AN INCUBATION STUDY TO ASSESS THE EFFECT OF WASTE SLUDGE ADDITIONS ON SOME CHEMICAL CHARACTERISTICS OF MINE SPOILS

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ABSTRACT

In 1985 a study undertaken by the New Zealand Soil Bureau identified a major shortfall in topsoils for mining rehabilitation works and the use of surrogate materials to overcome this shortfall was postulated (Wills, 1992). The Resource Management Act 1991 places constraints on the disposal of wastes and may act as a catalyst for research into the beneficial utilisation of once waste products for land rehabilitation.

The most common problem reclaiming of derelict and degraded land is a shortage of organic matter (Pulford, 1991) in the growing medium. The overall objective of the research reported in this study was to investigate chemical interactions between various mine spoils and sludge materials as organic amendments and to determine the level of sludge application (based on organic matter content) that maximised the chemical benefit to the mine spoils.

A controlled incubation study was used to achieve the objectives of the study. Six mine spoils from two sources (a gold mine and a coal mine) and three sludge amendments from two sources (municipal sewage sludge and paper sludge) were used. The sludge amendments were applied to the mine spoils to supply three different rates of organic matter (2, 5 and 10% in the amended spoils) and incubated for 38 weeks. The incubations were sampled every four weeks until week 20 and finally at week 38 for chemical analysis.

Results of the study revealed that organic matter, total and mineral N, total and Olsen P levels of the amended spoils could be predicted directly from the characteristics of the sludge and spoil constituents but pH, EC, CEC could not. The benefit of sludge addition on many of the chemical characteristics of the mined spoil increased with increasing level of sludge addition.

Manukau sewage sludge was the most beneficial sludge to apply with respect to P fertilisation. North Shore sewage sludge presented the greatest benefit for mine spoil rehabilitation with respect to N and it provided less risk of heavy metal contamination than Manukau sewage sludge. Paper sludge presented the most benefit with respect to pH and organic matter and the least risk of heavy metal contamination; however, nutritionally it was inferior to the sewage sludges.

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CHAPTER 5

DEFINITION OF TERMS USED

The various terms used in the thesis are defined as follows:

REHABILITATION:

A number of interpretations of the term rehabilitation are used in literature and there is often confusion or interchangeability between the terms rehabilitation, restoration and reclamation. These terms are used in issues relating to land disturbances caused by natural or human induced processes. They embody improvements of a visual nature to a natural resource- putting back into good condition or working order; restoring ecological attributes of particular interest to human society, but not all ecological attributes (Cairns, 1992).

WASTE:

Products of manufacturing, or of a physiological process (Sykes, 1987) which is of no value to the original process.

SLUDGE:

(As defined in the Collins English Dictionary 1991)"...4. (in sewage disposal) the solid constituents of sewage that precipitate during treatment and are removed for subsequent purification."

SPOIL:

Nelson and Nelson (1967) define spoil as the gangue, dirt or waste produced by underground mining or quarry or opencast operation, or by preparation plants, surplus excavated material as from pond, drainage ditch or other cut in engineering works. In this thesis the term spoil will be used as a general term to cover the materials that require rehabilitation, and are related to a mining operation i.e. tailings, oxidised waste, mudstone, subsoils, and fireclay. These specific terms will be defined in sections 3.1 and 3.2.

CHAPTER 1

INTRODUCTION

1.1   BACKGROUND

All systems with transformations have outputs, some of which may be considered undesirable. The safe disposal of effluent and solid wastes is hence an important part of many enterprise or company's activities. However, it is becoming increasingly realised that many once waste products have some economic value.

In 1985 a study undertaken by the New Zealand (NZ) Soil Bureau identified a major shortfall in topsoils and subsoils for mining rehabilitation works. The shortfall was estimated as 220 000 m^3 of topsoils and 1 200 000 m^3 of subsoil materials. It occurred largely as a result of poor stripping practice from 1945 to the late 1970's (Wills, 1992).

The use of surrogate materials to overcome the shortfall in topsoils was postulated by the NZ Soil Bureau (Wills, 1992) and research into potential materials has been undertaken by other countries in the past. Examples include the use of sewage and some other sludges on European and North American soils (and to a lesser degree mine sites) (Sopper, 1992, Lue-Hing *et al.*, 1992; Hall, 1991). Such work has until recently received little attention in New Zealand and the special characteristics of New Zealand soil and climate conditions may not allow extrapolation of overseas results to New Zealand soil and site conditions. However, the Resource Management Act (1991) places constraints on the disposal of wastes and may act as a catalyst in New Zealand for research into the beneficial utilisation of once waste products for land rehabilitation e.g. as surrogate topsoils.

The use of waste sludges to aid revegetation of mine land offers a route for otherwise unutilised resources to be usefully employed to assist in the production of surrogate soils. This appears to be consistent with the Resource Management law in that it utilises what was a waste product, disposed of to landfill, as a useful additive to improve soil quality in mine rehabilitation.

Levels of contaminants must be fully monitored in the soils, plants, waters and livestock at sites where sludge is applied. The need for such thorough monitoring may be relaxed

in future when the particular risks are better identified and appropriate management strategies developed.

1.2   OBJECTIVES

The information presented in 1.1 was the catalyst for the present research undertaken with the following objectives:

1. To investigate chemical interactions between various mine spoils and sludge amendments, applied to increase the organic matter content of the mine spoils.

2. To determine the level of sludge application for each of three sludges, that maximises the benefit to the mine waste with respect to chemical fertility (N, P, CEC, pH, EC) while not exceeding permissible concentrations of heavy metals.

Aims achieved by objectives:

1. To determine the most beneficial sludge (of three trialled) to amend a range of mine spoils with respect to addition of nutrients, amelioration of pH, low input of heavy metals.

2. To investigate the influence of incubation period on the effect of sludge addition to mine spoils with respect to chemical fertility.

1.3   STRUCTURE OF THE STUDY

A controlled incubation experiment was used to answer the objectives of the study.

In Chapter 2, Part 1 of the review of literature provides an overview of extractive industries, their productivity, by-products and associated problems in New Zealand. Mine spoils, and methods that have been employed to rehabilitate them are considered. Part 2 of the literature review considers the potential utilisation of sludges in mine spoil rehabilitation.

In Chapter 3, a description of the materials utilised in this research is given. These materials include six mine spoils that require rehabilitation, and three sludges that may be utilised as amendments. Details of the location of the spoils are also presented.

Chapter 4 describes the controlled incubation experiment used to assess the effect of the sludge additions on the chemical characteristics of spoils. Details of analytical procedures to assess the effects of sludge additions and the incubation on the spoils are presented.

The Results and Discussion section (Chapter 5) considers the results of the incubation study, and the implications for rehabilitation of the mine spoils.

Chapter 6 presents conclusions and suggestions for future research that may expand on the results obtained from this preliminary incubation study. Subsequent green house and field work is required to confirm the results presented in this thesis.

CHAPTER 2

REVIEW OF LITERATURE

2.1 EXTRACTIVE INDUSTRIES

2.1.1 Global overview

2.1.1.1 Extent of activities

In 1986, the area of land globally disturbed by mining was estimated to be approximately 386 000 ha/yr. This figure is projected to increase to 924·000 ha/yr. by 2000 A. D. (Soni and Vasistha, 1986).

2.1.1.2 Impacts of mining activities

Organic matter

The most common problem of derelict and degraded land (e.g. mine spoils) is a shortage of organic matter (Pulford, 1991; Hossner and Hons, 1992) in the growing medium. This results in the deterioration of soil texture and structure and a shortage of plant nutrients.

Organic matter is the substrate for soil microbiological life (Pulford, 1991), it aids nutrient (and heavy metal) retention, increases cation exchange capacity and improves pH buffering capacity. These effects are a result of its high number of negatively charged exchange sites (Brady, 1984). Organic matter accumulates in normal soils as a result of plant growth and decay (Brady, 1984). In most spoils however, the low level of biological activity results in minimal inputs of organic matter. One can therefore expect spoils low in organic matter to have a low cation exchange capacity and hence low nutrient and heavy metal retention and low buffering capacity.

Supply of nutrients

The problem of nutrient supply to plants growing on spoil is not simply providing sufficient quantity for establishment, but nutrient cycling over a long term period. This is particularly relevant to the supply of nitrogen which in most soils is derived mainly from organic matter (Pulford, 1991). Hall and Vigerust (1983) report that the major difficulty for restoration of disturbed and derelict land is establishing a nitrogen mineralisation cycle, as nitrogen and often phosphorus are usually very deficient. Nitrogen deficiency is the most frequent cause of failure for reclamation which at first appears successful.

Acid production

The production of acid by oxidation of pyrite, a sulphide containing mineral (FeS_2) is a common problem associated with mine spoils derived from coal and metals of sulphide origin. It commonly results in pH values below 3. On pyritic spoil, continued acid production by pyrite oxidation is likely to destroy any established vegetation cover (Pulford, 1991). Pyrite is a diagentic mineral formed in shales and coals as a result of the reduced environment under which they are deposited. Oxidation of pyrite occurs when pyritic spoil is exposed to the action of air and water (Pulford, 1991). Formation of sulphuric acid (Equation 2.1) decreases the pH of the spoil environment and results in increased solubility of metals that may be present.

$$2FeS + 2H_2O + 7O_2 \longrightarrow 2Fe^{2+} + 2H_2SO_4 \tag{2.1}$$
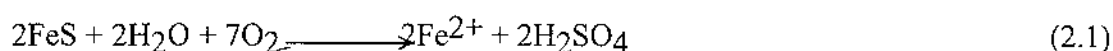
The resultant aluminium and heavy metal toxicity is the most important growth limiting factor for plants in many acid soils and mine spoils (Foy, 1983). Traditional guidelines used for applying limestone to neutralise acidity in agricultural soils often do not apply to highly acidic sulphide spoils (Sorensen *et al.* 1980; Caruccio *et al.*, 1988). Hydrolysis of aluminium species is the main cause of acidity in agricultural soils; hence methods developed for lime requirement determination in soils are based primarily on aluminium hydrolysis. These methods tend to grossly underestimate potential acidity where sulphide oxidation contributes substantial acidity (Sorensen *et al.*, 1980).

Spoil structure

The poor structure of many spoils manifests itself as instability leading to poor water holding properties and erosion of the spoil (Pulford, 1991). Mine tailings are normally variable in physical composition with depth (Hossner and Hons, 1992). Crusting and cracking of soil surfaces are also common and is brought about by differences in texture and variable mineralogy, as well as a lack of organic matter (Hossner and Hons, 1992). Erosion of tailings by wind and water with the associated environmental degradation is a universal concern (Johnson and Eaton, 1980; Sheppard *et al.*, 1984).

Effects on surrounding environment

Many areas of mine spoils visually disrupt scenic landscapes and cause environmental damage, such as sediment and acid drainage into streams, lakes and underground water supplies (Harwood, 1979). As a consequence of erosion, a common problem with unreclaimed tailings is blowing dust which pollutes air, streams and lakes, abrades vegetation, decreases aesthetics and creates health problems for communities near the tailings (Day and Ludeke, 1973).

Heavy metals and other toxic substances

Tailings (and some other mine spoils) may have elevated levels of heavy metals or other toxic materials associated with the processing of the ore. As the ore body is processed and the ore concentrated by recycling water, excess salts may accumulate (Hossner and Hons, 1992).

A number of consequences are possible due to high heavy metal contents in a spoil. The presence of heavy metals may inhibit revegetation of the spoil. Concentrations of heavy metals in the plants may be high enough to retard organic matter decomposition and the ability to support microbial and microfaunal populations may be reduced in the spoil resulting in reduced humus formation (Williams *et al.*, 1977; Tyler, 1981). Toxic heavy metals may also enter the human food chain (Department of Health, 1992).

In summary, mine spoils present a number of technical and practical problems for land rehabilitation. Concerns regarding air pollution to heavy metal leaching must be dealt

with. Problems associated with mine spoils have only recently been confronted and considerable research and practice is still required to enable successful rehabilitation of the range of current mine sites and those that may eventuate in the future.

2.1.1.3 Rehabilitation of mine spoils

Concern for rehabilitation of surface mined land is comparatively new, originating with the heightened environmental awareness of the late 1960's (Williams, 1987). Most legislative and technical experiences in land reclamation that have since occurred have involved land surface mined for coal. However, with appropriate modifications, this information may be applied to other types of disturbed land (Sopper, 1992).

Three general approaches have been used in the revegetation of tailings with toxic levels of heavy metals. Heavy metals may be immobilised through the addition of sewage sludge compost or similar wastes to the surface of the tailings site (Goodman *et al.*, 1973; Harwood *et al.*, 1987). A cap of non toxic material may be placed over the toxic materials and vegetation grown in this. Finally, genotypes collected from old metal mine sites with a genetic tolerance to heavy metal contaminants may be introduced to the contaminated site (Bradshaw *et al.*, 1978; Goodman, *et al.*, 1973; Hogan *et al.*, 1977; Morrey *et al.*, 1984; Palaniappan, 1974; Simon, 1978; Smith and Bradshaw, 1979).

2.1.2   The extractive industries in New Zealand

2.1.2.1 History and overview

The first mining in New Zealand was for manganese and occurred on Waiheke Island in 1841 (Isdale, 1981). In 1861, a gold rush that became known as the 50 year gold rush began (Taylor and Walker, 1987). Little reclamation occurred during this period and the Mining Act of 1926, which remained in force until 1970, allowed the payment of a Government levy in lieu of reclamation (Taylor and Walker, 1987). While the area of mined land in New Zealand has always been small (McKenzie and Cave, 1991), the result of many of these mining operations was the creation of disturbed land which has

remained both unsightly and unproductive to this day. The Mining Act of 1971 and the Mining Amendment Act of 1981 have required the development of land reclamation programmes with every mining operation. There has been an upsurge in prospecting and mining in New Zealand since the early 1980's (Taylor and Walker, 1987), especially in the Hauraki Goldfields of the Coromandel (Hansen, 1988) and these modern mines must abide by the new reclamation requirements. Since 1971 no licenses for large mining operations have been given without the production of an Environmental impact report or Environmental impact assessment by the applicants for the license (Taylor and Walker, 1987).

Aggregate mining is currently the largest extractive industry in New Zealand in terms of volume and value of product. However a number of other types of mining occur in New Zealand (Simcock, 1993) that include:

- Alluvial gold dredging
- Hard rock gold mining
- Coal mining
- Iron sand mining
- Topsoil mining
- Limestone mining

2.1.2.2 Rehabilitation of mine sites in New Zealand

There is an abundance of international literature on the rehabilitation of mine sites, however the applicability of overseas research to New Zealand depends primarily on similarities in climate, soils, vegetation, and post mining land use. Agricultural and horticultural reclamation techniques are most easily transferred at a general level from England, South Eastern Australia and lowland California as these areas have climates closest to New Zealand's (Simcock, 1993).

In NZ, reclamation research has mainly concentrated on determining guidelines for the suitability of mined materials for revegetation purposes and the management of these materials for maximum agricultural production. Traditionally, investigations have

started with chemical and physical analysis of potential rooting media, followed by pot trials and small scale field trials. The most commonly researched areas have been determination of the type and depth of optimum rooting mediums and rates of fertiliser application (Simcock, 1993).

Most research into mining reclamation in New Zealand has been associated with procedures related to environmental impact reporting (which have been required since the 1971 Mining Act). A significant proportion of recent research has been contracted by individual companies and a number of unpublished reports have been produced which are not widely available. Commercial research contracts in which clients require confidentiality of results thus limits technology transfer (Simcock 1993).

Adequate establishment of pasture is being achieved in experiments on gold (Waihi), topsoil (Wellington and Manawatu) and coal (Waimanu) mines. This is being achieved with the application of fertilisers, particularly nitrogen fertilisers (Simcock, 1993). New Zealand reclamation practitioners at a land reclamation workshop agreed that there was adequate information available on establishing pastures with similar productivity to undisturbed pastures but the ability to establish land with the same versatility or potential as the pre-mining state has not been established (Gregg *et al.*, 1990). Table 2.1 lists some of the rehabilitation research that has occurred in New Zealand.

Table 2.1

Some mine land rehabilitation research conducted in New Zealand

Cause of land disturbance	Location	Materials used for rehabilitation	Parameters assessed	Reference
Aggregate mining	Nelson	media present	soil physical and temperature changes and crop characteristics	McQueen, 1983 and Duck and Burton, 1985.
Alluvial gold dredging	Nelson	media present	physical and cropping measurements	McQueen, 1983 and Duck and Burton, 1985
Alluvial gold dredging	West Coast, South Island	topsoil and subsoil	pasture establishment, production and composition; soil chemical and physical properties	Morton and Harrison, 1990

Hard rock gold mining	Te Aroha	lime to establish pasture (short term)	crop measurements	Waikato Regional Council, 1991
Hard rock gold mining	Martha Hill, Coromandel Peninsula	soil over waste rock	soil physical properties	Horne et al., 1990
Hard rock gold mining	Martha Hill, Coromandel Peninsula	varying topsoil depths and fertiliser on oxidised waste	dry matter yield, soil P, K, pH and organic matter	Gregg et al., 1990
Hard rock gold mining	Martha Hill, Coromandel Peninsula	poultry manure on waste and tailings	soil physical and chemical properties, plant growth (e.g. lettuce and bean)	Mason et al., 1990
Hard rock gold mining	Union Hill, Coromandel Peninsula	varying topsoil depths and fertiliser on tailings	dry matter yield, soil P, K, pH and organic matter	Gregg et al., 1990
Hard rock gold mining	Coromandel Peninsula (Golden Cross mine)	pasture on different topsoil, subsoil, topsoil-subsoil depths	the productivity of the different media combinations	Cyprus Minerals (NZ) Ltd., 1987a and b.
Hard rock gold mining	Coromandel	various combinations of topsoil and subsoil and soil supplements	identify phytotoxic elements and the potential of the rooting mediums	Macraes Joint Venture, 1989
Hard rock gold mining	Macraes Flat, Otago	soil replacement techniques and topdressing	plant establishment. dry matter production and pasture composition; soil chemical analysis	Cossens and Keating, 1990
Hard rock gold mining	Reefton, West Coast	contouring and selection of suitable plants for shelter and pioneer planting e.g. willows, and legumes to return to indigenous beech	monitoring plant growth	Cawthron Technical Group, 1977
Hard rock gold mining	Westland	planting of indigenous and exotic plants on the present media, contouring and adding topsoil	monitoring tree growth	Mackenzie and Cave, 1991.
Hard rock gold mining	Reefton, West coast, (Giles Creek) Coal?	raw overburden and overburden covered with soil	overburden characteristics, monitoring a range of soil overburden characteristics (on going to 1997)	Davis and Crozier, 1991 and Ross 1992
Metal mining	Tui mine, Te Aroha,	lime, various metal tolerant grass varieties, composted sewage sludge	germination rates, dry matter yields, soil pH	Morrell et al., 1995
Coal mining	Southland	N fertiliser, mole drainage, soil replacement	chemical, physical and biological properties of soil and pasture production	Ross and Widdowson, 1987. Widdowson and McQueen, 1990.
Coal mining	Rotowaro, Huntly	lime and super phosphate	soil physical and chemical factors	Longhurst and O'Conner, 1990

Topsoil mining	Palmerston North	present media, pasture (return of clippings and clover), fertilisers.	worm numbers, herbage yield, chemical and physical soil characteristics	Sears *et. al.* 1965.
Topsoil mining	Wellington	present subsoil	effects of topsoil stripping on soil physical, chemical and biological characteristics and pasture production	Ross et. al., 1984 and Hart et. al. 1989.

Most research involving rehabilitation in New Zealand (Table 2.1) indicated that organic matter accumulation and decomposition is critical to the nutrient availability and productivity of drastically disturbed land. Higher accumulation rates of organic matter relate to increased plant yield. Based on these observations Hart *et al.*(1990) stated that one of the most pressing reclamation problems in New Zealand was to quantify the relationship between input of organic matter to soils and the rate of organic matter accumulation under different climates, planting and management regimes. Quantification of the relationship would allow the development of rational and effective restoration programs through plant species selection, grazing management, fertiliser applications and mulching (Hart *et al.*, 1990).

2.2   UTILISATION OF SLUDGES FOR MINE SPOIL REHABILITATION

2.2.1   Regulations

A number of countries and organisations around the world have developed regulations for the application of waste sludges to land. Most of these regulations apply to the application of waste sludges to agricultural land as a soil amendment and relate mainly to heavy metal contents (Table 2.2). Regulations have not been developed specifically for utilisation of sludge for land rehabilitation, although the Pennsylvania Department of Environmental Resources have issued guidelines (Table 2.2). According to Beckett (1992), the lack of directives related specifically to waste sludge utilisation for land rehabilitation may be for any one or a number of the following reasons:

1. Waste sludges are more commonly utilised on agricultural land.

2. Agricultural land, by definition, is always used for some form of human food production. Sludge is applied to this land to improve production, rather than for revegetation purposes as is usually the case in land rehabilitation.

3. Land to be rehabilitated is often already contaminated and/or a source of pollution. Application of sludge may improve existing conditions.

4. Sludge application to mine land for rehabilitation is often a one off application, there is no potential for an accumulation of toxic substances as in agricultural utilisation.

The regulations and directives under development are in order to enable waste disposal, or the beneficial uses of wastes to continue but without spoiling the soil and water environments (Beckett 1992). According to Beckett (1992), the processes involved in the mobilisation or immobilisation of sulphur, phosphorus, heavy metals and other toxic compounds from non agricultural wastes are the basis of the majority of research work relating to land reclamation. Table 2.2 lists some regulating authorities and references where regulations/guidelines can be found.

The Department of Health (1992) regulations (Table 5.20) were developed for New Zealand but based on overseas research. These regulations will be used in this thesis as the basis for any recommendations for constraints on sludge application to mine spoils in New Zealand based on heavy metal content. It is important to remember that the beneficial effects of the organic matter, N and P, and in some cases of the water in sewage sludge may overlie and to some extent compensate for the negative effects of the heavy metals (Davis and Zabel, 1990). Also the availability of added heavy metals to plants seems not to be well correlated with their extractability using conventional extractants. Further, heavy metal analyses are often very variable between and within different extracting procedures (Davis and Zabel, 1990).

Table 2.2 Authorities regulating the application of waste sludges to land, the nature of the regulations and the sludge constituents included

Authority or Country	Nature of regulations	Sludge constituents included	Source
Pennsylvania Department of Environmental Resources (PDER), 1988 [1]	Recommended maximum trace element loading rates for land reclamation 1	Cd, Cu, Cr, Pb, Hg, Ni, Zn	Sopper, 1992
United States Environmental Protection Agency (USEPA), 1979 [2]	Guidelines on metal loadings based on soil CEC.	Cd, Cu, Ni, Pb, Zn	USEPA, 1979
United Kingdom (UK), 1989	Guidelines for limits of addition of heavy metals in sewage sludge applied to agricultural land.	As, B, Cd, Cr, Cu, Hg, Ni, Pb, Zn	Alloway, 1990.
European Economic Community (EEC), 1986 [3]	Guidelines for limits of addition of heavy metals in sewage sludge applied to agricultural land.	Cd, Cr, Cu, Hg, Ni, Pb, Zn	Alloway, 1990.
EEC, 1986.	Upper permissible values for concentrations of heavy metals in agricultural soils (based on pH of soils).	Cd, Cu, Ni, Pb, Zn, Hg	Giller and McGrath, 1989.
Britain, 1989.	Upper permissible values for concentrations of heavy metals in agricultural soils (based on pH of soils).	Cd, Cu, Ni, Pb, Zn, Hg	Giller and McGrath, 1989.
Department of Environment (DoE), 1977, England..	Upper permissible values for concentrations of heavy metals in agricultural soils (based on pH of soils).	Cd, Cr, Cu, Hg, Ni, Pb, Zn	Giller and McGrath, 1989.
Germany, 1982	Upper permissible values for concentrations of heavy metals in agricultural soils (based on pH of soils).	Cd, Cr, Cu, Hg, Ni, Pb, Zn	Giller and McGrath, 1989.
Davis and Zabel, 1990	Maximum acceptable concentrations of elements in raw sewage.	As, Cd Cr, Cu, F, Hg, Mo, N, Pb, Se, Zn	Davis and Zabel, 1990.

1. The PDER guidelines state that due to the high permeability of mine spoils and low retention of organic matter, sufficient N in excess of the crop requirement must be provided in order to establish growth. To provide this N, a maximum of application of 134 metric tons N per ha is allowed.
2. The metal loadings suggested by the US EPA are based upon the soil CEC. The use of soil CEC is based upon the assumption that metal solubility and thus plant availability tend to decrease with increasing CEC in most soils in the USA
3. Regulations of member states of the European Community (EC), must lie within the limits specified in EC directives, but are commonly more detailed, and more relevant to local conditions (Beckett, 1992).

2.2.2 Examples of the utilisation of sludge in mine spoil rehabilitation

Options for disposal

A number of options exist for the disposal of sludge. These include (USEPA, 1983):

- Dedicated land disposal- a piece of land is set aside for the purpose of sludge disposal.

- Agricultural utilisation- as a source of nutrients and/or as a soil amendment to enhance crop production.

- Forest utilisation- to enhance forest productivity.

- Land rehabilitation utilisation- where sludge is applied to degraded land for the purpose of revegetation and reclamation.

Characteristics of sludge utilisation for land rehabilitation

Only the utilisation of sludge for land rehabilitation is considered here. The typical characteristics of this disposal option are (USEPA, 1983):

- Usually a one time application

- If additional applications occur they are likely to be at five to ten years intervals.

- Therefore this disposal option utilises a short life disposal/application site.

- Reduces or eliminates commercial fertiliser use.

- Allows soil to support vegetation and retards erosion.

- Potential harmful impact on vegetation is not usually a problem; because of the typical one time application

- Often the disturbed land is already a source of degradation. Therefore pertinent sludge application and management may alleviate existing problems.

The sources of sludges include municipal sewage sludge and industrial sludges, such as paper sludge. Although there has been extensive work on the use of sewage sludge for the rehabilitation of mine spoils (Sopper, 1992), only a limited information is available on the value of paper sludge as an amendment.

Paper sludge

Information regarding the utilisation of waste paper sludge is limited and this is presumably an indication that little work has been done on the subject. However, it could also be due in part to work being done as commercial research projects for which the clients request confidentiality of the results. Research may also be carried out by individual companies who do not publish reports on their work.

Paper sludge has been used as a metal immobilising soil amendment of metal contaminated substrates collected in the vicinity of zinc smelters (Vangronsveld and Clijisters, 1992). Other materials trialled concurrently included a refuse compost, alumino silicates and modified alumino silicate. Only the application of a modified alumino silicate and a town refuse compost significantly reduced soil phytotoxicity of heavy metals (Vangronsveld and Clijisters, 1992). Ritter *et al.* (1992), evaluated the use of paper mill sludge applied with soil, for revegetation of landfills. Greenhouse and field experiments were performed. From the field experiment, a mixture of one part sludge, two parts fly ash and one part soil was recommended without the risk of heavy metal contamination. It was recommended that a mixed pasture, including a legume be sown in the landfill surface amendment. Wills (1992) has considered the use of paper sludge as a surrogate topsoil for rehabilitation of Coal Corp mine areas in the Waikato region of New Zealand. Other materials considered were a dried digester sewage sludge and a bark mulch. The use of dried digester sludge showed some success but its application was limited by the topography and the poor drainage of the site.

Paper sludge composted with either fine or coarse wood bark was included in a study by Pichtel *et al.* (1994) that compared amendments and management practices for long term reclamation of abandoned mines. The composted paper sludge was compared with digested municipal sewage sludge, limed topsoil and powerplant fly ash. It was concluded that both the papermill and sewage sludges were suitable as substitutes for topsoil on the basis of nutrient content and plant growth. Assuming other environmental impacts of using these materials were acceptable, they could be viewed as beneficial materials rather than as solid wastes for disposal.

Feagley *et al.* (1994) undertook a study on the effect of a bleached primary papermill sludge on clover grown on a mine soil. The papermill sludge treatment was compared with lime and fertiliser treatments. It was concluded that fertiliser was necessary to revegetate mine soil when the sludge was applied. However improvements when sludge and fertiliser were applied over just fertiliser application were reported. These included an increase in nitrogen (N) fixation, higher uptake of potassium (K), calcium (Ca), and magnesium (Mg) by clover, and increased aggregation of the mine soil.

Sewage sludge

The agricultural benefits of sewage sludge are well published. As the human population increases and sewage treatment improves or increases, more sewage sludge is created for disposal. In Western Europe, 40 to 50% of the total sludge produced is utilised in agriculture (Matthews and Schenkel, 1983). Agricultural benefits include the addition of N, P, Ca as well as organic matter. The major contaminants/constraints are heavy metals, organic compounds and pathogens (Sopper, 1992, Lue-Hing *et al.*, 1992). Another constraint on the use of sewage sludge as a soil amendment is the view held by pollution and health authorities that sewage sludge is a waste product and as such, its distribution should be confined (Lawrie and Higginson, 1992).

Sopper and Seaker (1983) have extensively documented the beneficial effects of using digested municipal sewage sludge as a soil amendment for rehabilitation. This information relates specifically to mine sites in the humid eastern USA. In 1992, Sopper published a review paper dealing with reclamation of mine land using municipal sewage sludge (Sopper, 1992). This covers such topics as effects on vegetation, soil, water quality and on animal health and nutrition of applying sewage sludge. Also covered is reclamation acts and federal and state regulations governing the use of sludge on mine land. Again this information relates specifically to US mine sites and reclamation projects. It is however, a useful guide regardless of geographic location.

According to Seaker and Sopper (1988b), the reclamation success that is achievable with sewage (and some other) sludge is due to three factors relating to its organic content:

1.   The N content is in a slowly available organic form

2.   The high organic carbon content provides an immediate energy source for soil microbes

3.   Sludge organic matter improves the poor spoil physical conditions.

The persistence of the effects of sludge on soil physical properties and many chemical and biological properties is directly related to the persistence of sludge organic carbon in the soil medium. If part of the sludge organic carbon is resistant to degradation, the organic carbon content of the soil will increase under repeated sludge applications and an irreversible alteration of the physical properties is possible (Metzger and Yaron, 1987).

Seaker and Sopper (1988a) carried out research on coal mine spoils of the bitumous region of eastern USA. They compared sludge amended sites with chemically amended sites and found that above ground biomass, root biomass organic matter and detritus accumulation were superior on the sludge amended sites. They also reported these factors increasing with site age over five years. N levels were maintained over the five years. This was explained by the nitrogenous organic additions e.g.. proteins in the sludge, causing net mineralisation of N that builds up the N pool. Amendment of minespoil with sewage sludge at a rate of 120 to 134 Mg/ha (dry weight basis) provided an immediate nutrient and energy pool necessary for plant growth and microbial activity. This latter did not occur with chemical additions.

Topper and Sabey (1986), reported on the use of municipal sewage sludge as an amendment for a Colorado minespoil. Pasture growth responses were compared between sewage sludge amended sites and those amended with inorganic N and P fertilisers. The trial was conducted over two years, and the conclusion was that sewage sludge as a spoil amendment in environmental conditions similar to the study site (if sludge source is close) is economical. At rates less than 83 Mg/ha, seeded grass growth was benefited. The seeded grasses performed best at 15 Mg/ha and at levels greater than 83 Mg/ha sludge caused detrimental effects on plant growth. The reason for this was not determined but may have been due to high soluble salt concentrations.

In Poland, experiments on the suitability of different substances for the regeneration of the humus horizon on eroded loessal soils were conducted. A variety of materials were trialled, including mineral fertilisers, manure, humus rich soil, sewage sludge, bark compost, peat compost and rye green matter. After four years (first cycle of a crop rotation) it was found that application of organic substances resulted in rapid soil regeneration. The bark and peat composts and the humus rich soils contributed most benefit to the soil humus. The sewage sludge and the humus rich soil most positively affected the P and the K of the soil, although all treatments were beneficial in this respect (Jozefaciuk, *et al.*, 1990).

In the U.S., research has shown that organic amendments such as sewage sludge compost and animal manures can be used successfully to restore a high level of productivity on exposed subsoil within three years after reclamation. The areas thus restored include subsoils exposed through sand, gravel and topsoil mining. Prior to treatment, these subsoils did not support plant growth mainly due to their low fertility, pH and organic matter content. They were hence subject to severe erosion and surface runoff (Seaker and Sopper, 1988b).

Seaker and Sopper (1988a) conducted field trials on five coal surface mine sites reclaimed with sewage sludge as well as one site reclaimed with chemical fertiliser. They assessed the effects of sludge amendments and time on microbial populations. Specifically they studied populations of bacteria, fungi and actinomycetes, as well as microbial respiration and organic matter decomposition. Ecosystem recovery (as measured by microbial population and activity) appeared to occur more rapidly on sludge amended sites than on chemically amended sites. The study was conducted over a five year period. Microbial populations were not adversely affected by the heavy metals applied in the sludge.

Municipal sludge has been successfully used to stabilise and revegetate acidic dredge spoils along the Chesapeake and Delaware Canal (Palazzo, 1977).

According to Hall and Vigerust (1983), grass has been successfully established on a shale tip derelict for forty years. Five cm of sewage sludge, equivalent to 500 t/ha was incorporated into the surface which improved germination and moisture holding capacity. In another project, dewatered, digested sludge was applied at 86 tonnes dry solids (tds) and 180 tds/ha to colliery shale and this increased the mean annual yield of grass by 3.6 tonnes dry matter (tdm) and 5.0 tdm/ha respectively over a three year period. When sludge was applied at 180 tds/ha (the equivalent of 22t/ha of 11:9:0 N:P:K fertiliser), approximately 20% of the organic N was mineralised in the first year, five to ten percent in the second year and decreasing amounts in subsequent years (Kerr, *et al.*, 1979).

A lysimeter study (Hall and Vigerust, 1983) showed that nitrate N leaching losses from dewatered sludge was proportionately much less than fertiliser from shale. With crop cover, leaching losses from sludge were negligible over the winter period. Ayerst (1978) found that soils treated with sewage sludge had lower penetration resistance and that higher plant production with better root:shoot ratios were produced than when inorganic fertiliser was used.

Sewage sludge has been successfully used on metalliferous wastes. The organic matter of the sewage sludge formed complexes with the soluble metals and provided a long term source of nutrients. However, the vegetation root depth was generally restricted to the sludge layer (Sopper, *et al.*, 1982; and Gemmell, 1977).

Sewage sludge has been applied to a refuse tip, capped with about one metre of boulder clay. The clay had an organic matter content of 1 %, a pH of 8 and was deficient in nutrients, particularly N. After sludge incorporation, grass seed germinated readily and produced increases in yields in proportion to the application rate of sludge. Sludge was applied once at varying rates up to 289 tds/ha and in the first year after application, yields were up to 8 tdm/ha as opposed to 5 tdm/ha when 200 kg N/ha was applied, The sludge samples used in this experiment were an air dried digested sludge and a lime treated, undigested sludge cake. The undigested sludge cake was more effective than the air dried digested sludge (Coker, *et al.*, 1982). However it is expected that the stabilised

nature of digested sludge will ensure that its effects will persist for longer than the effects of undigested sludge as 60 to 80% of its organic carbon is in a form not easily biodegradable (Terry, *et al.*, 1979).

Hall and Vigerust (1983) undertook two experiments in Norway on land that had been levelled for cultivation. The surface after levelling consisted of unweathered clay, low in organic matter. The experiments trialled sewage sludge applied at up to 300 tds/ha and showed 60 to 100% increases in grain yields of oats and barley. Erosion risks were reduced on the sludged soils and the proportion of water stable aggregates was increased.

2.2.3   Effects of sludge addition on mine spoil characteristics

This review mainly relates to the utilisation of sewage sludge. Information regarding the effect of paper sludge on mine spoils is scarce.

2.2.3.1   Chemical characteristics

pH

Usually an improvement in the pH of a spoil occurs with addition of sewage sludge. Limed sludges which have a neutral to alkaline pH can raise the pH of acid spoils (Griebel, *et al.*, 1979). However, little information is available on long term effects on pH of a single high application of sludge to mine spoils. Sopper and Seaker (1990) reported that a sludge application of 184 Mg/ha increased the pH of strip mine spoil in Pennsylvania from 3.8 to 6.2 in the surface 15 cm, four months after application, and was still 5.4 after 12 years with excellent grass and legume cover. Pichtel *et al.* (1994) reported an increase in spoil pH with addition of paper sludge. Examples also exist of trials on spoil with an initially high (alkaline) pH where addition of sludge resulted in a decline of pH (Topper and Sabey, 1986).

Nutrients

An increase in the N and P content of spoils is generally associated with sewage sludge addition. Numerous studies have been reported on the nutritional benefits of sewage

sludge (Sopper, 1992; Pichtel *et al.*, 1994; Topper and Sabey, 1986; Ghorayshi, 1989; Furrer and Gupta, 1985). Werner *et al.* (1991) believe that it is on the basis of recycling and supply of plant nutrients that sewage sludge should be promoted as an amendment and nutrient source in agriculture.

Sewage sludges do not usually supply ergonomically significant amounts of K and contributions of K, Ca, Mg and S vary with sludge composition (Sopper, 1992).

Pitchel reported that when paper sludge was applied to a mine spoil, an increase in the content of K and Ca occurred (Pichtel *et al.*, 1994). Bellamy *et al.* (1995) reported that N immobilisation in sludge treated growing media is a constraint to paper sludge utilisation in crop culture.

Soluble salts

Effects on the soluble salt content of sludge amended spoils depend upon the particular sludge and the spoil it is applied to. Sopper (1992) gave a number of examples that demonstrated an increase in soluble salt content of the growing media when sludges were applied. Yet on other sites, the opposite effect has sometimes been reported (Lejcher and Kunkle, 1973).

CEC

Because of the high CEC of organic matter, the CEC of spoils amended with sewage or paper sludge is usually improved (Schneider *et al.*, 1981; Jones and Cunningham, 1979; Stucky and Newman, 1977; Flemming and Davis, 1986; Ghorayshi, 1989; Del Rosario, 1980). An increase in CEC results in an increase in the retention of nutrient cations and toxic heavy metals.

Heavy metals

A major problem with revegetation of mine spoils is the extreme acidity that releases metals such as Zn, Cu, Cd, Al, and Mn from the soil/spoil into the soil solution at concentrations inhibitory to soil micro-organisms (Mills, 1985). Reduced respiration and fungal populations in strip mine spoils have been attributed to high levels of metals

coupled with low nutrient levels and acid pH (Lawrey, 1977). In sludge that has been processed by digestion and composting, metals are bound to the organic components as sulphides, chlorides, carbonates, hydroxides, and other compounds not readily soluble (Lawrey, 1977). Corey *et al.* (1981) reported that the primary mechanisms involved in the retention of metals by sludges are precipitation as carbonates, phosphates, sulphides, silicates or hydrous oxides, and sorption onto organic matter and hydrous oxides.

The complete mechanism by which soil colloids (material less than 0.0002 mm) bind heavy metals is not well understood. However, it is generally agreed that the organic colloid may be five times as effective as the same percentage of the inorganic colloid (clay) in the retention of heavy metals (Leeper, 1978). The effect depends in part upon pH; a sharp increase in binding of heavy metals occurs from about pH 6 upwards (Leeper, 1978). Acid spoils are therefore at greater risk of damage or rehabilitation problems by heavy metals than those closer to or above neutrality.

Addition of sludge to a mine spoil usually results in an increase in the heavy metal content of the spoil, however the extent and the nature of the heavy metal depends upon the particular sludge (Sopper, 1992). Cd, Cr, Co, Cu, Fe, Pb, Mn, Hg, Ni and Sn are heavy metals commonly associated with industry and are hence likely to occur in sewage and other sludges (Leeper, 1978). In many cases however, increases are not significant in the amended spoil when sludge is applied (Sopper, 1992).

Cadmium is the heavy metal in sludge that has received the greatest attention with respect to human health. The concentrations of Cd in crops that may cause concern for human health are far below those that may reduce the crop yield. So phytotoxicity does not offer protection against excessive levels of Cd in crops (U.S. EPA, 1983; Alloway, 1990). Cd accumulates in the kidneys and may cause proteinuria, a chronic disease that causes increased excretion of protein in urine. However, it is difficult to predict the effect of sludge application on Cd in the human diet because crops vary in their uptake of Cd (e.g., cereals have a lower Cd content than leafy vegetables) and Cd uptake by plants is dependent on soil properties and the amount of Cd applied (U.S.EPA, 1983).

In general, Zn, Cu and Ni will be toxic to crops before their concentration in plant tissues reaches a level that presents a problem to human or animal health. The majority of crops do not accumulate Pb. However, these metals may enter the food chain by animals consuming amended soils along with forage (U.S. EPA, 1983).

Iron, Al, and Mn are usually present in acidic mine spoils at high concentrations (Leeper, 1978) and addition of a sewage sludge with high organic matter and relatively high pH can cause a decrease in the availability of these metals (Sopper, 1992). The addition of P in sewage sludge can also cause Fe, Al and Mn to become unavailable for plant uptake (Kardos et at., 1979; Sopper and Kerr, 1982; Kerr *et al.*, 1979; Seaker and Sopper, 1983; Seaker and Sopper, 1984). P antagonises the heavy metals inside the plant rather than in the soil (Leeper, 1978). Retention of P by soils causes an increase in CEC. As the CEC increases, generally the availability of heavy metals decreases (Adriano, 1986).

Increases in the spoil/soil extractable concentration of Cu, Zn, Cr, Pb, Cd, and Ni are common with sludge addition, although Sopper and Kerr (1982), Kerr *et al.* (1979), Seaker and Sopper (1983), and Seaker and Sopper (1984) reported minimal increases only in the top 15 cm depth. Peterson *et al.* (1982) and Fitzgerald (1982) reported an increase in spoil Cd, Zn, Ni and Cu concentrations when Chicago sludge, which has a high metal loading, was applied annually for four years. In Peterson's study, only Cd exceeded the values for normal ranges in agricultural soils. However, in Fitzgerald's study Cu, Zn, and Cd were at times above normal ranges and he also found that sludge addition resulted in large increases in Cr, Pb, and Hg (Fitzgerald, 1982).

Mercury may be carried along with fine suspended particles into water systems and may also endanger life by aerial contamination, however, it poses no risk by way of entering plants from the soil/spoil (Leeper, 1978).

On a weight for weight basis, Ni is considerably more toxic than Zn but is commonly present in sewage sludges in much lower amounts (Leeper, 1978).

The transfer of sludge constituents from the soil to crops is a function of soil pH, ion exchange capacity, crop species and plant variety and of course the characteristics and amount of sludge applied (Department of Health, 1992).

2.2.3.2 Biological characteristics

Sewage sludge application to soil generally raises the activity of soil micro-organisms by increasing the soil organic matter content (Stroo and Jenks, 1985; Seaker and Sopper, 1988a). Fesquez and Lindemann (1982) reported that sludge applied to a New Mexico coal mine spoil caused increases in the measured microbial parameters. However Brookes and McGrath (1984) found that at high levels, the heavy metals in the sewage sludge could have a toxic effect and reduce biomass. Microbial processes performed by specific or specialised micro organisms, such as nitrification are more sensitive to the effects of soil heavy metal contamination than processes carried out by a variety of micro organisms. There is evidence that the heavy metals in some sludges may affect particular soil microbial processes such as N fixation. The levels of heavy metal to have this effect exceed maximum soil limit concentrations (Smith, 1991).

2.2.3.3 Physical characteristics

Bulk density

Sludge application has been found to reduce bulk density of soils (Chang *et al.*, 1983; Kladivko and Nelson, 1977; Hall and Coker, 1983).Sludge additions have resulted in decreased bulk density in Illinois mine spoils high in compacted clay (Peterson *et al.*, 1979 and 1982)and coal refuse (Joost *et al.*, 1981). This is attributable to the sewage sludge being less dense than the mineral fractions of soils and spoils (Metzger and Yaron, 1987). The organic carbon added may also affect the bulk density by improving structural stability (Hall and Coker, 1983).

