An Investigation of Soil Quality Parameters Relating to Agricultural Reuse and Land Disposal Options for the Management of Biosolids

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DECLARATION

Declaration

This thesis has not previously been submitted to this, or any other college. With acknowledged exception, it is entirely my own work.

Aoife O Connor

ABSTRACT

An investigation of soil quality parameters relating to agricultural reuse and land disposal options for the management of biosolids.

Aoife O Connor

Abstract

Sludge provides valuable nutrients to soil. Application of sludge to land is subject to a number of limitations. Its use as a soil conditioner represents a 'beneficial reuse option'. Primary and secondary sludge from Dublin city is treated in Ringsend treatment plant where it undergoes thermal drying. This study investigates the feasibility of land application of thermally dried biosolids (TDB) from Ringsend treatment plant.

Greenhouse trials demonstrated the positive effects of TDB application on both agricultural soil and mine tailings from Silvermines Tailings Management Facility, Tipperary.

Both shoot height and dry matter yield of five of grass species used in trials were increased as a result of sludge addition to agricultural soil at 2 t/ha. The increase in these parameters was only significant at 20t/ha. TDB application to agricultural soil improved soil chemical properties. This included increases in pH, organic matter, organic carbon, cation exchange capacity, total kjeldahl nitrogen, available phosphorus and exchangeable potassium levels in the soil. TDB application to agricultural soil also caused slight increases in concentrations of copper, lead and zinc in the soil, and were only significant at 20 t/ha TDB application. Herbage metal levels were not significantly different with the application of TDB to agricultural soil at either application rate.

Silvermines Tailings Management Facility is a lead-zinc tailings, occupying 76.2 ha, and is partially covered in vegetation. TDB was used as a substrate ameliorant. Grass species established only where TDB was applied. *Agrostis stolonifera* performed best in these conditions. Only *Poa pratensis* and *Festuca rubra* exhibited a significant increase in dry matter yield on addition of 50t/ha TDB. The clover species, *Trifolium repens* did not survive on tailings substrate. The adverse chemical properties of the tailings were ameliorated by TDB. This included an improvement in the physical structure of the tailings. A reduction in pH, and increases in organic matter, organic carbon, cation exchange capacity, total kjeldahl nitrogen, available phosphorus occurred with TDB application to enhance the plant growth properties of the soil. Elevated metal concentrations in tailings were effectively reduced with TDB application, particularly, arsenic, nickel, cadmium, lead and zinc. This was due to the complexing of metals with the organic matter matrix and the dilution effect of mixing the tailings substrate with TDB. Herbage metal levels were extremely high in comparison with agricultural soil. Arsenic, lead, zinc and nickel in herbage decreased on application of TDB as a result of the decreased substrate metal levels.

Greenhouse trials demonstrated the positive aspects of TDB addition to mine tailings as a plant growth medium. No germination of seeds took place on tailings alone, therefore, grass growth was established with the use TDB. Uptake of metals from tailings was high, however, this was directly resulting from high substrate metal levels. Following the greenhouse trials, monitoring of herbage metal uptake over the long term is strongly advised. Additionally, the implementation of full scale field trials on Silvermines TMF is recommended.

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Appendix A

Percentage recovery for Plant Reference Material Poplar leaves GBW 07604

Percentage recovery for Sewage Sludge Reference Material CRM 029-050

1.0 Introduction

1.0 Introduction

1.1 Urban wastewater sludge and biosolids

Urban wastewater consists of domestic waste-water, or a mixture of domestic and industrial wastewater and/or rainwater. In general, the wastewater from these sources is collected and piped to treatment plants before discharge into rivers, lakes, estuaries or coastal waters. The level of treatment before discharge varies from primary treatment alone, to advanced treatment (EPAa, 2000). The constituents removed in wastewater treatment plants include screenings, grit, scum, solids and biomass. These are usually in the form of a liquid, or semisolid liquid, containing between 0.25% to 12% solids, by weight, depending on the operations and processes used. 'Biosolids' refer to wastewater solids which can be beneficially reused after treatment with processes such as stabilisation and composting. The term 'sludge' is used only before beneficial use criteria have been achieved (Metcalf and Eddy, 2003).

Dealing with solids and biosolids from biological treatment processes often presents complex problems since sludges are composed largely of the substances responsible for the offensive character of untreated wastewater. Thickening (concentration), conditioning, dewatering, and drying are primarily used to remove moisture from solids; digestion, composting, and incineration are used primarily to treat or stabilise the organic material in the solids (Metcalf and Eddy, 2003).

1.2 Urban wastewater sludge generation and disposal in Ireland

A number of items of legislation in recent years have resulted in increased sludge generation and the elimination of traditional disposal routes. The Urban Wastewater Treatment Directive (91/271/EEC) (CEC, 1991), introduced into Irish legislation by means of SI 419 of 1994, lead to the requirement of towns in Ireland, with a population in excess of 2000, to install secondary wastewater treatment facilities by the year 2005.

The Urban Wastewater Treatment Directive (91/271/EEC), also resulted in the implementation of the Dumping at Sea Act of 1996 (no. 14 of 1999) elimination the traditional disposal route for much of Irelands sludge generation (EPA, 2000b). Landfill dumping of unprocessed sludge discontinued following the introduction of The Waste Management Act of 1996 (no. 10 of 1996) and European Council Directive (1999/31/EEC) (*regarding the landfill of waste*).

According to the EPA (2000a) in 1998 in Ireland, total urban wastewater sludge arisings for agglomerations with a population equivalent ≥ 1,000, was estimated to be 37,577 tonnes of dry solids, equivalent in wet weight terms to approximately 493,000 tonnes. Of this, 15.8% was reused in agriculture, 41.1% was landfilled, 40.6% dumped at sea and the remaining 2% treated by some other unspecified route. The source also states that a significant amount of sludge arises from small scale wastewater treatment plants and septic tanks. It is estimated that this figure is approximately 507 tonnes of dry solids per annum, resulting in total estimated wet weight arisings for sewage sludges in 1998 of 505,686 tonnes. Although in 1998, only 15.8% of sludge was landspread, this figure is thought to have increased by 2000 with the move away from sea dumping of sludge.

According to the EPA (2000b) the sludge treatment plant at Ringsend, Co. Dublin accounts for 35% of biosolids arisings nationally. Operating since 1999, this is the first use of thermal drying technology in Ireland. In 1999, 14,445 tonnes of thermally dried biosolids was produced, all of which was landspread.

1.3 Land application of wastewater biosolids

Management of municipal sewage sludge remains a major issue for large urban populations. Land application of sludge is an economically appealing option since it is the natural disposal route and returns fertility in the form of mineral nutrients to the soil. However, land application has limitations (Olness *et al.*, 1998).

European Union waste disposal policy recognises recycling of sludge as the preferred option to incineration (with energy recovery) and landfilling (Davies, 1996). This is emphasised in the 'Use of Sewage Sludge in Agriculture' Directive No. (1986/278/EEC)(CEC, 1986), with the intention of promoting the beneficial use of sludge on land. The 'Waste Management (*Use of Sewage Sludge in Agriculture*) Regulations, 1998', (SI 148 of 1998), implement the requirements of 'Council Directive 86/278/EEC on the Protection of the Environment, and in particular of the Soil when

Sewage Sludge is used in Agriculture' (EPAb, 2000). According to the Regulations, any person using sludge is required (under Article 4) to ensure that the quality of the soil, surface and groundwater is not impaired. Limit concentrations of heavy metal in applied sludges and receiving soils are specified for cadmium, copper, nickel, lead, zinc and mercury. The Schedule to the Regulations sets out maximum values for concentrations of heavy metals in soil (Part I), of sludge for use in agriculture (Part II), conditions for soil sampling and analysis (Part III), conditions applying to sludge sampling and analysis (Part IV) and methods of analysis (Part V) (EPAb, 2000, SI 148 of 1998). The 1998 Regulations cite a definition of 'treated sludge', and concentrations of metals in both sludge and soil, which if exceeded prohibit its application to agricultural land (SI 148 of 1998).

Table 1.1 Maximum values for concentrations of heavy metals in soil, and in sludge for use in agriculture (SI 148 of 1998).

