.56	0.07	0.005
MANGANESE	26.5	1.7	0.07
IRON	540	10	0.03
ZINC	21.5	0.2	0.16

All results in mg/l except pH.

readily biodegradable material becomes broken down and the organic content of the leachate decreases. Hence the concentration of BOD, COD and TOC are lower as are BOD:COD and COD:TOC ratios (Crawford and Smith, 1985).

Most published studies concerning the characterization of organic chemicals in leachates cover analyses of the main classes of organics and to some extent analyses of free volatile fatty acids (Artiola-Fortuny and Fuller, 1982). A few investigations deal with analyses of individual compounds (Burrows and Rowe, 1975; Chian and Dewalle, 1976; Reinhard et al., 1984; Albaiges et al, 1986). Burrows and Rowe (1975) were among the first to identify the composition of the volatile carboxylic acids. C2 - C6 carboxylic acids were identified. Typical components of anaerobic fermentation, n- and i-butyric acids, have been shown to compose 40-90% of the organic extract (Johansen and Carlson, 1976; Chian and Dewalle, 1976; Harmsen, 1983). Other compounds identified include C2-C6 alcohols and amines, volatile esters, aliphatic and aromatic hydrocarbons and phenols (Khare and Dondero, 1977; Harmsen, 1983; Reinhard et al, 1984).

Ammonia (NH_4^+) contributes 60-90% of the total nitrogen compounds in leachate (Coker, 1984). Due to anaerobic conditions within the landfill, the concentration of oxidised nitrogen (nitrites and nitrates) is low (Chian and Dewalle, 1977; Johansen and Carlsen, 1976). High levels of ammonia often persist in leachates from aged wastes, even though the biodegradable organics may have fallen to low values (Harrington and Maris, 1986).

The metal content of leachate is generally highest during the acid formation stage (Ray and Chan, 1986). Among the heavy metals, iron has been found in highest concentration, followed by zinc, chromium, nickel, copper, cadmium, and lead (Cameron and Koch, 1980). Under anaerobic conditions, metals such as iron and manganese will be reduced from an insoluble to a soluble form (Table 2.5). The reversion of iron to the insoluble ferric form when leachate comes into contact with air is the cause of the characteristic rust-coloured deposits which are often seen at leachate seepages (County Surveyors' Society, 1984). Complexation reactions with humic and other organic substances (Chapter 3) attenuate the metal concentration towards the later stages of the landfill stabilization process (Knox and Jones, 1979).

Municipal solid waste may contain faecal material from a number of different sources and this raises the possibility that landfill leachate may contain enteric pathogens, including enteric viruses (Englebrecht and Amirhor, 1976; Peterson, 1974). Sobsey (1975, 1978) identified enteric viruses in only one leachate of the 21 different landfills tested in the USA. It would be expected that any viruses present in leachate would be reduced by dilution in ground and surface waters and by virus inactivation. Substantial virus reductions would also be expected if the leachate travelled through soil. Novello (1974) found that only 10 cm of gravelly, silty sand removed from 80.0 to 98.6% of poliovirus from experimentally contaminated leachate. Compared to domestic sewage, which has average virus concentrations of 103 to 105 per litre, the enteric virus contribution to the environment from municipal solid waste leachate is negligible.

2.5 LANDFILL LEACHATE TREATMENT

In the UK many landfills continue to operate on the dilute and disperse principle, with reliance being placed on the capacity of the underlying strata to attenuate contaminants in leachate. As leachate percolates through the underlying strata, many of the pollutants will be removed by physical, chemical and biological processes. The extent of the attenuation depends on the characteristics of the soil (Chapter 3).

In the USA and some European countries e.g. West Germany and Italy, it is becoming mandatory to install an impermeable liner to contain the leachate within the site (County Surveyors' Society, 1984). Almost certainly the need to treat leachate in the UK will increase as tighter environmental controls are imposed (Harrington and Maris, 1986).

The successful treatment of leachate is particularly difficult and the general problems include:

- the organic strength of undiluted leachate is typically many times greater than that of sewage, and high concentrations of ammoniacal nitrogen may also be present

- leachate production may only exist for 5-10 years and on many sites the composition and rates of flow may be subject to large seasonal variations

- leachate characteristics change significantly with age of landfill

- leachate may contain materials, e.g. heavy metals, that upset the efficiency of biological treatment and anaerobic digestion units

- leachate may lack some required nutrients e.g. phosphorus

- on-site technical back-up may be limited

On-site treatment options include (i) aerobic oxidation, i.e. lagoons, trickling filters, activated sludge plants (ii) anaerobic oxidation (iii) physical-chemical treatments (iv) recycle on landfill and (v) land application. Alternatively, the leachate may be treated off-site at the local sewage works.

In general, those systems which have been able to treat leachates most successfully (both in laboratory and full scale studies) have used aerobic biological treatment processes (Dewalle and Chian, 1977; Cook and Foree, 1974; Boyle and Ham 1974; Pohland and Kang, 1975; Chian and Dewalle, 1977; Farquhar and Rovers, 1975; Spencer and Farquhar, 1975; Carlson and Johansen, 1976; Uloth and Mavinic, 1977; Temoin, 1980; Robinson, 1980; Ehrig, 1984; Venkataramani and Ahlert, 1984; Maris et al, 1984). All studies showed that BOD and COD can be substantially reduced, particularly in leachates from recently emplaced wastes where readily degradable substances comprise a large proportion of the organic material. Several studies indicated that treatment is retarded by the low phosphorus concentrations in leachate, and additions of this nutrient were necessary (Boyle and Ham, 1974; Chian and Dewalle, 1977). Leachates from older, more decomposed wastes are less amenable to biological treatment because a higher proportion of the organic material consists of relatively refractory compounds such as humic and fulvic acids. With the exception of studies at the University of British Columbia (Zapfe-Gilje, 1979; Zapfe-Gilje and Mavinic, 1981; Graham, 1981) and at the Water Research Centre (Robinson, 1980; Robinson and Maris, 1983; Maris et al., 1984) most of this work was carried out at temperatures of 20°C and above. At the much lower temperatures of U.K. winter conditions, when greatest volumes of leachate are produced, treatment efficiency may be effected (Robinson and Maris, 1985). Full-scale aeration systems also need to accommodate fluctuating flows and changes in strength and composition of leachate. Nevertheless, several full-scale aerobic treatment plants are in operation in the U.K. (Dorset County Council, 1981; Knox, 1983; Robinson, 1986) and abroad (Steiner et al., 1977; Steiner and Growes, 1980; Stegmann and Ehrig, 1980; Keenan et al, 1984; Cossu, 1981).

Anaerobic biological treatment processes have several advantages over aerobic processes including generation of methane gas, lower production of biological solids, and no need for aeration equipment. (Foree and

Reid, 1973; Boyle and Ham, 1974, Chian and Dewalle, 1977; Bull et al, 1983; Henry, 1985).The main disadvantages of anaerobic treatment is the cost of construction, and the sensitivity of the anaerobic methanogenic bacteria to acidic pH and some metals. In addition, very little removal of ammonia is achieved. The system is also not able to withstand variable loads, which is one of the distinctive features of landfill leachate. The use of upward flow anaerobic digestors is currently being investigated (Mosey and Maris, 1982; Young and Maris, 1987).

A less sophisticated anaerobic treatment is recirculation of leachate through the landfilled refuse. The immediate appeal of this method is that by spraying liquid onto unsaturated refuse the volume may be reduced by evaporation and absorption by the waste. Pollutants which can potentially be reduced in concentration are volatile acids and hence BOD and COD, but there will be no significant effect on the content of chloride, sodium, potassium and ammonia (Emcon Associates, 1976; Pohland, 1976; Cameron and Koch, 1980; Pohland, 1980; Tittlebaum, 1982). A full-scale study of leachate recirculation has been carried out by the Water Research Centre (Robinson et al, 1982; Robinson and Maris, 1985). Although the BOD and ammonia concentration can be reduced, the resultant levels may still be unacceptably high; further treatment may well be required to remove these pollutants. Additionally, although the leachate volume can be reduced by evaporation from the surface during spraying, the overall volume of liquid discharging from the site is increasing with time as perched areas of saturation increase due to continued spraying.

The apparent difficulty in operating biological processes has led many workers to investigate physical and chemical processes. Chemical methods which have been used to treat leachate have involved the addition of chemicals to precipitate, oxidise or reduce inorganic or organic fractions. The use of lime, ferric chloride and alum have been shown to have little effect on organic matter removal (Bjorkman and Mavinic, 1977; Ho et al, 1974; Thornton and Blanc, 1973; Chian and Dewalle, 1976). Removal of colour, suspended solids and metals are good, although high sludge yields would require further disposal. Attempts have been made to remove organic matter using chemical oxidants. Experimental work (Ho et.al., 1974; Boyle and Ham, 1974) evaluating chlorine, calcium, hypochlorite, potassium permanganate and ozone gave excellent removal of colour and iron. Hypochlorite produced the best results and reduced the COD of the leachate by 48%. Activated carbon has been investigated and results indicated between 34-59% COD removal for untreated leachate (Bjorkman and Mavinic, 1977) and 81% for lime treated leachate (Uloth and Mavinic, 1977). Hydrogen peroxide has been used successfully in the amelioration of odours due to hydrogen sulphide (Fraser and Sims, 1983). The high concentration of ammonia present in landfill leachate can be reduced by the process of air stripping (Steiner et al., 1977; Smith, 1984; Arab, 1985). The pH of the leachate is first adjusted to between 10.5 and 11.5 by the addition of lime. This causes the formation of ammonia gas which is then removed by contact with air either in a pond system or stripping tower. In summary, physical and chemical treatment processes are inadequate as only low organic matter removals have been reported. Operating costs can be high because of excessive chemical dose rates and increased sludge production.

Spray irrigation of leachate to adjacent land or to a completed landfill has proved to be an effective process (Norstedt et al, 1975; Rowe, 1979; Newton, 1979; King, 1981; Hawley, 1983). Significant reductions in volume can occur due to evapotranspiration. In addition, as the leachate percolates vegetation and soil this provides opportunities for degradation of organic components, removal of inorganic ions by precipitation or ion exchange, and possible rapid uptake of components such as ammonia by plants. The process of land treatment will be reviewed more extensively in Chapter 3.

Direct discharge to sewer or tankering to a sewage works are the simplest disposal options. In principal a works should be able to accept leachate provided the proportion of the pollution load contributed by the leachate is not so great as to significantly disturb the normal biological treatment process at the works, or to exceed its treatment capacity (Boyle and Ham, 1974; Palit and Qasim, 1977; Chian and Dewalle, 1977; Raina and Mavinic, 1985). The important feature of leachate in this respect is that its pollution load per unit volume may be some 10-20 times that of sewage. In addition treatment charges will be levied by the water authorities based on the organic load of the leachate. Comparison of costs of on-site treatment and direct discharge to sewer (Water Research Centre, 1981) indicate that little economic benefit was to be obtained by using a direct discharge unless the strength of leachate was less than 2000 mg/l COD.

In the treatment of complex wastewaters such as landfill leachate, no single technology will prove to be a panacea. Different strategies are required to match treatment to the changes in leachate volume and strength as the landfill ages. Biological treatment methods will be particularly suited to leachate from freshly emplaced waste. Leachates from older wastes are less readily biodegradable and may require a combination of treatment methods including both physical-chemical and biological processes.

CHAPTER 3 SOIL AS A WASTE TREATMENT MEDIUM

3.1 SOIL PHYSICAL PROPERTIES AND REACTIONS

3.1.1 Introduction

The physical characteristics of the soil are equally as important as the biological and chemical characteristics for pollutant attenuation (Fuller, 1978; Fuller, 1977; Cope et al., 1983; Fuller et al., 1981; Korte et al., 1976). Some prominent physical soil characteristics and processes that influence movement and retention of pollutants in soils are: (a) soil texture, (b) surface area, (c) soil structure, (d) type of clay mineral, (e) stratification of materials, (f) compaction, (g) restrictive layers, (h) hydraulic conductivity, (i) shrinking and swelling, and (j) drying and wetting, as well as freezing and thawing (Fuller, 1980; Fuller, 1981; Soil Survey Staff, 1951). All of the factors that influence soil permeability play an important role in pollutant attenuation by soil.

3.1.2 Soil Texture

Soils may be divided on the basis of their dominating particle size into six arbitrary categories which are called boulders, cobbles, gravel, sand, silt and clay. These size ranges, as defined in British Standard 1377 (1975) and in Code of Practice CP 2001, are given in Figure 3.1. For the coarse soil fraction the proportions of the various sizes are determined from the sizes of square openings in sieves, whereas for fine soil particles they are based upon diameters for equivalent spheres obtained from a sedimentation analysis, notwithstanding that particles in the fine silt to clay range are far from spherical.

Particle size mm.	Designation		Test procedure
> 200		BOULDERS	Measurement of seperate pieces
200		COBBLES	
60	Coarse	GRAVEL	Sieve analysis
20	Medium		
6	Fine		
2	Coarse	SAND	
0·6	Medium		
0·2	Fine		
0·06	Coarse	SILT	Sedimentation analysis
0·02	Medium		
0·006	Fine		
0·002 and less		CLAY	

Figure 3.1 Classification of soils by particle size.

Many clay particles consist of thin flat plate-like or elongated particles (Figure 3.2). Texture names can be assigned to soils from mechanical analysis and plotted as a soil texture triangle (Figure 3.3).

Texture and the related surface area of the soil particles (Table 3.1) have been shown to dominate the migration rate of trace and heavy metals through soils (Korte et al., 1976; Fuller, 1981). Sand is found to be negatively correlated to heavy metal ion attenuation and clay positively correlated.

3.1.3. Mineral Constituents of Soils

The mineral constituents of a soil are dependent on the parent material from which they were derived. Quartz (SiO_2) commonly dominates the finer grades of sand as well as silt (Figure 3.4). Quartz and some other primary minerals have persisted with little change in composition from the original rock. Other minerals such as the silicate clays and iron oxides have been formed by the weathering of less resistant minerals and are therefore called secondary minerals (Brady, 1974).

The type of clay mineral dominating the soil influences the physico-chemical behaviour of the soil. Clay minerals vary considerably in composition and properties (Jackson, 1963). In a broad way, two groups of clays are recognised: the silicate clays and the hydrous oxide clays (Brady, 1974). The basic structural units of the silicate clay minerals are the silica tetrahedron and the alumina octahedron (Figure 3.5a). The basic units combine to form sheet structures which are represented symbolically in Figure 3.5b. The way in which these sheets are stacked, the bonding between sheets and the substitution for aluminium and silicon by other ions account for the compositional and physical variations in clay minerals (Grim, 1968). The three major silicate clay minerals are kaolinite, illite and montmorillonite.

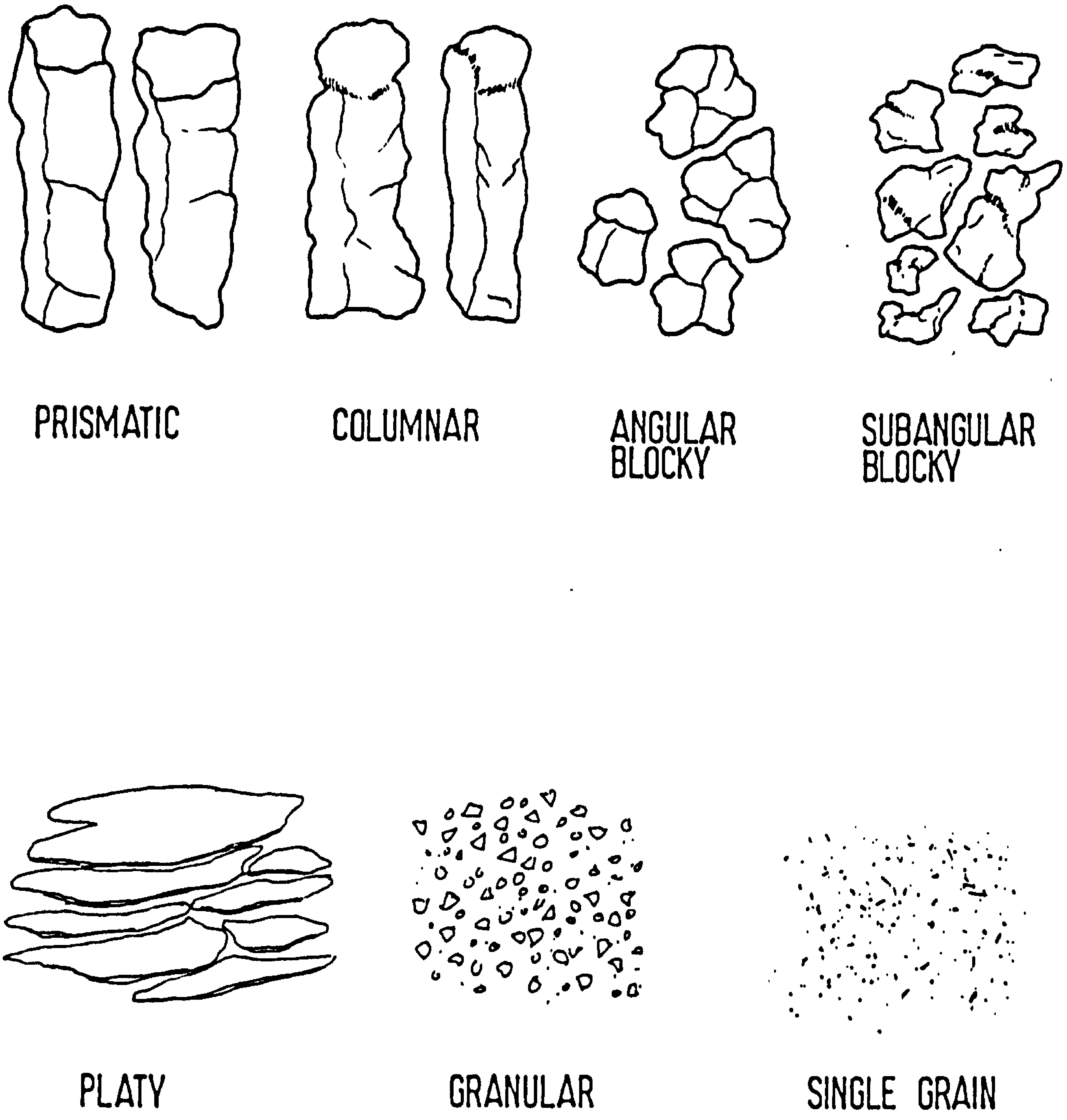


Figure 3.2 Diagrams of some naturally occurring and observable soil structure.

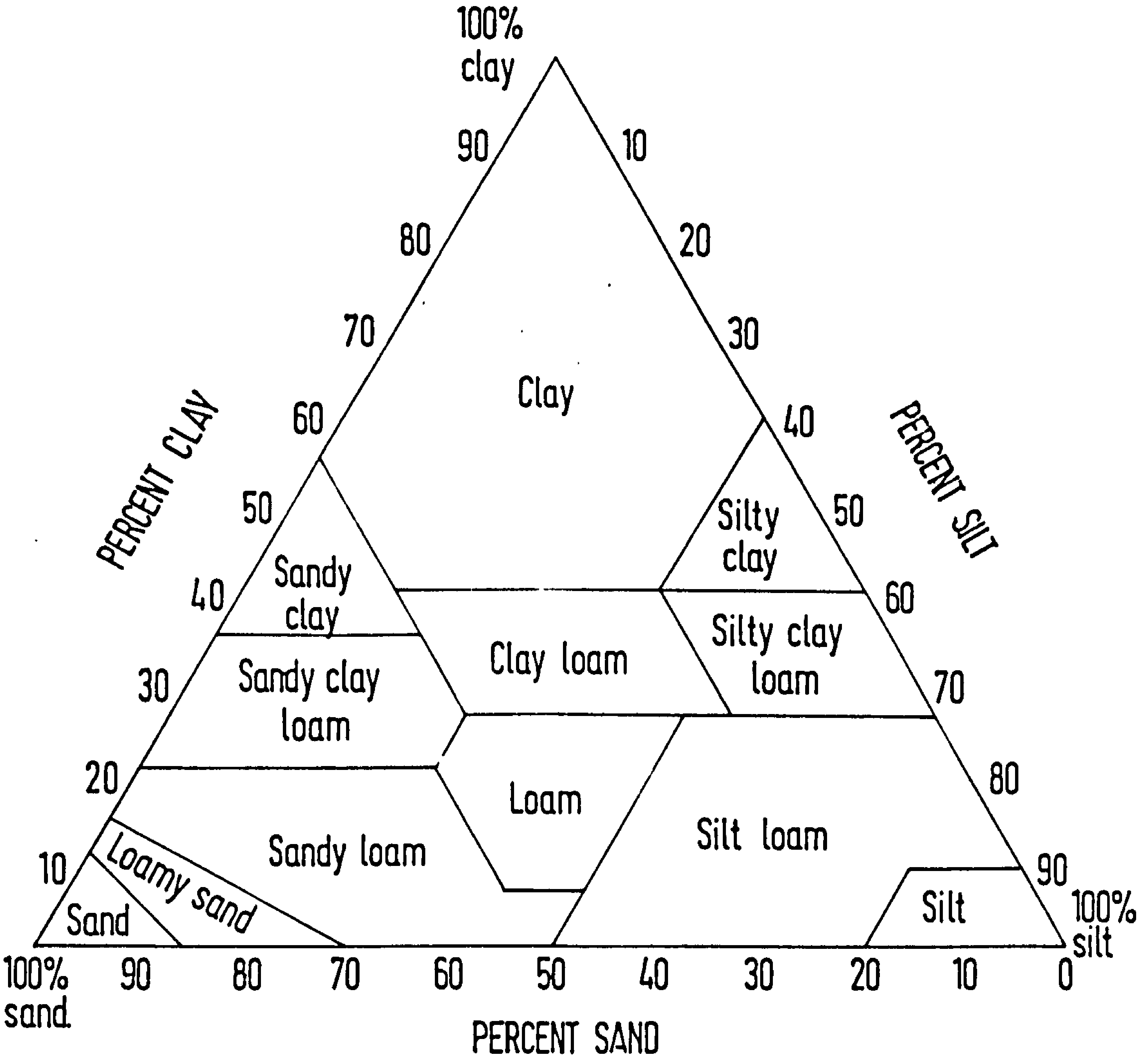


Figure 3.3 Soil Texture Triangle

TABLE 3.1 PARTICLE SIZE, MASS AND SURFACE AREA OF EQUAL SPHERES

Equivalent Soil Category	Particle size (mm)	Approximate mass of particle(g)	Approximate number of particles per gram	Approximate surface area	
				(mm^2/g)	(m^2/g)
Small cobble (largest 'soil' particle)	75	590	(1.7/kg)	30	
Coarse sand	1	0.0014	720	2300	
Fine sand	0.1	1.4×10^{-6}	7.2×10^{5}	23000	0.023
Medium silt	0.01	1.4×10^{-9}	7.2×10^{8}	23×10^{5}	0.23
Clay (smallest size measured)	0.001	1.4×10^{-12}	7.2×10^{11}	2.3×10^{6}	2.3

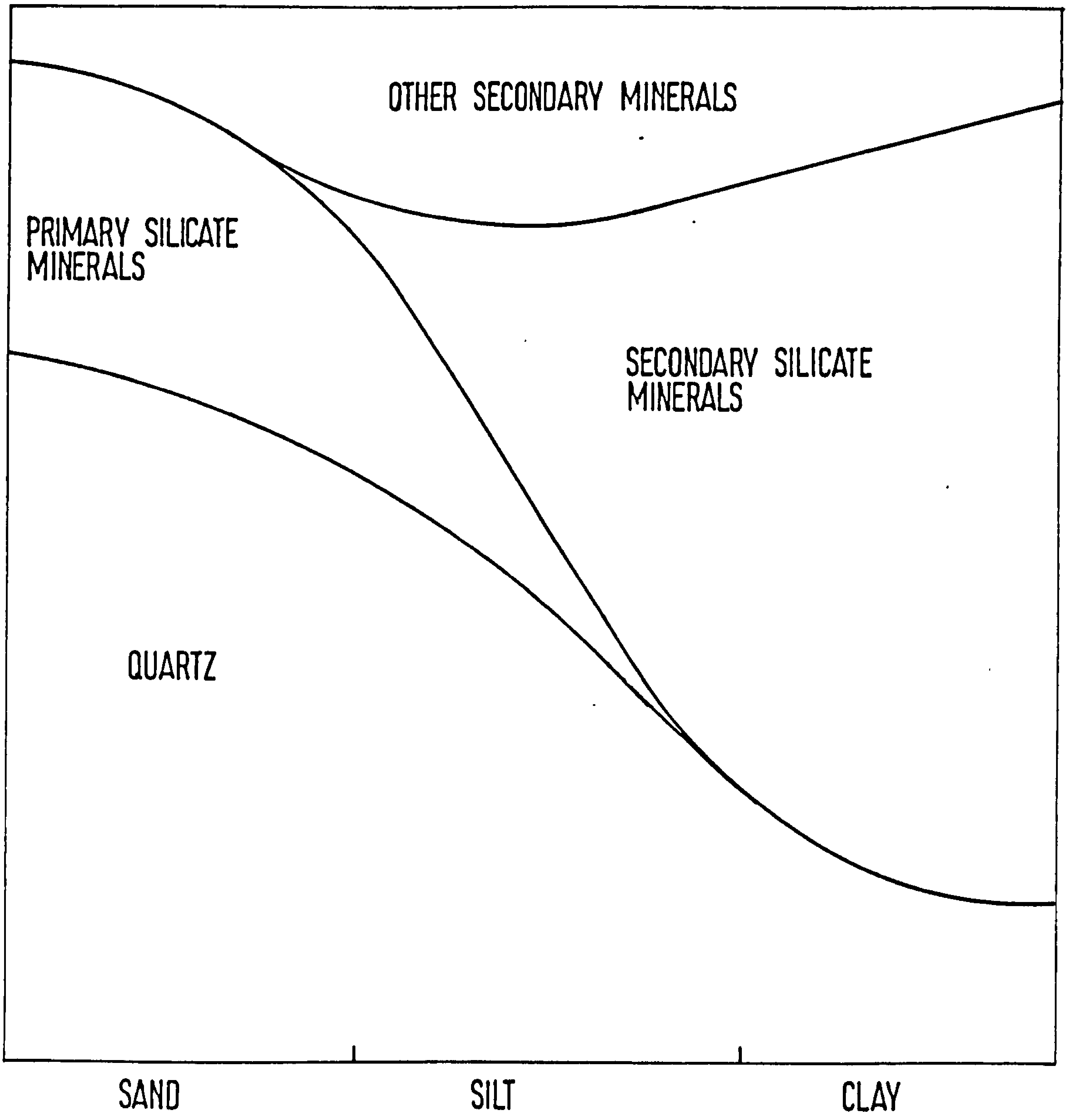


Figure 3.4 General relationship between particle size and kind of minerals present (Brady, 1984)

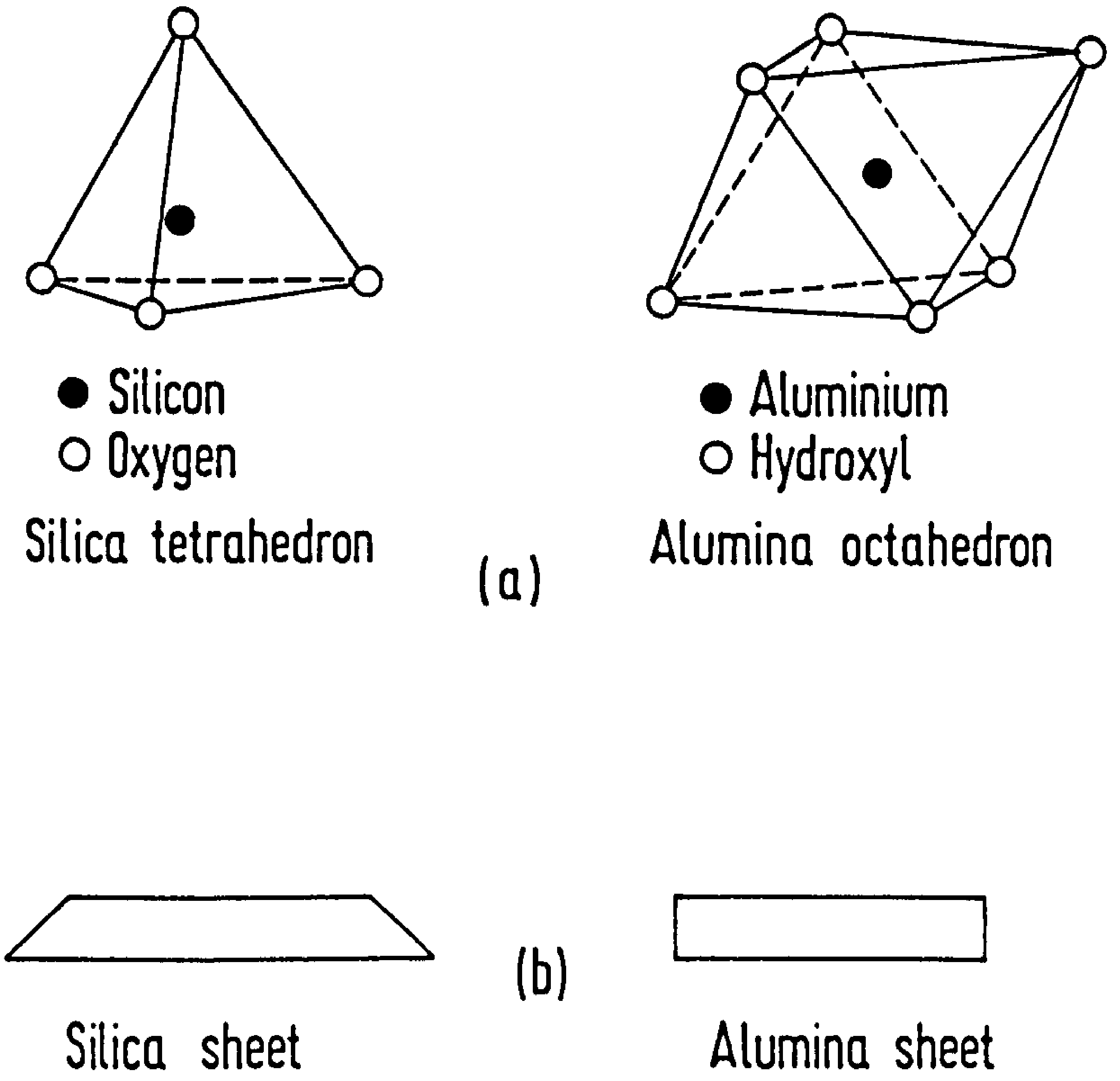


Figure 3.5 Clay Minerals: basic units

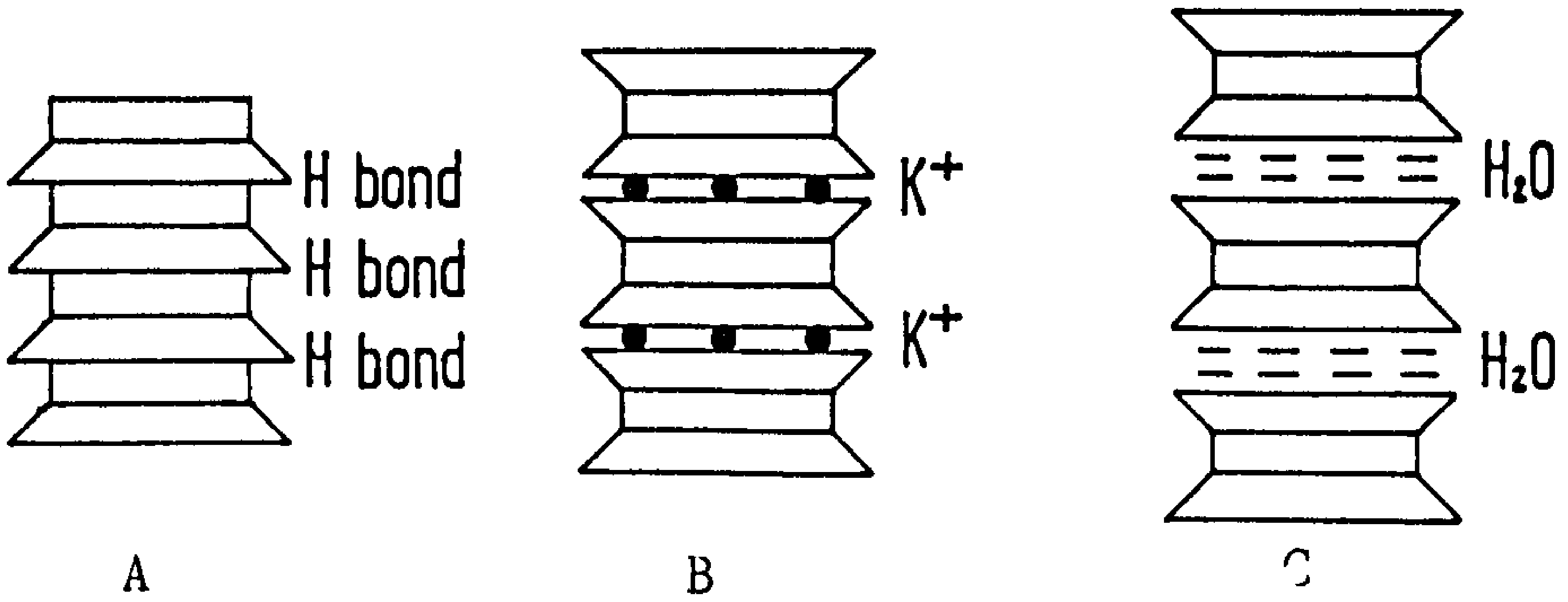


Figure 3.6 Clay Minerals: (A) Kaolinite (B) Illite
(C) Montmorillonite

Kaolinite consists of a structure based on a single sheet of silica tetrahedrons combined with a single sheet of alumina octahedrons and therefore it is a 1:1 type mineral (Figure 3.6a). The combined silica-alumina sheets are held together fairly tightly by hydrogen bonding (i.e. ionic bonding); a kaolinite particle may consist of over 100 stacks. Kaolinite is principally formed as an alteration product of feldspars, feldspathoids and muscovite as a result of weathering under acidic conditions (Bell, 1981).

Within the 2:1 family of clay minerals is a group commonly known as the smectites. They have a basic structure consisting of a sheet of alumina octahedrons between and combined with two sheets of silica tetrahedrons. Within the structure of these clay minerals, the sheets experience considerable isomorphous substitution. Isomorphous substitution occurs when, for instance, a magnesium atom substitutes for an aluminium atom on a 1 to 1 basis. Therefore, each substitution results in an unsatisfied negative valence. In the octahedral sheet there is partial substitution of aluminium by magnesium and iron, and in the tetrahedral sheet there is partial substitution of silicon by aluminium. In illite combined sheets are linked together by potassium molecules (Figure 3.6b). In montmorillonite clay minerals the space between the sheet is occupied by water molecules and (exchangeable) cations other than potassium (Figure 3.6c). There is a very weak bond between the combined sheets due to these ions. Considerable swelling of montmorillonite can occur due to additional water being adsorbed between the combined sheets. Montmorillonite virtually always has some octahedral sheet cations exchanged with magnesium or sodium. The layers, each consisting of three sheets, are generally stacked with bonding between successive layers by Van der Waals forces. Due to the charge deficiencies which exist within the lattice, resulting from frequent substitutions, cations may be present between the layers to balance charge deficiencies. These interlayer bonds are therefore relatively weak and easily separated by imposed stresses such as the adsorption of water or other polar liquids.

Due to the lattice substitutions within the basic sheets and the cations within the interlayer needed to balance charge deficiencies, the cation exchange capacity is relatively high.

Hydrous oxide clays are iron and aluminium oxides containing associated water molecules e.g. gibbsite ($Al_2O_3.3H_2O$) and goethite ($Fe_2O_3.H_2O$). They may carry negative charges and thus serve as a central micelle around which a swarm of cations are attracted. However, the much smaller number of negative charges per micelle means that cation adsorption is even lower than for kaolinite.

3.1.4. Soil Aeration

Soil aeration is the mechanism of gas exchange in soils that prevents oxygen deficiency and CO_2 toxicity. Thus, a well-aerated soil is one in which gas exchange between the soil air and the atmosphere is sufficiently rapid to prevent a deficiency of oxygen or a toxicity of CO_2 and thereby permits normal functioning of plant roots and aerobic microorganisms (Brady, 1974).

A soil in which aeration is considered satisfactory must have sufficient gas filled pores to allow gas exchange with the atmosphere and reduce the chances of localised anaerobic pockets or microsites developing which can greatly alter the rate of organic matter decomposition (Lynch, 1983). Most of the gaseous interchange in soils occurs by diffusion. Each gas tends to move in a direction determined by its own partial pressure. Diffusion also seems to be directly related to the volume of pore spaces filled with air. On heavy-textured soils, and in compact subsoils, the rate of gaseous movement is seriously slow (Table 3.2). Moreover, such soils allow very slow penetration of water into the surface layer. This prevents the rapid replacement of air high in CO_2 and the subsequent inward movement of atmospheric air. Boynton (1941)

TABLE 3.2 RELATIONSHIP BETWEEN OXYGEN DIFFUSION RATES (ODR) AND SOIL TYPE (STOLZY AND LETEY, 1961)

	ODR (x 10^{-8} g/cm^2/min) AT THREE SOIL DEPTHS		
SOIL TYPE	10 cm	20 cm	30 cm
LOAM	53	31	38
SILT LOAM	49	26	32
LOAM	27	27	25
LOAM	58	60	16
SANDY LOAM	36	32	34
CLAY LOAM	7	9	-
SANDY LOAM	64	45	39

found that the O_2% in the soil air decreased with depth, the rate of decrease being much more rapid with a clay soil than a sandy soil (Figure 3.7).

The total porosity of a soil is determined chiefly by the bulk density and this in turn is related to factors such as soil texture and structure. While clay soils may have a higher total porosity then sandy soils, most of their pores will be in the form of micropores as opposed to macropores. The macropores characteristically allow the ready movement of air and percolating water. In contrast, the micropores impede air movement and water movement is restricted primarily to slow capillary movement. Thus, in a sandy soil, in spite of the low total porosity, the movement of air and water is surprisingly rapid because of the dominance of the macropores. In fine textured soils the dominating micropores often maintain themselves full of water and aeration, particularly in the subsoil, is often inadequate for satisfactory root development and desirable microbial activity. Probably the most apparent effect of poor soil aeration on microbiological processes is a decrease in the rate of organic matter oxidation. If the soil porosity is reduced below 10-12%, soil oxygen renewal is extremely slow.

3.2 SOIL BIOLOGICAL PROPERTIES

3.2.1 Soil Microflora

The soil provides a suitable habitat for a diverse range of organisms which can help to render waste less hazardous. Hamaker (1971) reports that biological action accounts for approximately 80% of waste degradation in the soil. The range of organisms that degrade land applied waste is illustrated in Figure 3.8.

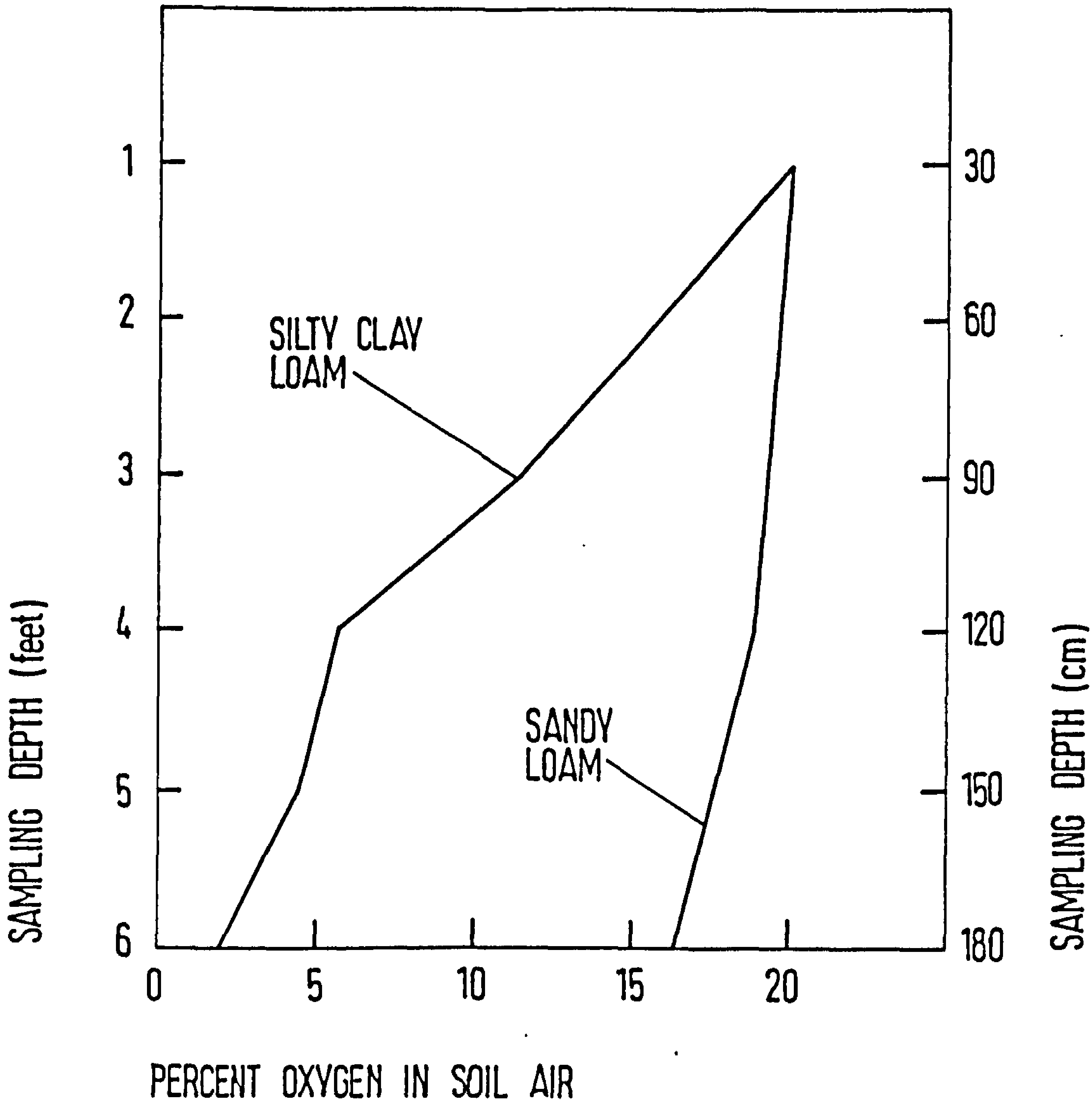


Figure 3.7 Average oxygen content of two orchard soils (Boynton, 1941)

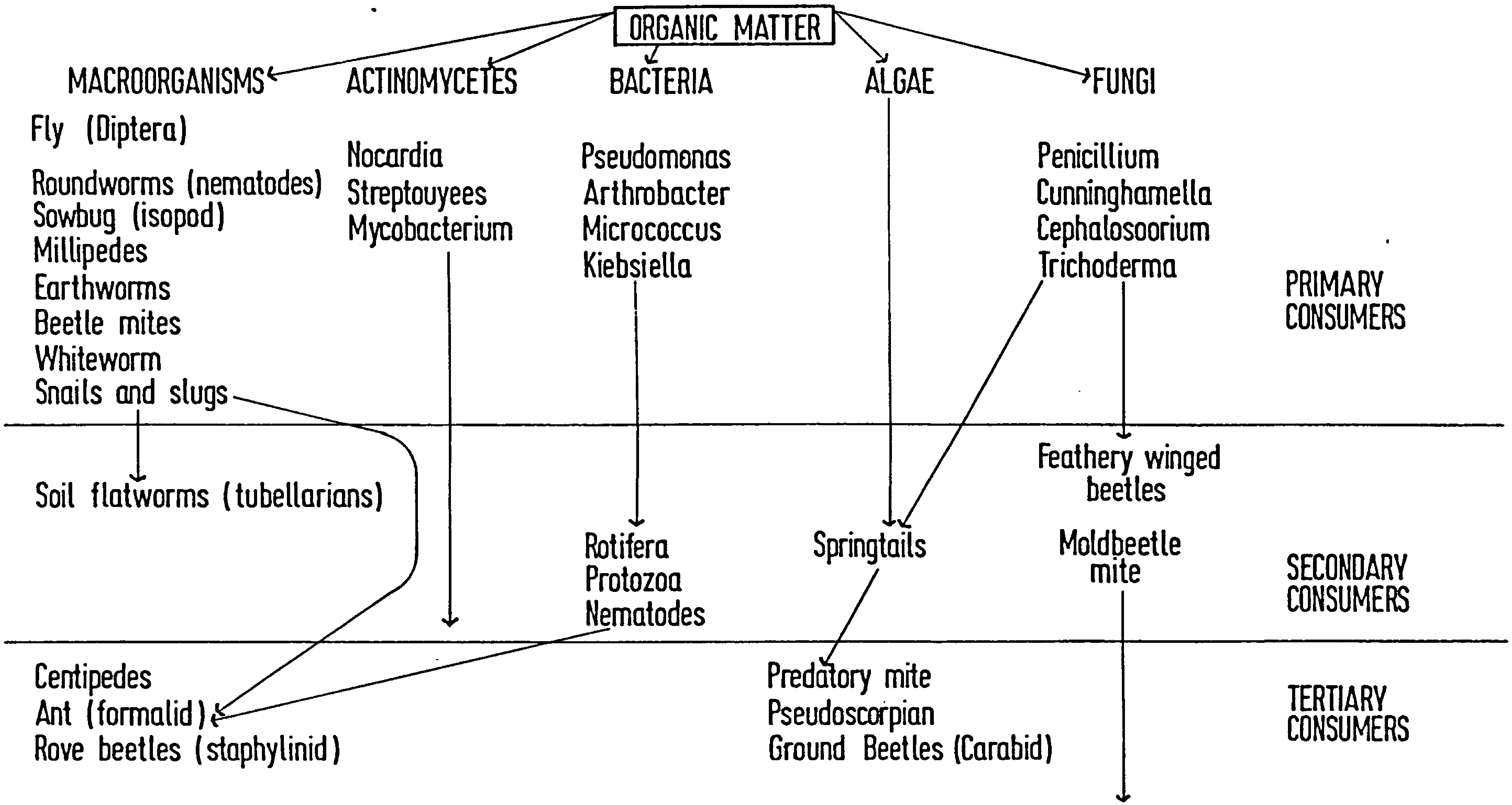


Figure 3.8 Cycle of organisms that degrade land applied waste.

The population establishment of decomposer organisms following the land application of a waste material begins with bacteria, actinomycetes, fungi and algae (Dindal, 1978). These organisms have diverse enzymatic capabilities and can withstand extremes in environmental conditions. Following establishment of microbial decomposers, the second and third level consumers establish themselves and feed on the initial decomposers and each other. Secondary and tertiary consumers include worms, nematodes, mites and flies. As these organisms use waste components, energy and nutrients from organic materials are released and distributed throughout the immediate environment.

Bacteria are the most abundant of soil micro-organisms (Table 3.3), yet they account for less than half of the total microbiological cell mass (Alexander, 1971). Bacteria found in soil may be indigenous to the soil or invaders which enter via precipitation, disease tissue, or land applied waste. The genera of bacteria most frequently isolated from soil include *Arthrobacter*, *Bacillus*, *Pseudomonas*, *Agrobacterium*, *Alcaligenes* and *Flabobacterium* (Alexander, 1971). Bacterial growth or inhibition is influenced by moisture, available oxygen, temperature, pH, organic matter content, and inorganic nutrient supply. In temperate areas, bacterial populations are generally greatest in the upper layers of the soil, although in cultivated soils the population is less dense at the surface due to the lack of moisture and the bactericidal action of sunlight (Alexander, 1971). Bacterial activity is usually greatest in the spring and autumn months but decreases during the hot, dry summer and during cold weather (Anderson and Domsch, 1973). Most bacteria, along with fungi, protozoa and animals, are heterotrophes (Payne, 1970).

Under conditions of limited nutrient supply, actinomycetes become the predominate micro-organisms and use compounds which are less susceptible to bacterial attack. They are heterotrophic organisms that utilise organic acids, lipids, proteins, and aliphatic hydrocarbons. These organisms are a transitional group between bacteria and fungi, and

TABLE 3.3 APPROXIMATE NUMBERS OF ORGANISMS COMMONLY FOUND IN THE SOIL

ORGANISM *	ESTIMATED NUMBERS PER GRAM OF SOIL		
BACTERIA	3,000,000	to	500,000,000
ACTINOMYCETES	1,000,000	to	20,000,000
FUNGI	5,000	to	900,000
YEASTS	1,000	to	100,000
ALGAE	1,000	to	500,000
PROTOZOA	1,000	to	500,000
NEMATODES	50	to	200

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* There are also large numbers of slime, moulds, virus, phages, insects, worms, anthropods and mycoplasma.

appear to dominate other microbes in dry or cultivated areas (Alexander, 1971). Preliminary ecological influences on actinomycetes include moisture, pH, temperature, and amount of organic matter present. Addition of organic matter to the soil greatly increases the density of these organisms. In addition, actinomycetes seem to influence the composition of the microbial community due to their ability to excrete antibiotics and their capacity to produce enzymes capable of inhibiting bacterial and fungal populations.

Fungi are heterotrophic organisms and are affected by the availability of oxidisable organic substrates (Griffin, 1972). Other environmental influences affecting the density of fungal populations include moisture content, pH, organic and inorganic nutrients, temperature, available oxygen, and vegetative composition. Fungi can withstand a wide range of pH and temperatures. They also have the ability to survive in a quiescent state when environmental conditions are no longer favourable for active metabolism. These organisms, because of their extensive mycelial or threadlike network, usually compose a significant portion of the soil biomass (Waid, 1960). One of the major activities of fungi in the mycelial state is the degradation of complex molecules. In addition, fungi are active in the formation of ammonium and simple nitrogen compounds.

Algae use light as a source of energy and carbon dioxide as a source of carbon. Thus, algae are abundant in habitats where light is plentiful and moisture is available (Lund, 1965). The population of algae is normally smaller than bacteria, actinomycetes or fungi. Due to the inability of algal populations to multiply beneath the zone of soil receiving sunlight, the most dense populations are found between 5-10 cm deep. Algae can generate organic matter from inorganic substances. Normally, they are first to colonize barren surfaces, and the organic matter produced by the death of algae produces a source of carbon for future fungal and bacterial populations (Silvey and Roach, 1964). Surface blooms produced by algae bind together soil particles contributing to soil structure and erosion control.

The major importance of small worms in decomposing organic material is their abundance and relatively high metabolic activity. When sewage sludge is land applied, the total number of earth worms in the biomass is enhanced with increasing treatment. Mitchell et al. (1977) found sludge decomposition was increased two to five times by the manure worm. Increased earthworm populations also enhance soil porosity and formation of water stable soil aggregates, thus improving the structure and water holding capacity of the soil.

As nematodes, flies and mites use waste components energy and nutrients are released and made available to other decomposers. Nematodes harvest bacterial populations while processing solid waste material. Mold mites will feed on yeast and fungi. Beetle mites and springtails will also feed on molds, but usually under drier and more aerobic conditions. Flies are vital in the colonisation of new organic deposits. These insects are used to transport the immobile organisms from one site to another.

3.2.2 Biodegradation

Degradation is the loss of organic constituents from soil by chemical change induced by either soil organisms, photolysis, or reactions catalysed by soil. While the non-biological sources of chemical change can play an important role in degradation, the primary mechanism of organic chemical degradation is likely to be biological.

The full range of soil organisms are important to organic waste degradation, although habitation by micro-organisms depends on microbial utilization and detoxification of waste constituents. Soil texture and water content as well as the source and availability of nutrients, total salt concentration, pH, and temperature may be expected to have complex interdependent effects on the rate of respiration in a soil (Clark, 1967; MacFadyen, 1971; Alexander, 1971).

Water, although essential for microbial growth and transport (Wildung et al., 1975) has a limited effect on the rate of waste degradation over a broad range of soil moisture contents. Only under excessively wet or dry conditions does soil moisture content have a significant effect on waste degradation (Brown et al., 1981). Dibble and Bartha (1979) found a negligible difference in the microbial activity of oil-amended soil at moisture contents between 30% and 90% of the water holding capacity of the soil. Problems may occur when soil water fully occupies the pore spaces so that anaerobic conditions determine the biodegradation processes. Waterlogging characterizes the soil and anaerobic and facultative anaerobes dominate; decomposition slows down and intermediate degradation products accumulate (Tate, 1979). Gases such as methane, hydrogen, nitrogen, carbon monoxide, and carbon dioxide are evolved.

The texture and structure of the soil exerts a significant influence on the rate of waste biodegradation (Edwards, 1973). In a laboratory study evaluating the biodegradation rates of two wastes in four soils, the most rapid degradation occurred in the silt loam soil and the least rapid in the clay soil (Table 3.4). The low degradation rate exhibited by the clay soils was at least partly due to anaerobic conditions that developed in these soils. It has been demonstrated that both inorganic and organic colloids such as clays and humic substances can stimulate microbial growth and metabolism (Filip, 1973; Martin et al., 1976; Marshall, 1978). The maintenance of a more favourable pH has been suggested as a reason for this as well as adsorption of micro-organisms and nutrients onto the colloid surfaces.

TABLE 3.4 THE EFFECT OF SOIL TEXTURE ON THE BIODEGRADATION OF PETROLEUM SLUDGE (Brown et al, 1981)

SOIL	TOTAL CARBON APPLIED(mg)	% CARBON DEGRADED AS DETERMINED BY	
		CO_2 EVOLVED	RESIDUAL C
Norwood Sandy Clay	2,100	15	34
Lakeland Sandy Clay	2,100	13	20
Nacog Doches Clay	2,100	9	32
Bastrop Clay	2,100	0.3	19

In general, the optimum pH for bacteria in soils is between 6.5 and 8.5. Verstraete et al. (1975) found the optimum pH for microbial activity to be 7.4 with inhibition occurring at a pH of 8.5. Dibble and Bartha (1979) noted a significantly higher biodegradation rate for oily sludge at soil pH of 7.0 to 7.8, than at pH 5 to 6.

Although microbial decomposition of organic materials occurs most rapidly in the mesophilic (25°C to 55°C) range, higher and lower temperature levels favour some other organisms, i.e. psychrophiles (0°C to 20°C) and thermophiles (45°C to 65°C). Thus biodegradation will occur over a wide range of temperatures, although it takes place more slowly near the extremes of 0°C and 65°C (Fuller and Warrick, 1985). In a six month laboratory study evaluating the rate of biodegradation of two API-seperator sludges in soil, the rate of biodegradation of both wastes doubled between 10°C and 30°C, but decreased slightly at 40 °C. (Brown et al., 1981). A 50 day laboratory study by Dibble and Bartha (1979) showed little or no increase in the rate of hydrocarbon degradation above 20°C. While temperature adjustments in the field are impractical, enhanced biodegradation rates may be achieved by delaying or reducing waste applications according to the soil temperature.

The speed and extent of microbial utilization of a substrate in soil will depend on either the diffusion of the substrate, the enzyme, or on the movement of the organisms (Adu and Oades, 1978). With insoluble substrates the ability of organisms to explore pore and aggregate surfaces will control the utilisation of the substrate. Fungal mycelium should be able to grow rapidly along the walls of coarse pores and even across the pores as the organism moves towards a potential substrate (Griffin, 1972). In the absence of continuous water pathways of requisite dimensions, spread of bacteria will be extremely slow as reproduction leads to the formation of another simple cell which may be pulled back within the boundary of the parent colony by surface tension.

The adverse effects of land treatment on the soil fauna may be reduced by a carefully planned program which may involve modifications of certain waste characteristics or environmental parameters. The factors affecting degradation which may be adjusted in the design and operation of a land treatment unit include soil parameters (moisture content, temperature, pH, available nutrients, available oxygen, and soil texture or structure) and design parameters (application rate and frequency). The frequency and rate of application of organic wastes to soil are design parameters that can be used to enhance waste biodegradation. The amount of residual solids in the soil influences both the availability of oxygen and the toxic effects of waste constituents on soil fauna. When small amounts of waste are applied frequently, the toxic effects of the waste on microbes are minimised and adequate time for re-aeration of the soil is available.