Porosity

Porosity is reported to increase with sludge addition due to an increase in total pore volume of the soil (Pagliai *et al.*, 1981). Pagliai reported an increase in the percentage of small pores (0.5-500 mm) and a reduction in the percentage of large pores (>500 mm). However Wei, *et al.* (1985) amended a clay soil with sewage sludge and found that the

large pore spaces were increased to the detriment of capillary pore space. Overall though an increase in porosity was reported.

Field and laboratory studies show that the application of sludge to soil, induces an increase in the number and size of water stable aggregates (Metzger and Yaron, 1987; Kladivdo and Nelson, 1979; Pagliai et al., 1981). Similar results have been reported with sludge application to a Mid-Western USA coal mine spoil (Hinesly et al., 1982). This is expected due to the increase in organic carbon (Metzger and Yaron, 1987) which acts as a binding material. However, this benefit may be reduced with time as a result of the decay of the added organic carbon (Kladivdo and Nelson, 1977). Nevertheless, Morel and Guckert (1983) found beneficial effects persisting four years after sludge application to a loamy clay and Wei et al. (1985) obtained beneficial effects six years after a single application (112 t/ha) of sewage sludge to a silty clay loam.

Hydraulic conductivity

It has often been observed that the addition of sewage sludges increases the saturated hydraulic conductivity of mine spoils (Kahaleel et al., 1981; Younos and Smolen, 1981). This is usually explained by parallel decreases in bulk density and increases in the total porosity (Kahaleel et al., 1981).Younos and Smolen (1981) found that sludge addition promoted infiltration, rapid saturation, and increased hydraulic conductivity. Feagley, et al. (1994) noticed an increase in aggregation of a mine soil when paper sludge was applied resulting in an increase in saturated hydraulic conductivity. However, there are a few reports of decreases in saturated hydraulic conductivity following additions of sludge to soil. These occurred in short term incubation experiments utilising raw sewage sludge, added to a silt loam (Epstein, 1975). Sludge decomposition products, microbial metabolites or fungal mycelia may be responsible for plugging the pores of these fine textured soils, when amended with sludges characterised by a relatively large content of easily degradable organic carbon (Metzger and Yaron, 1987).

Infiltration rates

Infiltration rates are usually improved on soils that are amended with sewage sludge. This is due to the enhanced macroporosity of the surface soils (Pagliai *et al.*, 1983). Griebel *et al.* (1979) stated that because sludge is about 50% organic matter (dry matter basis), it can improve water infiltration and retention. This feature is at least in part responsible for the reduction in erosion (that results from transport of soil particles in cases of high runoff) that can be achieved by sludge addition (Kladivdo and Nelson, 1979). Sutton and Vimmerstedt (1974) reported a reduction in runoff, erosion and sedimentation from coal mine spoils amended with sewage sludge. However, in some cases, negative results have been reported (Mazurak, *et. al.*, 1975; Khaleel, *et. al.*, 1981).

Hinesly, *et al.* (1982) reported an increase in available water holding capacity when sewage sludge was applied to a coal mine spoil in Mid Western USA.

2.2.3.4 Thermal characteristics

Organic matter has a lower thermal conductivity than the mineral constituents of soil. Sludge addition is therefore expected to bring about a decrease in soil thermal conductivity (Metzger and Yaron 1987).

2.2.4 Conclusion

While there are many reported benefits to be gained by using sludge to rehabilitate land, there is still some reluctance on the part of landowners and local citizens to accept its use for reclamation (Sharp, 1992). Due to the nature of degraded lands, larger amounts of sludge are used than for farmlands, but usually only a single application is made and this allows the vegetation to become self-sustaining. The greatest obstacle appears to be the lack of knowledge by the general public about the possible impacts of sludge on soils, groundwater, surface water, and animal and human health. These impacts must be known in order to make rational decisions concerning the benefits and risks of sludge utilisation in land rehabilitation.

CHAPTER 3

MATERIALS

Mine spoil samples from two sources (gold mine and coal mine) and sludge samples from two sources (municipal sewage sludge and paper sludge) were used.

3.1   GOLD MINE SPOILS

3.1.1   Source

The gold mine spoils originate from the Martha Hill Gold mine situated in the township of Waihi, at the southern end of the Coromandel Ranges, North Island, New Zealand. The gold mine spoils include tailings, oxidised waste and subsoil.

3.1.1.1 Background
Gold was first discovered at Martha Hill in 1878 and underground mining began in 1879 (McAra, 1988). The mine closed in 1952 but was opened again by Waihi Gold Mining Company Ltd. in 1987. This was a result of the upsurge in gold prices in 1979/80. In 1993 production from the Martha Hill gold mine was 1820 kg of gold and 8400 kg of silver annually. Along with this, 3 500 000 tonnes of ore and waste rock were extracted. The mining project is planned to extract approximately 8 million tonnes of gold and silver bearing ore and approximately 20-25 million tonnes of waste rock from Martha Hill over a 14-15 year operating period using an open pit method (Morrel *et al.*, 1995) .

3.1.1.2 Climate
The climate of the Martha Hill Gold Mine region is mild with abundant rainfall (mean annual rainfall is 2168 mm). Air temperatures are generally between 4 and 23 °C with frosts occurring during winter. The average number of sunshine hours is 1952 (Waihi Gold Company, 1985b).

3.1.1.3 Geography
The Martha Hill mine is located on an epithermal deposit developed in a fossil hydrothermal system hosted by Miocene pyroxene-quartz, and andesites. The ore comprises pyrite, sphalerite, galena, arsenopyrite, chalcopyrite, and chalcocite. Silver is

present mainly as a canthite and argentite and gold in the native form. The gangue minerals are quartz, calcite, chalcedony, chlonite and potassium feldspar (Morrell *et al.*, 1995).

3.1.1.4 Topography

The topography of the waste disposal area is flat river terraces to volcanic hills. It is an undulating topography. The parent materials' of the soils of the waste disposal area are approximately 1.5 m of Holocene and late Pleistocene volcanic ash. The river terraces comprise alluvium derived from tephra and weathered rhyolite and andesite. The soils are classified as yellow brown loams. They are well drained, have medium water holding capacities and are strongly leached. They are hence naturally low in nutrients. They have a high P retention due to the presence of allophane. Dairying and drystock farming are the predominant land uses of the area (Gregg *pers. comm.*).

3.1.2 Tailings

The gold rich pyritic ore is crushed and the gold is extracted using a cyanide extraction process. In order to immobilise cyanide, the residue is treated with lime. This waste material is known as tailings. Since the tailings are treated with lime during processing they consequently have a high initial pH, in the range of 9-10. This however is reduced over time exposed to the environment. The CEC is reported very low in tailings (Waihi Gold Company, 1985b). This indicates a limited ability to retain applied nutrients. The high pH may however immobilise trace metals essential for plant growth as well as toxic heavy metals.

3.1.3 Oxidised waste

Oxidised waste is the overburden pyritic material which has undergone oxidation. It comprises at least 65% of the total waste rock and is the major waste rock to be placed in the disposal area. The remaining waste rock is unoxidised and is a potentially acid forming waste. It is buried within the oxidised waste bunds so will not be available for rehabilitation (Waihi Gold Company, 1985a). Oxidised waste is used to build the tailings retention dam. Elemental concentrations of this material are either near the average or within the range normally expected for soils (Adriano, 1986). Oxidised waste contains sufficient fines to provide a suitable plant growth medium (Waihi Gold Company, 1985a), moisture storage is also adequate but macroporosity is low.

Lack of organic matter and nutrients are likely to be the major limiting factors to plant growth on both tailings and oxidised waste. Oxidised waste has somewhat higher CEC but lower pH than tailings (Waihi Gold Company, 1985b). These materials are capable of producing pasture with chemical amendments (Waihi Gold Company, 1985a); however, it is expected that the addition of organic matter will reduce the time required to establish a self perpetrating vegetative cover.

3.1.4   Waihi subsoil

The Waihi subsoil (Waihi ash) is of volcanic origin and is of coarse texture, with a low level of organic matter and biological life. This results in relatively slow nutrient cycling. It has a low pH and very high P retention (Gregg *pers. comm.*).

3.2   COAL MINE SPOILS

3.2.1   Source

The coal mine spoils originate from the mining activities of Coal Corporation of New Zealand Ltd (Coal Corp). around Huntly, in the Waikato, North Island of New Zealand. The coal mine spoil samples include fireclay, mudstone and subsoil.

3.2.1.1 Background

Coal Corp is the primary producer of coal in New Zealand and has mining operations in both the North and South Islands. Some of New Zealand's largest reserves of sub-bituminous coal lie under the Waikato region and these reserves are the focus of Coal Corps mining activities based at Huntly (Coal Corporation of New Zealand Ltd., 1993).

The formation of coal
Coal forms over millions of years. Vegetation decomposes to form peat, a combination of carbon, oxygen, nitrogen, sulphur and trace elements. As peat compresses, the oxygen and water content is reduced and the carbon proportion increases. Coal is hence formed. In the Waikato, about 15 m of peat is required to produce a 1m thick coal seam (Coal Corporation of New Zealand Ltd., 1989).

Coal mining methods
Coal Corp uses underground and opencast mining in the Waikato. The coal spoil samples used in this study originate from opencast mining, centred around Rotowaro.

Heavy machinery is used to remove the overburden and the coal is extracted using face shovels which load it on to trucks for removal. The overburden is transported to a holding area. When the mining is completed in a particular area, the overburden and soils are replaced, soil testing and fertilisation undertaken and pasture established (Coal Corporation of New Zealand Ltd., 1989). However there are some areas which have not been rehabilitated and there is concern that there will be a shortage of suitable topsoil to rehabilitate all disturbed land.

3.2.1.1 Climate

The climate of Huntly is characterised by mild winters and warm summers. The average annual rainfall is approximately 1300 mm. Mean air temperatures range from 19.2 $^\circ$C in February to 9.3 $^\circ$C in July. Fog occurs on an average of 30 days per year (State Coal Mines, 1986).

3.2.1.1 Geology

The geology of Huntly is dominated by Holocene Age coarse sediments which range in depth from 5 to 100 m. They overlie siltstones (mudstone), sandstones and claystones. Beneath these are the Waikato Coal Measures which are of Tertiary Age (State Coal Mines, 1986).

3.2.1.4 Topography

The topography of the land on which the coal mines are located is predominantly flat to rolling. Valleys dissect the rolling country.

The soils are a complex mosaic. They are predominantly yellow brown loams and brown granular loams. In low lying areas, organic soils, e.g. peats, predominate. The predominant land use is pasture, both low and high producing (State Coal Mines, 1986).

3.2.2 Fireclay

Fireclay lies immediately below a coal seam and is the buried soil of an old forest system. The coal represents the forest system (Dr. R. B. Stewart, pers. comm.).

3.2.3 Mudstone

Mudstone is a soft sedimentary rock formed from material with a high clay content. It is an overburden material (Edbrooke *et al.*, 1994) deposited over the coal seam.

3.2.3 Huntly Subsoil

Huntly subsoil is a Hamilton ash of andesite and rhyolite composition (Dr. R. B. Stewart, pers. comm.).

3.3 AMENDMENTS

Sewage sludge samples from two sources with different heavy metal contents and one industrial sludge (paper sludge) were used.

3.3.1 Manukau sewage sludge

Manukau sewage sludge is a by-product of the Manukau Sewage Purification Works (MSPW), operated by Watercare Services Ltd. Watercare Services Ltd. services the major part of the Auckland urban area (850 000 people). This includes the major industrial areas of Auckland. The sludge is an earth like material and is considered to contain relatively high levels of heavy metals.

The MSPW presently treats an average daily wastewater volume of 300 000 m^3/day including 2000 m^3 of sludge.

Treatment comprises both primary and secondary methods, the by-products of which are dried sludge and biogas which is produced during the sludge digestion process.

The treatment process
Waste water from sewers enters a mixing chamber where air is blown into it to keep it aerobic and to prevent solids from settling out. Odorous air and gasses are extracted as they are during subsequent processes.

Primary treatment occurs after screening for large refuse (rags, sticks etc.) which are dumped at a landfill. It occurs in pre-aeration grit removal tanks and primary

sedimentation tanks. Air is pumped into the sedimentation tanks through a perforated pipe running along the side of the tanks floors. It produces a rotary motion which reduces the effective density of the wastewater and allows the grit (sand, silt, gravel etc.) to settle out. Organic solids remain in suspension. The grit is used for landfill at the plant.

Organic solids settle out in primary sedimentation tanks. Scrapers along the sloping floors of the tanks collect the sludge and drop it into a hopper where open topped airlift pumps remove it to a sump. The sludge and scum (which is collected from the surface) are pumped to sludge digesters for secondary biological treatment. This phase is necessary to kill any pathogenic bacteria. Sludge is anaerobically digested. It is heated to 37 $^\circ$C and acid forming bacteria break down the organic substances to organic acids which are then converted to methane and CO_2 by methane forming bacteria.

The sludge is reduced in volume by 50% after approximately twenty days in the digesters. It is pumped to sludge lagoons where it remains at least a year. Harmful bacteria are destroyed in the sludge lagoons. Finally it is dried in dewatering beds with each bed taking about a year to fill (Water Care Services Ltd., 1993). The sludge is stock piled at the treatment plant after excavation from the ponds (Bradley et al., 1992). Prior to September 1990, the sludge was available to the public free of charge for landscaping, topdressing, backfill etc. However concerns about the heavy metals in the sludge and the unknown and unmanaged use of the material after leaving the site resulted in the practice being stopped (Bradley et al., 1992).

3.3.2 North Shore sewage sludge

North Shore sewage sludge is a product of the North Shore City Council's waste water treatment plant. About 203 m^3 of sludge is produced daily. The plant was designed to service 160 000 people. The connected population is 151,000. Five percent of the flow is from trade wastes.

The treatment process involves passing the wastewater through coarse screens, primary sedimentation tanks, trickling filters, secondary sedimentation tanks, oxidation ponds, sludge digesters, and sludge dewatering lagoons. The sludge is stock piled for two years. It has subsequently been used by home gardeners (North Shore City, undated); but this practice has been terminated due to public concerns about the safety of the

sludge (North Shore City Council, 1994). The North Shore sludge is considered to contain low levels of heavy metals.

3.3.3 Paper sludge

Paper sludge is a product of the deinking process of the New Zealand Forest Products Te Papa recycling mill. During the recycling process, cellulose fibres and components such as fillers are rejected into the water system and discharged along with the removed ink. This material is concentrated by sedimentation and screening processes and the paper sludge is formed (Kirkpatrick, 1991)

The expected benefits of applying the paper sludge to a mine site include nutrient and soil conditioning, also a reduction of acidic discharge in streams and encouraging vegetative growth. Possible problems include polychlorinateddibenxo-p-dioxins (PCDDs) and polychlorinateddibenzofurans (PCDFs) although these are slowly being phased out of the manufacturing process (Wills, 1992).

CHAPTER 4

METHODS

4.1   COLLECTION OF THE RAW MATERIALS

Bulk samples of the three sludges were taken from the spoil storage areas. Approximately one tonne of Manukau sewage sludge, 500 kg of North Shore sewage sludge and 100 kg of paper sludge were delivered to Massey University. The two sewage sludges were emptied out of the hessian sacks they were delivered in, and large bits of debris were removed. They were passed through a 5 mm sieve and then re bagged. From this re-mixed bulk sample, a sample was taken for the incubation. A large sample of the paper sludge was taken randomly from the bulk, large pieces of debris removed and passed through a 5 mm sieve.

4.2   PREPARATION OF THE MATERIALS

The sludge samples had any bulky material removed (e.g., bits of plastic and clay in the sewage sludge; sellotape and cardboard in the paper sludge). All sludge and mine spoils were ground with a wooden mallet to pass through a 2 mm sieve. An untreated wooden mallet rather than a ceramic or metal mortar was used to reduce the risk of heavy metal contamination.

Neither the sludges nor the mine spoils were dried before the incubation. The moisture contents of the materials were assessed by accurately weighing 5-10 g sample, drying the samples at $105^{\circ}C$ in an oven overnight and weighing again. Appendix 1 gives the moisture contents.

4.3   ADDITION OF SLUDGE TO THE MINE SPOILS

Sludge was added to the mine spoils on the basis of organic matter content. The objective was to obtain for each combination of sludge and spoil, an organic matter content of 2, 5 or 10 % i.e. three incubations for each sludge/spoil combination, with different ratios of sludge to spoil. Because the sludges were applied on the basis of organic matter, a sludge with a higher organic matter content was applied at a lower quantity than a sludge with a lower organic content. Similarly when the same sludge was applied to two or more different spoils, the spoil with the lowest organic matter content received the greatest amount of sludge.

From the initial estimate of organic matter contents of each material in the incubation, the amount of the sludge amendment required to give 2, 5, or 10 % organic matter in the mine spoil samples was calculated using Equation 4.1.

$$x = a \frac{(d-b)}{(c-d)}$$

(4.1)

   x = Dry weight of the sludge amendment required.

   a = Weight of mine spoil.

   b = Percent organic matter in the mine spoil.

   c = Percent organic matter in the amendment.

   d = Percent organic matter in the mixture.

The figures derived from Equation 4.1 were then adjusted (increased) to take account of the moisture contents of the individual materials.

Distilled water was added to bring the moisture contents of each sludge/mine spoil mixture up to 60 % of the field water holding capacity of the mine spoil in that mixture (Table 4.1). The mine spoil was the predominant constituent of each mixture, the sludge was added as an amendment. Note that only two levels of sludge were applied to the mudstone. This was because the organic matter content of the original mudstone was above 2%. Similarly, the fire clay had an organic matter content greater than 5% so only

one level of sludge was applied (Table 4.2). Particles of coal in these materials are the likely cause of the higher organic matter contents.

North Shore sewage sludge was used to amend both the coal and the gold mine spoils. Manukau sewage sludge was used to amend the gold mine spoils and paper sludge to amend the coal mine spoils.

Table 4.1

Field water retention capacity of the spoils*

Material	Field water retention capacity (%)
Tailings	37.88
Oxidised waste	42.01
Waihi Ash	45.73
Fire clay	29.88
Mudstone	44.39
Huntly subsoil	41.23

*The field water retention capacity (the water content of a saturated material at atmospheric pressure) of each material was estimated using the method described by Ritcey (1989).

A quantity of 900g of spoil was mixed with the required amount of sludge and water to achieve the appropriate organic matter status of each mixture (Table 4.2). The water was added drop wise and the mixtures mixed thoroughly before placing in the incubation jars.

Samples were taken from two sludge amended spoils and the C content measured to give an estimate of organic matter in the mixtures to check the accuracy of the method of addition. The results were within 0.4 % of the organic matter content expected.

Table 4.2

Quantity of each material in the incubations

Amendment	Mine Waste	Organic Matter (%)	Amount of Amendment (g)	Amount of Mine Waste (g)
Manukau sewage sludge	Tailings	2	43	900
		5	117	900
		10	270	900
	Oxidised waste	2	33	900
		5	106	900
		10	257	900
	Waihi subsoil	2	7	900
		5	78	900
		10	224	900
North Shore sewage sludge	Tailings	2	46	900
		5	126	900
		10	293	900
	Oxidised waste	2	35	900
		5	113	900
		10	279	900
	Waihi subsoil	2	7	900
		5	82	900
		10	243	900
	Fire clay Mudstone	10	52.8	900
		5	45	900
		10	199	900
	Huntly subsoil	2	26	900
		5	103	900
		10	267	900
Paper sludge	Fire clay Mudstone	10	31	900
		5	28	900
		10	117	900
	Huntly subsoil	2	16	900
		5	64	900
		10	157	900

4.4   THE INCUBATION

An incubation experiment may be a useful method for testing the effect of a treatment over time on selected characteristics of a soil or mine spoil material. Unlike a pot or

field experiment, an incubation is able to be conducted under strictly controlled conditions of temperature, light and aeration. This allows the effects of a treatment to be more clearly observed, i.e. with minimum external influences. For these reasons it was decided to use an incubation experiment for the study of the effects on spoil characteristics of sludge amendments. The incubation was initiated on 26 January 1993 and completed on 20 October 1993. It was designed to examine the effect of addition of each of three sludges on the chemical characteristics of six mine spoils as described in Chapter 3. The incubations were in sealed, one litre glass jars, in a darkened incubator at a temperature of 22 °C. The jars were placed randomly in the incubator and the lids were removed every second day for a few minutes to allow an aerated condition to be maintained in each jar. The contents were shaken upon replacement of the lids to ensure maintenance of an homogenous mix. Initially water was applied to the jars every second day to maintain the moisture content. Distilled water was added on a weight loss basis. Due to the small amount of moisture being lost, this period of replenishment was increased to once a week.

4.5   ANALYSES

Each incubation treatment (Table 4.2) was sampled initially and six times subsequently; at four weekly intervals until week 20 and finally at week 38. A bulk sample of approximately 50 g was taken from each jar at each sampling time. Three moist sub-samples were taken for ammonium and nitrate analysis, the rest of each sample was air dried and passed through a 2 mm sieve, put into sealed plastic bags and cool stored at 4 °C for future analysis. Triplicate sub samples were taken for each analysis performed for each treatment.

4.5.1   Organic matter

Sludge was applied to the mine spoils on the basis of organic matter. The Carbon (C) content of the spoils and sludges was measured prior to the incubation.

Samples were dried at 105 °C in an oven overnight. The C contents of the samples were measured using the Leco induction furnace. This method involves combustion of a dry sample in a stream of oxygen. The gases produced by the combustion are carried by an oxygen stream through a dust trap to a copper oxide catalyst to convert any carbon monoxide present to carbon dioxide, through a Manganese -dioxide trap to remove halogens and SO_2 and finally through Mg percolate to remove any moisture. Carbon dioxide is evolved and trapped in ascarite. The weight difference in the ascarite trap before and after each oxidation allows a measure of carbon dioxide to be made. From this the amount of total carbon is calculated i.e.:

$$\% \text{ total C} = \frac{\text{amount of } CO_2 \text{ (mg)} \times 0.02729}{\text{weight of sample (mg)}} \times 100$$

(4.2)

Organic C for the purpose of this study was assumed to be the same as total C i.e. all carbon present in the incubation materials is assumed to be organic carbon.

All analyses were done at least in triplicate, or until a consistent reading was achieved. Organic matter contents were estimated using the "Van Bemmelen factor" of 1.724 (Bremner and Tabatabai, 1971):

$$\text{Organic matter} = \text{organic carbon} * 1.724$$

(4.3)

The use of this factor is based on the assumption that soil organic matter contains 58% C (Allison *et al.*, 1965).

Calcite and to a lesser extent dolomite are the main components of the inorganic fraction of soil C (Allison *et al.*, 1965). If carbonates are absent from the sample or are removed form the sample prior to analysis, total C may reasonably represent organic C (Allison *et al.*, 1965) and the above procedure is valid.

A simple test to identify the presence of carbonate was undertaken on all materials initially. Two to five g of spoil/sludge material (less than 2 mm) was placed on a spot pallet and moistened with a few drops of water to displace air that might otherwise have been confused with carbon dioxide released from carbonates. A few drops of 4M HCl was added to the moist sample and any evidence of effervescence noted (Allison *et al.*, 1965).

4.5.2   pH

Initially the pH of the mixtures and individual materials was measured both in water as well as in 1M KCl.

Miller (1968) explained that the pH suspension of a salt solution is more artificial than the pH suspension in a water solution but that the salt solution gives a more stable and reproducible result; it is an expression of the surface pH. This is a stable property of a soil with particular significance for the study of chemical soil changes. Overall the pH in water was (as expected) more variable than that obtained in KCl and also consistently produced a higher pH reading although there was less than one pH unit difference. The salt solution method as described by Blakemore *et al.* (1987) was therefore used for subsequent pH analysis.

Five g of soil material was mixed in a pottle with 12.5 ml of 1M KCl. The mixtures were shaken vigorously in closed pottles and left over night before a pH reading was made. pH was analysed at all sampling dates.

A test was undertaken to determine whether or not a linear change in pH could be expected when successive increments of a sludge were applied to a mine spoil. Samples of each of four materials: tailings, mudstone, paper sludge and Manukau sewage sludge were taken. These were assumed to cover the range of material types presented. Analyses were in duplicate. Samples of 1, 2.5, 4, and 5 g of each material was added to

12.5 ml of 1M KCl in pottles. They were shaken vigorously and left overnight before a pH reading was made.

4.5.3   Electrical conductivity

The 1:5 solid:water extraction procedure was used to measure conductivity (Bower and Wilcox, 1965).

A five g air-dried sample (<2 mm sieved) was added to 25 ml of deionised water and stirred well. It was shaken in an end-over-end shaker for 30 minutes and filtered through Whatman No. 1 filter paper.

A conductivity cell connected to a self adjusting conductivity meter was calibrated in a 0.01 M KCl solution to 1.14 mmho/cm at 25 ^oC. The temperature and the conductivity of the extracted solutions were measured. The cell constant was arrived at by dividing the theoretical value for 0.01 M KCl by the measured value. The soil conductivity was corrected to standard temperature 25 ^oC using standard temperature factors (Massey University Soil Science laboratory methods, unpublished). Sample conductivity was then calculated using Equation 4.4.

$$Conductivity = a*b*c$$

(4.4)

where: a= measured conductivity

b= cell constant

c= temperature factor

4.5.4   Total nitrogen and phosphorus

The Kjeldahl Digestion method (McKenzie and Wallace, 1954) was used to determine the total N and P contents of the mixtures and the individual materials in the incubation

experiment. Analyses were performed on samples taken initially (week 0) and finally (week 38) of the incubation.

The Kjeldahl digestion method involves digesting 1 g of accurately weighed soil material with 4 ml of a digest mixture containing potassium sulphate, selenium and sulphuric acid. The digests were heated in aluminium blocks at 350 ^{o}C for four hours and cooled over night. They were then diluted with deionised water, thoroughly mixed in a vortex mixer and analysed using the auto analyser. Only 0.5 g accurately weighed sample was used for each of the 3 sludges as it was expected that they would contain a high level of N. Dilutions were made as necessary with deionised water to achieve levels of N that were within the linear range for the auto analyser. Two blanks were run with every set of 30 tubes.

4.5.5   Mineral nitrogen (nitrate and ammonium)

The inorganic N content of the incubation materials was analysed using the 2M KCl extraction procedure. Ammonium (NH_4^+) and nitrate (NO_3^-) in the extract were determined using a Technicon auto analyser (Searle, 1975; Technicron, 1976).
Two g of moist sample was added to 20 ml of 2 M KCl. The mixtures were shaken in an end over end shaker for 30 minutes and centrifuged at 9000 rpm for 5 minutes. They were filtered through Whatman #40 filter paper and the filtrate collected. NO_3^- and NH_4^+ were determined. Dilutions were made as necessary using 2M KCl.

4.5.6   Sodium bicarbonate extractable (Olsen) phosphorus

The sodium bicarbonate extractable P (Olsen et al, 1954) method was used to measure inorganic P, an estimate of plant available P, at each sampling time of the incubation.
The reagent used was 0.5M sodium bicarbonate ($NaHCO_3$), adjusted to pH 8.4 with 0.5 M sodium hydroxide (NaOH). One g, air dry samples (<2 mm) were accurately

weighed into 50 ml polypropylene centrifuge tubes. Twenty ml of 0.5M NaOH solution was added and the mixtures were shaken in an end over end shaker for 30 minutes. They were centrifuged at 9000 rpm for one minute and filtered through filter paper.

Inorganic P was determined using the phosphomolybdate method of Murphy and Riley (1962). This involved the formation of a phosphomolybdate complex which when reduced with ascorbic acid gives a blue colour.

A standard curve was made up to give 0 to 0.8 μg P/ml. The samples were made up with 4 ml of filtrate, 30ml of water and 10ml of Murphy and Riley solution. They were made up to 50ml volume with water, shaken vigorously and left for half an hour before reading the absorbance. The absorbance of the standards and the samples was read in a spectrophotometer at 712nm using a 1 cm cell. Samples with too dark a colour were diluted with $NaHCO_3$. The content of P was read off a standard curve in μgP/50ml.

4.5.7   Phosphate retention

The phosphate retention capacity of the original materials was assessed.
Phosphate retention is the ability of a soil to absorb P onto the surface of soil particles.
Phosphate retention of the materials in the incubation was measured using the method described by Blakemore et al. (1987). The reagents were: phosphate retention solution composed of Potassium di hydrogen phosphate, anhydrous sodium acetate and glacial acetic acid and Nitric Vanadomolybdate acid reagent. A set of standards were prepared using the phosphate retention solution to give a standard curve from 0 to 100% phosphate retention i.e., 0, 0.2, 0.4, 0.6, 0.8, and 1.0mg P/ml. This corresponded to 100, 80, 60, 50, 40, 20, and 0% phosphate retention respectively.

Five g triplicate samples of each mine spoil and sludge were mixed with 25ml of P retention solution and made up to 50ml with water. They were shaken for 16 hours and centrifuged for 5 minutes at 9000rpm. Absorbance was read on a spectrophotometer at 412 nm

4.5.7   Cation exchange capacity

Cation exchange capacity (CEC) is a measure of cation exchange in a surface active material, i.e.; the interchange of cations in solution with cations on the surface of the material. Exchangeable cations are thought to be available to plants by exchange with hydrogen (H^+) ions from root hairs and soil micro organisms. The principle soil exchangeable cations are the bases calcium (Ca^{2+}), magnesium (Mg^{2+}), sodium (Na^+) and potassium (K^+). However other cations may also be present such as H^+ and NH_4^+, aluminium (Al^+) and iron (Fe^+) (Blakemore *et al.*, 1987).

The 1M ammonium acetate (pH 7) method is currently the most widely used procedure for measuring CEC (Blakemore *et al.*, 1987) and was used in this study.

The measurement of CEC involved:
1.   Saturating the negatively charged exchange sites on the soil particles. This was done with a displacing cation (NH_4^+)
2.   Extracting and measuring the displacing cation.

One M ammonium acetate at pH7 was used as the saturating solution. The ammonium acetate was prepared as instructed by Blakemore *et al.* (1987).

Triplicate samples of 1 g (air dry <2 mm) material from each incubation were mixed with 2 g acid washed silica sand and packed into a leaching tube (pipette tip) which had a macerated filter paper plug (Whatman #41 filter paper). The columns were leached with 50 ml of 1 M ammonium acetate and the leachate collected in 50 ml volumetric flasks which were made up to volume with ammonium acetate. The blank was 2 g of acid washed silica sand.

The H^+ concentrations in the resultant solutions were determined by measuring the pH of each solution and subtracting from this the pH of a blank (ammonium acetate solution) and using the derived equation 4.5 to determine the H^+ concentration.

$$H^+(meq\%)= \frac{Blank\ pH - sample\ pH}{0.04} * 5$$

<div align="right">(4.5)</div>

The concentrations of calcium, magnesium, sodium and potassium were determined using the Atomic Absorption Auto Analyser GBC904AA.

4.5.8   Heavy metals

Total metal contents of the nine original materials were analysed by Plasma Emission Spectrometry. Initial and final incubation time analysis of available (0.1 M HCl extractable) elements in the individual materials and mixtures with 10% organic matter was undertaken using the same equipment. (The analysis was undertaken by AgResearch at the Grasslands Research Centre).

Total concentrations of metals were only analysed in the original sludge and mine spoil samples for the initial period as they were not expected to change with time in a closed system and they are not volatile. The results were extrapolated to give expected total values for heavy metals in each of the mixtures. The cost of analysis prevented more extensive assessment of heavy metals. Mercury was not analysed due to the cost of analysis.

The samples were ground using a tungsten carbide ring grinder, to less than 2 μm size. The available metals were extracted using 0.1 M HCl extractant. It is generally accepted that this extractant liberates more than the labile forms of metal in the medium, especially of Fe, Mn and Al. (Norvel, 1984).

Five g air dry material was accurately weighed into 50 ml polpropylene centrifuge tubes. Twenty five ml of the extractant was added and the samples shaken end-over-end for 16 hours. They were subsequently removed and centrifuged at 9000 rpm for five minutes, filtered through Whatman No. 42 filter paper and cool stored for analysis.

Twenty three elements were analysed for, these included aluminium, arsenic, boron, calcium, cadmium, cobalt, chromium, copper, iron, potassium, magnesium, manganese, molybdenum, sodium, nickel, phosphorus, lead, sulphur, selenium, silicon, tin, strontium and zinc.

4.5.9   Statistical analysis

For most parameters assessed, a comparison of actual experimental results with predicted results were made. Predicted results were calculated using equation 4.6.

$$\frac{(a*b)+(c*d)}{a+c} = x$$

(4.6)

a= quantity of mine spoil (g)

b= measured value for mine spoil

c= quantity of sludge amendment (g)

d= measured value for sludge amendment

x= predicted value for the amended spoil (sludge-spoil mixture)

A two factor analysis of variance at a 5 % level of significance was performed for all parameters where the effect of time as well as various rates of sludge addition were considered, i.e. for mineral nitrogen, Olsen P, pH, and electrical conductivity. A single factor analysis of variance at a 5 % level of significance was performed for all parameters where the effect of different rates of sludge addition only, was likely to impact upon results i.e. for total N and P, CEC, heavy metals and organic matter.

CHAPTER 5

RESULTS AND DISCUSSION

5.1   ORGANIC MATTER

5.1.1   Organic matter in the original materials

Table 5.1 gives the initial organic carbon and the organic matter contents of each material in the incubation. The organic matter was estimated using Equation 4.3.

Table 5.1

Organic carbon and the estimated organic matter contents of the original incubation materials

Material	Organic carbon (%)	Organic matter (%)
Manukau sewage sludge	25.1	43.3
North Shore sewage sludge	23.6	40.6
Paper sludge	36.1	62.3
Tailings	0.0	0.0
Oxidised waste	0.3	0.5
Waihi Subsoil	1.1	1.9
Fireclay	4.8	8.2
Mudstone	1.8	3.2
Huntly subsoil	0.5	0.9

In this study the Van Bemmelen factor of 1.724 was used to convert organic carbon to organic matter. Many studies have used a range of values for this factor indicating that it is at best only an approximation. Studies by Broadbent (1953) indicate that the factor for converting organic C to organic matter in surface soils is approximately 1.9, and that the factor for subsoils is about 2.5. Considerable variation exists in the carbon -to-organic matter ratio among different soils and also among horizons of the same soil (Allison, *et al.*, 1965). The values reported are therefore only estimates.

The sludges had high organic matter contents, Fireclay had a low organic matter content and the other spoils all had very low organic matter contents, according to New Zealand Soil Bureau ratings (Table 5.2).

The values obtained concur with other published data. Griebel *et al.* (1979) reported that sewage sludge is about 50% organic matter and Bayes *et al.*(1989) quoted an organic matter content of 43% for sewage sludge. Sopper (1992) reported that sewage sludge contains significant amounts of organic materials. Vasconcelos and Cabral (1993) reported that pulp mill sludge is characterised by a high level of organic matter. Waihi Gold Company (1985a) quoted very low values of organic matter in tailings and oxidised waste. Sopper (1992) reported that mine spoils lack organic matter.

5.1.2   Effect of amendments on the organic matter content of the mine spoils

Slightly less Manukau than North Shore sewage sludge was required to achieve a given organic matter content in the spoils. Considerably less paper sludge than North Shore sewage sludge was required to achieve a given organic matter content in the mine spoils. The greater effectiveness of Manukau sewage sludge and paper sludge compared to North Shore sewage sludge, at a given volume, is attributed to their higher organic matter contents.

5.1.3   Effect of the incubation on organic matter content

The percentage of organic carbon in each incubation was determined at the conclusion of the experiment. Organic matter contents of the incubations remained close to the initial values. There was no loss of organic matter, although there was some variation about the mean. The highest standard deviation was 1.27% and this was recorded for Waihi subsoil amended to 10% organic matter with Manukau sewage sludge.

There were no significant differences between the measured and predicted organic matter contents of the mixtures. The organic matter contents were predicted using Equation 4.6.

The largest deviation from the expected organic matter content was 2.6 and occurred in the Waihi subsoil amended to 10% with Manukau sewage sludge.

It is concluded that the incubation had no significant effect on organic matter in any incubation jar and that Equation 5.1 adequately predicted organic matter levels in prepared mixtures.

5.1.4 Explanation of the effects of sludge addition and incubation on the organic matter content of the mine spoils

The addition of sludge to the mine spoils not only increases their organic matter content but also their microbial population (Sundberg *et al.*, 1979; Seaker and Sopper, 1988b; Fresquez and Aldon, 1986). It was anticipated that this increased microbial activity would result in the breakdown of organic matter. However, the extremely low content of organic matter in all the mine spoils except fireclay precluded the measurement of any significant reduction in organic matter. The organic matter in fireclay is in the form of coal which is not readily broken down as coal is a condensed form of nearly elemental carbon (Allison *et al.*, 1965). The organic matter content of fireclay was hence unlikely to decline during the incubation due to microbial breakdown.

Given the high organic matter content of the sludges one may have expected some decomposition with a subsequent release of carbon dioxide and reduction in organic matter (Miller, 1974). This was not observed because the three sludges used were relatively stable products due to stabilising treatment at the processing plants from which they were sourced (section 3.3).

5.1.5 Implications for rehabilitation of the mine spoils

Soil organic matter includes (Allison *et al.*, 1965):
(i)   Fresh plant and animal residues capable of rapid decomposition and loss of identity, with simultaneous release of nutrient elements.

(ii)   Humus, which represents the vast bulk of resistant organic matter, having high adsorptive capacity for cations and capable of improving soil structure.

(iii)   Inert forms of nearly elemental C such as charcoal, coal, or graphite.

Organic matter stabilises soil structure, improves tilth and is active, along with clay minerals, in storing and releasing plant nutrients (Brady, 1984). It is particularly important in the plough layer because that is where the seed bed must be prepared and where many plant nutrients should be stored. The low infiltration rates and relatively unstable soil structure typical of low organic matter surface soils makes them susceptible to high runoff and high rates of water erosion.

Influence of soil organic matter on soil properties include (Brady, 1984):

1. Colour   Brown to black
2. Physical properties   Granulation encouraged
                                       Plasticity, cohesion reduced
                                       Water holding capacity increased.
3. High CEC   Two to thirty times as great as mineral
                                       colloids (weight basis)
4. Supply and availability of nutrients: Easily replaceable cations present

New Zealand Soil Bureau ratings for organic carbon and organic matter contents are given in Table 5.2. Based upon these values, increasing the organic matter content of a mine spoil to two percent is unlikely to have a significant effect upon spoil properties; however, beneficial additions of nutrients may be made. Increasing spoil organic matter to five percent is similarly unlikely to have a major impact. At ten percent organic matter some significant impact on spoil characteristics is expected.

Table 5.2   Ratings for organic carbon and organic matter

Organic C (%)*	Organic matter (%)	Rating*
<2	<3	Very low
2-4	3-7	Low
4-10	7-17	Medium
10-20	17-34	High
>20	>34	Very high

* From Blakemore, et al., 1987.

Greenland et al. (1975) suggested that non-calcareous soils with organic matter contents below 3.4% are likely to suffer structural deterioration whereas soils containing 4.3% or more are likely to be structurally stable. This indicates that increasing the organic matter content of spoils to five percent is expected to improve its structural stability.

If the pre-mining organic layer has been destroyed (as in the mine spoils), the only carbon source for microbial utilisation is the plant biomass that is expected to accumulate over several growing seasons on the site. Until such accumulation occurs, microbial activity remains at a low level, with little improvement of adverse soil physical and nutrient conditions.

Vegetation growth and maintenance are also inhibited. On sites reclaimed with chemical fertilisers and lime, vegetation may initially be established but poor physical conditions result in deterioration of the vegetative cover before it can begin to ameliorate the spoil (Stroo and Jenks, 1982). On both alkaline and acidic mine spoils, microbial activity, nutrient cycling, and spoil organic matter levels may take over thirty years to re establish (Segal and Mancinelli, 1987, Stroo and Jenks 1982, Mills 1985). A soil containing three percent organic matter contains approximately 75 t of organic matter over 1 ha to a plough depth of 150 mm. To increase this to four percent organic matter would take close to 100 years if 2 t/ha of crop residue were added annually (Cresser et al., 1993).

The amount of sludge required to apply in order to achieve two, five, or ten percent organic matter in each spoil, over one hectare, and to a depth of either 5, 10 or 15 cm, in one application is shown in Table 5.3.

Table 5.3   The amount of sludge(t/ha) required to provide the desired amount of organic matter in the mine spoils, to given depth

Sludge	Spoil	Organic matter (%)	5 cm depth	10 cm depth	15 cm depth
Manukau	Tailings	2	24.1	48.2	72.3
		5	65.2	130.3	195.5
		10	150.0	300.0	450.0
	Oxidised waste	2	18.2	36.3	54.5
		5	58.7	117.4	176.2
		10	142.7	285.3	428.0
	Waihi subsoil	2	3.6	7.3	10.9
		5	43.1	86.1	129.2
		10	124.6	249.2	373.9
North Shore sewage sludge	Tailings	2	25.7	51.4	77.2
		5	69.9	139.8	209.7
		10	162.7	325.4	488.2
	Oxidised waste	2	19.4	38.8	58.2
		5	63.0	126.0	189.0
		10	154.7	309.4	464.2
	Waihi subsoil	2	3.9	7.8	11.6
		5	45.7	91.3	137.0
		10	135.2	270.3	405.5
	Fireclay Mudstone	10	29.3	58.7	88.0
		5	25.2	50.4	75.7
		10	110.8	221.6	332.3
	Huntly subsoil	2	14.2	28.4	42.7
		5	57.4	114.9	172.3
		10	148.2	296.4	444.7
Paper sludge	Fireclay Mudstone	10	17.2	34.4	51.7
		5	15.7	31.3	47.0
		10	65.0	130.0	195.0
	Huntly subsoil	2	9.1	18.2	27.3
		5	35.8	71.6	107.3
		10	87.0	174.0	261.0

All other variables being equal between sludges, the lower organic matter content of North Shore sewage sludge will make it more expensive than either Manukau sewage sludge or paper sludge to apply to mine spoils as an organic matter amendment due to higher transport and spreading costs. Similarly Manukau sewage sludge would be more expensive than paper sludge. On the basis of the ratings by Blakemore *et al.* (1987), of the options assessed the most beneficial application rate of sludge to each mine spoil with regard only to organic matter, is that which achieves an organic matter content in the amended spoil of 10%, i.e. a medium value (and the highest value considered). The greater the depth of rooting medium with this organic matter content, the better.

5.2   pH

5.2.1   pH of the original materials

Table 5.4 gives the pH of the individual incubation materials.

Table 5.4
pH of the individual materials at the start and conclusion of the incubation experiment

Material	Initial pH	Final pH
Manukau sewage sludge	6.11	5.82
North Shore sewage sludge	6.39	5.75
Paper sludge	7.20	7.26
Tailings	7.93	7.80
Oxidised waste	3.86	3.13
Waihi subsoil	3.71	3.76
Fire clay	5.10	4.85
Mudstone	2.32	2.23
Huntly subsoil	3.75	3.71

The pH of paper sludge was considerably higher than the pH of either of the sewage sludges.

It was difficult to measure the pH of paper sludge because of its high moisture holding capacity; it formed a slurry with no supernatant. However, the pH reading of the slurry at a sludge:KCl ratio of 1:2.5 and 1:5 were not significantly different (<0.1) and the

latter was therefore assumed to be a comparable estimate of pH. Blakemore *et al.*(1987) stated that replicate determinations were expected to give results within 0.1 pH unit. All replicated results in this study were within 0.1 pH unit.

The high pH of paper sludge is attributable to the use of lime ($CaCO_3$) in the paper industry e.g. during sludge stabilisation (Simson *et al.*, 1988).

The high pH of the tailings reflects the addition of hydrated lime during processing of the ore (Waihi Gold Company, 1985b). Sodium cyanide is used in retrieval of gold from the ore and hydrated lime is used to maintain the cyanide solutions at a high pH to avoid the release of hydrogen cyanide gas (Macleod and Rouse, 1991).

Significant quantities of pyrite (FeS) frequently occur within coal measures and overburden. This results in high acid generating potential (Macleod and Rouse, 1991). The oxidation of pyrite in mine spoils commonly results in pH values below 3 (Pulford, 1991). The low pH of the oxidised waste may be explained by this phenomenon, however oxidation of most/all pyrite is expected to have occurred and further oxidation is unlikely (Senkay and Dixon, 1982).