Parameters	**Maximum values in soil (mg/kg)***	**Maximum values in sludge (mg/kg)**
Cadmium	1	20
Copper	50	1000
Nickel	30	300
Lead	50	750
Zinc	150	2500
Mercury	1	16

*mg/kg of dry matter in a representative sample of a soil with a pH of 5 to 7

This Regulation was amended by Statutory Instrument 267 of 2001 (Waste Management Regulations). The Council Directive 86/278/EEC and Regulation 148 of 1988, set absolute and stringent limits and allowed no flexibility for managing site specific circumstances. The 2001 Regulations provided for site specific conditions by basing the maximum loading per hectare based on a 10 year average subject to proper nutrient management planning.

1.3 Mineral exploitation in Ireland

At present, Ireland is the sixth largest producer of lead and zinc in the world. The extraction of minerals, unless properly controlled, can have serious localised environmental effects through air pollution, traffic generation, noise, leachate production from spoil heaps and tailings. Dust, depending on its composition, can affect people, agriculture and wildlife. Most existing mining operations, and all new mines, are now required to apply for an Integrated Pollution Control licence. This licence contains conditions regulating operations over the lifespan of the mine as well as the ongoing monitoring of the on-site mine waste (EPA, 2000a). According to EPA (2000a), in 1998, approximately 2,112,302 tonnes of mine tailings, which are classed as a non hazardous industrial waste, were produced in Ireland.

1.4 History of mining in the Silvermines area

Silvermines, Co. Tipperary, has a long history and tradition of mining that has ensured its place in almost every Irish mining 'boom', particularly in the seventeenth and nineteenth centuries, the 1950's, and in the more recent period of 1960 to 1990 (Grennan, 2000). The author states that the first substantive report of mining in the area is from the latter part of the 13th century AD, although the earliest records of mining in the area date back to early 9th century when argentiferous galena was mined by the Danes (Andrew, 1986). From the 16th to the 19th century, 'Silvermines Fault' operations produced copper, silver, lead, zinc and sulphur ores. The major base metal deposits were discovered by diamond prospecting in 1962 and worked until 1982 by Mogul of Ireland, Ltd. The Mogul mine produced some 10,783,859 tonnes of ore grading 2.7% lead and 7.36% zinc from 1962 to closure from underground workings of various zones (Andrew, 1986).

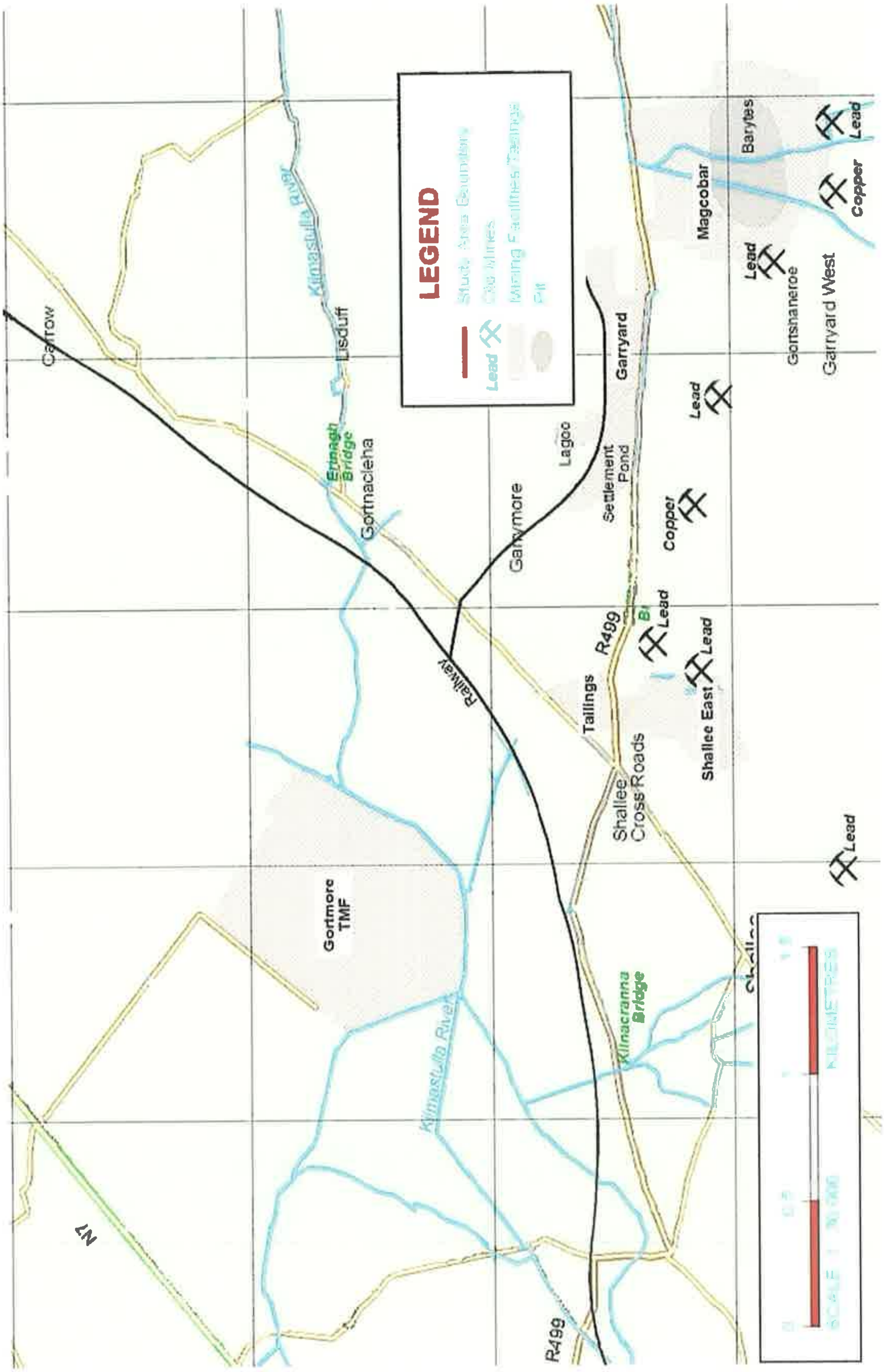
1.5 Gortmore Tailings Management Facility (TMF), Silvermines

Grennan (2000) states that mining at Mogul resulted in approximately seven million tonnes of material deposited as tailings although some sources (DAFRD, 2000) quote figures closer to nine million tonnes. The tailings (a wet slurry of water, fine rock and chemicals) were pumped into a tailings pond, an area which now covers 76.2 ha (Figure

1.1). In the spring of 1985, two years after closure, weather conditions were exceptionally dry, cold and frosty. The top or the surface of the tailings dried out and easterly winds caused a dust blow lasting for approximately three weeks intermittently. This was repeated in late summer and again the following spring (Grennan, 2000). As a result of these dust blows, trials were initiated at Silvermines and it was discovered that a cultivar of the species *Agrostis stolonifera* (cv. 'Seaside') was particularly suited to the conditions, i.e. high salt tolerance and its creeping nature (Johnson, 1990; Grennan, 2000). According to DAFRD (2000), following the dust blows of 1985, a family residing beside the (TMF) moved to another location and advice was given on the use of locally grown vegetables as a direct result of the contaminated dust blows. Lead concentrations above normal background were recorded on herbage and in blood samples from livestock in the area in 1985 (DAFRD, 2000).

1.6 Environmental exposure to Lead

Lead is ubiquitous in the human environment. However, environmental contamination by lead has become a cause for concern (Wixson and Davies, 1994), particularly in the Silvermines area (DARFD, 2000). The main sources of lead in the environment in industrialised countries are leaded petrol, lead based paints (Wixson and Davies, 1994) and mining and smelting activities. Toxicity can result from inhalation, ingestions, and less commonly by skin exposure. The danger from lead residues in soil and dust is now widely accepted (Wixson and Davies, 1994). Children are particularly susceptible to the toxic effects of lead. The most sensitive target of lead poisoning is the nervous system, although it can affect other systems in the body such as the production of blood, the kidneys, the reproductive system and the production of hormones (DAFRD, 2000). Lead accumulates in the surface layers in soil due to its low solubility and resistance to microbial degradation. Soil and dust act as pathways to children for lead deposited from a number of sources. As lead does not dissipate, biodegrade or decay, the lead in dust or soil has the potential to become a long term source of lead exposure to children (DAFRD, 2000).