3.3 SOIL CHEMICAL PROPERTIES

3.3.1 Soil pH

Soil acidity occurs when exchangeable bases are leached from the soil. Alkalinity occurs when there is a high degree of base saturation. In general, the soil pH should be maintained between 6 and 7 to give adequate nutrient availability for plants and microbes without danger of toxicity or deficiency (Figure 3.9).

The ability of the soil solution to resist abrupt pH changes (buffering capacity) is due to the presence of hydrolisable cations, specifically Al^{3+}, on the surface of the soil colloid. In the soil Al^{3+} sorbed on the clay surface maintains equilibrium with Al^{3+} ions in the soil solution. As the Al^{3+} ions in the soil solution are removed by hydrolisation and precipitation as $Al(OH)_3$, surface-bound Al^{3+} ions migrate into solution to maintain equilibrium. These Al^{3+} ions will hydrolise and remove OH^- ions from solution, thus maintaining a stable

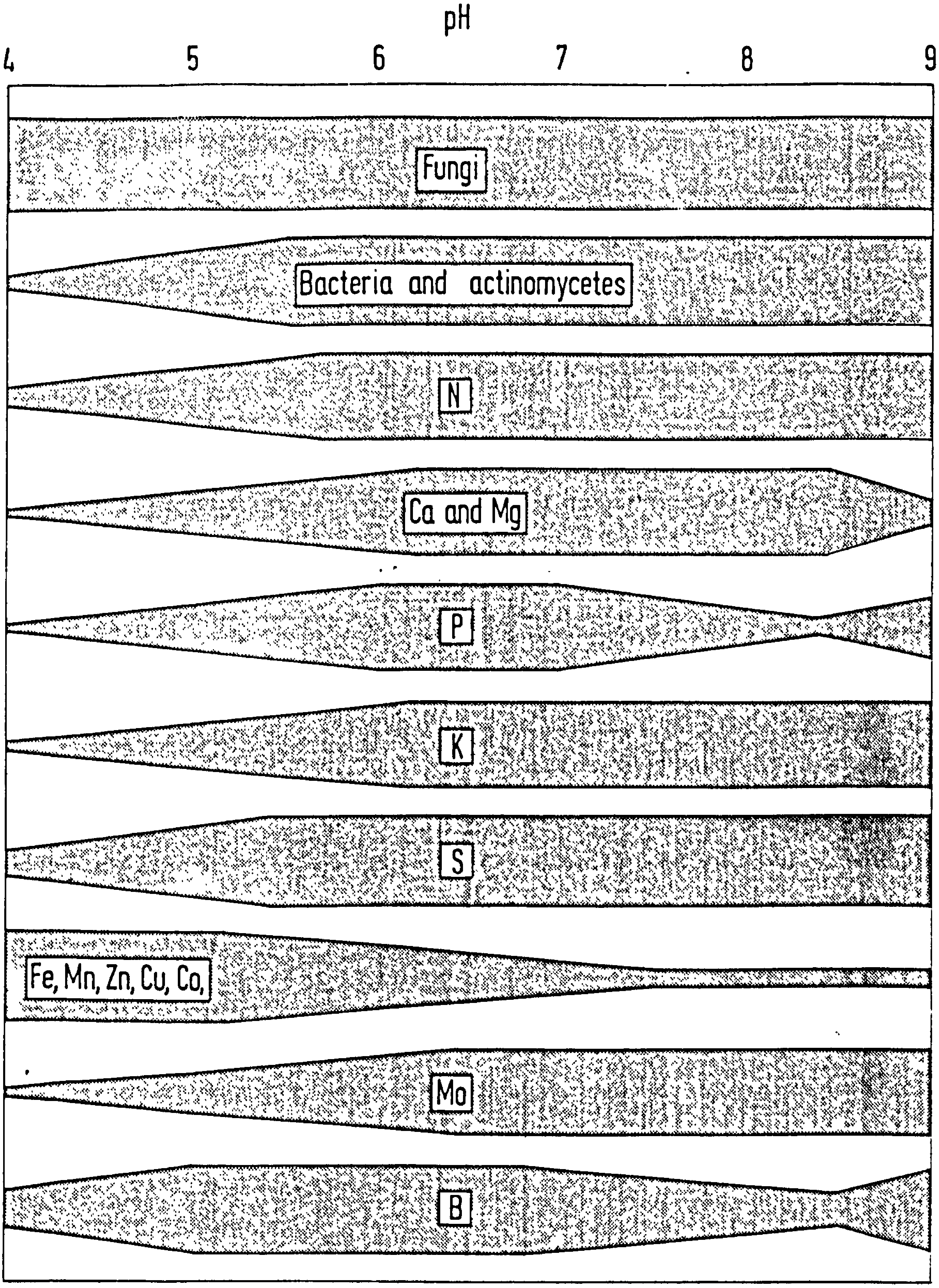


Figure 3.9 Relationships existing in mineral soils between pH and the activity of microorganisms and the availability of plant nutrients. The wide portions of the bands indicate the zones of greatest microbial activity and the most ready availability of nutrients.

pH. Simultaneously, as the sorbed Al^{3+} ions migrate into solution, other cations replace Al^{3+} ions on the soil colloid. As the pH of the soil solution is increased, the percentage of the cation exchange complex occupied by basic cations (base saturation) increases. There is a gradual rise in pH and the percentage base saturation. When an acid is added to a soil the reverse process occurs. The $Al(OH)_3$ dissolves and the available Al^{3+} ions replace the basic cations on the exchange complex.

The addition of large quantities of organic wastes may lower the pH of the soil due to the formation of organic and inorganic acids during decomposition. These not only supply H^+ for adsorption but also replace bases on the soil complex and encourage their solution from soil minerals. As the soil pH is lowered, there will be increasing solubilisation of metals which will affect both microbial growth and plant growth. Fuller and Warrick (1982) found that when acid wastes were added to soil, the pH of the soil assumed a much greater role in the rate and extent of metal movement. In acid soils almost all metals escaped sooner and in greater concentrations than soils of near neutral pH. This was due in part to the original low soil pH as well as to the lesser volume of acid required to bring the soil pH to a critical level for metal solubilisation. They found that the clay content of the soils tested influenced retention of soluble metals but with strong acids the retention was temporary and short-lived.

Two types of negative charges can be identified on soil colloids:- permanent charges and pH dependent charges. The first is associated primarily with the silicate clays resulting from isomorphic substitutions within the clay crystals. Cations are exchangeable at all pH levels at these sites. The second charge is directly related to soil pH rises. The effect of pH on the negative charge of soils is shown in Figure 3.10. It should be noted that at a pH of less than 6.5, cations are not readily adsorbed.

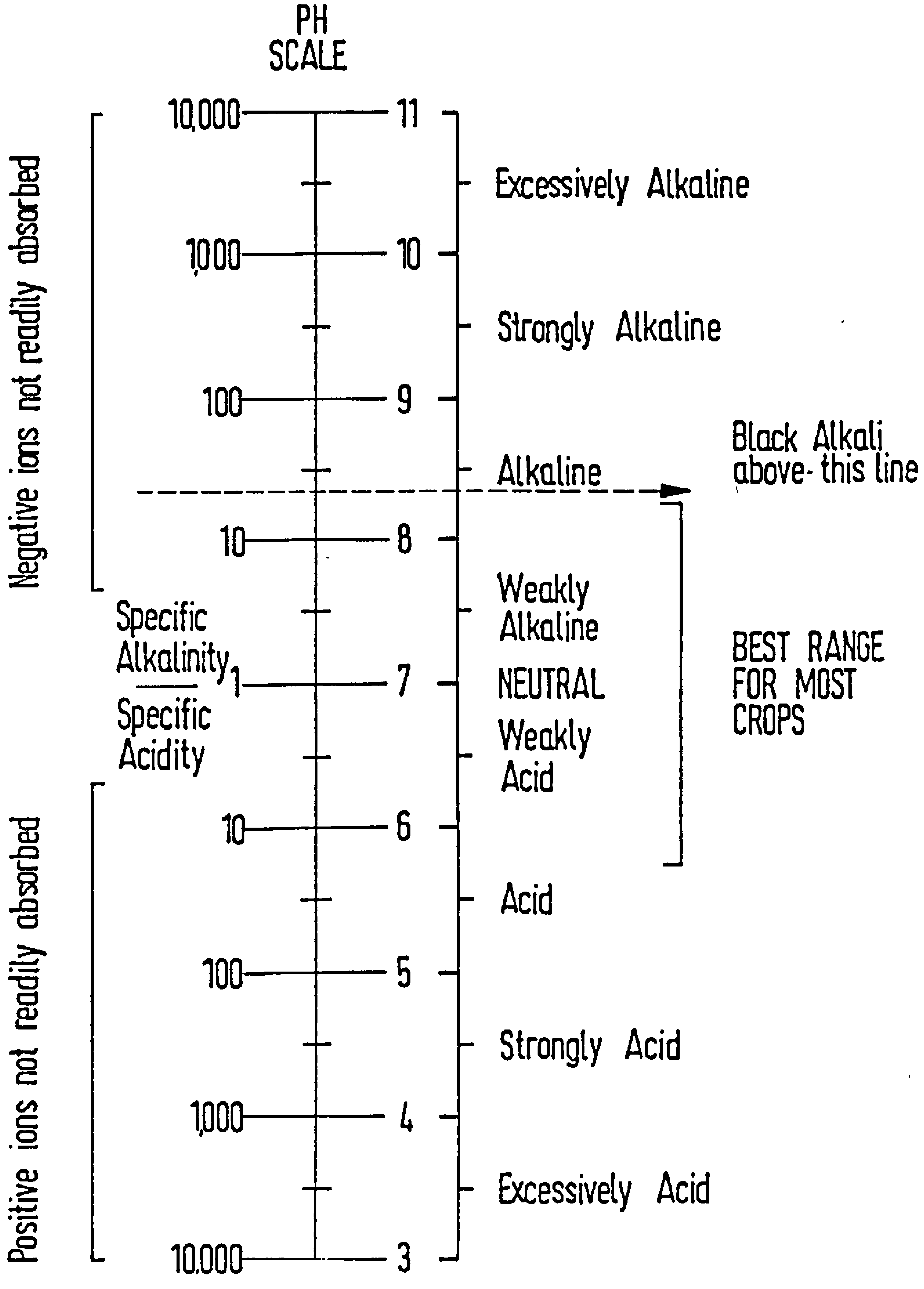


Figure 3.10 Effect of pH on ion adsorption.

3.3.2 Ion Exchange Reactions

All soil components contribute in some measure to ion exchange reactions. The ability of soil minerals to exhibit ion exchange properties is due primarily to the substitution of small amounts of divalent for trivalent cations, and trivalent for quadravalent cations, within the crystal structure of the soil minerals (section 3.1.3). The location within the mineral crystals, and the degree and types of substitutions that occur, differ from one mineral to another. This type of exchange capacity is relatively permanent.

The smectites, vermiculites, hydrous micas, chlorites and interstratified minerals, kaolins, feldspars, zeolites, allophanes, oxides and hydrous oxides are the most important of the inorganic constituents which contribute to cation exchange in soils (Gieseking, 1975). The source of negative charge resulting in cation exchange in the smectites, the micas and other related 2:1 layer silicates arises from the substitution of Mg^{2+} and Al^{3+} or Si^{4+} in the octahedral or tetrahedral sheets by isomorphic ions of smaller valency e.g Li^{+}, Mg^{2+}, Fe^{2+} and Al^{3+}. The smectites (e.g. montmorillonite) may have sufficient isomorphous substitution in either or both the tetrahedral and octahedral sheets to give a high interlayer negative charge and high cation exchange capacity (CEC) and to permit significant interlayer expansion and consequent shrinking and swelling of clay.

By contrast, the micas (e.g. illite) and related minerals, formed in K-rich environments, contain potassium ions (ionic radius = 0.133nm) to compensate for the negative charge resulting from isomorphous substitution. Its exact accommodation in hexagonal holes between the tetrahedral layers encourages interlayer sheets to approach very closely. Faults in the staking of 2:1 sheets only occur when the interlocking process is interrupted or when cations other than K occur as impurities. The K ion hydrates very weakly so that water and dissolved cations in it can only slowly penetrate the intersheet space along such faults.

The feldspars, which with micas form the two main K-bearing groups of soil minerals, are potassium and sodium aluminosilicates consisting of Si and Al tetrahedra randomly attached in the ratio 3:1. Negative charge arising from isomorphous substitution, as in the micas, does not occur but a pH dependent charge is measurable, increasing with smaller particle size (larger surface area). This arises from exposed hydroxyl groups at crystal edges, which may contribute to the CEC at the pH of equilibrium.

The kaolins (an aluminosilicate mineral of the 1:1 crystal lattice group; that is consisting of one Si tetrahedral sheet alternating with one aluminium octahedral sheet) are basically an octahedrally co-ordinated Al layer linked to a tetrahedral Si layer. Several hundred of such 1:1 layer sheets are close packed to form much larger platy crystals than those formed by the smectites, but with a smaller diameter: thickness ratio, and a smaller specific surface area. Only a small permanent negative charge (or CEC) is usually reported and it is not certain how much of this is related to either a small degree of isomorphous substitution of Al for Si or an equally small contamination with a hydrous mica.

The mineral fraction of soil also possesses an element of exchange capacity, which depends on the pH of the soil. This type of ion exchange is reflected in the retention of both cations and anions.

The nature of pH dependent exchange capacity of the mineral phase is not well understood but is thought to result primarily from the dissociation of hydrogen ions from structural elements at the crystal edges of aluminosilicate minerals (Aubert and Pinta, 1977). At pH values of 8 or more, the contribution of pH dependent changes to the total cation exchange capacity can be considerable. At pH values below 4 or 5 the retention of anions such as sulphates can be significant. However, in the pH range of 5 to 7 (characteristics of many soils) the retention of anions by this mechanism is small to insignificant.

In many soils organic matter is as significant as the mineral phase in determining ion exchange capacity, particularly for the surface soil at any location. For organic and peat soils, cation exchange due to organic matter predominates. The exact organic components that participate in exchange reactions are not well characterized. Organic matter in soils contains a variety of both acidic and basic chemical groups potentially available for cation and anion exchange respectively. The basic groups appear to have little activity, as evidenced by the relatively low anion exchange capacity of soils, except at very low pH. At normal soil pH values, acidic groups of humic material (e.g. carboxylic and phenolic functional groups) are weakly dissociated, providing opportunity for cation exchange (Bloom and McBride, 1979; Boyd et al., 1981).

At lower pH values the CEC of organic matter decreases, because fewer acidic groups are dissociated. Also, at lower pH considerably more Fe, Al, and heavy metal cations are present in solution. These types of cations interact strongly with exchange groups of organic matter and effectively block sites normally available to other types of cations. The CEC of organic matter increases significantly with pH. At pH values near neutral, the CEC of organic matter ranges from 50-400 meq/100 g, with values of more than 200 meq/100 g being common. Thus, on a unit weight basis, the organic fraction can contribute more than the clay fraction to the total CEC of a soil.

1 3.4 FATE OF ORGANIC COMPOUNDS IN SOIL

3.4.1 Introduction

To determine the suitability of a leachate for land treatment it is essential to understand the probable fates of the organic constituents in soil. Organic constituents of landfill leachates are frequently part of a complex mixture of organic and inorganic compounds. Many of the important types of organic compounds present in leachate are similar to the ones found in natural soils (Chian and Dewalle, 1977). Some of these are biochemicals such as proteins, lipids, carbohydrates and pigments that occur in living organisms.

Amending soils with high organic waste poses a stress on the available oxygen within the soil system. As long as that oxygen demand can be met the organic load should not be excessive. Under anaerobic conditions decomposition products will be organic acids such as lactic, butyric and citric acids. In addition, decomposition under anaerobic conditions proceeds much more slowly than under aerobic conditions (Schraa and Jewell, 1984). Under anaerobic conditions leachates having high levels of organic compounds will also have high levels of these low-molecular weight intermediates. These compounds have not yet been incorporated into the more stable group of large complex polymers, such as humic and fulvic acids, or have not decomposed further into smaller molecules such as CO_2, CO, NO_3 etc.

3.4.2. Organic Acids

Organic acids are organic constituents with carboxylic acid or phenolic functional groups. They compose the major organic fraction of landfill leachates (section 2.4).

Degradation of organic acids in soil can be relatively rapid under favourable environmental conditions. Martin and Haider (1976) showed that several carboxylic acids would degrade as rapidly as glucose in a sandy soil (Table 3.5). Higher molecular weight carboxylic acids may degrade more slowly (Moucawi et al., 1981). Hoeks and Borst (1982) studied the anaerobic digestion of free volatile fatty acids in soils below waste tips. Free volatile fatty acids i.e. acetic acid up to and including caproic acid, cause about 95% of the total COD value (Harmsen, 1983). Soil columns were percolated under anaerobic conditions with leachate containing varying amounts of free volatile fatty acids. The results are summarised in Table 3.6. They found that the higher the concentration of free volatile fatty acids, the longer the lag in the start of CH_4-fermentation. At the highest concentration level, equivalent to 26,624 mg/l acetic acid, fermentation did not start within the test period of 10 months. At 6471 mg/l acetic acid the lag phase lasted about 55 days and at 3046 mg/l acetic acid the lag phase was only 37 days. The COD of the effluent finally reached a value of about 7% to 8% of the leachate COD. No volatile fatty acids were left in the effluent; the remaining part of the COD represents persistent organic compounds. Sand, humic sand and clay soil were tested, but only at the highest acid concentration level of the influent. Apparently this concentration level was too high, for CH_4-fermentation did not occur in any of the last mentioned soils. The experiments with the sandy loam soil indicated that when the soil was capable of buffering the pH between 6.5 and 7.0 fermentation was more likely to take place.

Leaching and runoff of organic acids can be substantial due to the high water solubility of these compounds. Organic acids exist in soil as anions when the soil pH is greater than the dissociation constant (pKa) of the compounds. As anions, these compounds exhibit negative adsorption and are increasingly mobile in clay soils (Helling,1971).

TABLE 3.5 DECOMPOSITION OF THREE CARBOXYLIC ACIDS AND GLUCOSE IN SANDY SOIL (Martin and Haider, 1976)

Organic Constituent*	% Decomposition	
	After 7 days	After 84 days
Acetic Acid	52 - 76	71 - 87
Pyruvic Acid	47 - 83	70 - 93
Succinic Acid	52 - 89	71 - 95
Glucose	75	87

* All organics applied to soil at 1000 ppm

TABLE 3.6 SUMMARY OF RESULTS CONCERNING THE FINAL RATE OF CH_4 - FERMENTATION IN DIFFERENT SOIL COLUMNS AT 20°C (VFA = free volatile acids; AA = acetic acid equivalents; * = estimated; C_e = concentration in effluent; C_1 = concentration in influent leachate)

	Concentration in influent		Retention time in soil column (days)	Relative concentration in effluent (C_e/C_i)		Purification efficiency (%)	
	COD (mgl^{-1} O_2)	VFA (mgl^{-1} AA)		COD	VFA	COD	VFA
Sandy loam	6640	2740*	17	0.08	0	92	100
	6640	2740*	40	0.09	0	91	100
	7750	3046	18	0.06	0	94	100
	16000	6471	20	0.06	0	94	100
	60600	26624	21	1.00	1.00	0	0
Sand	21600	8900*	23	0.93	0.92*	7	8
Humic sand	64300	26179	19	0.98	0.98*	2	2
Clay	64300	26179	21	0.97	0.97*	3	3

3.4.3 Aliphatic Hydrocarbons

Aliphatic hydrocarbons are open chain compounds or cyclic compounds that resemble the open chain compounds. Included in this family are the alkanes, alkenes, alkynes and their cyclic analogs (Morrison and Boyd, 1975). While very few are hazardous they can often be the land limiting constituent in land application systems.

Degradation of aliphatic hydrocarbons in soil depends on molecular weight, vapour pressure, water solubility, number of double bonds, degree of branching and whether the compound has an open chain or cyclic configuration. Perry and Cerniglia (1973) ranked aliphatic and aromatic hydrocarbons from most to least degradable as follows: straight-chain alkanes (C12-C18) > gases (C2-C4) > straight-chain alkanes (C5-C9) > branched alkanes (up to C12) > straight-chain alkenes (C3-C11) > branched alkenes > aromatics > cycloalkanes. Microbial degradation of straight-chain alkanes proceeds faster than with branched alkanes of the same molecular weight (Humphrey, 1967). Degradation rate decreases with either the number and size of alkyl groups or the number of double bonds present. Straight or branched open chain aliphatics degrade much more rapidly than their cyclic analogs.

Microbial degradation of alkanes to carbon dioxide and water initially produces the corresponding organic acid (Morrill et al., 1982). Other degradation by-products of alkanes include ketones, aldehydes and alcohols, all of which are readily degradable in aerobic soil.

Cycloalkane and its derivatives are remarkably less degradable in soil than other aliphatic hydrocarbons. Haider et al. (1981) obtained no significant biodegradation of cyclohexane after the compound was incubated in a moist loess soil for 10 weeks. Moucawi et al. (1981) compared the biodegradation rates of saturated and unsaturated hydrocarbons in soil. Four soils were amended with 2,000 mg/kg of an alkane (octadecane) and the corresponding alkene (1-octadecene). While the percent of the added substrate that degraded varied between soils (16.4-32.3% degradation in 4 weeks), the amount of the alkane and alkene that degraded in a given soil was essentially the same. It was also noted that decomposition was consistently greater in non-acid as opposed to acid soils.

Volatilisation can be a significant loss mechanism for low molecular weight aliphatics which have a vapour pressure greater than 1 (Wetherold et al., 1981). Runoff and leaching of aliphatic hydrocarbons are generally thought to be minimal due to low water solubility (Raymond et al., 1976).

3.4.4 Aromatic Hydrocarbons

Aromatic hydrocarbons are cyclic compounds having multiple double bonds and include both mono- and polyaromatic hydrocarbons. Monoaromatic compounds are benzene and substituted benzenes such as nitrobenzene and ethylbenzene. Polyaromatic hydrocarbons are composed of multiple fused benzene rings and include compounds such as napthalene (2 fused rings) and anthracene (3 fused rings). Soluble aromatic hydrocarbons are reported to affect water quality and present potential health hazards when present at a concentration of 1 mg/l or even less (Blumer, 1972; El-Dib and Badawy, 1979; Cadena et al.,1984).

At very low dose levels, the decomposition rate of aromatic compounds depends more on substance characteristics than on the precise dosage (Medvedev and Davidov, 1981). Most substituted benzenes are biodegradable to some extent (Alexander and Lustigman, 1966; Marinucci and Bartha, 1979) although migration through the soil has been observed (Wilson et al., 1981).

Phenolic compounds are intermediates in the breakdown of organic compounds. They are of concern due to their inherent toxicity and increasing prevalence as by-products of industry (Finkle and Runeckles, 1967; Elias, 1972; Degering, 1973). The U.S.EPA has established a standard for phenols in drinking water of 1 ppb or less, due to their proven carcinogenic nature (Drinking Water Standards, 1972; Sax, 1979).

Artiola-Fortuny and Fuller (1982) studied phenols in municipal solid waste (MSW) leachates and their attenuation by clay soils. By means of simulated landfills they found that natural phenols are present in MSW leachates, both young and old. The conservative estimates of phenols found in leachates indicate that they can have levels well above drinking water standards for a long time. They can migrate through the clay soils tested relatively rapidly. The data indicates that the clays tested may act as a filter for general organics, but a large portion can finally migrate; phenols appear to migrate more rapidly than most of the other TOC constituents. Fine-textured soils with appreciable iron oxides are more able to slow the migration of phenols than clay soils low in iron oxides. High TOC and low pH values for leachates are correlated with low retention of phenols by soils, perhaps due to competing effects of the organics present in the younger, more concentrated leachates. Aeration of leachates was found to significantly lower the levels of phenols, both natural and enriched, in MSW leachates. The apparent fast reactivity of the high levels of fulvic and humic acids found in leachates seems to be responsible for the selective disappearance of high levels of enriched phenols in MSW leachates and may provide an excellent ground for quick disposal of low concentrations of such materials. It may follow that organic matter in the soil profile will aid in phenols retention. Nitrophenols are the least reactive of all phenols tested in MSW leachates, perhaps due in part to their strong polar character in water solutions.

Phenolic acids are rapidly degraded in soil at low concentrations but can cause a lag phase of low microbial degradation at higher concentrations. Scott et al. (1982) evaluated the curves representing cumulative adsorbed and microbially degraded phenol with two soils in a batch test using a 1:5 soil to solution concentration and continuous shaking. At concentrations less than 10^{-3}M phenol the curves had the following three characteristic phases:- 1. An initial lag phase whose length (of time) increased with increasing phenol concentration (time necessary for organisms to adapt). 2. An exponential growth phase whose rate of growth decreased with increasing phenol concentration; and 3. A stationary phase where essentially all the phenol that was not adsorbed had been degraded.

Baker and Mayfield (1980) found that phenols were rapidly degraded by aerobic soil microorganisms, but that no degradation occurred under anaerobic conditions. Medvedev et al. (1981) found that repeated applications of phenols to soil first increased and then decreased the rate at which phenol was biodegraded. The initial decomposition rate increase was thought to be due to rapid multiplication of the phenol-decomposing microorganisms, and the subsequent decrease due to a gradual accumulation of toxic metabolic by-products or the proliferation of another microbe that fed on phenol-decomposing bacteria.

Toluene is easily degraded in sewage sludge (Malaney and McKinney, 1966) and by a variety of soil microorganisms (Kaplan and Hartenstein, 1979). Nitrobenzene is extensively and rapidly degraded in adapted activated sludge (Pitter, 1976). However, degradation of nitrobenzene by soil microorganisms can be slow, with more than 64 days required for complete disappearance (Alexander and Lustigman, 1966). While general trends in the decomposition of aromatics can be related to substance properties there are nearly always exceptions. One general trend observed for aromatic compounds is that the higher the number of fused rings in the structure, the slower its decomposition rate (Cansfield and Racz, 1978).

Another general trend with respect to decomposition rates of aromatic compounds is that the higher the water solubility of the compound, the more rapidly it degrades in the soil.

A number of studies have noted short-term accumulation of aromatic hydrocarbons after land treatment of oily wastes. This is apparently due to the formation of aromatic hydrocarbons as by-products of aliphatic hydrocarbon decomposition (Kincannon, 1972). In a well managed land treatment unit, most of the rapidly degradable aliphatic hydrocarbons of oily wastes will decompose within a few months after application. After that point, aromatic hydrocarbons should decrease at a faster rate since they will no longer be added to the soil as decomposition by-products.

3.4.5 Halogenated Organics

Halogenated organics contain one or more halogen atoms (Cl, F, Br, or I) somewhere in their molecular structure. They can be further broken down into aliphatics, aromatics, and arenes (molecules that contain both aromatic and aliphatic parts). However, these compounds are generally recalcitrant to biodegradation (McConnell et al., 1975; Wilson et al., 1981).

Most of the interest in the past few years has been directed toward chlorinated aromatics such as chlorinated biphenyls (PCB), chlorinated benzenes and their phenolic metabolic by-products. Land treatment of halogenated organics should be avoided unless preliminary studies have assured that biodegradation (not volatilisation or leaching) will be essentially the only loss mechanism for these hazardous constituents (Brown et al., 1983).

Certain pesticides and other relatively complex organic compounds may be adsorbed to soil solids (Wilson et. al., 1981). These include several halogenated aliphatic hydrocarbons (Chiou et al., 1979), polynuclear aromatic hydrocarbons (Means et al., 1980) and benzene (Rogers et al., 1980). Trichlorobenzene can be degraded in soil, although very slowly (Marinucci and Bartha, 1979).

3.5 FATE OF NITROGEN IN SOIL

3.5.1. Introduction

Soil application of a waste high in nitrogen requires an understanding of the various forms of nitrogen contained in the waste and the transformations that may occur in soils. Nitrogen exists in waste, soil and the atmosphere in several forms. Organic N, such as alkyl or aromatic amines, is bound in carbon-containing compounds and is not available for plant uptake or leaching until transformed to inorganic nitrogen by microbial decomposition. Inorganic nitrogen is found in various forms such as ammonia, ammonium, nitrite, nitrate and molecular nitrogen. The nitrogen cycle illustrates the additions and removals of N from the soil system and the subsequent changes in form due to the prevailing soil environment which may occur when leachate is land applied (Figure 3.11).

3.5.2. Mineralisation and Immobilisation

Mineralisation is the conversion of plant unavailable organic nitrogen to available inorganic forms and includes such processes as ammonification and nitrification. The transformation of organic nitrogen compounds to ammonia or ammonium is termed ammonification.

$$R\text{-}NH_2 + H_2O \text{ ----------------> } R\text{-}OH + NH_3 + \text{energy}$$

$$2NH_3 + H_2CO_3 \text{ -------> } (NH_4)2CO_3 \text{ ----------> } 2NH_4^+ + CO_3^-$$

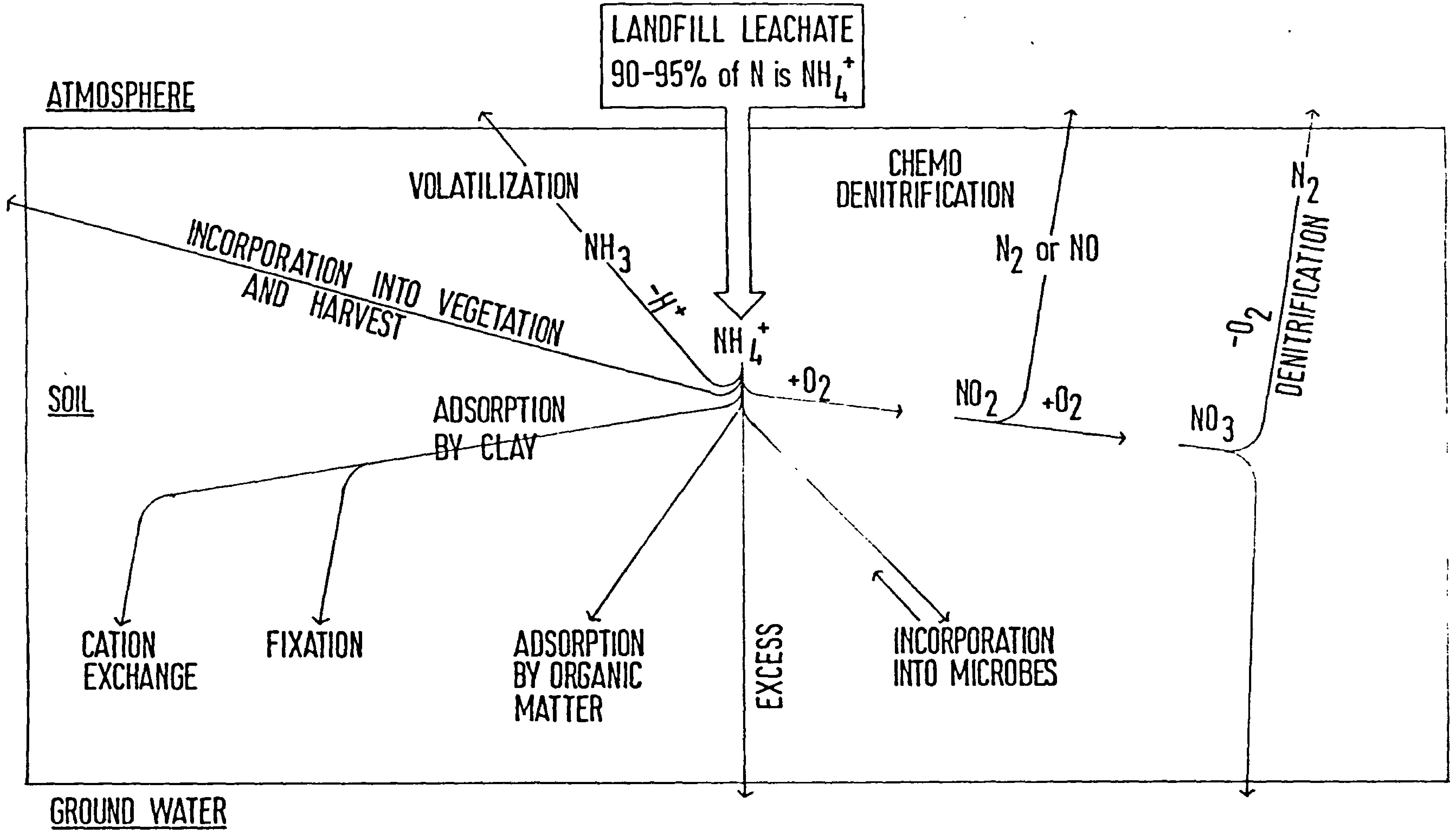


Figure 3.11 Nitrogen transformations during land disposal of leachate.

Hinesley et al. (1972) shows that 25% of the organic nitrogen in land applied sewage sludge is mineralised in the first year of application, and 3-5% of the organic N is converted to inorganic N during the next three years. Where the applied waste contains proteins, hydrolysis results in long-chain amino acid fragments of simple peptides, which, on continued hydrolysis, yield free amino acids. Amino acid may then be : (1) Metabolized by microorganisms; (2) transformed by microbial enzymes with the formation of ammonia; (3) adsorbed by clay minerals or incorporated into humus fraction; and (4) utilized by plants.

The next step is nitrification which is a two stage process carried out by specialised microorganisms:

$$2NH_4^+ + 3O_2 \text{------------------>} 2NO_2^- + 2H_2O + 4H^+ + \text{energy}$$

$$2NO_2^- + O_2 \text{------------------>} 2NO_3^- + \text{energy}$$

These reactions occur in rapid sequence and usually preclude any great accumulation of the highly mobile nitrite ion (NO_2^-). Nitrification has been shown to depend on the availability of substrate (Meikle, 1979; Keeney, 1980), oxygen, carbon dioxide, soil water (Sabey, 1969) and adequate temperature (Schmidt, 1982; Addiscott, 1983; Gilmour, 1984). The nitrifying organisms are strictly aerobic and cannot survive in saturated soils. The optimum temperature for nitrification is in the range of 26°C-36°C (Downing et al., 1964; Myers, 1975). Maximum oxidation rates for Nitrosomonas are found at pH 8.5-9.0 and at pH 8.9 for Nitrobacter (Downing et al., 1964). The activity of these bacteria may cease altogether where the pH is 4.0-4.5 or below.

3.5.3. Biological Denitrification

Denitrification is currently of major interest because of the increasing cost of fertilizer nitrogen and because of the potentially adverse effects of nitrate on environmental quality (Magdoff et al., 1984; Ritter and Manger, 1985). Biological denitrification is the reduction of nitrate to nitrogen gas by the following equation :

$$C_6H_{12}O_6 + 4NO_3^- \text{--------}> 2N_2 + 6H_2O + 6CO_2$$

Three conditions must be met for denitrification : (1) oxidation of ammonium ion to nitrate i.e. nitrification must occur before denitrification; (2) passage of nitrate through an anaerobic zone, and (3) provision of an adequate source of energy in the anaerobic zone for the denitrifying bacteria (Lance, 1972).

The denitrification rate depends on the organic matter content (Burford and Bremner, 1975), water content (Terry and Tate, 1980), soil type and degree of aeration (Blackmer and Bremner, 1978), pH (Waring and Gilliam, 1983) and temperature of the soil (Bremner and Shaw, 1958). Denitrification is strongly inhibited below pH 6.0 and is very rapid at pH 8-8.5 (Bremner and Shaw, 1958). The optimum temperature is 25°C and is slow below 10°C. Denitrification practically ceases at 2°C (Alexander, 1964). Most of the gas evolved above pH 6.0 is N_2, while N_2O and NO are predominant at low pH (Cooper and Smith, 1963). The reaction is facilitated by heterotrophic, facultative anaerobic bacteria living mainly in soil micropores where oxygen is limited (Brown et al., 1983).

The degree of water saturation of the soil has a profound effect on the rate of denitrification. Broadbent and Clark (1965) differentiated two soil water regimes under which denitrification occurs. In the first, the soil is waterlogged and losses are rapid. In the second, the soil is well-drained, but slow losses occur from anaerobic zones within the generally well-aerated soil matrix. Extensive losses of this type have been demonstrated by some workers (Stefanson, 1972), but Craswell and Martin (1974, 1975a, b) and Craswell (1978) have found that a soil with 70% clay exhibited denitrification only under waterlogged conditions.

Denitrification has been detected in well-drained soils and is thought to be due to the uneven distribution of water causing a volume of the soil to be sealed from the atmosphere by free water (Craswell, 1978). Clay soils tend to be well-structured and would not develop such an uneven water distribution. Terry and Tate (1980) concluded that the introduction of a flooded period on muck soils is an efficient means of removing nitrate from the soil.

Denitrification in waterlogged soils can be greatly promoted by addition of organic materials (Burford and Bremner, 1975). Bremner and Shaw (1958) found that the effect of organic materials on denitrification in waterlogged soils varied with their resistance to decomposition. Easily decomposable substances such as glucose, mannitol and sucrose have much greater effects than difficultly decomposable materials such as lignin and sawdust.

Although it is often assumed that N in coarse, as compared with fine-textured soils, is subject to less intense microbial transformations, results from a study by Kowalenko (1980) show this not to be the case. There was relatively more immobilisation during initial stages in a sandy loam than in a clay loam soil. Denitrification has been demonstrated with soil columns flooded with wastewater, but this did not account for the major portion of the nitrogen removed (Lance and Whisler, 1972). Broadbent and Clark (1965) estimated that total losses from denitrification amount to 10%-30% of the nitrogen applied in chemical fertilizers. However, under the optimum conditions of neutral to alkaline pH, high soil water or small pores filled with water, warm temperatures, and the presence of easily decomposable organic matter, almost 90% of the nitrate in wastewater can be converted to gaseous N and lost from the system (Bremner and Shaw, 1958).

Alternate aerobic and anaerobic conditions provide a favourable environment for N loss as NH_4^+ is nitrified during the aerobic period and undergoes denitrification during the anaerobic period (Reddy and Patrick, 1976).

3.5.4. Volatilisation of Ammonia

Nitrogen may be transferred to the atmosphere by nonbiological volatilisation of ammonia (Denmead et al., 1974; Terman, 1979; Rachhpal-Singh and Nye, 1986a; 1986b). Ammonia exists in equilibrium with ammonium ions in solution :

$$NH_4^+ + OH^- \text{------>} NH_3 + H_2O$$

The ratio of NH_4^+ to NH_3 in solution depends on pH and temperature (Hunt and Adamsen, 1985). Most of the nitrogen is present as ammonium ion at pH 7 and below, but an increase in pH shifts the equilibrium to the right so that a greater proportion of the nitrogen occurs as gaseous ammonia (Rachhpal-Singh and Nye, 1986c). However, the pH of leachate is usually less than 7 and hence this is not a major removal mechanism unless the leachate is made more alkaline by the addition of lime.

Mills et al. (1974) reported that when pH values were above 7.2, at least half of the N applied to a fine sandy loam was volatilised as NH_3, generally within two days of application. Ryan and Keeney (1975) reported NH_3 volatilization ranging from 11% to 60% of the applied ammonium-nitrogen from a wastewater sludge containing 950 mg/l of ammonium-nitrogen. The greatest losses occurred in low clay content soils with the highest application rate.

3.5.5. Sorption of Ammonium Ion

Ammonium ions (NH_4^+) may be sorbed by negatively charged clay and organic colloids of soil (Bartlett and Simpson, 1967). The cation exchange capacity of soils is commonly used to estimate the amount of nitrogen removed by this mechanism. However, the presence of other competing ions will have a limiting effect on NH_4^+ adsorption (Preul and Schroepfer, 1968) and only about 5% of the cation exchange capacity is available for ammonium adsorption (Lance, 1972). While the concentration of ammonium in leachate is generally high, the concentration of other more competitive ions may be higher. Hence ions, particularly divalent cations such as calcium and magnesium, will be preferentially adsorbed. In addition, retention in this exchangeable form is temporary. When oxygen and nitrifying bacteria are available, NH_4^+ may become nitrified.

Many investigators have demonstrated that ammonia reacts with the organic fraction of soil, forming complexes resistant to leaching and decomposition (Mortland and Wolcott, 1965; Sohn and Peech, 1958; Broadbent, 1970). In many cases the organic fraction played a greater role than the mineral fraction in the retention of ammonia in soil. Anhydrous ammonia was used in most of these studies, but Broadbent et al. (1960) added NH_4^+ to the surface of columns containing peat. Extensive leaching failed to remove all of the added nitrogen, and some of it was resistant even to refluxing with 6N HCl for 16 hours. Fixation of ammonia was slight under acid conditions, but increased rapidly as the pH was raised above 7 by adding $Ca(OH)_2$. The mechanism of this reaction and the exact chemical nature of the organic matter/ammonia complex are not well understood.

The adsorption of ammonia is not necessarily stable because it can be oxidised biologically to nitrate when oxygen becomes available between irrigations (Kowalenko and Cameron, 1978; Mengel and Scherer, 1981).

Only the ammonium adsorbed in a zone that remains anaerobic is stable. However, the adsorption process will retain nitrogen in the root zone for a time.

3.5.6 Fixation of Ammonium Ion by Clays

The ammonium ion may be fixed into the crystal lattice of a clay and does not exchange readily with other cations and is not accessible to nitrifying bacteria. Ammonium ions become trapped in the intermicellar layers of clay minerals with a 2:1 type structure such as montmorillonite and vermiculite (Bartlett and Simpson, 1967; Dalal, 1977). Nitrogen fixed in this way is stable because it is resistant to nitrification (Allison et al., 1953) and crop removal.

Nommik (1965) suggested that an equilibrium occurs between the different forms of NH_4^+ in the soil :

soluble NH_4^+ ------> exchangeable NH_4^+ --------> fixed NH_4^+

It was established previously that the amount of NH_4^+ removed by exchange is limited in most land disposal systems. The fixed NH_4^+ would also be limited even if the proper conditions for fixation are met. Soils with a high vermiculite content will remove NH_4^+ by this mechanism but arable land with this capacity is uncommon (Nommik, 1965). Broadbent and Clark (1965) found that a primarily kaolinite clay soil fixed no NH_4^+ and that soils containing vermiculite and montmorillonite were capable of fixing 20-40% of the applied NH_4^+ .

3.5.7 Nitrogen Uptake by Plants

The type of crop determines the amount of nitrogen utilised. For all crops, increasing amounts of nutrients will result in increased yields until an adequate supply of nutrients is achieved; additional amounts of nutrients do not result in additional yield. Furthermore, for some plants, adding N in excess of an adequate supply can result in a yield decrease (Ritter and Manger, 1985).

In general the efficiency of uptake is not high (Lance, 1972) and can only be thought of as a removal mechanism if the plants are harvested and removed from the soil environment. Grasses tend to be more efficient than row crops. A crop should be selected that has a long growing season and a high nitrogen requirement. The best crop from the standpoint of nitrogen removal from a land application site is a flood tolerant perennial grass because it has both characteristics (Lance, 1975).

3.6 FATE OF METALS IN SOIL

3.6.1 Introduction

The effect of a metal is determined primarily by its chemical form (Florence, 1977; Allen et. al., 1980). When a waste containing metals is land treated, soil characteristics such as pH, redox potential and mineralogy, as well as the form of the metal in the waste stream determine the solubility and thus the chemical form of the metal.

The most important factors governing the availability of metals in soils are the pH and the redox potential. Usually the most mobile forms of ions occur at a lower range of pH and at a lower redox potential. Therefore, a high level of soluble metal elements would be expected in a soil under acidic and/or waterlogged conditions. The normal recommendation for land treatment units is to maintain the pH above 6.5 (Brown et. al., 1981). It must be emphasised that the various guidelines for metal application given in the following sections become decidedly unsafe at pH values below 6.5.

Adsorption studies have indicated a direct correlation between soil pH and metal retention (Shuman, 1975; Anderson, 1977; Kuo and Baber, 1980). Harter (1983) found that the amount of Pb, Cu, Zn and Ni retained on two soils with an average CEC of 15meq/100g was dependent on the pH of the soil sample. Retention dramatically increased above pH 7.0 to 7.5. With the exception of Ni, at least 70-75% of the retained metal was extractable in 0.01N HCl. This casts some doubt on the concept of pH management for immobilising heavy metals since 0.01N HCl is often used to estimate plant availability of soil ions.

When the soluble form of a metal is in the soil solution it may undergoe one of the following reactions:-

1. Leached from the soil.
2. Precipitated.
3. Incorporated into minerals.
4. Adsorbed by a soil colloid.
5. Adsorbed onto or into organic matter.

The ion-exchange reactions and precipitation reactions which occur in soils are not permanent removal mechanisms since the soil is in equilibrium with the soil solution and heavy metals could exchange back into the solution if the equilibrium is disturbed (Figure 3.12). This disturbance is most likely to be caused by a change in pH dependent on the original soil pH, wastewater pH, formation of organic acids, nitrification and/or carbon dioxide concentrations.

Soil contamination with heavy metals is usually quite permanent (Davies, 1980; Johnson et. al., 1975; Purves, 1977; Kitagishi and Yamane, 1981). Metals accumulated in soils are depleted only slowly by leaching, plant uptake and erosion.

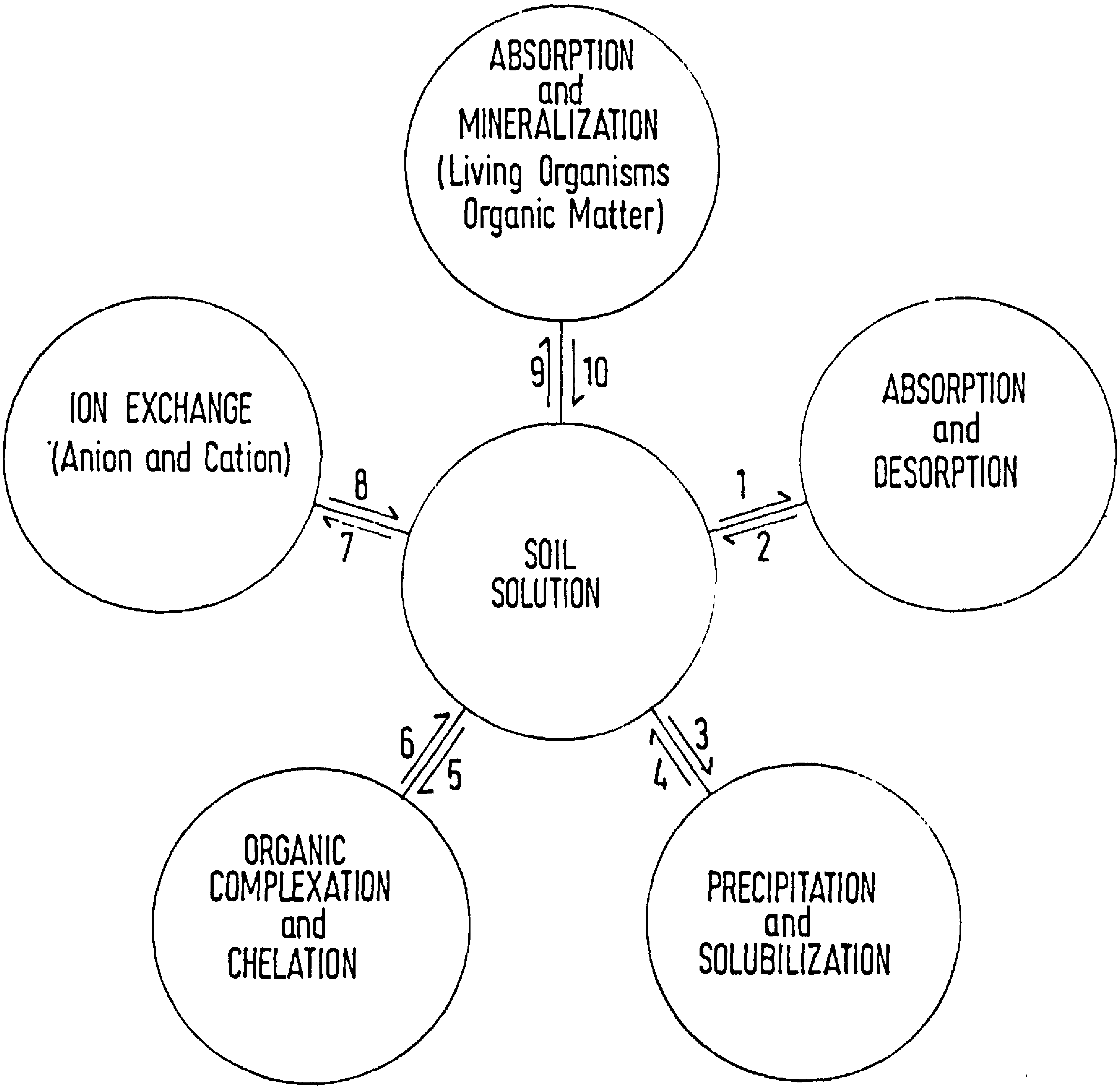


Figure 3.12 Reactions occurring in the soil solution.

While metals are taken up by plants, it is generally not possible to use plants to significantly decrease the metal content of soils. Plant uptake typically amounts to less than one percent of the metal content in the soil (Chaney, 1973). Plant uptake of most heavy metals has been shown to be greater on sludge-amended soils when the pH is less than 6.5 (Hyde et. al., 1979).

In the following sections a review of the metallic elements which may appear in municipal landfill leachate in significant quantities is given.

3.6.2. Iron

The chemistry of iron (Fe) in the environment is complex and is largely determined by the easy change of its valence states in response to physicochemical conditions. The general rules governing the mobilisation and fixation of iron are that oxidising and alkaline conditions promote the precipitation of iron, whereas acid and reducing conditions promote the solution of iron compounds. The released iron readily precipitates as oxides and hydroxides, but it substitutes for magnesium and aluminium in other minerals and often complexes with organic ligands. Transformations of iron compounds are also affected by microorganisms. Some bacteria species (e.g. *Metallogenium* sp.) are involved in iron cycling and are known to accumulate this metal on the surfaces of living cells (Trudinger and Swaine, 1979).

Detailed descriptions of the role and behaviour of iron in soils have been published by Krauskopf (1972), Norrish (1975), Schwertmann and Taylor (1977), Lindsay (1979) and Bloomfield (1981). Many reactions are involved in the solubility of iron in the soil, but hydrolysis and complexed species appear to be the most significant. Lindsay (1979) reported that the mobility of iron in soils is largely controlled by the solubility of Fe(3+) and Fe(2+) amorphous hydrous oxides. However, the formation of other iron compounds, such as phosphates, sulphides and carbonates, may greatly modify Fe solubilities. The content of soluble Fe in soils is extremely low in comparison with the total Fe content. Soluble inorganic forms include Fe(3+), $Fe(OH)_2^+$, $FeOH^{2+}$, Fe^{2+}, $Fe(OH)_3^-$, and $Fe(OH)_4^{2-}$. In well-aerated soils, however, Fe^{2+} contributes little to the total soluble inorganic Fe, except under high soil pH conditions. The concentration of iron in soil solutions within common soil pH levels ranges from 30 to 550 micrograms per litre, whereas in very acid soil it can exceed 2000 micrograms per litre. Acid soils are therefore higher in soluble inorganic iron than are neutral and calcareous soils. Thus, Fe^{2+} cations when in acid anaerobic soils (optimum conditions for solubilisation) may become toxic, but in alkaline well-aerated soils, the low concentration of soluble Fe species may not meet plant requirements for this metal. The Fe compounds produced are largely responsible for the colour of soils and have been used for the description of soil processes and for soil classification.

3.6.3. Manganese

Manganese (Mn) is one of the most abundant trace elements in the lithosphere and is essential to plant nutrition. On a world scale, the range of Mn in soils varies from 10 to around 9000 ppm and a maximum in the frequency distribution of values occurs approximately from 200 to 800 ppm (Bohn et al., 1979).

Mn is likely to occur in soils as oxides and hydroxides in the form of coatings on other soil particles (McKenzie, 1977; 1980). These Mn concretions are reported to accumulate Fe and several trace elements. The solubility of these Mn compounds is highly dependent on the soil pH and redox potential (Lindsay, 1972;1979). Mn compounds are known for their rapid oxidation and reduction under variable soil environments.

Oxidising conditions may greatly reduce the amount of Mn in the soil solution whereas reducing conditions may lead to the ready availability of Mn ions in solution (Krauskopf, 1972).

The most common ionic forms of Mn found in the soil are the divalent cation (Mn^{2+}) which is soluble and mobile and the tetravalent cation (Mn^{4+}) which is practically insoluble, non-mobile and unavailable (Aubert and Pinta, 1977). The trivalent cation (Mn^{3+}), as Mn_2O_3, is unstable in solution. At pH values of 5.0 or less, Mn is rendered very soluble and excessive Mn accumulation in plants can result. At pH values of 8 or above, precipitation of $Mn(OH)_2$ results in Mn removal from the soil solution.

Manganese may be fixed by clay soils but this has been shown to be highly pH dependent (Reddy and Perkins, 1976). Page (1962) believed that organic matter complexing rather than the formation of higher oxides caused reduced manganese availability. Hemstock and Low (1953) found that manganese was not adsorbed by manganese-saturated clay but was removed from solution due to oxidation.

Microbial activity is also known to be largely responsible for the oxidation and reduction of Mn compounds, as well as for the formation of Mn concretions (Letunova et al., 1976; Bromfield, 1978; Wada et al., 1978; Zajic, 1969 and Weinberk,1977).

Mn has not been considered to be a polluting metal in soils, yet Hemkes et al. (1980) reported the increase of Mn from 242 to 555 ppm (dry weight) in sludge-amended soil in five years. Grove and Ellis (1980) found more water-soluble Mn in soil after fertilisation with sludge. When Mn has accumulated in soil due to Mn application over a long period of time, toxic effects in some plants may be observed. Soil solution concentrations of 1-4 ppm Mn produce symptoms such as brown spotting on leaves in many plants (Black, 1968).

3.6.4 Zinc

Most soils contain between 10-300 ppm, with 50 ppm being the average (Bohn et al., 1979).

The predominant Zn species in solutions with a pH less than 7.7 is Zn^{2+}, while $ZnOH^+$ predominates at a pH greater than 7.7 (Figure 3.13). The relatively insoluble $Zn(OH)_2$ predominates at a soil pH between 9 and 11, whereas $Zn(OH)_3^-$ and $Zn(OH)_4^{2-}$ predominate at a soil pH greater than 11. The complexes, $ZnSO_4$ and $Zn(OH)_2$, control equilibrium Zn concentrations in soil at a low pH and high pH, respectively (Lindsay, 1972).

Soluble Zn^{2+} can form as a precipitated salt, it can be adsorbed on exchange sites of clay or organic colloids, or it can be incorporated into the crystalline clay lattice by isomorphic substitution for aluminium, iron or magnesium.

Zinc interaction with organic matter results in the formation of both soluble and insoluble Zn organic complexes. Soluble Zn organic complexes are mainly associated with amino, organic and fulvic acids and is easily exchangeable. Hodgson et al. (1966) reported an average of 60% of the soluble Zn in soil is present as organic complexes. The insoluble organic complexes are derived from humic acids.