5.2.2   Effect of amendments on the pH of mine spoils

Figures 5.1 to 5.4 show the effect on pH of ameliorating mine spoils with a sludge and Table 5.5 shows the effect of sludge addition to provide 10% organic matter, on the pH of the mine spoils.
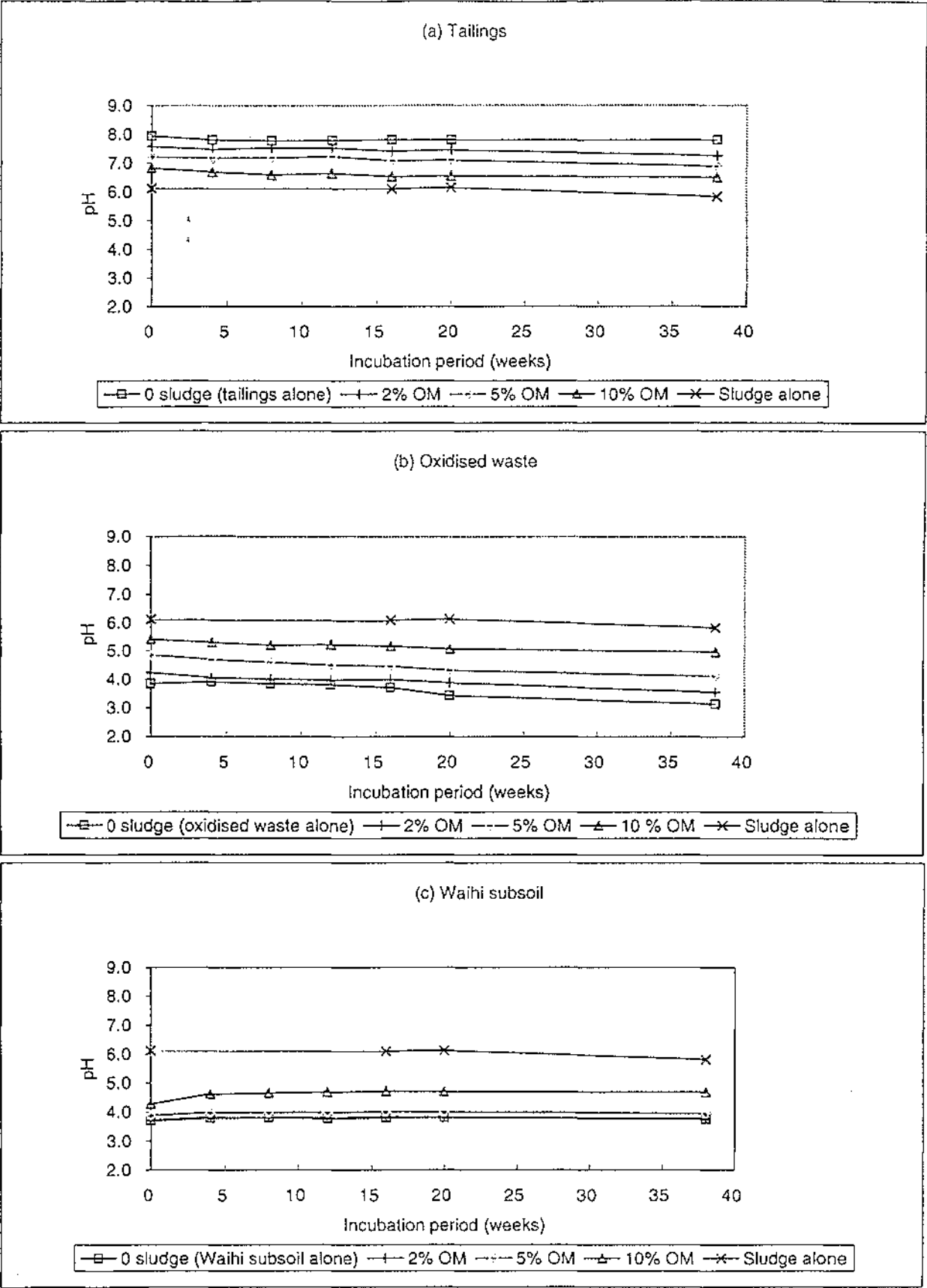
Figure 5.1   Effect of Manukau sewage sludge addition
to provide specified organic matter content
(OM) on the pH of gold mine spoils

(a) Tailings

—□— 0 sludge (tailings alone) —+— 2% OM —◇— 5% OM —·—10% OM —✕— Sludge alone

(b) Oxidised waste

—□— 0 sludge (oxidised waste alone) —+— 2% OM —◇— 5% OM ——— 10% OM —✕— Sludge alone

(c) Waihi subsoil

—□— 0 sludge (Waihi subsoil alone) —+— 2% OM —◇— 5% OM —·— 10% OM —✕— Sludge alone
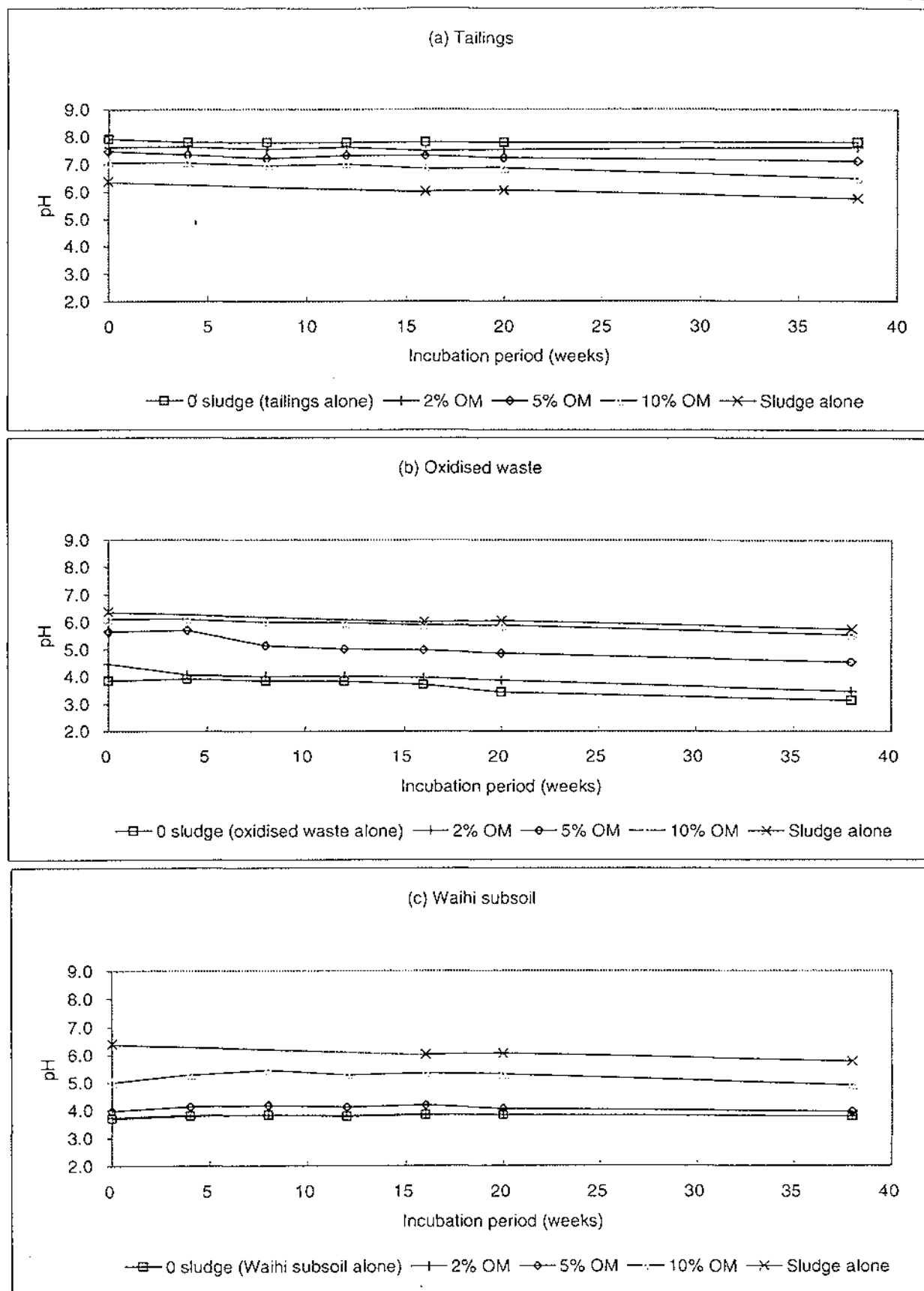
Figure 5.2   Effect of North Shore sewage sludge addition to provide specified organic matter (OM) content on the pH of gold mine spoils

(a) Fireclay

(b) Mudstone

(c) Huntly subsoil
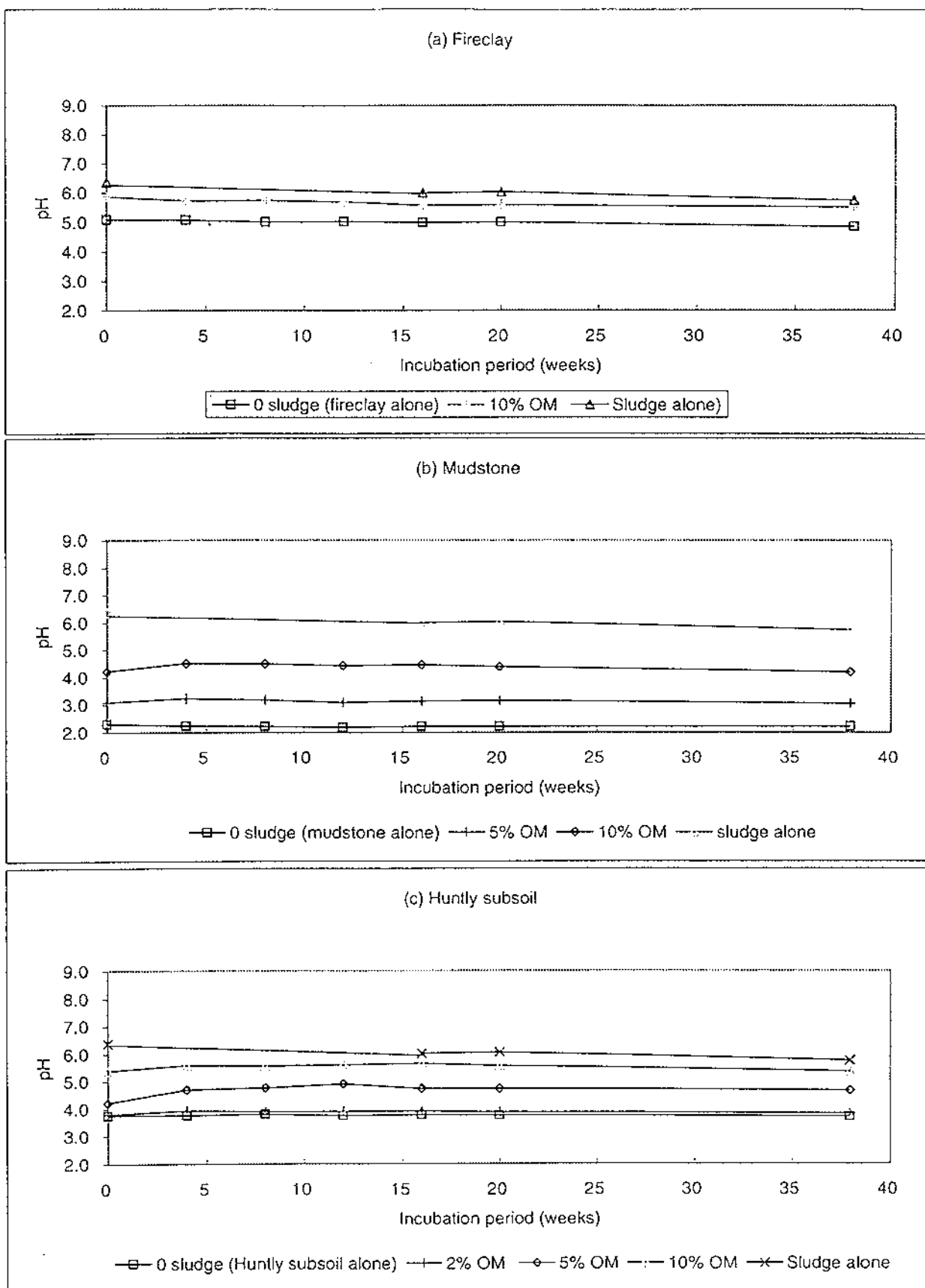
Figure 5.3   Effect of North Shore sewage sludge addition to provide specified organic matter (OM) content on the pH of coal mine spoils

(a) Fireclay

pH vs Incubation period (weeks)

Legend: —□— 0 sludge (fireclay alone) —◇— 10% OM —✕— Sludge alone

(b) Mudstone

pH vs Incubation period (weeks)

Legend: —□— 0 sludge (mudstone alone) —+— 5% OM —◇— 10% OM —··— sludge alone

(c) Huntly subsoil

pH vs Incubation period (weeks)

Legend: —□— 0 sludge (Huntly subsoil alone) —+— 2% OM —◇— 5% OM —··— 10% OM —✕— Sludge alone
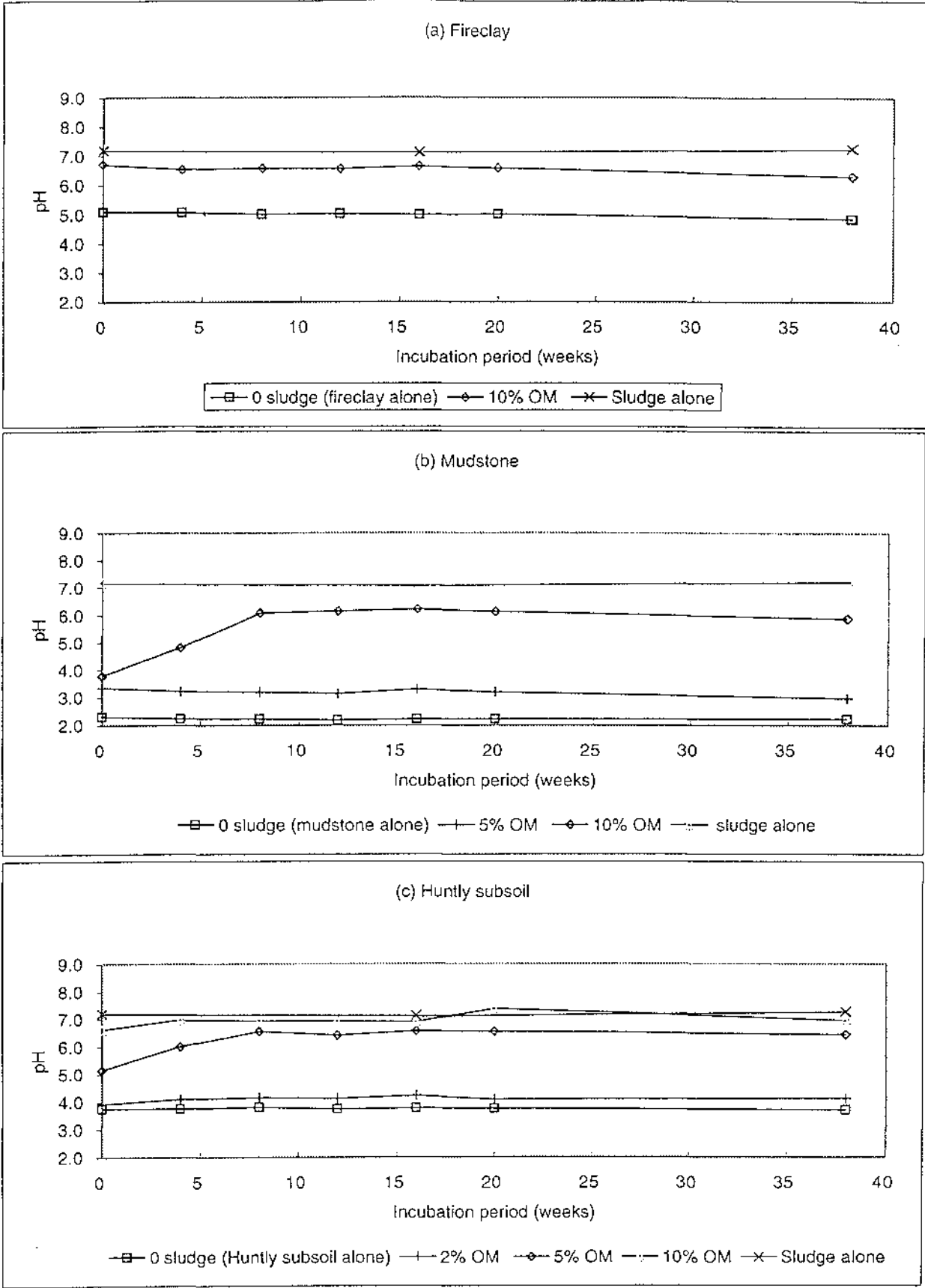
Figure 5.4   Effect of paper sludge addition to provide specified organic matter (OM) content on the pH of coal mine spoils

Table 5.5

The effect of sludge addition to provide 10 percent organic matter on the pH in the mine spoils

Sludge amendment	Amended spoil	Change in pH after addition of sludge
Manukau	Tailings	-1.12
	Oxidised waste	+1.55
	Waihi subsoil	+0.58
North Shore sewage sludge	Tailings	-0.87
	Oxidised waste	+2.24
	Waihi subsoil	+1.29
	Fireclay	+0.77
	Mudstone	+1.90
	Huntly subsoil	+1.61
Paper sludge	Fireclay	+1.62
	Mudstone	+1.47
	Huntly subsoil	+2.87

5.2.2.1   Manukau and North Shore sewage sludges

All levels of addition of Manukau and North Shore sewage sludge resulted in a reduction in the pH of tailings. The larger the quantity of sludge addition, the greater the reduction in pH bringing it closer to the pH of the sludge. When the sewage sludges were applied to either oxidised waste or Waihi subsoil, the pH of the mine spoil was increased. Successive increases in sludge addition resulted in an increase in pH, and similar to tailings, it became closer to the pH of the ameliorant.

The pH of Waihi subsoil appeared to be less affected by the addition of sewage sludge than the tailings and oxidised waste. This may be explained by a lower quantity of sludge being applied to this spoil to raise its organic matter content. Further, Waihi subsoil may have a greater pH buffering capacity than the tailings or oxidised waste. This may also explain why its pH was less affected by incubation period than the other gold mine spoils (Section 5.2.3).

North Shore sewage sludge had a greater effect on the pH of the mine spoils than Manukau sewage sludge, with the exception of tailings, where the effect was less. This

is due to the higher pH of the former. North Shore sewage sludge produced similar trends in the coal mine spoils as it did in the gold mine spoils (Figure 5.3).

5.2.2.2 *Paper sludge*

Paper sludge had a greater effect on the pH of the coal mine spoils than the North Shore sewage sludge due to its higher pH. It consistently produced a pH around one pH unit higher in the spoils than that produced when North Shore sludge was applied (Figure 5.4).

5.2.3 Effect of the incubation on pH

The pH of the sludge amended spoils remained fairly constant during the 38 week incubation with a general trend in the sewage sludge amended spoils to a slight reduction in pH during time (Tables 5.6 a and b and Figures 5.1 to 5.4).

The reduction in the pH may be attributed to the release of acid during the breakdown of organic matter and concurrent nitrification reactions producing organic acid (Peterson *et al.*, 1982). This was not evidenced by a significant reduction in organic matter (section 5.1), however slight reductions in organic matter content may have occurred that were not measured with the technique used in this study. In the case of paper sludge, any release of acid may have been neutralised by free $CaCO_3$.

Table 5.6a

Effect of time on the pH of the unamended mine spoil and sludge materials

Material	Initial pH	final pH	Change in pH
Tailings	7.93	7.80	-0.13*
Oxidised waste	3.86	3.13	-0.73*
Waihi subsoil	3.71	3.76	+0.05 NS
Fireclay	5.10	4.85	-0.25
Mudstone	2.32	2.23	-0.09 NS
Huntly subsoil	3.75	3.71	-0.04 NS
Manukau sewage sludge	6.11	5.82	-0.29*
North Shore sewage sludge	6.39	5.75	-0.64*
Paper sludge	7.20	7.26	-0.06 NS

Table 5.6b

Effect of time on the pH of spoils amended to 10% organic matter

Sludge amendment	Amended spoil	Initial pH	Final pH	Change in pH
Manukau	Tailings	6.81	6.49	-0.32*
	Oxidised waste	5.41	4.98	-0.46*
	Waihi subsoil	4.29	4.68	+0.39*
North Shore	Tailings	7.06	6.50	-0.56*
	Oxidised waste	6.10	5.54	-0.56*
	Waihi subsoil	5.00	4.91	-0.09*
	Fireclay	5.87	5.51	-0.36*
	Mudstone	4.22	4.20	-0.02 NS
	Huntly subsoil	5.36	5.36	0 NS
Paper	Fireclay	6.72	6.30	-0.42*
	Mudstone	3.79	5.87	+2.08*
	Huntly subsoil	6.62	6.96	+0.34*

*= Significant difference at 5% level   NS= Not significant.

5.2.4   Explanation of the effects of sludge addition and incubation on the pH of the mine spoils

The addition of sludges tends to buffer the pH of the mine spoils, resulting in the pH of the amended spoil coming closer to the pH of the sludge amendment. This effect is commonly reported by other authors (Sopper and Seaker, 1990; Sopper and Kerr, 1982; Sutton and Vimmerstedt; 1974, Haghiri and Sutton, 1982).

Paper sludge had a pH consistently higher than North Shore throughout the incubation. The difference became greater during the incubation due to the reduction in pH of North Shore sewage sludge.

Manukau had a pH closer to that of oxidised waste and Waihi subsoil than North Shore sewage sludge. The effect of Manukau sewage sludge on the pH of these materials was hence less than that of North Shore sludge. Similarly, the pH of North Shore sewage sludge was more similar to the pH of tailings than Manukau sewage sludge and hence it caused less pH change of this spoil than did Manukau sewage sludge.

The greater the difference in pH between a sludge amendment and mine spoil, the greater the effect on pH when the sludge was applied to the mine spoil.

5.2.5 Measured compared to predicted pH

Table 5.7 presents the results of the test undertaken to assess whether the pH of the mixtures could be predicted from the pH of the individual samples using equation 4.6. The data indicated that the pH is affected by the quantity of material present in the suspension used for pH measurement

Table 5.7

The pH of various ratios of solid material to KCl

Material	Quantity of material (g dry matter) in 12.5 ml of KCl	Measured pH
Tailings	1.0	8.16
	2.5	7.98
	4.0	7.95
	5.0	7.93
Mudstone	1.0	2.71
	2.5	2.42
	4.0	2.38
	5.0	2.32
Paper sludge	1.0	7.43
	2.5	7.29
	5.0	7.20
Manukau sewage sludge	1.0	6.36
	2.5	6.32
	5.0	6.11

The pH of a mixture is not a linear function of the pH values of the individual materials making up that mixture. Regression is not valid as pH is not an additive property, the change in pH recorded for a material when the ratio of the material to the solution was increased was less than that predicted; i.e., one would expect a two fold increase in the pH reading for a material when the quantity of that material in the solution is doubled. This less than predicted change in the pH of the soil solution is known as pH buffering, i.e., the solution resists changes in pH upon addition of a

certain amount of acid (pH) or base (OH-) (Evangelou and Sobek, 1988). Removal from, or addition of hydrogen ions in the soil solution results in their being largely replenished from or adsorbed on to the micelle. The higher the exchange capacity, of a soil material, the greater will be its buffer capacity, other factors being equal (Brady, 1984).

5.2.6 Implications for rehabilitation of the mine spoils

The New Zealand Soil Bureau (Blakemore *et al.*, 1987) uses the following ratings for pH of New Zealand soils:

Very high	pH >9.0 (extremely alkaline)
	8.4-9.0 (strongly alkaline)
	7.6-8.3 (moderately alkaline)
High	7.1-7.5 (slightly alkaline)
	6.6-7.0 (near neutral)
Medium	6.0-6.5 (slightly acid)
	5.3-5.9 (moderately acid)
Low	4.5-5.2 (strongly acid)
Very low	<4.5 (extremely acid)

The pH in unlimed topsoils in New Zealand is in the range 4.5 to over 6.0, except for peats which may be very acidic with pH 3.5-3.8 (During, 1984).

An indication of the significance of soil pH values for various crops is given in Cresser *et al.* (1993):

pH range	Crop and soil responses
<5.0	Possible failure of all crops
5.0-5.4	Possible failure of barley, oilseed rape, peas and beans
5.5-5.9	More sensitive crops may suffer from acidity symptoms
6.0-6.5	Suitable for most arable crops. Trace element problems may arise at the higher values
>6.5	Trace element deficiencies likely on many soils

Note: Grasses are more tolerant of low pH than are legumes

According to the above criteria, the oxidised waste, Waihi subsoil, mudstone, fireclay and Huntly subsoil have acidic pH values and do not provide a favourable medium for plant growth. These spoils are likely to have problems associated with deficiency of basic cations and toxicity of heavy metals, especially aluminium (Al) and manganese (Mn) (Berg and Vogel, 1973; Beyer and Hutnik, 1969; Fleming et al., 1974). Organic matter decomposes more rapidly in neutral than in acid soils. A low soil pH therefore reduces the mineralisation of organic matter and the subsequent availability of N, P, S and micronutrients (Kamprath and Foy 1971).

Normally P is most readily available to plants in the pH range of 6.5 to 7 (Tucker et al., 1987). Under acid conditions, much of the P is strongly adsorbed by hydrous oxides of Al and Fe (Cresser et al., 1993) and the solubility of P in these compounds decreases as pH decreases (Lindsay, 1979). Sulphur tends to behave similarly to P in acid conditions and the availability of sulphur falls with decreasing pH (Germida, et al., 1992) (Figure 5.5). The solubility of potentially toxic metallic ions increases rapidly as acidity increases (Lindsay, 1979).

Awad et al., (1989) stated that soils which can best retain heavy metals are those with a pH above 6 and an organic matter content of at least 10%. Soil pH levels less than about pH 5 to 5.5 present potential toxicity risks for agronomic species, particularly related to Al and Mn. However the soil pH at which Al becomes soluble in toxic concentrations varies with soils depending upon clay mineralogy and organic matter content (Tucker et al., 1987) and soils high in organic matter have lower critical pH levels than soils low in organic matter (Foy, 1974). Fuller (1977) reports that in acidic soils (pH 4.2 to 6.6) cadmium (Cd), mercury (Hg), nickel (Ni) and zinc (Zn) are relatively mobile, arsenic (As) and chromium (Cr) are slowly mobile.

Tailings have a high pH which may result in the deficiency of some trace elements e.g. Fe, Zn and Cu (Tucker et al., 1987). P availability may be restricted slightly as the optimum range is 6 to 7.5 (Tucker et al., 1987). The presence of free $CaCO_3$ in the tailings is likely to cause the precipitation of phosphate.

Copper is an essential trace element for plants and animals and its availability decreases when the pH exceeds 6 (Tucker et al., 1987). However, the availability of Cu in tailings was relatively high compared with the other spoils (Table 5.22).

The sewage sludges have a pH close to the pH ideal for most plant growth, and paper sludge is alkaline, likely to result in trace element deficiencies if maintained at that pH. New Zealand. public health guidelines (Department of Health, 1992) state that soil receiving a sewage sludge with a high heavy metal content should have a pH greater than or equal to 5 to reduce the availability of heavy metals to crops and leaching from the soil. The American Resource and Recovery Act of 1976 and the Clean Water Act of 1977 (Federal Register, 1979) require that, with regard to Cd additions to crop land, the pH of the soil must be greater than or equal to 6.5 at the time of sludge application. This requirement would exclude all but the tailings from amendment with the sewage sludge (however it is unlikely that the spoils can be considered crop land).

Addition of sludge to the spoils buffers the pH, resulting in a pH closer to the pH of the sludges. Addition of Manukau sewage sludge to tailings brings their pH to a value ideal for plant growth at 10% organic matter addition. Oxidised waste remains slightly acidic and Waihi subsoil is likely to present problems related to acidity for rehabilitation at all levels of sludge addition trialled. Lime remediation is hence required. Tailings amended with North Shore sewage sludge even at 10% organic matter will have an alkaline pH, however the oxidised waste amended to provide 10% organic matter is in the ideal range and Waihi subsoil is likely to require some remediation with lime. The coal mine spoils also remained rather acid and are likely to require remediation with lime. However, when amended with paper sludge to provide 10% organic matter, the pH of fireclay and Huntly subsoil were raised to a level ideal for rehabilitation but mudstone remained acidic and will require further amendment with lime.

For all spoils, amendment to provide 10% organic matter with sludge was the most ideal treatment with respect to pH. Therefore, to achieve ideal pH values by addition of sludge only, the sludge addition should be aimed to achieve at least a 10% organic matter level.

Finally, the pH of a growing medium is a valuable parameter to monitor reclamation efforts at mine sites. If unexpected shifts in pH occur, then it is likely that other changes may be occurring in the medium. Similarly, if pH remains stable, many other soil characteristics are also relatively stable (Tucker *et al.*, 1987). pH is hence discussed with respect to the other parameters that have been studied.

Figure 5.5

Relationship between mineral soil pH and nutrient availability (Brady, 1984)
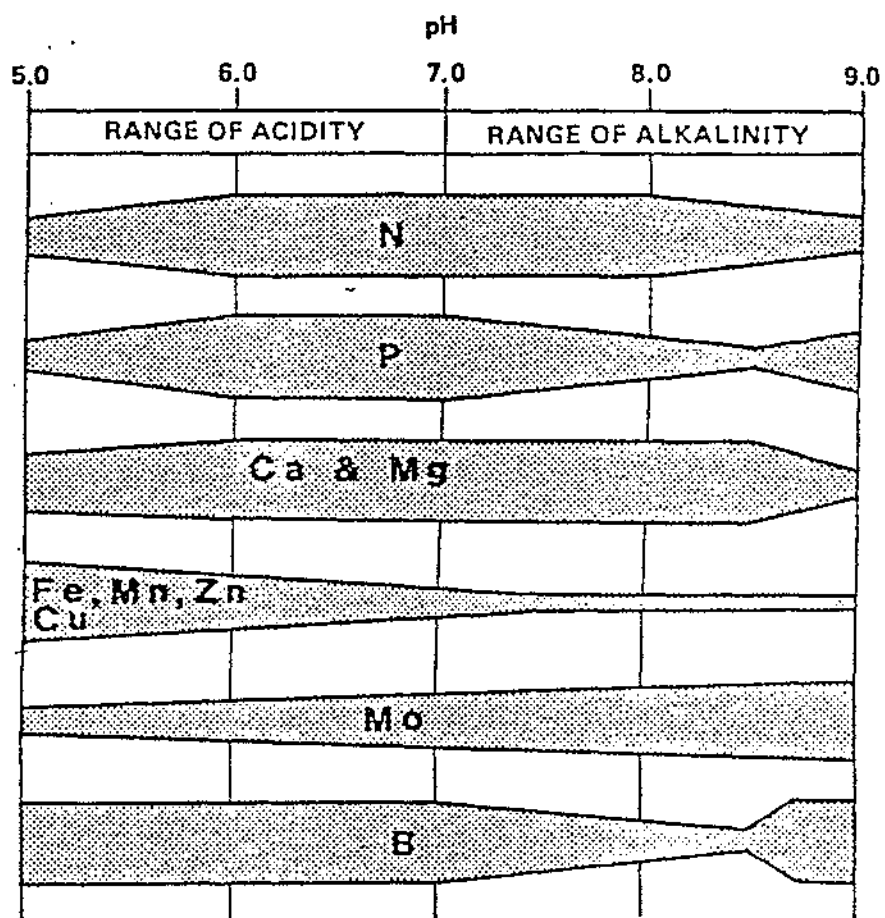
5.3   ELECTRICAL CONDUCTIVITY

5.3.1   Electrical conductivity of the original materials

The New Zealand Soil Bureau uses the following ratings for the electrical conductivity (EC) of New Zealand soils (Blakemore *et al.*, 1987):

>2000 µS/cm	Very high
800-2000	High
400-800	Medium
150-400	Low
<150	Very low

Based on Soil Bureau ratings, Manukau sewage sludge had a very high value for EC, North Shore sewage sludge had a high value and paper sludge had a medium value (Table 5.8). This is similar to the EC values reported for other sewage sludges (Bellamy et al, 1995; Sopper, 1992) and paper sludges (Feagley et al, 1994; Del Rosario, 1980). Sludges are a by-product of waste water purification works and hence are high in soluble salts removed as contaminants from the waste water (Auckland Regional Authority, 1989), hence the high EC of these sludges.

Tailings and mudstone had medium values for EC, oxidised waste had a low value and Waihi subsoil, fireclay and Huntly subsoil had very low values (Table 5.8).

Table 5.8
Electrical conductivity of the unamended mine spoil and sludge materials

Material	EC (µS/cm)	
	Initial	Final
Manukau sewage sludge	3307	4299
North Shore sewage sludge	1760	3427
Paper sludge	469	511
Tailings	411	467
Oxidised waste	261	1645
Waihi subsoil	60	61
Fireclay	133	148
Mudstone	672	1689
Huntly subsoil	72	98

EC values in mine soils/spoils are commonly lower than sludges used as amendments (Del Rosario, 1980; Feagley et al, 1994; Topper and Sabey, 1986). However, the EC value depends on the nature of mine spoils and waste materials used as amendments (Schneider et al, 1981; Lejcher and Kunkle, 1973).

5.3.2 Effect of amendments on the electrical conductivity of the mine spoils

Table 5.9 gives the values for EC in the amended spoils.

Table 5.9
The effect of sludge addition to provide desired organic matter values on the electrical conductivity of the minespoils initially and at the conclusion of the incubation

Sludge	Spoil	Organic matter (%)	EC at start of incubation (μS/cm)	EC at conclusion of incubation (μS/cm)
Manukau sewage	Tailings	2	1387	1608
		5	1707	1969
		10	2187	2393
	Oxidised waste	2	544	1720
		5	1067	1826
		10	1707	2318
	Waihi subsoil	2	107	80
		5	427	548
		10	1067	1439
North Shore	Tailings	2	491	642
		5	869	1146
		10	1003	1259
	Oxidised waste	2	427	1788
		5	597	1782
		10	816	1589
	Waihi subsoil	2	69	83
		5	155	374

		10	411	978
	Fireclay	10	256	474
	Mudstone	5	581	1047
		10	923	1813
	Huntly	2	149	212
	subsoil	5	277	623
		10	555	1209
Paper	Fireclay	10	197	196
	Mudstone	5	432	754
		10	432	1358
	Huntly	2	107	75
	subsoil	5	117	268
		10	443	312

5.3.2.1 Manukau sewage sludge

Manukau sewage sludge had a greater effect on the EC of the gold mine spoils than North Shore sewage sludge and increasing the rate of sludge addition, increased the EC in the gold mine spoils. Tailings ameliorated with Manukau sewage sludge had high to very high EC values. With increasing sludge addition the amended oxidised waste had medium to high EC values and Waihi subsoil EC values were very low at 2% organic matter (and not significantly different from the unamended spoil or the 5% organic matter value), increasing to a high value at 10% organic matter (Figure 5.6).

5.3.2.2 North Shore sewage sludge

When North Shore sewage sludge was applied to tailings, the EC value increased from a medium value at 2% organic matter to a high value at 10% organic matter; although there was no significant difference between the 5 and 10% organic matter treatments. There was no significant difference in EC values between any of the North Shore treatments of oxidised waste. In Waihi subsoil, values increased from very low to medium with increasing sludge application; however, similar to when Manukau sewage sludge was applied, there was no significant difference in EC values between the 2 and 5% levels of sludge addition (Figure 5.7).

The EC of fireclay was increased to a low value (from very low) with sludge addition; the EC value of mudstone at 5% organic matter was lower than the unamended spoil but it had a high value at 10% organic matter. In Huntly subsoil, the EC value was

increased with sludge addition, it was very low at 2% organic matter, increasing with sludge addition to a high value at 10% organic matter (Figure 5.8).

5.3.2.3   *Paper sludge*

Paper sludge had less effect on the EC values of the coal mine spoils than the sewage sludge. The EC of amended fireclay was low and in the case of mudstone the EC was lower than the unamended spoil at 5 and 10% organic matter (EC values at 5 and 10% organic matter were the same). In amended Huntly subsoil, EC values were very low at 2 and 5% organic matter and medium at 10% organic matter. The EC of the spoil increased with increasing sludge addition (Figure 5.9).

(a) Tailings

—□— 0 sludge (tailings alone) —+— 2% OM —◇— 5% OM —△— 10% OM —✕— Sludge alone

(b) Oxidised waste

—□— 0 sludge (oxidised waste alone) —+— 2% OM ——— 5% OM —△— 10% OM —✕— Sludge alone

(c) Waihi subsoil

—□— 0 sludge (Waihi subsoil alone) —+— 2% OM ——— 5% OM —△— 10% OM —✕— Sludge alone
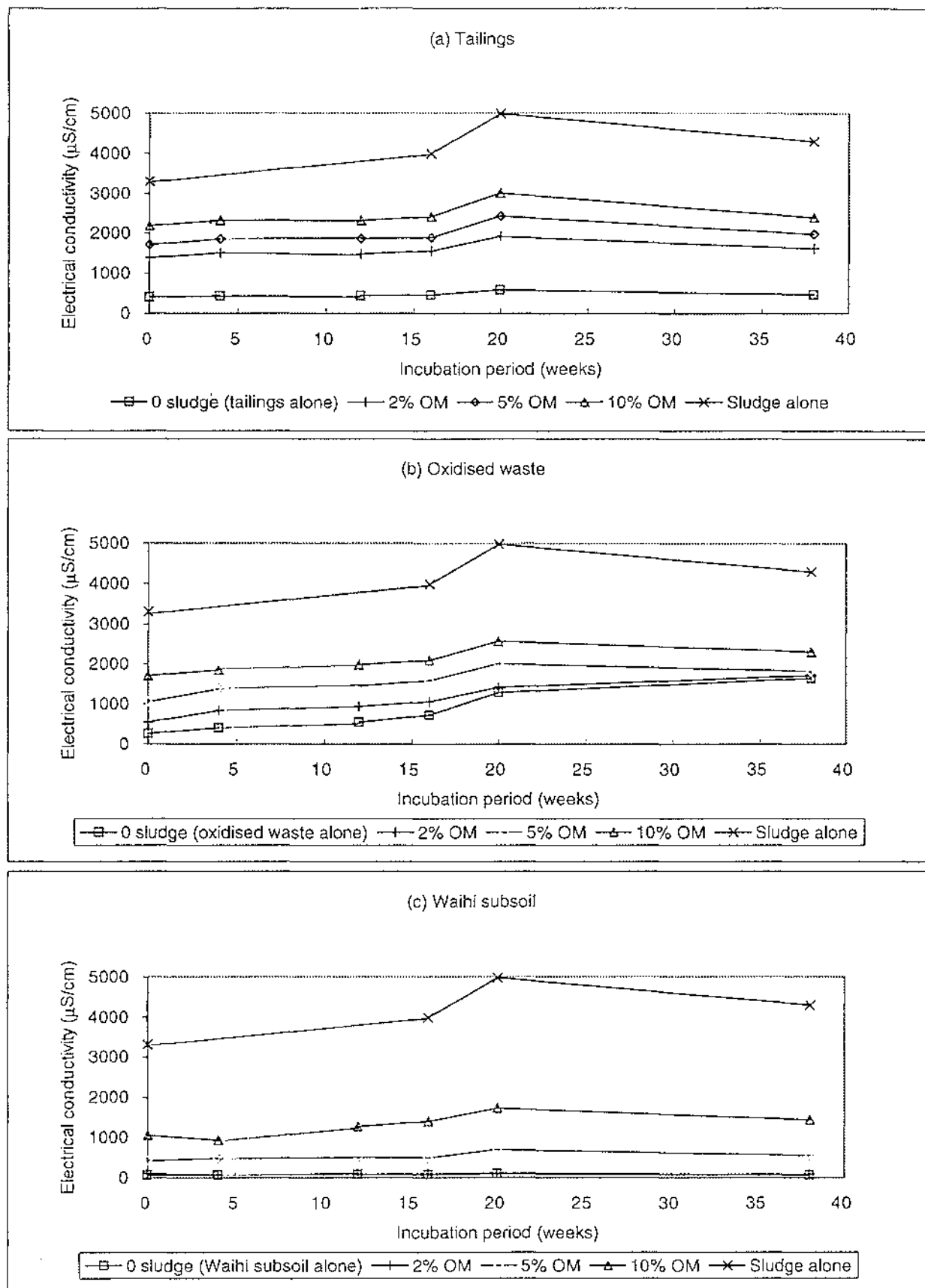
Figure 5.6   Effect of Manukau sewage sludge addition to provide
specified organic matter (OM) content on the
electrical conductivity of gold mine spoils

(a) Tailings

(b) Oxidised waste

(c) Waihi subsoil
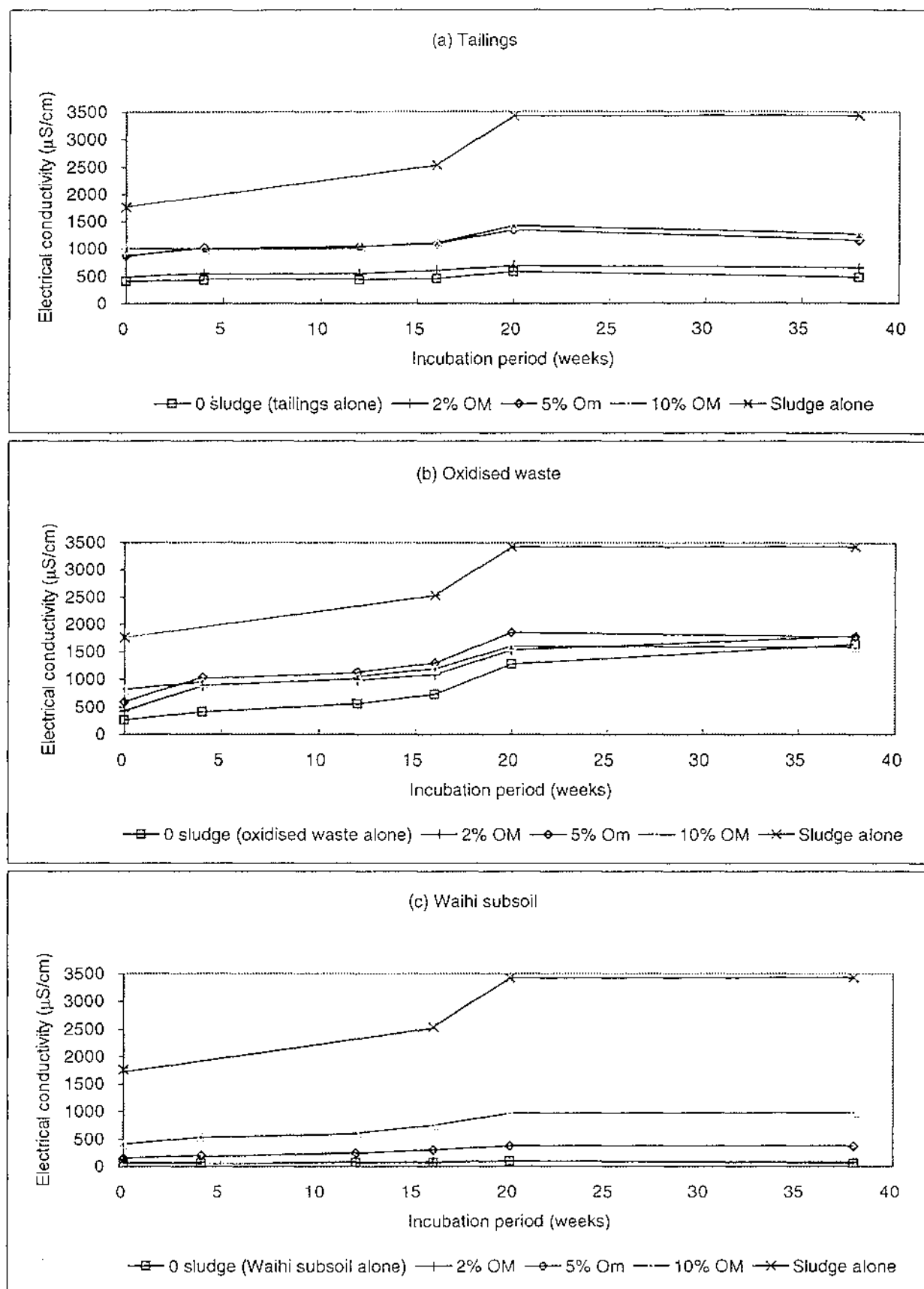
Figure 5.7 Effect of North Shore sewage sludge addition to provide specified organic matter (OM) content on the electrical conductivity of gold mine spoils