← North

Figure 1.1 Map of the Silvermines Area

1.7 Current status of Silvermines TMF

In 2000 the tailings pond was extensively covered in grass. However, there were a number of 'exposed' areas, devoid of vegetation (Grennan, 2000). DAFRD (2000) state that in early 1999, between 10% and 25% of the surface of the TMF had poor or no grass cover (Plate 1.1), with most of the embankment wall having no cover. These bare areas occurred as a result of regeneration of acidity causing local dieback of the sward (Johnson, 1990; DAFRD, 2000; Grennan, 2000) and also salinity, nutrient deficiencies, surface water-logging and water shortage during dry periods (DAFRD, 2000). The generation of this acidic water, and the development of acid mine drainage (AMD), are based on a chemical reaction involving the hydrolysis and oxidation of pyrite.

$$4\ FeS_2 + 8\ H_2O + 15\ O_2 \rightarrow 8\ H_2SO_4 + 2\ Fe_2O_3$$

The Gortmore TMF at Silvermines, Co. Tipperary is a tailings derived from a lead-zinc 'massive pyrite' orebody (Andrew, 1986). Initially revegetation of the site was hampered by the unusually high salinity of the material, derived from the complex chemical reactions within the substrate producing magnesium sulphate (Johnson, 1990).

Plate 1.1 Poor vegetation cover on Silvermines TMF surface

According to Johnson (1990), revegetation provides the only lasting method for simultaneously stabilising and landscaping tailings areas that have dried out following abandonment. Usually the behaviour of tailings is such that dewatering occurs progressively, depending on both the climate and the permeability of the substrate and ground beneath the tailings. The author also states that direct seeding or planting of mine waste is the most economically viable, especially in relation to cover-materials.

SRK (2002) in a recent report state that all areas of unvegetated tailings should be sufficiently amended with organic matter to 100mm depth. This report also encourages the development of a self-sustaining grass cover on the surface of the mine tailings. Sewage sludge, treated or applied in such a way that it does not pose a hazard to public health, is an ideal organic ameliorant for mine tailings low in organic matter (SRK, 2002). In addition, sludge has been widely used to date at other mine sites in Europe (Bergholm and Steen, 1989; Bradshaw and Johnson, 1992; Gallagher and O Connor, 1999; Kilkenny and Good, 1998), the U.S. (Harris and Megharaj, 2001; McNearny and Belyaeva, 1998; Pitchel, 1994; Seaker, 1991; Stuckey *et al.*; 1980; Sutton, 1974), and China (Ye *et al.*, 2001). At present, grass cover occupying greater than 50% of the tailings surface at Gortmore is dominated by *Agrostis stolonifera* and *Festuca rubra* in the more acidic and saline areas, and by *Festuca rubra* in the wetter areas being invaded by moss (SRK, 2002).

Thermally dried biosolids are an ideal ameliorant for mine waste being high in both organic matter and slow-release nutrients and low in pathogenic bacteria. Other advantages to the use of biosolids as a mine waste ameliorant include high cation exchange capacity, complexing of metals due to its organic matter content, increasing water retention during dry periods, raising pH and physically improving the soil (SRK, 2002).

A number of conditions need to be satisfied prior to application of biosolids to Gortmore tailings. These include communication and consultation with the owner, the local community and adjacent landowners in relation to the application of sludge. This would stress the use of biosolids as 'one waste treating another waste' as opposed to a 'biosolids disposal option'. The assessment of restrictions on application rates also requires consideration.

1.8 Objectives of this study

The objective of this study was to determine the effect of the addition of thermally dried biosolids to two contrasting substrates. The effect of this biosolids on an agricultural brown podzolic soil was assessed in relation to chemical characteristics and total metal content. Following on from this, metal uptake by grass species growing on this substrate was be assessed together with the effect, if any, of biosolids or elevated application rates on metal levels in the grasses grown thereon.

The second substrate which was analysed was mine tailings from the Tailings Management Facility at Silvermines, Co. Tipperary. These lead/zinc tailings are hostile medium for plant growth. An attempt to vegetate this substrate was made. Additionally, the effect of thermally dried biosolids on this substrate was observed. The use of thermally dried biosolids as a substrate ameliorant was examined in terms of chemical characteristics and total metal content. Vegetation established on the tailings and tailings plus biosolids treatments was analysed for metal uptake. Results were compared and contrasted in relation to biosolids effects and biosolids application rates.

2.0 LITERATURE REVIEW

2.0 Literature Review

2.1 Land disposal of sewage sludge

Sewage sludge is the residue produced from the treatment of domestic and industrial wastewaters (Alloway, 1995a) and has been applied to agricultural soils for many years both as a convenient means of disposal and, also, to utilize its fertilising and soil conditioning properties (Hooda and Alloway, 1994). However, sludge disposal must be controlled in order to obtain agricultural benefit from the sludge whilst protecting human and animal health and the general environment. Current practices in Europe are based on the requirements of the 1986 Directive on the Use of Sewage Sludge in Agriculture (86/278/EEC) (Carrington, 2001).

Constraints associated with the land application of sewage sludge are generally related to sludge composition, site characteristics, management limitations and public acceptance (Oberle and Keeney, 1994). The chemical composition of sewage sludge is of great importance when developing recommendations for the rates of sludge application on agricultural land (Sommers, 1977). It is also necessary to consider limitation of addition of toxic elements to land and any beneficial effects are secondary to this (Sterrit and Lester, 1980).

According to Sommers (1977), the heterogeneous nature of sewage sludges produced by different cities and the presence of potentially harmful trace metals necessitates knowledge of the composition of each individual sludge prior to land application.

There is little evidence of disease in man or animals arising from land application of sludge. The few documented cases that have occurred resulted when local regulations or codes of practice were not being observed (Carrington 2001).

Although guidelines limit the addition of toxic elements in sludges to soils, thus reducing the quantities of these elements accumulated by plants, total concentrations of toxic elements in soil provide no indication of their availability to plants (Sterrit and Lester, 1980). A potentially toxic element will be of significance if that element is commonly at a higher concentration in sludge than in soil, so that repeated applications raise the soil concentration, and this in turn may lead to increased concentration in plants (Coker, 1983).

Though well documented in many countries, according to O'Riordan (1986a), Ireland does not have a history of land spreading sewage sludge. Only 20,000 tonnes of dry matter was produced per annum in Ireland in 1986 and of this only 5% was applied to land.

2.2 Sludge Treatment

Municipal treatment systems and end products have varied greatly, but typically a community of 10,000 population produces about 1 metric ton of treated sewage sludge per day (dry weight) (Sabey and Hart, 1975).

Raw or primary sludge consists of 2-5% solid matter in water, inorganic solids, organic matter from undigested food and vegetable fibres in varying stages of lignification and faecal organisms. Activated and humus sludge solids (1.25-4.0% in water) consist mainly of bacterial floc and the associated microfauna. These are usually mixed with primary sludge before further treatment (Coker, 1983).

Treatment of sludge prior to its incorporation is of critical importance to the physical properties of the soil (Harris and Megharaj, 2001). Effective industrial pretreatment and monitoring by wastewater treatment facilities can ensure that the sludge produced is low in potentially toxic contaminants, both organic and inorganic, and high in nutrients and humus, thus rendering sewage sludge an effective and cheap alternative to commercial fertilizers (Frost and Ketchum, 2000).

The term biosolids is given to wastewater sludge that has been treated, often by stabilization and/ or dewatering, and is destined for beneficial reuse (Vesilind and Spinosa, 2001).

There are two aspects to sludge treatment; the reduction of putrescibility, i.e. stabilization, and the reduction in the levels of pathogens, i.e. hygenisation. For sludge to be aesthetically acceptable for land use, it must be hygenised. However, it must also be stabilized i.e. it must not putrefy further (Carrington 2001).

Sludge treatments determine the nature of the predominant fractions of organic matter in each sludge type. Activated sludge and those derived from anaerobic digestion contain high proportions of bacterial floc which decays rapidly and releases available nitrogen (N) and phosphorus (P). Undigested sludges, including primary sludges, contain a mixture of readily decomposable carbohydrates, fats, cellulose, lignin and other organic nitrogen compounds (Oberle and Keaney, 1994).