Zinc is a nutritionally valuable element which is deficient in many animals and humans (Miller et al., 1964). However, zinc toxicity and zinc tolerance in plants have recently been of special concern because of the prolonged use of zinc fertilizers, as well as its input from industrial pollution (Kabata-Pendias and Pendias, 1986). Chlorosis, mainly in new leaves, and depressed plant growth are the common symptoms of zinc toxicity. The toxicity limit for Zn depends on the plant species and genotypes, as well as on the growth stage. The normal range of Zn

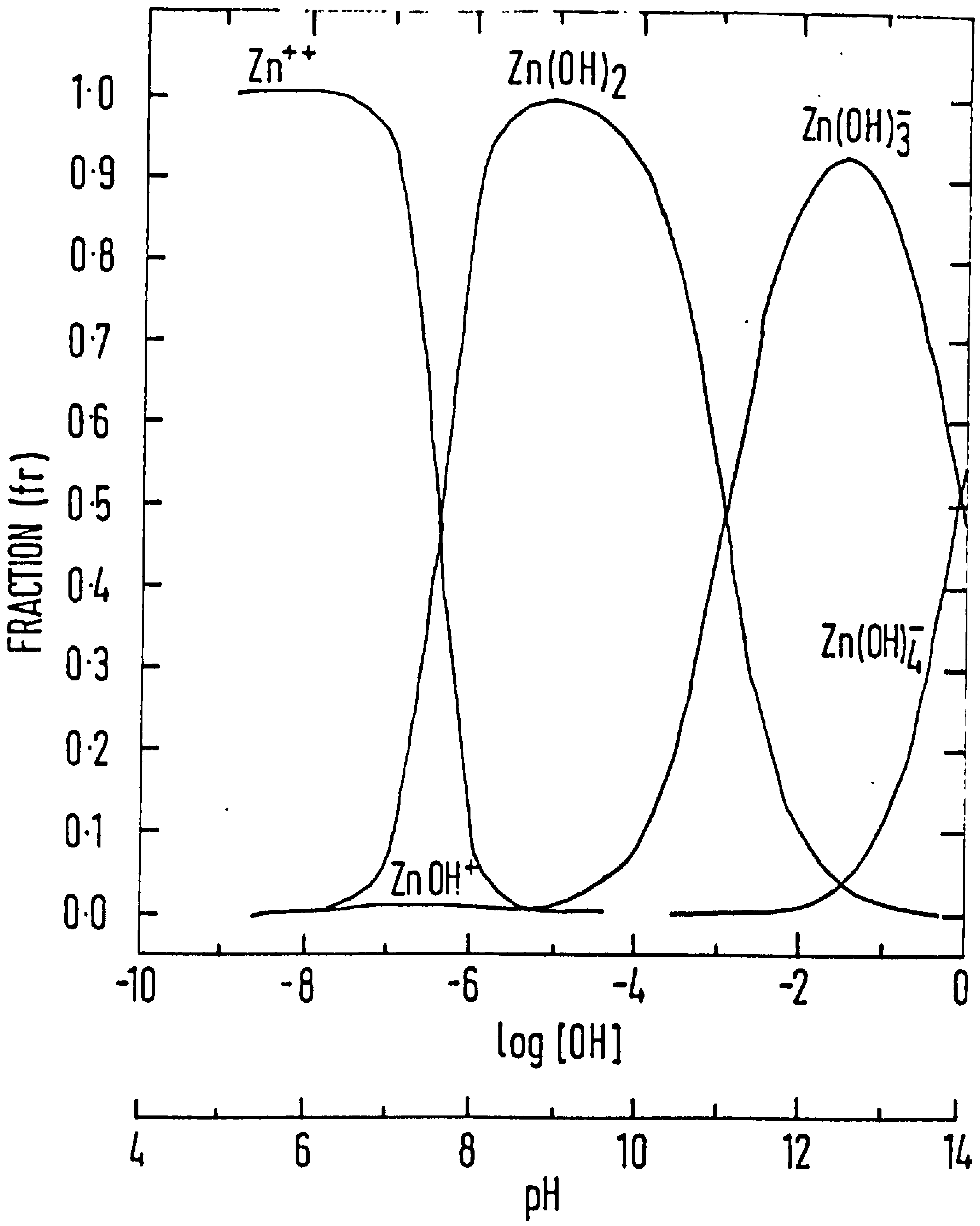


Figure 3.13 Distribution of molecular and ionic species of divalent zinc at different pH values (Fuller, 1977).

in leaves of plants is 15-150 ppm and the maximum suggested concentration is 300 ppm to avoid phytotoxicity (Melsted, 1973). Hyde et al. (1979) found that the concentrations of zinc in plant tissues on sludge-amended soils increased in proportion to the total amount of metals applied to the soil.

The loading rate of zinc bearing wastes can be estimated by using a zinc equivalent (Chumbley, 1971). This is based on observations that copper is twice as toxic and nickel eight times as toxic as zinc. It may be calculated thus:-

$$\text{Z.E. (ppm)} = Zn^{2+}\text{(ppm)} + 2Cu^{2+}\text{(ppm)} + 8Ni^{2+}\text{ (ppm)}$$

Chaney (1973) has recommended that the total zinc equivalents applied be limited to 5% of the cation exchange capacity. However, it should be noted that this equation takes no account of toxic effects due to elements other than zinc, nickel and copper and that no account is taken of pH .

3.6.5 Lead

A lead (Pb) concentration of about 10 ppm is average for surface soils (Barltrop et al., 1974). Lead is present in soils as Pb^{2+} which may precipitate as lead sulphates, hydroxides and carbonates. Below pH of 6, $PbSO_4$ is dominant and $PbCO_3$ is most stable at pH values above 7. The hydroxide $Pb(OH)_2$ controls solubility around pH 8, and lead phosphates, of which there are many forms, may control solubility at intermediate pH values (Chafer, 1984).

The availability of Pb in soils is related to moisture content, soil pH, organic matter and the concentration of calcium and phosphates. Under waterlogged conditions, naturally occurring lead becomes reduced and mobile. Organometallic complexes may be formed with organic matter and these soil organic chelates are of low solubility (Table 3.7). Increasing pH and calcium ions diminish the capacity of plants to adsorb Pb, as calcium ions compete with Pb for exchange sites on the soil and root surfaces (Fuller, 1977).

Lead is not an essential element for plant growth. It is, however, taken up by plants in the Pb^{2+} form. The amount taken up decreases as the pH, cation exchange capacity, and available phosphorus of the soil increases.

Griffin and Shrimp (1976) investigated the ability of two types of clay, kaolinite and montmorillonite, to remove Pb from landfill leachate. They found that Pb removal from the leachates increased with increasing pH values and with increasing concentration of Pb in solution. Under similar conditions, montmorillonite adsorbed substantially more lead than kaolinite. Lead adsorption by both clays was reduced drastically as the ionic strength was increased from that of pure $Pb(NO_3)_2$ to landfill leachate. The decrease in lead sorption at low pH values is apparently due to an increase in competition for adsorption sites by H^+ and the effect of the dissolution of Al^{3+} ions from the clay crystal lattice. At $pH > 6$, a sharp rise in Pb adsorption occurred coincident with the formation of hydroxyl Pb species. A white precipitate was formed which was identified as $PbCO_3$. They concluded that if lead-containing wastes are present in a landfill, a sudden decrease in pH may release large amounts of potentially toxic lead into the aqueous phase, especially in places where $PbCO_3$ has accumulated. Cations contained in the waste, especially di- and trivalent cations, compete with Pb and may exchange with it, thus allowing Pb to come into solution.

3.6.6 Copper

The most important statement on copper contamination of soils is the great affinity of surface soils to accumulate this metal. Soil copper contents range from 2-100 ppm with an average of 30 ppm (Bowen, 1966).

TABLE 3.7 STABILITY CONSTANTS EXPRESSED AS LOG K OF METAL FULVIC AND HUMIC ACID COMPLEXES AT VARIOUS pH LEVELS OF THE MEDIA. (Norvell, 1972; Schnitzer & Khan, 1978)

CATION	pH 3		pH 5		pH 7
	FA	HA	FA	HA	HA
Cu^{2+}	3.3	6.8	4.0	8.7	12.3
Ni^{2+}	3.2	5.4	4.2	7.6	9.6
Pb^{2+}	2.7	3.1	4.0	8.3	-
Zn^{2+}	2.3	5.1	3.6	7.2	10.3
Mn^{2+}	2.1	0	3.7	0	5.6
Cd^{2+}	-	5.3	-	6.3	8.9
Fe^{2+}	-	5.4	5.8	6.4	4.8
Ca^{2+}	2.7	0	3.4	0	6.5
Mg^{2+}	1.9	0	2.2	0	5.5
Fe^{3+}	6.1	11.4	-	-	6.6
Al^{3+}	3.7	-	-	-	-

LOG K <9 indicates a weak complex

Highest levels occur in the ferralitic soil group and lowest in the sandy soils and organic soils. Copper forms several minerals of which the common primary minerals are simple and complex sulphides. These minerals are quite easily soluble in weathering processes and release copper ions, especially in acid environments.

Copper retention in soils is dependent on pH; sorption of copper increases markedly with increasing pH (Tirsch et al., 1979). In kaolinitic soils where clay surfaces have a net negative charge with increasing pH, the amount of copper desorbed increased as the pH was lowered from 6 to 2 (Kishk and Hassan, 1973). The lack of adsorption of copper at a low pH may be due to competition from Mg^{2+}, Fe^{3+}, H^+ and Al^{3+} for sorption sites. Some copper may be removed from solution by precipitation as the pH is increased (Tirsch et al., 1979). It has been recommended that land treated copper waste should be limed if necessary to maintain a pH of 6.5 or greater to ensure the predominance of insoluble forms of copper i.e. $Cu(OH)_2$ and $Cu(OH)_3$ (Hodgson et al., 1966; Younts and Patterson, 1964).

Soil organic matter forms very stable complexes with copper due to their carboxyl and phenolic groups. Stevenson and Fitch (1981) found that 48 to 160 mg of copper is sorbed per gram of humic acid. However, the breakdown of organic matter through decomposition causes a significant decrease in this retention mechanism.

Copper is sorbed appreciably by quartz and even more strongly by clays. The strength of copper sorption of soil constituents are in the following order:-

manganese oxides < organic matter < iron oxides < clay minerals

The toxic leaf concentration has been defined as 20 ppm (Gupta, 1979), depending on species. A soil concentration of greater than 80 ppm Cu has been shown to cause adverse effects. Copper is essential in small amounts to the metabolic processes common to the decomposing bacteria, plants and animals.

3.6.7 Cadmium

The estimated mean cadmium concentration of soil is 0.06 ppm, ranging from 0.01 - 0.7 ppm (Siegel, 1974). During weathering cadmium goes readily into solution.

Soil chemistry of cadmium is largely governed by pH (Figure 3.14). Tirsch et al. (1979) found that over the pH range 5.0 to 7.4 the increase in cadmium removal ranged from a low of 30% to a high of 300% depending on soil type. At a pH of less than 8, Cd^{2+} is formed and very little sorption of cadmium by soil colloids, hydrous oxides and organic matter takes place (Anderson and Nilsson, 1974). Cadmium solubility is greatest between 4.5 and 5.5. Under high pH conditions (pH > 8) precipitation of cadmium occurs [$Cd(OH)_4$]. Precipitation of cadmium with carbonates ($CdCO_3$) and phosphates [$Cd_3(PO_4)_2$] may regulate cadmium concentration in the soil solution at low pH values.

Cadmium is strongly associated with zinc in its geochemistry but has a higher mobility than zinc in acid environments. Cadmium may also be sorbed by organic matter in the soil as soluble or insoluble organometallic complexes or by sorption to hydrous oxides of iron and manganese (Peterson and Alloway, 1979). Column studies by Emmerich et al. (1982) showed that no leaching of cadmium occurred from sewage sludge amended soils, all of which had cation exchange capacity values between 5 and 15 meq/l. The recommended limit for application in sewage sludge is not more than 10 ppm cadmium (Dowdy et al., 1976). Cadmium can be toxic to microbial populations. Williams and Wollum (1981) found that 5 ppm cadmium in the growing media retards actinomycetes and soil

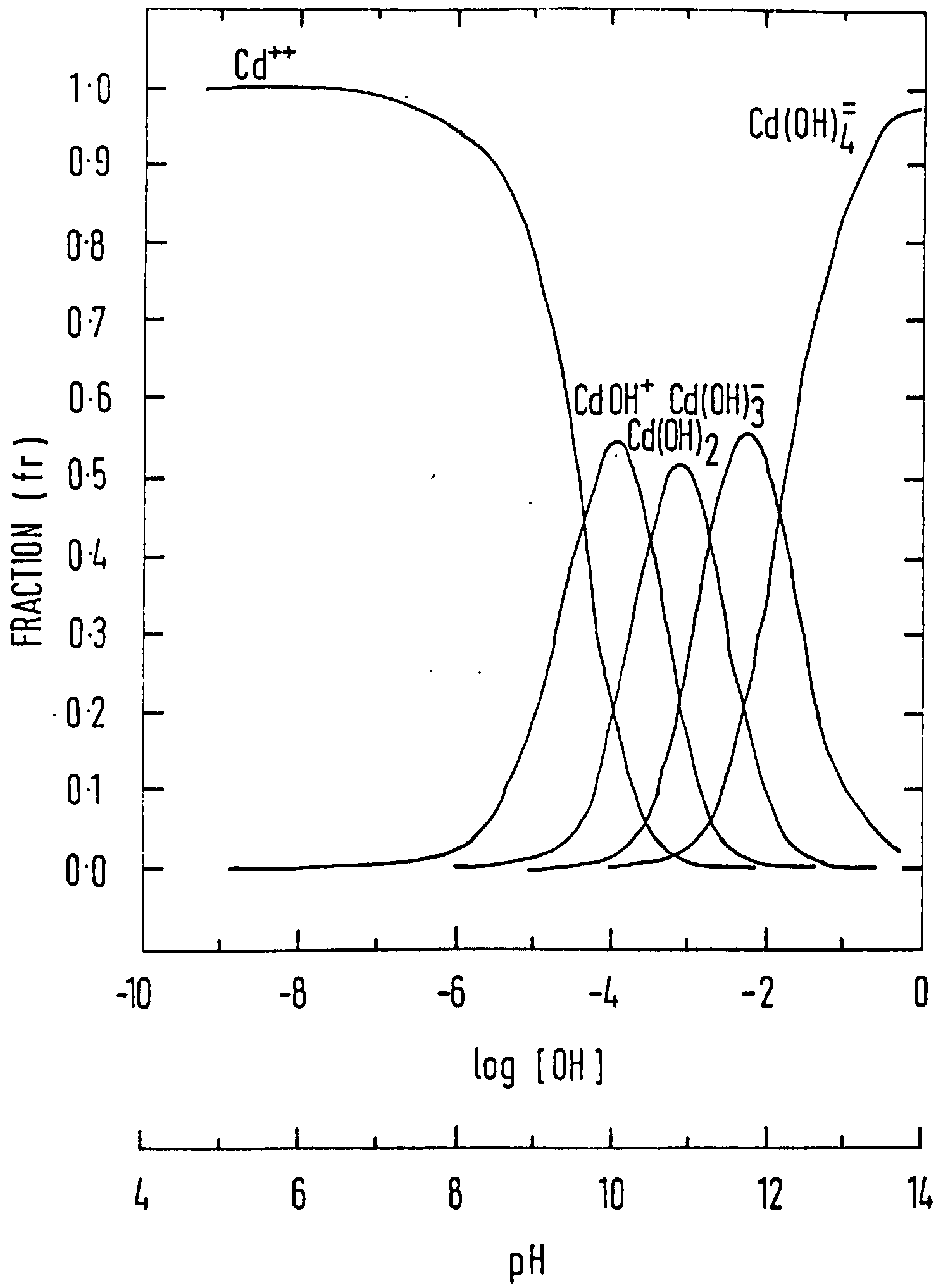


Figure 3.14 Distribution of molecular and ionic species of divalent cadmium at different pH values (Fuller,1977).

bacteria growth. However, at concentrations greater than 5 ppm, the microorganisms exhibited a tolerant response and the tolerant population attained dominance in the culture.

The foliar cadmium concentrations associated with phytotoxicity vary in different crops from 5 to 700 ppm (dry weight) (Chaney et al., 1981). Cadmium can be quite toxic to aquatic organisms at concentrations as low as 1 ppm. Therefore, runoff or movement of particles containing cadmium must be avoided.

3.6.8 Nickel

In soils the typical range of nickel is 5 - 500 ppm (Lindsay, 1979). Soils derived from serpentine may contain as much as 5000 ppm nickel (Vanselow, 1966).

Nickel (Ni^{2+}) in soil associates with O_2^- and OH^- ligands and is precipitated as nickel hydroxides at alkaline pH. In an aerobic system, nickel may be reduced to lower oxidation states when it will precipitate as nickel carbonate and nickel sulphide (Bohn et al., 1979).

The cation exchange capacity values and percentage of clay in soils have been found to be insignificant to nickel retention (Korte et al., 1975). It has been found to be correlated to the amount of iron and manganese oxides in the soil.

A column study by Emmerich et al. (1982) indicated that when 211 ppm nickel was added as sewage sludge, 94% of the nickel added was recovered from the column indicating essentially no nickel leached below the depth of incorporation.

Organic matter has the ability to hold nickel at levels up to 2000 ppm (Leeper, 1978); maximum sorption of nickel by soils is often near 500 ppm (Biddappa et al., 1981). However, other studies show nickel sorption is decreased in the presence of a strong chelating agent such as EDTA, and suggest nickel mobility would be enhanced when present with naturally occurring complexing agents such as sewage sludge (Bowman et al., 1981).

Nickel is not essential to plants and in many species produces toxic effects. The nickel content of plants falls in the range 0.1-1.0 ppm (dry weight). Toxic levels of nickel are considered to be 50 ppm in the plant tissue (CAST, 1976). Phytotoxic levels of nickel in soil ranges from 50 to 200 ppm. A soil accumulation of 100 ppm nickel appears to be acceptable based on phytotoxicity and microbial toxicity.

3.6.9 Chromium

The range of chromium in native soils is 1-1000 ppm with an average concentration of 100 ppm (Bowen, 1966). Sandy soils and histosols have the lowest chromium content; serpentine soils have the highest.

Chromium shows highly variable oxidation states (from +2 to +6). The chromium in most industrial wastes (e.g. tannery wastes, sewage sludge) is present in the +6 oxidation state as chromate (CrO_4^{2-}) or a dichromate ($Cr_2O_7^{2-}$). In the +6 or hexavalent form, chromium is toxic and quite mobile in both acidic and alkaline soil. Under acid conditions there is a conversion from chromate to dichromate. Soluble salts of chromium, such as sulphate and nitrate, are more toxic than insoluble salts of chromium such as oxides and phosphates. This toxicity becomes more important as soil acidity increases. Aubert and Pinta (1977) found that under the same redox potential of 500 mV, Cr^{3+} predominated at pH 5, $Cr(OH)_3$ was formed between pH 5 to 7, and CrO_4^{2-} occurred at pH greater than 7.

Cr^{3+} readily precipitates with carbonates, hydroxides and sulphides (Murrmann and Kountz, 1972) and these precipitation reactions are favoured by a pH greater than 6. In general, Cr^{3+} closely resembles Fe^{3+} and Al^{3+} in ionic size and geochemical properties.

The behaviour of chromium in soils may be modified by organic complexes of chromium. However, the dominant effect of organic matter is the stimulation of the reduction of soluble hexavalent chromium to insoluble Cr^{3+}, thereby reducing toxicity.

Chromium has been shown to be toxic to plants and animals and to soil microorganisms. Ross et al. (1981) found that levels as low as 7.5 ppm were toxic to gram negative bacteria. Rudolfs (1950) recommended a 5 ppm limit for hexavalent chromium in sewage sludge which is land treated. El-Bassam and Tietjen (1977) found that after 8 years of irrigation with sewage sludge containing 112 ppm chromium, the metal concentration in soil increased from 43 to 113 ppm. Many investigators have found that chromium is toxic to plants, dichromate being more phytotoxic than chromate (Pratt, 1966). Some plants (e.g. soybean) experience decreased yields at soil concentrations as low as 0.5 ppm chromium (Turner and Rust, 1971). Most mammals can tolerate up to 1000 ppm chromium in their diets. In animals, however, experimental evidence has shown conclusively that chromium in the hexavalent form can cause cancer. Hernberg (1977) and Enterline (1974) has shown the predilection of workers in chromium plants to respiratory cancer.

CHAPTER 4 SOIL COLUMN EXPERIMENTS

4.1 INTRODUCTION

The basic properties of soil have a major influence on the success of land treatment of wastes. These relevant properties include soil texture, soil structure, permeability, infiltration, available water capacity, and cation exchange capacity.

Land application systems are commonly classified in terms of vertical water transmission properties of soil. Soils with high transmission capabilities are considered suitable for "rapid infiltration" systems; soils with moderate transmission rates are suitable for use with conventional irrigation methods; gently sloping soils with low transmission capabilities are normally suitable only for "overland flow" systems. Clearly, the behaviour of water in soils is an important consideration. Equally important is the potential for removal or alteration of other waste constituents including organics, metals, dissolved salts and major nutrients such as nitrogen and phosphorus.

Site evaluation necessitates a basic understanding of soil components and properties, the treatment mechanisms operating in the soil, and limitations of these mechanisms in terms of polluting loading rates. For land treatment systems the vegetative cover and the rate of application of waste can be adapted to a particular site with relative ease. However, if the soil type is inappropriate it would be a major expenditure to import soil to the site. Therefore, the research programme has concentrated on the effect of soil type on the renovation of landfill leachate.

Soil-leachate interactions were studied by two different methods:-

1. column tests in which leachate was allowed to percolate through a column of soil; and

2. batch tests in which predetermined quantities of soil and solution were allowed to interact in a closed container.

The soil-column technique has the advantage of screening a large number of soils of wide variability for pollutant attenuation while avoiding the multitude of problems associated with field conditions. A large volume of data can be generated at a relatively low cost. In general, the column is regarded as a model of the natural movement of solutes in soil (Schweich et al., 1983). Soil columns allow leachate to percolate down slowly through the soil and hence there is longer time for the exchange reactions and absorption to take place than in batch tests. In addition, the use of soil columns is more suited to the study of organic compound removal from leachate by soils. No conceivable batch incubation experiment could provide soluble COD reduction data truly representative of the long-term conditions in a soil column. Over a series of irrigation cycles a distinctive population of microorganisms will become attached to the soil particulate matter. Near the soil surface, organisms acclimatised to the organic compounds in the entering leachate will predominate; deeper in the soil organisms acclimated to decomposition products of the original organic compounds, and to the conditions of temperature, pH, oxygen tension, available nutrients etc., will predominate. The resulting spatial variation of organism type (and presumably reaction rate) will not necessarily be the same as the temporal variation that may (or may not) occur in the soil sample incubated only as long as it takes adsorption to take place.

4.2 ANALYSIS OF EXPERIMENTAL SOILS AND LEACHATE

4.2.1 Introduction

The experimental programme was designed primarily to investigate the effect of different soil types on leachate treatment efficiency. Four types of soil were investigated:- topsoil, peat, sand, and clay. The soils chosen for testing were thought to give a good representation of the wide range of soil types. Sand was chosen to represent a soil normally regarded as inert. Clay and peat represented soils which are commonly regarded as reactive due to their cation exchange capacity; clay due to its mineral content and peat due to its organic content. Topsoil was chosen to represent a typical surface soil. The characteristics of the chosen soils are described in the following sections.

The applied leachate was collected from a domestic landfill site which lies six kilometres north of Glasgow city centre between the River Kelvin and the A879 road to Milngavie. This road forms the eastern boundary of the site whilst the River Kelvin runs along the north and west of the site. The site has been in operation since the late 1940's. At present the site receives about 4000 tonnes per annum of high density baled domestic refuse. The geology of the site is complex but not directly relevant to waste disposal activities. The hydrology and hydrogeology are also complex due to the position of the river, the site topography and the drainage pattern. The lower part of the site is prone to flooding by the River Kelvin and old drains underlying the site have been tipped over, providing an easy route for leachate from the balefill to enter the river. Some small springs within the site are also contaminated with leachate, as is surface water run-off at the north end of the site. All these sources drain to the River Kelvin. Surface water was observed lying on various parts of the site, in particular on the benches above the river where rainfall running off and through the bales had been trapped. However, at the moment it is considered desirable as it prevents leachate from flowing directly into the river. Leachate used for this study was collected weekly from a small terrace trench formed by the original landfill surface at the edge of the infill. The terraced area is saturated with leachate to about half a metre, the level increasing during wet weather. The leachate was peaty brown in colour and highly turbid. It has the faint odour of hydrocarbons and the pH when collected varied from 6.5 - 7.5. It is characterised by a high concentration of ammonia and particulate organic matter. An example of a full analysis of the leachate is given in Table 4.1.

In order to analyse the results of soil-leachate interaction tests, it is necessary to examine the character of the soils and refuse leachate tested. The leaching solutions were analysed each week prior to irrigation for selected parameters by standard chemical tests. The type and composition of the soils were identified by X-ray diffraction, moisture content and grain-size tests as well as chemical tests. The chemical properties of the soils are given in Table 4.2 and the analytical techniques described in sections 4.2.5 to 4.2.11.

Analysis of fresh or moist soils makes it difficult to relate one soil to another because the moisture status of each soil will affect the availability of constituents. Therefore, in order to standardise analyses, all soil samples were air-dried prior to analyses. They were then lightly ground with a pestle and mortar and sieved through a nylon 2 mm mesh to obtain the fine earth fraction which was subsequently used for analysis. All glassware used in the analysis was soaked in pyroneg for 24 hours, acid-washed for a further 24 hours and then rinsed in distilled water in order to ensure non-contamination of glassware.

TABLE 4.1 ANALYSIS OF LANDFILL LEACHATE USED IN SOIL COLUMN EXPERIMENTS.

PARAMETER	NUMBER OF SAMPLES	MEAN	STANDARD DEVIATION	MINIMUM	MAXIMUM
pH	20	7.01	0.2	6.72	7.97
COD	20	13,489	6939	3174	32,142
BOD	20	5,750	3028	1000	11,000
Total Solids	20	3,368	215	2850	3,900
Suspended Solids	20	163.1	22.5	105	200
Volatile Suspended Solids	20	129.5	10.0	105	140
Ammoniacal-N	20	332	135	114	550
Organic-N	20	21	18	2.5	68
Calcium	20	141.5	21.1	98	176
Magnesium	20	111.1	13.4	87	141
Potassium	20	89.5	7.6	80	110
Sodium	20	308.8	26.9	229	350
Iron	20	184.8	28.5	97	207
Zinc	20	2.0	0.5	1.0	2.5
Aluminium	20	0.01	-	-	-
Copper	20	0.02	-	-	-
Lead	20	0.01	-	-	-
Manganese	20	0.02	-	-	-
Chromium	20	0.02	-	-	-
Cadmium	20	0.01	-	-	-
Nickel	20	0.02	-	-	-

All Results in mg/l EXCEPT pH.

TABLE 4.2 CHEMICAL PROPERTIES OF SOIL SAMPLES

PARAMETER	SAND	SOIL		PEAT
		TOPSOIL	CLAY	
Organic Content (%)	1.37	5.72	21.37	83.0
Phosphate (%)	7.68	0.36	0.76	0.4
pH	4.54	5.8	4.88	3.64
CEC (meq/100g)	20.75	14.35	47.50	50.0
NH_4 (ppm)	200.0	1600	4200	11400
Exc. Ca (ppm)	2.0	41.0	66.0	30.0
Exc. Mg (ppm)	0.51	3.2	9.8	35.8
Exc. Na (ppm)	0.99	0.60	1.9	4.35
Exc. K (ppm)	0.54	0.98	11.5	8.10
Total Metals				
Fe (ppm)	8296.0	20311.0	14266.0	790.0
Mn (ppm)	17.54	5.39	5.95	6.38
Zn (ppm)	26.0	108.0	530.0	38.0
Cu (ppm)	11.0	24.0	53.0	37.0
Ni (ppm)	10.0	12.0	34.0	4.0
Pb (ppm)	6.20	183.08	127.85	9.11
Cr (ppm)	10.4	14.8	28.0	9.8
Cd (ppm)	<0.05	1.57	0.52	<0.05
Hg (ppm)	N/D	N/D	N/D	N/D

N/D = Not Detected

Exc. = Exchangeable.

4.2.2 Soil Description

A subjective description of soils is undertaken either in the field or on field-moist samples in the laboratory. This involves a visual examination of colour, rubbing soil between the fingers and moulding the soil to determine the texture. The natural colour of most minerals is white or light grey. The grey, brown, red and yellow colours of soil are due, in general, to chemical changes in the mineral constituents themselves (especially iron) associated with weathering phenomena. The dark colours in soils are usually due to accumulation of decayed organic matter, which imparts a dark grey or dark brown colour to soils. Where soils are not rich in organic matter, dark colourations may be due to the presence of excess calcium carbonate or anaerobic conditions. A subjective evaluation of soil texture is achieved by examining the soil by eye for individual grains and rubbing between thumb and fingers to determine grittiness; moulding the soil to determine cohesive properties and rolling soil into a thin wire to determine plasticity. A description of the soils used is given in Table 4.3.

4.2.3 X-ray Diffraction Analysis of Soil Minerals

Knowledge of the internal atomic arrangement in crystals was founded on x-ray diffraction analysis. X-rays consist of short wave lengths of electromagnetic radiation, comparable to visible light. Soil chemistry was given considerable impetus by the application of X-ray diffraction to soil colloidal mineral characterisation. The analytical characteristic of each different mineralochemical structure arises from the uniqueness of the atomic spacings of each. These spacings result in a unique array of different peaks for each mineral called a diffraction pattern which is used like a "fingerprint" to identify each structure qualitatively. Diffraction analysis of soil clay, silt and sand particles (organic colloids of soils are too heterogenous to show diffraction patterns) consists of mounting the specimens followed by x-radiation,

TABLE 4.3 DESCRIPTION OF SOILS USED IN SOIL COLUMN EXPERIMENTS

SOIL	DESCRIPTION
SAND	Coarse yellow sand, individual grains obvious to the eye, loose when dry, not sticky when wet.
TOPSOIL	Brown loam, friable, small degree of cohesion and plasticity when wet.
PEAT	Organic dark brown peat, high degree of cohesion and plasticity when wet.
CLAY	Dark grey clay, high degree of cohesion and plasticity, moulds readily when wet and very hard when dry.

and qualitative and quantitative interpretation of the patterns. The intensity of each diffraction peak is proportional to the number of diffracting planes, or simply the concentration of each kind structure in a mixture, if a number of other factors are held constant.

The sand, topsoil and clay were analysed by x-ray diffraction. This enabled the major soil minerals present in the soil to be identified. The results are qualitative and not quantitative, although for an individual soil sample the amount of a particular mineral may be related to that of another by the height of the peaks on the diffraction pattern. The results of the tests are given in Table 4.4 with the mineral present in greatest amount being indicated first and the others following in descending order of prevalence.

4.2.4 Soil Particle Size Distribution

Sieving is the simplest of all methods of particle size analysis. This method covers the quantitative determination of the particle size distribution in a soil down to the fine sand size. The combined clay and silt fraction can be obtained by difference. The procedure involves preparation of the sample by wet sieving to remove silt and clay sized particles followed by dry sieving of the remaining coarser material.

Approximately 2 kg of dried soil was weighed and sieved through a 20 mm sieve. The sieved soil is then weighed and this riffled fraction is then spread out in a large tray or bucket and covered with water. Sodium hexametaphosphate is added to give 2 g/l of water with the soil. The mixture was allowed to stand for at least one hour with frequent stirring. The sample is then washed with water through a 2 mm sieve in a 63 micrometre sieve.

TABLE 4.4 SOIL MINERAL CONTENT OF SAND, TOPSOIL AND CLAY

SOIL	MINERAL CONTENT
SAND	Quartz K - Feldspar Mica Kaolin
TOPSOIL	Quartz K - Feldspar Kaolin Mica
CLAY	Quartz Kaolin K - Feldspar Mica

A known weight of soil is placed on a tray and allowed to dry overnight in an oven maintained at 105°C. After drying to constant weight the whole specimen is allowed to cool and is then weighed. A selection of sieves with different sizes of apertures were used. The sieves are stacked with the largest aperture sieve at the top. The dried soil sample is placed in the topmost sieve and is shaken for long enough for all particles smaller than each aperture size to pass through. The material retained on each sieve is transferred to a balance and weighed. The masses retained are recorded against the sieve aperture size. In order to draw a particle size distribution curve it is necessary to calculate the cumulative percentage (by mass) of particles finer than each sieve aperture size i.e. passing each sieve. The cumulative mass passing each sieve is calculated first, from which the percentages passing are derived. The mass retained on the first sieve is denoted by m^{s1}. The mass passing the first sieve = $m_1 - m_{s1}$. The percentage passing the first sieve is given by :-

$$P_1 = \frac{(m1 - ms1)}{m_1} \times 100$$

The mass passing the second sieve = $m_1 - m_{s1} - m_{s2}$. The percentage passing the second sieve is given by :-

$$P_2 = m_1 - \frac{(ms1 + ms2)}{m_1} \times 100$$

and so on. The fine materials were then tested by pipette analysis to categorise the material which passed through the 63 micrometre sieve.

The particle size distribution curves for the soils tested is shown in figures 4.1 to 4.3. The position of a curve on the chart indicates the fineness or coarseness of the grains; the higher and further to the

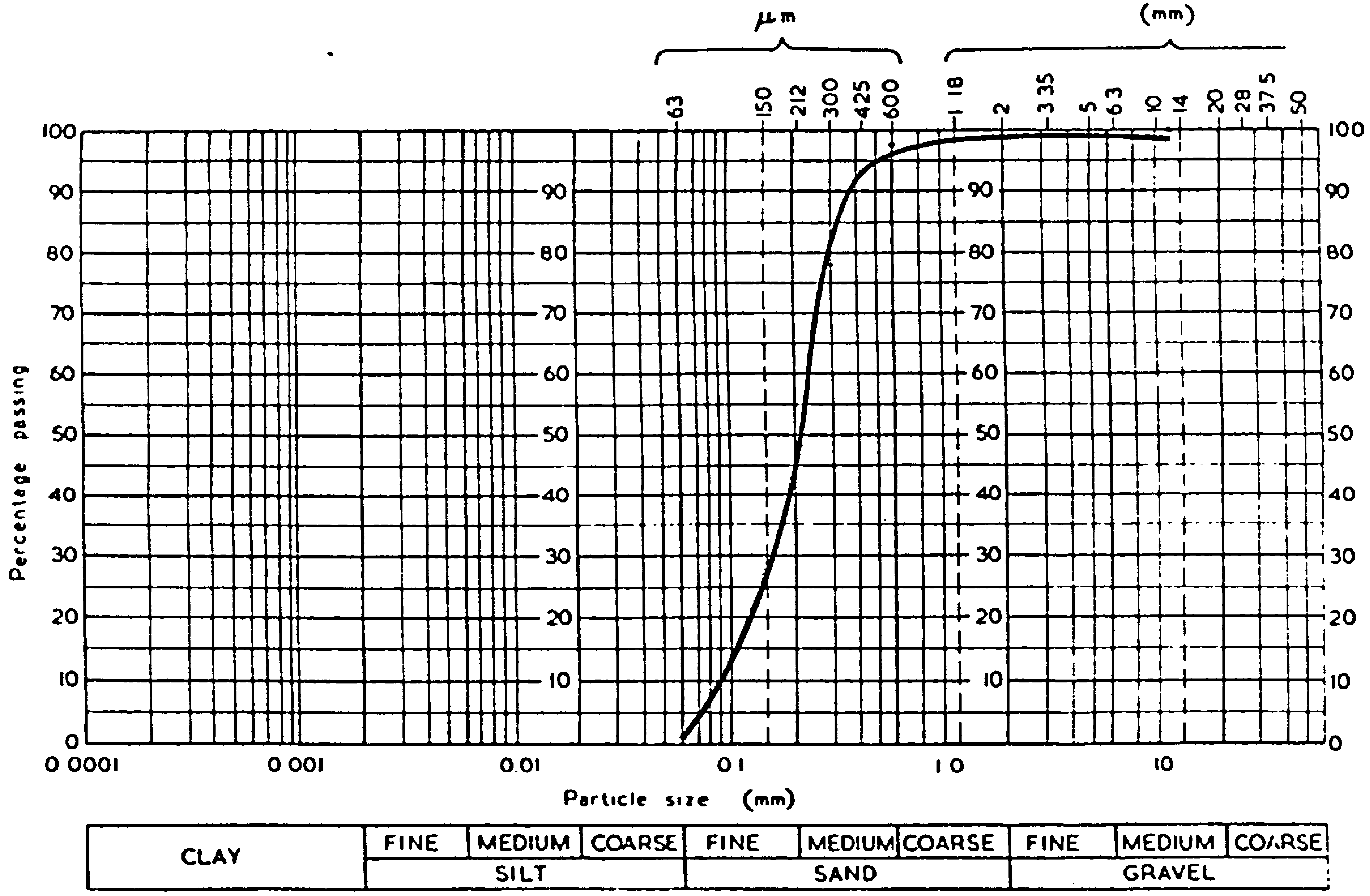


Figure 4.1 Particle size distribution curve for sandy soil

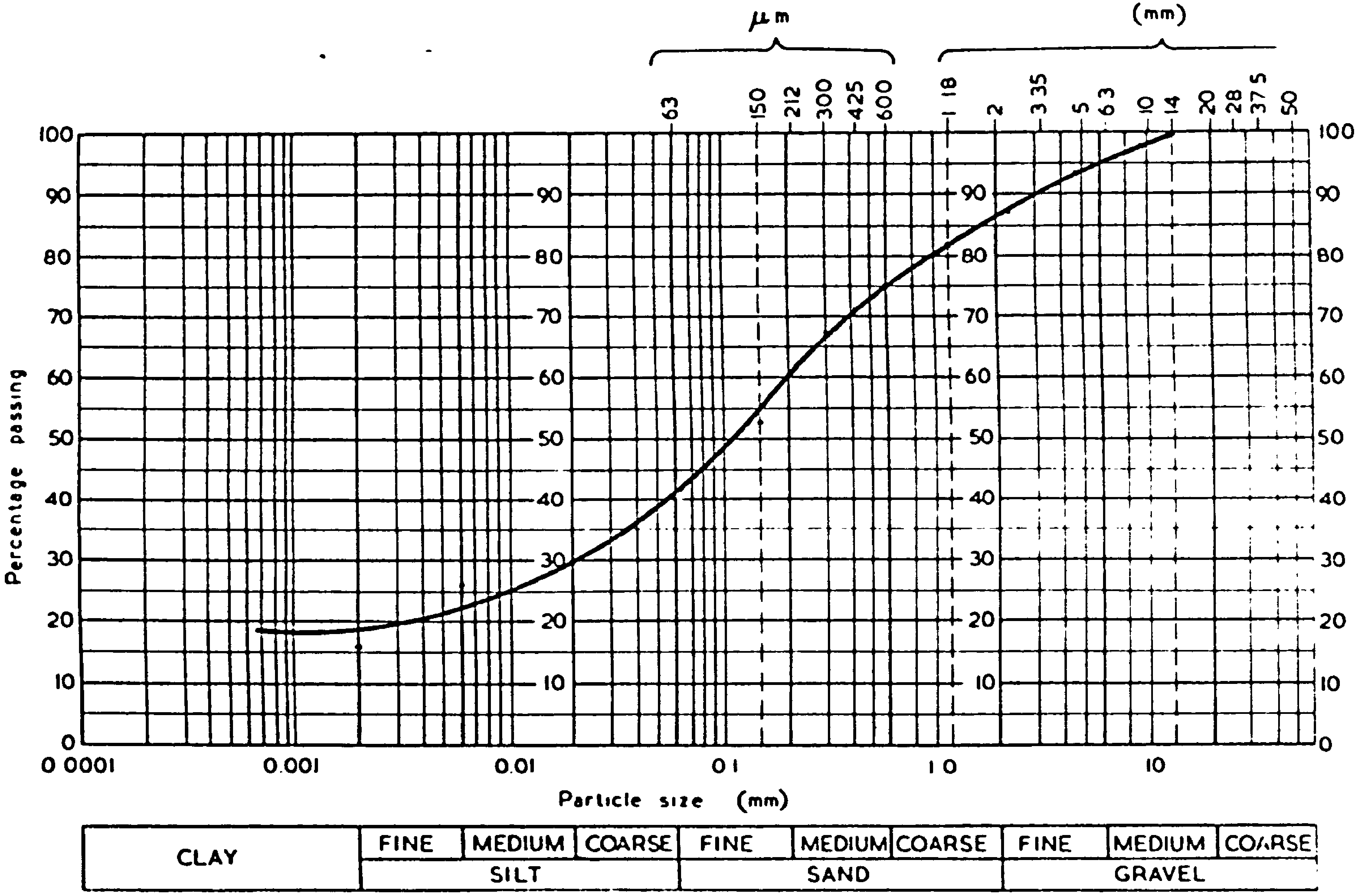


Figure 4.2 Particle size distribution curve for clay soil

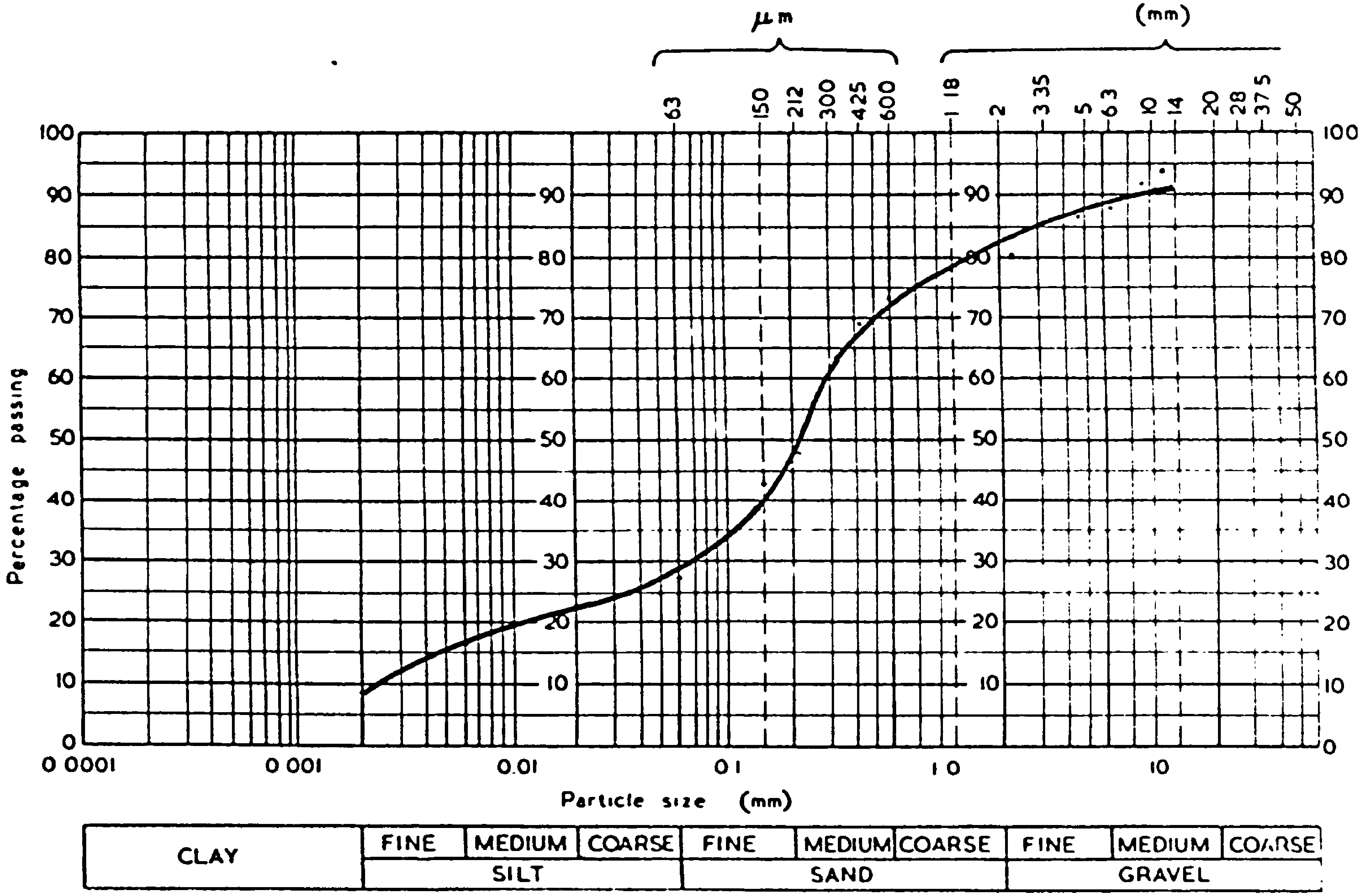


Figure 4.3 Particle size distribution curve for topsoil

left the curve lies, the finer the grains and vice versa. The steepness, flatness and general shape indicate the distribution of grain sizes within the soil.

4.2.5 Soil and Leachate pH

The pH of leachate was determined with a pH meter which had been previously calibrated against three buffers (pH = 4; pH = 7; pH = 9).

The pH of soils was determined by first shaking 10 g of soil with 25 ml of 0.01 M $CaCl_2$ for 30 minutes on an orbital shaker. The pH was then measured with a pH meter which had been previously calibrated against three buffers (pH = 4; pH = 7; pH = 9).

4.2.6 Soil Moisture Content

The moisture content of the soils was measured by weighing 20 g of fresh moist soil into a dry, weighed pyrex container. The container was then placed in an oven at 100°C and dried to a constant weight (when successive weighings differed by no more than 2 mg). The samples were cooled in a dessicator prior to weighing. The moisture content was calculated according to the following equation :-

$$\text{MOISTURE CONTENT (\%)} = \frac{\text{loss in weight on drying (g)}}{\text{original sample weight (g)}} \times 100$$

4.2.7 Soil Organic Matter Content

Organic matter content can be estimated for most soils by calculating the loss in weight of a dry soil on ignition (i.e heating to 440°C). Duplicate 1 g samples of air-dried soil were placed into previously weighed crucibles and oven dried to constant weight at 105°C. The soils were muffled at 440°C until completely ashed. After ashing the soils were cooled in a dessicator and reweighed. The organic matter content of each soil was expressed as a percentage and calculated from the following equation :-

$$\text{\% ORGANIC MATTER} = \frac{\text{(mass of oven dried soil)} - \text{(mass of ashed soil)}}{\text{mass of oven dried soil}} \times 100$$

4.2.8 Soil and Leachate Metal Content

The following digestion procedure was conducted on soil samples prior to analysis of metals. Two grammes of each soil was treated with 20 ml of a mixture of concentrated nitric and perchloric acids (4:1 v/v) and digested in a 300 ml Tecator digestion tube for 1 hour at 40°C and 3 hours at 140°C. The digest was allowed to cool to room temperature and then diluted to 20 ml with double distilled water. Each batch of digests contained a duplicate sample, an internal standard and a sample blank. This procedure helped to ensure compatibility between digests and account for reagent impurities. All chemicals used were of analytical grade.

The concentrations of calcium, magnesium, iron, cadmium, nickel, copper, manganese, lead, chromium, and zinc of both the soil digest and the leachate were determined by atomic adsorption spectroscopy using a Pye Unicam SP9 AAS. The concentrations of sodium, potassium and aluminium were determined by flame emission spectroscopy.

4.2.9 Leachate and Soil Ammonium Content

The ammonium content of the leachate and the digested soil extract were determined by the following method. Standard solutions were first prepared containing a range of N contents from 0 to 500 mg/l in order to prepare a calibration curve. The standard solutions were made up in a 1:4 mixture of digest acid:distilled water for use with the digested soil extracts. 0.5 ml of sample was pipetted into a cuvette and 2 ml of sodium tartrate was added (0.2% w/v in DDW). Nesslers reagent (1 ml) was then added and allowed to stand for 15-20 minutes to allow the development of colour. The optical density at 410 nm was then calculated on a colourimeter. Using the calibration curve the sample optical density was converted to ammonium concentration (mg/l).

4.2.10 Total Soil Nitrogen

Two grammes of air-dried and sieved (< 2 mm) soil was placed in a digestion tube with 10 ml concentrated H_2SO_4, a Kjeldahl catalyst tablet, 0.1 g selenium powder and 0.1 g sodium thiosulphate. The tubes were then placed in a Tecator digestion block and placed in the fume cupboard. The tubes were heated for 1 hour at 150°C before raising the temperature to 350°C for 3 hours (until the contents are clear). The tubes were then allowed to cool in the fume cupboard. The digests were then made up to 100 mls with distilled water, shaken vigorously and about 30 mls decanted into a clean storage container. This method converts organic N into NH_4 which is then measured according to the ammonium determination method (section 4.2.9).

4.2.11 Soil Cation Exchange Capacity

Cation exchange capacity is an expression of the number of potential cation exchange sites (i.e. negatively charged) per unit weight of soil and is an estimate of the ability of a soil to absorb cations and to retain them against losses from soil solution through leaching and root absorption.

The cation exchange capacity of a soil is determined by a basic two-stage process. The colloidal complex of the soil is first saturated with a selected cation (the saturating cation), all exchangeable cations originally associated with the complex are thus removed. Excess saturating solution is usually removed by washing the soil with ethanol. In the second stage the saturating cation is displaced quantitatively by another selected cation (the replacing cation) and the amount displaced is measured and expressed in terms of milliequivalents per 100 grams of oven dry soil.

Five grammes of air-dried and sieved (< 2 mm) soil was weighed into an acid-washed 100 ml beaker. Each soil was tested in triplicate. A blank solution was also tested which contained no soil. To this was added 50 ml of 1.0 M KCl and the mix was shaken on an orbital shaker for 60 minutes. The samples were then filtered through Whatman 540 filter papers. The filter paper and soil were washed at least four times with industrial alcohol (60% V/V) with the filtrate draining completely between each washing. This filtrate was then discarded and the filter paper and soil were placed into a fresh acid-washed 100 ml beaker. 50 ml of 1.0 M ammonium acetate (pH = 7) was then added and the mix was shaken on an orbital shaker for 60 minutes. The samples were then filtered through fresh Whatman 540 filter papers. The filtrate was retained and this was analysed for potassium ions by atomic adsorption spectroscopy. The cation exchange capacity was then calculated according to the following equation:-

$$\text{CEC (meq/l)} = \frac{\text{K concentration in filtrate (ppm)} \times \text{volume of extractant}}{391 \times \text{sample weight (g)}}$$

4.2.12. Chemical Oxygen Demand of Leachate

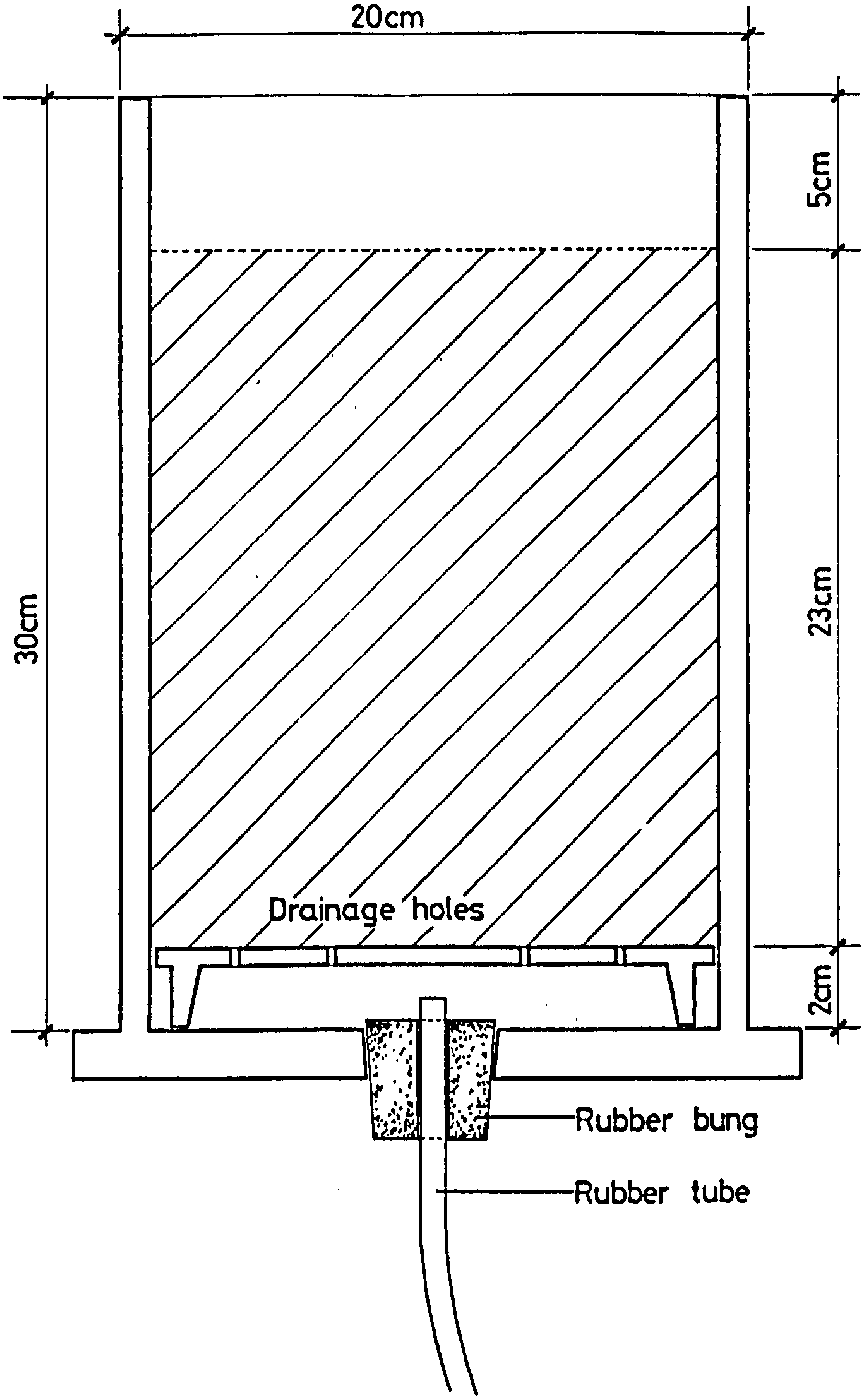
The chemical oxygen demand (COD) of the leachate was calculated according to the following method :- 50 ml or equivalent dilutions of leachate sample were refluxed with a mixture of potassium dichromate and sulphuric acid. After the complete oxidation of the organic matter the excess potassium dichromate is titrated with ferrous ammonium sulphate. Ferrion is used as an indicator giving a very accurate end point.

4.3 EXPERIMENTAL DESIGN

Four types of soil were chosen for the experiment and leachate treatment efficiency was tested on both the bare soil and soil which had a covering of perennial ryegrass. Sixteen P.V.C columns (height = 30 cm; diameter = 20 cm) were constructed as shown in Figure 4.4. The columns were fitted at the base with a perforated template to allow leachate drainage but to prevent soil flowing to the outlet pipe. The rubber outlet pipe was fitted with a jubilee clip so that flow was regulated until the time of collection. The columns were placed on two large specially constructed tables which had perforations to allow the outlet pipe through and collection containers were placed under these. Each particular soil column was constructed in duplicate to give the experimental design detailed in Table 4.5.

The soils were air-dried and placed in the columns to a standard height (23 cm) so that all columns had similar levels of soil. Compaction was assured by filling the columns in a series of layers which were compacted down before the next successive layer. Prior to irrigation the soils were saturated several times in order to ensure that all water soluble soil elements had been washed from the soil.

Leachate was applied to the top of the columns each week by means of a watering can and the filtrate was collected the following week. The leachate was collected fresh each week. During weeks 1 to 5 the columns were irrigated at a rate of 500 mls inside the laboratory. The columns were then placed in the external environment in order to monitor the effects of natural temperature variations on leachate renovation efficiency. The columns were situated in a sheltered alcove on the roof



Hatched area indicates soil infill.

Figure 4.4 Construction of soil columns.

TABLE 4.5 EXPERIMENTAL DESIGN

COLUMN	DESCRIPTION
1	Topsoil and Perennial Ryegrass
2	Topsoil and Perennial Ryegrass
3	Bare Topsoil
4	Bare Topsoil
5	Peat and Perennial Ryegrass
6	Peat and Perennial Ryegrass
7	Bare Peat
8	Bare Peat
9	Sand and Perennial Ryegrass
10	Sand and Perennial Ryegrass
11	Bare Sand
12	Bare Sand
13	Clay and Perennial Ryegrass
14	Clay and Perennial Ryegrass
15	Bare Clay
16	Bare Clay

of the University. During the first 5 weeks of external exposure (weeks 6 to 10) the columns were irrigated at 500 mls/week. The irrigation rate was increased to 1000 mls/week during weeks 11 to 13; to 1500 mls/week during weeks 14 to 16 and to 2000 mls/week during weeks 17 to 18. The filtrate from each column was collected after seven days and analysed for total volume, pH, chemical oxygen demand (COD) and ammonia.

4.4 RESULTS

4.4.1 General Observations

The following general observations were made during the column tests. The leachate collected after passing through the sand columns appeared free of most suspended matter and colour; that passing through the topsoil was slightly discoloured although not as dark as the original leachate; the effluents from the peat and clay columns were highly discoloured with a high suspended solids content. The vegetation which was lush on all columns except peat prior to irrigation suffered badly by week 4 with the grass becoming bare and sparse. This is thought to be due to the high organic content of the leachate. A slime layer was also observed to develop on the top of each column. The permeability of the columns was reduced as time, or the leachate volume added, increased. At different time periods during the study, each column exhibited a minimum permeability, and, thereafter the permeability increased, although not reaching its initial condition.