(a) Fireclay

—▣— 0 sludge (fireclay only) —+— 10%OM —·—·— Sludge alone

(b) Mudstone

—▣— 0 sludge (mudstone alone) —+— 5% OM —◇— 10% OM —·—· Sludge alone

(c) Huntly subsoil

—▣— 0 sludge (Huntly subsoil alone) —+— 2% OM —◇— 5% OM —·—· 10% OM —✕— Sludge alone
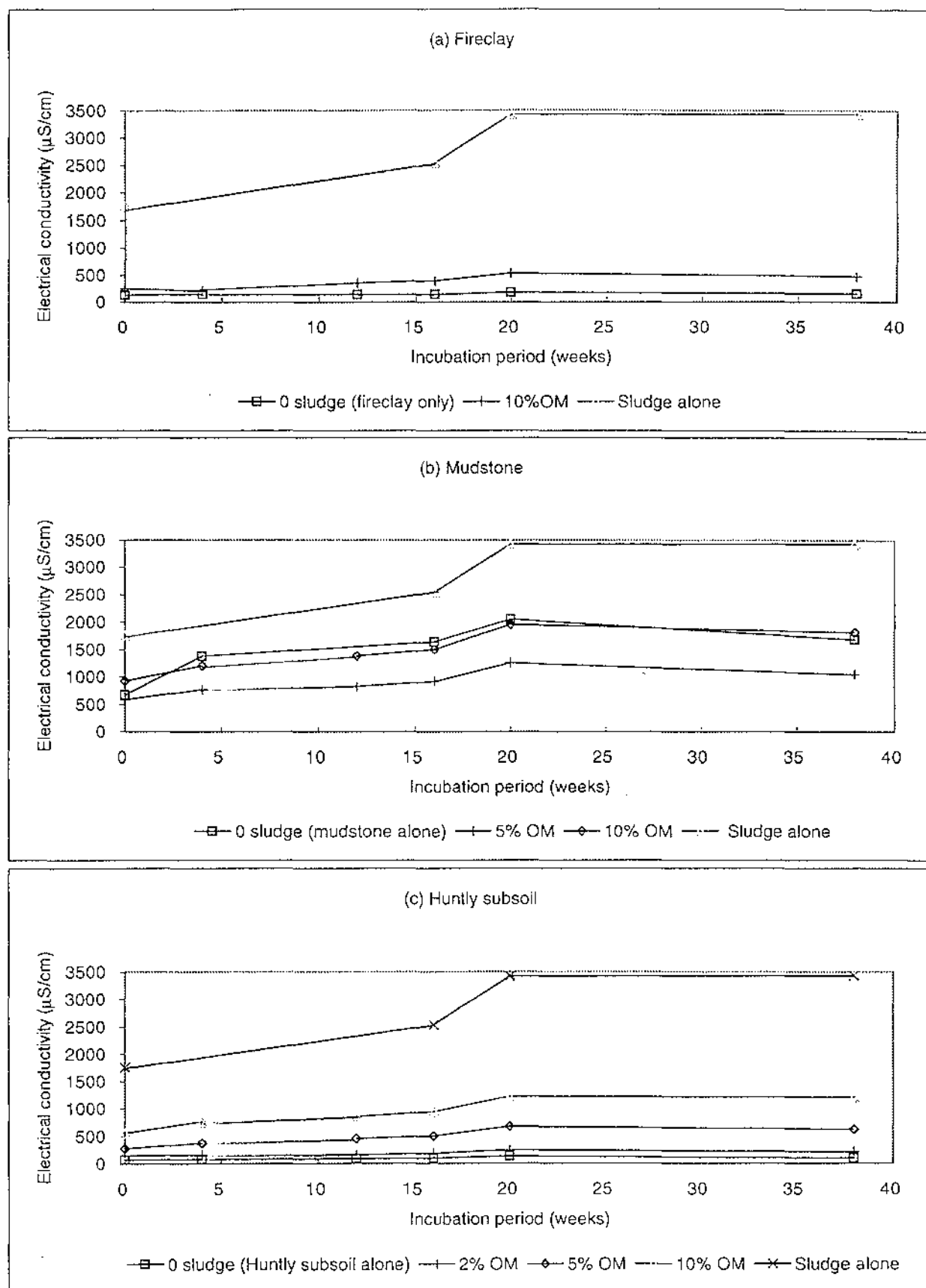
Figure 5.8   Effect   of   North   Shore   sewage   sludge   addition   to
              provide   specified   organic   matter   (OM)   content   on
              the   electrical   conductivity   of   the   coal   mine   spoils

(a) Fireclay

(b) Mudstone

(c) Huntly subsoil
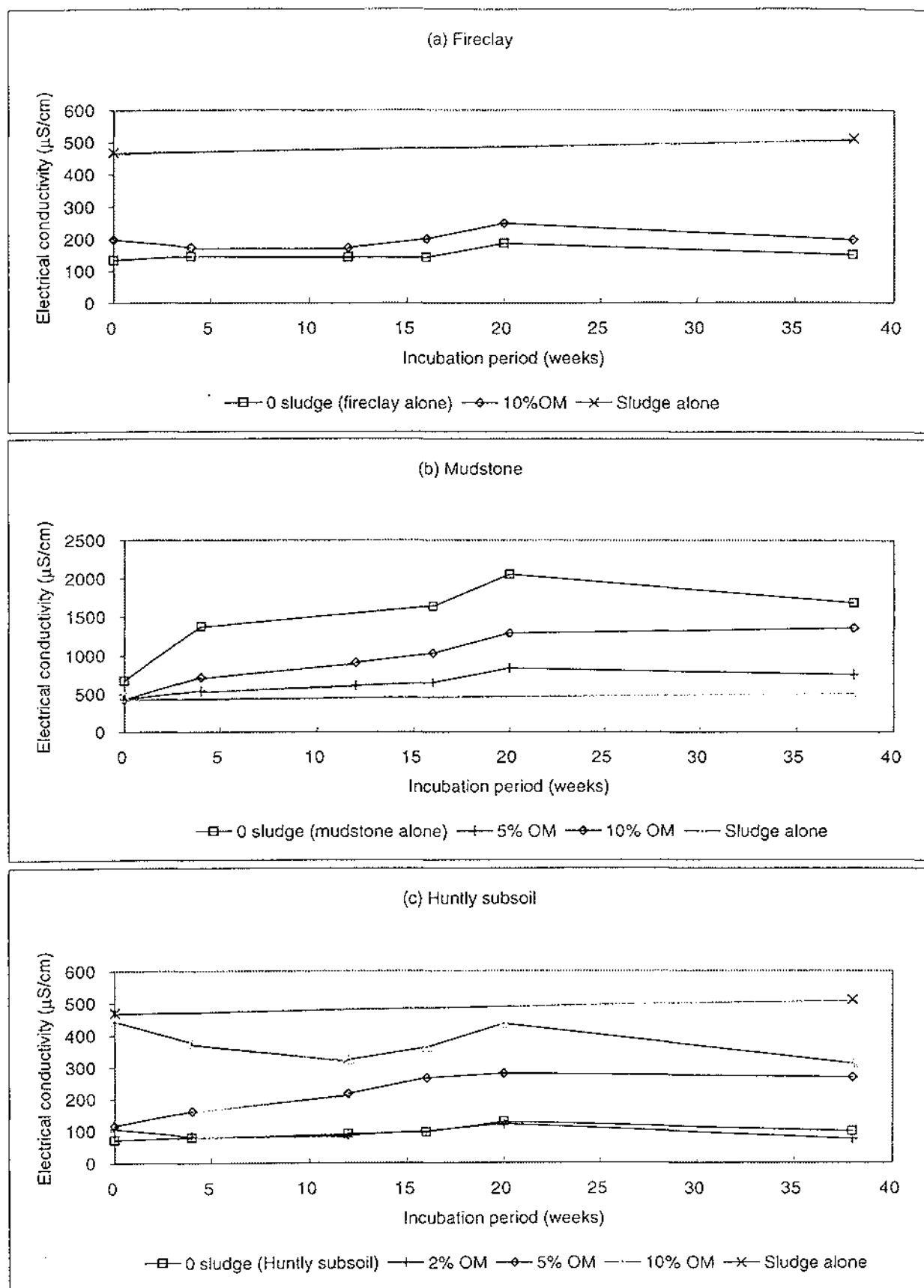
Figure 5.9   Effect of paper sludge addition to provide specified organic matter (OM) content on the electrical conductivity of coal mine spoils

5.3.3 Effect of the incubation on electrical conductivity

The EC of most of the amended mine spoils increased during time except in Huntly subsoil amended with paper sludge to achieve 2 and 10% organic matter and Waihi subsoil amended to 2% organic matter amended with Manukau sewage sludge (Table 5.9).

The EC of Manukau sewage increased up to week 20 and a decline occurred between then and the conclusion of the incubation. The final EC value was, however significantly higher than initial value (Figure 5.6). North Shore sewage sludge followed a similar trend but difference in EC values was not significant between the week 20 and week 38 incubation periods (Figure 5.7 and 5.8). The EC of paper sludge at the end of the incubation was not significantly different from the initial value (Figure 5.9). The EC of tailings, Waihi subsoil, fireclay and Huntly subsoil did not change significantly during the incubation. The EC of oxidised waste increased at each sampling and was a high value at week 38. The EC of mudstone increased with sampling time until week 20, between week 20 and 38 it declined slightly but still remained high.

Over all spoil treatments there was a trend to increasing EC up to week 20 and between then and week 38 little change and often a slight decline occurred (Figures 5.6 to 5.9).

When Manukau sewage sludge was applied to tailings and oxidised waste, the EC increased to week 20 then declined slightly in all treatments. At the end of the incubation, there was no significant difference in EC between unamended oxidised waste and oxidised waste amended to 2 and 5% organic matter with Manukau sewage sludge. The EC of oxidised waste at 2% organic matter increased to a high value by the end of the incubation and at 10% organic matter attained a very high EC value (Figure 5.6). A similar trend occurred when North Shore sewage sludge was applied but the increase was not as large in tailings and there was no significant difference between the 5 and 10% organic matter treatments from week 4. Similarly, there was no difference in EC between unamended oxidised waste and any of the North Shore treatments at the conclusion of the incubation, all values were high.

The change in EC of amended Waihi subsoil during time followed generally the change in EC during time of the sludge amendment. At 10% organic matter with either sewage sludge, Waihi subsoil had a high EC value at the conclusion of the incubation.

The EC mudstone amended with North Shore sewage sludge increased up to week 20 and then declined slightly. When amended with paper sludge the EC increased up to week 20 and then stabilised. At week 4 and subsequently, the EC of mudstone amended to 10% organic matter was higher than the EC of mudstone amended to 5% organic matter even though the unamended spoil had the highest EC value.

When fireclay was amended to 10% organic matter with North Shore sewage sludge, the EC was significantly higher throughout the incubation than the fireclay alone or the paper sludge amended fireclay, and attained a medium value by the conclusion of the incubation. The EC of fireclay amended with paper sludge was not significantly different from the unamended spoil and did not significantly change during the incubation. The EC of Huntly subsoil amended with North Shore sewage sludge increased in a similar way through the incubation as did the sludge and at 10% organic matter the EC was high at the conclusion of the incubation. Amended with paper sludge, there was no significant difference in EC between the spoil and 2% organic matter treatment from week 4 and the EC values of the two incubations increased up to week 20 and then stabilised. The EC at the conclusion of the incubation was lower than at the start for Huntly subsoil amended with paper sludge to 2 and 10% organic matter.

5.3.4   Measured compared to predicted electrical conductivity

The EC values of the mine spoils amended with sludge samples were predicted using Equation 4.6. The initial and the final measured EC values were generally higher than the predicted EC values; i.e. measured (or actual) EC was generally underestimated by equation 4.6 especially at higher EC values (Figure 5.10). This was especially so at the start of the incubation and indicates that an interaction occurred between the sludges and spoils when they were mixed resulting in a release of soluble salts, mostly from the sewage sludge. Generally the larger the sludge addition, the greater deviation between the measured and the predicted EC values indicating the difference was due to an effect of the EC in the sludge rather than the spoil.
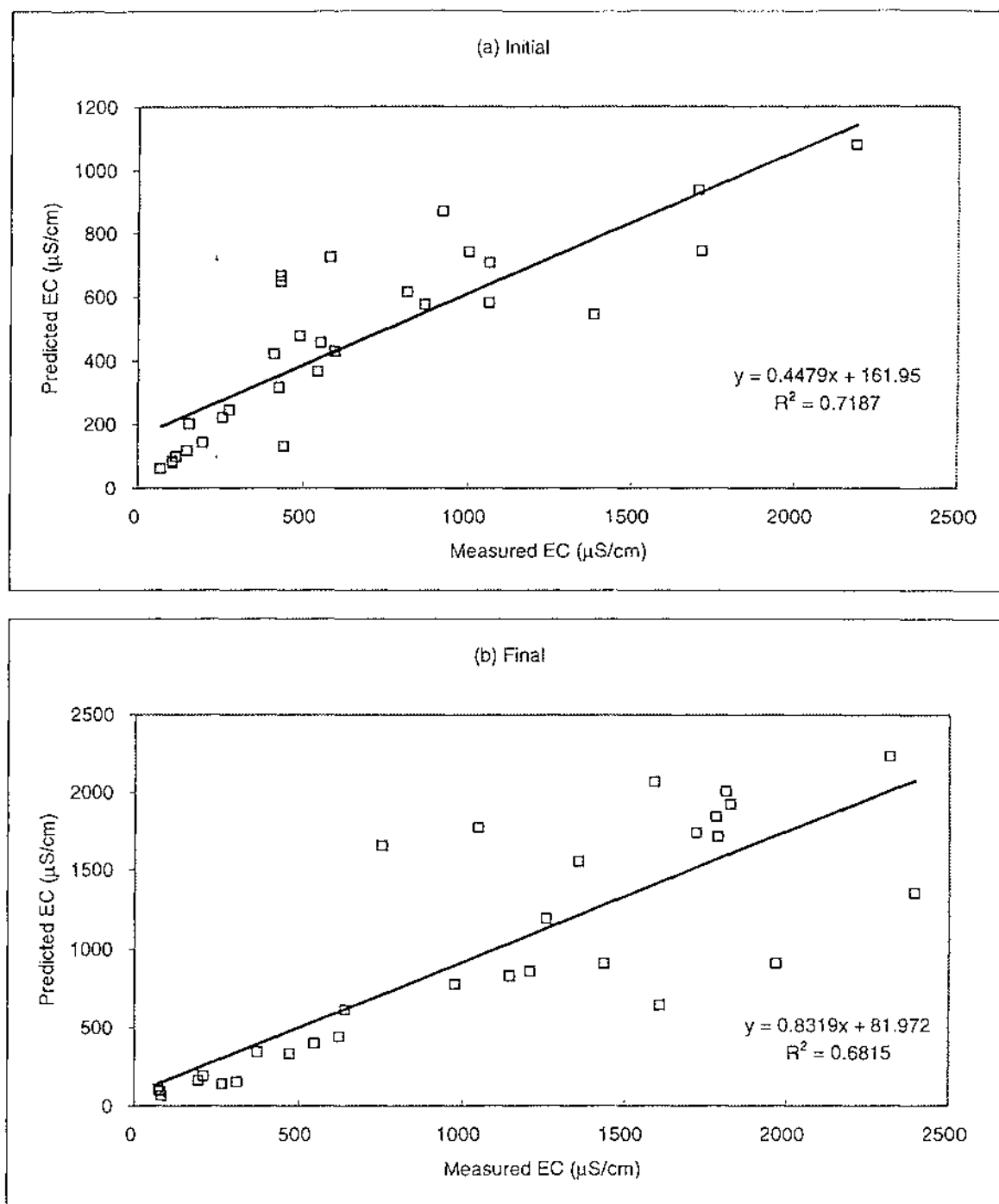
Figure 5.10 Relationship between predicted and measured electrical conductivity at the start (initial) and at the conclusion (final) of the incubation

5.3.5   **Explanation of the effects of sludge addition and incubation on the electrical conductivity of the mine spoils**

The general trend of increasing EC with incubation period is due to the release of salts in the sludge and sometimes the minespoil. Since leaching was not allowed from the incubations, salts accumulated. This trend has also been reported for a sewage sludge and a sludge amended sand-clay mixture by Gonzalez *et al.* (1992). An increase in EC with sludge addition is caused by the sludge having a higher content of soluble salts than the spoil and this phenomenon has been reported by several authors (Feagley *et al.*, 1994; Hinesly *et al.*, 1982; and Topper and Sabey, 1986). Conversely a reduction in EC may occur if the EC of the spoil is higher than the amending sludge (e.g. mudstone amended with paper sludge). The effectiveness of a sludge in affecting a change in the EC of the mine spoil was related to the difference in the EC between the sludge and spoil values. Generally, the sludge with the highest EC had the greatest effect on the EC of the amended spoil.

Not all the results follow the trends explained above. This may be explained by variation in water content. While every effort was made to keep the incubations well mixed and homogenous, it is possible that samples taken may have varied in moisture and salt content at different sampling intervals. The variability in sampling affecting a a given time may explain some of the unexpected results (e.g. no difference between initial EC of the mudstone amended with paper sludge to 5% and 10% organic matter (Table 5.9). The levelling off of increase in EC between week 20 and week 38 may indicate that no more soluble salts were available for release.

5.3.6   **Implications for rehabilitation of the mine spoils**

The major adverse effect of soil salinity is to reduce the availability of soil water to plants because of increased osmotic pressure, but supply of nutrients may also be restricted (Jurinak *et al.*, 1987). Salinity damage is most severe during germination and in the early stages of growth (Jansen and Melsted, 1988).EC effects on germination and establishment of vegetation are not discussed.

Conversely, electrolytes in the soil solution are essential to maintaining the permeability (hydraulic conductivity of a soil in the presence of high exchangeable Na (Frenkel *et al.*, 1978; Quirk and Schofield, 1955; Black, 1968), that is a soil with an exchangeable Na content at least about 15% of CEC (Black, 1968). Amended tailings

have the highest Na (Table 5.19) percentage of all the spoils but they also have high EC values and hence are unlikely to present a problem. Additionally, the addition of sludge while usually increasing EC, also supplies organic matter which will reduce bulk density, improve spoil structure; and in the field is therefore likely to improve infiltration, resulting in an increased movement of salt down through the profile resulting in a reduction in EC (Opeka and Morse, 1979).

The EC of a sludge amended spoil cannot be accurately predicted directly from the EC of the individual materials involved and periodic measurements of the EC of amended spoil will be beneficial to assess seasonal changes in EC with sludge addition. A high EC may be fairly easily remedied by the use of salt tolerant plants, i.e.; plants with a relatively high plant cell osmotic pressure (Jansen and Melsted, 1988); manipulation of water supply to encourage leaching of salts, or improvement in drainage. The former may not be practical because of the potential for heavy metals and other toxins to be leached into water systems. Jansen and Melsted (1988) reported that the salt effect is minimum when soil is wet. Both the coal mine and gold mine are in locations of relatively high rainfall (Chapter 3). Therefore if sludge is used as an amendment to spoils there is not likely to be a EC problem. Also where there is potential for a high salt problem, effort should be made not to use fertilisers high in soluble salts which will only add to the problem. According to Tisdale and Nelson (1975), usually the higher the analysis of the fertiliser, the lower the salt index per unit of nutrient supplied

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According to Jansen and Melsted (1988), Bellamy et al. (1995) and United States Salinity laboratory staff (1954) (Table 5.10), even the amended spoils with very high EC values based upon the Soil Bureau ratings for New Zealand soils are unlikely to present any restriction to spoil rehabilitation. According to the US Salinity Laboratory Staff (1954), non saline-non sodic soils have an EC less than 4 and a Na saturation of CEC less than 15 and do not generally present problems related to salts. All amended spoils are in this category.

Table 5.10

Plant response to the EC of soil saturation extract

EC of saturation extract (mmho/cm) at 25 0C	Plant response
0-2	Salinity effects usually negligible
2-4	Yield of very salt sensitive crops may be restricted
4-8	Yield of salt sensitive crops restricted
8-16	Only salt tolerant crops yield satisfactorily
>10	Only a few very salt tolerant crops yield satisfactorily

(United States Salinity Laboratory Staff, 1954)

1 mmho/cm= 1 mS/m

0.1 mS/m= 1 μS/cm

5.4   TOTAL (KJELDAHL) NITROGEN

5.4.1   Total nitrogen content of the original materials

The New Zealand Soil Bureau (Blakemore *et al.*, 1987) uses the following ratings for the total nitrogen content of New Zealand soils:

Very high	>1.0%
High	0.6-1.0
Medium	0.3-0.6
Low	0.1-0.3
Very low	<0.1

Based upon these ratings for New Zealand soils, Manukau and North Shore sewage sludges had very high levels of N (Table 5.11). This is in common with other sewage sludges (Sopper, 1992), although total N values of sewage sludge are slightly outside (lower) the range reported (2-6%) by Ghorayshi (1989) for sewage sludge of 2 to 6%. Paper sludge had a low content at 0.4%; this compares to other paper sludges. Bellamy *et al.* (1995) reported that primary paper mill sludges have low N contents, e.g., 0.1 to 0.25% (dry weight basis) and Feagley *et al.* (1994), reported a value of 0.18% total N

in papermill sludge. Pichtel *et al.* (1994) reported a total N value of 0.30% for paper mill sludge.

Table 5.11

Total nitrogen, carbon and the C/N ratio in sludge and spoils

Incubation material	Total C (%)	Total N (%)	C/N ratio
Manukau	24.9	1.6	15.1
North Shore	23.5	1.9	12.6
Paper	34.7	0.2	90.7
Tailings	0.0	0.3	0.1
Oxidised waste	0.2	0.0	3.7
Waihi subsoil	0.6	0.0	14.7
Fireclay	4.9	0.1	59.0
Mudstone	1.6	0.1	23.4
Huntly subsoil	0.4	0.2	2.6

Manukau and North Shore sewage sludges had significantly higher total nitrogen than paper sludge. This compares to values obtained by Pichtel *et al.* (1994) with 11% N reported for sewage sludge and 0.30% for paper mill sludge, and NCASI (National Council of the Paper Industry for Air and Steam Improvement,1984) with a value of 10 to 17% reported for sewage sludges and 0.05 to 8.75 for US paper mill sludges.

The values for N in the sludges are low compared to N fertilisers commonly used in New Zealand (e.g., Urea, which is the most concentrated solid nitrogenous fertiliser (46% N), and usually the cheapest per unit of N in New Zealand, calcium nitrate (16.5% N) and sulphate of ammonia (21.2% N) (During, 1984)).

Tailings and Huntly subsoil had low N values, fireclay and mudstone low to very low, and oxidised waste and Waihi subsoils had very low values for total nitrogen (Table 5.11). This is in common with other mine spoils (Whitby and Hutchinson, 1974; Hutchinson and Whitby, 1984; Pichtel *et al.*, 1994; Cassandra and Anderson, 1995; Li and Daniels, 1994).

The low N contents of the spoils and the high N contents of the sludges is a reflection of the organic matter content of the materials. Black (1968) states that soil N is mostly organically bound and usually less than 2% of the total N content of soils is in the

mineral N forms, and Hendreck (1993) reports that on most soils, more than 95% of the N present occurs in the organic matter.

5.4.2 Effect of amendments on the total nitrogen content of mine spoils

5.4.2.1 *Manukau and North Shore sewage sludges*

Successive increments of either Manukau or North Shore sewage sludge to a mine spoil resulted in a significant increase in the total N content of the mixture (Table 5.12).

5.4.2.2 *Paper sludge*

Addition of paper sludge to mine spoils increased slightly but significantly the total N content of the amended fireclay and mudstone but when paper sludge was applied to Huntly subsoil, there was not a significant increase in total N at any application rate (Table 5.12). This may be attributed to the low value of N in the sludge and relatively high N content in the spoil. Also because of the high organic matter content of the paper sludge, less of this compared to the sewage sludge was required to be applied to achieve the same level of organic matter in the amended spoils.

As Kjeldahl N does not measure nitrate, any increase in nitrate may be expected to be associated with a reduction in Kjeldahl N in the incubations. This was not observed because the amount of nitrate compared with Kjeldahl N was very small and changes in Kjeldahl N caused by an increase in nitrate were unlikely to be significant.

Table 5.12

Total nitrogen, carbon and the C/N ratio in sludge amended spoils

Sludge amendment	Amended spoil	Organic matter (%)	Total C (%)	Total N (%)	C/N ratio
Manukau	Tailings	2	1.5	0.14	10.5
		5	2.4	0.26	9.3
		10	5.5	0.50	10.9
	Oxidised waste	2	1.2	0.12	9.7
		5	2.2	0.25	9.2
		10	4.7	0.50	9.4
	Waihi subsoil	2	0.2	0.07	3.6
		5	1.5	0.17	8.6
		10	3.9	0.35	10.9
North Shore	Tailings	2	1.3	0.14	4.1
		5	2.7	0.28	9.6
		10	6.3	0.59	10.9
	Oxidised waste	2	0.9	0.12	7.3
		5	2.3	0.23	7.7
		10	4.6	0.56	8.2
	Waihi subsoil	2	0.3	0.06	4.9
		5	1.8	0.17	10.9
		10	4.5	0.38	11.8
	Fireclay	10	7.1	0.19	37.4
	Mudstone	5	3.1	0.16	19.0
		10	6.5	0.39	16.7
	Huntly subsoil	2	1.4	0.08	17.6
		5	3.0	0.21	14.3
		10	6.1	0.44	14.4
Paper sludge	Fireclay	10	6.5	0.10	63.8
	Mudstone	5	2.9	0.09	33.6
		10	4.7	0.08	57.3
	Huntly subsoil	2	1.5	0.04	43.0
		5	3.4	0.06	64.0
		10	7.2	0.09	80.5

Note some rounding errors are present in the calculation of the C/N ratio.

5.4.3   Effect of the incubation on total nitrogen

Total N values obtained from samples taken initially were not significantly different to those taken at the end of the incubation period (week 38). This was expected as very little total N was expected to be lost. Sources of nitrogen loss are:

1. Ammonia volatilisation which is likely to occur at the soil surface when the pH is greater than 6.5 (Brady, 1984; During, 1984). It may therefore be expected that some loss of N due to ammonia volatilisation could have occurred from tailings and the sludges, but not in the spoils or amended spoils. However, no loss was measured.

2. Denitrification which occurs under reduced conditions (Brady, 1984). The incubations were maintained in aerated conditions so losses of N by dentrification were unlikely.

3. Leaching (Brady, 1984), which was not possible from the incubations.

5.4.4   Explanation of the effects of sludge addition on the total nitrogen content of the minespoils

The effect of the sludges on the N content of the amended spoils was directly related to the N content of the sludge, the higher N content of the sludge, the greater the effect it had on the spoils. Paper sludge which had a low N content had little or no affect on the N content of the spoils, the sewage sludges had very high values for N and a large effect on the total N content of the spoils they were applied to. North Shore had a slightly higher N content than Manukau sewage sludge and application of it to the spoils resulted in more N being supplied. Further, the organic matter content of the amendment and the spoil to be amended affected the total N content of the mixture. Paper sludge had a higher content of organic matter than North Shore sewage sludge and hence less was applied to achieve the desired level of organic matter. Subsequently less nitrogen was applied.

5.4.5   Measured compared to predicted total nitrogen

Regression analysis was performed to compare the measured N content and N values predicted from Equation 4.6 (Fig 5.13). Measured N was closely correlated with predicted N in the amended spoils ($R^2= 0.85$). The exception was Huntly subsoil, where calculated N overestimated measured nitrogen. This appears to be a result of an

erroneous value for total N in the Huntly subsoil. Contamination of the sample may have occurred. This explains why there was a trend of increasing N in the spoil with increasing addition of sewage sludge but N in spoil amended to provide 2% organic matter was lower than the N in the unamended spoil. Similarly when paper sludge was applied to the spoil, there was a trend (though differences were not significant) of increasing N content with increasing sludge addition but the unamended spoil had a higher N content than any treatment.

The greater the sludge additions, the larger the difference between the measured and the predicted N values. This may be due to an inherent variability in the sludges (Awad *et al.*, 1989).

The mine spoils had low variability (standard deviations 0 to 0.04) in total N due at least in part, to the very low amount of N present and the relative homogeneity of the materials compared to the sludges. The spoils contributed very little to the total N in the incubations.
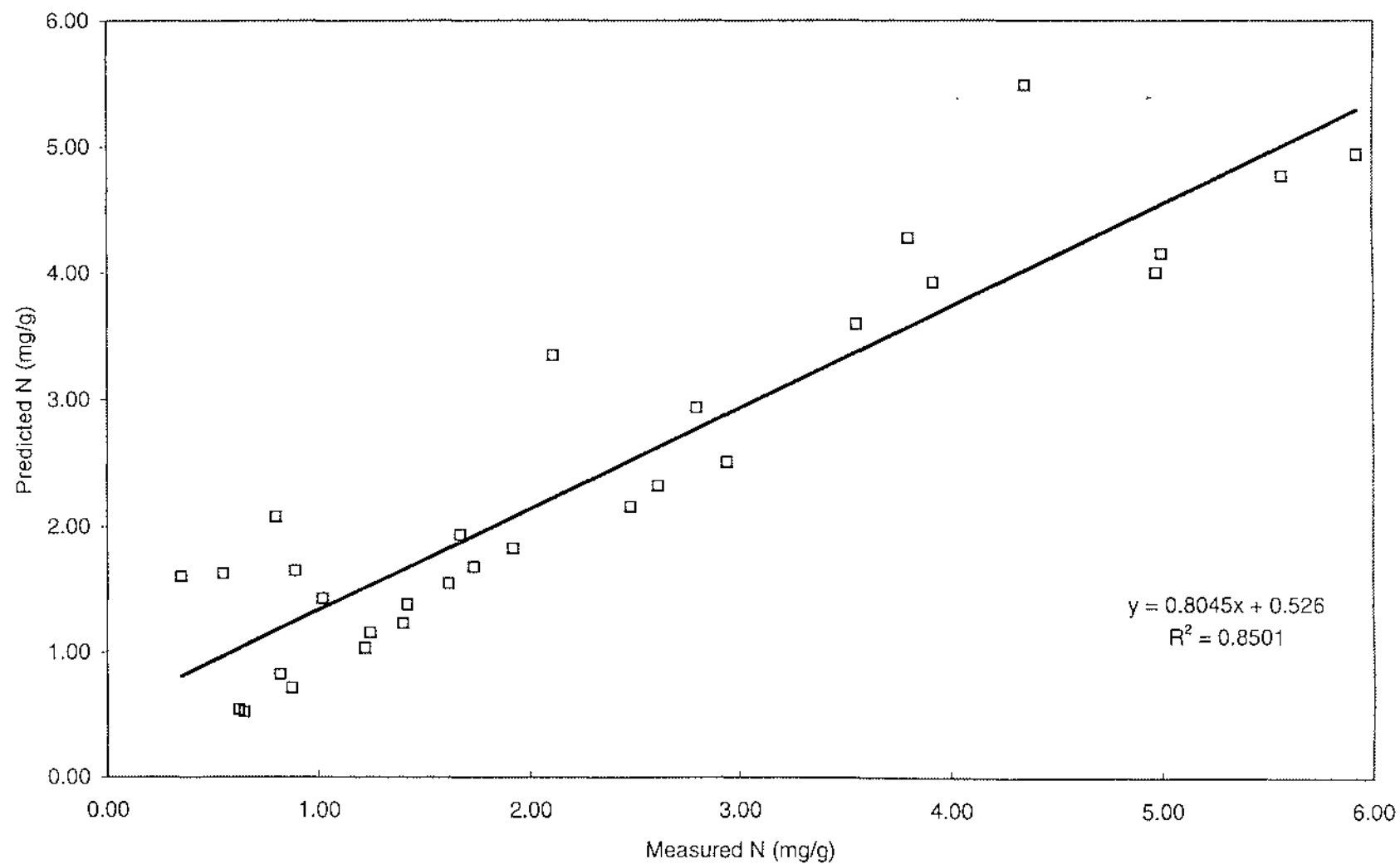
Figure 5.11   Relationship between predicted and measured total nitrogen content of the
incubation

5.4.6   Implications for rehabilitation of the mine spoils

Surface mining frequently results in a deficiency of plant available N (Reeder and Sabey, 1987) in the growing medium or spoil material. To achieve a self maintaining, desirable plant community, the re-establishment of an active biological nitrogen cycle is necessary (Chichester and Smith, 1983; Skeffington and Bradshaw, 1981). N is an essential component of chlorophyll, amino acids, plant growth enzymes, and ATP (adenosine triphosphate), which is the carrier of free energy needed for macromolecule synthesis and active transport of ions. N also stimulates root development and activity and supports the uptake of other nutrients, such as P (Olsen and Kurtz, 1982). Because of the high N requirement for growth and reproduction, more N than any other nutrient is removed from the soil by growing plants (Marrs and Bradshaw, 1982). Plant communities often fail to persist on severely N deficient sites despite initial seedling establishment and fertilisation because of a lack of continuing N supply from a mineralising cycle (Bradshaw et al., 1982). However, plant communities containing legumes which have an association with Rhizobium bacteria on their roots may be able to persist due to the ability of the legume/bacteria to fix N_2 from the atmosphere.

Organic N is not available for plant uptake, it must first be converted to mineral N. At any time in a soil the mineral N is likely to be no greater than 2% of total N (Black, 1968). The increase in total N may therefore not have a significant immediate effect upon plant growth but it does provide a source of N that may be slowly released over time for plant utilisation; organic N is not leached from the soil profile (During, 1984).

Since most derelict spoils/soils have little capacity for retaining inorganic N, the supply of organic, slow release N in dewatered sludge is advantageous in re-establishment of the nitrogen cycle. (Bayes et al., 1989).

Bradshaw and Chadwick (1980) suggested that for a low maintenance end use, a self-sustaining ecosystem requires a nitrogen budget of at least 1000 kg N/ha although the depth was not specified. If sludge is incorporated to provide the desired organic matter value to a depth of 15 cm, this value for total N is exceeded in all treatments of spoils except Waihi subsoil with 2% organic matter and Huntly subsoil with 2 and 5% organic matter. If sludge is only to be applied to the top 5 cm of spoil then this level is exceeded (in the top 5 cm) of tailings, oxidised waste and Huntly subsoil amended to 5% organic matter with sewage sludge and in Waihi subsoil amended to 10% organic matter. In fireclay it is not met and in mudstone it is exceeded at 10% organic matter with sewage sludge. When paper sludge is the amendment, this value is not exceeded

at 5 cm by any treatment and at 10 cm depth only in fireclay amended to 10% organic matter (Table 5.13).

Work at Rothamsted has determined estimates of the quantities of N in different forms for an arable field representative of arable fields throughout north-west Europe. The surface layer of an arable soil (depth not given) typically contains 2000 to 6000 kg N/ha in organic matter (Powlson, 1993). The values for the unamended spoils are considerably lower than this range except Huntly subsoil which is assumed to result from an erroneous N value. However, tailings, oxidised waste and Huntly subsoil will be within this range if amended with sewage sludge to provide 10% organic matter to a depth of 5cm. If the depth of amendment is increased to 10cm they will be within the range when amended to provide an organic matter content of 5 or 10%. Waihi subsoil will be within this range when amended to 10% organic matter to a depth of 10 cm, or 5% organic matter to a depth of 15 cm. Fireclay will be within the range when amended to 15cm depth with North Shore sewage sludge to provide 10% organic matter and mudstone treated similarly to a depth of 10 cm or amended to 5% organic matter with sewage sludge to 15 cm depth. Huntly subsoil is within this range when North Shore sewage sludge is applied to provide 5% organic matter to a depth of 10 cm or more.

On the basis of Blakemore's ratings, an application of sewage sludge to provide 10% organic matter is required to produce an appreciable increase in total N, i.e. to raise N values of the spoils from low values to medium values.

Paper sludge was ineffective at raising the N content of the spoils and N fertiliser will need to be applied for rehabilitation of the spoils amended with the paper sludge.

To conclude, according to the Department of Health (1992) these sludges have N contents too low to be considered useful as N fertilisers. However, from the above discussion it is obvious that as a source of slow release N, they may provide considerable benefit for the rehabilitation of the spoils.

Table 5.13

Predicted amount of N (Kg/ha) in amended mine spoil when the sludge materials are added to a depth of 5, 10 and 15 cm to achieve 2, 5 and 10% organic matter content*

Sludge amendment	Spoil	Organic matter %	5 cm	10 cm	15 cm
Manukau	Tailings	2	700	1400	2100
		5	1305	2610	3915
		10	2500	5000	7500
	Oxidised waste	2	610	1220	1830
		5	1240	2480	3720
		10	2485	4970	7455
	Waihi subsoil	2	325	650	975
		5	870	1740	2610
		10	1775	3550	5325
North Shore	Tailings	2	710	1420	2130
		5	1395	2790	4185
		10	2965	5930	8895
	Oxidised waste	2	625	1250	1875
		5	1470	2940	4410
		10	2785	5570	8355
	Waihi subsoil	2	315	630	945
		5	835	1670	2505
		10	1900	3800	5700
	Fire clay Mudstone	10	960	1920	2880
		5	810	1620	2430
		10	1960	3920	5880
	Huntly subsoil	2	400	800	1200
		5	1055	2110	3165
		10	2175	4350	6525
Paper sludge	Fireclay Mudstone	10	510	1020	1530
		5	440	880	1320
		10	410	820	1230
	Huntly subsoil	2	175	350	525
		5	275	550	825
		10	445	890	1335

* Bulk density is assumed to be 1 for all amended spoils.

5.5　　　　Mineral Nitrogen

5.5.1　　　Mineral nitrogen content of the original materials

The mineral N contents of the original mine spoil and sludge samples, as a percentage of total N, are presented in Table 5.14. Black (1968) reports that N is mostly organically bound and usually less than 2% of the total N content of soils is in the mineral N (nitrate and ammonium forms). Manukau sewage sludge and tailings had 6% and 3.4% of their total N, respectively as mineral N. In tailings the mineral N was predominantly in the ammonium form. This may be geologic N present in the tailings. Stevenson (1962) reported that geologic N (within mineral structures) is usually in organic form or as ammonium fixed within the lattice structures of silicate minerals.

Sewage sludges

It is common for sewage sludges to have a higher percentage of total N in mineral form than soils. Sjoquvist and Wikander-Johansson in Ghorayshi (1989) reported that generally in sewage sludge, a large amount of total N is in organic forms (2-5% of dry matter) and about 0.65% of dry matter is mineral N. This equates to 13 to 32% of total N present as mineral N. EPA (1983) reported that aerobic sewage sludges contain 2.6% of total N in the form of ammonium (NH_4^+) and nitrate (NO_3^-) although a wide variation is reported. In the aerobically digested sewage sludge assessed by Topper and Sabey (1986) mineral N was 4.8% of total N. Manukau therefore has a mineral N content more consistent with other sewage sludges than does North Shore (Table 5.14). The contribution of mineral N to total N in North Shore sewage sludge initially is more consistent with soils.

The high content of nitrate compared to ammonium in the sewage sludges (Table 5.14) is unusual. Most literature reports ammonium contents of sludge being considerably higher than nitrate, which is often considered negligible (Lerch *et al.*, 1992; Topper and Sabey, 1986; Wen et al, 1995; Ghorayshi, 1989; Awad *et al.*, 1989). However there are some reports of sludges having high nitrate to ammonium ratios although no explanation of this is given (Sloane and Basta, 1995; Medalie *et al.*, 1994; Lerch *et al.*, 1992).

Black (1968) provides information that may explain why the nitrate contents of the Manukau and North Shore sewage sludges are higher that those commonly reported for sewage sludges. As in unfertilised soils, the mineral forms of N in the sewage sludges

arise almost entirely from decomposition of the organic nitrogenous compounds. The steps in the process are:

$$\text{Organic N} \rightarrow \text{NH}_4^+ \rightarrow \text{NO}_2^- \rightarrow \text{NO}_3^-$$
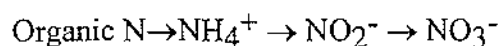
In general, the rate controlling step is the conversion of organic N to ammonium. Consequently nitrate is usually the most abundant form of mineral N in soils and is the principle form of mineral N utilised by plants. In fallow soils, that remain in a warm, moist condition without addition of organic matter or loss of mineral nitrogen from leaching, the content of mineral N gradually increases. This is because the net quantity of N tied up in microbial tissue remains approximately the same while the organic N in the organic matter is undergoing gradual mineralisation. According to Reeder and Sabey (1987), storage of samples in a warm, moist condition prior to analysis may stimulate micro-organisms to mineralise organic N and result in accumulation of ammonium and or nitrate. The final step in Manukau sludge treatment is storage for at least one year in dewatering beds and storage on site for at least two years (Bradley *et al.*, 1992). Similarly, North Shore sewage sludge is stored for about two years in lagoons in open air and sunlight before use. Other sludges not stored for this length of time are released from treatment works with mineral N predominantly in ammonium form (Bradley et al, 1992). They are expected to produce nitrate after application to soils which may lead to contamination of ground and surface water supplies (Awad *et al.*, 1989).

The sludge storage sites will presumably have prevented the leaching of nitrates and the sludges will have been maintained under conditions not conducive to denitrification so that nitrate has accumulated. Additionally the C to N ratio of the sludges (Section 5.6.1) will have favoured mineralisation (Black, 1968). If the sewage sludges are compared to organic soils to which they do have similar qualities, then a high rate of nitrification is expected. This may be due to the presence of adequate calcium and the inactivity of part of the C. The effective C to N ratio may hence be similar to that of mineral soils and specific nitrifying organisms are comparatively more active than the non specific heterotrophic organisms responsible for ammonification (Brady, 1984).

Paper sludge

The mineral N content of paper sludge as a percentage of total N is similar to values quoted in Bellamy *et al.* (1995).

Paper sludge has an ammonium to nitrate ratio of 16:1 This is similar to values quoted for other paper sludges (Bellamy *et al.*, 1995).

Mine spoils

In the mine spoils, mineral N was in very low quantities due to low total N content, and most mineral N occurred as ammonium. This may be in the form of geological N as discussed above or as a result of loss of nitrate through leaching and denitrification from the spoil at a faster rate than mineralisation occurs. Nitrification of indigenous ammonium in geologic materials depends upon the suitability of the chemical and physical properties of the material for nitrifying bacteria (Reeder and Sabey, 1987). Nitrification only occurs under aerobic conditions and production of ammonium occurs under both aerobic and anaerobic conditions (Black, 1968). Ammonification will take place to some extent under almost any conditions because of the great number of different organisms capable of the process. Autotrophic bacteria (*Nitrobacter*) are responsible for the conversion of ammonium to nitrate or more specifically the conversion of nitrite to nitrate. They are most active in well aerated but moist soils at temperatures between 27 and 32 $^\circ$C and at pH levels above 6; below pH 6 nitrification drops rapidly (Kamprath and Foy, 1971). This accounts for the weak nitrification in the acid spoils. Nitrification proceeds most rapidly where there is an abundance of exchangeable bases (Brady, 1984).