2.1.1 Thermal Drying

Thermal drying is an attractive alternative to existing dewatering options, for wastewater treatment plants to decrease their volume of sludge. In addition the sludge is pasteurised and is therefore easier and safer to store and handle. Dried sludge pasteurised by this process can be landfilled or landspread. Sludge granulates can be used as a slow release fertilizer or as a fuel source (Weemaes and Verstraete, 2001).

There have been a number of developments in the field of thermal drying of sludges in recent years. Heat drying of sludge involves the use of active or passive dryers to remove water from biosolids. It is used to destroy pathogens and eliminate most of the water content, which greatly reduces the volume of biosolids. Thermally dried biosolids generally do not have an objectionable odours when stored dry. It has the advantage of conserving nitrogen and significantly reducing transport costs in comparison with other forms of biosolids with higher moisture contents. Variations of the process include convection drying, contact drying and vacuum drying. Sludge is dried to a water content of less than 10% at a temperature in excess of 80°C (Carrington 2001).

Carrington (2001) reports that a short period, i.e. less than 10 minutes at this temperature of 80°C should be lethal to most pathogens. The hygenisation of the sludge is further enhanced by the reduction in the water content, which will inhibit the growth of bacteria.

Thermal drying of raw undigested sludge results in the structure of the dried sludge being light and fluffy with a low density, as opposed to being granular. This is primarily due to the high fibre content of raw sludge, possibly as a result of the use of soft lavatory paper and its subsequent disposal into the sewer system (Weemaes and Verstraete, 2001).

2.3 Sludge Characteristics

Sludges vary in their chemical, biological and physical properties, depending on such factors as the source and composition of the sewage, the treatment system, the extent to which the material is digested and stabilized, and how the material is handled between processing and application to the soil (Oberle and Keeney, 1994).

2.3.1 Nitrogen

According to Sommers (1977), the nutrient content of sludges varies considerably with ranges of <1 to 17.6% for total N. The author exhibited values of 5 to 67, 000 mg/kg for ammonium (NH_4) N, 2 to 4,900 mg/kg for nitrate (NO_3) N. Most sewage sludges contain greater than 1% total N (Barnhisel, 1988). Olness *et al,* (1998) give a range of <0.1 to 5.0% with a median of 3.9% whilst Sommers (1977) states that total N in sludges is quite variable with median values ranging from 2 to 4%, a significant proportion of which may be present as NH_4^+. O'Riordan *et al* (1986a) found that sludges from activated sludge plants in Ireland had a mean dry matter content of 6.3%, with values ranging from 0.2 to 36.4%. Mean N content was 0.3% but ranged from 0.025 to 0.852%. This sludge type also contained quantities of NH_4- N (351 mg/kg) and NO_3- N, (4 mg/kg) representing 10.8% and 0.1% of total N, respectively. Digested sludge had a mean N content of 10.7 % but ranged from 0.018 to 40.78%. Analysis of Irish sludges shows that 85-90% of the N is present in organic form and that 10-15% is in the ammonium form, the proportions depending on sludge treatment. The dry matter has an important bearing on the relative forms of N in sludge (O'Riordan *et al,* 1986a)

If sludges are dewatered by centrifugation, vacuum filtration or filtering beds the NH_4 and NO_3 contents of sludge are reduced due to the soluble nature of these constituents. The decrease in NH_4 and NO_3 will depend on the amount of water removed. Depending on the solids content of the sludge, from 50 to 90% of the total N in liquid sludge may be in organic combinations (Sommers, 1977). Nitrogen in sludges is rapidly mineralized and nitrified (Olness *et al.*, 1988).

2.3.2 Phosphorus

Olness *et al.* (1998) state that total P in biosolids is in the range < 0.1 to 14.3% with a median of 3.9%. Sommers (1977) states that P concentration in sewage sludge may equal or exceed the amount of N present. Total P concentrations range from 1.2 to 3.0%. Irish activated sludges have mean P content of 1.4% and digested sludges had a mean of 0.83% in sludge dry matter (O'Riordan *et al.*, 1986b).

Phosphorus in sludges generally exists in both organic and inorganic forms with the inorganic forms generally predominating (Coker, 1983; Oberle and Keeney, 1994). Organic P must undergo mineralisation in the soil before the P is available for plant uptake (Oberle and Keeney, 1994). Due to the association of P with sludge solids, sludge handling does not influence total P and thus variability for P levels in sludges is seldom encountered (Sommers, 1977).

2.3.3 Potassium

Sommers (1977), found potassium (K) in sludge to be in the range 200 to 26,400 mg/kg. Concentrations of sodium (Na) and K are strongly influenced by sludge handling procedures but most contain less than 0.5% K and 0.5% Na expressed on a dry matter basis. Irish activated and digested sludges contained 0.6% and 0.4% K (O'Riordan *et al.*, 1986b). The K in sludges is normally assumed to be fully available for plant uptake. Sewage sludges are generally considered to be poor sources of plant available K, primarily due to low concentrations of K in sludges. Potassium is a soluble constituent in sludges and, when relatively high K concentrations (>10,000 mg/kg) are reported, this often reflects sludges with low solids content that have been dried down prior to analysis (Oberle and Keeney, 1994).

2.3.4 Organic carbon

According to Sommers (1977), the organic carbon (C) content of sewage sludges range from 6-48% with a median of approximately 32%. Digested sludges and composts have lower organic C, a median of 28% and 32% for anaerobically and aerobic digested sludges, respectively and 33% for other forms (Sommers, 1977). In comparison, dried plant material content often has organic C content of 39-44% (Olness *et al.*, 1998).

2.3.5 Metals

The occurrence of metals in sludges arises from the scavenging action of sewage and sludge solids for soluble metals present in wastewater. The efficiency of metal recovery in sludges during wastewater treatment processes depends on the total metal load and the efficiency of the treatment process (Sommers, 1977). The solids content of sludges is a reflection of the digestion process and subsequent handling methods. Concentration of water-soluble constituents (i.e. K, Calcium (Ca), Na and Magnesium (Mg)) will be decreased by dewatering through filtration or centrifugation (Sommers, 1977).

Metals may be present in biosolids as carbonates, sulphides, organically bound, adsorbed or exchangeable forms (Illera, *et al.*, 2000). Of the numerous trace metals present in sludges, cadmium (Cd), lead (Pb), mercury (Hg), arsenic (As), selenium (Se), zinc (Zn), copper (Cu) and nickel (Ni) are identified as the elements of primary concern (Hooda and Alloway, 1994). Heavy metals may be defined as those having a density >6 g/cm^3 (Davies, 1987).

In a study of samples from 150 wastewater treatment plants in six north American states, data generated by Sommers (1977) show that the typical sewage sludge from a city relatively free of industrial inputs will still have adequate metal levels to warrant carefully controlled application rates to soil. Metal constituents present in plumbing systems, urban drainage runoff, etc., can continue to enter the waste treatment system resulting in a sludge containing significant amounts of metals. The author also states that Pb, Zn, Cu, Ni and Cd concentrations in sludge are extremely variable. However, median concentrations obtained for aerobically digested sewage sludges were Pb, 300 mg/kg; Zn, 1800 mg/kg; Cu, 970 mg/kg; Ni, 31 mg/kg; and Cd 16 mg/kg.

2.3.5.1 Lead Levels in sludge

O'Riordan *et al.* (1986c) state that mean Pb level in Irish sewage sludge was 269 mg/kg, ranging from 29 to 1772 mg/kg with a median of 135 mg/kg. Sommers (1977) reports in his study, that Pb levels ranged from 13-19,700 mg/kg with a median of 500 mg/kg. Coker and Matthews (1983) state that the typical concentration of Pb in human faeces is 11mg/kg dry solid whereas the median content of sludge from a non-industrialised area is 121mg/kg Pb, with additional lead arising as a result of Pb water pipes and road drainage run off. They also state that a 90% removal of Pb occurs in sewage treatment (primary plus secondary). It is generally accepted that a typical sludge contains <1000 mg Pb/kg and is commonly present in sludges at up to 400 mg Pb/kg DS (Coker, 1983).