4.4.2 Effluent Volumes

The relative volume of the effluent collected each week was calculated according to the formula V/Vo where V is the quantity of collected effluent (mls) and Vo is the original leachate volume added to the top of the column for that irrigation cycle.

Figure 4.5 displays a histogram of V/Vo for topsoil during the 18 week experimental period. Throughout the experimental period both vegetated topsoil and unvegetated topsoil produced a lower quantity of effluent than the applied influent (which is reflected in relative values less than 1). During the first 5 weeks of the experiment the effluent from the unvegetated topsoil was relatively constant and consistently less than that of the vegetated column effluent. The vegetated topsoil column had a relatively large effluent volume during the first two weeks of the experiment which then decreased to values approaching that of the bare topsoil columns. This may be due to the vegetation 'opening up' the structure of the topsoil and allowing more rapid passage of liquid. A similar pattern of vegetated columns producing a greater effluent was followed by clay (Figure 4.6) and sand columns (Figure 4.7). This difference between vegetated and unvegetated soils is most marked in the sand columns. Again this is thought to be due to vegetation allowing greater passage of liquid through the soil. The difference in effluent production between vegetated and unvegetated columns is not as marked in the peat soil columns (Figure 4.8) and this is thought to be due to the sparse establishment of perennial ryegrass on the vegetated columns. For all soil columns there appeared to be a decrease in effluent volume during the initial period of exposure to the external environment. This is probably due to an increase in evaporation of liquid from the soil surface. All columns then tended to show a general increase in relative values as the irrigation rate increased. The pattern is erratic however and is probably due to a differing time lag between leachate application, soil liquid storage and final effluent collection.

The unvegetated sand columns produced negligible or low amounts of effluent during the first eleven weeks of irrigation. This is probably due to the larger pore space of this soil being able to store larger volumes of water. As the leachate application rate increased the volume of effluent produced increased which would indicate that increased hydraulic loading is forcing the stored water to the outlet.

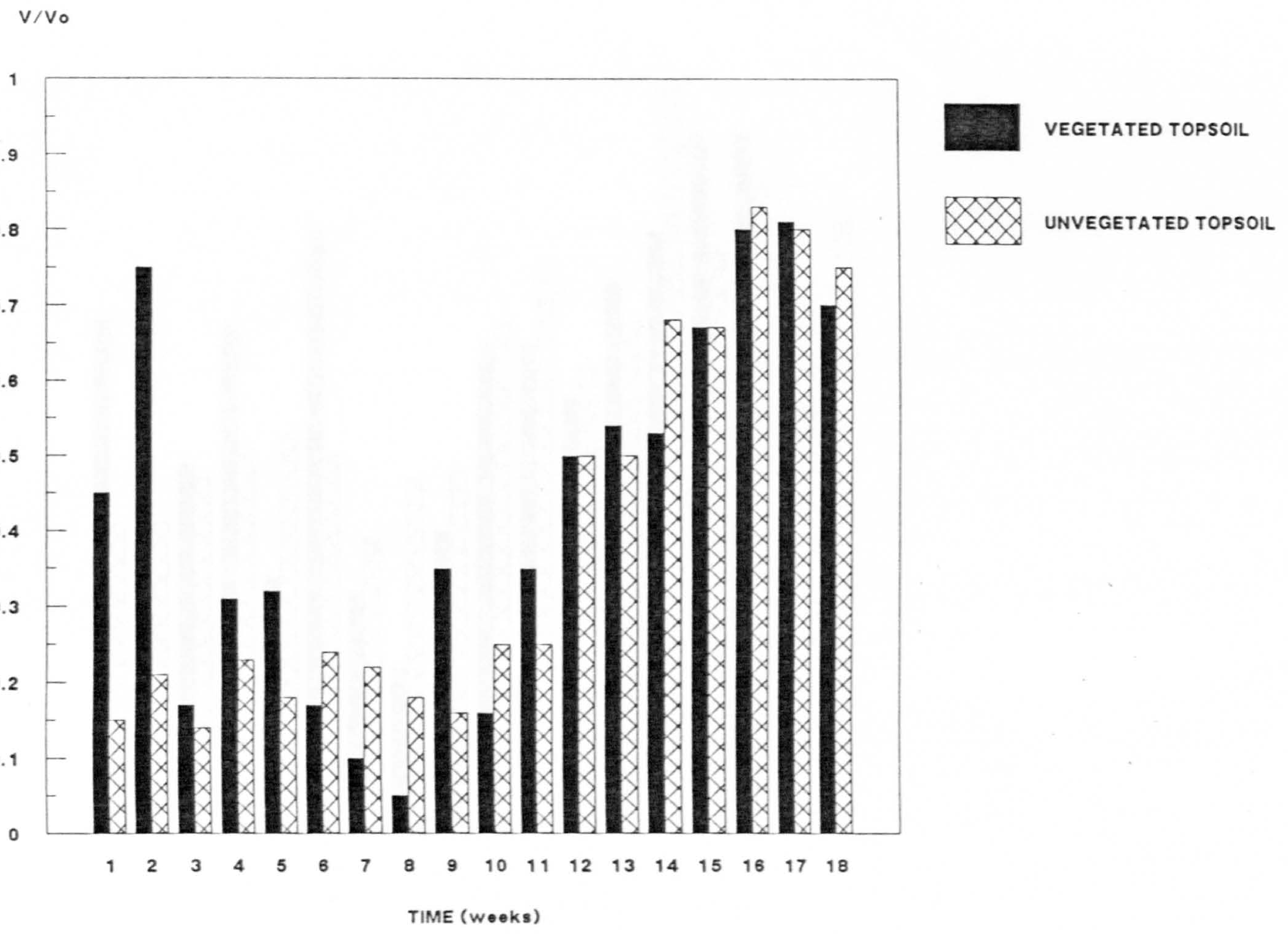


FIGURE 4.5 V/Vo VALUES FOR TOPSOIL COLUMNS

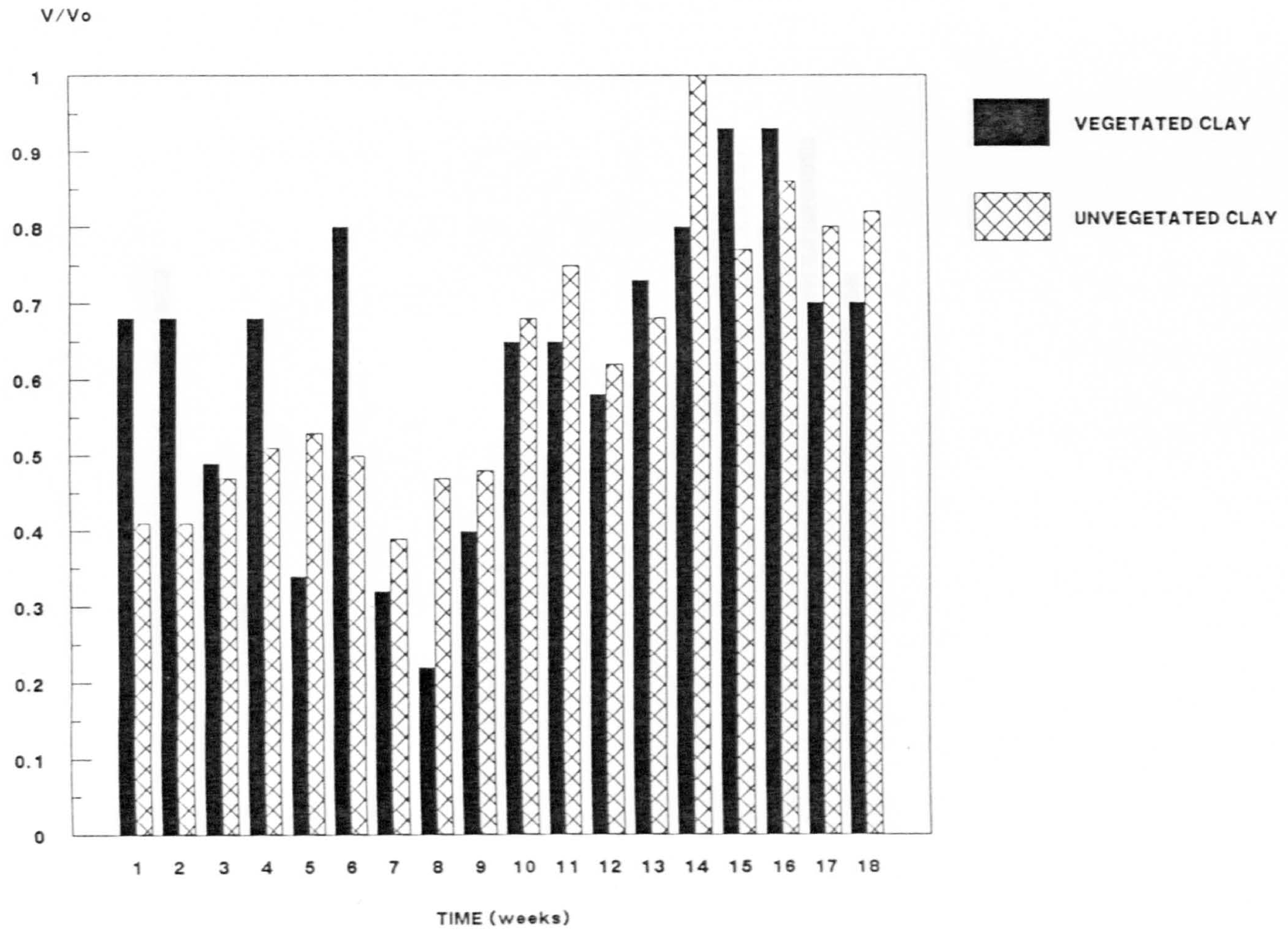


FIGURE 4.6 V/Vo VALUES FOR CLAY COLUMNS

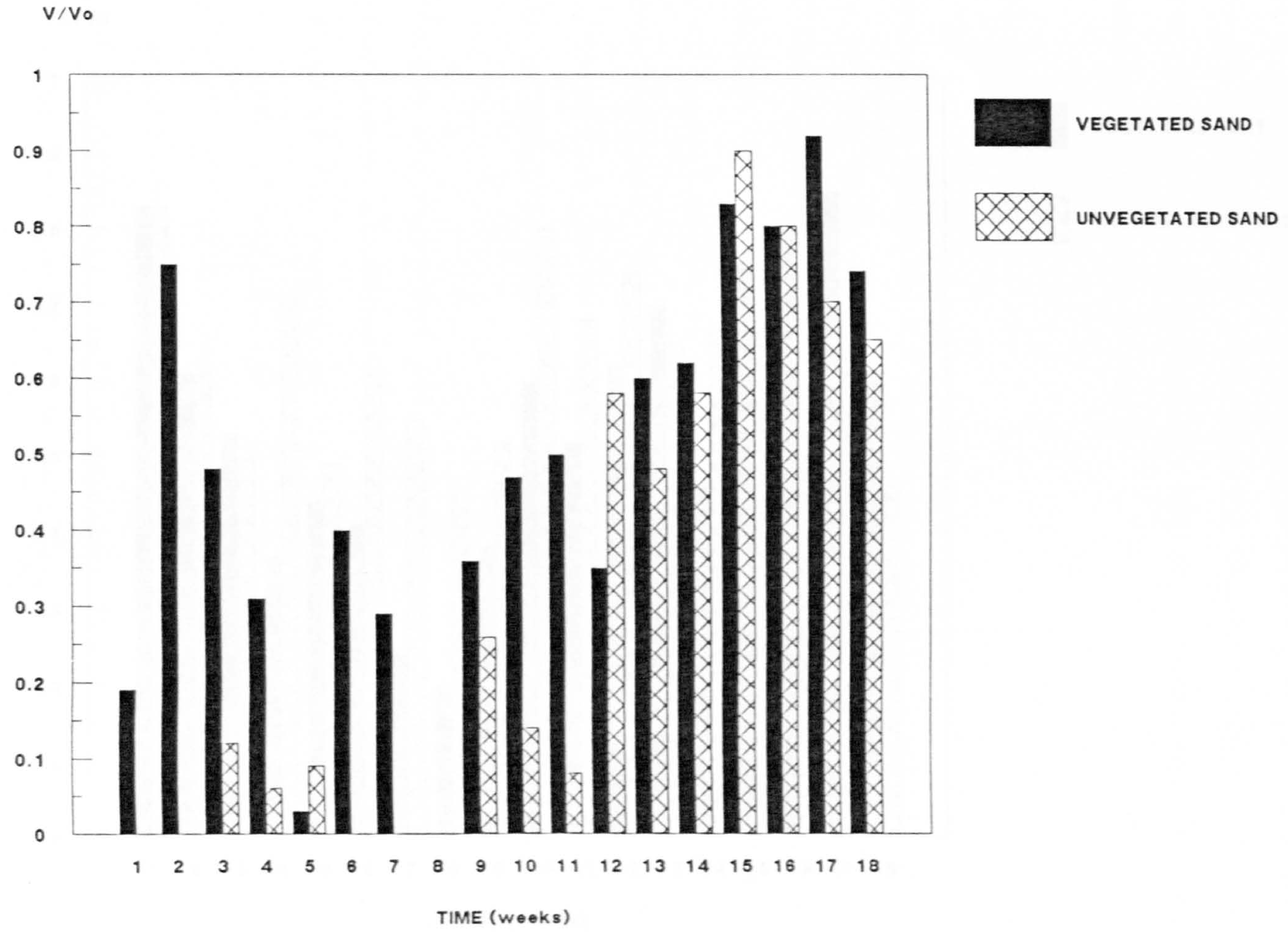


FIGURE 4.7 V/Vo VALUES FOR SAND COLUMNS

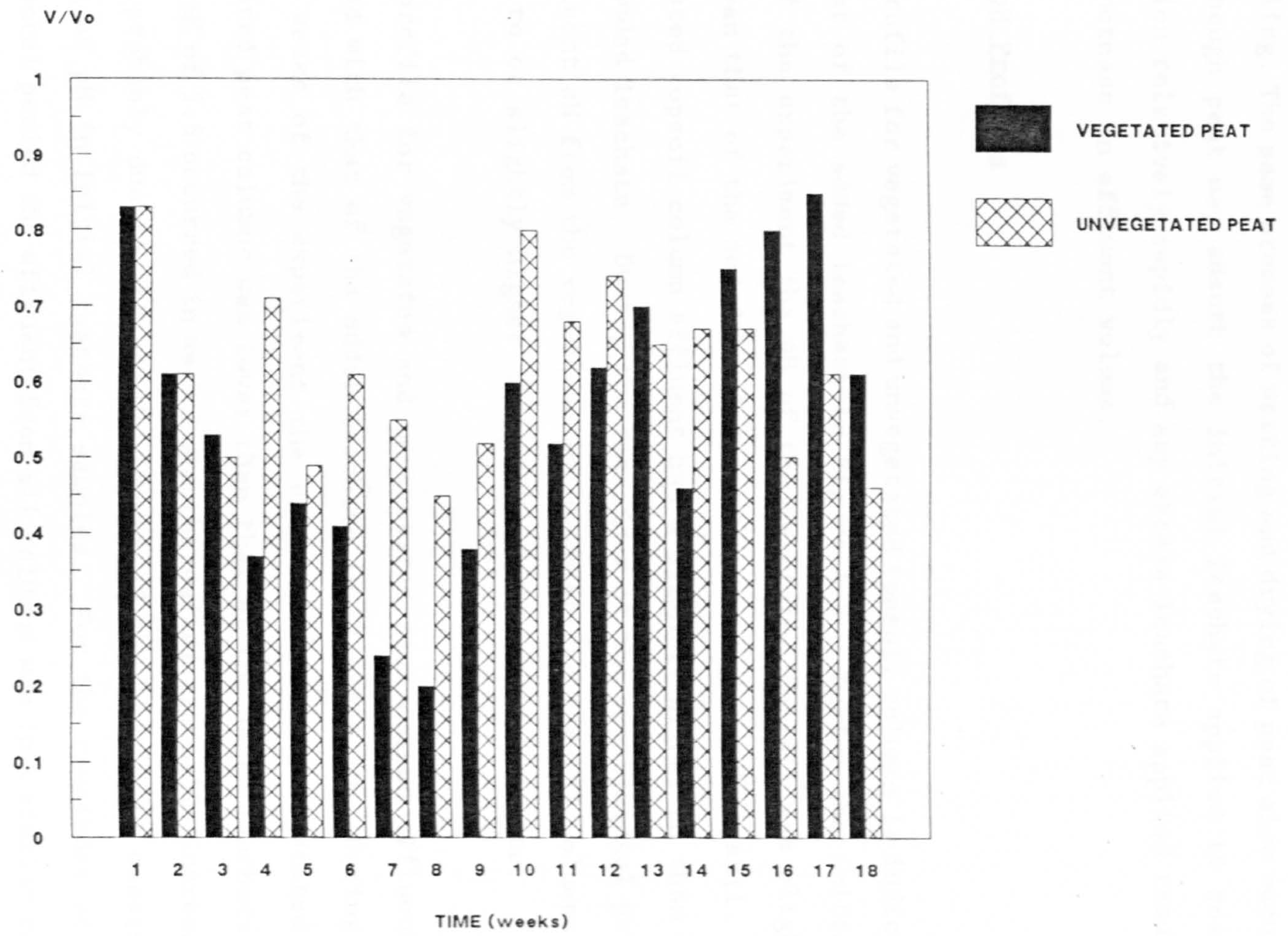


FIGURE 4.8 V/Vo VALUES FOR PEAT COLUMNS

Overall, the clay and peat columns appear to produce the largest total quantity of effluent. In the case of clay this may be due to channelling within the column as in the interim between irrigation cycles the clay had the opportunity to dry and subsequent wetting and re-drying would lead to cracking of the clay core. It is also possible that the leachate is causing a breakdown in the clay structure which could again lead to channelling. The same process of wetting and drying of peat also occurred and although peat may adsorb the initial leachate applied it reached saturation relatively rapidly and any excess leachate applied resulted in an increase in effluent volume.

4.4.3 pH Profiles

The pH profile for vegetated and unvegetated topsoil columns is indicated with that of the added leachate in Figure 4.9. During the initial 4 weeks of the experiment the pH of the vegetated topsoil was slightly lower than that of the added leachate and the unvegetated topsoil. The unvegetated topsoil column effluent had a slightly higher pH than that of the added leachate. During the remainder of the experimental period the effluent pH from the vegetated and unvegetated topsoil columns was similar to or slightly higher than that of the added leachate.

The pH profile for vegetated and unvegetated peat column effluent is indicated with that of the added leachate in Figure 4.10. During the first 4 weeks of the experiment the effluent from the vegetated and unvegetated peat columns was lower than that of the added leachate. A minimum pH of 5.5 occurred in week 1 and thereafter gradually increased. This is probably due to the acidic nature of the peat soil causing a lowering of pH in initial leachate samples. For the remainder of the experimental period the effluent from all columns was in a similar range to that of the added leachate.

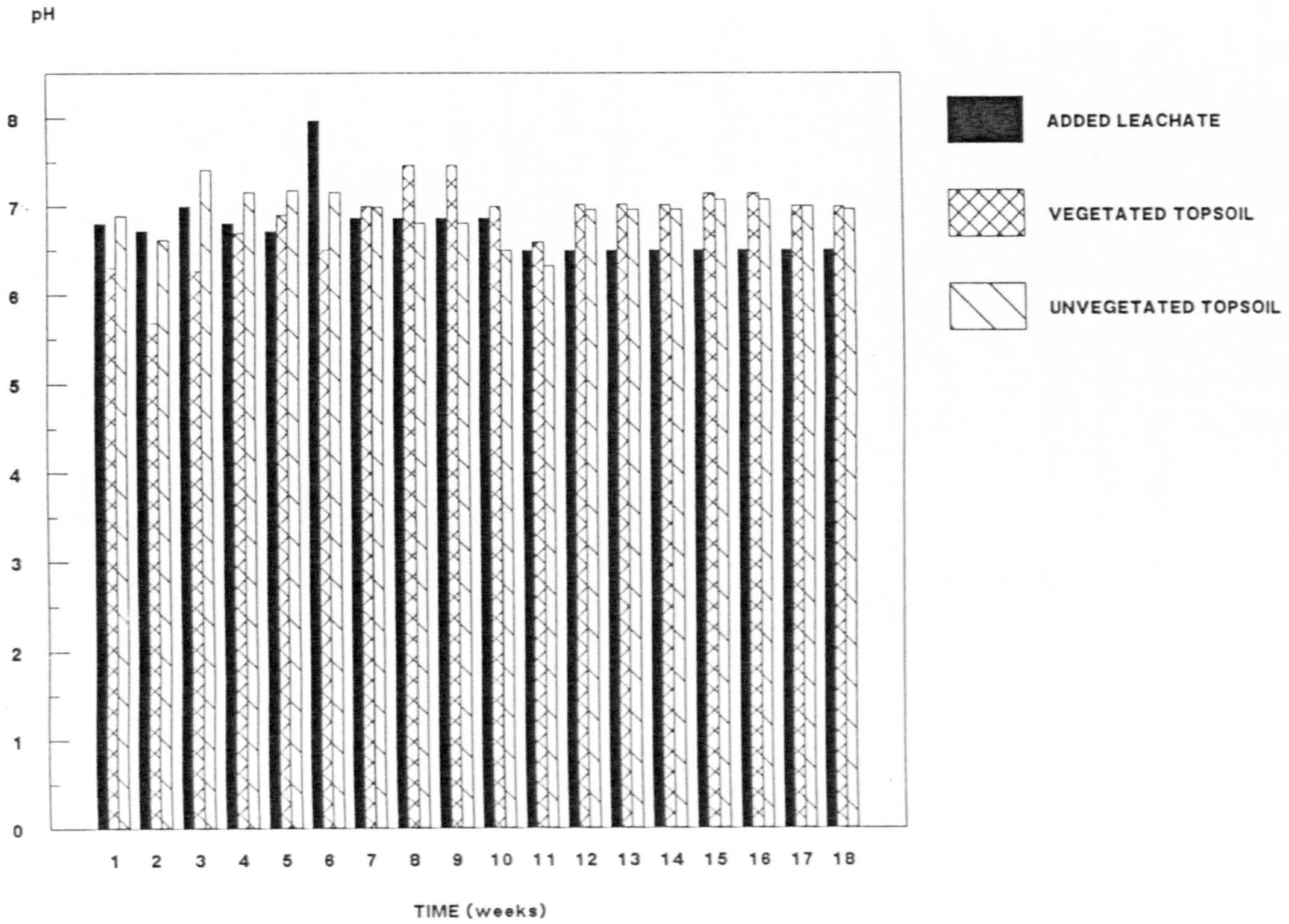


FIGURE 4.9 pH PROFILE FOR TOPSOIL COLUMNS

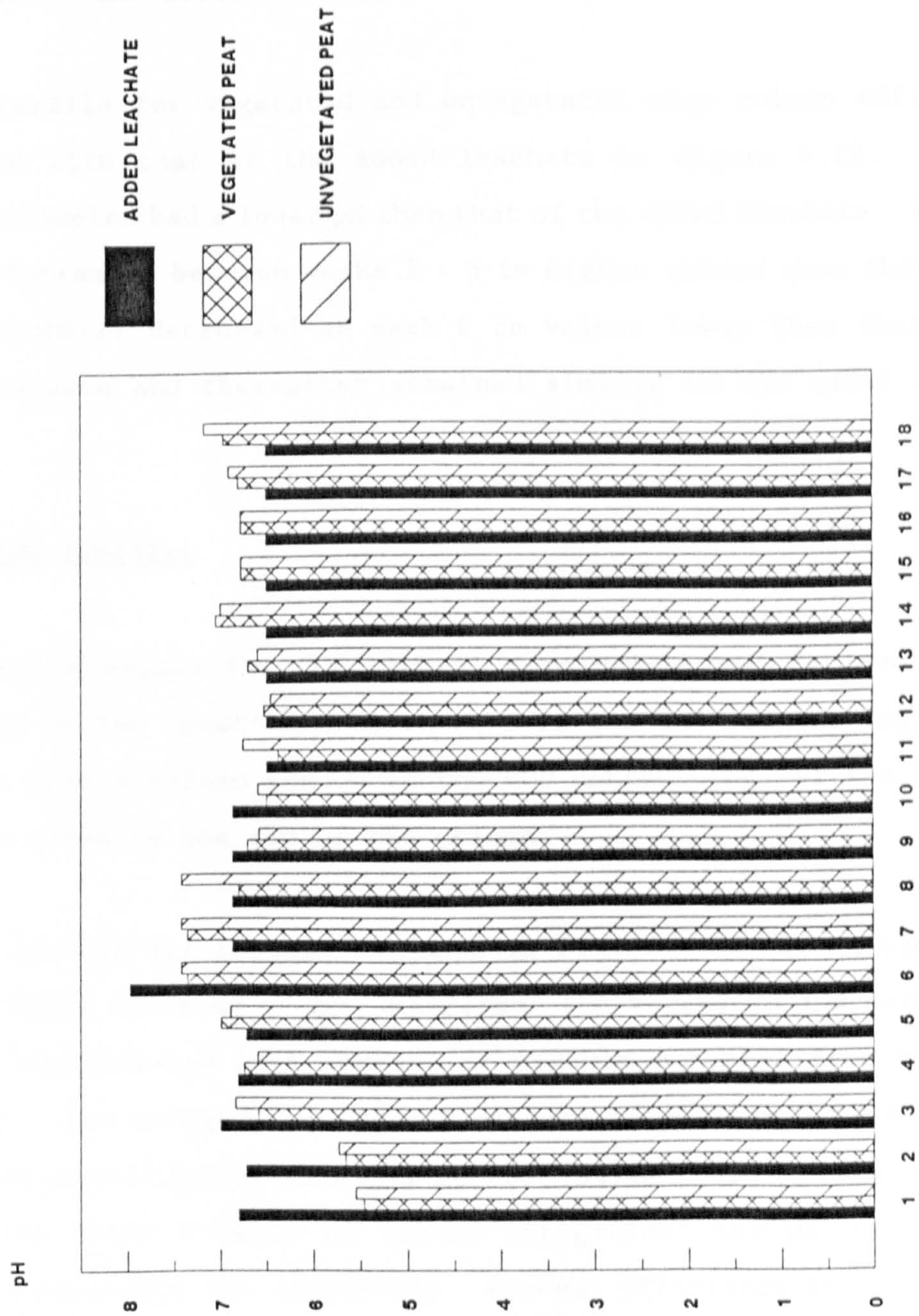


FIGURE 4.10 pH PROFILE FOR PEAT COLUMNS

The pH profile for vegetated and unvegetated sand column effluent is indicated with that of the added leachate in Figure 4.11. The effluent from the vegetated sand columns were initially low but gradually increased to slightly higher levels than that of the added leachate by week 5. During weeks 5 - 10 the effluent leachate was slightly lower than that of the added leachate. From week 11 onwards the effluent pH was higher than that of the added leachate.

The pH profile for vegetated and unvegetated clay column effluent is indicated with that of the added leachate in Figure 4.12. Initial effluent samples had a lower pH than that of the added leachate. Effluent pH then increased between weeks 3 - 5 to higher values than that of the added leachate; decreased at week 6 to values lower than that of the added leachate and thereafter remained similar to the added leachate pH.

4.4.4 COD Profiles

The relative values for COD removal were calculated for each column according to the equation C/Co where C is the COD content (mg) of the effluent from a column and Co is the COD content (mg) of the original leachate added to the top of the column.

The COD profile for topsoil is shown in Figure 4.13. It is clear that for the first 13 weeks of the experiment the vegetated and unvegetated topsoil demonstrated high removal of organic material from the added leachate. The unvegetated topsoil appears to perform better than the vegetated topsoil during this time period. Highest removal rates occurred during the first 5 weeks of column irrigation; the period when the columns were within the laboratory. Removal efficiency for COD was 90% or more. This is probably due to highly favourable environmental conditions for microbial establishment. A gradual decrease in removal efficiency occurred in the vegetated topsoil from week 6 to 9, although

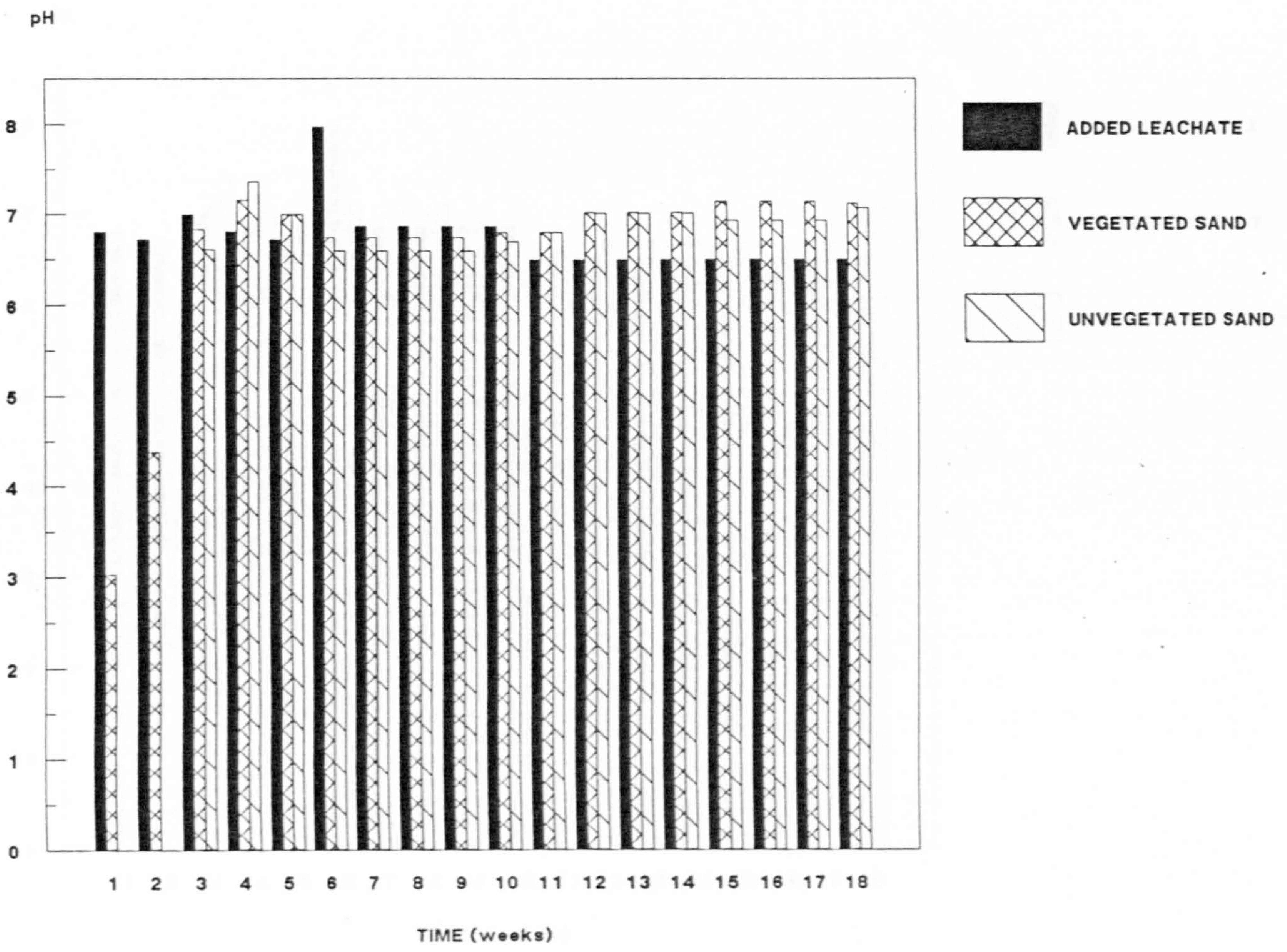


FIGURE 4.11 pH PROFILE FOR SAND COLUMNS

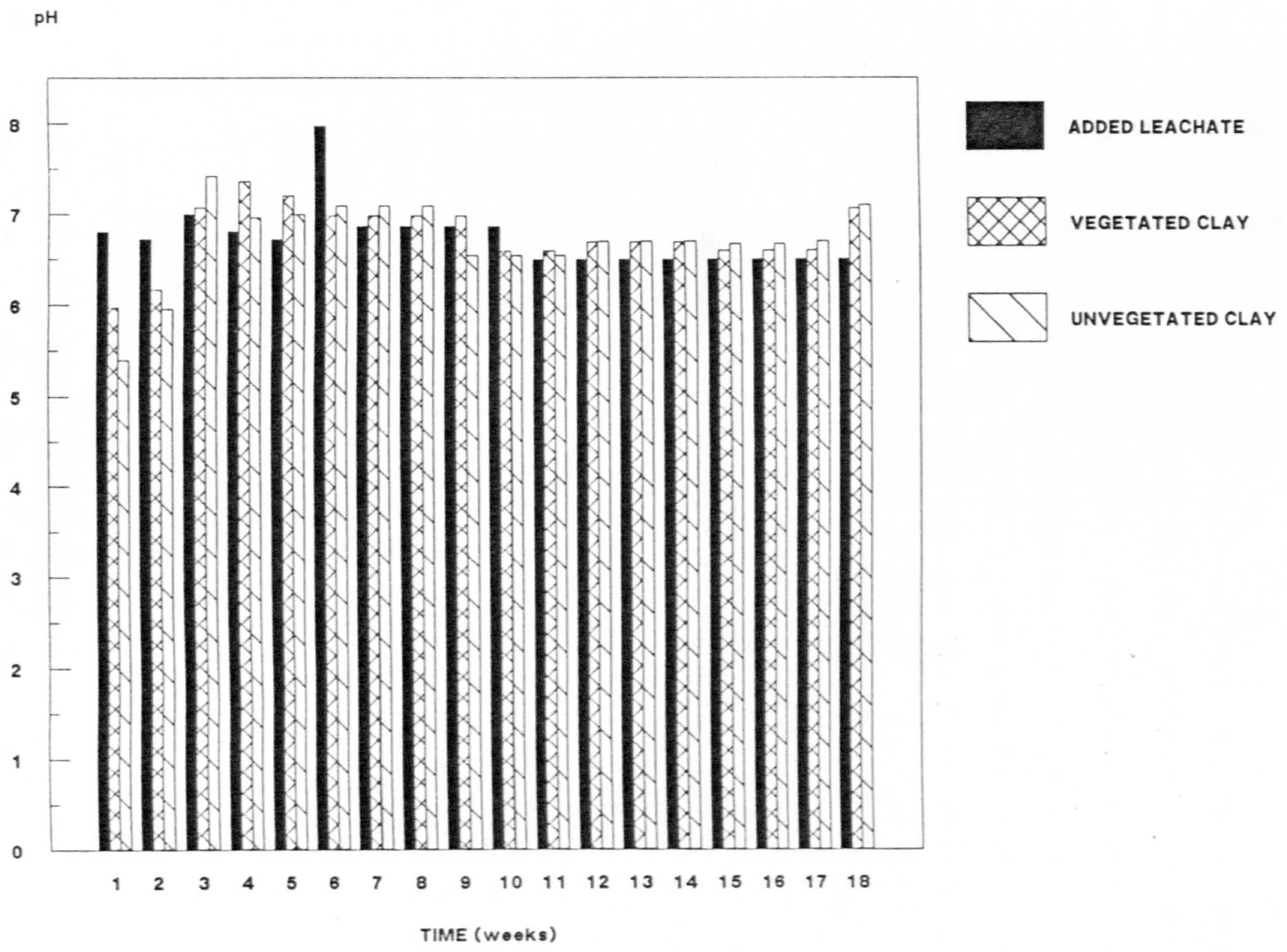


FIGURE 4.12 pH PROFILE FOR CLAY COLUMNS

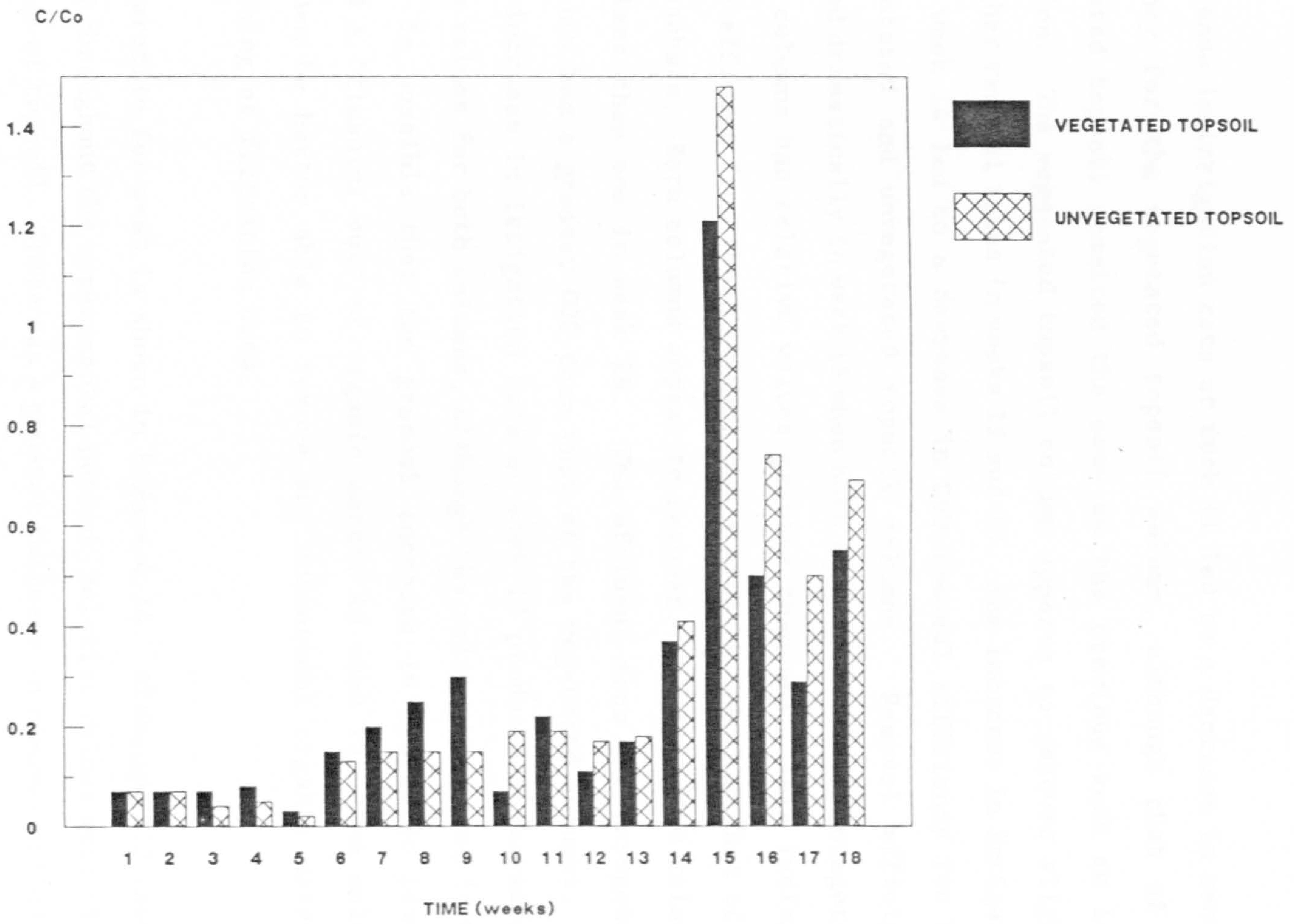


FIGURE 4.13 COD PROFILE - C/Co VALUES FOR TOPSOIL COLUMNS

removal efficiency increased on week 10. This is probably due to some die-back in microbial populations on initial exposure to the environment and the recovery in week 10 could be due to acclimatisation of microbes to the new environmental conditions. Although the unvegetated topsoil demonstrated a decrease in removal efficiency at week 6, the relative value remained constant to week 10.

The increase in irrigation rate at week 11 led to a decrease in removal efficiency for the vegetated topsoil column, although that of the unvegetated topsoil remained the same as the previous week at lower irrigation. The vegetated topsoil column appears to recover slightly with higher removal rates in weeks 12 and 13. The increase in irrigation rate at week 14 led to a decrease in COD removal efficiency for both the vegetated and unvegetated topsoil columns. Removal efficiency decreased dramatically in week 15 when both the vegetated and unvegetated topsoil columns had relative values greater than one. This indicates that the effluent from these columns has a greater COD than that of the added leachate. Both columns appear to recover, however, with relative values less than one in week 16. The effluent from the unvegetated columns now had a greater COD than that of the vegetated columns. The further increase in irrigation rate at week 17 produced a decrease in relative values for both columns, although the values increased in week 18. It is possible that the gradual increase in hydraulic loading produced a 'flushing out' of organic matter in week 15. The columns would then be better able to remove any subsequent organic material c.f. washing of filtration beds.

The COD profile for peat is shown in Figure 4.14. Although COD removal occurred throughout the experimental period, relative values were higher than those of topsoil. There was a general increase in removal efficiency during the first 5 weeks for the vegetated peat while that of the unvegetated remained relatively constant. The relative values for both columns increased in week 6 on exposure to the external environment.

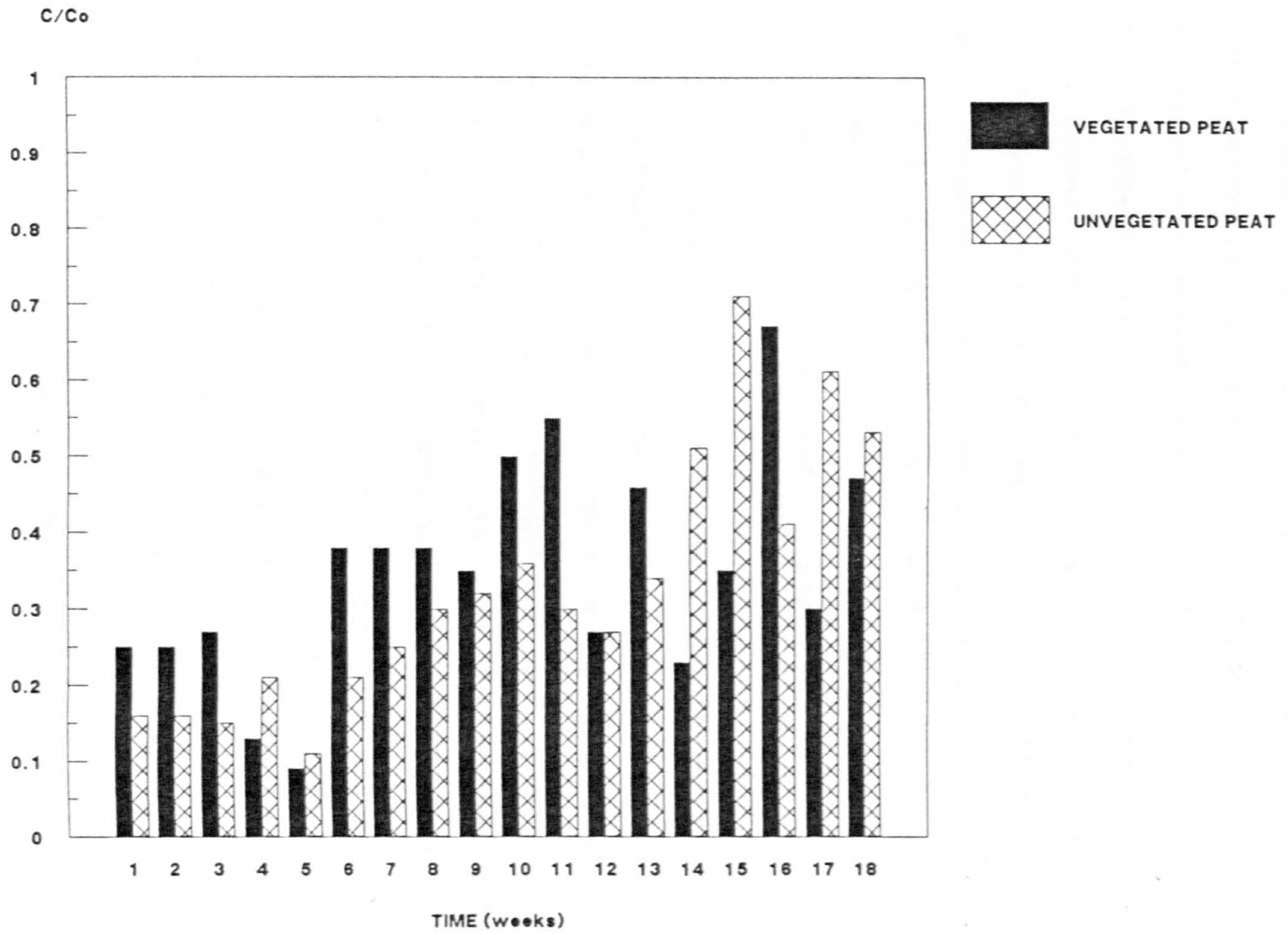


FIGURE 4.14 COD PROFILE - C/Co VALUES FOR PEAT COLUMNS

The relative values for unvegetated peat columns increased gradually to week 10. The relative values for vegetated peat columns remained constant between weeks 6 - 8, decreased in week 9 and increased in week 10; the COD of effluent from vegetated peat columns was continually higher than those of unvegetated peat during this time period. On increasing the irrigation rate at week 11 the relative value for vegetated peat columns increased while that of unvegetated peat decreased. The vegetated peat column appears to recover during week 12; but relative values for both columns increase in week 13. Increasing the irrigation rate in week 14 increased the removal efficiency for vegetated peat but decreased the removal efficiency for unvegetated peat. There was a decrease in removal efficiency during weeks 15 and 16 for vegetated peat columns; unvegetated peat column effluents increased in relative value in week 15 but appear to recover in week 16. The final increase in irrigation rate at week 17 improved removal in vegetated peat columns but decreased removal rate in unvegetated peat.

The COD profile for sand is shown in Figure 4.15. During the first 14 weeks of the experiment both the vegetated and unvegetated sand columns demonstrated substantial removal of COD from the added leached; the highest of the four soils tested. Unvegetated sand columns performed better than vegetated sand columns. At week 15, however, both the vegetated and unvegetated sand columns had peak relative values indicating that the COD of the effluent from these columns was greater than the'COD of the added leachate. The relative value for unvegetated sand is higher than that of the vegetated sand. The relative values for both columns decrease from week 15 to 18 although they do not reach the low levels of the initial 14 weeks. This would seem to indicate a 'flushing' of organic matter from the soil columns at week 15 due to the increase in hydraulic loading c.f. topsoil columns. However, this flushing appears to allow the sand beds some amount of recovery.

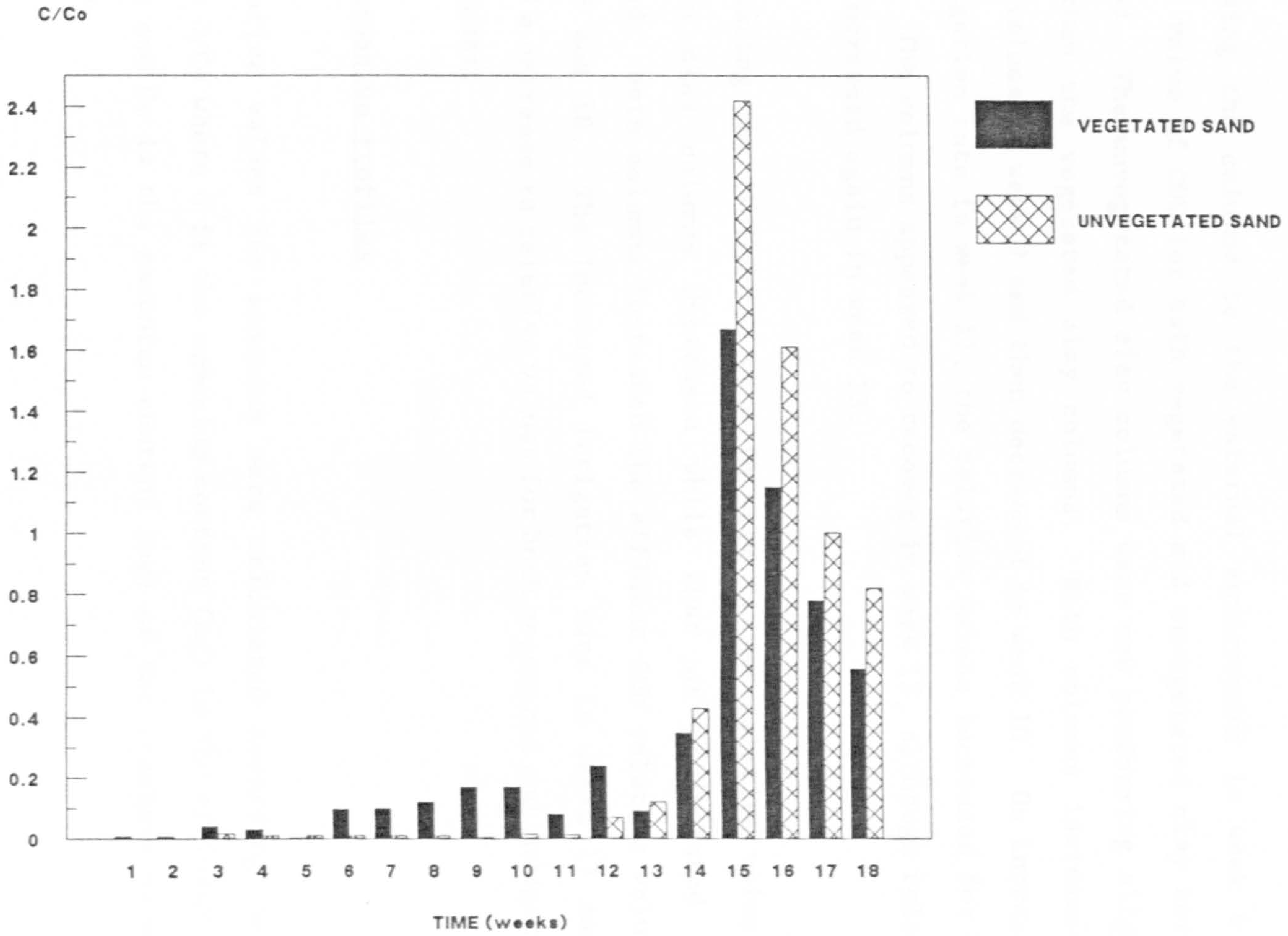


FIGURE 4.15 COD PROFILE - C/Co VALUES FOR SAND COLUMNS

The COD profile for clay is shown in Figure 4.16. Although COD removal occurred throughout the experimental period, clay did not perform as well as topsoil and sand at organic removal. During the first four weeks of irrigation the removal rate was constant with vegetated clay performing slightly better than unvegetated clay. The removal rate for both columns decreased in week 5.

On exposing the columns to the external environment in week 6 the relative value of COD for both vegetated and unvegetated clay columns increased. The unvegetated clay columns were now performing slightly better than the vegetated clay columns. Both columns increased to maximum values at week 9 and then decreased in week 10. On increasing the irrigation rate in week 11, the relative values increased for both columns. The columns appeared to recover in week 12, although relative values increased again in week 13.

On increasing the irrigation rate in week 14 the relative value for vegetated clay columns decreased while that of unvegetated clay increased. Both columns increased the effluent COD relative value in weeks 15 and 16. The increased irrigation rate in weeks 17 and 18 produced a decrease in relative values for both vegetated and unvegetated clay columns.

4.4.5 Ammonium Profiles

The relative values for ammonium were calculated according to the equation C/Co where C is the ammonium content (mg) in the effluent from a column and Co is the ammonium content (mg) of the leachate added to a column.

The ammonium profile for vegetated and unvegetated topsoil column effluents is illustrated in Figure 4.17. Both topsoil columns demon-

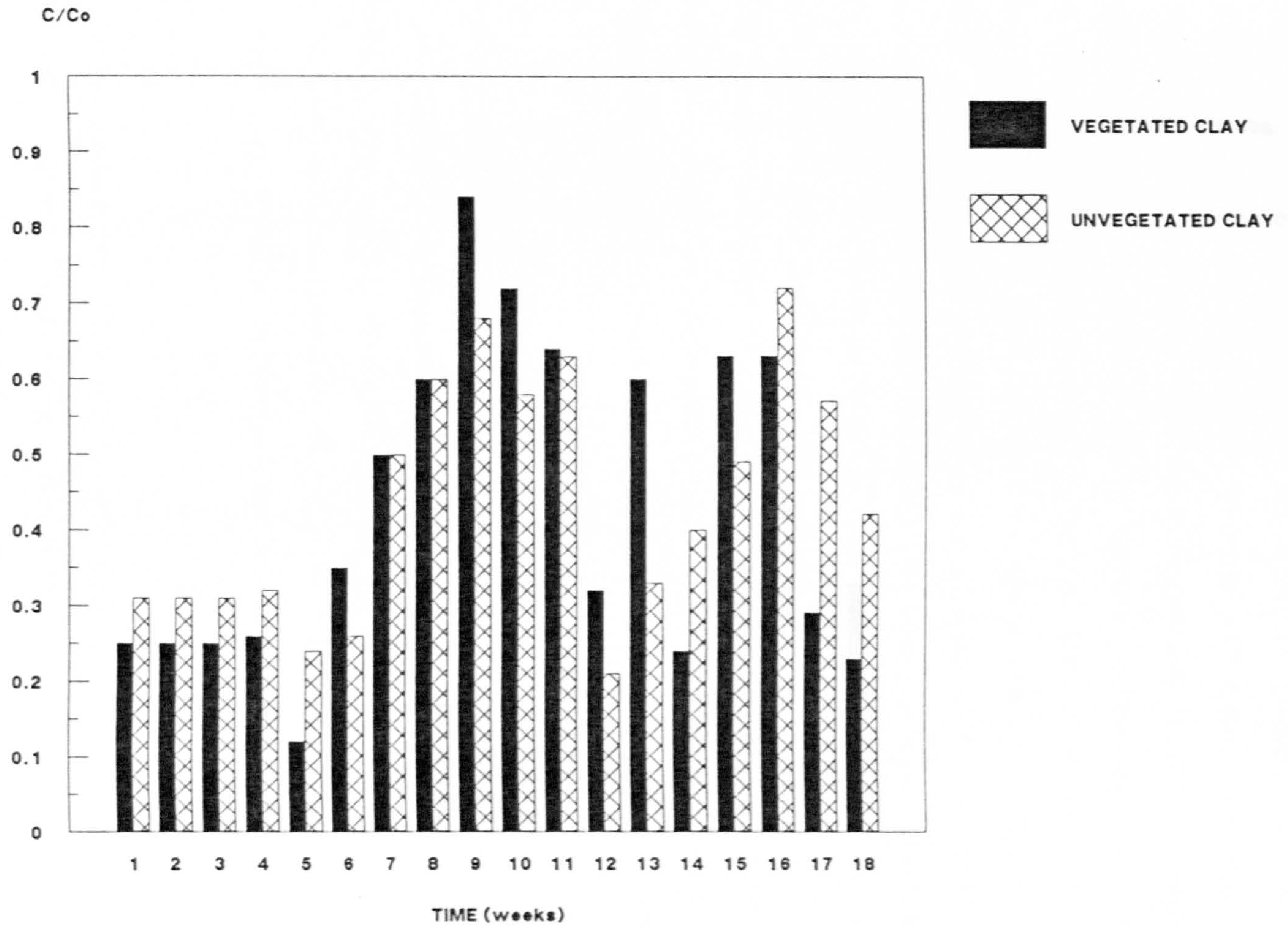


FIGURE 4.16 COD PROFILE - C/Co VALUES FOR CLAY COLUMNS

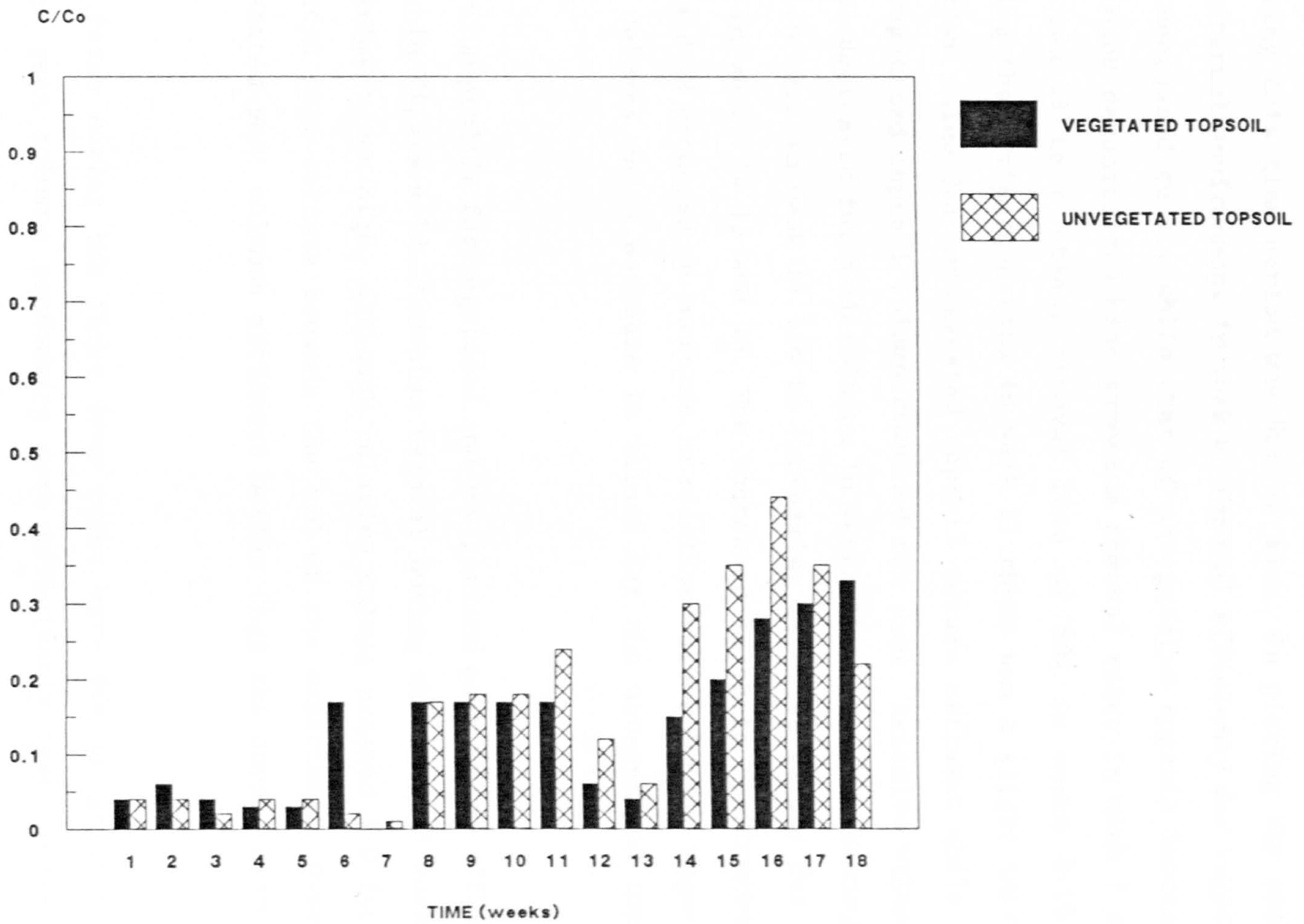


FIGURE 4.17 AMMONIUM PROFILE - C/Co VALUES FOR TOPSOIL COLUMNS

strated ammonium removal from the added leachate of 50% or more throughout the experimental period. Overall, the vegetated topsoil columns removed more ammonium than the unvegetated topsoil columns.