Table 5.14

Nitrogen characteristics in the original materials

Material	Total N (mg/g)	Mineral N (μg/g)		Mineral N as a % of total N		Ammonium as % of mineral N		Nitrate as a % of mineral N	
		Initial	Final	Initial	Final	Initial	Final	Initial	Final
Manukau Sewage Sludge	16.4	1066	1694	6.5	10.3	1	1	99	99
North Shore Sewage Sludge	18.7	216	917.8	1.2	4.9	10	3	90	97
Paper Sludge	3.8	15.8	30.3	0.4	0.8	94	100	6	0
Tailings	0.5	17.1	16.2	3.4	3.2	77	86	23	14
Oxidised Waste	0.5	9.6	14.6	1.9	2.9	77	95	23	5
Waihi Subsoil	0.4	8.1	16.3	2.0	4.1	94	100	6	0
Fire Clay	0.9	7.9	12.5	0.9	1.4	95	95	5	5
Mudstone	0.7	15.5	17.4	2.2	2.5	93	100	7	0
Huntly Subsoil	1.6	28.0	45.2	1.75	2.8	46	72	54	28

5.5.2 Effect of amendments on the mineral nitrogen content of mine spoils

5.5.2.1 Manukau sewage sludge

Manukau sewage sludge significantly increased the mineral N content of the gold mine spoils and the mineral N content increased with increasing levels of sludge application. Nitrate levels were significantly increased in the spoils but there was no significant effect on ammonium contents, except in Waihi subsoil where a small but significant increase in the ammonium content occurred with addition of sludge (Figures 5.12 and 5.16).

5.5.2.2 North Shore sewage sludge

North Shore sewage sludge had a similar but smaller effect on the mineral N content of the gold mine spoils than Manukau sewage sludge (Figures 5.13 and 5.17). When applied to Waihi subsoil to provide a 2% level of organic matter, it did not significantly affect mineral N in the subsoil, however mineral N content was increased between the 2, 5 and 10% levels of organic matter addition (Figure 5.13c).

Similar to Manukau sewage sludge, application of North Shore sewage sludge had no significant effect on ammonium levels. This was true irrespective of the spoil it was applied to (Figures 5.17 and 5.18).

When North Shore sewage sludge was applied to the coal mine spoils, the nitrate and hence mineral N content of the spoil was significantly increased (Figure 5.14).

5.5.2.3 Paper sludge

Addition of paper sludge to the coal mine spoils did not significantly affect their mineral N contents (Figures 5.15 and 5.19). However, in fireclay, the ammonium content was slightly but significantly reduced when paper sludge was applied (Figure 5.19a). Paper sludge had a lower ammonium content than fireclay and Huntly subsoil. Huntly subsoil also had a higher nitrate content.

(a) Tailings

—□— 0 sludge (tailings alone) —+—2% OM —◇—5% OM —·—10% OM —×—Sludge alone

(b) Oxidised waste

—□— 0 sludge (oxidised waste alone) —+—2% OM —◇—5% OM —·—10% OM —×—Sludge alone

(c) Waihi subsoil

—□— 0 sludge (Waihi subsoil alone) —+—2% OM —◇—5% OM —·—10% OM —×—Sludge alone
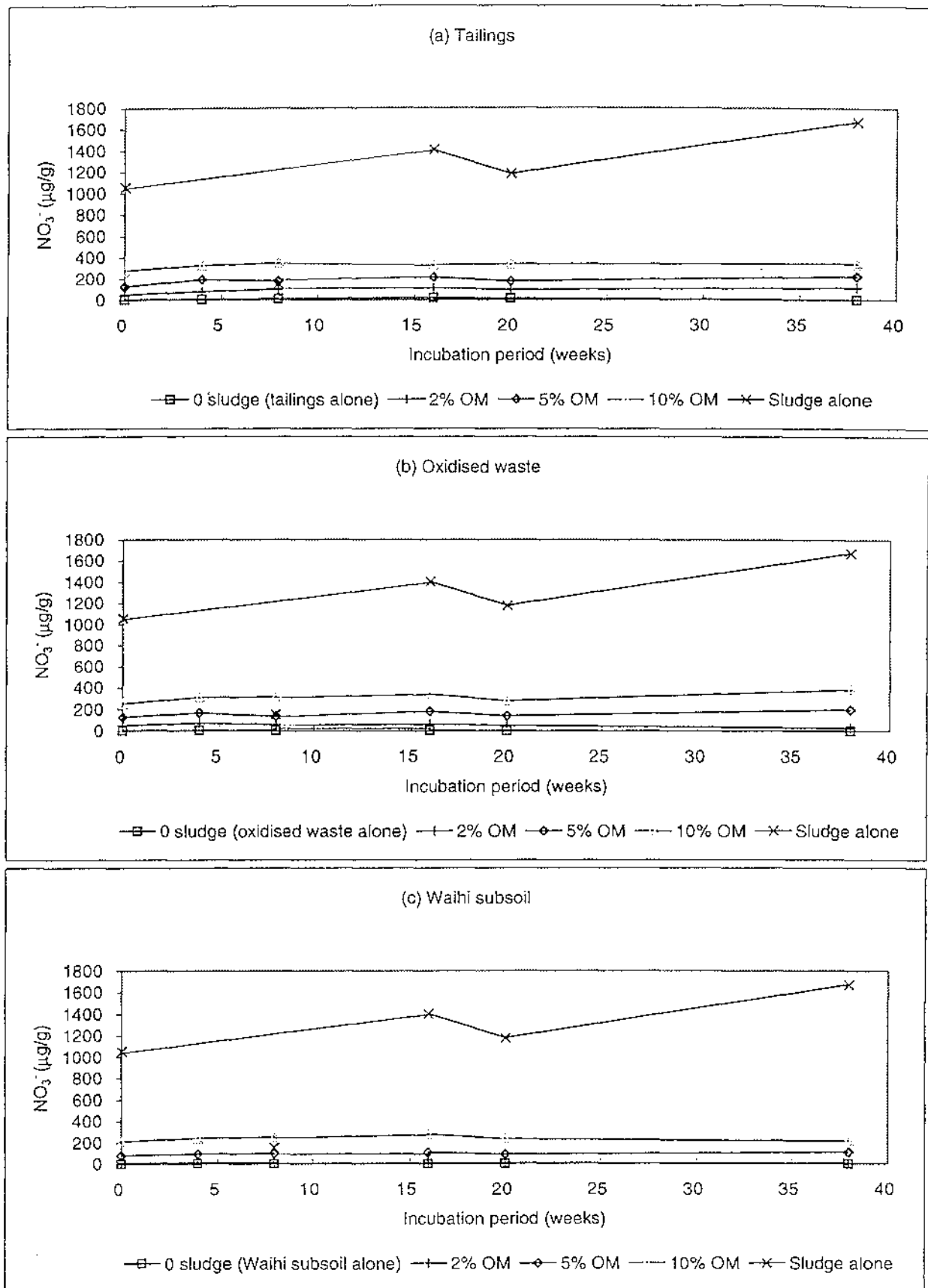
Figure 5.12   Effect of Manukau sewage sludge addition to provide specified organic matter (OM) content on the nitrate content of gold mine spoils
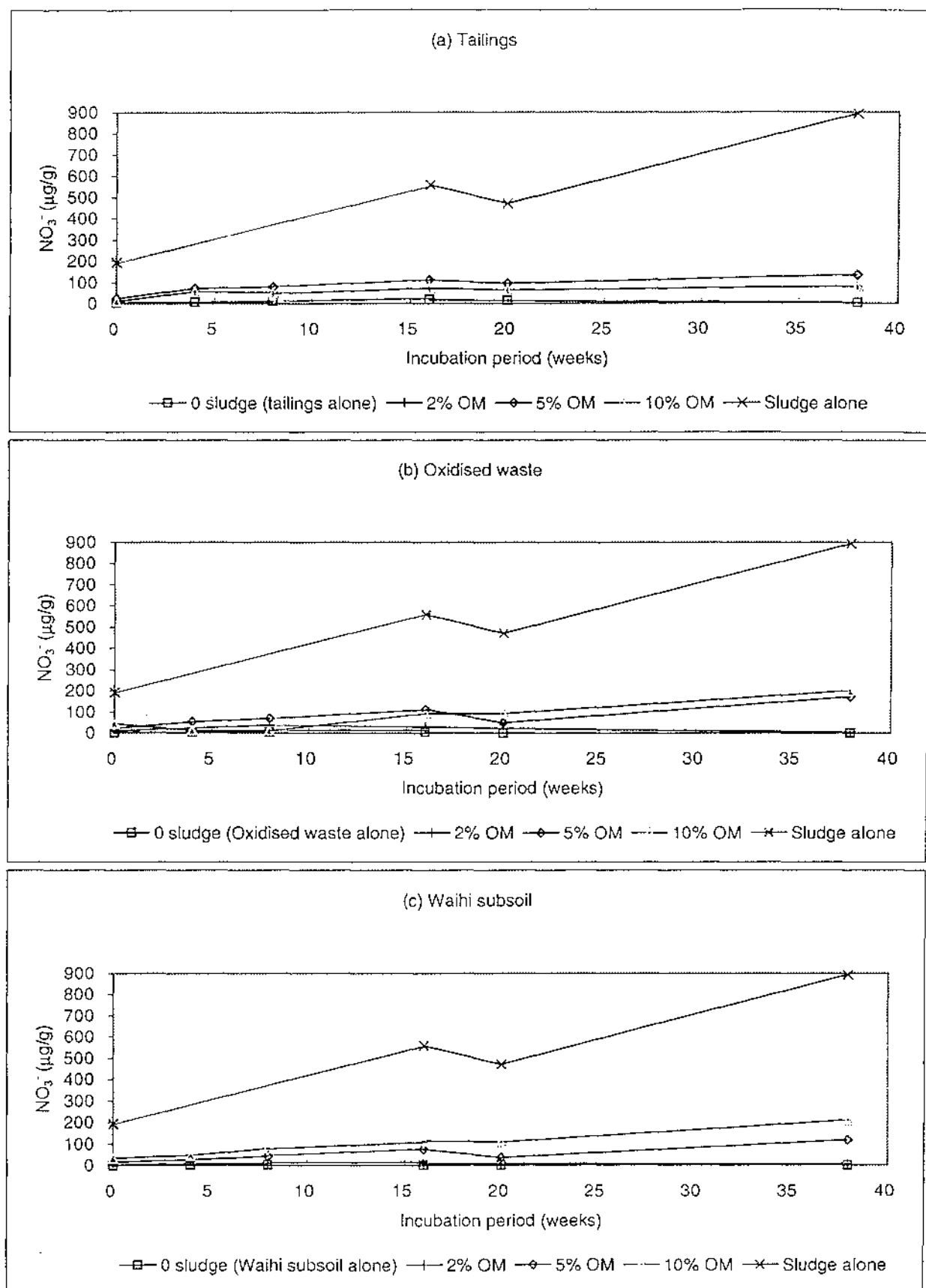
Figure 5.13 Effect of North Shore sewage sludge application to provide specified organic matter (OM) content on the nitrate content of gold mine spoils

(a) Fireclay

NO$_3^-$ (μg/g)

Incubation period (weeks)

—□— 0 sludge (fireclay alone)   —+— 10% OM   —◇— Sludge alone

(b) Mudstone

NO$_3^-$ (μg/g)

Incubation period (weeks)

—□— 0 sludge (mudstone alone)   —+— 5% OM   —◇— 10% OM   —·— Sludge alone

(c) Huntly subsoil

NO$_3^-$ (μg/g)

Incubation period (weeks)

—□— 0 sludge (Huntly subsoil alone)   —+— 2% OM   —◇— 5% OM   —·— 10% OM   —×— Sludge alone
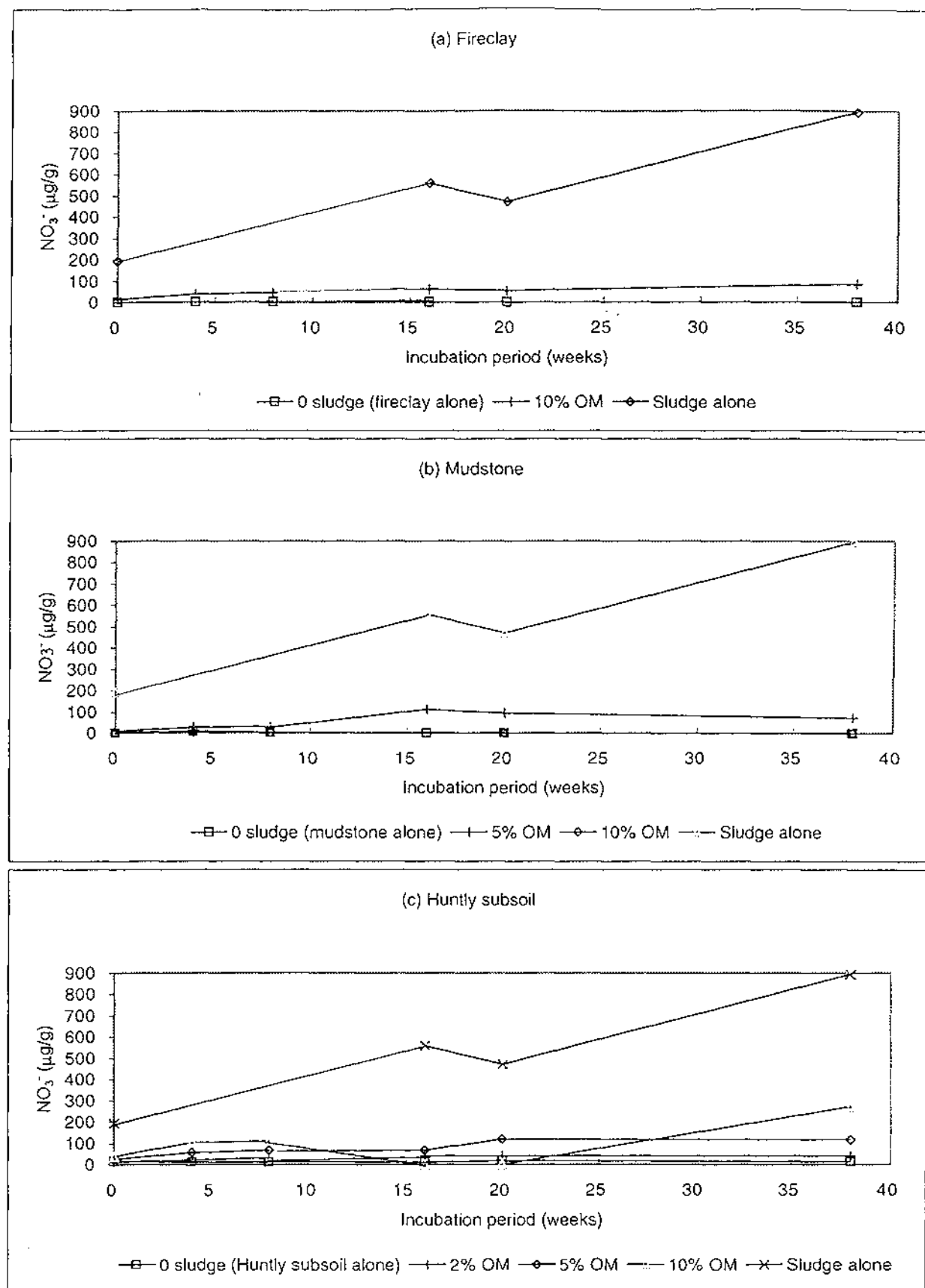
Figure 5.14 Effect of North Shore sewage sludge application
to provide specified organic matter (OM) on the
nitrate content of coal mine spoils

(a) Fireclay

(b) Mudstone

(c) Huntly subsoil
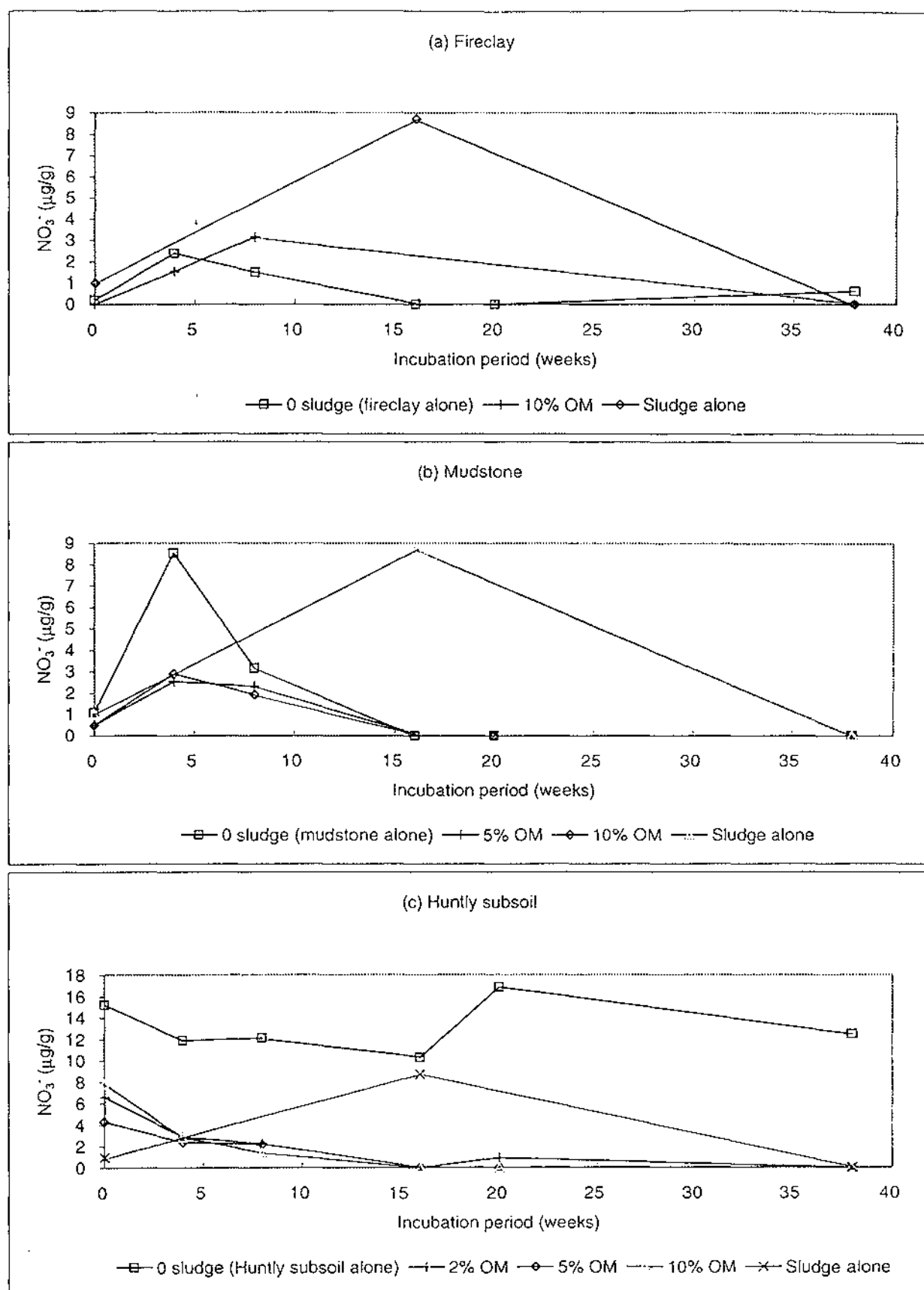
Figure 5.15 Effect of paper sludge addition to provide specified organic matter (OM) content on the nitrate content of coal mine spoils

(a) Tailings

NH$_4^+$ (µg/g)

Incubation period (weeks)

—□— 0 sludge (tailings alone)　——— 2% OM　—◇— 5% OM　—·—· 10% OM　—×— Sludge alone

(b) Oxidised waste

NH$_4^+$ (µg/g)

Incubation period (weeks)

—□— 0 sludge (oxidised waste alone)　——— 2% OM　—◇— 5% OM　—·—· 10% OM　—×— Sludge alone

(c) Waihi subsoil

NH$_4^+$ (µg/g)

Incubation period (weeks)

—□— 0 sludge (Waihi subsoil alone)　——— 2% OM　—◇— 5% OM　—·—· 10% OM　—×— Sludge alone
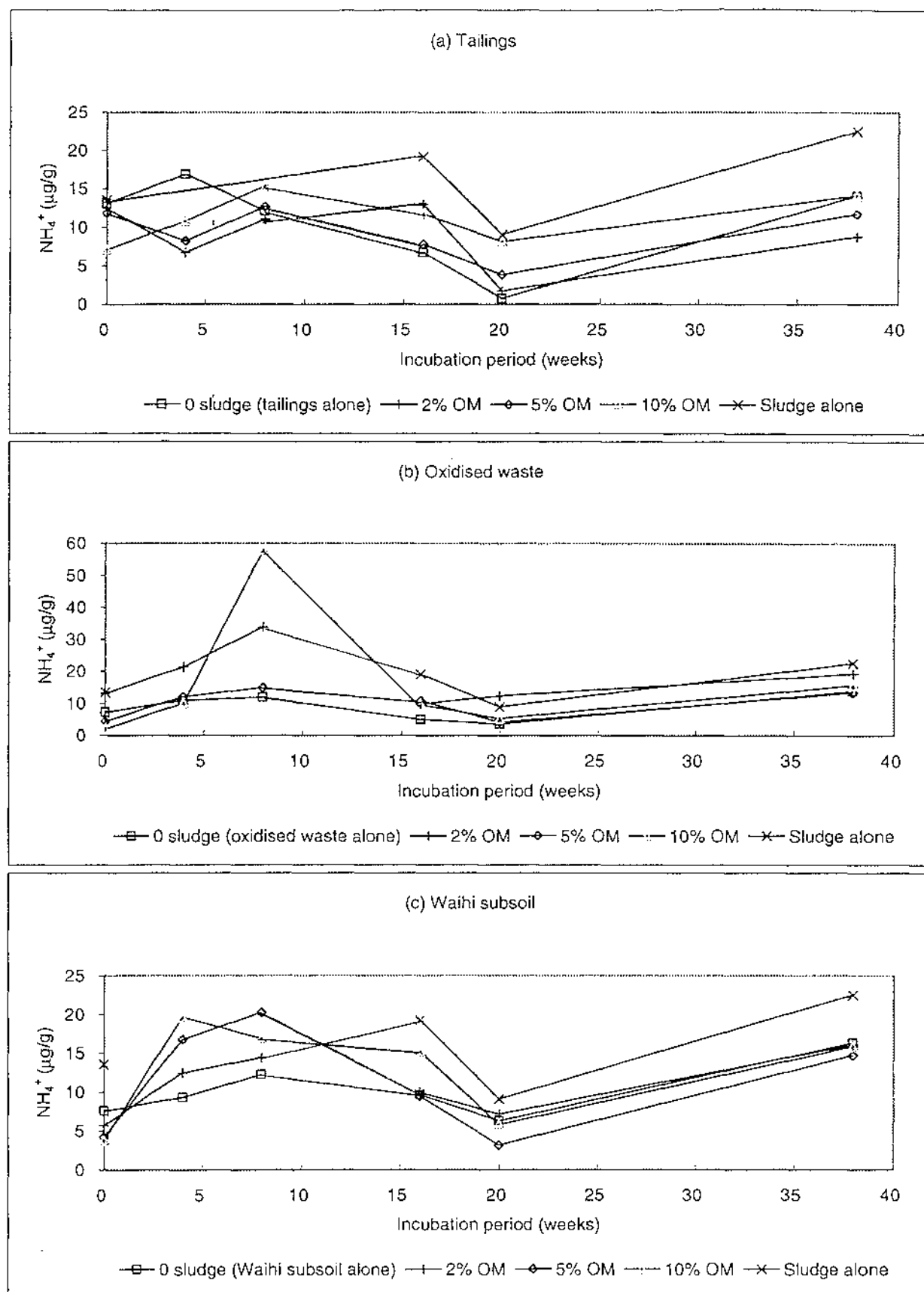
Figure 5.16 Effect of Manukau sewage sludge addition to provide specified organic matter (OM) content on the ammonium content of gold mine spoils
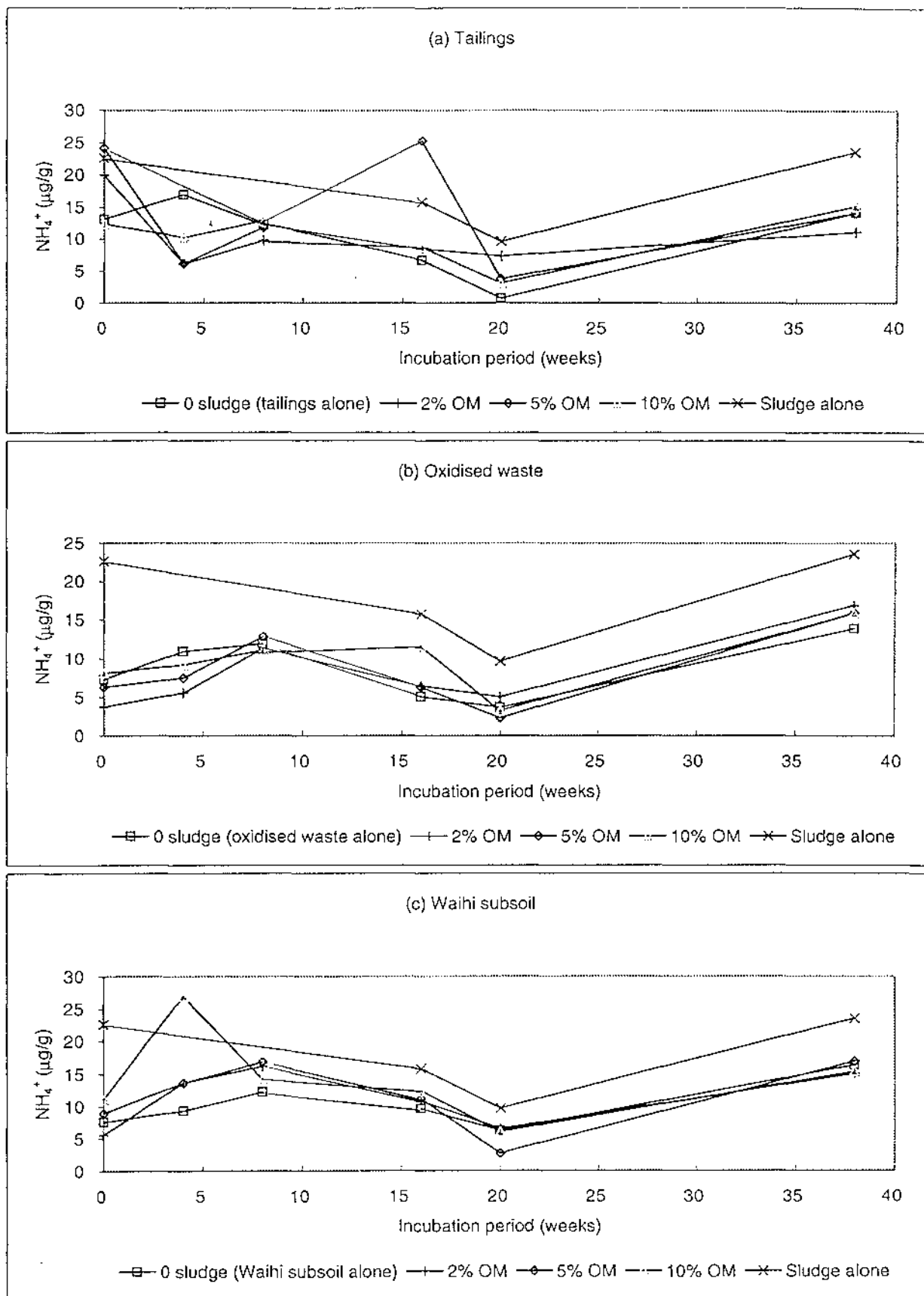
Figure 5.17 Effect of North Shore sewage sludge addition to provide specified organic matter (OM) content on the ammonium content of gold mine spoils

(a) Fire clay

Incubation period (weeks)

—□— 0 sludge (fireclay alone) —+— 10%OM —·—Sludge alone

(b) Mudstone

Incubation period (weeks)

—□— 0 sludge (mudstone alone) —+— 5% OM —◇— 10% OM —·—Sludge alone

(c) Huntly subsoil

Incubation period (weeks)

—□—0 sludge (Huntly subsoil alone) —+— 2% OM —◇— 5% OM —·— 10% OM —✕— Sludge alone
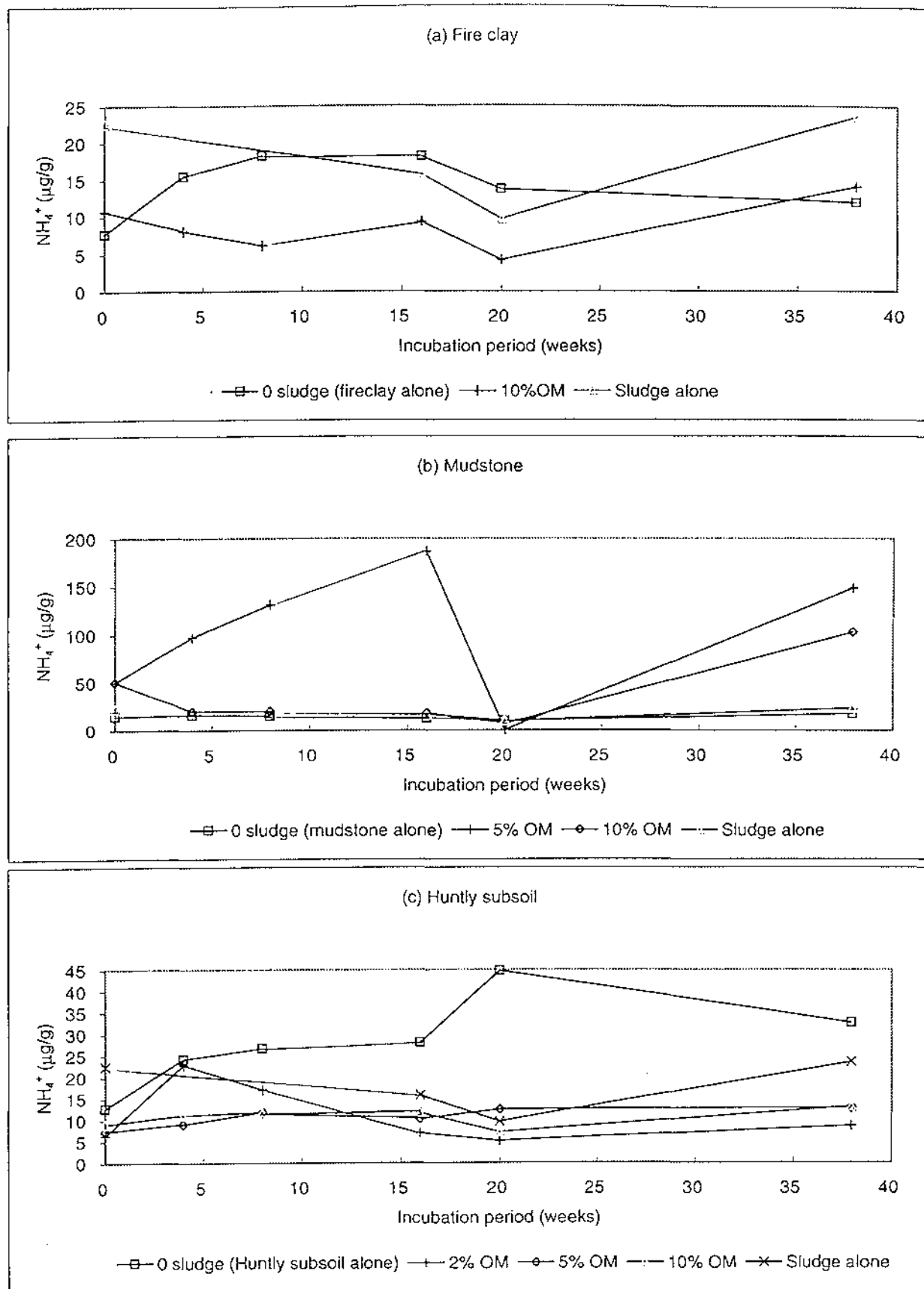
Figure 5.18 Effect of North Shore sewage sludge addition to provide specified organic matter (OM) content on the ammonium content of coal mine spoils

(a) Fireclay

—□— 0 sludge (fireclay alone) —◇— 10% OM —✕— Sludge alone

(b) Mudstone

—□— 0 sludge (mudstone alone) —+— 5% OM —◇— 10% OM —·—· Sludge alone

(c) Huntly subsoil

—□— 0 sludge (Huntly subsoil alone) —+— 2% OM —◇— 5% OM —·—· 10% OM —✕— Suudge alone
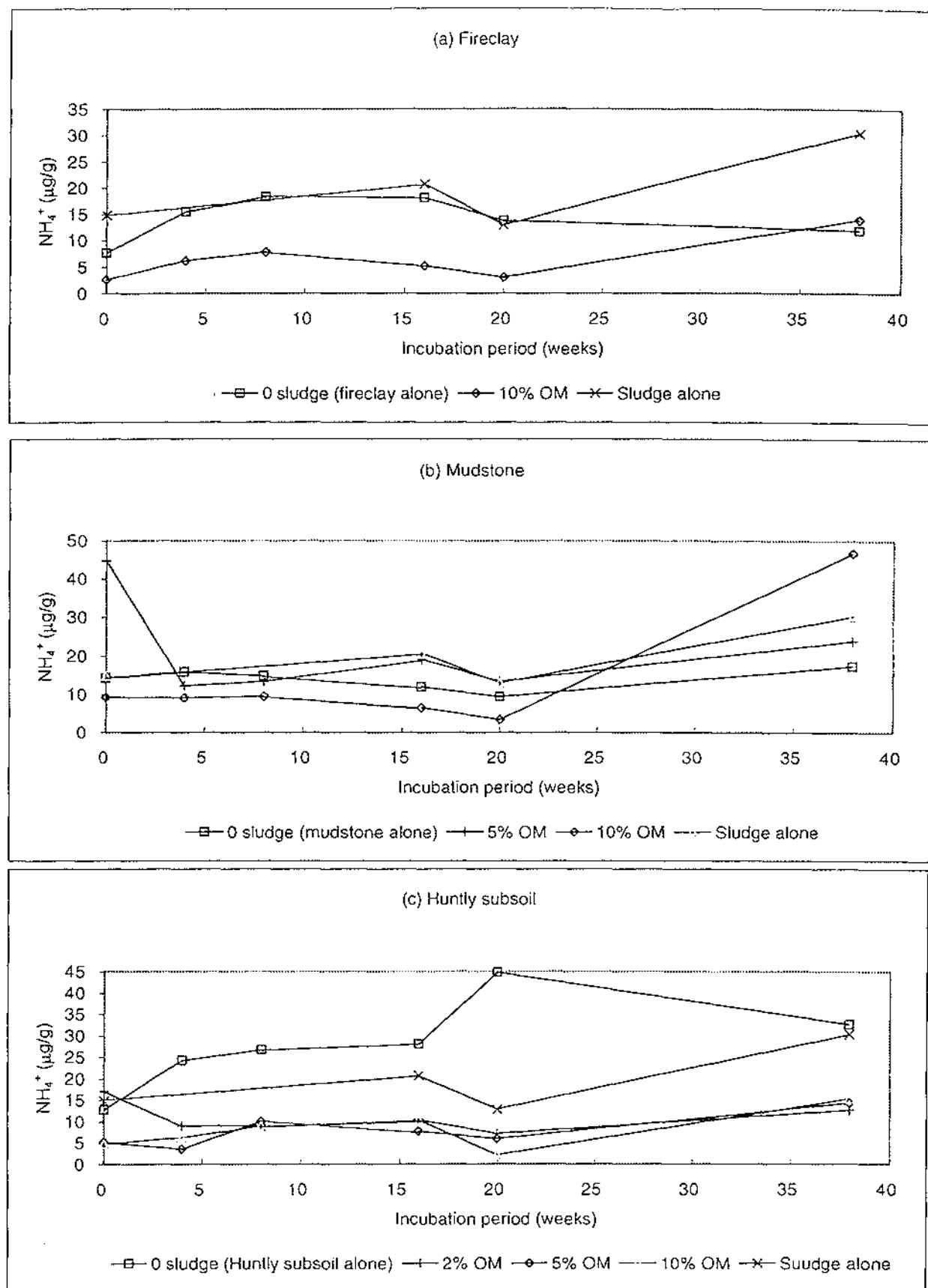
Figure 19   Effect of paper sludge addition to provide specified organic matter (OM) content on the ammonium content of coal mine spoils
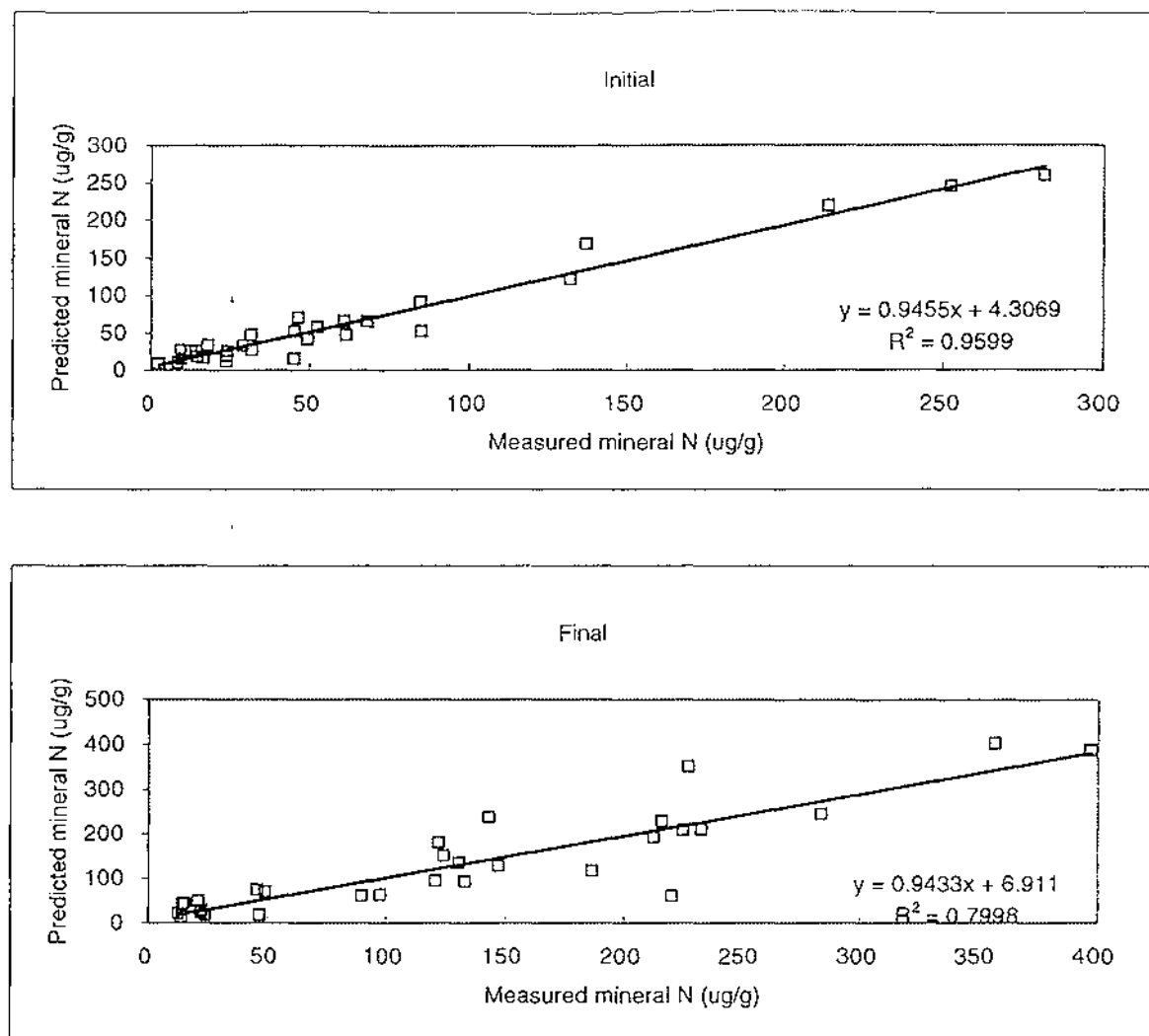
Figure 5.20   Relationship between predicted and measured mineral
               nitrogen at the start (initial) and at the
               conclusion (final) of the incubation
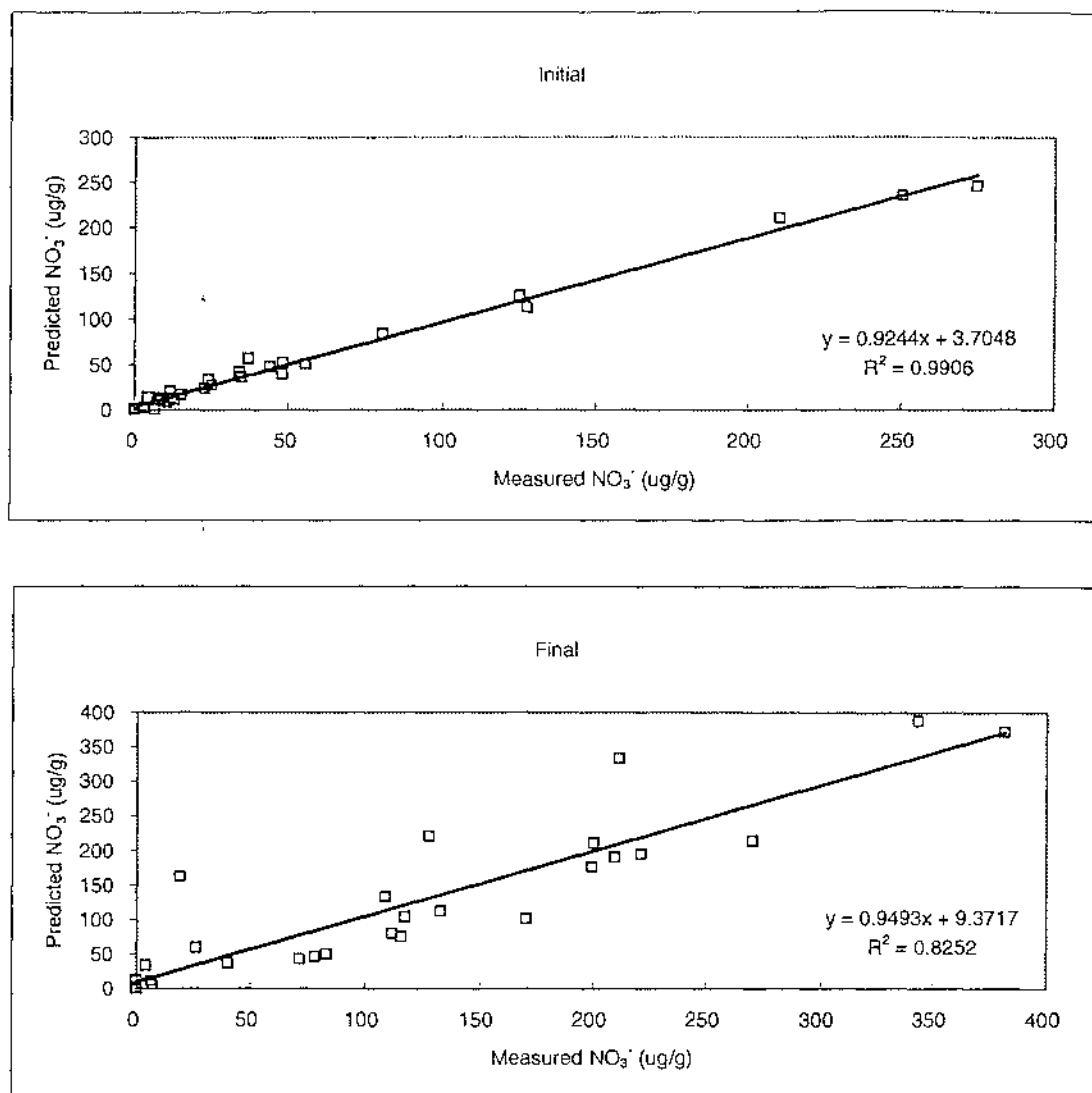
Figure 5.21   Relationship between predicted and measured nitrate
at the start (initial) and at the conclusion
(final) of the incubation
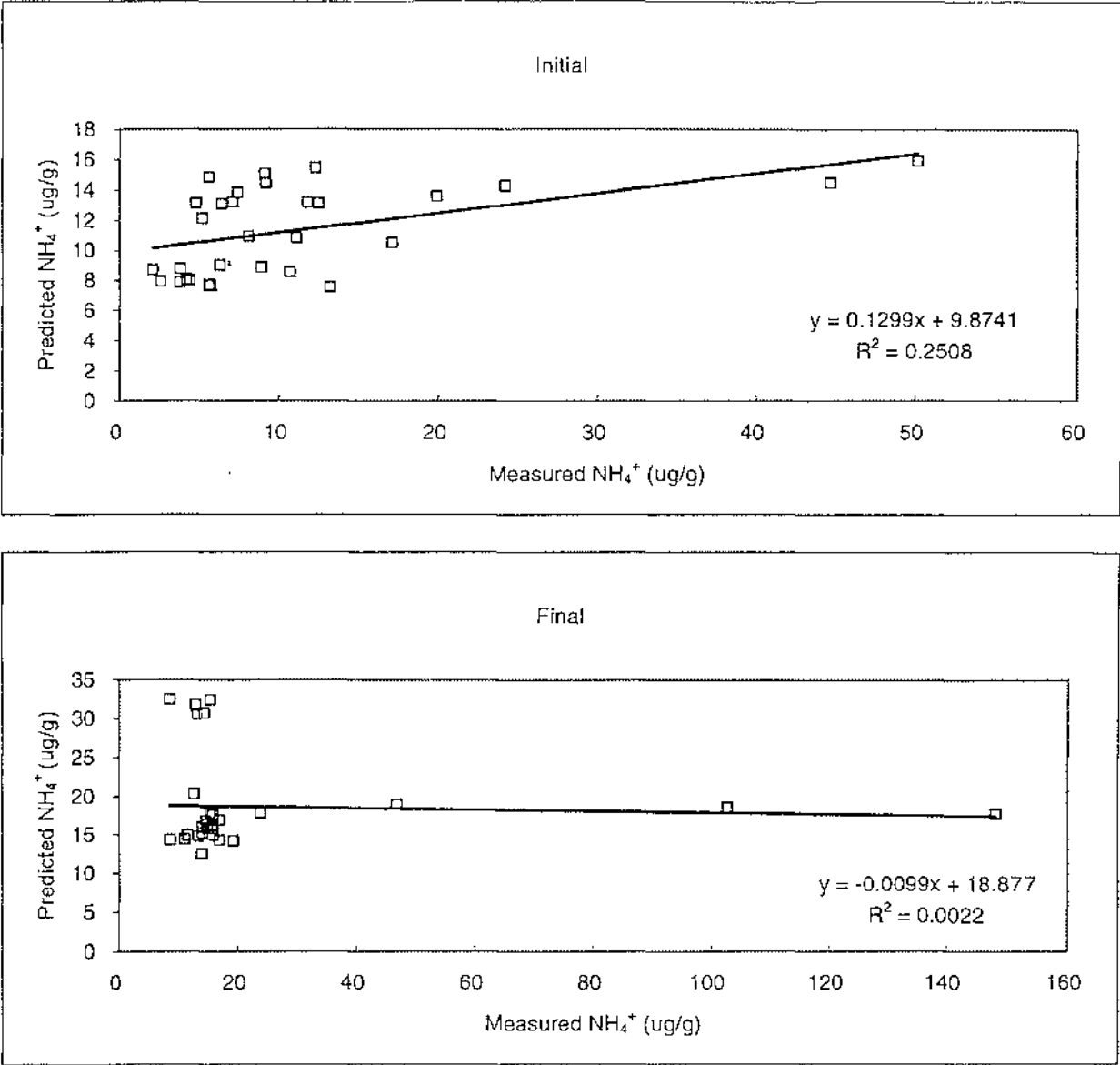
Figure 5.22 Relationship between predicted and measured ammonium at the start (initial) and at the conslusion (final) of the incubation

5.5.3 Effect of the incubation on mineral nitrogen

Figures 5.12 to 5.19 show the effect of incubation period on the nitrate and ammonium contents of the mine spoils, sludges and the amended spoils.