2.3.5.2 Zinc, Copper, Nickel, Cadmium, Chromium, Cobalt, Manganese, Mercury and Molybdeunum

Sludges are abundant in Cu, Zn and Cd in comparison with soil and plants (Baker and Senft, 1995). O'Riordan *et al.* (1986c) in a study of 45 sewage treatment plants in Ireland found that mean sludge Zn levels were 1,579 mg/kg, ranging from 91 to 28,766 mg/kg with a median of 876 mg/kg. Sommers (1977) in his North American study found total Zn levels to range from 101-27,800 mg/kg, with a median of 1,740 mg/kg. Zinc in sewage tends to be associated with suspended solids and is partitioned into the sludge during treatment. Conventional sewage treatment removes 40-74% Zn from the influent (Davis, 1980).

In Irish sewage sludges, mean total Cu was 493 mg/kg, ranging from 86 to 5,550 mg/kg with a median of 283 mg/kg (O'Riordan *et al.*, 1986c). According to Sommers (1977), total Cu in sludges is in the range 84-10,400 mg/kg with a median of 850 mg/kg.

O'Riordan *et al.* (1986c) found Cr values ranged from 8 to 1294 mg/kg with a mean of 88 mg/kg and a median of 47 mg/kg. Chromium in sludges is in the range 10-99,000 mg/kg with a median of 890 mg/kg (Sommers, 1977); Coker (1983) cites a mean value in sludge of 400 mg Cr /kg with a range of 40-14,000 mg Cr /kg.

In general, sludge from rural areas will have the lowest Cr and Ni concentrations, whilst fields receiving urban sludge will have significant concentrations of these metals (Mc Grath, 1995).

Mean Ni levels in Irish sludges were 83 mg/kg, ranging from 6 to 2890 mg/kg with a median of 135 mg/kg and Cd was in the range of < 1 mg/kg to 90 mg/kg with a mean of <1 mg/kg (O'Riordan *et al.*, 1986c). Sommers (1977), states that total Ni in sludges is in the range 2-3,520 mg/kg, with a median of 82 mg/kg, and Cd in the range 3-3,410 mg/kg with a median of 16 mg/kg. Sewage sludges vary in composition and contain Cd from various sources, including human excretion, domestic products which also contain Zn, storm waters containing particles of rubber tyres and various industrial effluents. Almost all the Cd accumulates in the insoluble sludge produced during sewage treatment (Alloway, 1995a).

Cobalt (Co) levels in Irish sewage sludge ranged from 1 to 48 mg/kg with a mean of 14 mg/kg, molybdenum (Mo) ranged from 3 to 39 mg/kg with a mean of 11 mg/kg and boron (Bo) ranged from 19 to 236 mg/kg with a mean of 72 mg/kg. The mean manganese (Mn) level in sewage sludge was 340 mg/kg with values ranging from 65 to 3,018 mg/kg with a median value of 253 mg/kg (O'Riordan *et al.*, 1986c). Mercury is present in sludges at concentrations of 0.2-18, common value 5 mg/kg (Coker, 1983). Steinnes (1995) states that 5-10 mg/kg is a typical Hg level in sludge, however, values of 100 mg/kg have been reported. Arsenic in sludges ranges from 3-30 mg/kg with a mean value of 20 mg/kg (Coker, 1983). The levels of As in sewage sludge reflect the degree of industrialization of the area served by the sewage system. Ranges of 0 to 188 mg/kg for As have been quoted by O'Neill (1995).

2.3.5.3 Calcium, Magnesium, Iron, Aluminium and Sodium

These elements are present in sludge solids but may be added to sludges in the form of lime, alum etc. This is indicated by the range of concentrations for these elements. General trends for median levels in sludge are; Calcium (Ca), 3.1-4.9 %; Magnesium (Mg), 0.40-0.48 %; Iron (Fe), 0.1-1.2 %; and Aluminium (Al), 0.1-0.5% (Sommers, 1977). Expressed on a dry matter basis, Irish activated and digested sludges contained

0.3% and 0.2% Mg, 2.4% and 3.0% Ca, 0.2% and 0.2% Na respectively (O' Riordan *et al.*, 1986b).

2.3.5.4 Sulphur

Sulphur (s) is a plant nutrient present in significant quantities in sludge; the median concentration found by Sommers (1977) is approximately 1%.

2.4 Effects of sewage sludge addition on soil physical properties

Fine textured soils with insufficient organic matter are difficult to cultivate and lack friability (Coker, 1983). Physical changes in soil associated with sludge application to land include enhanced soil organic matter and water holding capacity; as well as improved soil structure, aggregation and water infiltration. This can lead to reduced runoff and erosion (Oberle and Keeney, 1994). Soil aggregation and aggregate stability are the chief physical properties which affect its susceptibility to the impact of raindrops, runoff water and, consequently, soil erosion (Harris and Megharaj, 2001).

For these reasons, sewage sludge has been used in many areas for the reclamation and revegetation of disturbed lands and for the improvement of marginal soils. Addition of sludge to marginal and disturbed soils can restore productivity and quality, and in general provide a more favourable environment for plant growth (Oberle and Keeney, 1994). Due to the coarse structure of mining remnants, the water storage capacity is often too small to allow plant roots survive during dry spells. Soils containing large amounts of clay minerals, in addition to a shortage of organic material, can be compacted and this in turn hampers penetration of roots and their supply with sufficient oxygen thus affecting metal speciation (Ernst, 1996).

As decomposition proceeds in sludge, individual organic particles decrease in size, and organic matter particles no larger than the individual clay edges cause clay particle dispersion (Harris and Megharaj, 2001). Research has shown that sewage sludge as an ameliorant results in immediate improvement of soil physical conditions, increasing soil water content and retention, and cation exchange capacity (Epstein *et al.*, 1976).

Treated sludges, are the products of prior bacterial decomposition and therefore are sometimes lower in decomposable organics, as opposed to raw sludge. Thus they may lack sufficient latent energy to sustain microbial production and, therefore, sufficient changes to soil structure seem likely to only occur at high application rates of treated sludge (Harris and Megharaj, 2001).

2.4.1 Water Holding Capacity

Clay content and organic matter content determine the water holding capacity of a soil. Plants use between 200 to 400 g of water to produce a gram of dry matter. Therefore, water storage is vital to crop yield in most soils. Water holding capacity is generally determined by clay and organic matter contents (Olness *et al.*, 1998). Sludge applications at 50-60 tds / ha increased available water in the topsoil by 30-35% (Coker, 1983). On a weight basis, organic matter is more efficient at retaining available water than soil mineral particles alone (Olness *et al.*, 1998). Bergholm and Steen (1989) in field trials concerning the establishment of plant cover on a deposit of Zn mine waste in Sweden, found addition of topsoil and sewage sludge to the Zn sand was more than twice as effective at increasing water holding capacity compared with compost and liquid treatments. On average, organic carbon residues resulting from plant decay will retain approximately 2.5 times their weight in water against the pull of gravity (Olness *et al.*, 1998).

2.4.2 Organic Matter

Organic matter may improve the structure and water holding capacity of poor soils and the N and P in sludge have fertilizer value (Sterrit and Lester, 1980). In addition, soil organic matter binds together soil particles into aggregates, between which are large (non-capillary) pores spaces through which air can penetrate to roots, and surplus water can drain away (Coker, 1983).

Within the soil profile, the organic matter content is always highest in the surface horizon (Alloway, 1995). Soils in continuous cultivation are often deficient in organic matter as cultivations speed up decay and the return from crop residues is insufficient to the make up losses (Coaker, 1983). The following are summarized results from a study by Mc Grath and Loveland (1992) for soil pH and organic matter content in a range of soils in England and Wales.

Table 2.1 Organic matter and pH of soils in England and Wales*

No. of samples	Parameter	Minimum	Median	Maximum
5679	**pH**	3.1	6.0	9.2
5666	**% Organic carbon**	0.1	3.6	65.9

*after Mc Grath and Loveland (1992)

Organic matter content of normal soils is in the region of 3-5%, compared with mine tailings and waste rock having values of 0-1% (Williamson *et al.*, 1982).

2.4.3 Bulk Density

Mineralisation from organic sources depends on soil aeration, with optimal aeration occurring when approximately 66% of the soil pore space is filled with water (Skopp *et al.*, 1990). Additions of organic carbon added in the form of sewage sludge produces changes in soil bulk density similar to naturally produced organic matter (Olness *et al.*, 1998).