Highest removal rates for both columns occurred during the first five weeks of irrigation when the columns were within the laboratory. Removal rate during this time period was 90% or more. On placing the columns in the external environment in week 6, removal efficiency for vegetated topsoil decreased to 80% while that of unvegetated topsoil increased. Both columns demonstrated high ammonium removal rates in week 7 which then decreased to a steady removal rate of 80% in weeks 8-10. On increasing the irrigation rate in week 11 there was a slight increase in relative value for unvegetated topsoil column effluent while that of the vegetated topsoil column remained the same. Relative values of effluents decreased for both columns in weeks 12 and 13. Increasing the irrigation rate in week 14 led to increasing relative values for both columns in weeks 14,15 and 16. The increased leachate application in week 17 and 18 produced an increase in relative values for the vegetated topsoil columns and a decrease in values for the unvegetated topsoil columns.

The ammonium profile for vegetated and unvegetated peat column effluents is shown in Figure 4.18. Ammonium removal during the initial weeks of the experiment was high, although relative values reached 1.0 for the unvegetated peat columns towards the end of the experiment. Overall, the vegetated peat columns performed better than the unvegetated peat columns.

Removal rates during the first five weeks were 60% or greater with vegetated peat columns performing more efficiently than unvegetated peat columns. On placing the columns in the external environment the unvegetated peat demonstrated a peak relative value indicating twice as much ammonium in the effluent as in the added leachate. The removal

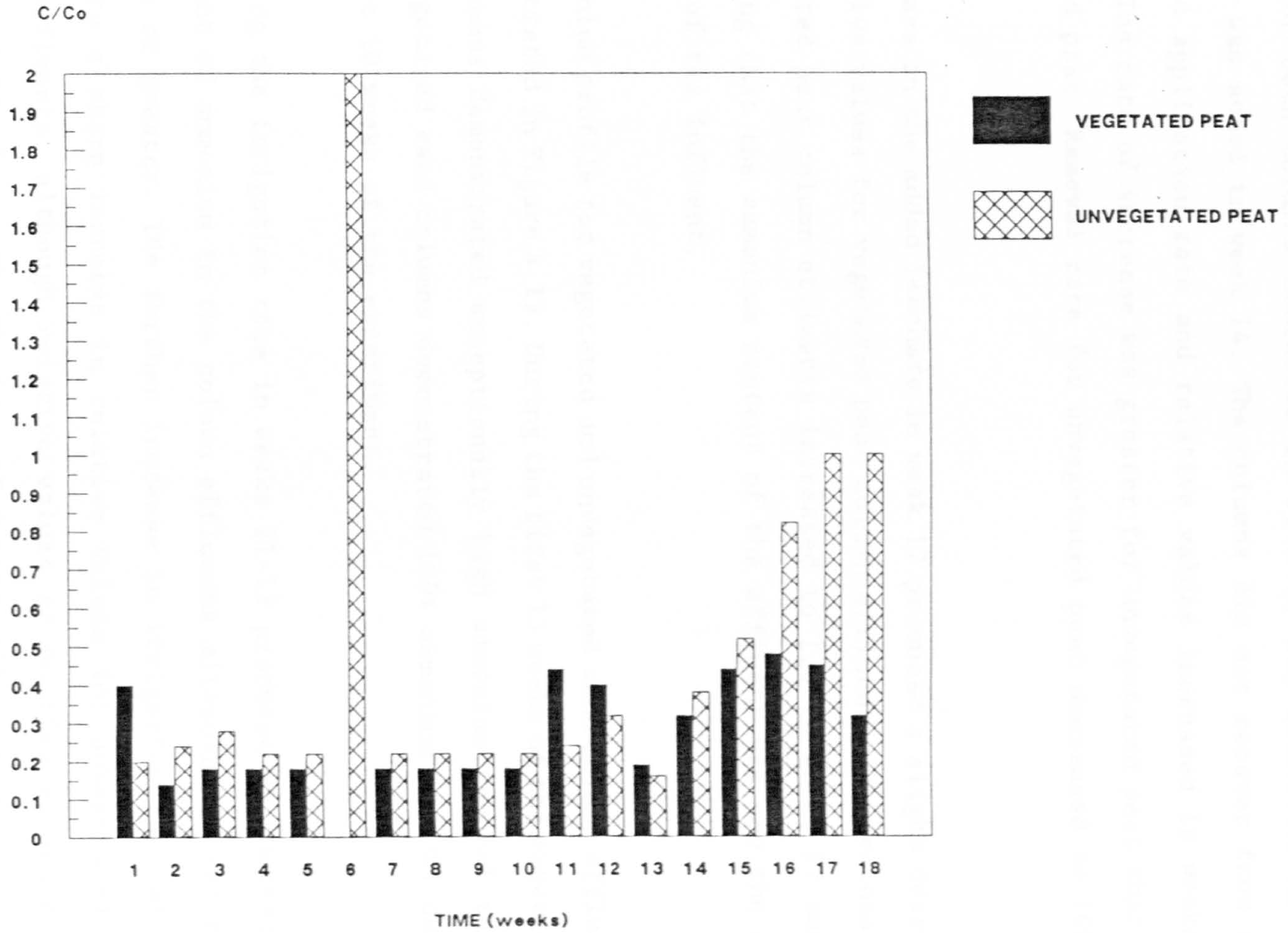


FIGURE 4.18 AMMONIUM PROFILE - C/Co VALUES FOR PEAT COLUMNS

efficiency of the vegetated peat columns was unaffected by exposure to external conditions. The removal rates for both columns was constant during weeks 6 to 10 at approximately 80% for vegetated peat and 75% for unvegetated peat. Increasing the irrigation rate in week 11 increased the relative values, with the increase for vegetated peat columns being greater than that for the unvegetated peat column effluents. The relative values for both columns decreased in week 13 but increased as more leachate was added in week 14. The columns did not recover from this increased application rate and relative values increased in weeks 15 and 16. The rate of increase was greater for unvegetated peat than for vegetated peat. Removal rate for unvegetated peat decreased to 10% in week 16.

An increase in the added leachate in week 17 produced a slight decrease in relative values for vegetated peat column effluents. The values for unvegetated peat column effluents increased to 1.0 in weeks 17 and 18 indicating that the ammonium content of the effluent was now the same as that of the influent.

The ammonium profile for vegetated and unvegetated sand column effluents is illustrated in Figure 4.19. During the first 13 weeks of the experiment both columns demonstrated exceptionally high ammonium removal rates; the unvegetated sand columns demonstrated 100% ammonium removal during the first 10 weeks of the experiment.

Increasing the irrigation rate in weeks 11-13 produced an increase in the amount of ammonium in the column effluents although removal rates were 85% or greater. The further increase in irrigation rate at week 14 led to a sharp increase in relative values for unvegetated sand column effluents, although relative values at no time exceeded 1.0. This is probably due to the flushing of stored pollutants from the sand as was demonstrated in the COD profile for sand. After the high relative value of 0.99 the unvegetated sand columns appear to recover and the

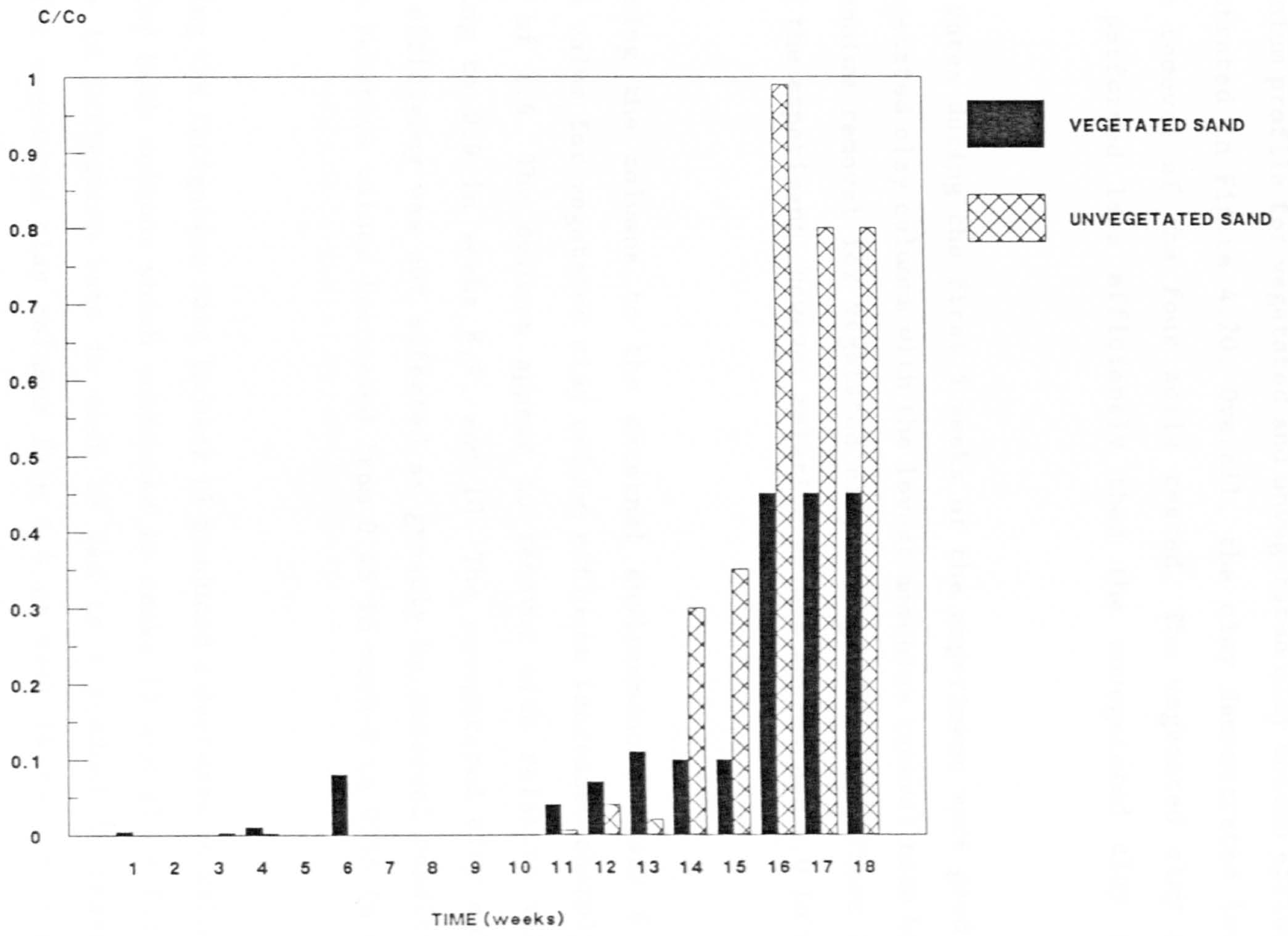


FIGURE 4.19 AMMONIUM PROFILE - C/Co VALUES FOR SAND COLUMNS

increased irrigation rate in weeks 17 and 18 led to a decrease in relative value for the unvegetated sand column effluents. The vegetated sand columns were unaffected by the increase in irrigation rate at week 14, although removal efficiency decreased to 55% during weeks 16,17 and 18.

The ammonium profile for vegetated and unvegetated clay column effluents is illustrated in Figure 4.20. Overall, the clay demonstrated lowest ammonium removal of the four soils tested. The vegetated clay soil columns performed less efficiently than the unvegetated clay soil columns.

Removal rates during the first 5 weeks of the experiment were good for the unvegetated clay columns with the lowest ammonium removal rate being 65%. Ammonium removal for vegetated clay was good for the first four weeks of the experiment; however relative values approached 1.0 in week 5.

On exposing the columns to the external environment in week 6 the relative value for vegetated clay column effluent increased sharply to a value of 2.6. The columns appear to recover with relative values decreasing to 0.9 in weeks 8,9, and 10. The unvegetated clay column removal efficiency was not affected as greatly by external conditions although relative values increased from 0.45 in week 6 to 0.55 in week 10.

Increasing the irrigation rate in week 11 produced a decrease in relative values for both columns which continued in weeks 12 and 13. A further increase in irrigation rate in week 14 led to a gradual increase in values for vegetated clay columns from 0.4 at week 14 to 0.8 at week 16. The unvegetated clay column effluents did not demonstrate as sharp an increase in relative values, increasing from 0.3 at week 14 to 0.35 at week 16. The final increase in leachate application rate at week 17

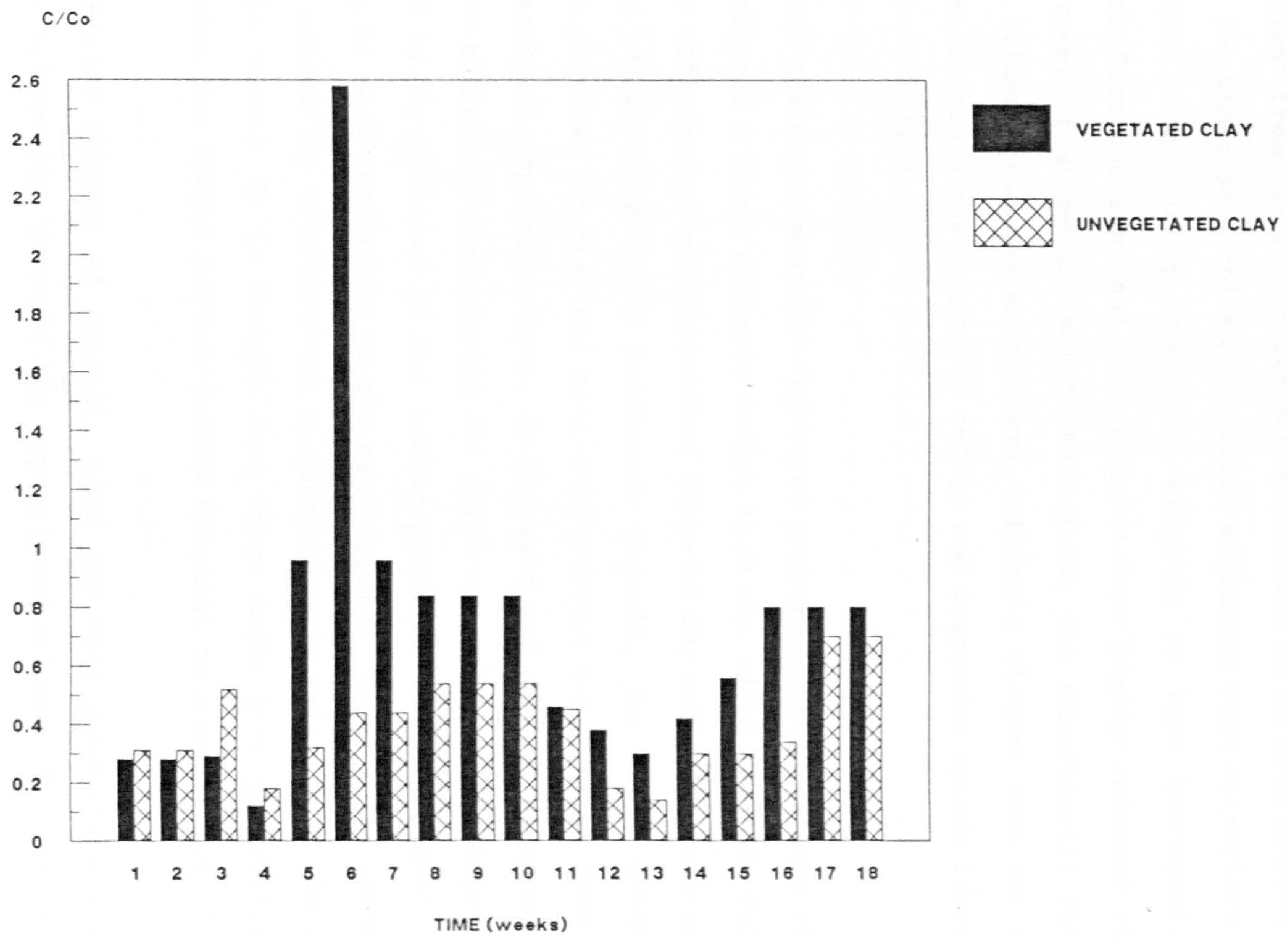


FIGURE 4.20 AMMONIUM PROFILE - C/Co VALUES FOR CLAY COLUMNS

did not alter the relative values of the vegetated clay column effluents; the unvegetated clay column effluent relative values increased to 0.7 in weeks 17 and 18.

4.5 DISCUSSION AND CONCLUSIONS

The effluent from the sand columns was observed to be much clearer than that of the other soil columns. Initial effluents were colourless with the degree of colouring increasing slightly as time increased. The effluents from the peat and clay columns were highly coloured with a large amount of suspended solids throughout the experimental period. Topsoil columns produced an effluent initially clearer than the added leachate, although the degree of colour and suspended solids increased markedly with time.

Throughout the experiment the vegetated and unvegetated columns of all soils produced a lower effluent volume than the added leachate volume, although effluent volumes approached those of the added leachate as the quantity of leachate added increased. Overall, the total volume of effluent produced by clay and peat soil columns was greater than that of the sand and topsoil columns. In the sand and topsoil columns there was a low effluent volume during the first ten weeks of the experiment followed by an increase in the latter parts of the experiment. This time lag is most noticeable in the sand columns. These soils contain a greater proportion of macropores to micropores in relation to the other two soils tested. It is thought that these soils have the ability to store water for longer periods before eventual release of liquid.

The vegetated columns of topsoil, sand and clay produced a greater effluent volume than those of the unvegetated columns. This is thought to be due to the vegetation allowing more rapid passage of liquid through the soil due to the plant roots "opening up" the soil structure. The difference between the vegetated and unvegetated peat columns is not as marked as there was poor vegetation establishment on these soils.

The pH of the effluent from all soil columns appears to undergo a short period of adjustment within the initial weeks of the experimental period. Thereafter, the effluent pH from all soil columns appears to be similar to that of the added leachate pH.

The main method of removal of organic material from leachate is thought to be biological degradation. This reaction relies on a reservoir of oxygen within the soil.

One of the most important soil properties affecting oxygen content is the relative proportions of micropore and macropore space. A fine textured soil (in which micropore spaces predominate) is least desirable while a coarser soil will have larger pore spaces and hence a greater oxygen content. Excessive hydraulic loading and soil surface clogging impede aeration. Anaerobic microbial decomposition of leachate is very slow, and adding large amounts of leachate to a soil could create anaerobic conditions. Leachate not only occupies the pore space because of its high dissolved solids content, thus excluding air from the soil, but it also greatly increases the oxygen demand for bio-oxidative metabolic activity. Soils with a high ratio of macropores tend to be rapidly drained so that aeration is maintained.

Pore size also plays a role in the development of microbial colonies in the soil and in their ability to degrade organics. Establishment of a microbial population requires that organisms reproduce and spread through the soil. Hence the smallest diameter along the length of the pore must be large enough to permit the passage of the bacterium by Brownian or flagellar movement. Microorganisms disappear more rapidly from the soil surface than below the surface, apparently because of dessication, effects of sunlight, and other factors at work at the soil surface. Therefore the ability of organisms to travel easily through the soil column will lead to their long-term survival and hence a more effective removal rate for organic material. Due to the small inter-pore space in clay the organisms will not be able to travel freely through the soil and hence will be trapped at the surface. They may therefore have a low survival rate. In contrast, the more aerated soils such as sand and topsoil will allow more rapid passage of organisms through the soil and allow population establishment which is more beneficial to long-term organic removal.

Sand and topsoil demonstrated greatest removal of organic material. This is thought to be due to the fact that they have a larger proportion of macropores than the clay soil. Hence an active microbial population is maintained and there is oxygen available for the biodegradation process. Sand was consistently better at removing organics than topsoil. The greater removal of suspended solids and colour in sand columns may indicate that a greater amount of particulate organic material is being trapped in sand pores and hence is available for biodegradation.

Peat demonstrated a lower removal efficiency for organics than sand and topsoil. Peat tended to drain rapidly and hence the leachate retention time in the soil and the trapping of particulates was minimal. Therefore, less time and material are available for biological degradation. Peat tends to form in fibrous layers so that channelling of leachate through the column tended to occur. This is reflected in the low suspended solids and colour removal from the added leachate.

Clay demonstrated lowest organic removal efficiency. This is thought to be due to the large ratio of micropores to macropores within the soil. Also, channelling is thought to have occurred in this soil as the clay was subject to a drying and wetting cycle which can lead to cracks in the soil core. The largest difference in removal efficiency between vegetated and unvegetated columns occurred with the clay soil. This is thought to be caused by the vegetative roots opening up the clay structure and maintaining aeration. Therefore, greater organic removal occurs in vegetated clay soil columns than in unvegetated clay soil columns.

A reduction in biological activity in the presence of clay minerals has been noted by several workers. Stotzky and Rem (1967) found that montmorillonite clay, and to some extent kaolinite, markedly inhibited the respiration of 27 species of fungi. Lavie and Stotzky (1986) found that the respiration of the fungi, *Histoplasma capsulatum*, was markedly reduced in the presence of increasing concentrations of montmorillonite, kaolinite and attapulgite clays. The reduction followed a pattern that suggested saturation-type kinetics :- an initial sharp reduction in respiration with low concentrations of the clays (0.01% - 0.5%) followed by a slight reduction with higher concentrations. Results of scanning electron microscopy indicated that montmorillonite and kaolinite were bound to the surface of the fungal mycelium and the amount of adhesion increased as the concentration of the clays increased. This coating was thought to interfere with the movement of nutrients, gases and waste products across the mycelial wall. There was a high direct correlation between the specific surface area of the clay containing systems and the reduction in respiration. Many fungi excrete polysaccharides with adhesive qualities (Martin and Adams, 1965) that may also have been involved in the apparent tight adhesion of the clays to the surface of *Histoplasma capsulatum*.

Adu and Oades (1978) found that in a sandy loam soil the fungi were considerably more active than bacteria due to their ability to explore aggregate surfaces and pores. In a grey clay the bacteria were more active than the fungi which was thought to be due to more favourable pH for bacteria and ready availability of substrate. Decomposition of organics requires contact between the organism and the organic substrate. If the material is in micropore space then insufficient bacteria can gain access to breakdown the particles. Ou and Alexander (1974) found that when substrates are in macropores in the soil i.e. easily accessible, bacteria play an equally important role in utilisation of the substrate.

Brown and Donnelly (1983) evaluated biodegradation in each of four soils at a 5% sludge application rate incubated at 30°C and moisture retention equal to 33 kPa. The greatest rate of CO_2 evolution occurred in Norwood soil (sandy clay), while CO_2 evolution in Nacogdoches (clay) and Lakeland (sandy loam) soils, was intermediate, and least evolution occurred in Bastrop clay.

Most of the nitrogen in landfill leachates is in the form of ammonium ions (NH_4^+). This positively charged ion may react with the cation exchange complex in the soil. However, competition with other cations in leachate such as calcium, magnesium, sodium and potassium limit this removal mechanism (Chapter 7).

Ammonium can also undergo nitrification. Nitrification essentially regenerates the capability of the soil to adsorb ammonium ions. Nitrification requires oxygen and is thus favoured in well aerated soils. The process is also affected by temperature and soil moisture.

Biodenitrification occurs when nitrate is converted into the gaseous forms N_2O or N_2 by microorganisms. The process occurs under anoxic conditions and the bacteria involved require organic carbon as an energy source.

In all columns, ammonia removal increased rapidly during the first three weeks of irrigation. The nitrifying population in soil is relatively small but it increases rapidly upon addition of ammonium to the soil.

Topsoil and sand performed more efficiently than clay and peat during the experiment. As with biodegradation of organics, this is thought to be due to the maintenance of aerobic conditions within these soils.

The soil column experiments have shown that different soil types have differing effects on leachate parameters. Vegetation will aid the treatment in some cases but the major removal occurs in the soil itself.

Topsoil and sand will give good leachate renovation as long as surface clogging is avoided. Peat and clay soils appear to be less efficient at treatment. This finding is particularly important in regard to the use of clay liners in landfill sites. If fissures occur in the clay, leachate passing through may not receive adequate treatment before reaching groundwater.

In these experiments the hydraulic and organic loading appeared to be the pollutant limiting waste application and not ammonia. Organic breakthrough occurred in week 15 for peat and clay and in week 18 for sand and topsoil.

In summary, topsoil and sand appear to be better at ammonia and organic removal than the other soils tested. It is believed to be due to the ability of these former two soils to maintain aeration in the soil - an essential requisite for efficient biodegradation.

The mechanisms in the soil which act to remove pollutants can be divided into three categories :- a. physical mechanisms; b. chemical mechanisms; c. biological mechanisms. Work detailed in the following chapters is an attempt to demonstrate the influence of each of these mechanisms on soil treatment of landfill leachate.

CHAPTER 5 INVESTIGATION OF PHYSICAL REACTIONS OCCURRING IN THE SOIL

5.1 INTRODUCTION

Essentially the only mechanism in soil that may be considered entirely physical is filtration. Once contaminants have reached the groundwater, dilution and dispersion are physical mechanisms that aid in spreading and reducing the concentration of pollutants. These alterations, however, should be attributed to the groundwater system rather than soil interaction.

The seepage of rainfall and runoff into porous soils and rocks and the storage and movement of groundwaters in open-textured geological formations, are important elements in the resource and quality management of water and wastewater. Although fine-textured granular materials remove pollutants, the water drawn from them is acceptable only when natural filtration together with the time lapse between pollution and use prevent the transport of pollutants to springs, wells and infiltration structures.

The ability of soil to act as a filter is related to several physical properties which also affect soil permeability. Grain size, particle size distribution, particle shape and packing determine the ability of a soil to pass liquids and retain solids. In theory soils will remove wastewater particulates smaller than the passages between the adjacent soil grains. This can be explained by the concept of a soil possessing, in the aggregate, a relatively huge surface area or interface in contact with the wastewater and its impurities that pass by. Surface forces are brought into play- among them van der Waals forces- that bind particles to the surfaces even though they may bear the same electrical charge as the filter grains. The substances removed during filtration are distributed irregularly over the grain surfaces. Therefore, the filter formed by soil is not planear as is, for example, a wire mesh; the soil is a filter in depth similar to a Whatman filter paper.

Interstices are narrowed down by accumulating deposits, and some of them are undoubtedly closed. Particulates entering pores still open are then transported deeper into the soil, until they reach grain sites able to accept them. Only if they fail to find sites of this kind do they escape into the effluent. Proof of the ability of soils, even the coarse grain soils, to filter liquids is the use of sand and gravel as an integral part of water treatment processes. Finer soils can of course filter finer materials, but flow application rates are limited. In addition to the solids originally present in the applied effluent, soils may also effectively filter out any solids formed as a result of chemical precipitation.

Adsorption is a physico-chemical mechanism that occurs in soils. The solid components in soils are capable of adsorbing or releasing solutes from or to the soil solution. It is difficult to separate physico-chemical adsorption from ion exchange. The former differs from the latter in that the total number of solutes in solution is affected (Dutt, 1960). Adsorption is a function of the types of materials which compose the soil fraction, the solute material, temperature and pH. Such adsorption is utilised in sewage treatment in the activated sludge and trickling filter processes. Constituents in solutions that are most likely to be adsorbed by this mechanism are dissolved gases such as ammonia, organic molecules such as humic acid, proteins and petroleum products, and non-polar molecules (Grim, 1968).

5.2 EXPERIMENTAL APPARATUS AND PROCEDURE

In order to investigate filtration it was decided to use filter papers rather than the soils themselves. To isolate leachate renovation by filtration through soil it is first necessary to prevent the action of biological and chemical mechanisms. Removal of leachate constituents by biological mechanisms could be avoided by sterilizing samples of the soil prior to application of leachate; provided the duration of the experiment was such to prevent microbial growth on soil particles. However, leachate composition changes due to physical adsorption and chemical reactions (particularly cation exchange reactions) with the soil may be instantaneous. Therefore, if soil samples are used to investigate filtration effects on leachate, it is impossible to attribute changes in leachate composition to this mechanism alone.

The use of filter papers in laboratory analysis necessitates that they do not contaminate the filtering sample. Two sizes of Whatman hardened ashless filter paper were chosen for the study:- Whatman 541 and Whatman 542. The 541 filter paper has a fast filter speed and is designed to retain coarse and gelatinous precipitates (particles of diameter greater than 20-25 micrometres). This was intended to model the actions occurring in a coarse textured soil such as sand. The 542 filter paper has a slow filter speed and is designed to retain fine crystalline material (particles of diameter greater than 2.7 micrometres). This was intended to model a fine-textured soil such as clay.

Leachate was applied under gravity to the filter papers at two application volumes:- 100 mls and 500 mls. Each filter/application volume combination was carried out in duplicate. The filtrate was collected in acid-washed containers. It was then analysed for pH, suspended solids, COD, calcium, magnesium, potassium, sodium, iron and ammonia. The methods of analysis are given in Chapter 4.

5.3 RESULTS

The results of the filtration experiments are given in mg/l in Table 5.1.

The most obvious result of the experiment is that there is very little change in most of the leachate parameters after filtration. The concentration of calcium, magnesium, potassium, sodium, iron and ammonia is only slightly less than that of the original leachate.

The pH of the leachate filtered through the 542 filter papers was observed to increase by 0.7 units; that filtered through the 541 papers increased by only 0.14 units. This difference is thought to be due to the effect of time rather than to the effects of filtration itself. Filtration through 541 papers took several minutes while the flow through the 542 papers took approximately 1 hour for 100 mls and 3 hours for 500 mls. It is also possible that filtration has removed organic acids from the leachate which would have the effect of increasing the pH. However, the difference in COD removal between the 541 and 542 filter papers is not great; therefore it is likely that the same, if any, degree of organic removal is occurring with both filter papers. Hence, if this was the mechanism for the rise in pH, then a similar pH change would be expected with both filter papers.

There was a substantial decrease in suspended solids with the 542 filter paper at the 500 mls application volume. At all other applications the decrease was not as significant. At the 500 mls application volume, the time taken for filtration to occur may have allowed precipitation-/coagulation to occur and therefore reduced the suspended solids. It is noted that the suspended solids concentration of the original leachate was low. However, if the leachate used had a high suspended solids concentration this could have increased the following effects on the

TABLE 5.1 RESULTS OF FILTRATION EXPERIMENTS

Sample	pH	suspended solids	COD	Ca	Mg	K	Na	Fe	NH_3
ORIGINAL LEACHATE	7.59	0.24	3250	67.2	136.5	50.2	300	0.10	480
541/100ml	7.73	0.2	3234	61.95	133.3	48.7	291	0.09	465
542/100ml	8.31	0.23	3124	63.5	127.1	47.0	290	0.09	450
541/500ml	7.73	0.21	2992	66.4	136.5	49.1	292	0.09	470
542/500ml	8.31	0.14	2500	70.4	138.6	49.9	295	0.09	470

ALL RESULTS IN mg/l EXCEPT pH

experiment:- 1. Creation of extra filter depth; 2. Varied filter depth and; 3. Formation of an organic layer i.e. a bio-filter. These effects would lead to mechanisms of removal other than filtration.

It is interesting to note that as the amount of suspended solids is reduced, the COD of the leachate is also reduced. This indicates that the suspended solids comprise a major portion of the COD. Regression analysis established a high correlation between the suspended solids in solution and the COD value of the leachate ($r = 0.98$; $P = 0.0004$). The equation relating these two variables is :-

$$\text{COD (mg)} = 7670 \text{ suspended solids (mg)} - 4.7.$$

There also appears to be a greater reduction in COD at the higher application rate.

The results of these experiments show that for the majority of leachate constituents, filtration is not considered to be a major removal mechanism in soils. Since little removal of leachate inorganic constituents occurred in these experiments, it suggests that the main physical mechanism acting in soils to remove inorganics from leachate is physical absorption and/or bioadsorption. Adsorption applies to the adsorption of inorganic or organic solute on soil particles. This type of adsorption differs from cation exchange in that the species being adsorbed or desorbed is not ionic. Biological adsorption refers to the adsorption of organic matter by microbial organisms such as the organic layer in the soil columns or activated sludge in the aerated treatment of sewage.

In regard to the column tests (Chapter 4), it seems reasonable that compacted soil columns would form filters that would be effective in removing suspended matter. The build-up of organic matter in the upper layer of the soil column would form a bio-filter similar to the bacteria covered medias utilised in trickling filters in wastewater treatment plants. The effect of this mechanism would be to retard the movement of suspended matter, as well as some dissolved organic matter through the bio-layer. The column tests performed with sand are believed to indicate the potential species removal by these mechanisms since sand is generally regarded as an inert medium and would not partake in chemical reactions. Hence, the high leachate renovation rate by sand is less likely to be due to chemical interaction and more probably due to filtration/physical adsorption and bio-adsorption.

5.4 SUMMARY

The experiments described in this section were designed to investigate species removal from leachate by purely physical means. In order to investigate this it is difficult to remove the effects of other mechanisms in soil which may act on leachate e.g. chemical reactions. Therefore, it was decided to use filter papers to investigate physical mechanisms.

The concentration of calcium, magnesium, potassium, sodium, iron and ammonia in leachate after passage through filter papers was only slightly less than that of the original leachate.

This would seem to indicate that the effect of the physical mechanism of filtration on inorganic species is negligible.

There was some reduction in the amount of suspended solids and COD of the leachate after passage through the filter papers. The degree of reduction was greater at a higher applied leachate volume and at a slower rate of filtration.

Regression analysis established a high correlation between suspended solids and the COD value of the leachate. This indicates that suspended solids comprise a major portion of the COD and hence removal of suspended solids will lead to a consequent decrease in the COD value.

CHAPTER 6 STUDIES OF BACTERIAL ACTIVITY IN THE VARIOUS SOIL TYPES

6.1 INTRODUCTION

The major aim of these experiments was to determine if a difference in oxygen profile, and hence bacterial activity, occurred in the different soil types. A secondary aim was to determine the soil to leachate ratio which will allow optimum bacterial activity for degradation.

The measurement of gas volumes at various temperatures and pressures, and the conversion of these volumes into the molar quantities of gas that they represent, is a common task in biological investigations. Sometimes comparatively large amounts of gas are involved; for example, when the yield of gaseous products is measured during the fermentative growth of microbial cultures. More frequently, the evolution or consumption of gases by biological materials is studied on a micro-scale using manometric methods.

Two manometric methods may be used:

Constant pressure manometry, which measures a change in the *volume* of a gas at constant pressure and constant temperature.

Constant volume manometry, which measures a change in the *pressure* of a gas whose volume is kept constant at a constant temperature. The Warburg manometer which operates on this principle is the most frequently used form of 'micro-respirometer' in biochemical laboratories.

The Warburg Constant Volume Respirometer was used to study the bacterial activity present in various soil types and at various soil to leachate ratios.

6.2 EXPERIMENTAL DESIGN

Bacterial activity was tested on four soil:leachate ratios i.e. 1:10, 1:5, 1:4 and 1:2. The leachate used had a COD value of 275 mg/l and a pH of 7.59. This leachate was obtained from the domestic landfill described in section 4.2.1. It is noted that the COD is lower than that used in the soil column experiments due to changes in leachate organic matter content with age of the fill. Solutions were made up which contained 5.0 or 10.0 grams of soil and 50 ml leachate for the 1:10 and 1:5 ratios respectively; the 1:4 and 1:2 ratios were made from 10 grams of soil and 40 or 20 ml leachate respectively. The mixture was then shaken for several minutes to ensure adequate mixing of the soil and leachate.

A sample size of 5.0 ml was withdrawn by pipette from each mixture and placed in the respirometer. Samples were shaken for 10 minutes to reach equilibrium and the manometer readings were then taken every 5 minutes. Measurements were continued until the manometer readings had approached equilibrium (where there was no significant alteration in the manometer reading over the period of one hour). Each soil was analysed in duplicate and if there was significant variation in the readings then the respirometer study was repeated for the soil concerned. A negative reading indicates that there is oxygen uptake and aerobic bacterial activity; a positive reading indicates that there is methane generation and anaerobic activity.

6.3 RESULTS

The oxygen profile for the topsoil, clay, sand and peat at the 1:10

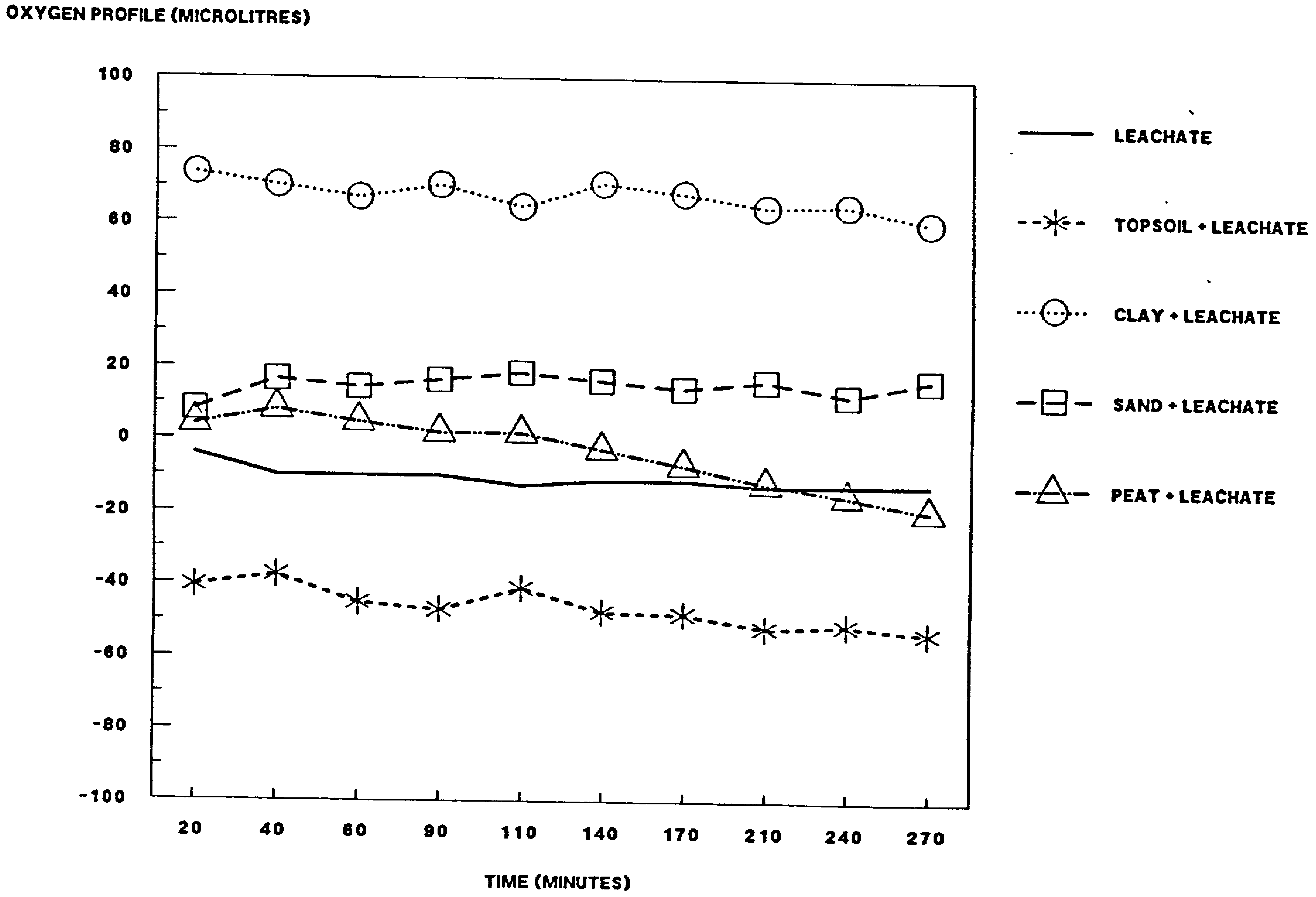


Figure 6.1 Oxygen Profiles for topsoil, clay, sand and peat at 1:10 soil:leachate ratio.

soil:leachate ratio is shown in Figure 6.1. Throughout the experimental period the flasks containing sand and clay demonstrated anaerobic respiration. Oxygen uptake was observed throughout the experimental period in the flask containing topsoil and leachate. The peat:leachate mixture initially produced anaerobic conditions; at 140 minutes this soil/leachate combination began to take up oxygen. Therefore, of the four soils tested at the 1:10 ratio, topsoil had the highest oxygen uptake rate.

The oxygen profile for sand, peat topsoil, and clay at the 1:5 soil:leachate ratio is shown in Figure 6.2. The increase towards positive values after 210 minutes is thought to be due to the sudden change in weather i.e. there was a large drop in pressure which meant that the respirometers gave erratic readings. The flasks containing peat and clay began to take up oxygen after approximately 30 minutes with a slight increase in oxygen uptake with time until the sudden decrease in pressure at 210 minutes. The topsoil and leachate mixture took approximately 100 minutes until oxygen uptake occurred, but from this point in time the uptake increased markedly to the highest of the four soils tested. The sand/leachate combination was anaerobic throughout the experimental period. Topsoil again demonstrated the highest bacterial activity of the four soils tested.

The oxygen profile for topsoil, clay, sand and peat at the 1:4 soil:leachate ratio is shown in Figure 6.3. All soil/leachate combinations took up oxygen at the 1:4 soil:leachate ratio. The general trend for each soil is for the amount of oxygen taken up - and therefore bacterial activity - to increase with increasing time. Clay took up the

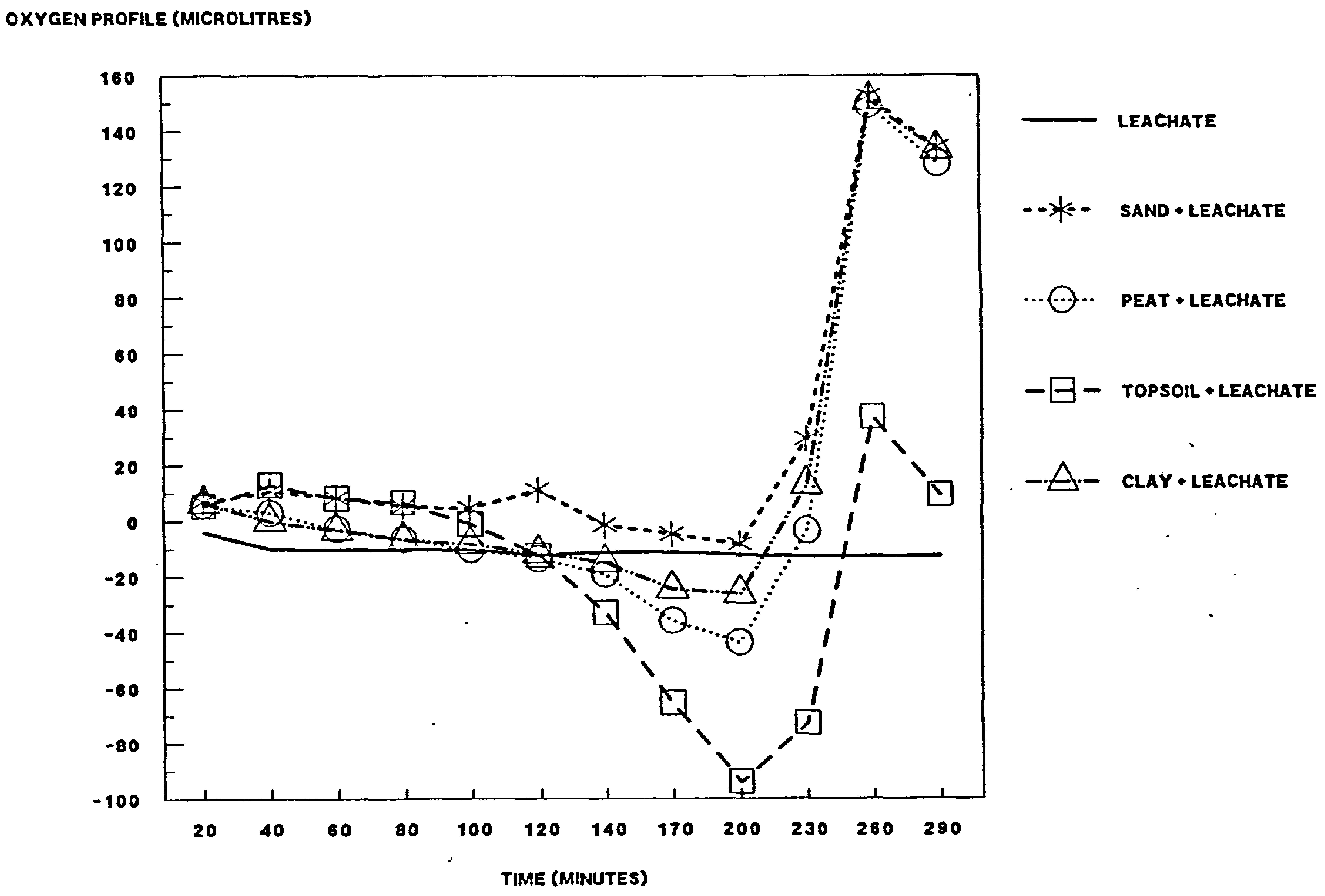


Figure 6.2 Oxygen Profiles for topsoil, clay, sand and peat at 1:5 soil: leachate ratio

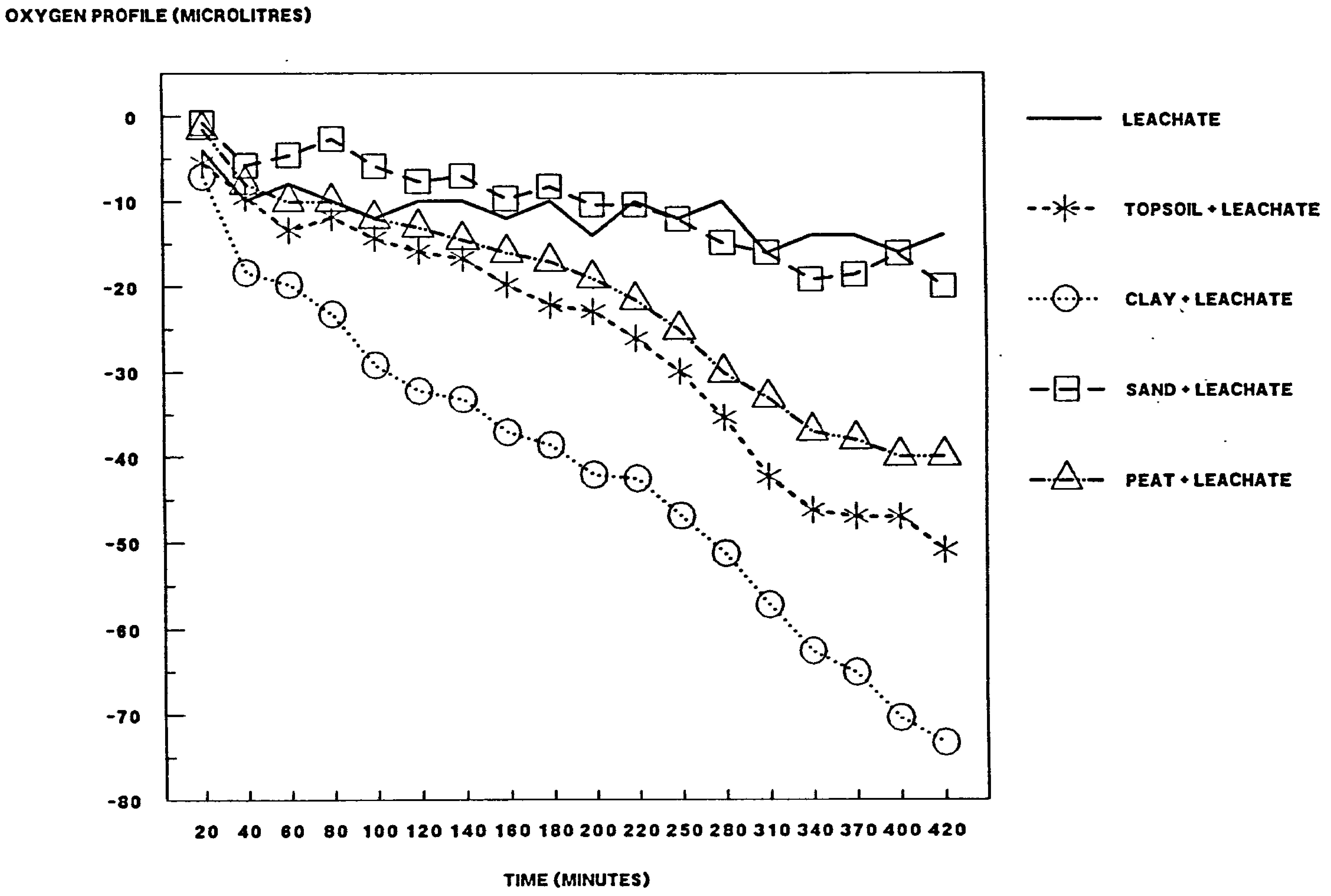


Figure 6.3 Oxygen Profiles for topsoil, clay, sand and peat at 1:4 soil:leachate ratio.

most oxygen, followed by topsoil and then sand. This would seem to indicate that microbial activity is greatest in the leachate combined with the clay soil. Leachate only was also tested in the respirometer and while there was uptake of oxygen showing the presence of aerobic bacterial activity, it was not as large as those with the soils. This would seem to indicate that either the presence of soils allows more rapid multiplication of organisms or that the soils themselves have an inherent microbial activity. Since the soils were air-dried prior to addition to the flask, it is unlikely that large populations of soil organisms would be present. Therefore, it appears that rapid microbial growth is occurring at the 1:4 soil:leachate ratio.

The oxygen profile for topsoil, clay, sand and peat at the 1:2 soil:leachate ratio is shown in Figure 6.4. The clay/leachate combination shows rapid uptake of oxygen, to a much greater extent than that of the other soils tested. The topsoil, sand and peat soils combined with leachate demonstrated similar levels of oxygen uptake, with final uptake values of approximately 30 microlitres. The topsoil also demonstrated an uptake of 60 microlitres at 180 minutes, this pattern of sudden increase in oxygen uptake at this time interval also being followed by the leachate. Therefore, as the volume of leachate added to the soil has decreased, clay is the soil demonstrating greatest bacterial activity.