The sludges and the spoils

The nitrate content of the sewage sludges increased during the incubation period, although there was a decline in mineral N content between week 16 and week 20 in both sewage sludges. In paper sludge there was a small but significant increase in ammonium and mineral N between the start and the conclusion of the incubation, but it varied during the incubation.

The mineral N content of the spoils did not change significantly during the incubation.

Manukau amended spoils

When Manukau sewage sludge was used to amend tailings and oxidised waste to provide 5 and 10% organic matter, there was a large increase in nitrate between the start of the incubation and week 4 and a small but significant increase from week 4 until the conclusion of the incubation. At 2% organic matter the nitrate content of oxidised waste did not significantly change during the incubation. There was no significant change during incubation in amended Waihi subsoil, except in the 10% mixture where there was an increase in nitrate to week 12 and then a small decrease to the end of the incubation. The final nitrate (mineral N) value was however higher than the initial.

North Shore amended spoils

Tailings amended with North Shore sewage sludge followed a similar trend to the Manukau treatments during the incubation. When North Shore sewage sludge was applied to oxidised waste there was no significant effect of time at the 2% organic matter level. There was, however a significant increase during the incubation at the 5 and 10% organic matter level although in the latter, there was a decline in nitrate between the start of the incubation and week 4 and no significant increase until week 8. The nitrate content of Waihi subsoil amended with North Shore sewage sludge increased during the incubation except in the 2% organic matter treatment which did not change significantly during the incubation.

A general trend in the sludge amended gold mine spoils was a reduction in the nitrate content at week 20.

There was no significant change in ammonium content in any of the Manukau sewage sludge amended spoils during incubation.

In fireclay amended with North Shore sewage sludge there was a significant increase in nitrate and ammonium during the incubation period, although ammonium varied significantly during the incubation. The incubation had no significant effect on the mineral N content of amended mudstone, and in Huntly subsoil, the nitrate content increased during the incubation.

Paper sludge amended spoils

The mineral N contents of paper sludge amended coal spoils did not change significantly during the incubation.

5.5.4 Explanation of the effects of sludge addition and incubation period on the mineral N content of the mine spoils

Sludge addition

Paper sludge was less effective than the sewage sludges in increasing the mineral N content of the minespoils. This was because it had a very low mineral N content compared to the mine spoils. Neither the sludge nor the spoils had high reserves of organic N that could be mineralised and contribute to the mineral N. The high carbon to nitrogen ratio of the paper sludge (Section 5.6) may have been expected to cause the rate of immobilisation to exceed the rate of mineralisation in sludge amended spoils resulting in a net reduction in mineral N (Brady, 1984). This was not evident, presumably because of the very low levels of mineral N already present.

In all treatments of spoils with sewage sludge, the ammonium contents of the sludge and spoil were more similar than the nitrate contents. In the short term, a greater effect on the nitrate than the ammonium contents of the spoils is therefore expected when sludge is applied.

As Kjeldahl N does not measure nitrate N, an increase in nitrate is expected to coincide with a reduction in Kjeldahl N; this was not evident. The largest increase (0.62 mg) in nitrate occurred in Manukau sewage sludge during the incubation. The variability in total N results for Manukau sewage sludge was ± 1.25 mg, any change brought about by a change in nitrate content was therefore not significant. Further, mineral N contributes to only less than 6% of the total N.

The increase in mineral N content with sludge addition is directly related to the mineral N content of the individual incubation materials as shown in section 5.5.4. North Shore sewage sludge was hence less effective in increasing the mineral N content of the spoils than Manukau due to its lower mineral N content, even though, due to its slightly lower organic matter, more was added for each treatment.

Incubation period

The increase in nitrate and hence mineral N in the sewage sludges during the incubation may be attributed to the slow oxidation of organic matter and the lack of leaching and denitrification enabling nitrate to build up in the incubations. There was no significant change in the ammonium content of the sludges. Conversion of organic N to ammonium N occurs at a slower rate than conversion of ammonium to nitrate (assuming conditions favour nitrification). The decline in ammonium and nitrate at week 20 of the incubation is unusual. The reduction probably occurred as a result of immobilisation exceeding mineralisation. Denitrification is unlikely to have occurred, as aerobic conditions were maintained, although microscale anaerobic conditions may have existed. A change in temperature may have occurred although it is unlikely that any unreported change in the incubation chamber temperature would have had a large enough effect on either nitrate formation or immobilisation to cause the decline in ammonium and nitrate.

5.5.5 Measured compared to predicted mineral nitrogen

Measured mineral N was closely correlated to expected mineral N both at the start of the incubation (R^2= 0.96) and the conclusion of the experiment (R^2=0.80) (Figure 5.20).

Nitrate contents followed similar trends (Figure 5.21). The close correlation between the measured and the predicted nitrate contents at the end of the incubation is partly because no loss of mineral N by leaching occurred.

Both the initial and the final measured ammonium differed from the predicted (Figure 5.22) with measured generally being lower than predicted. Ammonium was present in small quantities in the incubations and there was a greater degree of experimental error in the analysis of ammonium using the auto analyser.

The property of ammonium fixation is exhibited more strongly by subsoils than by surface soils. It seems to be associated with clay minerals such as illite and vermiculite (Black, 1957). Ammonium fixation may have occurred when the sludges were applied to the spoils. This could explain why the measured ammonium was lower than that predicted when the sludges were applied, and also why this difference between expected and measured results was greater at the conclusion of the incubation. The 2M KCl used for the extraction of mineral N is unlikely to remove the fixed ammonium.

The amount of mineral N in a mixture was in direct proportion to the amounts present in the constituents. The amount of nitrate in general increased over time in the amended spoils in direct proportion to the increase that occurred in the individual constituents over the same period, most importantly the sludge amendments. This indicates that there was no interaction between the constituents that affected the nitrate content when they were mixed.

5.5.6 Implications for rehabilitation of the mine spoils

The conversion of ammonium to nitrate is expected to cause a lowering of pH as H^+ ions are released:

$$NH_4^+ + 1/2O_2 \xrightarrow{\text{bio oxidation}} NO_2^- + H_2O + 2H^+ + \text{energy}$$

$$NO_2^- + 1/2O_2 \xrightarrow{\text{bio oxidation}} NO_3^- + \text{energy.}$$
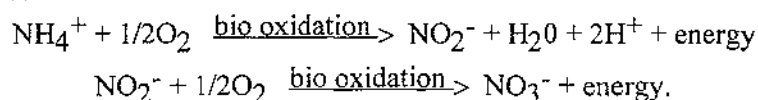
The general trend in pH (Tables 5.6a and b and Figures 5.1 to 5.4) appears to follow this rule.

Sewage sludges are expected to produce nitrate after application to soils. This may lead to contamination of ground and surface water supplies (Awad et al., 1989). Danneberg et al., (1983) reported that if sludge application rates are too high, excess nitrate accumulates in the soil and may be taken up by crops in excess of requirements or reach the ground water. Consequently restrictions on N application have been placed e.g. in Switzerland, the UK, Germany and the Netherlands (Bradley et al., 1992).

The sludge will be applied to the spoils prior to sowing a crop. It will not therefore be taken up by plants for at least several weeks (Powlson, 1993). Nitrate then, is at risk of loss from leaching, however, the smaller the amount of nitrate present, the less available to be leached or denitrified.

The slow release of nitrate from the sludges will allow a supply to plants over an extended period in addition to the initial flush. However, additional quick release fertiliser may be required at different stages of crop growth.

Mineral N (ammonium, nitrate and nitrite) occurs in the soil solution and may be absorbed and utilised by plants (Black, 1957). The mineral forms of N constitute the bulk of the N present in available form at a given moment. In general however, the content of mineral N does not provide a good estimate of the availability of the soil N to crops. This is because the mineral N present at a given moment represents a small and variable proportion of the total amount of mineral N that will be available through out a season (Black, 1957). Munson and Stanford (1955) found that the best estimate of the yield of N to plants was provided by the sum of the initial nitrate and the nitrate produced during a two week laboratory incubation. In this study, the value for initial nitrate was obtained but net mineralisation rather than gross mineralisation was measured over time; i.e.: nitrate mineralised minus nitrate immobilised, denitrified etc.

Nitrate is lost more rapidly from coarse than from fine textured soils because of greater water loss (Black, 1957). Loss is also greater from a fallow soil than from a cropped soil because of the absence of a crop to absorb nitrate in water. When the soil is dry, the time of application of nitrogenous fertiliser before planting has little effect on N losses, under wetter conditions, much may be lost by leaching (Black, 1957). These factors are likely to have an impact on the effect of mineral N applied with sludge on the rehabilitation of the mine spoils.

The low amount of ammonium in the sludges means once the initial high content of nitrate is lost, the release of N for plant use is likely to be slow i.e., the sludges will provide a slow release source of N (Williams and Hall, 1985).

The highest initial rate of nitrate applied was 127 kg/ha, applied to tailings in Manukau sewage sludge applied to provide 10% organic matter. The value for N that may be taken up from an arable field is estimated to be 200 kg/ha in one year (Powlson, 1993). However, while the N applied through sludge is not as high as the average value for crop removal in a season, leaching may be a problem because of the time of application relative to crop growth. The final values in the incubation are in reality unlikely to be realised in the spoil due to losses e.g. leaching, plant uptake etc.

5.6   CARBON TO NITROGEN RATIO

5.6.1   Carbon to nitrogen ratio of the original materials

New Zealand Soil Bureau ratings for carbon to nitrogen ratios (C/N) are as follows (Blakemore et al, 1987):

>24	Very high
16-24	High
12-16	Medium
10-12	Low
<10	Very low

The C/N ratios for the incubation materials are given in Table 5.11.

Based on the New Zealand Soil Bureau ratings for soils, the sewage sludges had medium C/N ratios, and paper sludge had an extremely high C/N ratio. This is similar to figures for recycled paper mill sludge reported by Bellamy *et al.* (1995) of 100-150:1 and is considerably lower than the value (200:1) reported for a paper mill sludge by Feagley *et al.* (1994). The values for sewage sludge are within the range of values reported for some US sewage sludges (Lerch *et al.*, 1992). North Shore had a lower C/N ratio than Manukau sewage sludge.

Tailings, oxidised waste and Huntly subsoil had very low C/N ratios, Waihi subsoil had a medium value, mudstone high and fireclay a very high value for C/N based on Soil Bureau ratings. This compares with studies by Chichester and Smith (1983) where they observed that the C/N ratio of coal spoils was high.

5.6.2   Effect of amendments on the carbon to nitrogen ratio of the mine spoils

5.6.2.1   Manukau sewage sludge
Addition of Manukau sewage sludge increased the C/N ratio of the amended spoils but successive increments did not necessarily cause an increase in the ratio, except when the sludge was applied to Waihi subsoil. This is because there was a greater difference in C contents between the sludges and the spoils than in N contents (Table 5.13). C/N ratios remained in the low to very low range in all amended spoils (Table 5.14).

5.6.2.2   North Shore sewage sludge

Addition of North Shore sewage sludge increased the C/N ratio in all gold mine spoils and the C/N ratio increased with increasing application rates, however values remained in the low to very low range. In the coal mine spoils North Shore sewage sludge was more likely to reduce the C/N ratio, i.e. bring the level of C closer to the level of N.

The C/N ratio of fireclay was reduced but remained very high, in mudstone successive increments of sewage sludge resulted in a reduction of the C/N ratio but values were still medium to high. The result was more variable in Huntly subsoil. The value for N in the subsoil amended to provide 2% organic matter was lower than the unamended spoil. This is assumed to be due to analytical error in measuring total N as discussed in section 5.4. If this value is taken out, a trend of increased C/N ratio with addition of sewage sludge is observed and the C/N ratio is increased to a medium value. (Table 5.12).

5.6.2.3   Paper sludge

The C/N ratio of mine spoils was increased by addition of paper sludge and the larger the sludge addition, the greater the C/N ratio. All additions of paper sludge resulted in very high C/N ratios. This is a result of the relatively high C, and low N content of the paper sludge (Table 5.11).

5.6.3   Implications for rehabilitation of the mine spoils

The critical ratio of C/N lies between 15 and 33, above which negative recoveries of added N occur due to immobilisation by soil micro-organisms (Bellamy *et al.*, 1995) and below which the N added is mineralised to inorganic N. The critical value is not constant but depends on such factors as time and temperature for decomposition, the supply of mineral N in the soil and the quantity and composition of the organic material (Black, 1968).

When Manukau sewage sludge was applied to minespoils, at all rates the C/N ratio remained in the low to very low range, implying that the organic N present in the sewage sludge may be readily mineralised and made available for plant uptake.

North Shore sewage sludge had a medium C/N ratio, it is hence likely to release N, available for plant use. When applied to tailings which had negligible amounts of C and N, the C/N values remain in the very low to low range. This would suggest that N

is likely to be rapidly released from the organic matter (mineralised) in the presence of suitable micro organisms (Brady, 1984). However, given the low N values of the mixtures, an additional N fertiliser may still be required. The same is true for oxidised waste and Waihi subsoil.

The very high C/N ratio of fireclay is a reflection of the high C content which is held in coal. As stated earlier (section 5.1) coal is a very stable form of carbon, resistant to breakdown and it is therefore unlikely to have a significant affect on the availability of nitrogen in the spoil.

Paper sludge has a very high C/N ratio. This is likely to cause what little nitrogen is supplied in the sludge to be significantly tied up and very little to be available for plant uptake (Black, 1957). Where it is used as an amendment a supplementary nitrogen fertiliser is likely to be required to supply nitrogen to plants.

The very high C/N ratio of the paper sludge is reflected in the very low (0.4% initially and 0.8% finally) of total N that was in mineral form in the sludge. The slow or small release of mineral N from the organic matter due to the high C/N ratio is evident if the percentage change in net mineral N during the incubation is calculated for spoils amended with either North Shore sewage or paper sludge. In every case, a lower percentage of net mineral was released in the paper sludge treatments than the sewage sludge and in some situations (e.g. paper sludge amended fireclay) the mineral N content declined from the beginning to the conclusion of the incubation.

5.7 TOTAL PHOSPHORUS

5.7.1 Total phosphorus content of the original materials

New Zealand Soil Bureau ratings for total phosphorus (P) contents in New Zealand soils are as follows (Blakemore et al., 1987):

>120 mg/100g	Very high
80-120	High
40-80	Medium
20-40	Low
<20	Very low

The values for P in the original incubation materials are given in Table 5.15.

Manukau and North Shore sewage sludges had similar P values, 12.9 and 12.3 mg/g respectively. According to the NZ Soil Bureau ratings for New Zealand soils, these values are very high; however, they are similar to other sewage sludges (National Council of the Paper Industry for Air and Steam Improvement, 1984; Topper and Sabey, 1986; Sjoquist and Wikander-Johansson in Ghorayshi, 1989). Sharp (1992) gave a typical figure for P in New Zealand "biosolids" (sewage sludge) of 0.2% and Adams, et al. (1992) gave a figure for P in sewage sludge from Bromely sewage treatment plant at Christchurch of 1.6%. Sjoquist and Wikander-Johansson (quoted in Ghorayshi, 1989) reported that the P content of sewage sludge is usually between 1 and 3.5% (dry matter).

The high content of P in the sewage sludges is due to the use of P in such products as washing powder and to the high efficiency of the chemical P elimination in sewage treatment plants (Furrer and Gupta, 1985). Most of the P is removed from the effluent and retained in the sludge.

The P content of paper sludge is medium based on the NZ Soil Bureau ratings and is within the range (0.001-25.4 mg/g) reported for US paper mill sludges (National Council of the Paper Industry for Air and Steam Improvement, 1984; Bellamy et al., 1995).

All the spoils except Huntly subsoil had low values for total P based on the NZ Soil Bureau ratings, Huntly subsoil had a medium value. Low values for total P and N are expected for mine spoils (Barnhisel, 1988, Bradshaw and Chadwick, 1980).

Table 5.15   Phosphorus characteristics of the original materials

Material	P Retention (%)	Total P (mg/g)	Total P (% of dry wt)	Olsen P (mg/g)	
				Initial	Final
Manukau sludge	61	12.9	1.29	202.1	228
North Shore sludge	43	12.3	1.23	273.9	183
Paper sludge	33	0.7	0.07	13.9	15.4
Tailings	25	0.3	0.03	5.3	11.8

Oxidised waste	31	0.2	0.02	2.8	0
Waihi subsoil	45	0.2	0.02	1.5	0
Fireclay	22	0.2	0.02	2.0	0.3
Mudstone	41	0.2	0.02	6.1	6
Huntly subsoil	26	0.5	0.05	0	0

5.7.2 Effect of amendments on the total phosphorus content of mine spoils

5.7.2.1 Manukau and North Shore sewage sludges

When Manukau sewage sludge was applied to achieve 5% organic matter, the P values of the mixtures were high to very high and when applied to achieve 10% organic matter all P values were very high (Table 5.16). At 2% organic matter, the amount of P in tailings and oxidised waste was a medium value and in Waihi subsoil was low.

North Shore sewage sludge produced similar trends although had slightly less effect on total P in the incubation mixtures than did Manukau. Coal mine spoils amended with North Shore sewage sludge to provide 10% organic matter had very high P values, the exception was mudstone which had a medium value. When applied to provide 5% organic matter in mudstone the P value was in the medium range and in Huntly subsoil the P value was high; at 2% organic matter, the P value was low in Huntly subsoil (Table 5.16).

5.7.2.2 Paper sludge

The effect of paper sludge on the P content of coal mine spoils was smaller than the effect of sewage sludge addition. This was a result of the paper sludge's lower P content and its higher organic matter content, resulting in less being applied than sewage sludge to achieve the same amount of organic matter in the mixtures. The total P in fireclay was not significantly affected by paper sludge addition, in mudstone at 5% organic matter it was not significantly affected but at 10% organic matter, a slight reduction in the total P value occurred. In Huntly subsoil the P content was slightly but significantly increased with increasing sludge addition, however, values remained very low.

Table 5.16

Total phosphorus and Olsen phosphorus initially in the incubations

Sludge amendment	Amended spoil	Organic matter (%)	Total P (mg/g)	Olsen P (µg/g)
Manukau	Tailings	2	0.79	28
		5	1.7	54
		10	0.25	77
	Oxidised waste	2	0.66	23
		5	1.90	44
		10	2.72	66
	Waihi subsoil	2	0.29	3
		5	0.95	21
		10	2.73	46
North Shore	Tailings	2	0.73	32
		5	1.54	59
		10	2.95	95
	Oxidised waste	2	0.63	24
		5	1.46	44
		10	2.50	73
	Waihi subsoil	2	0.27	0
		5	0.83	17
		10	2.07	48
	Fireclay	10	0.63	29
	Mudstone	5	0.56	44
		10	1.80	111
	Huntly subsoil	2	0.32	9
		5	0.90	30
		10	1.95	60
Paper sludge	Fireclay	10	0.25	3
	Mudstone	5	0.23	5
		10	0.18	6
	Huntly subsoil	2	0.14	2
		5	0.16	3
		10	0.17	6

5.7.3   Effect of the incubation on total phosphorus

The total P content of the materials did not significantly change during time. P is neither absorbed from the atmosphere nor volatilised (Brady, 1984), no changes in the total P contents of the incubations were therefore expected.

5.7.5   Measured compared to predicted total phosphorus

Measured and calculated total P values were closely correlated ($R^2=0.91$, Figure 5.23). This indicates that the effect of sludge addition on the total P content of the amended spoils was additive, there were no interactions between the two materials in any mixture that affected the total content of P. The 'Woburn Market Garden Experiment' summarised by Johnston (1975) produced similar results, the total P in soil amended with sewage sludge was well related to the P added in the sludge.

5.7.6   Implications for rehabilitation of the mine spoils

A measure of total P in a soil or spoil is not very revealing as to the likelihood of plants establishing on the material. In most soils the amount of the total P that is in an available form is very low, seldom exceeding 0.01% of the total P (Brady, 1984). Additionally, when soluble fertiliser salts of P are supplied to the soils, the P is often rendered insoluble or unavailable to higher plants (Brady, 1984). Soil nutrient status in the case of P is normally expressed in terms of 'available' fractions. P is an element that can be stored in many soils without considerable risk of loss by leaching. For this reason, high rates of P fertilisation in preceding years, have led to a continuous increase of the P content of many soils and accumulation or enrichment is apparent in measurements of total P (Cottenie and Kiekens, 1981). The CEC-Workshop on standardisation of analytical methods for manure, soils, plants and water held in Ghent in June 1978, proposed the determination of total P in order to observe soil enrichment with P and to make nutrient balances (Cottenie and Kiekens, 1981).

High levels of P (which occur in the sewage sludge amended spoils) can sometimes cause nutrient imbalances such as P induced zinc, iron, Manganese and molybdenum deficiencies (Olsen, 1972). Potential for transport of P into bodies of water also exists.

While the total P in sewage sludge amended spoils is high to very high at 10% organic matter, P available to plants will not necessarily be high. The availability of P to plants

is dependent most significantly upon P retention (section 5.9) and pH of the spoils (Cresser *et al.*, 1993),

Additional P fertiliser application to paper sludge amended spoils will be required.

5.8 SODIUM BICARBONATE EXTRACTABLE (OLSEN) PHOSPHORUS

A large number of methods may be used for determination of plant available P and results obtained depend upon the method used. It is for this reason that the CEC-expert group on analytical methods strongly recommend that P contents are given in terms of the element and not of its oxide and that they be expressed in mg/kg of soil (Cottenie and Kiekens, 1981). Values for P contents of spoils and sludges are usually given as total P, and where an estimate of the available P content of a material is given the method used to determine it may not be the same as the one used here and cannot be reliably compared. However, according to Williams and Coker, (1981), the fraction of soil P which is extractable with 0.5 M sodium bicarbonate ($NaHCO_3$) gives a good indication of plant available P.

5.8.1 Olsen phosphorus content of the original materials

New Zealand Soil Bureau ratings for Olsen P contents of New Zealand soils are as follows (Blakemore et al, 1987):

>50 ($\mu g/g$)	Very high
30-50	High
20-30	Medium
10-20	Low
<10	Very low

Based on these ratings, both Manukau and North Shore sewage sludges had very high levels of Olsen (available) P. The percentage of total P that was in available form was greater in North Shore sewage sludge than Manukau. This may be because of a higher heavy metal loading in Manukau sewage sludge (Section 5.11). According to Williams and Coker (1981), industrial sludges high in metals are likely to contain appreciable amounts of P precipitated as metal phosphates. Harkness and Jenkins (1958) showed that at two works treating mainly industrial sewage, there was considerably less soluble P (63%) compared with a sewage sludge that was of domestic origin (84%).

Sewage sludges are expected to have high percentage of P in available form to plants (Ghorayshi, 1989). Estimates of the average availability of the P present in sewage sludge varies between 50 and 70% although EAWAG (1977) in Switzerland suggested a value of 80% (Williams and Coker, 1981).

Paper sludge had a low level of available P based upon NZ Soil Bureau ratings.

All spoils had very low levels of available P. Bradshaw and Chadwick (1980) list colliery spoil as having a severe P deficiency and gold wastes a moderate deficiency. The low level of available P in the spoils is due to a deficiency in total P rather than a locking up of P in unweathered minerals (Table 5.15).

5.8.2   Effect of amendments on the Olsen phosphorus of mine spoils

5.8.2.1   *Manukau and North Shore sewage sludges*

In the amended spoils, both Manukau and North Shore sewage sludge caused significant increases in available P. Each successive increase in sludge addition resulted in an increase in the Olsen P value of the amended spoil except when Manukau sewage sludge was applied to Waihi subsoil to provide 2% organic matter (Figures 5.24 and 5.25). When tailings were amended with either sewage sludge to provide 5% and 10% organic matter, Olsen P values were very high. In oxidised waste Olsen P values were very high at the 10% organic matter level with both sludges, Huntly subsoil amended with North Shore sewage sludge to provide 10% organic matter was also very high. Mudstone and tailings amended with North Shore sewage sludge to 2% organic matter, oxidised waste amended with North Shore and Manukau sewage sludge to 5% organic matter, Waihi subsoil amended with either sewage sludge 10%, mudstone and Huntly subsoil amended with North Shore sewage sludge to 5% all had high Olsen P values (Figures 5.24-5.26). North Shore sewage sludge was more effective than Manukau sewage sludge at increasing available P in the gold mine spoils.

5.8.2.2   *Paper sludge*

Paper sludge had no significant effect on the available P content of Fire clay or Huntly subsoil (Figure 5.27a and c). When it was applied to mudstone, there was a slight increase in available P compared to the untreated spoil at 10% organic matter (Figure 5.27b). The Olsen P as a percentage of total P in paper sludge amended spoils was lower than in the sewage sludge amended spoils.

Huntly subsoil had an initially high Olsen P value, which had reduced by week 4 of the incubation and remained fairly constant (Figure 5.27c). It is suspected that the initial (time 0) result was erroneous.

5.8.3   Effect of the incubation on Olsen phosphorus

Figures 5.24-5.27 show the effect of time on the Olsen P contents of the incubations. The Olsen P values of Manukau sewage sludge and paper sludge increased slightly during the incubation, in North Shore sewage sludge it did not change significantly during the incubation. The Olsen P in the spoils did not significantly change during the incubation.

There was a slight but significant increase in Olsen P in the Manukau sewage sludge amended tailings throughout the incubation. This was due to an increase in Olsen P in the sludge during the incubation. There was no significant change in the Olsen P content of tailings during time, when amended with North Shore sewage sludge.

Similar results were achieved when the sludges were added to oxidised waste except there was a gradual increase in Olsen P in the treatments during incubation regardless of sludge.

At 5 and 10% organic matter in Waihi subsoil, the available P increased slightly during the incubation up to week 20, then stabilised. At 2% organic matter, there was no significant change.

In Mudstone amended with North Shore sewage sludge, the Olsen P content increased significantly over time. Olsen P slightly but significantly increased during the incubation when fireclay was treated with North Shore sewage sludge. In Huntly subsoil amended with North Shore to achieve 5 and 10% organic matter, the Olsen P level increased slightly during the incubation. There was no significant effect of time on Olsen P at 2% organic matter.

The Olsen P in the paper sludge treated spoils did not alter significantly during the incubation.

Olsen P values in amended spoils at the conclusion of the incubation were at very high levels in all treatments of tailings with Manukau sewage sludge and at 5 and 10%

organic matter with North Shore sewage sludge. Oxidised waste amended to 5 and 10% organic matter with Manukau sewage sludge and 2, 5 and 10% organic matter with North Shore sewage sludge also had very high values for Olsen P. Olsen P values were very high in Waihi subsoil amended to 5 and 10% organic with North Shore sewage sludge. They were also very high at 5 and 10% organic matter in North Shore sewage sludge amended mudstone and Huntly subsoil.

5.8.4 Explanation of the effects of sludge addition and incubation on the Olsen phosphorus content of the mine spoils

The increase in Olsen P in the mixtures with sewage sludge addition is attributable to the high Olsen P in the sewage sludges. Manukau sewage sludge addition to Waihi subsoil at 2% organic matter was not sufficient to cause an increase in Olsen P.

Due to the low available P in paper sludge and its high organic matter content (requiring less sludge be applied to achieve desirable organic matter contents), paper sludge had little effect on the Olsen P in the spoils. The amount of paper sludge required to raise the organic matter content of the spoils to 10% (fireclay- 76.5 kg/t, mudstone- 362 kg/t and Huntly subsoil- 269 kg/t).was directly related to the effect it had on the Olsen P content of the different materials.

A small amount of inorganic P is released continually from the pool of organic P (organic P mineralisation) in organic matter by the same decomposition processes that release N in mineral form (Black, 1957). The increase in Olsen P may be attributed to its slow release from the sludges and lack of loss from the system, i.e., it was not taken up by plants or leached.

5.8.5 Measured compared to predicted Olsen phosphorus

Regression relationships between the measured and predicted Olsen P at the beginning and conclusion of the incubation are given in Figure 5.28.

Measured trends were closely correlated to predicted trends. With increasing sludge addition an increase in Olsen P occurred. However, measured values for Olsen P were not well correlated with predicted values ($R^2 = 0.66$ initially and $R^2 = 0.45$ at the conclusions of the incubation). The more sludge applied, the closer the predicted results were to measured results.

When Manukau sewage sludge was applied to tailings and oxidised waste, the Olsen P values were considerably higher than predicted. When Manukau sewage sludge was applied to Waihi subsoil, measured Olsen P values were well correlated with predicted.

When North Shore sewage sludge was applied to tailings, the Olsen P values were higher than predicted, when applied to oxidised waste to achieve 2 or 5% organic matter, results were lower than predicted but very close to predicted at 10% organic matter. When North Shore sewage sludge was applied to Waihi subsoil, Olsen P values were lower than predicted. The same is true when the sludge was applied to Huntly subsoil. However, when applied to Fireclay and Mudstone, results were higher than predicted.

Results were higher than predicted when fireclay was amended with paper sludge and lower than predicted when mudstone and Huntly subsoil were amended with paper sludge.

Most of the available P is from the sludge rather than the spoil. Any interaction between the sludge and the spoil affecting Olsen P is likely to be as a result of an effect of the spoil characteristics on sludge characteristics. Addition of sludge to all but tailings, resulted in a reduction in pH relative to the sludge. Below about pH 6.5, the lower the pH, the lower the P availability (Cresser et al., 1993; Brady, 1984; Tucker et al. 1987). P is combined with iron and aluminium in soils below about pH 6.5 and in soils above this pH, calcium plays an increasing part in binding P (Brady, 1984).

Low P availability occurs most in soils with high acidity or alkalinity and least in the soils with pH approximately neutral. According to Black (1957), a variety of experimental evidence indicates that soil behaviour usually follows this pattern. Treatments that have a moderate acidifying effect usually increase the P availability in alkaline soils (Black, 1957). The reason for this is thought to be that the inorganic P in alkaline soils is predominantly in combination with calcium as calcium phosphate. Calcium phosphates are dissolved by acids because the tendency of the phosphate ion to associate with hydrogen instead of calcium increases rapidly as the acidity increases. However, neither the water solubility nor the availability of soil P is necessarily always increased when acid soils are limed.

Based on the effect on the pH of the sludge of addition to the spoils, it is unlikely that actual Olsen P values can be derived using equation 4.6 as this equation only takes into account the Olsen P value of each material and does not consider any possible effects

of other changes on the Olsen P of the mixtures. When the pH of the sludges and the amended spoils are considered then one would expect (as occurred) Manukau and North Shore sewage sludge amended tailings to have a higher Olsen P than predicted. However all other mixtures may be expected to have Olsen P values lower than predicted. This was the case for all except Waihi subsoil amended with North Shore sewage sludge to provide 2% organic matter, oxidised waste amended with Manukau sewage sludge, fireclay and mudstone amended with North Shore sewage sludge, and fireclay amended with paper sludge.
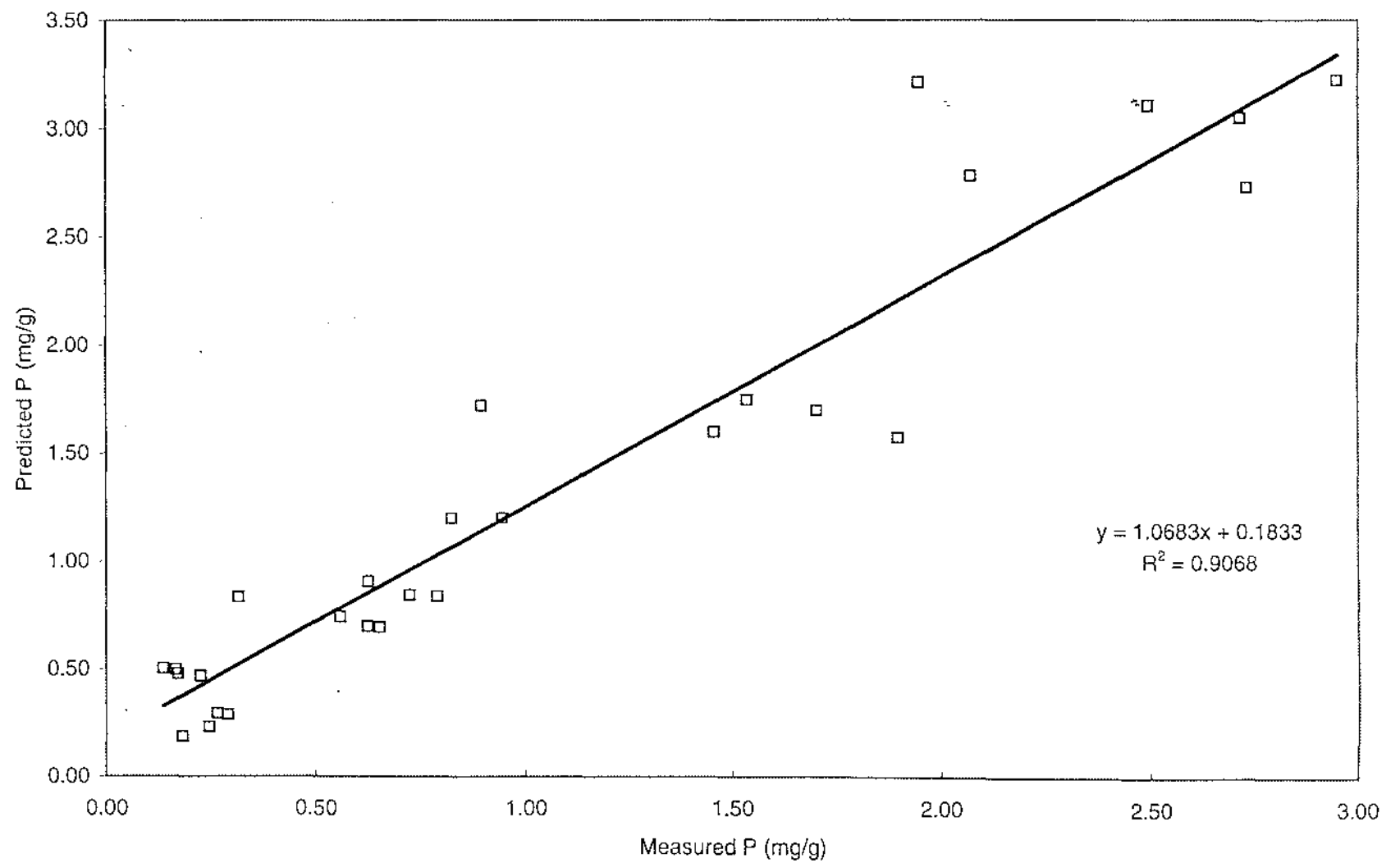
Figure 5.23 Relationship between predicted and measured total phosphorus content of the incubations
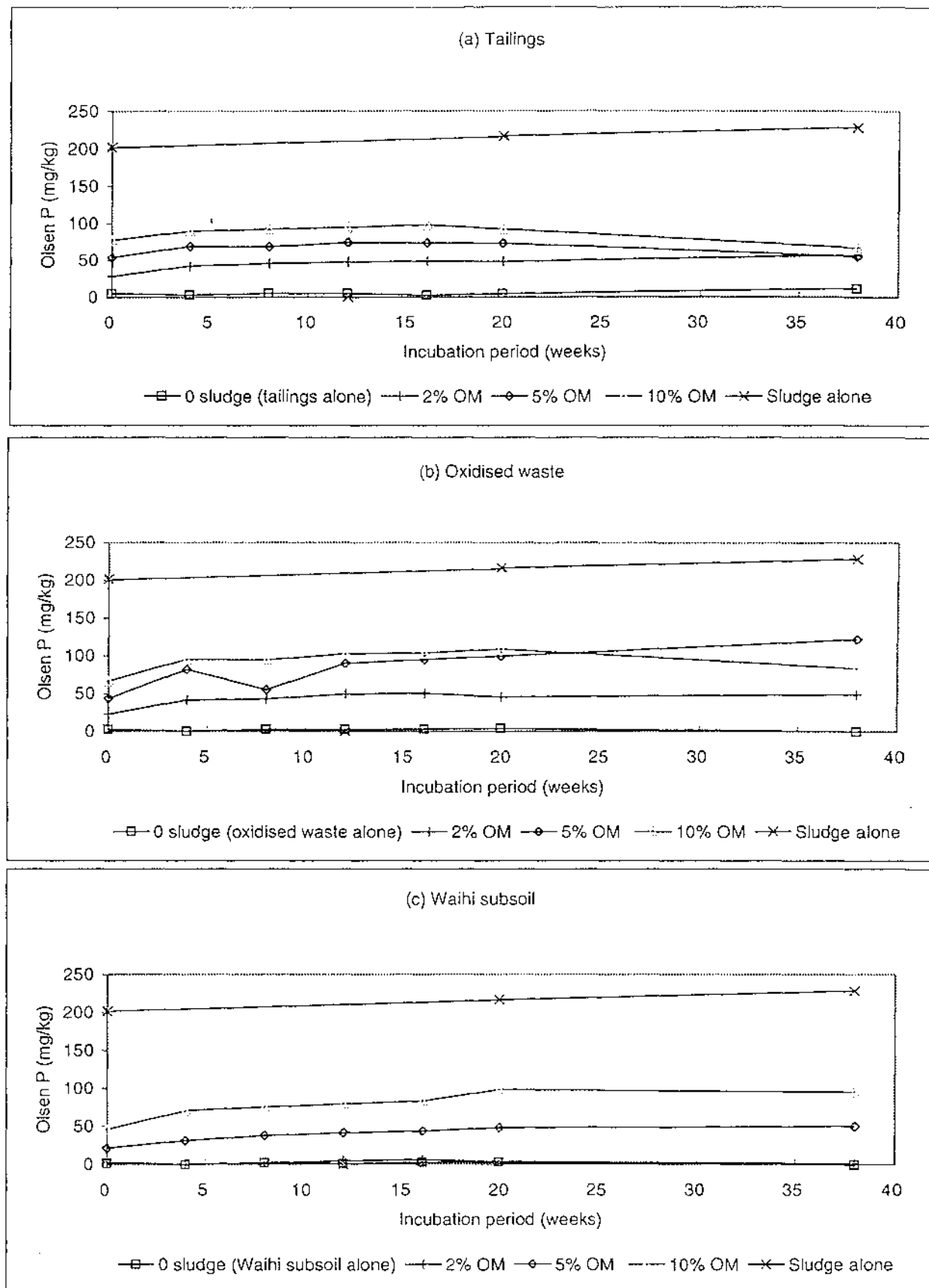
Figure 5.24   Effect   of   manukau   sewage   sludge   addition
to   provide   specified   organic   matter   content
(OM)   on   the   Olsen   phosphorus   content   of
gold   mine   spoils

(a) Tailings

—□— 0 sludge (tailings alone) —+— 2% OM —◇— 5% OM —·—· 10% OM —✕— Sludge alone

(b) Oxidised waste

—□— 0 sludge (oxidises waste alone) —+— 2% OM —◇— 5% OM —·—· 10% OM —✕— Sludge alone