Data compiled by Clapp *et al.* (1986) suggest that for every tonne of organic carbon added per hectare in the form of sewage sludge, the bulk density of the soil will increase by about 0.0037 t/m^3 and this effect will last for two or more years.

2.5 Effects of sewage sludge on soil biological characteristics

Biological considerations in land application of sludge are usually related to the presence of pathogens. Due to the potential for animal and human health effects from improper land application, pathogen removal is necessary before sludge is suitable for agricultural use (Oberle and Keeney, 1994).

Seaker and Sopper (1988) found that populations of aerobic heterotrophic bacteria, fungi, *Nitrobacter*, and their respiration rate in the soil, were significantly increased by a high rate of organic matter input. Application of sewage sludge to soil may temporarily increase general microbial population in a soil; however, this will drop quickly thereafter (Olness *et al.*, 1988).

Soils have very strong buffering capacities to balance microbial populations. Recycling sewage sludge to soil does not significantly change the general population of the soil over the long term, although short-term increases can occur, and the populations of soil bacteria, actinomycetes and fungi can be stabilised (Olness *et al.*, 1998).

Mycobacterium spp. survives in soil for several months, however, pathogens in sludge are fragile, in that, outside the environment of the human gut, they are rapidly reduced in numbers by sunlight, drying and soil competition (Coker, 1983).

There are concerns that land application of sewage sludge can lead to the transport of pathogens through bioaerosols downwind of sludge storage or spreading sites, through contamination of groundwater, drinking water wells, stock ponds and surface waters, or through food contamination from eating food grown in sludge spread land. Pathogens can be transported to humans who walk through sludge spread fields. Wild animals, farm animals, birds, rodents and pets may become infected by or transmit sludge pathogens (Reilly, 2001).

2.6 Effects of sewage sludge on soil chemical characteristics

Chemical changes in soil resulting from sludge additions largely depend on the assimilative capacity of the soil. Sludge additions require management in order to control the loading of nutrients and other chemical constituents such as metals, toxic organics and salts (Oberle and Keeney, 1994).

The large amounts of organic N, the total P, and the lesser amounts of K and the range of other elements including nutrients and metals make sewage sludges ideal fertilizers for crop production (Olness *et al.*, 1998).

In Ireland, agriculture has experienced considerable change over the past few decades and this has put pressure on the farming community to concentrate, specialise and intensify production. Practices such as increased fertilisation of the land and the spread of organic waste have impacted on the environment to a significant degree. There is now considerable evidence to show that a large excess of P over and above agronomic requirements is being applied to land in Ireland. Reducing the loss of P from lands requires the development of nutrient management plans in which nutrient inputs are balanced with outputs (EPA, 2000a).

2.6.1 Nitrogen

Nitrogen is the nutrient element most limiting to plant growth and crop yield and the relatively rich supply contained in sewage sludge led to the encouragement for application of sludge to land (Olness *et al.*, 1998). It is usually the primary factor determining increases in crop yield where the land is treated with sludge (Coker, 1983).

Nitrogen in the soil occurs mainly in organic form and is not immediately available to crop plants. The amount of total N in mineral soils ranges from trace to slightly more than 0.5% in the surface soil, with decreasing amounts with depth. The available nitrogen in the soil is, for the most part, in the nitrate form. Arable soils have a variable nitrogen content ranging from 2 to 60 mg/l NO_3-N. This NO_3 content varies throughout the growing season.

According to Sabey and Hart (1975), it takes several years for all of the N applied to land to become mineralized depending on the environmental conditions that affect biological activity.

In a study by Kelling *et al.* (1977b) on a silt loam in Wisconsin, accumulations of >100 mg/l NO_3 were found in the soil solution to depths of 120 to 150 cm after application of 30 t/ha sewage sludge. This accumulation occurred within 10 weeks of application, demonstrating the potential adverse affects of addition of excessive amounts of N in the form of sludge. The authors state that considerable amounts of N may be lost by nitrification, volatilization, or both, where > 30 t/ha are applied to soil.

Nitrogen supply largely controls the growth and fruiting of most plants. In the physiology of a plant, it is a very mobile element, entering into many compounds and being influenced by many internal and external factors. A shortage of N results in the reduction of the amount of chlorophyll in the leaf and, hence, a loss of green colour. Nitrogen deficiency symptoms may develop in the presence of adequate levels of NO_3-N in the soil. Nitrogen excess may cause excessive vegetative growth with consequent loss of fruit production (Jones, 1966). Rogers and Murphy (2000) state that Irish grass displays levels of between 0.86% and 6.3% total nitrogen with an average value of 3.5%.

Nitrate nitrogen moves with water in the soil (Jones, 1966). However, measurement of nitrate nitrogen does not indicate long term N availability (Berg, 1975). Ammonia nitrogen is fixed on the clay particles until it is changed to NO_3. Nitrogen excess may be exhibited in the soil as a salt because a high level of N application adds to the salinity of a soil (Jones, 1966).

Nitrogen contained in biosolids is mineralized to NO_3-N, the form used in greatest amounts by most plants grown (Olness *et al.*, 1998). The C:N ratio is greater for geological materials than for surface soils (Berg, 1975). The N contents of harvested grass, in a study by Sabey and Hart (1975), was almost three times greater on sludge treated plots as opposed to non-treated plots.

According to Coulter *et al.*, (1999) heavy N dressings cause a reduction in the concentration of Cu, Zn and Se in herbage and crops, possibly to the point of deficiency. Where adequate levels of zinc exist in the soil, N causes increased levels of Zn in herbage grown theron.

2.6.2 Phosphorus

The use of different sludge treatments and P removal treatments gives rise to sludges in which the availability to crops of the contained P varies considerably. The data for optimum levels of application of N and P to the major farm crops are economic optima, which take account of fertilizer costs and do not necessarily occur at the peak of the yield curve (Coker, 1983). According to Coulter *et al.* (1999), P levels in Irish soil ranged between 5.0 mg/l and 10.4 mg/l. The average of over 20,000 samples nationwide was 7.7 mg P/l.

Irish grasses show P levels of between 0.08% and 1.27% with the average value for P in Irish grass being quoted by Rogers and Murphy (2000) as 0.4%. The range of total P levels in plant tissues usually varies from 0.05 % to 0.1 % for deficiency, and 0.2% to 0.4% in the satisfactory range (Bingham, 1966).

Seedlings are much more sensitive to P deficiency than established plants; thus, adequate fertilization may supply enough P for establishment and continued growth (Berg, 1975). P excess is associated with impeded uptake of Cu and in some cases Zn (Bingham, 1966).

2.6.3 Potassium

Potassium availability is generally unaffected by its source, and thus K in biosolids should be equally effective at remediating deficiencies as other K sources (Olness *et al.*, 1998). Most of the K and some of the P contained in the sludge is available during the first year of incorporation (Sabey and Hart, 1975). Coulter *et al.* (1999) state that K distribution in Irish soil is between 88.8 mg/l and 148.3 mg/l with an average of 113.3 mg/l.

Irish grass contains levels of K between 0.5% and 6.6%. The average value is 2.8% (Rogers and Murphy, 2000). For most plants, the critical K level in leaves ranges from 0.70% to 1.5% on a dry weight basis. Critical level of K for *Trifolium repens* was stated to be 0.8% K in dry matter (Ulrich and Ohki, 1966).

2.6.4 Cation Exchange Capacity

The term Cation Exchange Capacity (CEC) is intended to give a means of integrating the soil adsorption capacity for cations; but this is not a fixed value for any soil, because the CEC of the organic fraction is modified by change in soil pH (Coker and Matthews, 1983).

Cation Exchange Capacity is an important factor in determining the availability of heavy metals to plants. The higher the CEC, the greater the binding of toxic metals and the less available they become to plants. In a study by Epstein *et al.* (1976) the CEC of untreated soil ranged from 5.5 to 6.4 meq/100g but increased progressively with increasing rates of sludge addition. However, after 2 years, the CEC associated with the higher rates had decreased considerably, whilst that of the lower rates had decreased less.

According to Williamson *et al.* (1982), the CEC of a soil rich in humus can be as high as 300 meq/100g, compared with a typical mine tailings value of 1-2 meq/100g.