The results of the four dilution rates for each soil have been plotted on separate graphs. These are shown in Figures 6.5 to 6.8. The clay soil (Figure 6.5) demonstrated a changeover from oxygen uptake at the lower soil:leachate ratios (1:2; 1:4 and 1:5) to anaerobic conditions at the

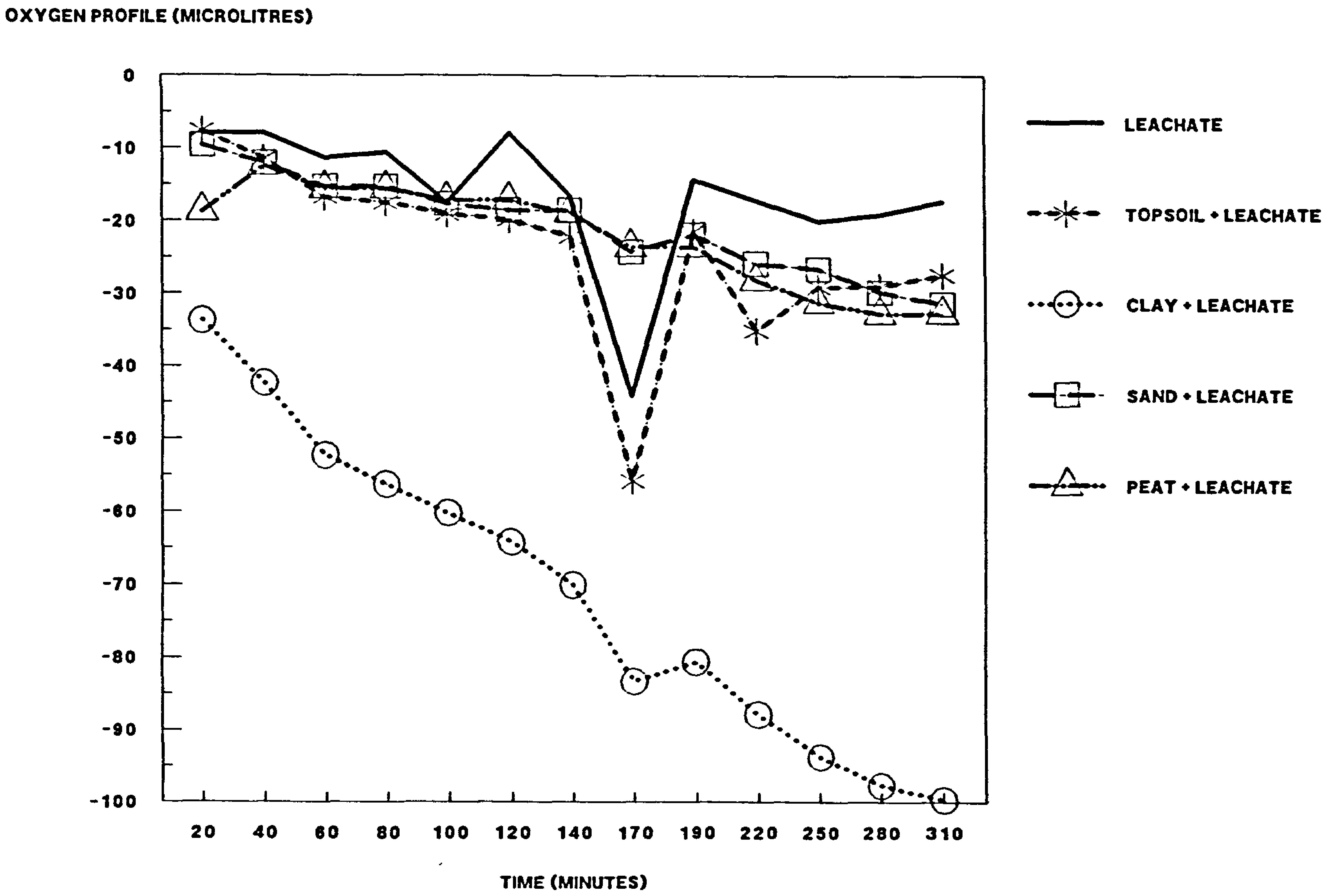


Figure 6.4 Oxygen Profiles for topsoil, clay, sand and peat at 1:2 soil:leachate ratio

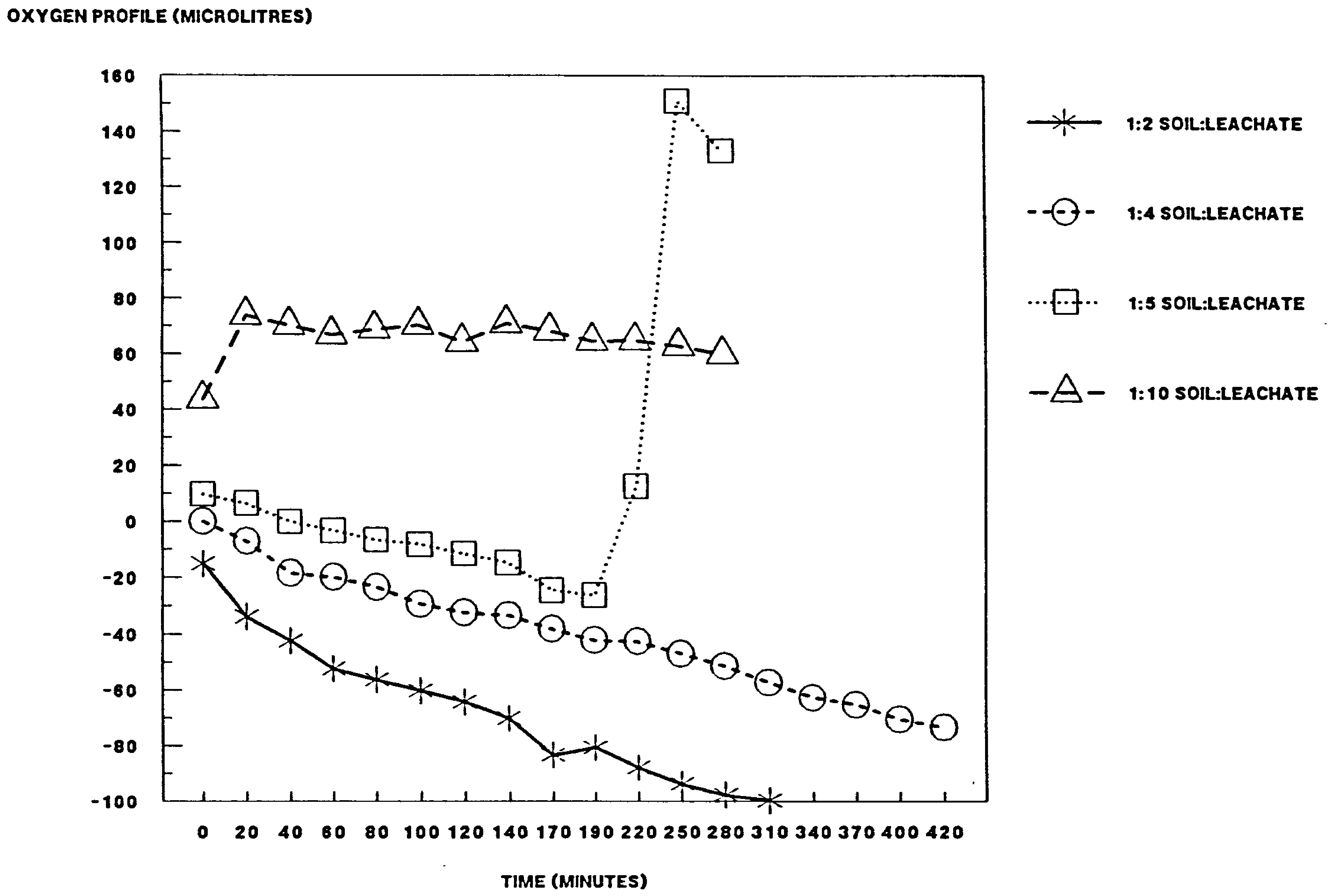


Figure 6.5 Oxygen Profiles for clay at 1:2; 1:4; and 1:10 soil:leachate ratios

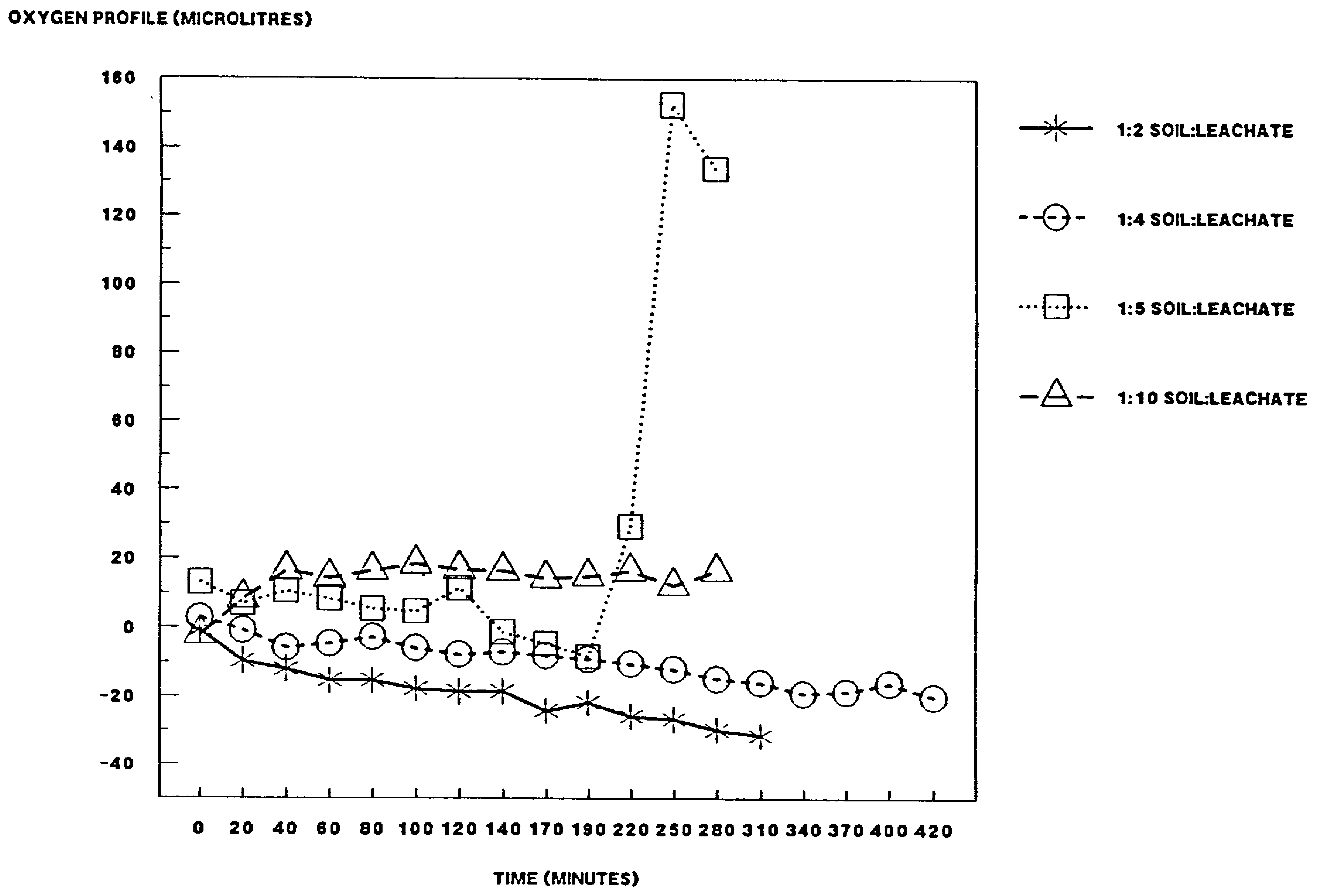


Figure 6.6 Oxygen Profiles for sand at 1:2; 1:4; 1:5 and 1:10 soil:leachate ratios

highest soil:leachate ratio (1:10). Greatest oxygen uptake and hence microbial activity was obtained with the 1:2 ratio; followed by the 1:4 and the 1:5 soil:leachate ratios. It is possible that the lower soil/leachate ratio pipetted samples contained more soil in the pipetted volume relative to the larger soil:leachate ratios tested. In addition, increasing the quantity of leachate in a flask will increase the levels of elements which are toxic to microbes e.g. Fe, Mn, which may have an adverse effect on bacterial activity.

The sand soil combined with leachate had the highest oxygen uptake at the lowest soil:leachate ratio (Figure 6.6). The amount of oxygen taken up decreased at the 1:4 ratio. At the 1:5 ratio there is a change from aerobic to anaerobic conditions; anaerobic conditions are also present at the 1:10 ratio.

The topsoil/leachate combination took up oxygen at all soil:leachate ratios (Figure 6.7), although there was an initial anaerobic period at the 1:5 ratio. Highest oxygen uptake occurred at the higher soil:leachate ratios (i.e. 1:5 and 1:10) and decreased as the amount of leachate added to the soil decreased.

The oxygen uptake from the peat/leachate combination (Figure 6.8) appears to be the highest at the 1:2 ratio, followed by the 1:4 ratio, the 1:5 ratio and the 1:10 ratio.

In addition to the respirometry studies, dilution plating techniques were also carried out. This involved using soil which had been in contact with leachate and untreated control soils. Leachate was added to

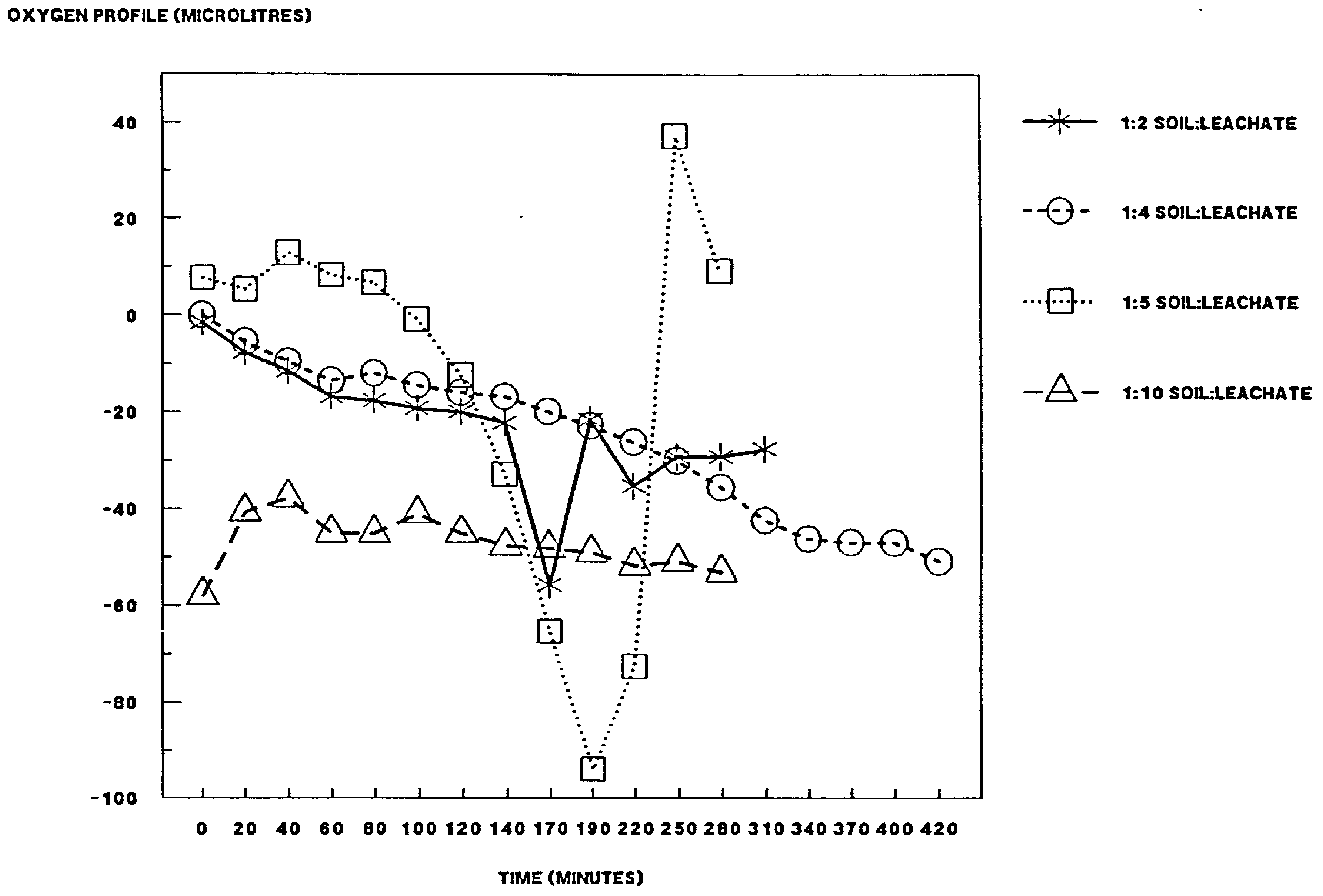


Figure 6.7 Oxygen Profiles for topsoil at 1:2; 1:4; 1:5 and 1:10 soil:leachate ratios

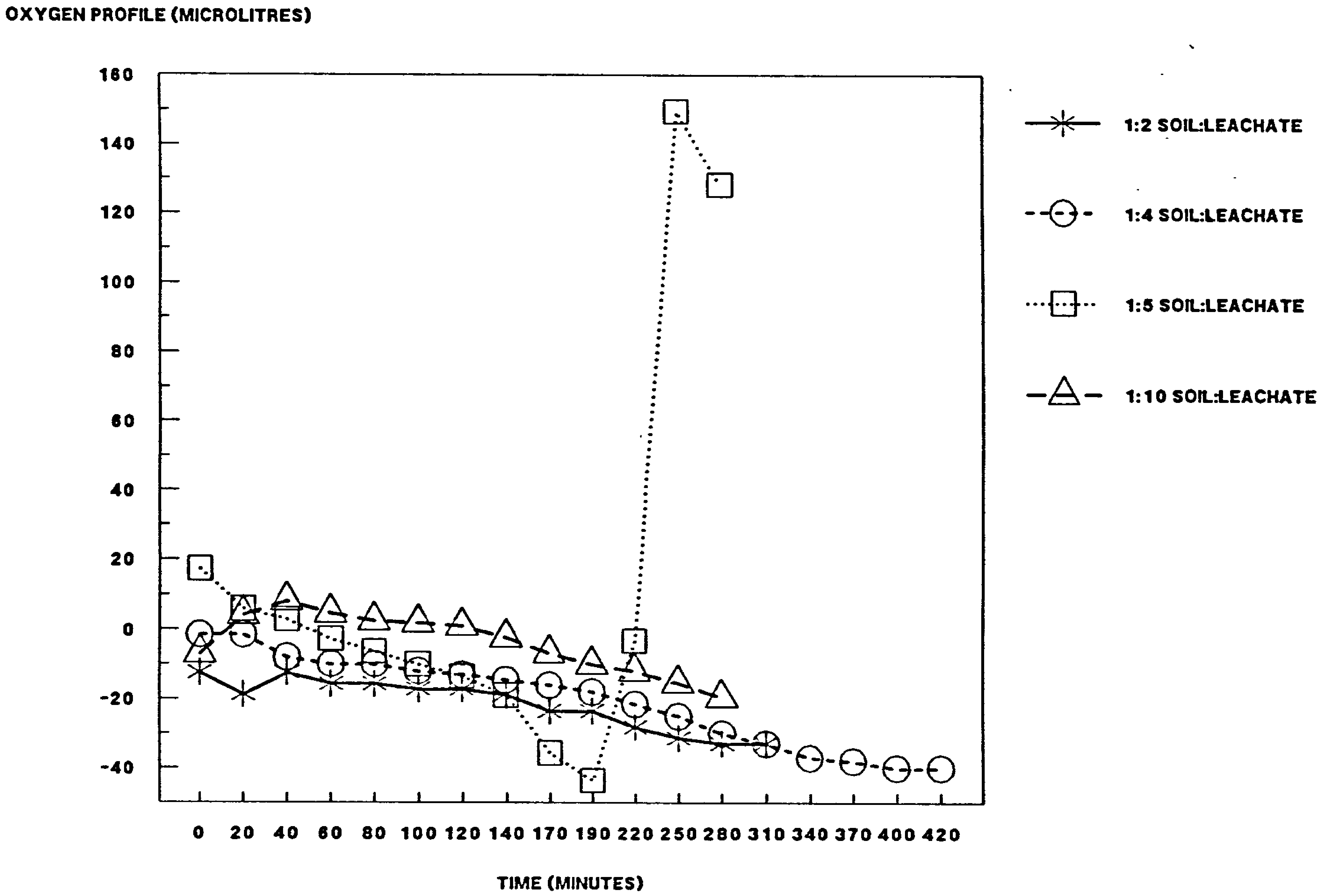


Figure 6.8 Oxygen Profiles for peat at 1:2; 1:4; 1:5 and 1:10 soil: leachate ratios.

the soils at graduated rates before incubation for seven days. Plate counts of soil microorganisms were determined before and after soil treatments. This was accomplished by removing 10 grams of soil and suspending it in a 90 ml water blank to obtain a 1:10 dilution. The serial dilution was continued until a $1:10^6$ dilution was achieved. Aliquots (1ml) of the serial dilutions were cultured in triplicate on nutrient agar (beef extract, 3g; peptone, 5g; and agar, 15g, in 1 litre of water at pH 6.8), and colony forming units (CFUs) were determined by plate colony enumeration after incubation for 8 days at 28°C. The results obtained were inconclusive in that there was no clear trend in the number of colonies in relation to the soil type studied. Therefore, the results are not reported here.

6.4 DISCUSSION

These batch experiments cannot provide biological data truly representative of conditions in a soil column or in the field. Over a series of irrigation cycles, a distinctive population of microorganisms will become attached to the soil particulate matter. Although soils vary in quantity and kinds of microorganisms, most soils contain many millions or billions of microorganisms per gram with the greatest numbers usually found in the surface layers. Landfill leachate is a complex mixture of organic material so it is probable that few, if any, microbial species will attack all fractions. A mixed population of microorganisms, rather than any single species, would probably be most efficient in breakdown of leachate components. Near the soil surface, organisms acclimated to the organic compounds in the entering leachate will predominate; deeper in the soil organisms acclimated to decomposition products of the original organic compounds, and to the conditions of temperature, pH, oxygen tension, available nutrients, etc., will predominate. The resulting spatial variation of organism type (and presumably reaction rate) will not necessarily be the same as the temporal variation that may (or may not) occur in a soil sample incubated for a short period of time in the respirometer flasks.

Overall, the topsoil and clay soils appeared to have a greater microbial activity than the other soils tested. It is possible that since the clay and topsoil have finer particles than the other soils tested and hence are easier to suspend in solution, that a greater quantity of soil is contained in the 5 mls sample pipetted into the manometer flask. In particular, it was difficult to maintain the sand grains in suspension as they tended to settle out as soon as the initial shaking ceased. Different patterns of oxygen uptake were followed by the clay and topsoil. Greatest oxygen uptake was observed at the lowest leachate volume added (1:2) to the clay soil. This may be an indication that increasing the amount of leachate added to the clay soil has an adverse effect on the bacterial population. Greatest oxygen uptake was observed at the highest leachate volume added (1:10) to the topsoil, indicating an increase in bacterial activity as the applied leachate volume is increased.

The sand soil demonstrated oxygen uptake at the lower ratios (1:2 and 1:4) but anaerobic conditions at the higher ratios (1:5 and 1:10). Peat followed a similar pattern to clay in that the highest oxygen uptake occurred at the lowest leachate volume added. however, uptake values were lower than those of clay.

If equipment had allowed further investigation of biological mechanisms, the following studies would have been undertaken:

The use of respirometry to investigate CO_2 evolution and hence microbial activity. This method allows longer term studies of microbial activity and also the use of larger quantities of soil. One such method would be to investigate the CO_2 evolved from 100 grams of soil alone and of soil with various leachate additions at regular intervals up to 14 days. The soils are incubated in 250 ml biometric flasks and CO_2 is absorbed by standard alkali contained in the tube connected to the reaction flask. Absorption samples can be withdrawn periodically to determine the rate of microbial activity.

Long-term incubation tests could be carried out to allow developement of the diverse range of microorganisms that would normally populate a soil irrigated with leachate. In addition to monitoring the total number of organisms at selected time intervals, specific media could be used to detect the presence of particular organisms.

CHAPTER SEVEN INVESTIGATION OF CHEMICAL INTERACTION OF LANDFILL LEACHATE AND SOILS

7.1 INTRODUCTION

Many adsorption systems relevant to behaviour in soils involve interactions which fall into a category between physical and chemical designations. Chemisorption usually involves an activation energy in the process of adsorption i.e. as an adsorptive molecule approaches the adsorbent surface an energy barrier has to be overcome for the reaction to take place. Chemisorption tends to occur at specific adsorption sites, and it does not proceed past the monolayer stage. By comparison, physical adsorption is a rapid, non-activated process which occurs at all interfaces. Detailed studies of adsorption processes take into account the mechanisms of binding of the adsorptive to the adsorbent. Mechanistic studies of chemical composition consider the various single processes which make up the overall reaction, the intermediates formed, and the transition states which are involved in going from the reactants to the final products. If the mechanism of an adsorption process is to be understood to this degree of detail it is necessary to have information about: 1) kinetic aspects of the interaction, and especially the rates of transfer of adsorptive to the adsorbent surface; 2) the interaction which takes place at the surface; 3) the initial and final equilibrium conditions; and 4) the composition and structure of the final adsorption complex.

The factors of immediate interest in leachate/soil interactions are the extents to which leachate constituents are held by given amounts of soil or soil components, and the selectivities of these soils for adsorptive species of different chemical structures. In whole soils, structural details of the adsorbing surfaces are precluded because of the complexities of the mixtures of the component colloidal structures e.g. oxide and hydrous oxide materials and organic colloids. Each of these different types of colloidal structure may have an independent existence in the soil, or they may be associated. Thus, laboratory studies of adsorption by whole soils provide only macroscopic descriptions of the processes involved without reference to the detailed microscopic structure and behaviour of matter. Therefore, one approach to the study of adsorption by a whole soil is to set aside considerations about the composition of the soil and to regard it first as a macroscopic body. This refers to the bulk quantities of materials or samples of macroscopic size in which details of molecular structure, which are revealed only by observations on a microscopic level, are ignored. In general, measurements made on a macroscopic scale reflect the average behaviour over a period of time of Avogadro's number of molecules per mole of substance.

Adsorption studies investigate the relationship between the amount of a chemical species which is adsorbed and its bulk phase concentration. An adsorption process will continue until the system in question reaches a state of equilibrium. Adsorption equilibrium is said to be achieved when the concentration of adsorptive in the bulk phase does not change between measurements made at an appropriate time interval. If a sufficient time interval is allowed, and biological activity is controlled, equilibrium will eventually be attained for soil adsorption systems in the laboratory. Equilibrium conditions are unlikely to be obtained in the field however because mixing of the interactive species is imperfect, and biological degradation of the adsorptive and adsorbate cannot be readily controlled, and because the soil system is continually subjected to mechanical and thermal disturbances.

Laboratory studies of the extent and reversibilities of binding of leachate constituents by soils can provide useful indications for the probable fate of these parameters when leachate is applied to the same soils under field conditions. In a more general sense knowledge of the processes of interaction between leachate constituents and soils will allow predictions to be made about their reactivity in soils when some information is available about the content and composition of the soil colloids.

Batch shaking tests offered several favourable characteristics with respect to experimental problems observed in column testing. Batch tests remove the effects of flow variations completely so that the effect of the soil itself as regards its cation exchange capacity and exchangeable cations is studied in regard to leachate attenuation. Also, there is little time for biological growth during the test period so it could be said that it pinpoints those attenuation mechanisms which are due to chemical means. Batch tests enable a more rapid formulation of chemical removal of leachate constituents than the corresponding soil column tests. An equilibrium state can be reached in a relatively short time (< 24 hours) which keeps the time variation effects of the leachate to a minimum. By keeping the soil weight constant and increasing the leachate volume added, the increasing cation concentration effect on the exhaustibility of the soil exchange complex can be evaluated.

7.2 EXPERIMENTAL DESIGN

The.batch tests were conducted in glass, polyvinyl chloride or polyethylene containers. These materials are all commonly used as sample containers in laboratories and are considered to be inert with respect to their effect on the soil-leachate interaction. To minimize the void space, each container selected from those available was the smallest one that could provide sufficient volume to contain the soil and solution. In addition all flasks were sealed to prevent air entrance. Each batch container was first acid-washed to ensure there was no pre-contamination of the containers. The containers were then filled with 100 grams of air-dried and sieved (< 2 mm) soil. Every soil-to-solution ratio was tested in duplicate and a control sample of leachate only was used to allow for deterioration of the leachate due to shaking and time. The specified volume of leachate was then added and containers were then sealed. The reaction vessels were then shaken on an orbital shaker at slow speed for 24 hours.

Samples of the leachates were taken from each soil/leachate combination and analysed. The parameters were those which were considered the major species which could be determined with reasonable accuracy. The major cations involved in soil-leachate interaction were monitored because cation exchange was the principle mechanism being examined. In addition, testing of certain trace elements was also carried out as attenuation of these constituents is one of the most important arguments for the use of clay or other soils as a material for landfill lining and for land treatment of landfill leachates.

The batch testing was conducted in three phases. Phase I was conducted to investigate the effect of contact time on soil-leachate reactions. Test conditions for the second phase of the batch testing were selected after studying the results of Phase I i.e. establishment of the minimum time to obtain equilibrium. Phase II was conducted to investigate the effect of soil:leachate ratio on conditions at equilibrium. This also allowed the effect of increasing cation concentration on equilibrium conditions to be investigated. The results of the Phase I and Phase II studies produced unusual results, in that the adsorption of leachate constituents was not as expected. In many cases the concentration of cations in leachate increased after contact with the soil; in particular, an increase in heavy metals in the leachates in contact with some soils was noticed. Therefore, the Phase III experiments were carried out with a different leachate and seven other soil types to verify this trend.

7.3 PHASE I EXPERIMENTS

7.3.1 Experimental Design

The Phase I experiments were designed to investigate the interaction between the major cations in landfill leachate and soils. The cations monitored in these initial experiments were calcium, magnesium, sodium, iron, zinc and aluminium.

Adsorption reactions are generally assumed to be instantaneous. In order to verify this the samples were shaken for a total of twenty-four hours and sub-samples taken during this time period. The contact time of 24 hours was to ensure that equilibrium would be reached. The aim was to obtain a profile for each of the metals tested with time and to determine whether time effected adsorption or release of cations into solution. The time intervals at which sub-samples were taken were 2 hours, 4 hours, 8 hours and finally at 24 hours. At each time interval, a sample size of 25mls was taken.

The soils tested were those that had been used previously in the soil column experiments (Chapter 4) i.e. sand, topsoil, clay and peat. The chemical and physical properties of these soils is shown in Table 4.2. The soils were air dried and passed through a 2mm sieve. 100 grams of each of these soils was then placed in acid-washed polyethylene containers. Most quantitative laboratory measurements of adsorption from solution use excess moisture to soil ratios and extensive mixing. These factors provide every opportunity for adsorption-desorption equilibria to be rapidly established. In this Phase of the testing, the soil:leachate ratio was not a variable being tested, and an arbitrary added volume of leachate of 200mls was chosen. The chemical composition of the leachate is shown in Table 7.1.

TABLE 7.1 CHEMICAL COMPOSITION OF LEACHATE USED IN PHASE I EXPERIMENTS

CONSTITUENT	CONCENTRATION
pH	7.58
COD	2995
AMMONIA	45
CALCIUM	266
MAGNESIUM	35
SODIUM	140
IRON	44.9
ZINC	0.12

It was attempted to use 100 grams of peat and 200mls leachate, but the hydrophylic nature of peat meant that as soon as leachate was added it was adsorbed by the peat. Hence, the quantity of peat used was reduced to 20grams and the volume of leachate added was the same as in the other experimental units. All soil/leachate combinations were tested in duplicate. A control, containing 200mls of leachate only, was also included in the experimental design. Thus, cation removal by association with leachate particulates or due to the effects of time and/or shaking was not confused with cation removal by reaction with the soil.

The containers were then sealed and placed on an orbital shaker. The samples were shaken continuously at medium speed for 24 hours, the shaker only being switched off at the chosen time intervals in order that 25mls could be removed for analysis.

A total of 180 analysis were carried out on the experimental units. Having measured the cation concentration by atomic adsorption spectroscopy, the actual quantity of a particular cation in solution was calculated in milligrams based on the volume in the container being 200mls at 2 hours, 175 mls at 4 hours, 150 mls at 8 hours and 125 mls at 24 hours. The results are displayed in a graphical form in the following pages.

The difference between the cation content in the sub-sample taken at each time interval and the amount of cation in the control leachate at that time interval was taken as the amount of metal adsorbed or released by the soil. This is most easily described by the calculation of a relative value (R.V.) for each soil at each time interval. The R.V. is defined as C/Co, where C is the cation content (mg) of leachate in contact with soil at time t and Co is the cation content (mg) in the control leachate at time t. This ensures that any loss of metal from the leachate in contact with soils is genuinely due to the action of

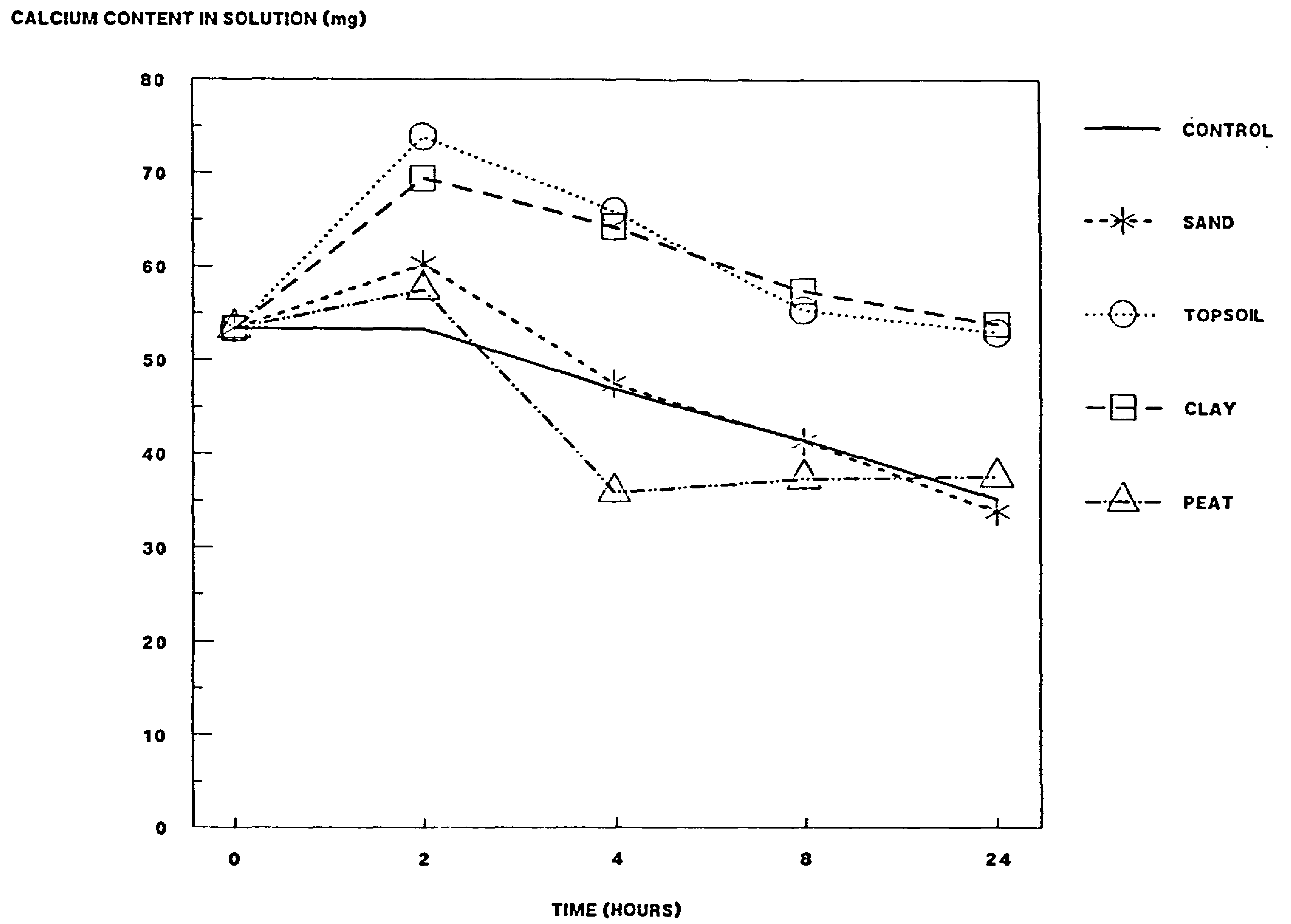


Figure 7.1 Calcium profile for sand, topsoil, clay and peat - Phase I experiments.

the soils and not due to the effects of shaking. Thus a R.V. less than 1.0 indicates that the soil has adsorbed that particular cation and a relative value greater than 1.0 indicates that there has been a release of that cation into solution.

7.3.2 Results

7.3.2.1 Calcium

The control leachate demonstrated a gradual reduction in calcium content in solution in samples taken from 2 hours onwards (Figure 7.1). This may be due to oxidation of calcium as a result of aeration or precipitation of calcium with other leachate constituents such as carbonates, oxides and/or hydroxides.

The calcium content with time for leachates in contact with soils is also shown in Figure 7.1. The calculated relative values are shown in Table 7.2.

TABLE 7.2 AVERAGE RELATIVE VALUES FOR CALCIUM.

	TIME (HOURS)			
SAMPLE	2	4	8	24
SAND	1.13	1.01	1.00	0.96
TOPSOIL	1.38	1.40	1.34	1.50
CLAY	1.30	1.37	1.38	1.53
PEAT	1.08	0.77	0.91	1.07

After 2 hours of shaking, all of the leachates in contact with soils had a higher concentration of calcium in solution than that of the control. This is reflected in relative values greater than 1.0 . Topsoil released the highest amount of calcium into solution, followed by clay, sand and peat.

Although the 2 hour result for the sand had a slightly increased calcium level relative to the control leachate, in general the sand had little or no effect on the calcium concentration. The peat results were erratic, but leachates in contact with both the topsoil and clay indicated increases in calcium concentration of 50% and 53% respectively after 24 hours.

The results would seem to indicate that sand had little interaction with calcium in the leachate; the remaining soils gave release of calcium to solution in the order of clay > topsoil > peat. An examination of the chemical composition of the initial soils illustrates that clay has the highest content of exchangeable calcium (66.0ppm), followed by topsoil (41.0ppm), peat (30ppm) and sand (2.0ppm).

7.3.2.2 Magnesium

The control leachate demonstrated a gradual decline in magnesium concentration with time from an initial value of 7.02 mg to a final value after 24 hours of shaking of 4.4 mg (Figure 7.2).

The magnesium content of each sample taken at each time interval is also shown in Figure 7.2. The relative values are shown in Table 7.3. All leachates in contact with soils demonstrated a higher magnesium concentration than that of the control leachate throughout the experimental period. This would appear to indicate that all soils are releasing, rather than adsorbing magnesium with the rate of release being peat > clay > topsoil > sand. A review of the chemical properties of the original soils shows that peat has the largest amount of

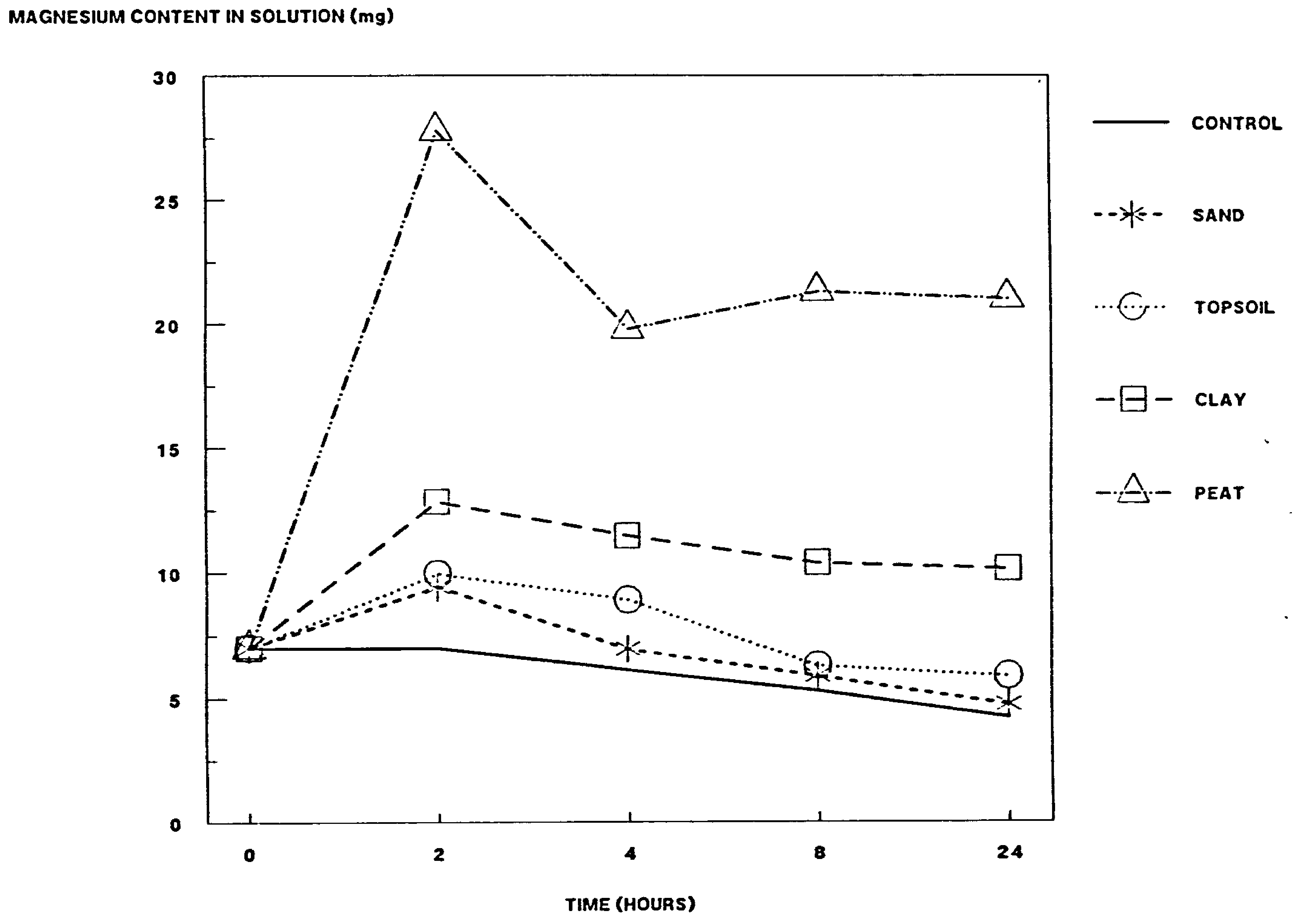


Figure 7.2 Magnesium profile for sand, topsoil, clay and peat - Phase I experiments.

exchangeable magnesium (35.8 ppm), followed by clay (9.8 ppm), topsoil (3.2 ppm) and sand having a low concentration of exchangeable magnesium (0.51 ppm). It is interesting to note that magnesium is the major exchangeable cation in peat, whereas calcium is the major exchangeable cation for the other three soils tested.

TABLE 7.3. AVERAGE RELATIVE VALUES FOR MAGNESIUM.

	TIME (HOURS)			
SAMPLE	2	4	8	24
SAND	1.34	1.14	1.07	1.12
TOPSOIL	1.42	1.46	1.20	1.39
CLAY	1.83	1.88	1.98	2.38
PEAT	3.96	3.22	4.04	4.93

7.3.2.3 Sodium

The sodium content of the control leachate decreased with time from an original content of 28.0 mg to a minimum value of 19.7 mg after 24 hours (Figure 7.3).

The sodium content of each sample taken at each time interval is illustrated in Figure 7.3. The relative values are shown in Table 7.4. All leachates in contact with soils demonstrated a higher sodium concentration than that of the control leachate at all time intervals. This would appear to indicate that all soils are releasing, rather than adsorbing sodium.

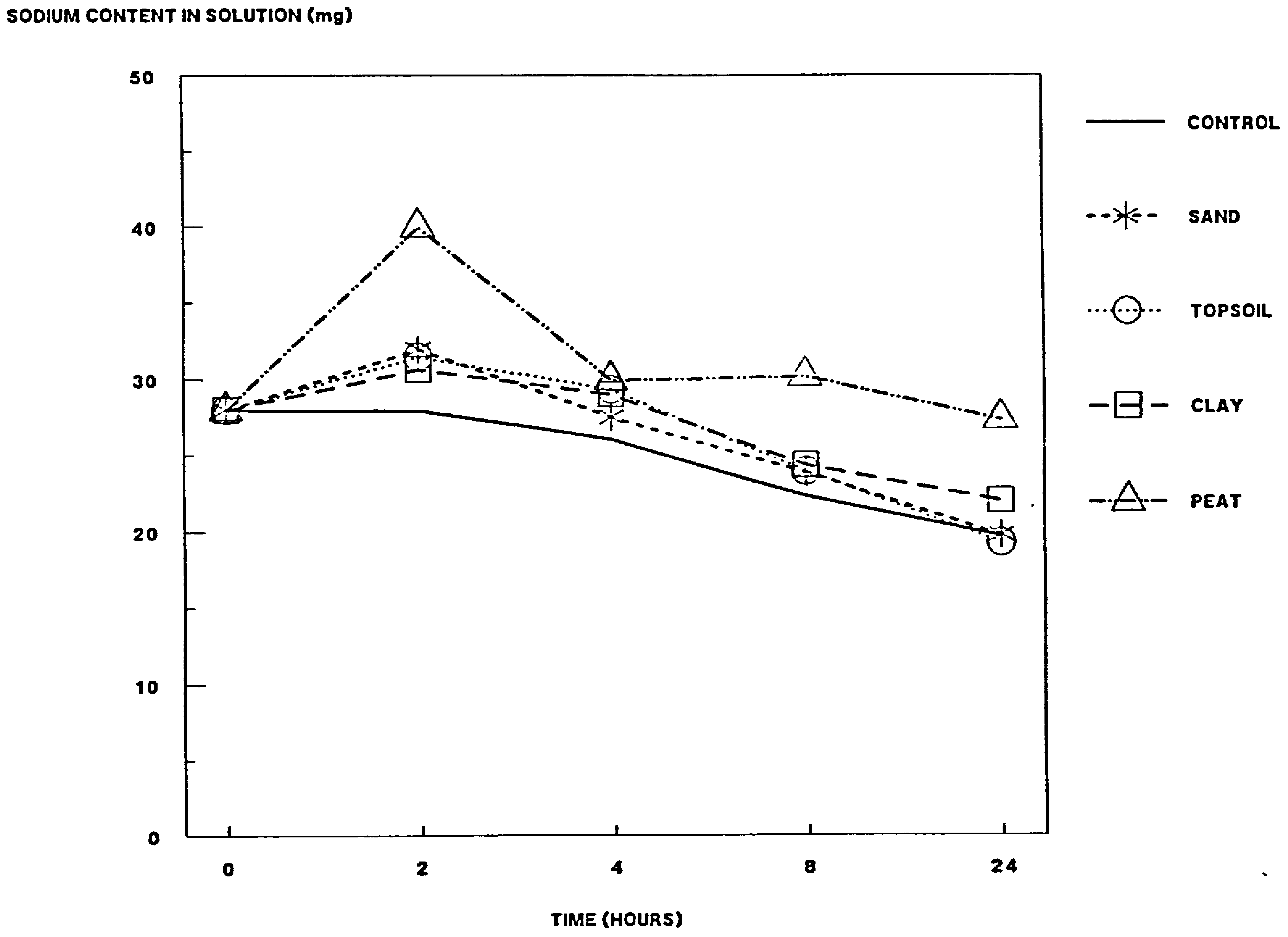


Figure 7.3 Sodium profile for sand, topsoil, clay and peat - Phase I experiments.

TABLE 7.4. AVERAGE RELATIVE VALUES FOR SODIUM.

	TIME (HOURS)			
SAMPLE	2	4	8	24
SAND	1.14	1.06	1.07	1.05
TOPSOIL	1.13	1.13	1.09	1.03
CLAY	1.10	1.11	1.09	1.17
PEAT	1.45	1.17	1.35	1.45

However, the amount of sodium released from the soils was low compared to the amount of other cations that were released. The order of release is as follows :- peat > clay > sand > topsoil. A revision of the chemical properties of the original soils revealed that the exchangeable sodium content of all soils is low in relation to the other exchangeable cations. Peat has the highest exchangeable sodium (4.35ppm), followed by clay (1.9ppm), sand (0.99ppm) and topsoil (0.6ppm).

7.3.2.4 Iron

The iron content of the control leachate decreased markedly with time, from an initial content of 8.98 mg to a value of 0.1 mg after 24 hours (Figure 7.4). This would suggest that iron is being lost from solution by oxidation during shaking or by precipitation with other leachate constituents.

The iron content of each leachate sample taken at each time interval is illustrated in Figure 7.4. The relative values are shown in Table 7.5. All samples taken throughout the experimental period contained higher concentrations of iron than that of the control leachate. This is reflected in relative values greater than one and indicates that the

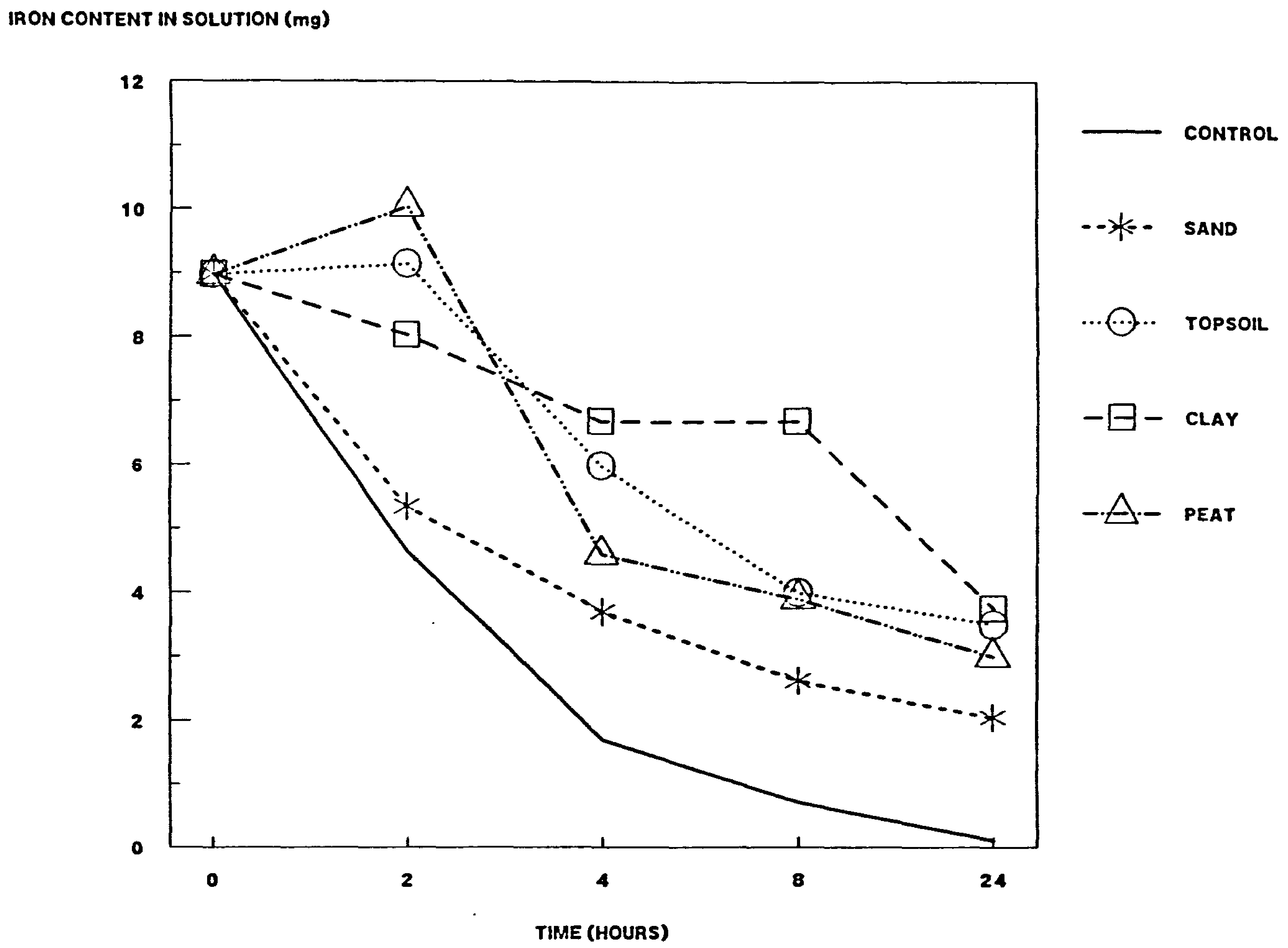


Figure 7.4 Iron profile for sand, topsoil, clay and peat - Phase I experiments.

soils are releasing, rather than adsorbing, iron. It is also possible that the presence of soil is hindering iron precipitation which would normally occur in a shaken leachate.

TABLE 7.5. AVERAGE RELATIVE VALUES FOR IRON.

	TIME (HOURS)			
SAMPLE	2	4	8	24
SAND	1.15	2.14	3.71	19.4
TOPSOIL	1.96	3.48	5.60	32.8
CLAY	1.73	3.89	9.52	34.2
PEAT	2.16	2.67	5.48	28.2

For all soils there was an increase with time in relative values; the values at 24 hours being markedly higher than those in samples taken at 2 hours. The clay soils released particularly high levels of iron to leachate; final iron concentrations in solution were approximately 34 times those of the control leachate. Topsoil also demonstrated high releases of iron giving final iron concentrations in the added leachate of approximately 33 times that of the control leachate. Leachates in contact with peat and sand for 24 hours had approximately 28 and 19 times the iron content of the control leachate, respectively. Therefore, the'order in which the soils tested released iron is as follows :- clay > topsoil > peat > sand. This release of iron by soils is an important finding in view of the fact that iron is often present in landfill leachates in significant quantities. It is commonly believed to be adsorbed by the soil if leachate migration from a landfill site should occur.

7.3.2.5 Zinc

The zinc content of each sample taken at each time interval is illustrated in Figure 7.5. The relative values are shown in Table 7.6. All soils, except sand, demonstrated release of zinc to solution at all time intervals.

TABLE 7.6 AVERAGE RELATIVE VALUES FOR ZINC.

	TIME (HOURS)			
SAMPLE	2	4	8	24
SAND	1.66	0.88	1.5	1.00
TOPSOIL	7.21	1.84	4.6	3.26
CLAY	33.4	26.20	46.5	39.5
PEAT	19.6	18.75	22.10	17.3

Leachates mixed with clay and peat demonstrated large increases in zinc in solution relative to the control leachate, throughout the experimental period. The topsoil samples showed slightly higher zinc concentrations than the control leachate, with final zinc solution concentrations of approximately 3 times that of the control leachate. The sand samples had similar levels of zinc in solution to that of the control leachate indicating little interaction with the leachate.

It is apparent from the results that the order for zinc release from the soils tested is as follows :- clay > peat > topsoil > sand. Sand was the only soil to show adsorption at certain time intervals. A review of the chemical analysis of the original soils shows that clay had a much greater zinc content (530 ppm) than that of topsoil (108 ppm), peat (38 ppm) and sand (26 ppm).

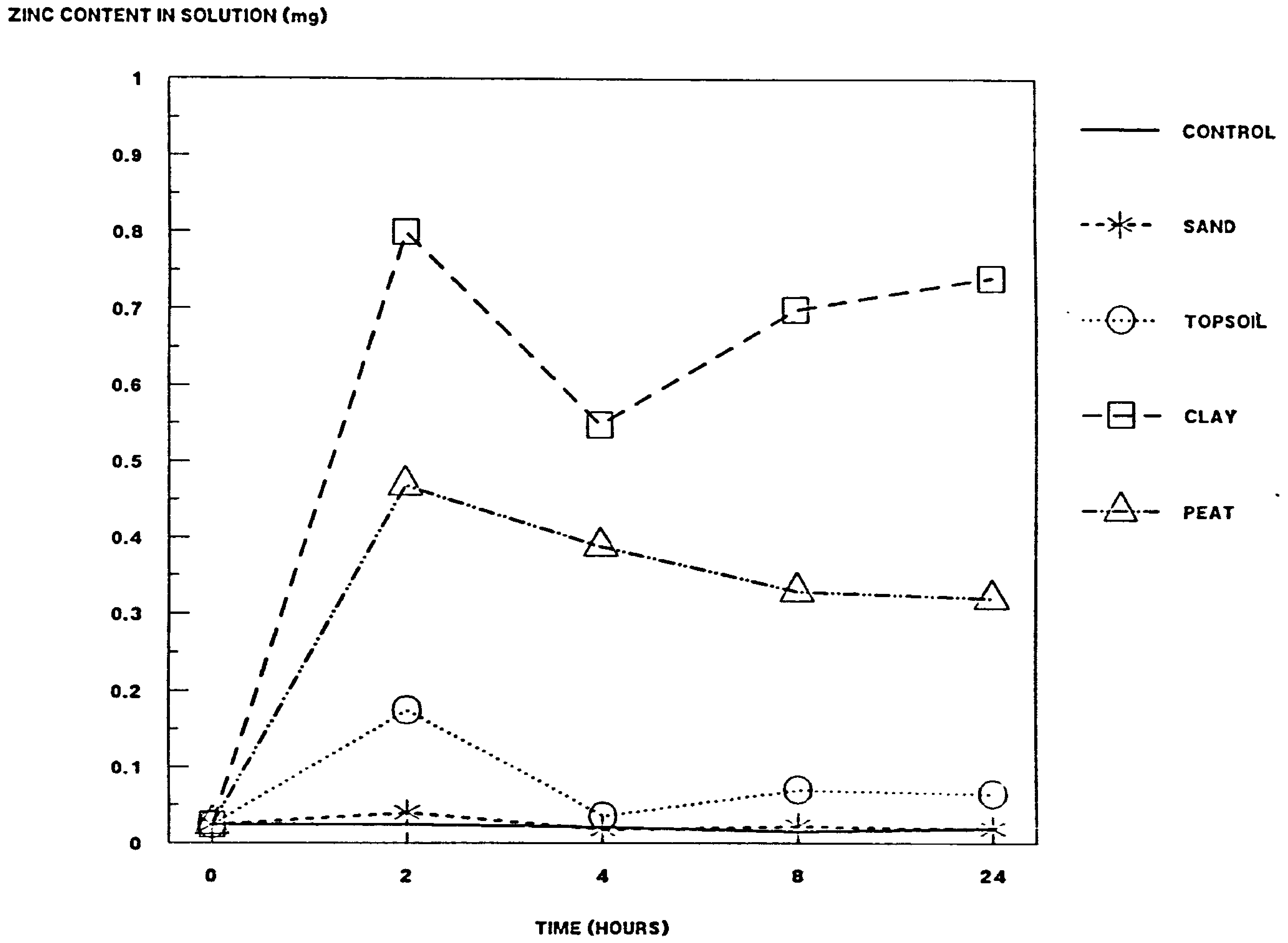


Figure 7.5 Zinc profile for sand topsoil, clay and peat - Phase I experiments.