(c) Waihi subsoil

—□— 0 sludge (Waihi subsoil alone) —+— 2% OM —◇— 5% OM —·— 10% OM —✕— Sludge alone
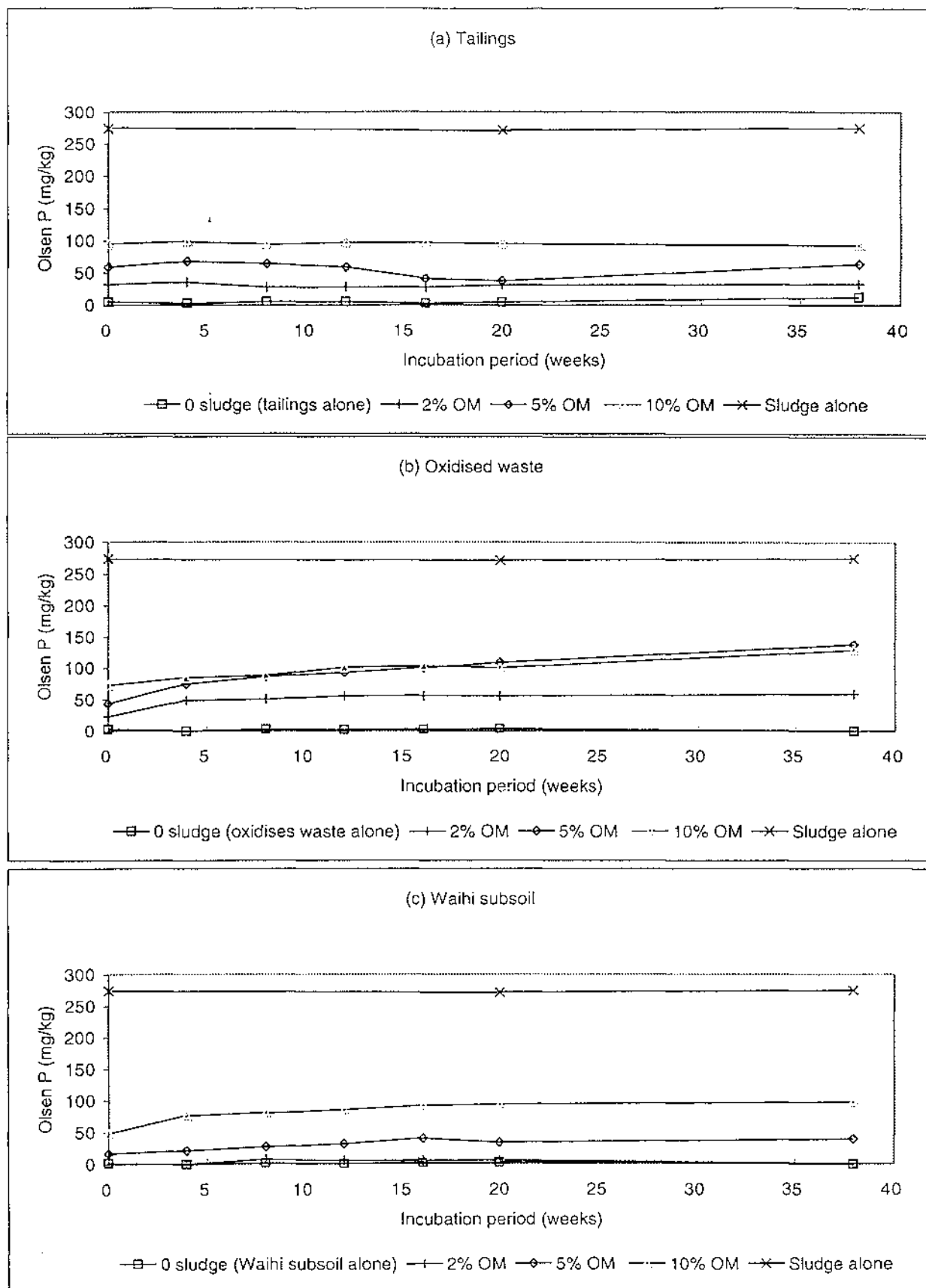
Figure 5.25   Effect of North Shore sewage sludge addition
to provide specified organic matter content
(OM) on the Olsen phosphorus content of
gold mine spoils

(a) Fireclay

—□— 0 sludge (fireclay alone) —·— 10% OM —△— Sludge alone

(b) Mudstone

—□— 0 sludge (mudstone alone) —·— 5% OM —◇— 10% OM —△— Sludge alone

(c) Huntly subsoil

—□— 0 sludge (Huntly subsoil alone) —+— 2% OM —◇— 5% OM —·— 10% OM —✕— Sludge alone
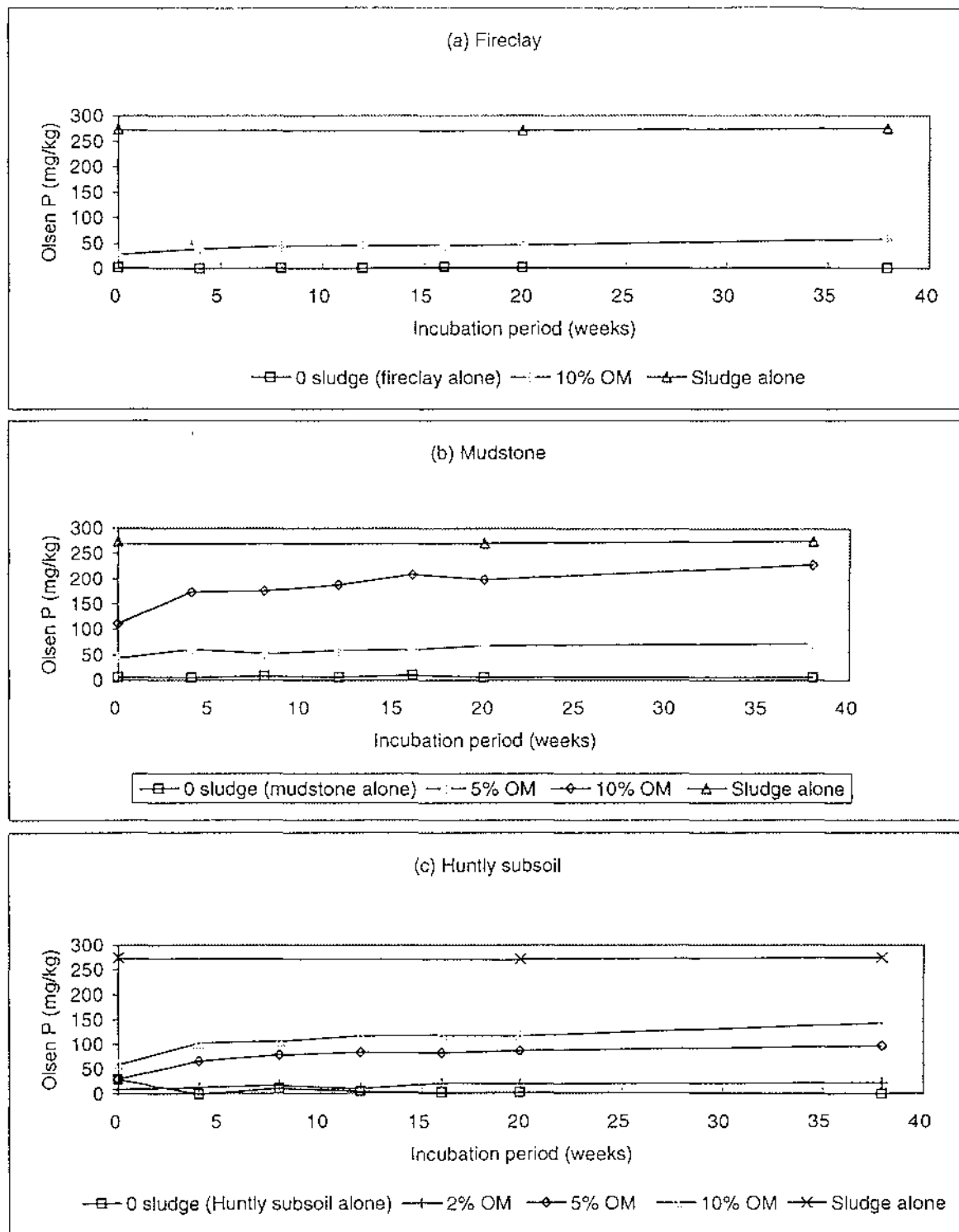
Figure 5.26   Effect of North Shore sewage sludge addition to provided specified organic matter (OM) content on the Olsen phosphorus content of coal mine spoils
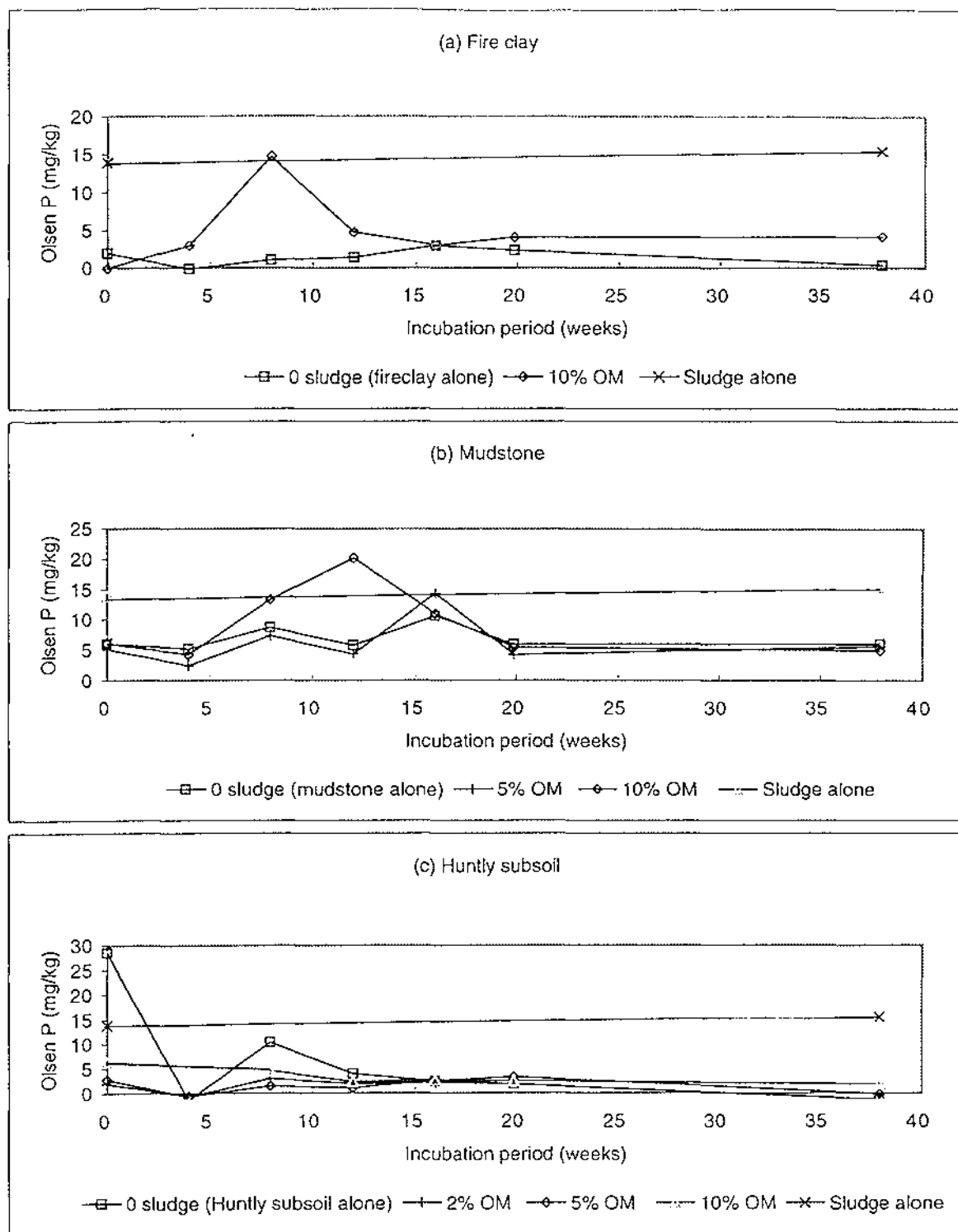
Figure 5.27   Effect of paper sludge addition to provide
              specified organic matter (OM) content on
              the Olsen Phosphorus content of coal mine
              spoils
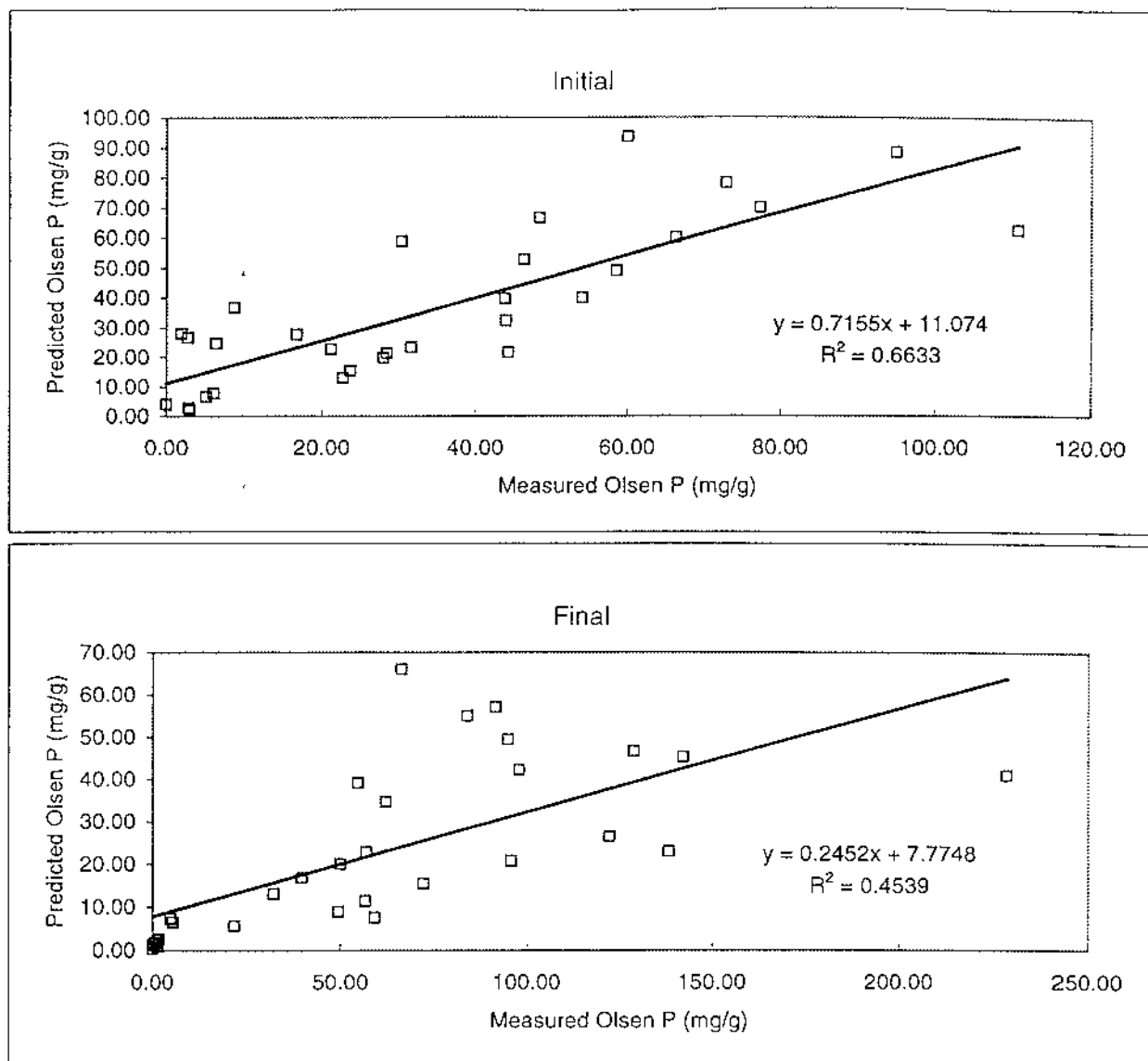
Figure 5.28   Relationship between predicted and measured Olsen phosphorus at the start (initial) and conclusion (final) of the incubation

5.8.6 Implications for rehabilitation of the mine spoils

Because Olsen P could not be accurately predicted, a soil test after sludge addition to spoils to assess P availability is required before a decision on P fertiliser application is made.

The relationship between the Olsen P and the expected response to applied fertiliser is as follows: <5 ppm, a response; between 5 and 10 ppm, a probable response; and > 10 ppm, a response unlikely. These responses depend on soil type. The crops used in field experiments to establish these levels were wheat, oats, alfalfa, and cotton (Olsen *et al.*, 1954). Similar response levels were observed by Martin and Mikkelsen (1960); and Moser *et al.* (1959) found a high correlation between $NaHCO_3$ extractable P and uptake of P by plants. On this basis, the only treatments likely to respond to additional P fertiliser (depending upon crop) are Waihi subsoil amended with either sewage sludge to provide 2% organic matter, fireclay amended with paper sludge, and Huntly subsoil amended with paper sludge to 2 and 5% organic matter. In Huntly subsoil amended with North Shore sewage sludge to 2% organic matter and with paper sludge to 10% organic matter and in mudstone amended with paper sludge to 5 and 10 % organic matter, a response is probable but not certain. All other treatments are likely, at least in the short term to supply sufficient P for plant growth. The concern with the treatments with high Olsen P values is the possibility of leaching of excess available P. However, some studies have shown that while an increase in soluble P in a soil profile may occur due to sludge application, this is not accompanied by an increase in P leaching (Furrer, 1981; De Haan, 1981). The P retention ability of the sludge receiving soils will largely determine the potential for P leaching through the spoil. This is considered in section 5.9.

5.9 PHOSPHATE RETENTION

5.9.1 Phosphate retention of the original materials

The phosphate retention values for tailings, fireclay and Huntly subsoil were low based upon New Zealand Soil Bureau ratings for soils (Blakemore *et al.*, 1987):

90-100%	Very high
60-90	High
30-60	Medium
10-30	Low
0-10	Very low

Waihi subsoil, oxidised waste, mudstone, North Shore sewage and paper sludge all had medium phosphate retention values. Manukau sewage sludge had a high phosphate retention (Table 5.15). These values do not correlate to the initial percentage of total P that was available in each material (Table 5.15) or to the increase in available P over time (Figures 5.24-5.27).

The phosphate retention of the individual materials does not follow the trend one would expect when considering the pH (Table 5.6a). Based on pH (Black, 1957), mudstone (pH 2.32), Huntly subsoil (pH 3.5) and tailings (pH 7.93) were predicted to have high P retention capacity.

However, the Olsen P in the sludge amended gold mine spoils when expressed as a percentage of total P does reflect the phosphate retention of the spoils (Table 5.17), i.e., the higher the phosphate retention of a spoil, the lower the percentage of total P that is in available form when amended with a sludge. The coal mine spoils do not follow this trend with either North Shore or paper sludge amendments.

5.9.2 Implications for rehabilitation of the mine spoils

The low P retention values of the tailings, fireclay and Huntly subsoil are likely to mean that a relatively high proportion of P applied will be available for plant uptake. This should have been reflected in Olsen P results which should be relatively higher for these spoils than Waihi subsoil, oxidised waste and mudstone when sludge is applied. This was the case except mudstone had a higher Olsen P value than expected based on P retention. The percentage of total P that was available in mudstone when either North Shore or paper sludge was applied was higher than the percentage total P available in fireclay and Huntly subsoil with the same amendment at 10% organic matter (Table 5.17).

None of the spoils have high phosphate retention values so if P is applied in a fertiliser, it is likely to be relatively readily available to plants. However, one would expect that

the high phosphate retention of the Manukau sewage sludge would mean that the P content of this amendment would be relatively unavailable to plants and this was initially the case (Table 5.15). Even if a high amount of total P was supplied in the sludge, further P fertiliser may be required to meet the demands of plants growing on the amended spoils. However, the Olsen P results do not reflect this (Table 5.16).

Table 5.17

Olsen P (initially) as percentage of total P and phosphate retention in sludges amended with sludge to 10% organic matter

Spoils and sludge in incubation	Olsen P as a % of total P	P retention of the spoil (%)
Tailings and Manukau	1.8	25
Tailings and North Shore	1.9	25
Oxidised waste and Manukau	1.7	31
Oxidised waste and North Shore	1.5	31
Waihi subsoil and Manukau	1.3	45
Waihi subsoil and North Shore	1.1	45
Fireclay and North Shore	1.6	22
Fireclay and paper	0.2	22
Mudstone and North Shore	2.8	41
Mudstone and paper	0.75	41
Huntly subsoil and North Shore	1.1	26
Huntly subsoil and paper	0.4	26

5.10 CATION EXCHANGE CAPACITY

5.10.1 The cation exchange capacity of the original materials

Table 5.18 gives the effective cation exchange capacity (CEC) of the individual incubation materials. The New Zealand Soil Bureau uses the following ratings for CEC of New Zealand soils (Blakemore *et al.*, 1987):

>40 me/100g (cmol/kg)	Very high
25-40	High
12-25	Medium
6-12	Low
<6	Very low

Based upon the Soil Bureau ratings for soils, all the spoils had medium CEC's and the sludges had very high CEC values.

The high CEC of the sludges is attributed to the high content of organic matter which has a high CEC (Fleming and Davis, 1986; Stucky and Newman, 1977; Schneider *et al.*, 1981). On a weight basis, humus has a much higher CEC than the inorganic components (Metson and Blakemore, 1968). The CEC obtained for paper mill sludge was very similar to that obtained by Feagley *et al.* (1994) who reported a CEC of 62.80 cmol/kg for a US papermill sludge. Similarly, the spoils with low organic matter content were expected to have a relatively lower CEC compared with the sludges. Feagley *et al.* (1994) reported very low CEC for minespoil in their study.

Calcium (Ca) dominates the exchange sites of tailings and the sludges. This is in common with the exchange properties of a typical arable soil (Metson and Blakemore, 1968; Miller, 1968). The reason is that Ca ions along with magnesium (Mg) ions are divalent and hence are the most strongly absorbed of the common soil cations (Metson and Blakemore, 1968). In the sewage sludges Mg is the second most common cation.

The high exchangeable Ca of tailings is attributed to the addition of hydrated lime during processing of the ore (Waihi Gold Company, 1985a). In the other spoils hydrogen (H) is the dominant cation on the exchange sites. This is a reflection of their low pH values (Metson and Blakemore, 1968). Paper sludge and tailings have very high concentrations of sodium (Na), higher than the Mg content. Sodium hydroxide, sodium meta-bisulfite and sodium silicate are used in paper manufacturing and are major sources of Na^+ (Bellamy *et al.*, 1995). In tailings the high value for Na is attributed to the addition of sodium cyanide during processing of the ore (Waihi Gold Company, 1985a).

Table 5.18

CEC and exchangeable bases of the original materials

Material	CEC (meq%)	Ca^{2+} (meq%)	Mg^{2+} (meq%)	K^+ (meq%)	Na^+ (meq%)	Total bases (meq%)
Manukau sludge	78.84	64.55a (82)	11.61a (15)	0.57b (0.7)	0.47b (0.6)	77.20a (98)
North Shore sludge	58.28*	52.26a (90)	4.08b (7)	0.87a (2)	1.07b (2)	58.28b (100)
Paper sludge	60.31*	54.27a (90)	2.20c (4)	0.56b (0.9)	3.28a (5)	60.31b (100)
Tailings	14.65	7.54 (51)	1.43 (10)	0.50 (3)	2.58 (18)	11.18 (76)
Oxidised waste	16.24	2.29 (14)	4.16 (26)	0.44 (3)	0.62 (4)	7.51 (46)
Waihi subsoil	18.22	2.79 (15)	2.65 (15)	0.43 (2)	0.77 (4)	6.63 (36)
Fireclay	13.71	4.95 (36)	2.23 (16)	0.33 (2)	0.83 (6)	7.32 (53)
Mudstone	23.30	0.67 (3)	1.19 (5)	0.27 (1)	0.67 (3)	2.8 (12)
Huntly subsoil	15.82	0.36 (2)	1.42 (9)	0.18 (1)	0.13 (0.8)	2.09 (13)

\#   Mean values for sludges with the same letter are not significantly different from other treatments of the same spoil; using Duncan's multiple range test at 5% significance level.

\#   The values within brackets give percent saturation.

*   For North Shore sewage and paper sludge, only the sum of the exchangeable bases was obtained as the acidic cation (H^+) could not be measured- it gave a negative result when subtracted from the standard solution and is not considered to contribute significantly to the CEC of the sludge.

5.10.2 Effect of the amendments on the cation exchange capacity of the mine spoils

5.10.2.1 Manukau sewage sludge

The effect of the sludge on the CEC of the spoils was variable (Table 5.19) although all the Manukau sludge amended spoils had higher CEC than the unamended spoils. Tailings amended to 5% organic matter had a significantly higher CEC (very high) than when amended to 10% organic matter (high) and at 2% organic matter the CEC was lower than at 5 and 10% organic matter.

In oxidised waste, successive increases in sludge addition resulted in an increase in CEC. Both 5 and 10% organic matter levels had high CEC values compared to a medium value at 2% organic matter. In Waihi subsoil, the 10% organic matter amendment resulted in the highest CEC (high), although it was not significantly different from the 2% organic matter amendment (medium value).

5.10.2.2 North Shore sewage sludge

In all mine spoils except Waihi subsoil, addition of sewage sludge resulted in an increase in CEC. When applied to tailings, to provide 10% organic matter, the CEC was significantly higher than at 5% organic matter, but there was not a significant difference in CEC between the 10% and 2% organic matter levels. All results were in the medium range. Results were similar in oxidised waste; although at 2 and 10% organic matter, values were high. In Waihi subsoil, there was no significant difference between any of the treatments (all had medium values) and the CEC's of the 2 and 5% organic matter treatments were lower than the unamended spoil. When applied to fireclay the CEC was increased (medium value) but when applied to mudstone to provide 5% organic matter, a CEC not significantly different from that of the spoil was recorded, however, at 10% organic matter it was a high value. Amended Huntly subsoil had a higher CEC than the unamended spoil and each successive addition of sludge resulted in an increase in CEC. The 2% and 5% organic matter levels had medium CEC values and the difference between them was not significant. At 10% organic matter, the CEC was high (Table 5.19).

5.10.2.3 Paper sludge

The CEC of fireclay amended with paper sludge was lower than the unamended spoil. There was no significant difference in CEC values between the treatments of mudstone, and similarly there were no significant differences between treatments of Huntly subsoil,

Table 5.19

CEC and basic cations of the amended mine spoils

Spoil	Amendment	Organic matter (%)	Ca (meq%)	Mg (Meq%)	K (meq%)	Na (meq%)	CEC (meq%)
Tailings	None		7.54f	1.43c	0.50b	2.58c	14.65d
	Manukau	2	10.79de	1.66bc	0.61b	2.81c	16.26d
		5	14.75c	2.03ab	0.70b	23.18a	43.08a
		10	20.67a	2.11ab	0.64b	12.67b	38.04b
	North Shore	2	9.76e	1.91ab	1.65a	3.08c	17.66cd
		5	12.48d	1.79a-c	0.64b	4.82c	16.92d
		10	16.97b	2.16a	0.64b	1.59c	22.19c
Oxidised waste	None		2.29e	4.16a	0.44e	0.62c	16.24c
	Manukau	2	5.03de	4.11a	0.67bc	0.81bc	19.30bc
		5	11.12b	4.37a	0.75b	0.97ab	30.87a
		10	17.97a	4.53a	0.88a	1.10a	33.17a
	North Shore	2	7.58cd	4.16a	0.70bc	0.66c	26.39ab
		5	9.09bc	4.12a	0.52de	0.73bc	20.92bc
		10	16.03a	4.10a	0.60cd	0.71bc	29.49a
Waihi subsoil	None		2.79c	2.65a	0.43a	0.77a	18.22b
	Manukau	2	2.99c	2.48a	0.50a	0.67a	23.54ab
		5	6.85b	2.33a	0.43a	0.72a	22.38b
		10	15.91a	3.38a	0.64a	1.15a	31.90a
	North Shore	2	2.89c	2.70a	0.53a	1.16a	16.17b
		5	8.25b	2.88a	0.54a	0.98a	17.96b
		10	14.77a	3.01a	0.64a	0.99a	22.91ab
Fireclay	None		4.95b	2.23c	0.33b	0.83a	13.71a
	North Shore	10	8.4a	2.41a	0.67a	1.10a	15.32a
	Paper	10	7.33a	2.08b	0.65a	1.91a	13.75b
Mudstone	None		0.67c	1.19b	0.27a	0.67a	23.30a
	North Shore	5	7.46b	1.45b	0.21a	0.72a	21.53a
		10	7.13a	1.84a	0.30a	0.96a	29.46a
	Paper	5	6.22b	1.21b	0.28a	0.90a	25.75a
		10	13.41a	1.19b	0.27a	0.83a	24.47a
Huntly subsoil	None		0.36b	1.42b	0.18a	0.13a	15.82d
	North Shore	2	3.62c	1.62b	0.28a	0.71a	18.21bc
		5	9.61b	1.92b	0.33a	1.11a	21.98b
		10	15.90a	2.52a	0.28a	0.92a	29.15a
	Paper	2	2.60c	1.77b	0.14a	0.64a	16.49cd
		5	9.84b	1.87b	0.14a	0.63a	18.42bc
		10	12.32a	1.19b	0.45a	1.03a	19.96cd

\#   Means with the same letter are not significantly different from other treatments of the same spoil; using Duncan's multiple range test at 5% significance level.

5.10.3 Effect of the incubation on the cation exchange capacity

CEC was determined at the beginning and at the conclusion of the incubation experiment for all the samples, however, there were no significant differences between initial and final measurements.

5.10.4 Explanation of the effects of sludge addition and incubation on the cation exchange capacity of the amended mine spoils

An increase in CEC with increasing organic matter was expected (Brady, 1984). This was the general trend but did not always occur, possibly because of the variability between replicates. Also, as the pH in the incubations generally increased slightly during the incubation, an increase in CEC was expected. However, the variability of CEC results will have prevented any slight change in CEC being observed. A change in CEC with pH was expected because as pH is raised, the hydrogen ions held by the organic colloids and silicate clays become ionised and are replaceable, leaving additional exchange sites on the colloids. An increase in the negative charge on the colloids occurs and in turn an increase in the CEC (Metson and Blakemore, 1968). Brady (1984) reported that within the pH range of 5-6, a ratio of roughly 5% base saturation change for every 0.1 change in pH is applicable for humid temperate mineral soils. However, since the CEC was measured using ammonium acetate buffered at pH 7, it is unlikely that any differences in CEC between the samples is attributed to the difference in pH.

The general trend of an increase in CEC of the spoils associated with additions of sewage sludge also reported by Stucky and Newman (1977), Schneider *et al.* (1981), Fleming and Davis (1986), and Ghorayshi (1989). In a field study by Daudin *et al.* (1991), addition of an industrial sewage sludge to an acidic, infertile soil did not significantly affect the CEC between rates of 0 to 60 t/ha applied. However, the reason given was that neither the organic matter level nor the clay level varied significantly; in this study the organic matter level did significantly vary between application rates.

Similar to the results in this study, Del Rosario (1980) reported an increase in the CEC of mine soil when paper sludge was applied, although a significant increase with increase in sludge addition was not always recorded.

5.10.5 Measured compared to predicted cation exchange capacity

Measured CEC was not well correlated with predicted CEC (Figure 5.29). Because the sludges had significantly higher CEC than all the spoils, then successive increases in sludge addition were predicted to result in significant increases in CEC in the mixtures; this did not always occur, as discussed in 5.10.2 and 5.10.4. CEC is affected by pH. Since the pH of the amended samples are different from the individual spoil and sludge samples it is unlikely that the CEC of the amended spoil will be the weighted mean of the individual components.

Because humus has an abundance of both positively and negatively charged dissociable groups, it is generally assumed that there is interaction or complex formation between clay and organic matter within the soil resulting in a CEC that is different and probably less than the sum of the capacities of the separate components (Metson and Blackemore, 1968). This phenomenon may in part explain why results did not always follow predicted trends In this study, 13 out of the 30 spoil treatments had lower, and the remaining 17 had higher CEC than the CEC predicted from the CEC of the individual constituents (Section 5.10.5).
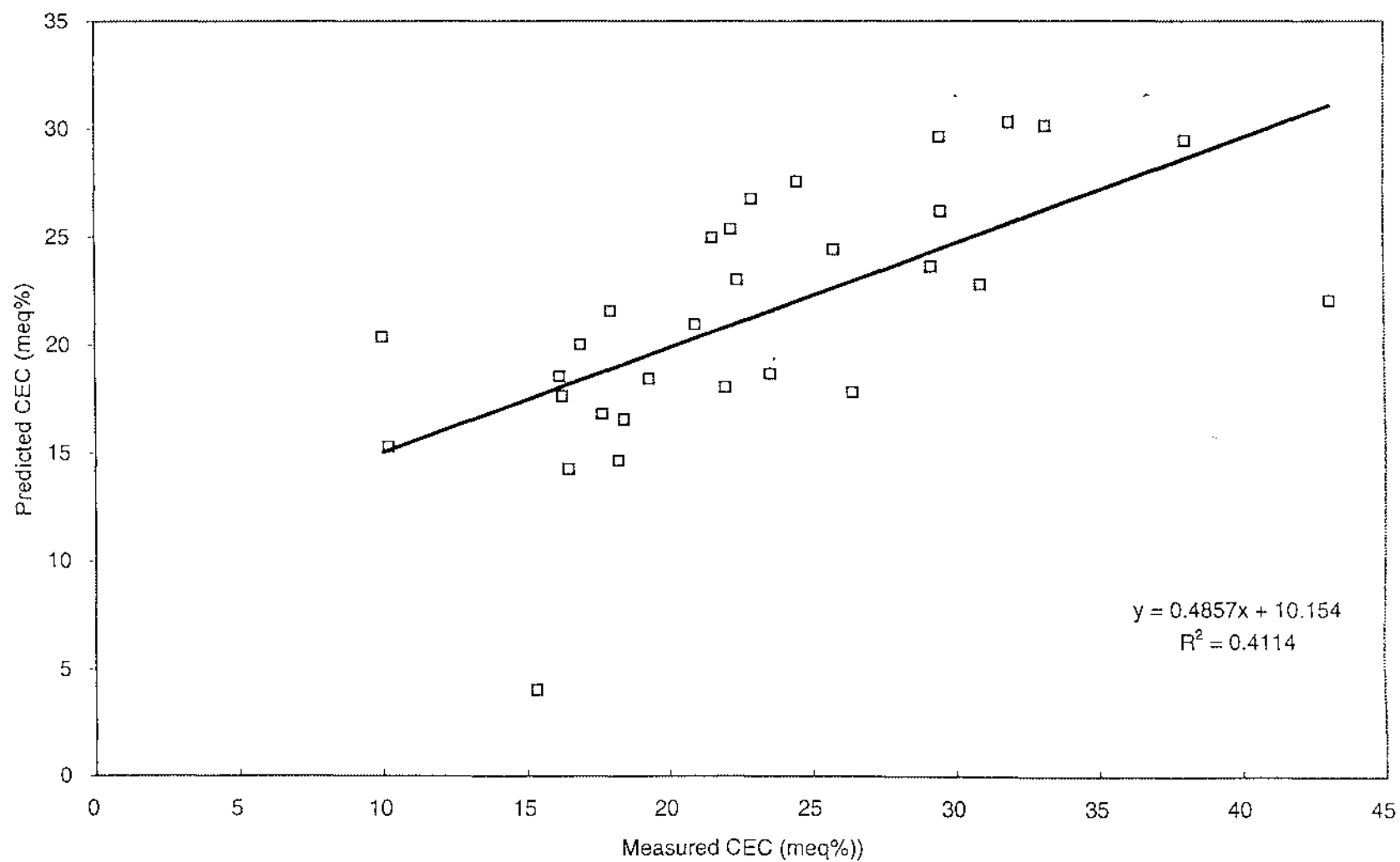
Figure 5.29 Relationship between predicted and measured cation exchange capacity of the incubation

5.10.6 Contribution of the basic cations to cation exchange capacity and implications for the rehabilitation of the mine spoils

5.10.6.1 Calcium

Calcium (Ca) is an essential plant nutrient (Brady, 1984). It has a strong influence on percentage base saturation, pH and other related properties that depend on the acid/base balance in the soil; it has a buffering effect on pH (Cresser *et al.*, 1993; Bellamy *et al.*, 1995). High values of exchangeable Ca in soils are favoured by high levels of Ca in parent materials, high CEC, and high % base saturation (Miller, 1968).

The Soil Bureau of New Zealand uses the following rating for Ca content of New Zealand soils (Blakemore *et al.*, 1987):

>20 me/100g	Very high
10-20	High
5-10	Medium
2-5	Low
<2	Very low

In comparison with New Zealand soils (Blakemore *et al.*, 1987), the exchangeable Ca of the three sludges and of the tailings was very high. In all spoils, as sludge rate increased, so did the content of Ca. In tailings amended with Manukau sludge, the exchangeable Ca content was high at 2 and 5% organic matter , and very high at 10% organic matter. When amended with North Shore sewage sludge, at 2% organic matter the Ca value was medium and at 5 and 10% organic matter, it was high based on the Soil Bureau ratings. Oxidised waste had medium to high values with both sludges and Waihi subsoil amended with both sludges had a low value at 2% organic matter, a medium value at 5% organic matter and high value at 10% organic matter. The same was true for Huntly subsoil. In amended fireclay, the percentage Ca saturation was medium and in mudstone was medium at 5% organic matter, and high at 10% organic matter (Table 5.19).

5.10.6.2 Sodium

Although sodium (Na) is not considered an essential for all plants.(Brady, 1984), it is required by at least a few plants (Black, 1957; Brownell and Wood, 1957), and plants such as sugar beet, mangolds and some brassicas, show reduced yield if the available supply of Na is low (Cook, 1967 and Russell, 1987). High levels of Na can result in defloculation and reduced permeability, especially in clay soils and inhibit plant root

development (Bellamy *et al.*,1995). In plants, potassium (K) and Na are the two principle monovalent metallic cations and an increase in one generally results in a reduction in the other (Black, 1968). Soils normally contain only small amounts of Na because it is readily leached (Black, 1968).

No trend was apparent in exchangeable Na contents of the spoils with increasing additions of sludge; however, in most cases sludge amended spoils had higher Na contents than the unamended spoils.

The Soil Bureau ratings for Na in New Zealand soils are as follows (Blakemore *et al.*, 1987):

>2 me/100g	Very high
0.7-2	High
0.3-0.7	Medium
0.1-0.3	Low
<0.1	Very low

Based on these ratings, values for Na were very high in amended tailings and high in all other spoils amended to 10% organic matter, regardless of the amendment. Values were medium or high in all other treated spoils. This may be attributed to the high level of Na present in the sludges and the lack of leaching from the incubations (Del Rossario, 1990).

A 15% saturation with Na is generally accepted as being deleterious to plant growth (Black, 1968, Brady, 1984). Na then in unamended tailings may inhibit plant growth, the Na value of the other amended spoils are not expected to impact on spoil rehabilitation efforts.

5.10.6.3   Potassium

Potassium is an essential plant nutrient. It is essential for photosynthesis, for starch formation and for the translocation of sugars and it increases crop resistance to certain diseases. Potassium is involved in the formation of strong root and stem systems and hence can counteract the negative effects of excessive nitrogen causing excessive vegetative growth which often results in plant lodging. In some plants, sodium has been found to partially take the place of potassium if there is a deficiency of the latter (Brady, 1984).

The New Zealand Soil Bureau use the following ratings for K in New Zealand soils (Blakemore et al., 1987):

>1.2 me./100g	Very high
0.8-1.2	High
0.5-0.8	Medium
0.3-0.5	Low
<0.3	Very low

Exchangeable K was a minor contributor to CEC in the individual materials and in the sludge amended spoils. Based on the New Zealand Soil Bureau ratings, exchangeable K was medium in Manukau and paper sludges and high in North Shore sewage sludge. Tailings had a medium exchangeable K value, oxidised waste, Waihi subsoil and fireclay had low values and mudstone and Huntly subsoil had very low values for exchangeable K (Table 5.18). There was a general trend of increasing exchangeable K values in the spoils associated with increasing sludge addition although differences were not significant (Table 5.19. In the amended gold mine spoils, values for exchangeable K were mostly medium, as was the K value in the amended fireclay. In mudstone and Huntly subsoil the values were low to very low. K values are therefore likely to be suitable for rehabilitation in all treated spoils except Huntly subsoil and mudstone; in the latter two, a K fertiliser will be beneficial.

5.10.6.4   Magnesium

Magnesium (Mg) is an essential plant nutrient used in relatively large amounts and derived purely from soil solids (Brady, 1984). It has a function in the chlorophyll molecule and several other physiological functions in plants (Metson, 1968). New Zealand Soil Bureau ratings for Mg in New Zealand soils are as follows (Blakemore et al., 1987):

>7 me./100g	Very high
3-7	High
1-3	Medium
0.5-1	Low
<0.5	Very low

Generally, in the spoils there was a trend of increasing exchangeable Mg with sludge addition (Table 5.19).

All tailings treatments had medium exchangeable Mg values based on Soil Bureau ratings, and in treated oxidised waste the values were high. Waihi subsoil amended to 2 and 5% organic matter with both the sewage sludges had medium exchangeable Mg values and 10% organic matter amended samples had high values. All amended coal mine spoils had medium exchangeable Mg values. A value of around 0.3 meq% of exchangeable Mg in soils seems to be a critical level for an absolute deficiency (Metson, 1968). No spoils or amended spoils therefore had an absolute deficiency. However, an induced deficiency may occur at much higher Mg levels when levels of exchangeable K or Ca are very high resulting in Mg/K or Mg/Ca ratios depressing uptake of Mg by the plant. In order to assure favourable ratios of Mg to other cations some workers consider a minimum of about 6-10% of the CEC should contain Mg (Metson, 1968). Only paper sludge amended mudstone has a lower Mg contribution (5%). Tailings with 10% organic matter amended with Manukau sewage sludge had a very high Ca value and the only very high value for K was recorded in tailings amended with North Shore sewage sludge at 2% organic matter. Mg is therefore unlikely to be a limitation or require amendment for successful rehabilitation of the amended mine spoils.

5.10.7 Implications for the rehabilitation of mine spoils

CEC is an important factor in the availability of cations, both nutrient (Ca, Mg, K and Na) and trace metals (Cu, Zn, Pb, Cd) to plants and also affects their movement in ground water (Sopper, 1992). Base cations on cation exchange sites are to a large degree available to growing plants and available base cations tend to come virtually exclusively from the cation exchange sites in non calcareous soils (Cresser et al., 1993).

A high CEC can hold cations against leaching, improving the availability and efficiency of fertiliser (Brady, 1984). Conversely, a soil with a very low CEC is poorly buffered and has a low capacity to retain nutrients against leaching.

High concentrations of exchangeable Ca and Mg are important in reducing potential adverse effects of Na (Bellamy et al., 1995). This has potential to be important only in amended tailings which have high Ca and Na values.

All amended spoils had medium to high values for CEC and hence, CEC is likely to be adequate for rehabilitation of the amended spoils at any of the rates of sludge addition

trialled and is unlikely to present a limitation or require special consideration for rehabilitation. The effect of CEC on the availability/retention of potentially harmful heavy metals is considered in section 5.11.

5.11   HEAVY METALS

5.11.1   Introduction

One of the major concerns in the rehabilitation of mine spoils is the toxicity of heavy metals. Depending on the source, mine spoils contain a range of heavy metals. Municipal and industrial sludge can act both as a source and sink for heavy metals. It is therefore important to ascertain the contribution of heavy metals from sludge when used as an amendment.

Due to the large variation in concentrations of the elements analysed, elements with low concentrations have not been measured accurately, but to the detection limit for the machine. It is possible that some of these elements were present in lower concentrations than quoted. Seven of the elements analysed will be discussed here, as the objective of the analysis was to ascertain those heavy metals that may cause deleterious impact upon utilisation of the sludges. Most of the literature concerned with chemical contaminants in waste sludges or mined materials considers all or a combination of the following major heavy metals: arsenic (As), cadmium (Cd), chromium (Cr), copper (Cu), lead (Pb), mercury (Hg), nickel (Ni) and zinc (Zn) (Table 2.2).

New Zealand Department of Health regulations are the reference standards used to assess the degree of contamination by heavy metals of the waste sludges and mined spoils (Table 5.20). These regulations are only "recommendations" and apply to sewage sludges intended for application to arable land. No regulations or guidelines exist in New Zealand for application of sewage sludge to mined lands or utilisation in land rehabilitation projects. In such situations the potential risks must be considered in conjunction with the potential benefits that may be gained by applying the waste sludge.

Neuman *et al.* (1987) reported that mine soil conditions are probably dramatically different than those of native soils, and the relative importance of each of these sources (mine soils and native soils) of metals will not be the same. Regulations that need to compare metal concentrations in native soils and mine soils are inappropriate because mine soils represent a youthful stage of soil development, rapid changes in their

chemical equilibria can be expected. The sedimentary materials that were previously confined to presumed reducing and biologically inactive zones are exposed by mining to an oxidising environment that is biologically active.