2.7 Metal Accumulations and Interactions

2.7.1 Metal Accumulation

A major concern associated with the use of municipal sludge on land is that it contains varying quantities of heavy metals. These heavy metals may be assimilated by plants and may enter the food chains of animals that consume the plants (Sterrit and Lester, 1980; Stucky *et al.*, 1980; Frost and Ketchum, 2000). In addition, where heavily contaminated sludges and excessive rates of application are used, plants may accumulate concentrations which are phytotoxic (Sterrit and Lester, 1980; Pertruzelli *et al.*, 1981). Many metals, such as Cu and Zn, are essential trace elements at low concentrations, but toxic to plants at high levels. Others such as Hg and Pb are less toxic to vegetation but hazardous to livestock that may graze vegetation which has accumulated such metals (Bradshaw and Johnson, 1992).

All plants respond to increases in heavy metals in their immediate environment. The nature, direction and magnitude of these responses will depend on the sensitivity of the individual, the intensity (concentration and duration) of exposure, the metal concerned and the form in which it is in (Baker and Walker, 1989). The plant abundance of essential micronutrients generally rank in the order Fe > Mn > Bo > Zn > Cu > Mo > Cl (Baker and Senft, 1995).

Uptake of metals by plants growing in sewage sludge-amended soils frequently exhibits a plateau response at high sludge loading rates, associated with high total concentrations of metals in the soil. This type of response has generally been attributed to attenuation of metal bioavailability by increased sorption sites provided by the sludge constituents at the high sludge loading rates (Hamon *et al.*, 1999). This study concluded that plant physiological factors were responsible for the plateau in plant metal concentration resulting from sludge application to soil. Phytotoxicity is most likely to occur on coarse textured acid soils which have a low CEC (Coker and Matthews, 1983).

2.7.2 Availability of metals

Environmental risk is related to the bioavailability of soil heavy metals. Humans assimilate bioavailable heavy metal from contaminated soil through several exposure pathways. These exposure pathways include exposure to Cd and Pb through the food chain via plant uptake, and exposure to Pb and Cd through incidental ingestion of contaminated soil (Basta and Gradwohl, 2000). Bioavailability of metals to plant species is regulated by physical, chemical and biological processes and their interaction (Ernst, 1996). Metals in sewage sludge are generally organically bound and, therefore, less available for plant uptake (Frost and Ketchum, 2000).

Petruzelli *et al.* (1981) state that addition of organic materials produced an increased extractability of some metals originally contained in the soil, possibly being ascribed to modification of some chemical conditions which regulate the solubility of heavy metals. Reduction of pH, increased salinity and development of bacterial activity may lead to the decomposition of complexes among heavy metals and organic matter.

Chemical methods based on solutions containing chelates such as diethylene-triaminepentaacetic acid (DTPA) can be used to estimate heavy metal phytoavailability in soil (Basta and Gradwohl, 2000).

Metals in sludges may be in cationic form; these react freely within the cation exchange system of a soil. Metals may be in inorganic form as hydroxides, carbonates, phosphates and sulphides. Some are complexed or chelated in organic molecules of varying levels of solubility which are subject to different rates of decay (Coker and Matthews, 1983). Illera *et al.* (2000) state that the percentage of the total extracted metal in the more available and mobile forms was very low for Cd, Cr, Cu, Ni, Pb and Zn in waste materials.

2.7.3 *Effect of pH on Metal Availability*

The pH of a soil is the hydrogen ion (H^+) concentration in soil pores, which is in dynamic equilibrium with the predominantly negatively charged surfaces of soil particles. Hydrogen ions are strongly attracted to the surface negative charges, and they have the power to replace most other cations. Heavy metal cations are most mobile under acid conditions. Increasing the pH by liming reduces their bioavailability. In a typical temperate environment, soils usually have a pH in the range 4-8. The optimum pH for most arable crops is 6.5 on mineral soils and 5.5 on peaty soils (Alloway, 1995).

Soil texture takes account of soil organic matter and the clay content of soil. Organic matter, particularly humic acids, bind metal ions over a wide range of pH values in soil, but particularly in the middle and upper parts of the pH range of agricultural soil (Coker and Matthews, 1983).

Increasing soil pH from a very acidic condition to near neutrality often causes favourable growth response (Olness *et al.*, 1998). In acidic soils, metals are more soluble and therefore both more available to plants and more mobile through the soil profile and eventually into ground water (Coker and Matthews, 1983; Palazzo and Reynolds, 1991) apart from molybdenum and selenium for which the reverse applies (Coker and Matthews, 1983).

Uptake of heavy metals by plants from soils through roots is influenced by soil parameters, such as acidity or redox potential, and different species absorb metals to different extents (Davies, 1987).

According to Jackson and Alloway (1991) in a UK study, liming sewage sludge amended soils to a neutral pH reduced the mean concentration of Cd in lettuce and cabbage. In addition, mean concentrations of DTPA extractable soil Cd were reduced by the application of lime. In the pH range 5-7, the solubility of Zn was reduced 30 fold for every unit rise in soil pH, above pH 5.5. The solubility of Zn in soils was primarily determined by adsorption with Fe and Al oxides (Coker, 1983).

Stuckey *et al.* (1980) found in trials on acidic mine spoil amended with sewage sludge in Illinois, USA, that, in general, plants established where the pH was greater than 5.5 accumulated lower quantities of metals than plants grown on spoils with a pH of less than 5.5. After three growing seasons, the authors found that accumulations of all elements in plant tops were within ranges which are not considered toxic or harmful.

It is clear that strongly acidic soils increase plant uptake of Zn, Cd, Ni, Mn and Co and increase the potential for phytotoxicity from Cu, Zn and Ni (Chaney, 1994). Soil pH is a significant factor in sorption of Cd, Zn, Ni and Co and in the fixation of Ni (King, 1988b).

In trials on acidic mine spoil amended with sewage sludge in Illinois, USA, the initial pH of the soil was approximately 3.0 and applications of sludge increased mean pH of sites in the trial area from 4.4 to 5.5 (Stucky *et al.*, 1980).

2.7.4 Metal mobility

Metal mobility in amended soils is influenced by various factors such as pH and redox status, type and quantity of soil present, the concentration and type of competing ions, and mainly the presence of complexing ligands, both organic and inorganic. Complex formation between a metal and soluble organic matter affects metal adsorption and, hence, their mobility (Illera *et al.*, 2000).

Changes in the soil environment over time, such as the degradation of the organic waste matrix, presence of different absorbing surfaces (such as Fe and Mn oxihydroxides), changes in the pH, redox potential or soil solution concentration due to natural weathering processes will affect metal mobility (Illera *et al.*, 2000).

According to a study by Chang *et al* (1984) in sludge treated soils, Cd, Cr, Cu, Ni, Pb and Zn accumulated almost entirely (>90%) in the 0-15 cm depth. Little movement of heavy metals occurred below 30 cm depth.

2.7.5 Persistence of contamination in soils

Pertruzelli *et al* (1981) showed that extractable amounts of heavy metals showed a typical pattern over two years, with a maximum value 30 days after each 150 tonnes/ha addition of sludge.

Purves (1985) has demonstrated that contamination of topsoil can persist for a period of six years after a single application of sludge (150 t/ha dry matter). Over this period, there was little change in 'available' levels of B, Cd, Cu, Pb, and Zn in the top soil and the degree of enhancement of these elements in perennial ryegrass grown in the sludge treated area remained unchanged.

Frost and Ketchum (2000) found from an examination of metal content in roots during wheat growth on sludge amended soil, that metal uptake occurred in the first 20 days of plant growth. From their studies they also concluded that metal concentration in roots was greater for Cd, Cr, Cu and Pb when two sludge applications were used as opposed to one. The residence time of metals derived from sludge is probably in the order of 10^3-10^4 years (Mc Grath, 1995).

2.8 Heavy metals of concern in regard to land disposal of sludge

2.8.1 Cadmium

Cadmium has no essential biological function and is highly toxic to plants and animals. In general, soils contain < 1 mg Cd/ kg and this is normally found concentrated in the surface horizon. However, unlike Cu and Pb, Cd (together with Zn and Ni) does have a tendency to move down the profile (Alloway, 1995). In soils treated with sewage sludge little downward movement of heavy metals occurs in the short term (5-10 years).