7.3.2.6 Aluminium

The leachate added to each soil contained no detectable aluminium. Throughout the test period the samples taken from the control leachate at each time interval also had no detectable aluminium. This verifies that no aluminium was being solubilised within the leachate itself due to the effects of shaking.

The leachate in contact with the sand had no detectable aluminium in solution throughout the shaking period. However, the topsoil, clay and peat had aluminium in solution at all the time intervals sampled (Table 7.7).

TABLE 7.7. AVERAGE ALUMINIUM CONCENTRATION (mg/l).

	TIME (HOURS)			
SAMPLE	2	4	8	24
SAND	0	0	0	0
TOPSOIL	6.0	2.2	1.6	1.9
CLAY	25.8	8.1	8.6	9.8
PEAT	2.6	2.0	1.6	2.0

Maximum release of aluminium for each soil was obtained after 2 hours of shaking. Clay samples released 25.8 mg/l; topsoil samples released 6.0 mg/l and peat released 2.6 mg/l. After 4 hours of shaking the aluminium content of topsoil solutions decreased to 2.2 mg/l; the clay solutions decreased in zinc concentration to 8.1 mg/l; the peat sample zinc concentration decreased to 2.0 mg/l. This may be due to readsorption of solubilised aluminium. After 8 hours there was a further decrease in the aluminium concentration for the topsoil samples (1.6 mg/l); the peat samples also decreased slightly in aluminium content (1.6 mg/l). However, the clay samples demonstrated an increase in aluminium concentration to 8.6 mg/l.

At the end of the 24 hour shaking period, the topsoil samples had an average aluminium solution concentration of 1.9 mg/l; the clay had an average solution concentration of 9.8 mg Al/l; the peat solutions had an average aluminium concentration of 2.0 mg/l. Therefore, the sand gave no release of aluminium, the topsoil and peat had similar aluminium solution concentrations and clay gave the highest release of aluminium.

7.3.3 Discussion

The relative values for all soils and cations tested after 24 hours shaking is given in Table 7.8. The topsoil, clay and peat did not adsorb any of the cations analysed for at the end of the 24 hour testing period. The sand did not release calcium, zinc, aluminium and released low levels of magnesium, sodium, and zinc. The clay and peat soils had particularly high relative values for iron, zinc and aluminium.

The results of the first set of batch experiments were not as would be expected from a review of the literature. Soil scientists generally recognise that among the factors affecting the mobility of the chemical constituents of water in soils, ion exchange and sorption/desorption are of prime importance. Soils with the highest cation exchange capacity would normally be expected to remove the greatest amount of cations from the leachate. Soils, such as sand, which are generally regarded as inert, would not be expected to adsorb or remove pollutants from landfill leachate.

TABLE 7.8 RELATIVE VALUES FOR ALL SOILS AND CATIONS TESTED AFTER 24 HOURS

SOIL	CATION				
	CALCIUM	MAGNESIUM	SODIUM	IRON	ZINC
Sand	0.96	1.12	1.05	19.4	1.00
Topsoil	1.50	1.39	1.03	32.8	3.26
Clay	1.53	2.38	1.17	34.2	39.50
Peat	1.07	4.93	1.45	28.2	17.30

The experimental results appear to indicate that the clay, peat and topsoil released to solution all the cations monitored. Therefore, rather than removing these constituents from solution these soils are increasing the amount of calcium, magnesium, sodium, iron, zinc and aluminium in leachate. The sand tested released magnesium, sodium and iron in lower quantities than the other soils tested and did not release calcium, zinc or aluminium. One difference between the sand and the other three soils tested is the differing concentrations of the original soil cations. The original sand has low levels of cations and hence cannot release these cations to solution in any great quantity. The other soils, however, have greater concentrations of these cations and hence can release greater quantities into solution. There also appears to be a relationship between the original soil cation content and the release of that particular cation into solution; the greater the original cation content of the soil, the greater the concentration of that particular cation in solution after 24 hours.

Most soil adsorption studies are carried out with solutions which are relatively simple in composition when compared to that of a landfill leachate. The types of solution used include single and mixed metal synthetic solutions or trade effluents. These solutions will not have the same activity in soil reactions, with regard to cation competition, as landfill leachates which contain a diverse range of cations. Hence their results are not directly applicable to landfill leachate-soil interactions.

The argument proposed after the results of these first experiments is that due to the large number of different cations and anions in landfill leachate and their wide range of concentrations (from mg/l for sodium to ug/l for heavy metals) that the results from simple or less complex solutions are not applicable. Due to the higher number of cations competing for exchange sites within a landfill leachate, simple calculation of exchange ratios is not possible. In addition, soil adsorption studies normally analyse the equilibrium solution for only the particular metal(s) under observation. Therefore, the release of other cations to compensate for those being adsorbed may have passed unnoticed.

The results of the Phase I study would also seem to indicate that a contact time of 8 - 24 hours is required for the soils to reach equilibrium. This is best observed by referral to the graphs in preceding pages. Solution concentrations generally became constant between 8 hours to 24 hours. The results also seem to indicate that while adsorption may occur in the first few hours, the final equilibrium content indicates a net release of the cations.

In order to examine more closely the effect of complex leachate on soil chemical action, it was decided to repeat the experiments and include measurement of a greater number of cations in the study. This led to the Phase II experiments.

7.4 PHASE II EXPERIMENTS

7.4.1 Experimental Design

The Phase II experiments were designed to investigate the equilibrium concentration of a greater number of cations in leachate contacted with soil. The cations measured in this phase of the experiments were ammonia, magnesium, calcium, sodium, potassium, iron, aluminium, zinc, copper, lead, manganese, chromium, cadmium and nickel. In addition the alteration in leachate COD and pH on contact with soil was monitored. A total of 520 determinations were carried out.

The Phase II experiments were also designed to investigate the effect of soil:leachate ratio or increasing cation content added on changes in leachate chemistry. The soil weight used was constant at 100 grams of air-dried and sieved (<2mm) soil. The volume of leachate was altered to give ratios of 1:1, 1:2, 1:4 and 1:10. As previously noted the hydrophylic nature of peat prevented use of the 1:1 and 1:2 ratios; after shaking all leachate had been adsorbed by the peat and hence there was not adequate solution remaining for analysis. The experimental design is shown in Table 7.9. Each soil/leachate combination was carried out in duplicate. Two blank samples containing leachate only were also monitored. Thus a total of thirty-two experimental containers were shaken for 24 hours in order to ensure equilibrium. The contact time of 24 hours had been shown by the Phase I experiments to be required for equilibrium conditions and it allowed ample time to conduct the sampling. It was believed that any changes in solution that would occur after 24 hours would result from biological rather than exchange or chemical interaction.

The leachate used was obtained from the same source as the Phase I leachate. It is noted that the concentration of the leachate in Phase II is reduced in comparison with the leachate used in the Phase I study. However, this allowed comparison of the effects of a high cation leachate with that of a low cation leachate. Due to the large number of experimental containers, the shaking had to be undertaken in two batches. This meant there were slightly different concentrations of cations in the added leachates; the 1:1 and 1:10 ratios were shaken together and the added leachate chemical composition is shown in Table 7.10. The 1:2 and 1:4 ratios were shaken together and the added leachate concentrations are shown in Table 7.11. The leachate concentrations are given in mg/l and meq/l. It is important to note that the results in meq give a different impression as to the cations present in highest concentration than when the results are quoted in mg/l. The term "equivalent" is defined as 1

TABLE 7.9 EXPERIMENTAL DESIGN OF PHASE II EXPERIMENTS

SOIL (100 gms)	LEACHATE ADDED (mls)	SOIL:LEACHATE RATIO
SAND	100	1 : 1
SAND	200	1 : 2
SAND	400	1 : 4
SAND	1000	1 : 10
TOPSOIL	100	1 : 1
TOPSOIL	200	1 : 2
TOPSOIL	400	1 : 4
TOPSOIL	1000	1 : 10
CLAY	100	1 : 1
CLAY	200	1 : 2
CLAY	400	1 : 4
CLAY	1000	1 : 10
PEAT	400	1 : 4
PEAT	1000	1 : 10
BLANK	400	-
BLANK	1000	-

TABLE 7.10 ANALYSIS OF LEACHATE USED IN 1:1 AND 1:10 SOIL:LEACHATE RATIOS.

CONSTITUENT	CONCENTRATION (mg/l)	CONCENTRATION (meq/l)
COD	331.6	
AMMONIA	11.2	0.62
CALCIUM	98	4.9
MAGNESIUM	80.4	6.6
POTASSIUM	56.1	1.4
SODIUM	314.5	13.7
IRON	0.09	3.2×10^{-3}
ZINC	0.01	
ALUMINIUM	<0.01	
COPPER	<0.02	
LEAD	<0.01	
MANGANESE	<0.02	
CHROMIUM	<0.02	
CADMIUM	<0.01	
NICKEL	<0.02	

TABLE 7.11 ANALYSIS OF LEACHATE USED IN 1:2 AND 1:4 SOIL:LEACHATE RATIOS.

CONSTITUENT	CONCENTRATION (mg/l)	CONCENTRATION (meq/l)
COD	265.4	
AMMONIA	11.2	0.62
CALCIUM	110.0	5.5
MAGNESIUM	80.4	6.6
POTASSIUM	54.8	1.4
SODIUM	319.0	13.9
IRON	0.09	3.2×10^{-3}
ZINC	0.01	
ALUMINIUM	<0.01	
COPPER	<0.02	
LEAD	<0.01	
MANGANESE	<0.02	
CHROMIUM	<0.02	
CADMIUM	<0.01	
NICKEL	<0.02	

gram atomic weight of hydrogen or the amount of any other ion that will combine with or displace this amount of hydrogen. For monovalent cations such as Na^+ the equivalent weight and atomic weight are the same since they can replace or react with one H^+ ion. Divalent cations such as Ca^{2+} and Mg^{2+} can take the place of two H^+ ions. Consequently, their atomic weight must be divided by 2 to obtain the equivalent weight. In terms of concentration in mg/l the amount of calcium in the leachate used would appear to be greater than the amount of magnesium. However, in terms of meq/l (the use of which is more applicable when studying soil chemical interactions) the magnesium concentration is greater than that of calcium. It is therefore recommended that leachate analyses should be quoted in both mg/l and meq/l when leachate-soil interactions are being studied.

7.4.2 Results

7.4.2.1 pH

The average pH values for all soil:leachate ratios after 24 hours contact are given in Table 7.12. The values are plotted with that of the control leachate in Figure 7.6.

TABLE 7.12 AVERAGE pH VALUES.

SOIL:LEACHATE RATIO	SOIL.			
	SAND	TOPSOIL	CLAY	PEAT.
1:1	7.54	8.16	5.92	-
1:2	6.78	7.86	5.94	-
1:4	7.58	7.86	6.89	3.73
1:10	7.27	7.25	6.56	4.11

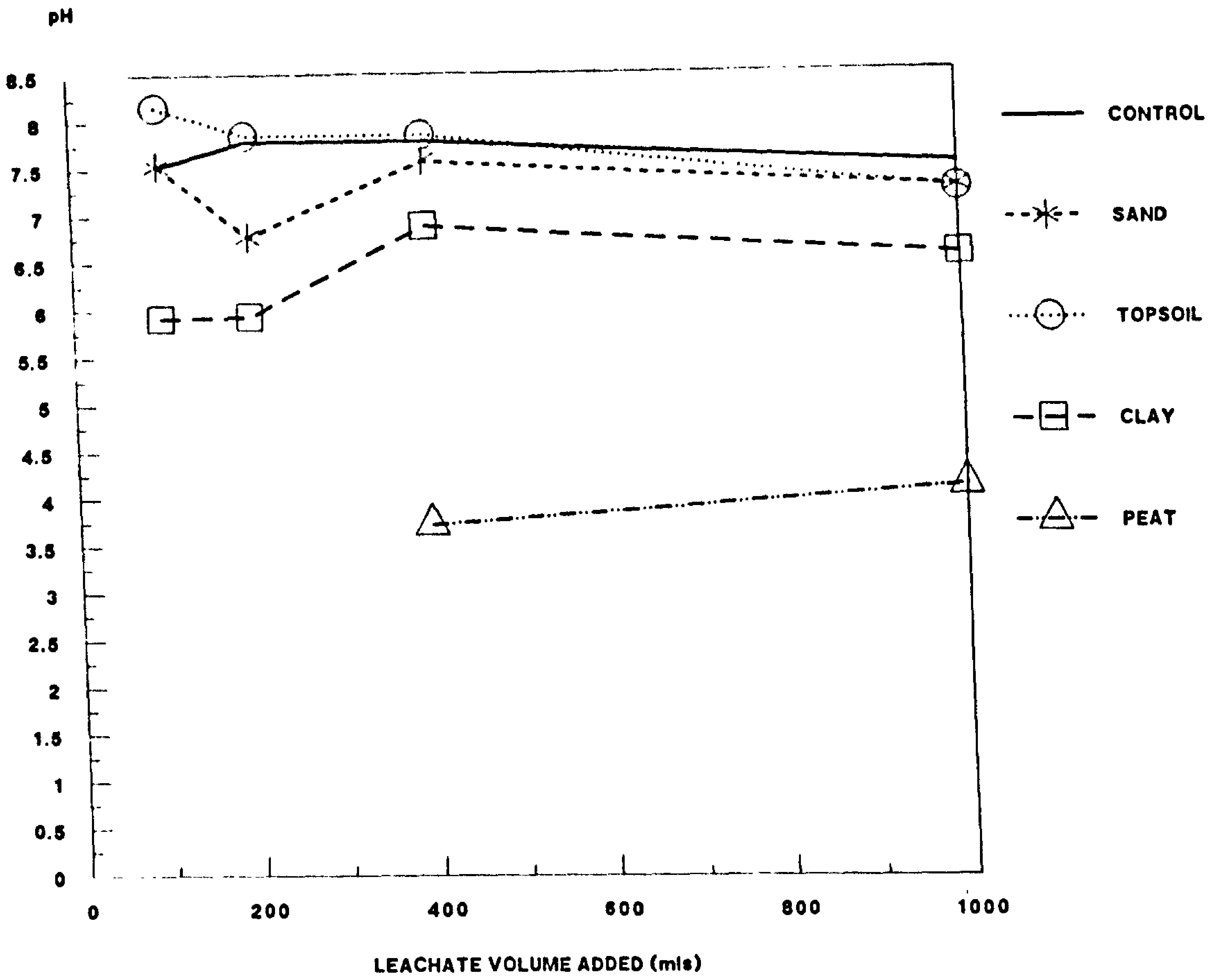


Figure 7.6 pH profile for sand, topsoil, clay and peat - Phase II.

The initial leachates added had a pH of 7.82 (1:1 and 1:10) and 7.87 (1:2 and 1:4) which declined to 7.53 and 7.80 respectively in the control leachates after 24 hours of shaking.

The pH of leachates in contact with sand and topsoil closely resembled those of the control leachate. Leachates in contact with clay had a lower pH than the control leachate at all added volumes. The pH difference was greatest at 100mls and 200mls applied leachate volumes. Leachate in contact with peat demonstrated the greatest drop in pH of the soils tested. The pH of the leachate decreased to approximately 4.0 at 400mls and 1000mls applied leachate volume.

The breakdown of organic materials within the leachate into organic acids could release hydrogen ions into solution and cause a decrease in pH; however contact times were very short in terms of biological acclimation and activities. During these short contact periods the pH changes of the control leachate would be of a similar magnitude if this process was occurring. It is probable that the large decrease in leachate pH on contact with peat is due to the dissociation and/or dissolution of some of the organic compounds in the peat.

The most likely explanation for the decrease in pH in clay is due to the leaching out of water-soluble hydrogen and in view of the other resùlts there may also be some released due to the accelerated weathering effect the leachate has on these soils. Ion exchange reactions will also affect the pH of soil solutions. As sodium and potassium ions move into the soil complex, other less alkali cations move out of the soil.

7.4.2.2 COD

The COD of the equilibrium solutions was measured and the values in mg are illustrated in Figure 7.7. The calculated relative values are given in Table 7.13.

The results show that a decrease in COD occurred at the 1:1 ratio for sand and topsoil, but at all other soil:leachate combinations there was an increase in leachate COD values after contact with soil.

TABLE 7.13 AVERAGE RELATIVE VALUES FOR COD.

SOIL:LEACHATE RATIO	SOIL.			
	SAND	TOPSOIL	CLAY	PEAT.
1:1	0.5	0.5	27.04	-
1:2	1.49	2.06	6.43	-
1:4	1.32	1.45	3.86	20.3
1:10	2.29	1.86	11.01	40.8

Therefore, none of the soils tested in this batch study removed COD to any appreciable extent. The largest relative values occurred in the peat soil. This soil had a higher initial organic content than the other soils tested. It is possible that the increase in COD of leachate with this soil is due to the leaching of organic acids.

7.4.2.3 Ammonia

The ammonia content of equilibrium solutions for all soil:leachate ratios is illustrated in Figure 7.8. The calculated relative values are given in Table 7.14.

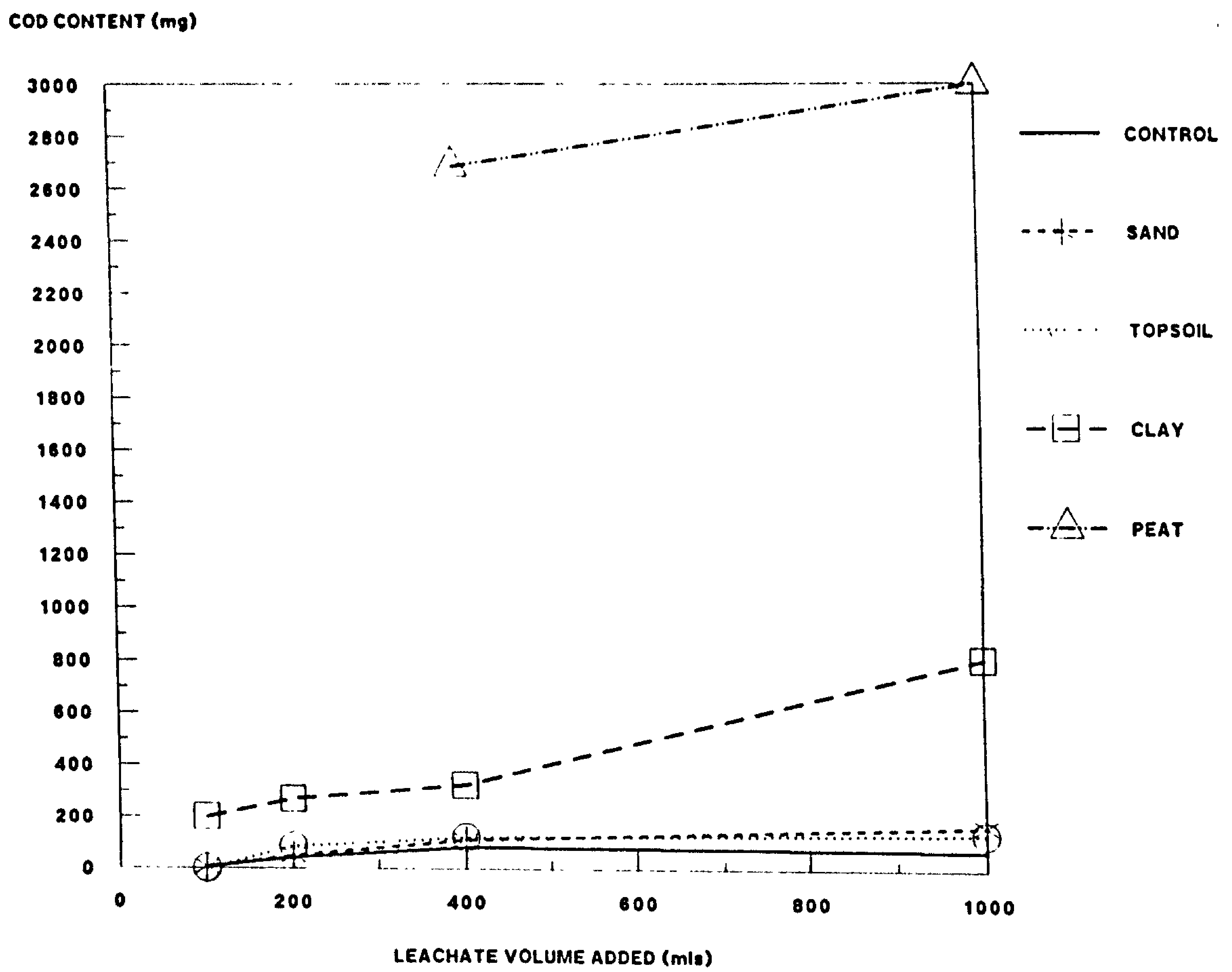


Figure 7.7 COD profile for sand, topsoil, clay and peat - Phase II.

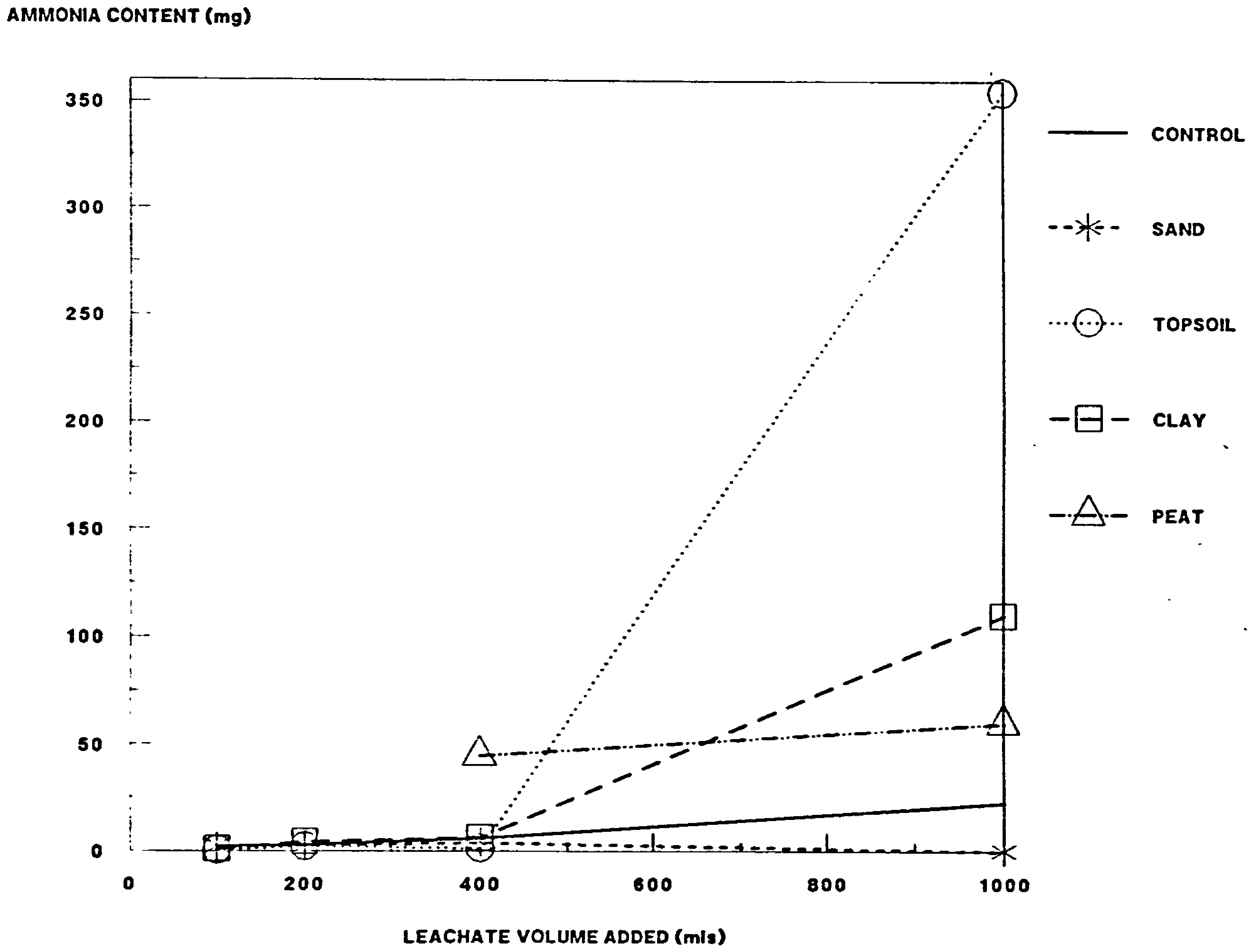


Figure 7.8 Ammonia profile for sand, topsoil, clay and peat - Phase II.

TABLE 7.14 AVERAGE RELATIVE VALUES FOR AMMONIA.

SOIL:LEACHATE RATIO	SOIL. SAND	TOPSOIL	CLAY	PEAT.
1:1	1.0	0.26	0.5	-
1:2	0.83	0.72	1.5	-
1:4	0.67	0.25	1.07	7.47
1:10	nd	15.80	4.89	2.67

As the volume of leachate added to the sand increased then the relative values decreased indicating increasing removal of ammonia from the leachate. The topsoil adsorbed ammonia from the added leachate at the 1:1, 1:2 and 1:4 ratios but released large amounts of ammonia at the 1:10 soil:leachate ratio. The clay soil adsorbed ammonia at the lowest applied leachate volume, released small amounts of ammonia at the 1:2 and 1:4 ratios and had approximately 5 times the ammonia in solution as the control leachate when 1000 mls was applied. The peat soil did not adsorb ammonia at either the 400 mls or 1000 mls applied leachate volume.

The ammonia concentration of the initial leachate is low, particularly in relation to other cations such as sodium. It is possible therefore that due to the effect of competing cations, ammonia is released from the soil complex rather than adsorbed.

7.4.2.4 Calcium

The profile for calcium content in leachates contacted with soil (Figure 7.9) and the calculated relative values (Table 7.15) show that at all soil:leachate ratios for all soils (except sand when 100 mls leachate was applied) calcium was released into solution.

TABLE 7.15 AVERAGE RELATIVE VALUES FOR CALCIUM.

SOIL:LEACHATE RATIO	SOIL			
	SAND	TOPSOIL	CLAY	PEAT
1:1	0.79	2.10	3.30	-
1:2	1.20	2.20	2.40	-
1:4	1.36	1.81	1.81	2.12
1:10	1.44	1.50	1.54	1.23

As the volume of leachate, and hence the amount of calcium added to the sand, increased the amount of calcium in solution increased.

This pattern was reversed with the clay soil. The highest relative value was obtained when 100 mls leachate was added to the soil; the calcium concentration in solution being approximately three times that of the control leachate. The values decreased with increasing volume of leachate added to a minimum calcium concentration of 1.5 times that of the control leachate when 1000mls of leachate was added. This is a similar pattern to that of magnesium.

The topsoil solutions demonstrated similar relative values at 100mls and 200mls of leachate application. Further increases in applied leachate volume led to a decrease in relative values.

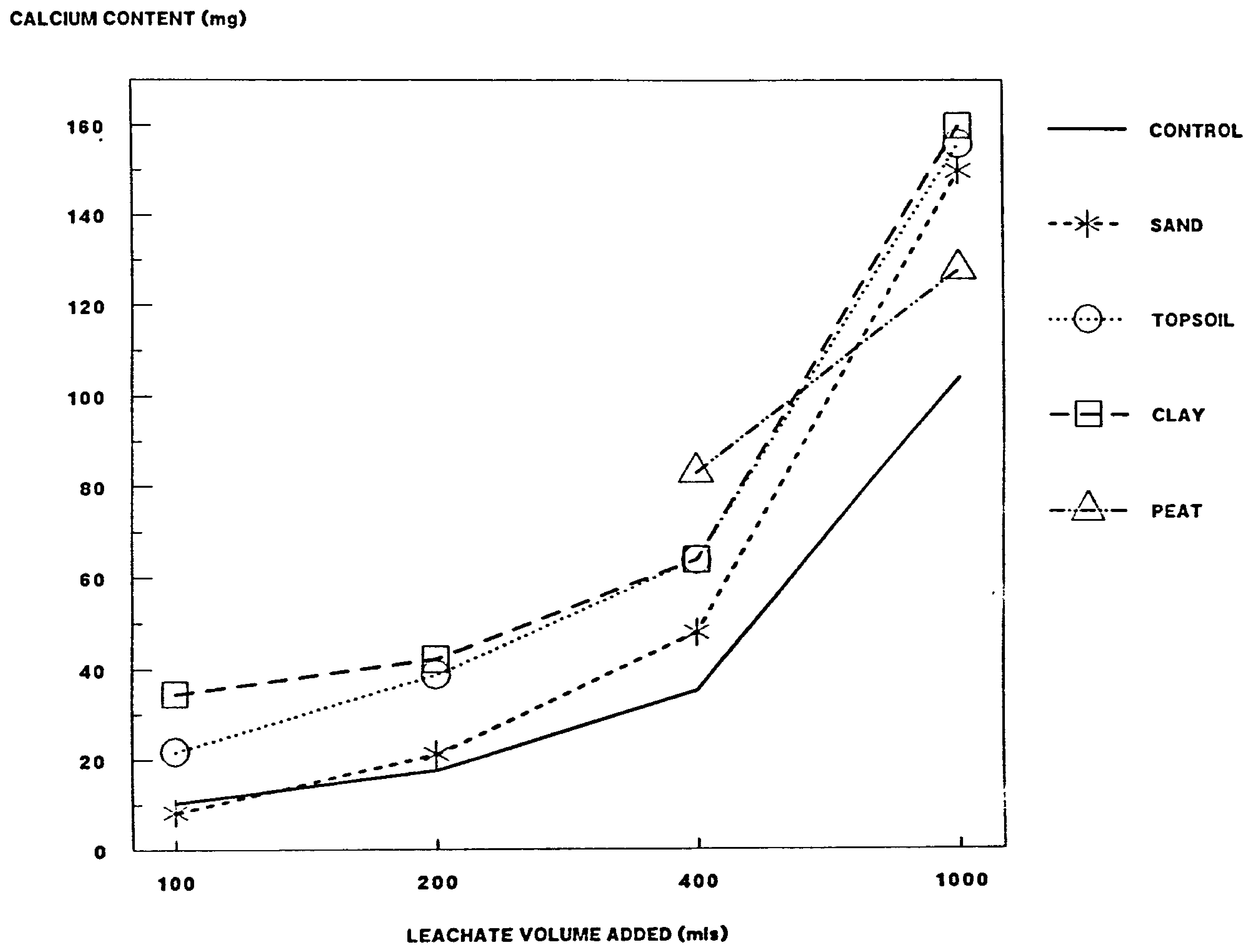


Figure 7.9 Calcium profile for sand, topsoil, clay and peat - Phase II.

Peat also demonstrated a reduction in calcium in solution with increased leachate volume applied; although release of calcium occurred at all volumes.

Clay gave greatest release of calcium at all application volumes in relation to the other soils tested; topsoil and peat were intermediate in release of calcium and sand had the lowest release of calcium at all application volumes. This is similar to the pattern of release that was found in Phase I and again it is noted that the calcium content of the original soils is in the order of clay > topsoil > peat > sand and that calcium is the major exchangeable cation in clay, topsoil and sand. No significant correlation was found between the original calcium content of the soils and the calcium content of the leachate after contact with the soils. However, a high correlation between the amount of calcium added to the soils and the calcium content of the leachate after 24hours contact with the soil was found. The correlation coefficients and the regression equations are given in Table 7.16.

7.4.2.5 Magnesium

The amount of magnesium in the control leachate and the leachates in contact with soil are shown in Figure 7.10. The calculated relative values are shown in Table 7.17.

TABLE 7.16 CORRELATION BETWEEN THE CALCIUM CONTENT OF LEACHATE CONTACTED WITH SOIL FOR 24 HOURS AND THE CALCIUM CONTENT OF THE ORIGINAL LEACHATE.

SOIL	CORRELATION COEFFICIENT r	REGRESSION EQUATION
SAND	1.00	Ca AFTER CONTACT(mg) = 1.50 Ca ADDED (mg) - 5.93
TOPSOIL	0.998	Ca AFTER CONTACT(mg) = 1.40 Ca ADDED (mg) + 11.8
CLAY	1.00	Ca AFTER CONTACT(mg) = 1.35 Ca ADDED (mg) + 18.6
PEAT	1.00	Ca AFTER CONTACT(mg) = 0.69 Ca ADDED (mg) + 56.1

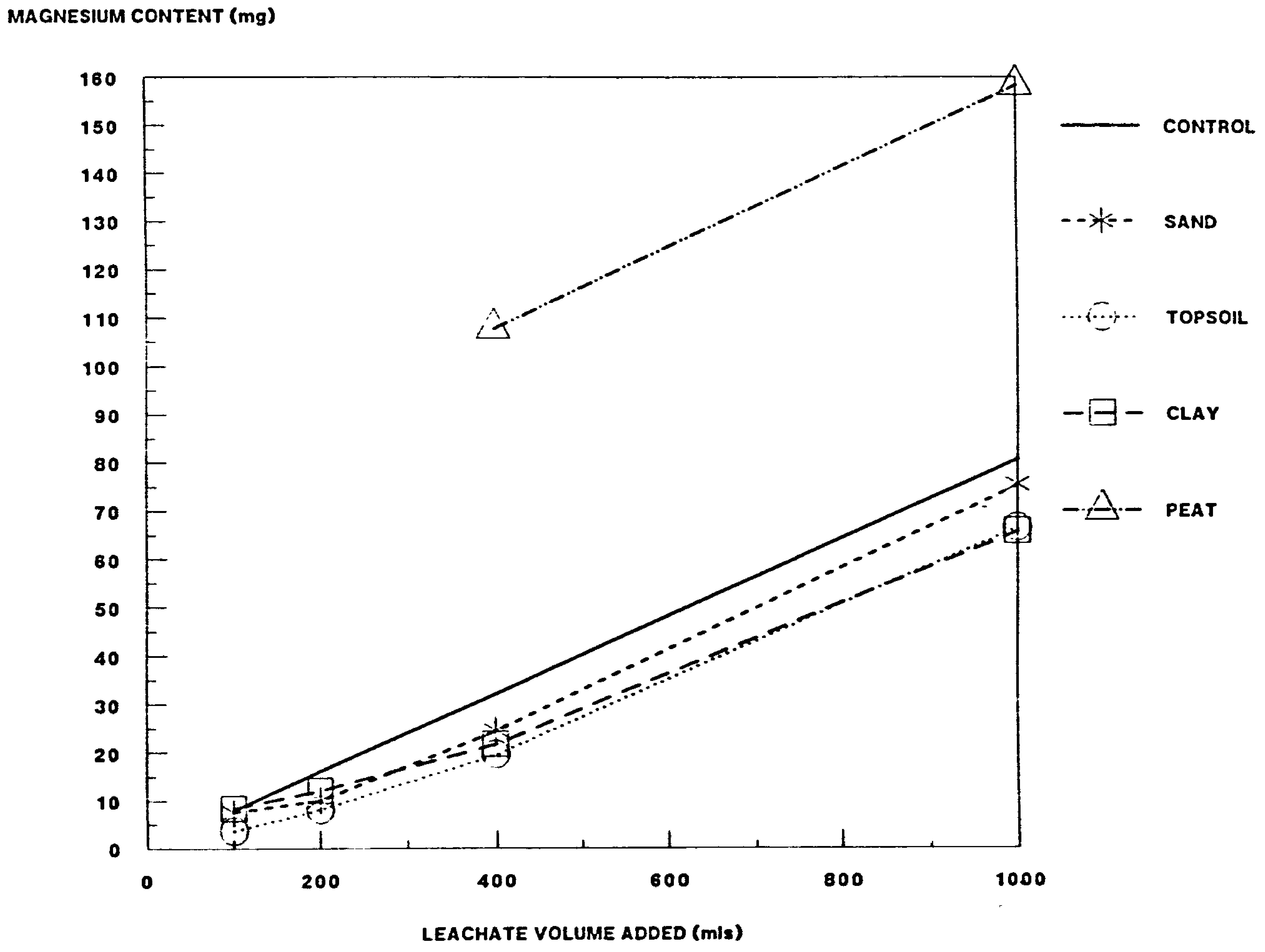


Figure 7.10 Magnesium profile for sand, topsoil, clay and peat - Phase II.

TABLE 7.17 AVERAGE RELATIVE VALUES FOR MAGNESIUM.

SOIL:LEACHATE RATIO	SOIL			
	SAND	TOPSOIL	CLAY	PEAT
1:1	0.50	0.45	1.05	-
1:2	0.62	0.50	0.75	-
1:4	0.76	0.61	0.68	3.35
1:10	0.94	0.83	0.82	1.97

At all leachate application volumes the sand demonstrated lower concentrations of magnesium in solution than that of the control leachate. The rate of magnesium adsorption by sand decreased with increasing leachate volume applied or increasing amount of magnesium added.

A similar pattern was followed by the topsoil; adsorption of magnesium occurred at all applied leachate volumes but the relative values increased as the quantity of leachate applied increased. Maximum absorption occurred when 100 mls leachate was applied (relative value of 0.45) and minimum absorption occurred when 1000 mls was applied (relative value=0.83). Therefore, topsoil demonstrated a slightly greater magnesium removal from leachate than sand.

The·clay and peat soil solutions demonstrated the opposite pattern to the above two soils; as the leachate volume applied and hence the amount of magnesium added increased the relative values decreased. Clay released magnesium at the lowest applied volume (100 mls) and at all other volumes adsorbed magnesium from solution. The relative value at 1000 mls applied leachate is similar to that of topsoil. Peat demonstrated release of magnesium at all applied volumes, the release being greatest when 400 mls leachate was applied.

The results from Phase I show that magnesium was released from the four soils tested; in Phase II all soils, except peat, adsorbed magnesium. The magnesium content of the leachate used in the Phase II study was approximately double that of the leachate used in Phase I. In addition, the magnesium content calculated in meq/l indicates that its content is greater than that of calcium in terms of ability to compete for exchange sites. Therefore, magnesium in the Phase II leachate may have a greater potential for adsorption due to its greater concentration. The release of magnesium from peat is thought to be due to the same reason as release in Phase I i.e. magnesium is the major exchangeable cation in peat whereas calcium is the major exchangeable cation in the other soils tested.

No significant correlation between the original magnesium content of the soil and the magnesium content in the leachate after contact with that soil could be found. A high correlation between the magnesium content of the added leachate and the amount of magnesium in the leachate after contact with the soils was found. The correlation coefficients and the regression equations are shown in Table 7.18.

7.4.2.6 Sodium

The profile for sodium content in leachates contacted with soil and for that of the control leachate are shown in Figure 7.11. The calculated relative values are shown in Table 7.19. Sodium was adsorbed by all soils (except peat when 400 mls was applied).

TABLE 7.18 CORRELATION BETWEEN THE MAGNESIUM CONTENT OF LEACHATE CONTACTED WITH SOIL FOR 24 HOURS AND THE MAGNESIUM CONTENT OF THE ORIGINAL LEACHATE

SOIL	CORRELATION COEFFICIENT r	REGRESSION EQUATION
SAND	0.999	Mg AFTER CONTACT (mg) = 1.0 Mg ADDED (mg) - 5.79
TOPSOIL	0.997	Mg AFTER CONTACT (mg) = 0.886 Mg ADDED(mg) - 5.86
CLAY	0.995	Mg AFTER CONTACT (mg) = 0.811 Mg ADDED(mg) - 0.77
PEAT	1.00	Mg AFTER CONTACT (mg) = 1.04 Mg ADDED (mg) + 74.5

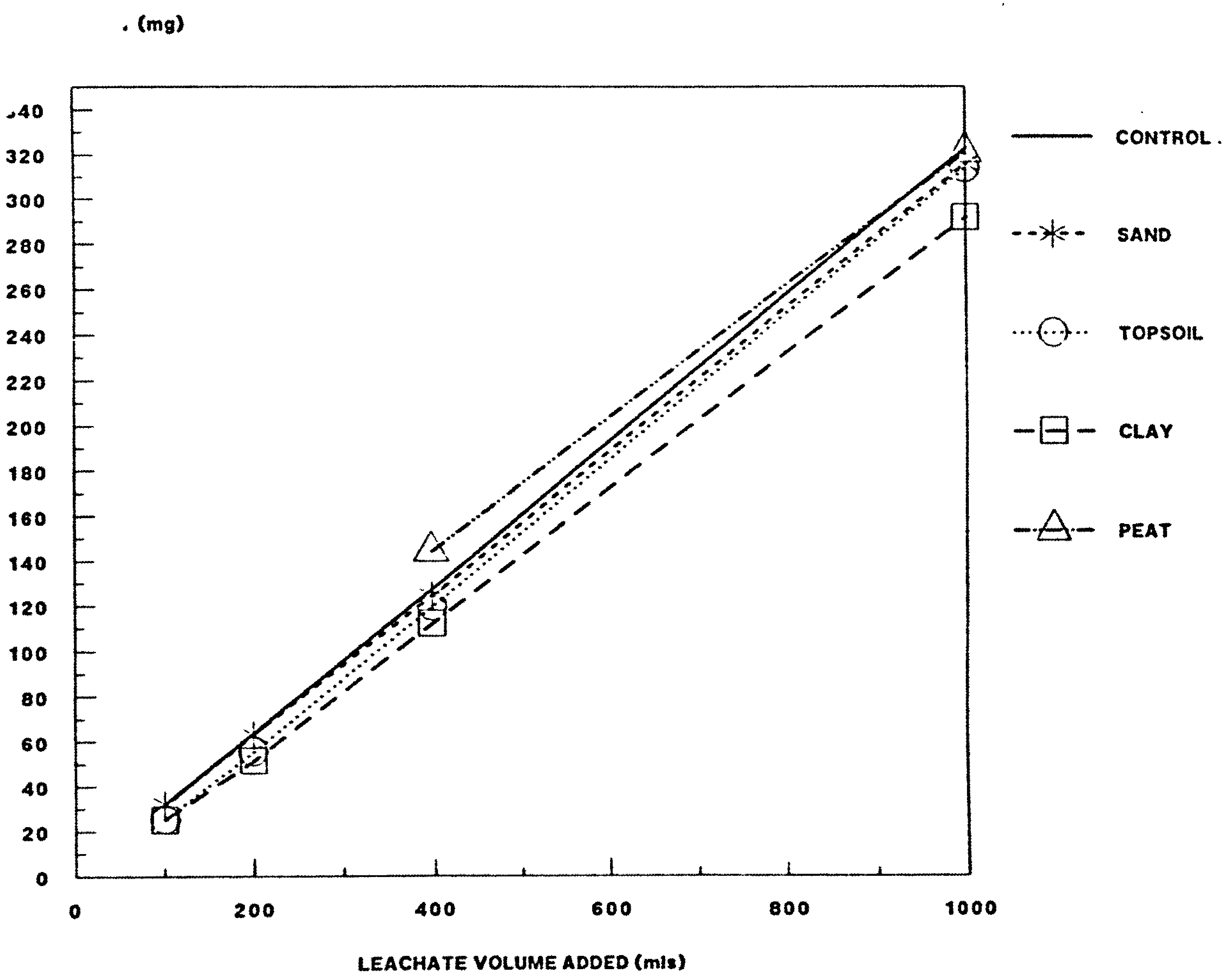


Figure 7.11 Sodium profile for sand, topsoil, clay and peat - Phase II.

TABLE 7.19 AVERAGE RELATIVE VALUES FOR SODIUM.

SOIL:LEACHATE RATIO	SOIL			
	SAND	TOPSOIL	CLAY	PEAT
1:1	1.00	0.79	0.79	-
1:2	0.99	0.87	0.81	-
1:4	0.98	0.94	0.88	1.15
1:10	0.98	0.97	0.90	0.99

The sodium content of the leachate used in these Phase II experiments (314 mg/l) was approximately twice that of the leachate used in the Phase I experiments (140 mg/l). All soils demonstrated release of sodium in the Phase I experiments. Therefore, the increase in sodium concentration may allow this cation to overcome the other more strongly attracted cations (such as calcium) in the competition for exchange sites.

The relative values for sand solutions remained approximately constant and similar to that of the control leachate throughout the range of applied leachate volumes. The relative values of the clay and topsoil samples increased with increased leachate application. A minimum relative value of 0.79 was obtained for clay when 100mls leachate was applied and rose to 0.9 when 1000mls was applied. Topsoil had a minimum relative value of 0.79 at 100 mls application volume, rising to 0.97 when 1000 mls was applied. This would seem to indicate that the ability of the topsoil and clay to adsorb sodium is not infinite and will be exhausted at some point.

The relative values for leachate in contact with peat appear to decrease as the volume of leachate applied increases. At 400 mls applied leachate the relative value indicates that sodium is released into solution, whereas when 1000 mls of leachate is applied adsorption of sodium from solution occurs.

Clay was the most efficient soil at adsorbing sodium at all applied volumes; followed by topsoil, sand and peat. The original soils all had low initial sodium contents as compared to other cations. The amount of sodium in the soil in increasing order is topsoil (0.6ppm), sand (0.99ppm), clay (1.9ppm) and peat (4.35ppm). No significant correlation between the original sodium content of the soil and the sodium content in the leachate after contact with that soil could be found. However, a high correlation was found between the amount of sodium in the leachate added to the soil and the amount of sodium in the leachate after 24 hours contact with the soil. The correlation coefficients and the regression equations are given in Table 7.20.

7.4.2.7 Potassium

The potassium content for leachate in contact with each soil at each soil:leachate ratio and the potassium content of the control is shown in Figure 7.12. The calculated relative values are given in Table 7.21.

TABLE 7.21 AVERAGE RELATIVE VALUES FOR POTASSIUM.

SOIL:LEACHATE RATIO	SOIL			
	SAND	TOPSOIL	CLAY	PEAT
1:1	0.50	0.29	1.43	-
1:2	1.3	0.45	1.41	-
1:4	0.93	0.60	1.05	2.11
1:10	0.88	0.78	0.92	1.59

TABLE 7.20 CORRELATION BETWEEN THE SODIUM CONTENT OF LEACHATE CONTACTED WITH SOIL FOR 24 HOURS AND THE SODIUM CONTENT OF THE ORIGINAL LEACHATE.

SOIL	CORRELATION COEFFICIENT r	REGRESSION EQUATION
SAND	1.00	Na AFTER CONTACT (mg) = 0.976 Na ADDED (mg) + 0.604
TOPSOIL	1.00	Na AFTER CONTACT (mg) = 0.994 Na ADDED (mg) - 0.307
CLAY	1.00	Na AFTER CONTACT (mg) = 0.921 Na ADDED (mg) - 5.59
PEAT	1.00	Na AFTER CONTACT (mg) = 0.894 Na ADDED (mg) + 32.4

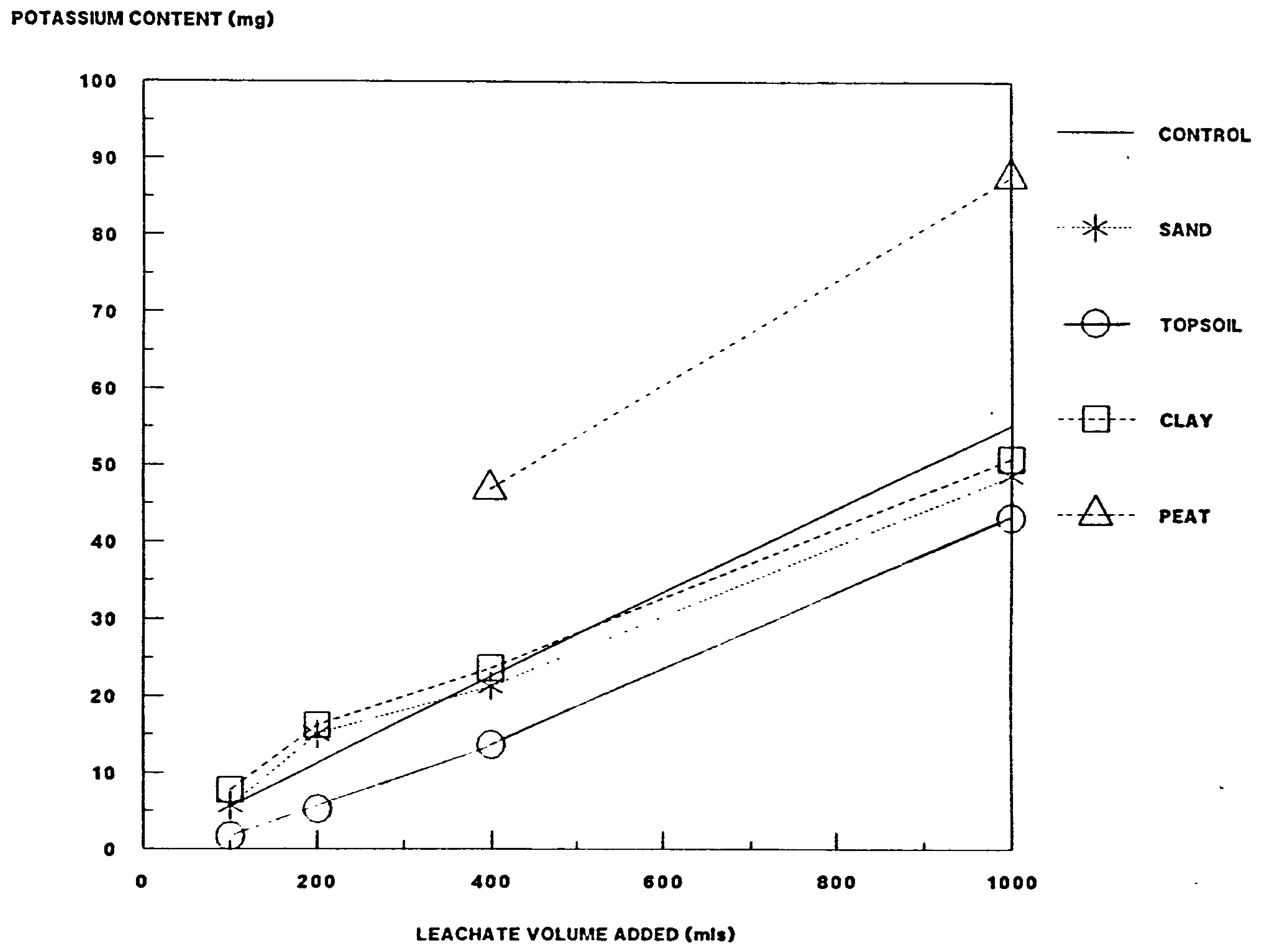


Figure 7.12 Potassium profile for sand, topsoil, clay and peat - Phase II

Topsoil adsorbed potassium at all leachate application volumes; the clay (except at 1000 mls applied leachate) and peat released potassium into solution. The potassium content of leachate in contact with sand was similar to that of the control.

The topsoil decreased in potassium absorbing capacity as the leachate volume increased. This would seem to indicate that while the topsoil adsorbs potassium, this adsorption is not unlimited and decreases as the potassium content added increases.

The clay and peat demonstrated a reverse pattern to the above soils in that the relative values decreased as the volume of leachate applied increased. The clay soil released gradually less potassium as the quantity of potassium applied increased until at 1000 mls applied leachate the clay adsorbed potassium from solution (relative value = 0.92). This would seem to indicate a mass effect in the ability of the potassium to compete for exchange sites. Peat demonstrated maximum release of potassium when 400 mls was applied.

The order of affinity of the soils for potassium appears to be topsoil > sand > clay > peat. A review of the chemical composition of the original soils illustrates that clay had the highest potassium content (11.5 ppm), followed by peat (8.1ppm), topsoil (0.98ppm) and sand (0.54ppm). No significant correlation between the original potassium content of the soil and the amount of potassium in the leachate after contact with the soil was found. However, a high correlation between the amount of potassium in the leachate added to the soil and the amount of potassium in the leachate after 24 hours contact with the soil was found. The correlation coefficients and regression equations for all soils are given in Table 7.22.

TABLE 7.22 CORRELATION BETWEEN THE POTASSIUM CONTENT OF LEACHATE CONTACTED WITH SOIL FOR 24 HOURS AND THE POTASSIUM CONTENT OF THE ORIGINAL LEACHATE.

SOIL	CORRELATION COEFFICIENT r	REGRESSION EQUATION
SAND	0.997	K AFTER CONTACT(mg) = 0.925K ADDED(mg) - 1.80
TOPSOIL	0.998	K AFTER CONTACT(mg) = 0.848K ADDED(mg) - 4.11
CLAY	0.997	K AFTER CONTACT(mg) = 0.837K ADDED(mg) + 4.82
PEAT	1.00	K AFTER CONTACT(mg) = 1.24 K ADDED(mg) + 19.3

7.4.2.8 Iron

The iron profile for leachates contacted with soil is shown in Figure 7.13 and the calculated relative values are given in Table 7.23.

TABLE 7.23 AVERAGE RELATIVE VALUES FOR IRON.

SOIL:LEACHATE RATIO	SOIL			
	SAND	TOPSOIL	CLAY	PEAT
1:1	0.44	1.11	17.80	-
1:2	2.10	1.30	4.8	-
1:4	2.60	3.00	16.5	122.0
1:10	0.55	5.40	6.0	36.7

The sand soils removed iron from solution at 100 mls and 1000 mls applied leachate volume and released iron at all other applied volumes. The topsoil released iron at all leachate volumes, with the amount released increasing as the volume of leachate or the amount of iron added increased.

The clay soil solutions had high relative values at 100 mls applied leachate (17.8) and at 400 mls applied leachate (relative value = 16.5). Lower release of iron into solution occurred when 200 mls and 1000 mls of leachate was applied. Peat also released iron at the 400 mls application volume (relative value= 122.0) and when 1000 mls of leachate was applied (relative value = 36.7).

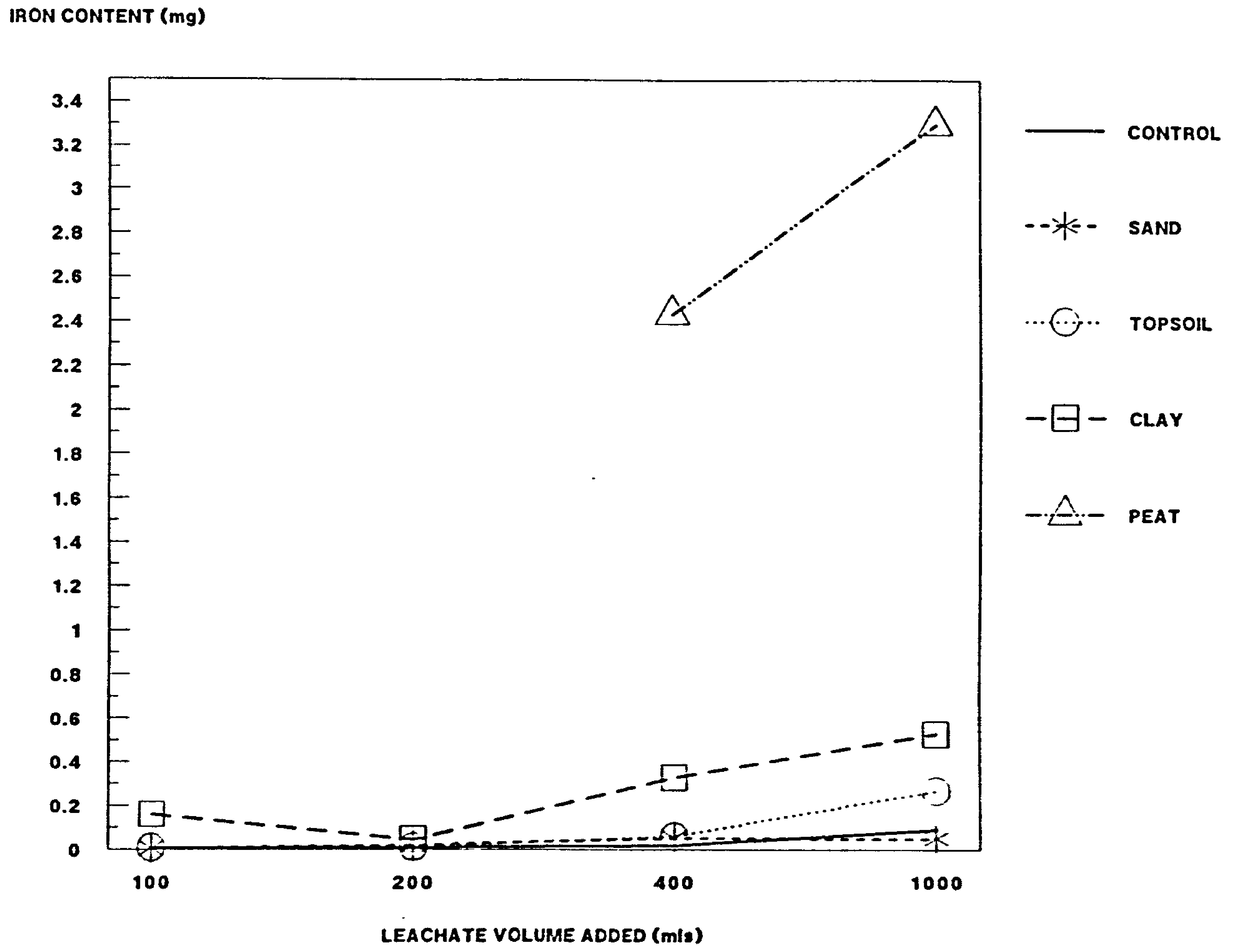


Figure 7.13 Iron profile for sand, topsoil, clay and peat - Phase II.