While the Department of Health regulations for sewage sludge have been set to bring New Zealand into line with practice in the U.K., European Community and Australia (Department of Health, 1992), the Australian guidelines (Awad et al., 1989) allow the same level of As in sewage sludge but considerably more (4 kg/ha as opposed to 0.2 Kg/ha) annual loading and maximum cumulative loading (20 kg/ha compared to 2.5 kg/ha in NZ). Other metal limits between the two countries compare favourably.

Table 5.20

Recommended limits for 'heavy metals' in sewage sludge intended for application to arable land

Element	Maximum acceptable concentration in dry sewage sludge (mg/kg)	Limit values allowable in soil (mg/kg)	Maximum annual application to land (kg/ha)	Maximum cumulative loading (kg/ha)
As	15	10	0.2	2.5
Cd	15	3	0.2	2.5
Cr	1000	600	15.0	125.0
Cu	1000	140	12.0	100.0
Pb	600	300	15.0	125.0
Hg	10	1	0.1	1.0
Ni	200	35	3.0	20.0
Zn	2000	300	30.0	250.0

Notes: The soil receiving soil sludge should have a pH of 5 or above.

The limit values for arable land apply to the top 200 mm of soil.

Site specificity is important and may invalidate some of these restrictions.

(Reference= Department of Health, 1992)

5.11 2　Heavy metal content of the original materials

5.11.2.1　Total heavy metal contents

Department of Health (1992) limit values for heavy metals in sewage sludge (Table 5.20) were exceeded in Manukau sewage sludge by As, Cr, Pb and Zn. In North Shore sewage sludge and in paper sludge, they were exceeded by As (Table 5.21). The content of each heavy metal in Manukau sewage sludge was higher than that reported for the same sludge by Department of Health (1992) but the relative amounts of each heavy metal were similar. The possible sources of these heavy metals are discussed below.

Arsenic is used in wood preservatives, pesticides and herbicides as well as other industrial processes (Adriano, 1987), and it arrives in sewage sludges mainly as a result of surface runoff which contains atmospherically deposited. Arsenic and residues from pesticides. Metal processing industries can also add a significant amount and a small amount may be added from phosphate detergents (O'Neill, 1990). As is not commonly included in the analysis of sewage sludges (Table 2.2). This may be because the As uptake is small by most terrestrial plants (O'Neill, 1990).

Chromium enters sewage systems from metal plating, anodising, ink manufacture, and textile industries; it is present in dyes, glass, ceramics, glues, wood preservatives, tanning solutions and corrosion inhibitors in cooling waters (McGrath and Smith, 1990). A large number of these industries will have occurred in the area from which the Manukau sewage sludge is collected and not the North Shore (5% of the flow into the North Shore waste water treatment plant is trade waste), hence the difference between Cr quantity in the two sewage sludges. It may be possible to reduce the heavy metal content of domestic sewage by isolating from the industrial effluent

Sources of Pb in sewage sludge include road runoff, Pb water pipes (Davies, 1990) and human faeces. According to Coker and Mathews (1983), the typical concentration of Pb in human faeces is 11 μg/g dry solids. Lead is also present in all soils in a range from 1 ppm for 'normal' soils to much greater than 10% in ore materials (Davies, 1990).

Zinc is used for galvanising (e.g. water pipes) and corrosion of this may contribute to the Zn content of sewage sludge. Zinc is also used in cosmetics, pharmaceuticals, paints, varnishes, rubber, electrical apparatus, including dry cell batteries; also in printing and dying of textiles, as hardeners in cement and concrete and in fertilisers and insecticides, among other things (Kiekens, 1990).

All of the gold mine spoils exceed the Department of Health soil limit values for As, Cd and Ni. No limits are exceeded in fireclay. In mudstone, limit values for As, Cd, Cr and Ni are exceeded; and the concentration of Ni is very high in mudstone. In Huntly subsoil, limit values for As and Cd are exceeded. In tailings, oxidised waste, Waihi subsoil, mudstone and Huntly subsoil, the limit value for Cd in soils is only slightly exceeded (Table 5.21).

It is common for elevated levels of As to occur in gangue minerals associated with an economic ore mineral. Arsenic is commonly associated with gold mine tailings and coal wastes such as fly ash and furnace bottom ash (O'Neill, 1990).

A certain amount of Ni can be expected to be associated with coal mining and coal (Australian bitumous coal) normally contains Ni in the range <1 to 90 ppm (Adriano, 1986). However, the value for Ni in mudstone is extremely high and without knowing the mudstone's exact source, it is difficult to explain the high level of Ni. It is considerably higher than occurs in sedimentary rocks, but is in the upper range of what can occur in igneous rocks, and is around the average value expected for serpentine. However, serpentine rocks also contain high Cr, Mg, and Fe and low Ca. Their Mg to Ca ratios are extremely high, e.g., 200 000:15 (Adriano, 1986). This was not the case with mudstone which had a ratio of 1158:169 and Ca and Fe were not exceptionally high (Appendix 2). It would appear then that although unlikely, contamination of the mudstone sample with Ni may have occurred.

Table 5.21

Total metals in the incubation materials (μg/g)

Material	As	Cd	Cr	Cu	Ni	Pb	Zn
Manukau	*47	11.1	1840	747	210	912	2268
North Shore	*29.	4.7	153	606	135	239	1517
Paper	*38.5	*3.9	41.5	96	67	68	211
Tailings	64	*3.1	68	37.5	44.5	*31.5	59
Oxidised waste	46	*3.2	100	30	69	38.5	89
Waihi subsoil	41.5	*3.5	79	25	48.5	*34.5	54
Fireclay	*3.3	*0.33	20	28	16	*3.3	62
Mudstone	*38.4	*0.3	725	13.3	2861	65	38.5
Huntly subsoil	*33	*3.3	26.5	22	17.9	*33	44.5

Note: Values marked with a * indicate that the element in that sample had a concentration below the instruments detection limit; the concentration given is the dilution corrected lower quantitative limit for that element.

5.11.2.2   Availability of heavy metals

There was no relationship apparent between the pH of the original materials (Table 5.6a) and the percentage of heavy metals extractable with HCl. This may be because of leaching of available heavy metals down the profile of the low pH mine spoils prior to sample collection.

Fireclay followed by Huntly subsoil had the highest percentage of total metals extractable by 0.1M HCl. Waihi subsoil, mudstone and tailings had the lowest percentage of HCl extractable metals (Table 5.22).

The most extractable metals in the incubation materials were Zn and Pb followed by Cu. Chromium was the least soluble of the metals because it forms insoluble oxide and is rendered unavailable for uptake (Leeper, 1978).

The results indicate that the application of Manukau sewage sludge to mine spoils presents the greatest risk for heavy metal contamination of the rehabilitation site; and fireclay possibly presents the greatest potential for rehabilitation with waste sludges, due to its low metal loadings.

Overall, paper sludge poses the least risk to contamination of mine spoils by heavy metals when applied on an organic matter basis. This is due both to its relatively low metal loading and to its high organic matter content which allows it to be applied in less quantity to allow the same level of organic matter in the sludge/spoil mix.

Table 5.22

Heavy metals extractable with 0.1 M HCl as a percentage of total heavy metals in the original materials

Material	As	Cd	Cr	Cu	Ni	Pb	Zn
Manukau sludge	0.43	0.67	0.003	0.02	0.49	0.04	0.75
North Shore sludge	0.68	0.55	0.02	0.02	0.57	0.17	0.4
Paper sludge	0.52	0.51	0.05	0.06	0.06	0.59	0.41
Tailings	0.03	0.06	0.1	0.568	0.26	0.30	0.37
Oxidised waste	0.05	0.09	0.04	0.71	0.54	0.44	0.52
Waihi subsoil	0.06	0.06	0.01	0.308	0.03	0.26	0.13
Fireclay	6.0	6.06	0.1	1.38	0.83	12.12	2.01
Mudstone	0.05	0.06	0.00	1.29	0.001	0.06	0.64
Huntly subsoil	0.17	0.3	0.39	3.94	2.01	0.7	7.35

5.11.3 Effect of amendments on the total and available heavy metal contents of mine spoils

From the analysis of heavy metals in the sludges and mine spoils, it is possible to predict the heavy metal content of the mixtures (Table 5.23). Table 5.22 gives the HCl extractable heavy metals in the original materials as a percentage of total heavy metals and Table 5.24 gives the HCl extractable heavy metal content of the spoils amended to 10% organic matter with sludge.

There appears to be an anomaly in the Department of Health guidelines for sewage sludge application to land (Table 5.20). Assuming a normal bulk density for soil (e.g., a bulk density of 1), the maximum allowable cumulative loading is considerably lower than that calculated from the 'limit value allowable' to a depth of 200 mm. For example, in the case of As the maximum cumulative loading is 2.5 kg/ha and the limit value allowable in soil is 10 mg/kg or 0.01kg/t. With a bulk density of 1, there is 2000t of soil/ha to 200mm depth. This equates to an As content of 20 kg/ha. Consideration is given to maximum cumulative loadings in section 5.11.5.

5.11.3.1 Manukau sewage sludge
The application of Manukau sewage sludge is predicted to reduce the total content of As in amended tailings, and slightly increase it in oxidised waste and Waihi subsoil.

The concentration of Cd, Cr, Cu, Ni, Pb and Zn is predicted to be increased in all gold mine spoils (Table 5.23).

The HCl extractable As, Cd, Cu, Ni and Zn as a percentage of predicted total heavy metals was increased in the spoils when amended with Manukau sewage sludge to 10% organic matter. The exception was Ni in Waihi subsoil which was reduced. There was little change in the availability of Cr, and Pb was reduced in all spoils except Waihi subsoil where it was increased (Table 5.22 and 5.24).

5.11.3.2 North Shore sewage sludge
The application of North Shore sewage sludge is predicted to have the following effects on total heavy metals in the spoils:

As- reduced in all spoils except fireclay in which an increase is predicted.
Cd- increased in all spoils.
Cr- increased in all spoils except mudstone in which a reduction is predicted.

Cu- increased in all spoils.

Ni- increased in all spoils except mudstone where a reduction is predicted.

Pb and Zn- increased in all spoils.

Application of North Shore sewage sludge to the gold mine spoils resulted in an increase in HCl extractable As, Cd, Cu, Ni, Pb, Zn, and Cr, although Cr was reduced in tailings. When North Shore sewage sludge was applied to the coal mine spoils, results were not so clear. HCl extractable As and Cd were reduced in fireclay, Cu was reduced in mudstone and Huntly subsoil, the HCl extractable Ni and Pb were reduced in fireclay and Huntly subsoil, and HCl extractable Zn was reduced in Huntly subsoil (Tables 5.21 and 5.23).

5.11.3.3 *Paper sludge*

Addition of Paper sludge to the spoils is predicted to have the following effects on total heavy metal contents:

As- increased in fireclay and Huntly subsoil and unaffected in mudstone.

Cd- increased in all spoils, most significantly in fireclay.

Cr- increased in fireclay and Huntly subsoil, reduced in Mudstone.

Cu- increased in all spoils.

Ni- increased in fireclay and Huntly subsoil and reduced in mudstone.

Pb and Zn- increased in all spoils, but only slightly in mudstone.

Paper sludge application resulted in a reduction in the HCl extractable As, Cd, and Cr in all spoils except mudstone where they remained the same as a percentage of total. Cu was reduced in Huntly subsoil and mudstone and increased in fireclay. HCl extractable Zn increased in fireclay and mudstone but was reduced in Huntly subsoil with application of paper sludge (Tables 5.21 and 5.23).

5.11.3.4 *Heavy metal content of the amended spoils with respect to limit values allowable in soils*

The following heavy metals are predicted to exceed Department of Health maximum limit values for soils in the specified amended spoils:

As: All amended spoils except fireclay.

Cd: All amended spoils except fireclay, however only Manukau amended tailings (10% organic matter) and Waihi subsoil (5 and 10%) exceed the limit by more than 1 mg/kg.

Cr: All treatments of mudstone.

Table 5.23

Predicted total heavy metal content of amended spoils (mg/kg)*

Amendment	spoil	Organic matter (%)	As	Cd	Cr	Cu	Ni	Pb	Zn
Manukau sewage sludge	Tailings	2	63.2	3.5	149.5	70.1	52.1	72.0	160.6
		5	62.0	4.0	272.3	119.3	63.6	133.0	313.7
		10	60.1	4.9	476.9	201.2	82.7	234.7	568.8
	Oxidised waste	2	62.3	3.2	72.2	65.3	48.9	41.7	130.3
		5	59.8	3.3	78.4	107.2	55.6	56.9	237.8
		10	55.5	3.5	88.9	177.1	66.7	82.4	417.0
	Waihi subsoil	2	46.0	3.5	161.0	55.1	73.9	69.1	165.4
		5	46.1	4.0	282.9	105.4	83.8	130.3	318.0
		10	46.2	5.0	486.3	189.2	100.3	232.4	572.7
North Shore sewage sludge	Tailings	2	45.4	3.3	102.0	51.5	71.5	46.0	142.3
		5	44.2	3.4	105.9	94.5	76.4	60.9	248.8
		10	42.1	3.6	112.5	166.1	84.6	85.9	426.5
	Oxidised waste	2	41.5	3.6	91.7	30.2	49.7	40.8	70.0
		5	41.9	4.1	218.6	82.2	61.3	104.1	229.5
		10	42.6	5.0	430.3	169.1	80.7	209.6	495.7
	Waihi subsoil	2	41.4	3.5	79.6	29.5	49.2	36.1	65.3
		5	40.5	3.6	85.2	73.6	55.7	51.6	176.4
		10	38.9	3.8	94.7	148.6	66.9	78.0	365.3
	Fireclay Mudstone	10	4.8	0.6	27.4	60.0	22.6	16.4	142.6
		5	4.5	0.4	20.7	30.3	17.7	5.5	67.0
		10	38.1	3.4	697.5	41.8	2730.1	73.4	109.5
	Huntly subsoil	2	36.9	3.6	621.3	120.8	2366.6	96.6	306.7
		5	38.5	3.3	704.2	15.8	2776.1	65.1	43.7
		10	38.5	3.4	646.4	22.8	2539.6	65.3	58.3
Paper sludge	Fireclay	10	32.9	3.3	30.0	38.2	21.1	38.7	85.2
	Mudstone	5	32.6	3.4	39.5	82.2	30.0	54.2	196.2
		10	32.2	3.6	55.4	155.5	44.7	80.1	381.2
	Huntly subsoil	2	33.1	3.3	26.8	23.3	18.8	33.6	47.5
		5	33.4	3.3	27.5	26.9	21.2	35.3	55.6
		10	33.8	3.4	28.7	33.0	25.2	38.2	96.2

*Predicted from Equation 4.6

Table 5.24

HCl extractable heavy metals (mg/kg) initially and at the conclusion of the incubation in spoils amended with sludge to 10% organic matter

Incubation materials	As		Cd		Cr	
	Initial	Final	Initial	Final	Initial	Final
Tailings + Manukau	*0.2 #(0.30)	*0.02	0.06 (1.20)	*0.002	0.520 (0.10)	0.012
Tailings + North Shore	*0.2 (0.36)	*0.2	0.03 (0.86)	0.072	0.075 (0.08)	0.7
Oxidised waste + Manukau	*0.2 (0.43)	*0.2	0.057 (1.14)	0.038	0.730 (0.15)	0.124
Oxidised waste + North Shore	*0.2 (0.48)	*0.2	0.031 (0.86)	0.074	0.106 (0.09)	1
Waihi subsoil + Manukau	0.054 (0.13)	*0.2	0.048 (0.96)	0.044	0.760 (0.18)	0.14
Waihi subsoil + North Shore	*0.2 (0.51)	0.064	0.029 (0.76)	0.058	0.106 (0.11)	0.76
Fireclay + North Shore	0.04 (0.80)	*0.2	0.012 (2.00)	0.034	0.032 (0.12)	0.116
Fireclay + Paper	*0.11 (2.40)	0.04	*0.013 (3.25)	0.012	*0.011 (0.05)	0.036
Mudstone + North Shore	*0.143 (0.39)	*0.02	0.024 (0.67)	0.006	0.099 (0.02)	*0.002
Mudstone + Paper	0.026 (0.07)	*0.2	*0.002 (0.06)	0.032	0.019 (0.002)	0.11
Huntly subsoil + North Shore	*0.2 (0.62)	0.034	0.029 (0.80)	0.002	0.108 (0.19)	0.016
Huntly subsoil + Paper	0.021 (0.06)	*0.02	*0.002 (0.06)	*0.002	0.022 (0.08)	*0.002

Continued...

Incubation materials	Cu		Ni		Pb		Zn	
	Initial	Final	Initial	Final	Initial	Final	Initial	Final
Tailings + Manukau	1.510 (0.75)	0.01	1.090 (1.31)	0.016	*0.4 (0.17)	*0.04	15.2 (2.7)	*0.00 2
Tailings + North Shore	1.800 (1.02)	1.86	1.960 (2.9)	1.18	*0.4 (0.5)	*0.4	13.3 (3.2)	16
Oxidised waste + Manukau	2.040 (1.08)	2.64	1.200 (1.2)	1.04	*0.4 (0.17)	*0.4	14.4 (2.5)	13.2
Oxidised waste + North Shore	2.760 (1.66)	2.7	1.050 (1.24)	1.48	*0.4 (0.47)	0.62	12.6 (2.95)	17
Waihi subsoil + Manukau	2.150 (1.3)	3.26	0.830 (0.01)	1.2	1.22 (0.58)	*0.4	11 (2.4)	14.2
Waihi subsoil + North Shore	2.740 (1.8)	2.32	0.760 (1.14)	0.96	0.45 (0.58)	1.3	11 (3.0)	12.8
Fireclay + North Shore	1.440 (2.4)	3	0.350 (0.02)	0.76	0.25 (1.52)	0.56	3.75 (2.6)	11
Fireclay + Paper	1.580 (5.2)	1.34	0.131 (0.74)	0.32	*0.249 (4.5)	0.2	3.2 (4.8)	4.2
Mudstone + North Shore	2.850 (0.02)	0.46	0.700 (0.03)	0.126	*0.259 (0.27)	0.082	9.7 (3.2)	1.54
Mudstone + Paper	0.240 (1.05)	3.04	0.037 (0.001)	0.82	0.057 (0.09)	*0.4	0.81 (1.4)	11.2
Huntly subsoil + North Shore	3.250 (2.1)	0.26	0.820 (1.8)	0.032	0.42 (0.00)	0.044	11.9 (3.1)	0.72
Huntly subsoil + Paper	0.290 (0.9)	*0.006	0.013 (0.05)	*0.004	0.199 (0.52)	*0.04	1.19 (1.72)	*0.00 2

\# values in brackets are available heavy metals as a percentage of estimated total heavy metals.

Note: Values marked with a * indicate that the element in that sample had a concentration below the instruments limit of quantitation therefore, the concentration given is the dilution corrected lower quantitative limit for that element.

Cu: Treatments of the gold mine spoils with Manukau or North Shore sewage sludge to provide 10% organic matter, Huntly subsoil amended with North Shore sewage sludge to 10% organic matter.

Pb: not exceeded in any amended spoil.

Ni: in all treatments of the gold mine spoils, in mudstone and Huntly subsoil amended to 10% organic matter with North Shore sewage sludge.

Zn: All gold mine spoils amended to 10% organic matter, tailings and oxidised waste amended with Manukau sewage sludge to 5% organic matter also exceed the limit. Mudstone and Huntly subsoil amended to 10% organic matter with North Shore sewage sludge exceed the limit for Zn.

5.11.4   Effect of the incubation on HCl extractable (available) heavy metals

Table 5.24 summarises the effect of incubation period on the availability of heavy metals in the spoils amended with sludges to 10% organic matter.

Gold mine spoils amended with Manukau sewage sludge

When Manukau sewage sludge was applied to tailings, the availability of all heavy metals (As, Cd, Cr, Cu, Pb, Ni, Zn) was reduced with incubation period. In oxidised waste amended with Manukau sewage sludge, the availability of As and Pb was not affected by time, but Cd, Cr, Ni, and Zn availability declined and extractable Cu increased during the incubation.

When Waihi subsoil was amended with Manukau sewage sludge, the availability of As, Cu, Ni, and Zn increased during the incubation, there was no change in the availability of Cd during time and the availability of Cr and Pb declined with time (Table 5.24).

Gold mine spoils amended with North Shore sewage sludge

In tailings amended with North Shore sewage sludge, the availability of As and Pb was not affected by incubation and the availability of Cd, Cr, Cu, Ni and Zn was increased during the incubation.

In oxidised waste amended with North Shore sewage sludge, incubation period did not affect the availability of As and the reduction in Cu during time was very small. The availability of Cd, Cr, Ni, Pb and Zn was increased during the incubation.

In Waihi subsoil amended with North Shore sewage sludge, the availability of Cd, Cr, Ni, Pb and Zn was increased during the incubation and the availability of As and Cu declined slightly.

Coal mine spoils amended with North Shore sewage sludge

In fireclay amended with North Shore sewage sludge, the availability of all heavy metals increased with time. The opposite occurred in mudstone and Huntly subsoil amended with North Shore sewage sludge; the availability of all heavy metals declined during the incubation period. In Huntly subsoil, Cd did not change significantly.

Coal mine spoils amended with paper sludge

In fireclay amended with paper sludge, the availability of As, Cd, Cu and Pb declined during the incubation and the availability of Cr and Ni increased. In mudstone amended with Paper sludge, the availability of all heavy metals increased during the incubation and in paper sludge amended Huntly subsoil, the availability of As did not change during the incubation, the availability of Cd, Cu, Ni, and Zn increased and the availability of Cr, and Pb was reduced.

There was no observable relationship between the availability of any one metal and time across all the treatments. The constraints of the analytical procedure (i.e. the true value of some of the elements in some of the materials could not be measured) may have compounded the lack of trends. Also the quantities and concentrations being analysed were very small and the natural variation of the materials may have masked the effect of time on the availability of the heavy metals.

In general, the capacity of soil to retain most trace elements is increased with increasing pH (Adriano, 1986) and in a CAST report, (CAST, 1980), it was concluded that soil pH was the most critical factor in controlling plant uptake of Cd and Zn from sludge treated soils (Adriano, 1986). Adriano (1986) also stated that generally as CEC increased, availability of the heavy metals was reduced. The availability of heavy metals in the amended samples was predicted to decline during the incubation as generally there was a decline in pH during the incubation (Section 5.2).

According to Adriano (1986) adsorption of As from solution is maximal at about pH 5; therefore, as the pH of an incubation came closer to pH 5, a reduction in As content was expected. A reduction in available As during the incubation was therefore predicted in all incubations amended to 10% organic matter except Waihi subsoil amended with North Shore sewage sludge and Huntly subsoil amended with paper sludge where an

increase may have been predicted and mudstone and Huntly subsoil amended with paper sludge where no change was predicted. This did not occur.

Further analysis of the incubations may elucidate the reasons for changes in the availability of heavy metals both upon application of sludge and during the incubation period e.g. the complexation of the metals with other components of the materials may have occurred.

5.11.5   Implications for rehabilitation of the mine spoils

Metal constraints depend on the future use of the reclaimed land. If the land is to be used for agricultural crops entering the human food chain (including pasture), limits apply to sewage sludge application. If however, the land is to be reforested or planted in vegetation not entering the human food chain, the metal accumulation may be limited only by potential phytotoxicity to the trees and vegetation (U.S. EPA, 1983). Cu, Zn, and Ni are the elements of most concern in plant phytotoxicity. If the soil pH is maintained above 6.0 to 6.5, these elements should not be taken up by the vegetation in amounts great enough to cause phytotoxicity (Gshwind and Pietz, 1992; U.S. EPA, 1983). In addition, Cr is also phytotoxic (Kiekens, 1990). Since Cr occurs both as a cation (Cr^{3+}) and an anion (Cr^{2-}) (Adriano, 1986), it may not be easy to control the plant uptake through the manipulation of soil pH.

The risk of heavy metals entering the food chain from contaminated soil will be minimised if pasture growing on the soil is managed to prevent it being grazed so low that grazing stock are likely to ingest soil along with pasture.

It is necessary to consider the depth of incorporation as well as the ratio of soil to sludge when considering maximum loadings of heavy metals per ha. A shallow application will allow a greater organic matter level to be achieved.

It is difficult to discuss the likely environmental impact of various metals in the amended spoils because the effect depends upon other factors such as end use, plant type and species. Further experiments are required to determine uptake by plants and leaching from the amended spoils. There is however, little evidence of significant downward movement of metals in sludge amended soils even after prolonged periods of time (Alloway, 1990).

Alloway (1990) and Adriano (1986) among other authors give details of the effects of the individual heavy metals on plants, water systems and humans. These are not therefore discussed here; only the likelihood of exceeding threshold limits will be discussed. It is worth pointing out however, that Zn, Cu, Ni and Cr are phytotoxic and hence unlikely to reach humans via the food chain (unless in water) as plants will be killed before they accumulate levels toxic to humans or animals. Concern about these metals is mainly directed at crop yield and soil fertility (Kiekens, 1990).

The discussion here has centred around the NZ Department of Health guidelines for application of heavy metals in sewage sludge to arable land. These guidelines may not be very relevant as it is doubtful that any of the spoils will be used for arable agriculture. However, in the absence of more suitable guidelines they are used.

The cumulative loadings based on total heavy metal content are not very useful as most amended spoils exceed the limit allowable in arable soil for at least two heavy metals (Table 5.25). If limits recommended for heavy metals in arable land were adhered to, North Shore sewage and paper sludge could only be applied to fireclay, and Manukau sewage sludge is not suitable for application to any of the gold mine spoils (Table 5.25). This is based on the total heavy metal loading in the soil. Sludge addition although sometimes contributes to heavy metal accumulation in soils, it may reduce the plant availability of heavy metals already present in the soil. For example in this study the paper sludge addition reduced the availability of As, Cd and Cr in the coal mine spoils. It is therefore important that the guidelines for heavy metals in soils consider soluble or plant available content.

The values for total heavy metals in the individual incubation materials were extrapolated to provide values for the amount of each heavy metal that would occur per hectare of land if the sludges were added to the mine spoils to a depth of 5, 10 or 15 cm to achieve an organic matter content of either 2, 5, or 10% in the amended spoil (Appendix 3). Equation 5.1 was used:

$$y \ (g/ha) = ax * 10000m^2$$
$$y \ (kg/ha) = (ax * 10000m^2)/1000$$
$$\mathbf{y = 10ax}$$

(5.1)

y= quantity of element (kg) per ha of sludge amended spoil

a= depth of incorporation (m)

x= value from equation 4.6 (mg/kg=g/t)

Assumption: The bulk density of the spoil/sludge mixture is equal to 1.

From these extrapolated results, applications that are likely to exceed Department of Health regulations for maximum cumulative loadings of heavy metals were derived. Results have been evaluated with respect to limits for maximum cumulative loadings of heavy metals (Department of Health, 1992) because it is predicted that only one application of sludge to the mined materials may occur. As noted however, there is some uncertainty about the validity of the cumulative limits.

With a theoretical mixing depth of 5 cm, the cumulative loading limit for the heavy metals likely to be exceeded in the given spoil treatments is listed below:

As- exceeded in all treatments except the fireclay treatments

Cr- exceeded in all treatments of mudstone.

Cu- exceeded in tailings ameliorated with Manukau sewage sludge to provide 10% organic matter.

Ni- in all spoils ameliorated with Manukau sewage sludge, in mudstone ameliorated with either North Shore or paper sludge, and in Huntly subsoil amended with North Shore sewage sludge to provide 10% organic matter.

Zn- exceeded in oxidised waste and tailings when Manukau sewage sludge is applied to provide 10% organic matter.

With a theoretical mixing depth of 10 cm, cumulative loading limits for heavy metals are likely to be exceeded in the following spoil treatments:

As- exceeded in all treatments

Cd- exceeded in all (but only slightly) except the fireclay treatments.

Cr- in all treatments of tailings and oxidised waste with Manukau sewage sludge, in Waihi subsoil amended with sewage sludge to provide 5 or 10% organic matter and in all mudstone treatments.

Cu- exceeded in tailings amended with both sewage sludges to provide either 5 or 10% organic matter, in oxidised waste amended with Manukau sewage sludge to provide 5 or 10% organic matter and North Shore sewage sludge to provide 10% organic matter, Waihi subsoil amended with either Manukau or North Shore sewage sludge to provide 10% organic matter. Mudstone amended with North shore sewage sludge to provide 10% organic matter and Huntly subsoil amended with North Shore sewage sludge to provide 10% organic matter.

Ni- in all except Huntly subsoil ameliorated with paper sludge to provide 2% organic matter and Fireclay amended with Paper sludge.

Pb- in tailings and oxidised waste amended with Manukau sewage sludge to provide 5 and 10% organic matter and Waihi subsoil amended with Manukau sewage sludge to provide 10% organic matter.

Zn-in tailings and oxidised waste when Manukau sewage sludge is applied to provide 5 and 10% organic matter, and in Waihi subsoil when Manukau sewage sludge is applied to provide 10% organic matter. The Zn limit is exceeded when North Shore sewage sludge is applied tailings to provide 5 and 10% organic matter, to oxidised waste, Waihi subsoil, mudstone and Huntly subsoil to provide 10% organic matter .

When sewage sludge is applied to the spoils to 15 cm depth , the maximum cumulative loading for As is predicted to be exceeded in all treatments, Cd in all treatments except Fireclay, Cr in all treatments except tailings amended with North Shore sewage sludge to provide 2 and 5% organic matter, Waihi subsoil amended with North Shore sewage sludge to provide 2% organic matter, and all fireclay and Huntly subsoil treatments.

Copper will be exceeded in all but tailings, oxidised waste and Waihi subsoil amended with North Shore sewage sludge to provide 2% organic matter. It is not exceeded when Manukau sewage sludge is applied to oxidised waste or Waihi subsoil to provide 2% organic matter. It is not exceeded in fireclay amended with either sewage or paper sludge or mudstone amended with North Shore sewage sludge to provide 5% and with paper to provide 5 or 10% organic matter, in Huntly subsoil amended with paper or in Huntly subsoil amended with North Shore sewage sludge to provide 2%.

Nickel limits will be exceeded in all treatments.

Lead limits will be exceeded in tailings, oxidised waste and Waihi subsoil when Manukau sewage sludge is applied to provide either 5 or 10 % organic matter. It will also be exceeded in oxidised waste, Waihi subsoil and mudstone when North Shore sewage sludge is applied to provide 10%.

Zinc limits will be exceeded in tailings, oxidised waste and Waihi subsoil when amended with Manukau sewage sludge to provide 5 and 10% organic matter and in tailings, oxidised waste, Waihi subsoil and Huntly subsoil when North Shore sewage sludge is applied to provide 5 or 10% organic matter. It will be exceeded in mudstone when North Shore sewage sludge is applied to provide 10% organic matter.

Table 5.25

The maximum amount of sludge that may be applied to each spoil before the maximum limit allowable in soil is exceeded by the limiting heavy metal*

Sludge	Spoil	1st most limiting metal	Maximum quantity of sludge that may be applied without exceeding limit (kg sludge/kg of spoil)	2nd most limiting metal
Manukau	Tailings	As	0	Ni
	Oxidised waste	As	0	Ni
	Waihi subsoil	As	0	Ni
North Shore	Tailings	As	0	Ni
	Oxidised waste	As	0	Ni
	Waihi subsoil	As	0	Ni & Cd
	Fireclay	Ni	0.14	Zn
	Mudstone	Ni	0	As
	Huntly subsoil	As	0	Cd
Paper	Fireclay	As	0.17	Ni
	Mudstone	Ni	0	Cr
	Huntly subsoil	As	0	Cd

*Equation 5.2 was used to calculate the values in the table:

$$(a-b)/c = z$$

(5.2)

a = limit value (mg/kg)

b = quantity of element in spoil (mg/kg)

c = quantity of element in sludge (mg/kg)

z = quantity of sludge that may be applied to spoil   (kg/kg)

The values given are actually higher than is allowed in 1 kg of soil e.g. 0.14 kg of North Shore sewage sludge applied to fireclay actually means the limit is reached in 1.14 kg of soil and is exceeded in 1 kg.

CHAPTER 6

CONCLUSION AND RECOMMENDATIONS

1. Disturbed land and waste materials resulting from mining activities often becomes unproductive and erodible and sometimes causes ground water pollution. The common characteristic of most mine waste and disturbed soils is that they contain negligible amounts of organic matter resulting in poor buffering for plant nutrients, weak soil structure and low retention of heavy metals. There is growing interest in the use of industrial waste materials as an amendment to improve both the physical and chemical fertility of mined soils/spoils. Use of these waste materials not only assist in the revegetation of the mine waste materials but also overcomes the problems associated with their disposal.

2. A number of studies overseas, have examined the potential use of organic carbon rich waste materials, such as sewage sludges in the reclamation of mined soils/spoils (Sopper, 1992). In New Zealand, however, there has been only limited work on the effect of sludge addition on the chemical characteristics of mine spoils.

3. In this study the effect of addition of two sludge sources, sewage and industrial sludge, on the chemical characteristics of six mine spoils from coal and gold mining sites was examined. An incubation experiment was used in which various chemical characteristics of the mine spoils amended with three levels of sludge addition (2, 5, and 10%) were monitored over a period.

4. An attempt was made to predict the chemical characteristics of the sludge amended mine spoils using the following equation:

$$\frac{(a*b)+(c*d)}{a+c} = x$$

a = quantity of mine spoil (g)

b = measured value for mine spoil

c = quantity of sludge amendment (g)

d = measured value for sludge amendment

x = predicted value for the amended spoil (sludge-spoil mixture)

Organic matter, total and mineral nitrogen, total and Olsen phosphorus contents of the sludge amended spoils were adequately predicted from the characteristics of the individual sludges and mine spoils.

The pH of the amended mine spoils could not be predicted and an interaction causing the release of salts from sewage sludge when applied to the mines spoils resulted in EC values being generally higher than predicted. An interaction between the mine spoils and the sludge also prevented the accurate prediction of CEC.

6.   Amendment with Manukau sewage, North Shore sewage or paper sludge to provide 10% organic matter in the amended mine spoils maximised the benefit to the mine spoils with respect to chemical fertility (N, P, CEC, pH, EC) although values for EC, C/N, P retention and CEC were adequate in most amended spoils. This level of amendment often resulted in New Zealand Department of Health guidelines for heavy metals being exceeded. However, limits for heavy metals were often exceeded in the unamended spoils also.

7.   Incubation, as an indicator of potential changes with time had the following effects on the chemical characteristics of the amended mine spoils:

Electrical conductivity was increased due to a release of salts and prevention of leaching from the incubations.

Nitrate and mineral N increased during time

The trend in Olsen P values was a slight increase during the incubation
There was a slight reduction in pH during time.

There was no significant change in total N, P, CEC, C/N ratio or organic matter with time and no trend to the changes in 0.1M HCl extractable heavy metals.

8. Manukau sewage sludge presented the most benefit for mine spoil rehabilitation with respect to P having the highest value for total and Olsen P.

9. Of the three sludges trialed, North Shore sewage sludge presented the greatest benefit for mine spoil rehabilitation with respect to nitrogen fertilisation. It had the highest value for total N but less mineral N than Manukau sewage sludge thus reducing the risk of N leaching, at least in the first season after mine spoil amendment. North Shore sewage sludge also had the lowest C/N ratio, meaning that if additional N is applied, it should be relatively easily available for uptake by vegetation planted in the amended mine spoil. A greater percentage of total P was in available (Olsen P) form than in Manukau sewage sludge and it also had a lower P retention than Manukau sewage sludge. The heavy metal content of North Shore sewage sludge was lower than Manukau sewage sludge.

10. Paper sludge was the most beneficial sludge to apply to the mine spoils for improvement of organic matter content and pH. Of the three sludges applied, it presented the least risk of contamination by heavy metals. However, its application resulted in a high C/N ratio which will result in available N being held unavailable and it provided very little N. It provided some benefit with respect to total P but very little was in available (Olsen P) form.

11. It is recommended that the physical characteristics of the mine spoils and sludges be determined in greater detail to aid interpretation of the results of amendment of the mine spoils with sludges.

12. Pot and field experiments are recommended to assess the effect of sludge amendment of the mine spoils on vegetation germination and development and that leaching through the profile and runoff from amended sites also be monitored under field conditions.

13. Although the addition of heavy metal enriched sludge materials (e.g. Manukau sewage sludge) increased the heavy metal content of the mine spoils, it is likely that the plant availability of the heavy metals originally present in some of the spoil materials (e.g. tailings) is likely to be inhibited. Further investigation of heavy metals is recommended, particularly the form the heavy metals present their availability to plants and movement in the amended mine spoil profile.

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Moisture contents of the sludges and mine spoils

Material	Moisture Content (%)
Tailings	1.9
Oxidised Waste	11.7
Waihi Subsoil	17.7
Fireclay	27.6
Mudstone	14.0
Huntly subsoil	13.6
Manukau sewage sludge	39.9
North Shore sewage sludge	28.9
Paper sludge	58.4

Concentration of various elements in the original sludge and mine spoil materials analysed by plasma emission spectrophotometry (ug/g)

Material	Al	As	B	Ca	Cd	Co	Cr	Cu	Fe	K	Mg	Mn
Tailings	38339	64	15.1	1841	3.1	156	68	37.5	33542	6911	2362	2110
Oxidised waste	52217	46	7.6	533	3.2	72	100	30	44289	6829	4592	3147
Waihi subsoil	80080	41.5	6.9	585	3.5	40.5	79	25	64858	6934	3706	419
Fireclay	42916	3.3	31.5	1429	0.33	6.1	20	28	12845	2239	1115	127
Mudstone	46989	38.5	41	338	3.3	3.3	725	13.3	35856	7434	2316	50
Huntly subsoil	99643	33	22	140	3.3	7	26.5	22	51747	2416	1812	80
Manukau sludge	27155	47	70	30785	11.1	96	1840	747	22593	1640	3325	383
North Shore sludge	21818	29.5	17.1	32441	4.7	14.9	153	606	13329	1059	2340	184
Paper sludge	22945	38.5	21	33666	3.9	25	41.5	96	2749	607	1986	84

Material	Mo	Na	Ni	P	Pb	S	Se	Si	Sn	Sr	Zn
Tailings	3.1	530	44.5	250	31.5	408	63	773	6.8	16.8	59
Oxidised waste	3.2	91	69	332	38.5	3914	63	252	6.3	11.9	89
Waihi subsoil	3.5	64	48.5	236	34.5	91	69	301	6.9	7.3	54
Fireclay	0.33	114	16	236	3.3	456	6.6	233	0.66	163	62
Mudstone	463	391	2861	224	65	7071	66	578	6.6	37	38.5
Huntly subsoil	3.3	100	17.9	98	33	119	66	219	6.6	20	44.5
Manukau sludge	18.6	1227	210	15067	912	12074	94	234	117	183	2268
North Shore sludge	15.9	508	135	11745	239	6460	59	241	71	95	1517
Paper sludge	18.7	602	67	470	68	1017	77	193	7.7	46.5	211

Predicted heavy metals (kg/ha) in sludge amended spoil to a depth of 5, 10 and 15 cm to achieve 2, 5 and 10% organic matter

To 5 cm depth

Spoil	Sludge	Organic Matter (%)	As	Cd	Cr	Cu	Ni	Pb	Zn
Tailings	Manakau	2	32	1.7	75	35	26	36	80
		5	31	2.0	136	60	32	67	157
		10	30	2.5	238	101	41	117	284
	North Shore	2	31	1.6	36	33	24	21	65
		5	30	1.6	39	54	28	28	119
		10	28	1.7	44	89	33	41	208
Oxidised Waste	Manakau	2	23	1.7	81	28	37	35	83
		5	23	2.0	141	53	42	65	159
		10	23	2.5	234	95	50	116	286
	North Shore	2	23	1.6	51	26	36	23	71
		5	22	1.7	53	47	38	30	124
		10	21	1.8	56	83	42	43	213
Waihi subsoil	Manakau	2	21	1.8	46	15	25	20	35
		5	21	2.1	109	41	31	52	115
		10	21	2.5	215	85	40	105	248
	North Shore	2	21	1.8	40	15	25	18	33
		5	20	1.8	43	37	28	26	88
		10	19	1.9	47	74	33	39	183
Fireclay	North Shore	10	2	0.3	14	30	11	8	71
	Paper	10	2	0.2	10	15	9	3	33
Mudstone	North Shore	5	19	1.7	349	21	1365	37	55
		10	18	1.8	311	60	1183	48	153
	Paper	5	19	1.7	352	8	1388	33	22
		10	19	1.7	323	11	1270	33	29
Huntly subsoil	North Shore	2	16	1.7	15	19	11	19	43
		5	16	1.7	20	41	15	27	98
		10	16	1.8	28	78	22	40	191
	Paper	2	17	1.7	13	12	9	17	24
		5	17	1.7	14	13	11	18	28
		10	17	1.7	14	16	13	19	35

To 10 cm depth

Spoil	Sludge	Organic Matter (%)	As	Cd	Cr	Cu	Ni	Pb	Zn
Tailings	Manakau	2	63	3	150	70	52	72	161
		5	62	4	272	119	64	133	314
		10	60	5	477	201	83	235	569
	North Shore	2	62	3	72	65	49	42	130
		5	60	3	78	107	56	57	238
		10	56	3	89	177	67	82	417
Oxidised Waste	Manakau	2	46	3	161	55	74	69	165
		5	46	4	283	105	84	130	318
		10	46	5	486	189	100	232	573
	North Shore	2	45	3	102	52	71	46	142
		5	44	3	106	94	76	61	249
		10	42	4	113	166	85	86	426
Waihi subsoil	Manakau	2	42	4	92	30	50	41	70
		5	42	4	219	82	61	104	230
		10	43	5	430	169	81	210	496
	North Shore	2	41	4	80	29	49	36	65
		5	40	4	85	74	56	52	176
		10	39	4	95	149	67	78	365
Fireclay	North Shore	10	5	1	27	60	23	16	143
	Paper	10	4	0	21	30	18	5	67
Mudstone	North Shore	5	38	3	698	42	2730	73	110
		10	37	4	621	121	2367	97	307
	Paper	5	39	3	704	16	2776	65	44
		10	39	3	646	23	2540	65	58
Huntly subsoil	North Shore	2	33	3	30	38	21	39	85
		5	33	3	40	82	30	54	196
		10	32	4	55	156	45	80	381
	Paper	2	33	3	27	23	19	34	47
		5	33	3	28	27	21	35	56
		10	34	3	29	33	25	38	69

To 15 cm depth

Spoil	Sludge	Organic Matter (%)	As	Cd	Cr	Cu	Ni	Pb	Zn
Tailings	Manakau	2	95	5	224	105	78	108	241
		5	93	6	408	179	95	200	471
		10	90	7	715	302	124	352	853
	North Shore	2	93	5	108	98	73	62	196
		5	90	5	118	161	83	85	357
		10	83	5	133	266	100	124	625
Oxidised Waste	Manakau	2	69	5	242	83	111	104	248
		5	69	6	424	158	126	195	477
		10	69	7	729	284	150	349	859
	North Shore	2	68	5	153	77	107	69	213
		5	66	5	159	142	115	91	373
		10	63	5	169	249	127	129	640
Waihi subsoil	Manakau	2	62	5	138	45	74	61	105
		5	63	6	323	123	92	156	344
		10	64	8	646	254	121	314	744
	North Shore	2	62	5	119	44	74	54	98
		5	61	5	128	110	84	77	265
		10	58	6	142	223	100	117	548
Fireclay	North Shore	10	7	1	41	90	34	25	214
	Paper	10	7	1	31	45	27	8	100
Mudstone	North Shore	5	57	5	1046	63	4095	110	164
		10	55	5	932	181	3550	145	460
	Paper	5	58	5	1056	24	4164	98	66
		10	58	5	970	34	3809	98	88
Huntly subsoil	North Shore	2	49	5	45	57	32	58	128
		5	49	5	59	123	45	81	294
		10	48	5	83	233	67	120	572
	Paper	2	50	5	40	35	28	50	71
		5	50	5	41	40	32	53	83
		10	51	5	43	49	38	57	104