7.4.2.9 Zinc

The applied leachate had a low initial zinc content as did the leachates in contact with sand and topsoil after 24 hours shaking (Figure 7.14). This is further illustrated by the calculated relative values (Table 7.24).

TABLE 7.24 AVERAGE RELATIVE VALUES FOR ZINC.

SOIL:LEACHATE RATIO	SOIL			
	SAND	TOPSOIL	CLAY	PEAT
1:1	2.0	3.0	424.0	-
1:2	1.0	2.0	65.5	-
1:4	1.0	2.0	34.0	207.5
1:10	1.0	2.0	45.0	111.0

Leachates added to clay and peat soils had large relative values at all applied leachate volumes. At 100 mls applied leachate the zinc concentration of leachate in contact with clay was 424 times that of the control leachate. This concentration value decreased when 200 mls, 400 mls and 1000 mls leachate was applied. Peat gave maximum release of iron when 400 mls leachate was applied, having 207.5 times the zinc concentration of the control leachate. The amount in solution decreased to 111 times that of the control leachate when 1000 mls was applied.

7.4.2.10 Aluminium, Copper, Lead, Manganese, Chromium, Cadmium, Nickel

The relative values of the remaining metals analysed for (aluminium, copper, lead, manganese, chromium, cadmium and nickel) could not be calculated as the added leachate and control leachates had non-detectable amounts of these metals in solution. However, leachates in contact with

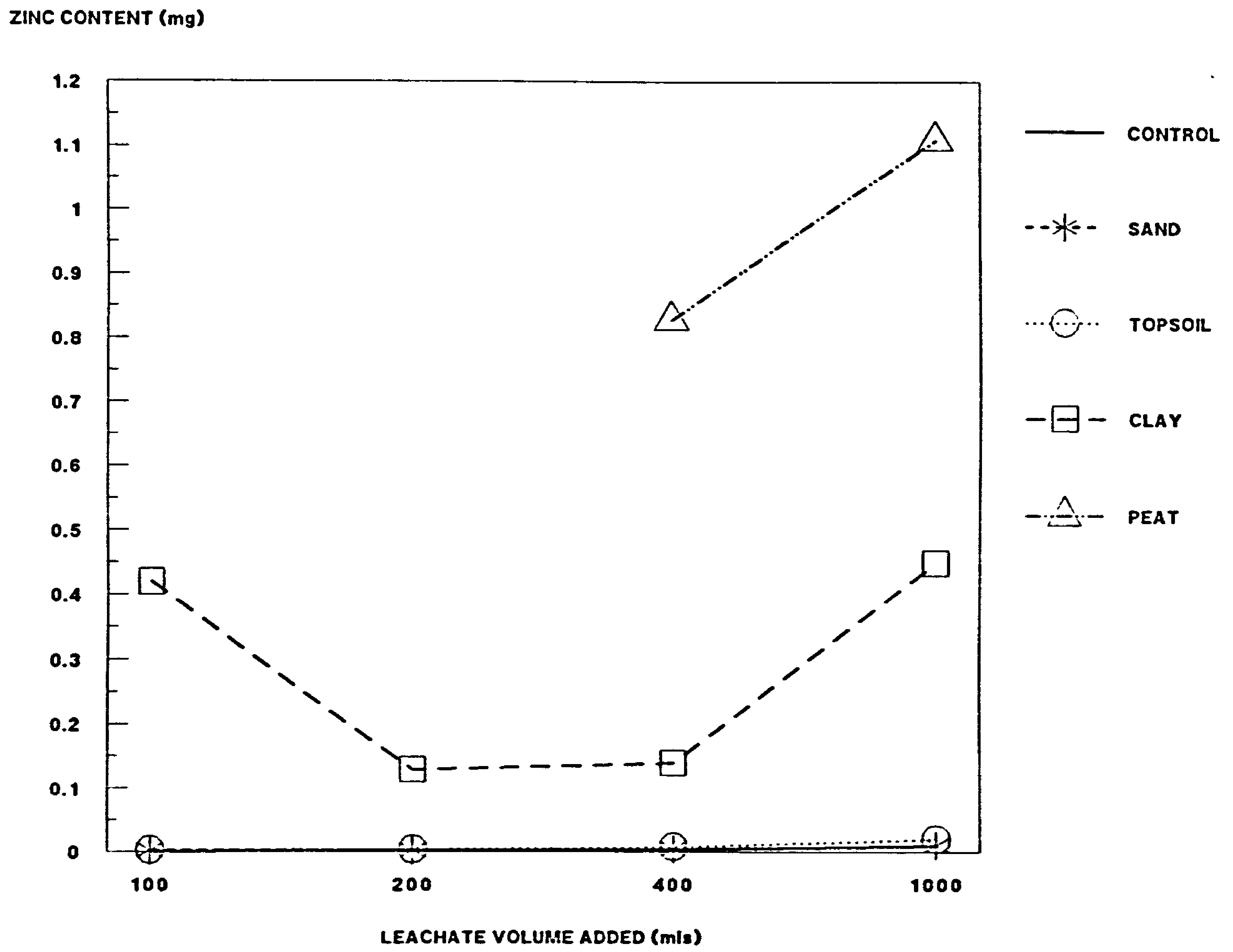


Figure 7.14 Zinc profile for sand, topsoil, clay and peat - Phase II.

clay and peat had detectable levels of these metals in solution after 24 hours of shaking. Topsoil also released some of these metals into solution. The leachate concentrations of the remaining metals after contact with the soils for 24 hours is given in Table 7.25.

The control leachate and the leachates in contact with sand and topsoil had non-detectable amounts of aluminium in solution after 24 hours of shaking. However, the clay and peat soils had detectable levels; peat released particularly high amounts of aluminium (7mg when 400 mls leachate was applied and 14mg when 1000 mls was applied). The release of aluminium from a clay soil may be an indication of a breakdown in the structure of the clay.

The control leachate and leachates in contact with sand and topsoil had either non-detectable or low levels of copper in solution. The amount released from the peat and clay soils was low, although the trend to release copper rather than adsorb copper should be noted.

All soils released manganese to some degree as illustrated by the fact that the added leachate contained no detectable manganese but the leachates in contact with soils contained detectable amounts of manganese at the end of the test period. The amount released from the sand and topsoil was relatively small. The amounts released from clay and peat were significantly higher and appear to increase as the amount of leachate added increases.

The amount of lead, chromium, cadmium and nickel released from the clay and peat is not high but it should be noted that the amount in the added leachate is non-detectable and at certain soil:leachate ratios with these soils the amount in the leachate becomes detectable.

TABLE 7.25 CONCENTRATION OF METALS AFTER 24 HOURS - PHASE II EXPERIMENT

All Results in mg/l.

SAMPLE	Al	Cu	Pb	Mn	Cr	Cd	Ni
CONTROL	<0.1	<0.02	<0.1	<0.02	<0.02	<0.01	<0.02
SAND (1:1)	<0.1	<0.02	<0.1	0.51	<0.02	<0.01	<0.02
SAND (1:2)	<0.1	<0.02	<0.1	0.33	<0.02	<0.01	<0.02
SAND (1:4)	<0.1	0.02	<0.1	0.19	<0.02	<0.01	<0.02
SAND (1:10)	<0.1	<0.02	<0.1	0.04	0.02	<0.01	0.04
TOPSOIL (1:1)	<0.1	0.03	<0.1	0.32	<0.02	<0.01	0.03
TOPSOIL (1:2)	<0.1	0.03	<0.1	0.11	0.02	<0.01	<0.02
TOPSOIL (1:4)	<0.1	0.03	<0.1	0.10	<0.02	<0.01	<0.02
TOPSOIL (1:10)	<0.1	0.03	<0.1	0.04	0.02	0.01	<0.02
CLAY (1:1)	6.6	0.25	0.2	16.4	<0.02	<0.01	0.13
CLAY (1:2)	0.1	0.04	<0.1	2.5	<0.02	<0.01	0.05
CLAY (1:4)	1.3	0.04	<0.1	2.7	0.02	<0.01	<0.02
CLAY (1:10)	0.2	0.07	0.1	3.10	0.02	<0.01	0.02
PEAT (1:4)	17.8	0.11	0.1	2.34	0.02	<0.01	0.12
PEAT (1:10)	14.0	0.17	<0.1	1.12	0.02	<0.01	0.08

7.4.3 Discussion

In the Phase II experiments the major cations involved in soil-leachate interaction were monitored as cation exchange was the principle mechanism being examined. In addition, testing of certain trace elements was also carried out. A summary of the relative values at all soil:leachate ratios for sand, topsoil, clay and peat is given in Table 7.26 to Table 7.29.

All leachates in contact with soils had a net increase in COD values, except when 100 mls was applied to the sand and clay. Sand adsorbed ammonia at all soil:leachate ratios, the rate of removal increasing as the volume of leachate applied increased. Topsoil adsorbed ammonia at all except the highest applied leachate volume. Clay and peat increased the amount of ammonia in the contacted leachate. Sand demonstrated adsorption of magnesium, sodium and potassium and increasing release of calcium as the volume of leachate applied increased. Topsoil demonstrated adsorption of magnesium, sodium and potassium and release of calcium, the amount released decreasing as the applied leachate volume increased. Clay adsorbed magnesium and sodium, but released calcium and potassium. The peat released calcium, magnesium, sodium and potassium. All soils tested demonstrated release of iron and zinc, with the amount released being greatest for the clay and peat soils. As previously stated these latter two soils also released trace metals in significant quantities.

Due to the positive charge of cations and the negatively charged soil complex, the cations are attracted to and may be retained on the surface of soil colloids. The rate of adsorption is dictated by both their concentration in solution and their relative intensity of attraction. Adsorbed cations are also liable to be exchanged at a later date if there is a shift in the cation concentration in solution. Thus, the

TABLE 7.26 SUMMARY OF RELATIVE VALUES FOR SAND AT ALL SOIL:LEACHATE RATIOS.

RATIO	CATION							
	COD	AMMONIA	CALCIUM	MAGNESIUM	SODIUM	POTASSIUM	IRON	ZINC
1 : 1	0.5	1.0	0.79	0.50	1.00	0.50	0.44	2.00
1 : 2	1.49	0.83	1.20	0.62	0.99	1.3	2.10	1.00
1 : 4	1.32	0.67	1.36	0.76	0.98	0.93	2.60	1.00
1 : 10	2.29	0	1.44	0.94	0.98	0.88	0.55	1.00

TABLE 7.27 SUMMARY OF RELATIVE VALUES FOR TOPSOIL AT ALL SOIL:LEACHATE RATIOS

RATIO	CATION							
	COD	AMMONIA	CALCIUM	MAGNESIUM	SODIUM	POTASSIUM	IRON	ZINC
1 : 1	0.5	0.26	2.10	0.45	0.79	0.29	1.11	3.0
1 : 2	2.06	0.72	2.20	0.50	0.87	0.45	1.30	2.0
1 : 4	1.45	0.25	1.81	0.61	0.94	0.60	3.00	2.0
1 : 10	1.86	15.80	1.50	0.83	0.97	0.78	5.40	2.0

TABLE 7.28 SUMMARY OF RELATIVE VALUES FOR CLAY AT ALL SOIL:LEACHATE RATIOS.

RATIO	CATION							
	COD	AMMONIA	CALCIUM	MAGNESIUM	SODIUM	POTASSIUM	IRON	ZINC
1 : 1	27.04	0.5	3.30	1.05	0.79	1.43	17.80	424.0
1 : 2	6.43	1.5	2.40	0.75	0.81	1.41	4.8	65.5
1 : 4	3.86	1.07	1.81	0.68	0.88	1.05	16.5	34.0
1 : 10	11.01	4.89	1.54	0.82	0.90	0.92	6.0	45.0

TABLE 7.29

SUMMARY OF RELATIVE VALUES FOR PEAT
AT ALL SOIL:LEACHATE RATIOS

RATIO	CATION							
	COD	AMMONIA	CALCIUM	MAGNESIUM	SODIUM	POTASSIUM	IRON	ZINC
1 : 4	20.3	7.47	2.12	3.35	1.15	2.11	122	207.5
1 : 10	40.8	2.67	1.23	1.97	0.99	1.59	36.7	111.0

introduction of a leachate with a high concentration of one or more cations in solution will displace other cations from the exchange complex. The results of these experiments illustrate that while some of the major cations in leachate may be adsorbed onto the soil complex, other cations are released into solution in exchange. This may lead to a resultant leachate which is equally as polluting as the original leachate.

In general, it could be said that those cations present in highest concentration in the added leachate in terms of meq/l (sodium and magnesium) are adsorbed from the leachate by all soils. Those cations present in highest concentration in the original soils are released into solution and the greater the original content of this cation on the soil then the greater will be the amount in solution. Thus, sand, topsoil and clay release calcium into solution since it is the major exchangeable cation in these soils and peat demonstrates greatest release of magnesium since this is the major exchangeable cation for this soil. Iron and zinc appear to be released from the soils to compensate for the adsorption of cations in all soils. In addition, the clay and peat soils appear to release other heavy metals to restore the charge balance in the soil. It is possible that the lower leachate pH obtained after contact with these soils will cause some dissolution of these metallic elements although no direct correlation between the pH and amount of metal in the leachate could be found. It is also possible that the organic content of the leachate accelerates the process of weathering in the clay and peat soils.

Carbonates and carbonate-containing minerals of both soils and geologic formations are readily susceptible to dissolution by acids. The increase in permeability is well known and when carbonates of Ca, Mg or Fe for example, form encrusting barriers in wells or excavations, organic acids have been used as solubilisation agents. The effects of acids on clay soils are considered to be largely associated with failure mechanisms due primarily to the solubilisation of the clay mineral with the release of the structural aluminium. Concurrent release of other clay mineral elements also occurs, resulting in porosity changes associated with the dissolution and altering effect on the exposed surfaces of soil pores and channels.

Landfill leachate contains a variety of soluble organic acids such as low-molecular aliphatic (e.g. citric, oxalic) and aromatic acids (e.g. vanillic, hydroxybenzoic), as well as fulvic acids with much higher molecular weights and containing both phenolic and carboxylic groups. These acids may considerably enhance mineral weathering and cause dissolution and migration of cations and heavy metals. Weathering of soils containing secondary minerals will lead to the solubilisation of ions such as Na, K, Ca and Mg, as well as heavy metals. If the soil is calcareous, dissolution of calcite may occur according to the reaction:-

$$CaCO_3 \ + \ H_2CO_3 \ \text{------------>} \ Ca^{2+} \ + \ 2HCO^{3-}$$

Clay and peat soils contain a wide variety of major and trace elements. After mixing with landfill leachate, these elements will be subject to both displacement from the soil colloid by competing ions and also to solubilisation if there is a lowering of pH. The high organic content of leachate may also produce an accelerated weathering affect which will in turn cause release of major cations and also of heavy metals. Sand is accepted as being relatively inert due to its high quartz content. However, it should be noted that quartz is highly resistant to dissolution. Therefore, sand irrigated with leachate may not have the inherent ability to reduce the cation concentration of the leachate, but at the same time sand will not increase the levels of cations in the added leachate.

In order to further investigate the release of metals by soils contacted with leachate the Phase III experiments were undertaken. In these studies a wider variety of soils were tested and leachate from a different landfill site was chosen.

7.5 PHASE III EXPERIMENTS

7.5.1 Experimental Design

The data reported previously has shown that soils with a relatively high initial metal content will release these metals into solution when they are contacted with leachate. This discovery of the effect of leachate on heavy metals in soils is particularly important in determining the effectiveness of land application as a method of leachate treatment and also in the use of clay as a lining material for landfill sites.

Accumulation of heavy metals in the soil or in the surrounding soil solution can affect the soil in several ways. Toxicity of these metals to microorganisms would reduce their ability to degrade organic compounds and ammonia in the leachate. The metals might also be toxic to future crops grown on the site. Uptake and accumulation of high concentrations of the metals in plant tissues could make the crop unsafe to feed to animals or humans, or animals feeding on the crop may become unsafe for humans to eat. Furthermore, if the metals are not immobilised in the soil or accumulated by crops, they may enter the groundwater system thereby posing a public health threat.

In order to verify that contact of leachates with certain soils causes an increase in the amount of metals in solution the Phase III experiments were conducted. This consisted of experiments using leachate obtained from a different landfill site and increasing the number of soils tested.

The experimental work was part of a preliminary study for a full-scale leachate treatment system to be installed at a landfill site on restoration. The system will involve a series of three stages through which the leachate will pass.

The initial stage involves passage through a plot of vegetated topsoil. The intermediate stage is passage through a sand bed filter or other soil as decided by the soil experiments. The final stage of the treatment is passage of the liquid through a reed bed system, the resulting effluent then being discharged subject to meeting discharge consent standards.

The soil studies were conducted in order to isolate the most appropriate soil for the intermediate stage of the full-scale treatment system. The proposed soil was a sand as this has been shown in the previous experiments to give the most effective treatment. The size of sand grains most suitable for treatment was open to question and for this reason the preliminary tests involved four different grades of sand. The sand types tested, listed in increasing particle size were as follows :- fine sand (diameter = 1.0 mm), coarse sand (diameter = 3 mm), small-stoned gravel (diameter = 10 mm) and large-stoned gravel (diameter = 20mm).

It also had to be established if one particular soil type would be more efficient for use in the soil bed system. Therefore two types of clay were obtained from the site; these clays to be used in the final capping of the landfill site. In addition, a topsoil being used as final cover over the clay cap was also selected for testing.

The seven different soils underwent a full metal analysis prior to contact with leachate and the results are shown in Table 7.30. The clay (1) soil has the highest metal content of all the soils tested; the sand and stones have lower metal contents than the clays and topsoil.

TABLE 7.30 METAL CONTENT OF ORIGINAL SOILS

SOIL	METAL CONTENT (mg/100g)							
	Cu	Zn	Pb	Cd	Ni	Mn	Fe	Cr
Coarse Sand	0.05	0.67	<0.02	0.009	0.52	1.99	663.6	0.22
Fine Sand	0.11	0.68	<0.02	0.009	0.39	2.30	682.1	0.31
Small Stones	0.09	0.52	<0.02	0.009	0.60	1.14	469.7	0.41
Large Stones	0.05	0.40	<0.02	0.009	0.43	1.38	416.2	0.09
Clay (1)	1.18	6.27	3.36	0.06	2.68	127.6	2769.6	2.18
Clay (2)	0.70	4.08	0.64	0.171	1.62	9.69	596.6	1.45
Topsoil	1.14	3.66	3.36	0.017	0.91	12.0	813.1	1.04

The leachate used in the experiments was obtained from the same landfill site as the soils and the chemical composition of this leachate as used in the experiments is given in Table 7.31. The leachate is characterized by a high ammonia content; typical of a landfill leachate which could normally be land applied.

All soils were air-dried for 24 hours; all soils, except the coarse sand and stones, were then passed through a 2 mm sieve. 100 grams of each soil was added to acid-washed, PVC containers. 400 mls of leachate was then added and a sealed lid put on each container to prevent air ingress. Each soil/leachate combination was carried out in duplicate. The containers were then inverted for several minutes to ensure thorough mixing of soil and leachate. Included in the experimental design were two containers containing 400 mls of leachate only in order to evaluate the effects of shaking on leachate constituents. Thus, metal removal by association with leachate particulates or due to the effects of aeration was not confused with metal removal by reaction with the soil.

The sixteen containers were then shaken for a total of 24 hours. Sub-samples of solution (40 mls) were taken from each container after a time period of 0.5 hours, 2 hours, 4 hours, 8 hours and a final sample at 24 hours. The solutions sampled were then analysed for the following metals :- iron, manganese, zinc, copper, lead, cadmium, nickel, and chromium. The pH and ammonia content of all solutions was also measured. The difference between the metal content in the sub-sample taken at each time interval and the amount of metal present in the control leachate sample at that time interval was taken as the amount of metal adsorbed or released by the soil. The metal content of the control leachate at each time interval is given in Appendix. The relative values were calculated as detailed in section 7.3.1.

TABLE 7.31 CHEMICAL COMPOSITION OF LEACHATE USED IN PHASE III EXPERIMENTS

CONSTITUENT	CONCENTRATION
pH	8.43
AMMONIA	252.0
IRON	5.71
MANGANESE	0.11
ZINC	0.03
COPPER	0.04
LEAD	0.67
NICKEL	0.07
CHROMIUM	0.19
CADMIUM	ND

ALL RESULTS IN mg/l EXCEPT pH

7.5.2 Results

7.5.2.1 pH

The pH levels with time for each leachate/soil combination are shown in Table 7.32. The initial pH of the added leachate was 8.43. The pH of leachate mixed with coarse sand, fine sand, small stones and large stones remained relatively constant and similar to the level of the initial leachate. The pH of leachate mixed with clay (1), clay (2) and topsoil was slightly less than that of the added leachate, although the difference was at no time greater than 0.5 pH units.

7.5.2.2 Ammonia

The control leachate demonstrated a gradual reduction in ammonia content with time from an initial value of 100 mg to a final value after 24 hours of 60.24 mg. This reduction may be due to the effects of aeration. The relative values for ammonia in leachate in contact with soils at a particular time are calculated in relation to the ammonia content in the control leachate at that time. This ensures that any change in the ammonia content in leachate in contact with soils is genuinely due to the presence of the soils and is not due to the effects of time or aeration. The relative values are given in Table 7.33.

The leachate in contact with coarse sand and fine sand had similar levels of ammonia to the control leachate during the experimental period; as did leachate in contact with small stones and large stones. The leachate in contact with topsoil, clay (1) and clay (2) had lower ammonia concentrations than the control leachate throughout the experimental period; the clay soils demonstrating highest adsorption of ammonia.

TABLE 7.32 AVERAGE pH VALUES -
PHASE III EXPERIMENTS

SAMPLE	TIME (HOURS)				
	0.5	2	4	8	24
Coarse Sand	8.45	8.48	8.50	8.44	8.42
Fine Sand	8.38	8.45	8.50	8.52	8.50
Small Stones	8.55	8.55	8.50	8.52	8.51
Large Stones	8.50	8.55	8.50	8.51	8.45
Clay (1)	7.95	8.00	7.90	8.00	8.13
Clay (2)	8.00	8.15	8.15	8.21	8.19
Topsoil	8.05	8.15	8.06	8.11	8.18

TABLE 7.33 AVERAGE RELATIVE VALUES FOR AMMONIUM - PHASE III

SAMPLE	TIME (HOURS)				
	0.5	2	4	8	24
Coarse Sand	0.99	1.19	1.02	0.96	0.99
Fine Sand	1.28	1.21	1.00	0.99	1.01
Small Stones	0.98	1.08	0.99	1.03	0.98
Large Stones	1.05	1.04	1.01	0.96	0.97
Clay (1)	0.81	0.63	0.59	0.51	0.53
Clay (2)	0.56	0.63	0.58	0.65	0.64
Topsoil	0.82	0.76	0.83	0.79	0.84

7.5.2.3 Iron

There was a gradual reduction in the iron concentration of the control leachate samples with time. This could be due to oxidation of iron as a result of shaking or due to precipitation of iron with other constituents of leachate. The calculation of relative values compensates for this reduction in iron that occurs on aeration of leachate (Table 7.34).

After 30 minutes all soils, except the coarse sand, showed adsorption of iron. The clays performed particularly well, having relative values less than 0.05. After 2 hours the leachates mixed with the clays and topsoil continued to show a loss of iron from solution. The sands and stones were performing less well and showed an increase in the amount of iron in solution. Between 2 and 8 hours the results followed this general trend i.e. the clays and topsoil showing substantial adsorption while the sand and stones showed some release of iron to solution.

After 8 hours the situation appeared to change with the leachate in contact with clay (1) soil being the only soil to show a reduction of iron from solution. The remaining leachate/soil combinations had relative values greater than 1.0, with particularly high values for the clay (2) soil and topsoil. The results after 24 hours would seem to suggest that while the iron may be adsorbed onto the soil exchange complex almost instantaneously, it is not permanently adsorbed and can be released back into solution.

7.5.2.4 Manganese

The calculated relative values for manganese are given in Table 7.35. After 30 minutes of shaking all soils, except the clay (2), gave

TABLE 7.34 AVERAGE RELATIVE VALUES FOR IRON - PHASE III

SAMPLE	TIME (HOURS)				
	0.5	2	4	8	24
Coarse Sand	1.16	1.73	1.52	0.88	2.5
Fine Sand	0.73	1.50	1.72	1.45	2.6
Small Stones	0.89	1.13	1.04	1.00	1.02
Large Stones	0.92	0.98	0.98	1.26	2.56
Clay (1)	0.04	0.03	0.03	0.05	0.04
Clay (2)	0.03	0.08	0.42	2.98	4.33
Topsoil	0.22	0.27	0.08	0.09	4.92

TABLE 7.35 AVERAGE RELATIVE VALUES FOR MANGANESE - PHASE III

SAMPLE	TIME (HOURS)				
	0.5	2	4	8	24
Coarse Sand	0.26	0.24	0.20	0.22	0.18
Fine Sand	0.15	0.75	0.25	0.12	0.46
Small Stones	0.6	0.87	0.43	0.38	0.13
Large Stones	0.71	0.70	0.02	1.00	0.33
Clay (1)	0.15	0.54	0.30	1.22	1.69
Clay (2)	14.92	15.12	9.86	6.16	8.28
Topsoil	0.38	0.57	0.42	0.60	3.14

substantial adsorption of manganese from leachate. The clay (2) soil showed a large increase in the amount of manganese in solution which is reflected in the relative value of approximately 15.

The coarse sand followed a pattern of high removal over the 24 hour period; as did the fine sand, small stones and large stones. Topsoil adsorbed manganese during the first 8 hours, but had 3 times the manganese content of the control leachate at the end of 24 hours.

Throughout the experimental period the clay (2) soil released manganese to solution, although a peak initial release of 0.7 mg decreased to 0.3 mg after 24 hours. The leachate in contact with clay (1) soil also had higher manganese concentrations than those of the control leachate from 8 hours onwards.

Therefore, the clay (1), clay (2) and topsoil appear to be releasing manganese whereas the sand and stones are adsorbing manganese.

7.5.2.5 Zinc

The zinc concentration of the control leachate appears to increase after 30 minutes of shaking to approximately three times the amount in the leachate prior to shaking (Appendix B). This phenomena of an increase in zinc concentration in a leachate after aeration was also noted by Fuller et al. (1979). A possible cause of this is that zinc bound to organic compounds in the leachate prior to shaking is released during the shaking process. The calculated relative values for zinc are given in Table 7.36.

At the end of 24 hours, leachates in contact with both coarse sand and fine sand had substantially lower zinc concentrations than the control leachate. The large stones released zinc throughout the experimental

TABLE 7.36 AVERAGE RELATIVE VALUES FOR ZINC - PHASE III

SAMPLE	TIME (HOURS)				
	0.5	2	4	8	24
Coarse Sand	0.84	1.77	1.83	0.56	0.36
Fine Sand	0.21	1.83	1.70	0.96	0.49
Small Stones	0.11	2.5	0.73	1.41	0.92
Large Stones	1.13	3.88	1.82	1.72	2.46
Clay (1)	0.23	2.03	1.13	0.6	0.82
Clay (2)	0.28	1.12	1.58	2.26	1.9
Topsoil	0.86	2.41	0.98	0.96	3.16

period. The small stones released zinc at 2 hours and 8 hours, although the final zinc solution concentration was slightly less than that of the control.

Both clay soils initially adsorbed zinc during the first 2 hours of shaking. From 2 hours onwards the clay (2) soil released increasing amounts of zinc to solution; after 24 hours there was a zinc concentration of twice that of the control leachate. The clay (1) soil released zinc at 2 hours and 4 hours but from that time onwards had lower zinc concentrations than that of the control leachate.

The topsoil appears to remove zinc from solution at 0.5, 4 and 8 hours, although at the end of the experimental period there is three times the zinc in solution as compared to the control leachate.

7.5.2.6 Copper

The copper concentration of the control leachate decreased with time to a minimum value after 24 hours of shaking. This could be due to the effects of aeration or due to the precipitation of copper with other leachate constituents. The calculated relative values are given in Table 7.37.

The leachate in contact with coarse sand and fine sand had higher copper contents than the control leachate at all time intervals. The large stones also appeared to increase the concentration of copper in leachate throughout the experimental period. The small stones adsorbed copper during the first four hours of shaking but thereafter had higher levels of copper in solution than the control leachate.

TABLE 7.37 AVERAGE RELATIVE VALUES FOR COPPER - PHASE III

SAMPLE	TIME (HOURS)				
	0.5	2	4	8	24
Coarse Sand	2.84	1.80	1.77	3.10	8.22
Fine Sand	1.53	1.45	1.64	3.10	6.56
Small Stones	1.0	0.54	0.74	1.52	5.44
Large Stones	3.10	1.22	1.90	4.15	13.19
Clay (1)	4.68	1.91	3.55	6.0	12.60
Clay (2)	0.73	0.10	0.74	2.32	2.11
Topsoil	2.84	1.45	2.66	4.42	9.89

The clay (1) soil appears to release large amounts of copper and the leachate in contact with this soil had a higher copper content than that of the control leachate throughout the experimental period. The clay (2) soil had some initial adsorption of copper but from 8 hours onwards there was release of copper into solution.

The leachate mixed with topsoil had relative values greater than one throughout the experimental period. The relative values increased with time to a final value of 9.89 after 24 hours.

Poor binding of copper may be because of pH effects, cation competition and complexation with organic compounds. The pH of all samples after 24 hours was greater than 8.0, therefore it is unlikely that pH is causing the solubilisation of copper. It is more probable that since copper is low in the added leachate relative to the other heavy metals, that cations present in stronger concentration are more able to attach to binding sites on the soils. As these cations are taken up by the soil, release of other metals to compensate takes place. This may be a reason for copper increase in solution. The possible association of copper with soluble organics, which would thereby reduce the effective concentration of copper available for soil binding, cannot be ruled out. The organically associated copper would be included in the analytical determination of copper by atomic adsorption spectroscopy.

7.5.2.7 Chromium

The chromium concentration of the leachate control sample showed a gradual reduction with time from an initial content of 0.07 mg chromium to a content after 24 hours of shaking of 0.03 mg. Chromium readily precipitates with carbonates, hydroxides and sulphides at pH greater than 6.0. Removal could also be due to complexation with organic matter or oxidation to chromate ($Cr_2O_4^{2-}$) or dichromate due to aeration during shaking. The calculated relative values for chromium are given in Table 7.38.

Leachates in contact with coarse sand, fine sand, small stones and large stones closely followed the pattern of the control leachate for the amount of chromium in solution at any time.

The clay (1) soil appeared to adsorb chromium from solution throughout the experimental period, as reflected in relative values less than 1.0. The leachate in contact with clay (2) had lower chromium levels in solution than the control leachate, except at eight hours when there appeared to be a relatively large release of chromium to solution. Leachate in contact with topsoil largely followed the pattern of the control leachate, except at 8 hours when there was a release of chromium to solution.

7.5.2.8 Lead

The lead concentration of the control leachate declined with time from an initial lead concentration of 0.268 mg Pb/l to a final solution concentration of 0.041 mg Pb/l after 24 hours. This would suggest that lead is being lost from solution due to oxidation or precipitation with other leachate constituents. The calculated relative values for lead are given in Table 7.39.

After 30 minutes of shaking all soils had adsorbed lead from the added leachate. The fine sand and clay (1) soils gave particularly high adsorption of lead. After 2 hours of shaking, however, all leachates in contact with soil had an increase in the amount of lead in solution. The clay (2) soil was the only soil to adsorb lead at this time interval. The values at 2 hours appear to be peak releases, as the samples taken

TABLE 7.38 AVERAGE RELATIVE VALUES FOR CHROMIUM - PHASE III

SAMPLE	TIME (HOURS)				
	0.5	2	4	8	24
Coarse Sand	1.08	1.24	1.00	1.00	0.99
Fine Sand	1.16	1.67	0.92	1.20	0.91
Small Stones	1.07	1.25	1.00	1.31	0.90
Large Stones	1.33	0.82	1.24	1.10	0.99
Clay (1)	0.90	0.73	0.84	1.00	0.82
Clay (2)	0.82	0.73	0.68	2.15	0.73
Topsoil	0.90	0.90	1.0	1.42	0.99

TABLE 7.39 AVERAGE RELATIVE VALUES FOR LEAD - PHASE III

SAMPLE	TIME (HOURS)				
	0.5	2	4	8	24
Coarse Sand	0.45	7.32	0.88	0.79	1.78
Fine Sand	0.08	3.87	0.43	2.62	1.72
Small Stones	0.36	1.0	1.23	1.38	0
Large Stones	0.46	3.3	0.21	1.38	3.18
Clay (1)	0.08	2.14	0.21	0.97	0.31
Clay (2)	0.17	0.5	0.10	1.41	0
Topsoil	0.91	2.8	0.78	0.77	2.81

at 4 hours show a decline in lead in solution for all soils except the small stones. All soils, except the small stones were now adsorbing lead from solution.

The lead levels from four hours onwards are erratic. The final relative values at 24 hours seem to indicate that the small stones and the clay (2) samples had adsorbed all the lead in the added leachate. The final relative value for the clay (1) soil also indicates that removal of lead from leachate is taking place. The leachates in contact with the other soils had a net increase in the amount of lead in solution. From the final relative values the order of release would appear to be large stones > topsoil > coarse sand > soft sand.

7.5.2.9 Nickel

The control leachate sample showed an initial increase in the amount of nickel in solution to 0.075 mg which then gradually declined to a minimum of 0.02 mg in the sample taken at 24 hours. This reduction could be due to oxidation or to precipitation e.g. nickel carbonate and/or nickel sulphide. The relative values will compensate for this loss of nickel from solution due to shaking. The relative values are given in Table 7.40.

After 30 minutes of shaking all soils had shown adsorption of nickel. After 2 hours the situation had changed in that all soils showed an increase in the amount of nickel in solution with relative values greater than one. The clay (2) samples had particularly high relative values followed by the clay (1) samples; these two soils had the highest initial nickel content.

TABLE 7.40 AVERAGE RELATIVE VALUES FOR NICKEL

SAMPLE	TIME (HOURS)				
	0.5	2	4	8	24
Coarse Sand	0.78	1.06	1.98	1.48	2.09
Fine Sand	0.45	1.37	1.13	1.73	1.61
Small Stones	0.95	1.16	1.11	1.48	1.24
Large Stones	0.23	1.57	1.24	1.36	1.73
Clay (1)	0.72	1.78	1.60	1.73	2.09
Clay (2)	0.72	2.50	1.36	1.73	1.36
Topsoil	0.45	1.16	1.98	1.24	0.88

Throughout the experimental period all soils, except topsoil samples at 24 hours, had relative values greater than 1.0, indicating a greater nickel concentration in leachate in contact with soils as opposed to the control leachate. The coarse sand and clay (1) samples had the highest relative values, followed by large stones, fine sand, clay (2), small stones and topsoil giving the lowest nickel solution concentration after 24 hours.

7.5.2.10 Cadmium

No cadmium was detected in either the added leachate or the leachates in contact with soils at any time interval.

7.5.3 Discussion

Ammonia was the major cation present in the leachate used in the Phase III experiments. All soils tested demonstrated adsorption of ammonia from the leachate. The greatest rate of adsorption was observed with the two clay soils and the topsoil. However, the two clay soils appear to be releasing iron, manganese, copper, nickel and zinc to compensate for this adsorption of ammonia. The topsoil released iron, manganese, zinc, copper and lead to the added leachate. These soils had the highest initial metal content (Table 7.30). The sand and stones had only slight adsorption of ammonia. However, they also released lower levels of iron and copper and adsorbed manganese, zinc and chromium. These soils had a low initial metal content.

The Phase III experiments have demonstrated that soils will release metals in order to compensate for the adsorption of the major cations in leachate. Generally, metals are seldom present in landfill leachate at the levels of other cations (e.g. calcium, ammonium). Therefore, it seems likely that this release of metals is a phenomenon that would normally occur with soils which have an inherent metal content.

The results from the Phase I, Phase II and Phase III studies of soil-leachate interactions have questioned the whole concept of leachate renovating power of soil, especially clay and peat which are often assumed to be the most efficient renovating soils. The assumption that soils have unlimited adsorption capacity, or even any adsorbing power in certain cases, should no longer be accepted without qualification. The disposal of leachates on land will subject the environment to two sources of potential pollutants, namely, those originally present in the leachate and those which may be leached from the soil. It is recognised that under alkaline conditions or with simple metal solutions clay and peat soils have the ability to retain metals due to their higher cation exchange capacity. However, these soils may fail to attenuate the pollutants in leachate in the presence of a high soluble salt level and/or low pH.

CHAPTER 8 DISCUSSION

8.1 INTRODUCTION

This study of the interaction between landfill leachate and soil was experimental in nature. The purposes of this investigation were:

1. To ascertain if significant interaction between leachate and soil actually occurs. 2. Providing interaction occurs, to observe and note the types of alterations; to identify the active mechanisms responsible for the various alterations and determine their relative influence; to examine the relationships among the soil type (especially the clay mineral fraction), the relative masses of soil and solution, the contact time and soil-leachate interactions and to develop criteria to qualitatively and quantitatively predict interactions between the selected soil-leachate combinations.

Four soils were analysed and classified as to mineralogical content, soil particle size, chemical composition and cation exchange characteristics. The soils chosen for testing were thought to give a good representation of the wide range of soil types. Sand was chosen to represent a soil normally regarded as inert. Clay and peat represented soils which are commonly regarded as reactive due to their cation exchange capacity; clay due to the mineral content and peat due to the organic content. Topsoil was chosen to represent a typical surface soil.

Field leachates were obtained from a local domestic waste landfill each week and analysed for selected parameters. Interactions between leachates and soils were assessed by comparing the chemical composition of samples from leachates that had been contacted with soils to those that had not been contacted (control samples). The alterations in leachate resulting from soil contact were recorded for both fixed-bed column and batch tests. The relative degree of interaction was assessed by measuring concentration changes in the leachates that occurred after contact with soil. In addition, studies of the effect of filtration and biological activity on the renovation of landfill leachate were undertaken.

When dealing with materials as variable and complex as soil, it is difficult to accurately identify the solid phase prior to contact. Owing to the large number and variety of concentrations of leachate constituents, it is considerably more difficult to quantitatively establish the results of interaction and assign alteration values to responsible mechanisms. However, this investigation did reveal the following: (1) interaction does occur, but this interaction is not unlimited; (2) the degree of interaction is different for different soil types; (3) the relative influence of the mechanisms of interaction; (4) the influence of soil types, soil to solution ratios, and contact times; and (5) soils previously thought to attenuate leachate have been found not to do so.

The first question to be asked is whether or not leachate alterations occur after contact with soil. Leachate concentrations were altered as a result of contact with soil. These alterations were observed in both column tests and batch tests. Whether a particular leachate constituent concentration decreased or increased, and the extent of this decrease or increase was dependent on the soil type under consideration.

8.2 RESULTS AND CAUSES OF ALTERATIONS IN LEACHATE CONCENTRATIONS

In the initial samples of effluent collected from the soil columns (Chapter 4), the concentration of all parameters measured were reduced with the exception of hydrogen ion concentrations. However, a fraction of this general reduction in species concentrations may partially be attributed to dilution and dispersion that resulted from the distilled water added initially to allow the soil to reach saturation capacity. Analysis of soil column effluents after sufficient amounts of effluent had passed through the soil columns, and tests performed on samples taken from the batch tests, indicated that other more specific mechanisms than dilution-dispersion had altered the leachate.

Analyses of the soil-leachate column and batch experiments revealed several trends. Sand and topsoil gave greater removal of ammonia and organic material in the soil columns than did the clay and peat. Clay and peat also demonstrated lower removal of leachate constituents than sand and topsoil in the batch tests. In addition, leachate in contact with clay and peat soils in the batch tests showed an increase in the concentration of certain cations.

Observation of the soil column effluent samples also revealed that soils, with the exception of sand, exhibited limited removal capability for suspended matter, colour, ammonia and organic matter. The limitations of these removal capabilities were evidenced by reduced concentration changes in these parameters as the volume leachate passed through the column increased.

Batch experiments also revealed alterations in leachate significantly different for each soil type. Tests with the sand mixture exhibited the least variations from those observed in tests on the control sample. Generally the concentration changes (including pH) resulting from contact with the sand and topsoil were similar in that there was a net reduction in the amount of cations in solution. Interaction with the clay and peat soils resulted in a net increase in the amount of cations in solution. In particular, the finding that these latter two soils release metals into solution after contact with leachate was unexpected.

Leachate concentrations of those cations that were dominant on the soils before contact were found to have an increased concentration in the leachate after contact with the soils. On the other hand, generally, it was found that the concentrations of those cations in the leachate that were relatively high prior to contact with the soil were reduced after contact with the soil.

Conducting batch experiments with a constant soil to solution ratio provided the opportunity to observe the effect of contact time on soil-leachate interactions. These experiments revealed that, generally, longer contact periods produced greater alterations in leachate. Longer contact times generally led to a release of a particular cation into solution despite an initial adsorption.

In order to evaluate the effect of increasing the amount of cations applied to the soil system, the volume of leachate added in the Phase II and Phase III experiments was varied while the amount of soil was kept constant. In almost all experiments conducted, the greater the soil to solution ratio, the greater the concentration changes in the leachate.

It is difficult to identify the mechanisms that are active in leachate interaction. However, the literature review and the analyses of these experiments indicate that the following mechanisms may contribute to concentration changes in refuse leachate caused by contact with soil: 1. Dilution-dispersion 2. Filtration 3. Adsorption-bioadsorption 4. Cation exchange 5. Oxidation 6. Precipitation 7. Evolution of gases 8. Complexation.

1. **Dilution-dispersion.** Although dilution-dispersion is a part of geologic soil-rock-groundwater systems, it is not a mechanism considered to be of major importance with respect to the chemical alteration or attenuation of leachate constituents. Dilution is not a mechanism by which leachate constituents are

chemically altered or attenuated by the soil. However, it may reduce the concentration of leachate constituents.

2. **Filtration.** It is difficult to estimate the percentage of attenuation through filtration for any parameter. Howver, this will be an operative mechanism whenever chemical precipitation, biological growth and other processes produce undissolved solid particles. The effect of this mechanism may be to retard the movement of suspended matter, as well as some dissolved organic matter through the bio-layer. Reduction of the suspended matter would directly affect the measured concentrations of other species, such as BOD and COD.

The results of the filtration experiments in Chapter 5 demonstrated that there is little attenuation of inorganic species by filtration. There was some removal of suspended solids and a high correlation was found between the measured COD of the leachate and the concentration of suspended solids. With regard to the column tests, it seems reasonable that compacted soil columns would form filters (similar to those used in water filtration plants) that would be effective in removing suspended matter. The build-up of organic matter in the upper layer of the soil column may have formed a bio-filter similar to bacteria covered medias utilised in trickling filters in wastewater treatment plants.

3. **Adsorption.** Adsorption is the process of adhesion by molecules onto the surface of individual soil particles. Due to the difficulty in distinguishing adsorption from exchange reactions experimentally, the process is sometimes referred to as adsorption-exchange reactions. The basic difference between adsorption and exchange reactions, however, is that adsorption will cause a

lowering of the total dissolved solids (TDS) in the leachate whereas exchange reactions will not lower TDS in the leachate. Adsorption, therefore, will attenate leachate whereas exchange reactions will simply change the type of ions present in the leachate.

The results in Chapter 7 indicate that a wide range of leachate parameters increased in concentration after contact with clay, peat and to a lesser extent topsoil. Therefore, there has not been attenuation of leachate by these soils but only a 'reshuffling' of cations. As a result, the major mechanism acting on cations is thought to be exchange reactions and only limited adsorption is thought to have occurred. The batch tests performed on sand are believed to indicate the species removal by adsorption since the cation exchange capacity of sand is low. Therefore, any change in cation concentrations in leachate in contact with sand may be as a result of adsorption.

4. **Cation Exchange**. Cation exchange, by definition, means that for every cation absorbed by the soil an equivalent cation must be released by the soil. Cation exchange was the mechanism of primary concern in the batch experiments, and it proved to be responsible for an appreciable fraction of the alterations observed. Although considered by many as a mechanism in the soil with available renovating power, the results of these experiments show that when a high ionic strength solution such as landfill leachate is tested, the resultant reshuffling of cations leads to the release of certain elements from the soil which may have a deleterious effect e.g. metals.

The ease of replacement of cations depends on ion size, valence, and mass action. As far as cation exchange in landfill leachate is concerned, the well-known 'replaceability series' ($Na^+ < Li^+ < K^+ < Rb^+ < Cs^+ < Mg^{2+} < Ca^{2+} < Ba^{2+} < Cu^{2+} < Al^{3+} < Fe^{3+} < Th^{4+}$) is of little help because it appears that most exchange occurs by mass action. In mass action, a cation of higher replacing power is replaced in the soil by a cation of lower replacing power because of a higher concentration of the lower replacing power cations in the leachate. The batch experiments showed that although soils adsorb some of the major cations from leachates e.g. sodium, calcium, magnesium, ammonium, other cations which are more polluting may be released in exchange e.g. metals. This has previously been undiscovered in soils such as clays and peats.

The reason that this has not been detected in previous research is thought to be due to the tendency of researchers to monitor only a small number of cations when investigating soil-cation reactions. Therefore, they may have noted a concentration change in the metals being considered but have not noticed an increase in concentration of other elements which are being released into solution to compensate for the adsorption.

In addition, the solutions used in most soil-cation investigations contain only a small number of cations. Therefore, the results from soil-cation investigations using low ionic strength solutions (which have found clay and peat soils to be good adsorbers of cations) are of no value when evaluating the effect of a soil on leachate renovation. Landfill leachate will contain a large range of cations at varying concentrations. This will place stress on the soil to release cations from exchange sites in order to 'make way' for those which are present in the leachate in high concentration. Leachates normally have a relatively low metal concentration so that metal cations may be released from the soil to the leachate by the laws of mass action.

Since the concentration of cations will vary tremoundously between leachates from different landfill sites and within the same site over a period of time, this makes predictions of the renovating power of certain soils for leachate extremely difficult.

Actual breakdown of the soil minerals could also be a source of soluble calcium in the leachate and also the increase in certain other metallic elements. Similar breakdown of mineral structure also could be attributed to the increases in hydrogen ion concentration observed after leachate contact with the clay and peat soils. If sufficient breakdown had occurred soils such as clay may have provided appreciable quantities of calcium, hydrogen and metallic elements.

5. Oxidation. With regard to cation removal, it is believed that the influence of oxidation was second only to cation exchange. Oxygen was available to leachate passing through the soil columns and to a lesser extent to the leachate in the batch tests. In the former, air was most likely trapped initially in void spaces in the soil and the column systems could be resupplied with air to some extent, especially during the earliest part of the column experiments (weeks 1 to 5) when columns underwent saturated-unsaturated cycles. The batch vessel systems were closed to exclude air from the vessels; however, there is little doubt that air was entrapped within the unsaturated soil mass, and this air provided oxygen for oxidation reactions. The extent of oxidation reactions would not be as great in the control leachate because the control samples were kept in closed vessels with no soil masses to introduce air.

6. Precipitation. Chemical precipitation involves a phase change in which dissolved chemical species are crystallized and deposited from solution because their total concentration exceeds their solubility limit. The solubility limits depend on factors such as ionic species

and their concentration, temperature, pH, redox potential, concentration of dissolved substances, and solvent. Of these, pH and redox potential are the most important.

Precipitates of metals formed with hydroxides, carbonates, sulphates or phosphates could coagulate with suspended organic matter and then settle, be filtered out, or be bio-physically adsorbed. This mechanism is by no means independent and would depend on the respective species and the environment and on mechanisms such as filtration, settling or adsorption to prevent these precipitates from remaining in the leachate after contact.

7. Evolution of gas. If either ammonia or carbon dioxide had been dissolved or evolved as gases the net concentrations of NH_3 or pH, respectively, would have been altered. However, the pH conditions during the test were such that ammonia would have been predominantly in the NH_4^+ form rather than in the NH_3 form. As for carbon dioxide it is very doubtful that this gas would have been adsorbed or released during the short-term, closed-environment batch tests although the release of CO_2 gas from the column effluents and the control could be a source of the gradual, long term increase in pH in the soil column studies. Generally it can be summarised that this mechanism was considered to have no appreciable effect on the alterations observed as a result of soil-leachate interaction.

8. Complexation The effect of reactions such as the chelation of iron by organic material cannot be accurately determined. However, unless such complexes formed settleable or readily adsorbable complexes, complexes would remain in suspension and would not be recorded as concentration alterations from those of the control. Therefore, although the effect of this mechanism could not be determined directly, its effect is not believed to be significant.

Of the eight mechanisms discussed, dilution-dispersion is not considered a direct mechanism of the soil but rather a property of the groundwater system. With regard to the removal of the organic fraction of the leachate, filtration and bioadsorption are believed to be the most significant mechanisms. In soils with a significant cation exchange capacity, cation exchange is responsible for the majority of concentration alterations in the inorganic fraction. These changes, however, do not necessarily produce a resultant leachate which has a lower total dissolved solids. In certain cases the cations released in exchange reactions may be potentially more harmful than the original leachate components. Oxidation and formation of hydroxides followed by filtration and/or precipitation are the next most significant mechanisms altering concentrations of the inorganic fraction of leachate, and these mechanisms would be most significant in soils with very low cation exchange capacities. With the exception of special cases or rare circumstances the effects of the other mechanisms would be minor.

8.3 RECOMMENDATIONS AND PROJECTIONS FOR FUTURE RESEARCH

Burial of solid wastes in the ground is still a viable option for much of our solid waste materials. Sensitivity of society to uncontrolled ocean and land surface dumping is keen, and legislation prohibiting such operations is continually being written into more restrictive language. In addition, land is becoming a valuable commodity and preservation of the environment for future generations is of the utmost importance. The demand for acceptable burial techniques and methods, therefore, must remain as one of our top waste disposal priorities.

The lagging in the development of better burial techniques and landfill site operations has not been due as much to indifference by communities or industries as to lack of knowledge of the complex physical and biological systems involved. These include:-

1. Soil-waste reactions (chemical, physical and biological) under both controlled and natural conditions.

2. Migration rates of specific pollutants (e.g. heavy metals, organic compounds and organic solvents) through the complex porous medium.

3. Loading or concentration factors.

4. The host of highly different potential pollutants in a single waste stream.

5. The way one constituent affects another with respect to attenuation or retention in soils.

The multitude of reactions that are operative when contaminants in leachate are put on or into the soil can be theoretically identified. However, due to the highly complex leachate/soil interactions, no leachate migration model exists that can simulate all of the physical, chemical and biological processes occurring in a typical landfill system. Since environmental conditions differ from one climatic region to another and even within a single region, no two disposal sites will be the same. Similarly, solid wastes vary from community to community and no two leachate streams will be identical.

This research does not attempt to fully explain the reactions occurring in the leachate/soil system. What has been shown is that the common assumptions of soil removal of leachate pollutants, in particular metals, may not be correct. It is suggested that immediate research is needed into clay-leachate interactions as clay is commonly accepted as an ideal material for use in landfill. In particular, the effect of acidic leachate in relation to the solubilisation of metals should be investigated. The research has highlighted some of the areas where data is not yet available for landfill or where data derived by external bodies is inappropriately used for landfill e.g. adsorption isotherms for simple metal solutions. The assumption that soils have unlimited renovating power, or even any renovating power in certain cases, should no longer be accepted without qualification. It is envisaged that this three year project will be part of a continuing effort to obtain a better understanding of landfill hydrology, leachate quality and leachate interactions.

Two testing procedures were developed as part of this research and were found to be useful in evaluating leachate - soil interactions. Soil columns allow leachate to percolate down slowly through the soil and hence there is longer time for the exchange reactions and adsorption to take place. In addition the use of soil columns is more suited to the study of organic compound removal from leachate by soils. No conceivable batch incubation experiment could provide soluble COD reduction data truly representative of conditions in a soil column. Over a series of irrigation cycles, a distinctive population of micro-organsisms will become attached to the soil particulate matter. Further modifications to this soil column technique would have been undertaken had time allowed and it is suggested that this is an area for future research. Development would include use of both aerobic and anaerobic soil columns, study of a wider range of soil types and investigation of the rate of cation and heavy metal movement through the soil.

The'use of field lysimeters would also fulfil a great number of objectives relating to soil water movement, salt and plant nutrient transport in soil, biodegradation assessments, and element transformations. Their position in waste disposal has been rather limited mainly because of cost disadvantages over other simpler field methods. However, there are advantages where highly toxic substances require more realistic testing than is possible in the laboratory and strict confinement of leachates, solvents and solutions are required which are often unsuited for "open" field exploration. They enable verification of laboratory and controlled-environment plot results and identification of field-oriented problems not detectable in the laboratory.

The batch tests were found to be useful for determining alterations to the inorganic fraction of leachate. This type of test is flexible and can be performed in a relatively short time. The use of this type of test is suggested as a preliminary method to determine the alterations between any leachate-soil mixture and also to gain information useful in developing an extensive testing programme. The method will allow rapid identification (24 hours) of soils unsuitable for use in landfill either because of a lack of attenuation capacity and/or release of undesirable substances from the soil to leachate.

A further development of these batch tests would be the use of soil thin-layer chromatography. This is a variation of the conventional thin-layer chromatology. The difference is in the composition of the stationary phase; soil is used in place of such better-known materials as alumina, silica gel, resins and cellulose. A disadvantage, however, is that flow is rapid, minimizing the adsorption-desorption kinetic effects and contact between leachate and soil is maximised so that it most closely simulates intra aggregate flow and negates the attenuating effects of soil aggregation.

The analysis of organic matter in this study was made under the general nature of the COD test. It is suggested that research should be directed toward the actual composition of the organic compounds in leachate. In particular their character, relative interaction with soil, and the relative influence of the active mechanisms should be investigated.

The final recommendation is concerned with the concept of "engineered landfills". There is presently a move towards leachate collection and treatment in many situations. In order to prevent migration of leachate, landfills are commonly lined with bentonite, asphalt, or rubber/synthetic liners. Use of these liners to enable landfill leachate collection has been initiated relatively recently. The durability and resistance of these materials to leachate and possible character change of these materials should be investigated in long range experiments. As an example of possible material alterations, consider how a clay bentonite lining (composed primarily of montmorillonite) might withstand a low pH, high ionic strength leachate.

To conclude, it is believed that the information from this study provides a foundation of knowledge and guidance as to the most productive avenues of future research. In addition, it has provided disturbing information as to the quality of certain soils to attenuate leachate constituents.

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2

CONCENTRATION OF CONSTITUENTS IN THE CONTROL LEACHATE USED IN THE PHASE III EXPERIMENTS

Time (Hours)	CONSTITUENT									
	pH	NH_4^+	Fe	Mn	Zn	Cu	Cr	Pb	Ni	Cd
0	8.43	100.8	2.28	0.046	0.01	0.015	0.075	0.269	0.03	ND
0.5	8.50	86.0	2.14	0.046	0.025	0.015	0.059	0.219	0.068	ND
2.0	8.53	53.6	1.95	0.027	0.006	0.031	0.053	0.039	0.03	ND
4.0	8.55	67.8	1.78	0.056	0.011	0.025	0.052	0.175	0.03	ND
8.0	8.58	57.7	1.52	0.041	0.012	0.025	0.034	0.171	0.022	ND
24.0	8.51	60.2	1.17	0.037	0.014	0.004	0.035	0.041	0.02	ND

All results in mg except pH.