According to Jackson and Alloway (1991), soil extraction with DTPA gave the best overall prediction of lettuce, cabbage and potato tuber Cd concentrations. The authors also refer to an enhanced uptake of Cd by plants grown in greenhouses.

2.8.2 Copper

Copper plays an important primary role in plant and animal metabolism (Reuther and Labanauskas, 1966; Baker and Senft, 1995). Analytical studies show that most mineral soils with textures ranging between loam and clay have a native total Cu content of between 10 and 200 mg/l in dry soil with a majority of soils between 25 and 60 mg/l (Reuther and Labanauskas, 1966).

According to Baker and Senft (1995), average Cu range for soils is 20-30 mg/kg. Subsoil contains less Cu than topsoil (Reuther and Labanauskas, 1966). Irish soils contain on average, 6.0 mg/kg of extractable Cu, but can range between 3.8 mg/kg and 10.7 mg/kg (Coulter *et al.*, 1999).

The abundance of Cu in soils and plants is less than that of Zn, unless soil has been contaminated with an industrial Cu source. Copper deficiency is characterised by levels of less than 4 mg/l in dry matter, normal growth between 5 and 20 mg/l in dry matter (Baker and Senft, 1995; Reuther and Labanauskas, 1966), and data indicates that plant tissue in excess of 20 mg/l should be looked upon with suspicion of toxicity (Reuther and Labanauskas, 1966). Rogers and Murphy (2000) quote an average of 9.2 mg/kg copper in Irish grass within a range of 1.6 mg/kg and 23.7 mg/kg of copper.

Copper is specifically adsorbed or 'fixed', being one of the trace metals that is most immobile. Toxic amounts of Cu in soil or nutrient medium reduce growth and may depress the Fe concentration in leaves, causing Fe chlorosis symptoms. In addition, this condition may interfere with the uptake of certain other heavy metals and P and otherwise interfere with the normal process of nutrient accumulation by roots.

No reports of plant toxicities from Cu resulting from sludge addition, when grown in fertile limed soil, were reported in the literature (Baker and Senft, 1995).

Soil organic matter has a major influence on Cu retention. As little as 10 mg/kg DTPA-extractable Cu has been shown to decrease soil enzymatic activity (Baker and Senft, 1995). Somewhat similar toxic effects can be produced by other heavy metals such as

Ni, Co, Zn and Mn. Nickel is appreciably more toxic than Cu, Co less toxic and Zn and Mn progressively less toxic (Reuther and Labanauskas, 1966).

In a study by Jeffery *et al.* (1974) using *Festuca rubra* spp. Commutata and *Trifolium repens* (white clover) it was found that the addition of 320 mg/l copper resulted in an 80-90% reduction in dry weight of both species. The authors also state at least an 80% reduction in growth of these species occurred when grown on mining wastes as compared with a normal soil.

Clover is very sensitive to copper toxicity, with the authors citing values in the range 7 to 16.4 mg/l exhibited by *Trifolium pratense* grown on soil in New Jersey, USA (Reuther and Labanauskas, 1966).

According to Coulter *et al.* (1999), fertilizer applications affect the Cu content of pastures and here N is of greatest significance. Where the initial soil Cu is low, application of N reduces Cu levels in herbage, consequent to the dilution effect of extra growth. However, when soil Cu supply is adequate, application of N can actually increase the Cu content of pasture herbage.

2.8.3 Nickel

Soils usually contain from 5 to 500 mg/l of Ni, with an average of 100 mg/l. Total Ni content is not a good measure of the availability of the element; the Ni content of plants appears to be closely correlated to the exchangeable Ni of soils, as determined by neutral normal ammonium acetate (Vanselow, 1966; Mc Grath, 1995).

Excessive acidification of ordinary soils sometimes results in greater uptake of Ni by plants. Liming of soils not only reduces availability of Cr and Ni but also tends to overcome the unfavorable Mg/Ca ratio (Vanselow, 1966).

In the early or incipient stages of Ni toxicity, the only visible symptoms are dwarfing or repression of growth. Nickel is readily taken up by plants (Vanselow, 1966).

Plants contain very low quantities of Ni, usually less than 1 mg/l, Vanselow (1966) found 1.9 mg/l Ni in *Trifolium pratense,* various grass species exhibited values within the range 0.2-3.0 mg/l in the intermediate range and some grasses in the higher range of 9.0-56.0 mg/l (Vanselow, 1966).

2.8.4 Lead

The earth's lithosphere contains approximately 16 mg/l of Pb. Total Pb in agricultural soils may vary between 2 and 200 mg/l. Most of the Pb in soils is only sparingly soluble and largely unavailable to plants (Brewer, 1966).

Lead is present in uncontaminated soils at concentrations < 20 mg/kg (Davies, 1995). Brewer (1966) states that, in general, it has been found that soils contain between 0.05 and 5 mg/l of lead.

According to Davies (1995) there is little evidence that Pb is readily lost from soil profiles by leaching. Like most heavy metals it remains in an insoluble or stable form in surface layers after sewage sludge application.

Lead compounds entering the soil are partitioned among several compartments, namely the soil solution, the adsorption surfaces of the clay-humus exchange complex, precipitated forms, secondary Fe and Mn oxides and alkaline earth carbonates, the soil humus and silicate lattices. Cation fixation studies indicated that Pb was more tenaciously held or "fixed" by humus soils than any of the other cations used (Brewer, 1966).

In broad terms, there is a positive relationship between soil concentration of Pb and that of plants grown thereon, only a small proportion of the Pb in soil is available for uptake by plants (Mc Grath, 1983; Davies, 1995).

Lead is not especially toxic to plants; however, high substrate concentrations do result in stunted growth or death. Some grasses can evolve tolerance to high Pb (Davies, 1995). Chang and Broadbent (1982) reported that Pb did inhibit N mineralisation and nitrification; the order of decreasing inhibition was Cr>Cd>Cu>Zn>Mn>Pb.

In a study by Jeffery *et al.* (1974) using *Festuca rubra* spp. *commutata* and *Trifolium repens* (white clover) it was found that the addition of 3000 mg/l Pb resulted in a 78-88% reduction in dry weight of both species. The concentration of lead in Irish mining wastes may be up to ten times this level.

Lead and Cr applied in biosolids are not absorbed to any significant extent at any pH (Chaney, 1994). Differences in the extractability between Pb and Cu, Zn, Cd and Ni suggest that Pb is held in a different chemical form to the other metals in the organic materials (Petruzelli *et al.*, 1981). The study confirmed that plants grown in low pH conditions might accumulate potentially harmful quantities of Pb.

In their study, Stucky *et al.* (1980), concluded that all species planted accumulated quantities of Pb between <1 mg/l to 15 mg/l, which were considered by the authors to be harmful.

In a study with *Festuca ovina* (sheep's fescue) growing in solution cultures, root growth was measurably retarded with 10 mg/l Pb, markedly reduced by 30 mg/l Pb and stopped at 100 mg/l of Pb (Brewer, 1966).

The extremely low Pb content of edible parts of the majority of crops is reassuring in light of the potential toxicity of Pb to animals, including man (Brewer, 1966). *Trifolium* species grown on unsprayed orchard soil showed Pb content on a dry weight basis of 6.17 mg/l while that grown on orchard soil sprayed with lead arsenate showed a content of 13.72 mg/l (Brewer, 1966).

Jeffery *et al.* (1974) state that there is a mutual antagonism between the growth promoting effects of P and the toxic properties of Pb, and that P additions may be used to quantitatively reduce Pb toxicity.

2.8.5 *Zinc*

Zinc is an essential trace element for humans, animals and higher plants. The common range for total Zn concentrations in soils is 10-300 mg/kg (Chapman, 1966; Kiekens, 1995) with an average of 50 mg/kg. Zinc is usually more concentrated in surface than in sub-surface horizons (Chapman, 1966).

According to Coulter *et al.* (1999), Irish soils contain extractable Zn levels of between 2.3 mg/kg and 9 mg/kg Zn, with a national average of 4.7 mg/kg.

Higher plants predominantly absorb Zn as a divalent cation (Zn^{2+}), which acts either as a metal component of enzymes or as a functional, structural, or regulatory co-factor of a large number of enzymes. In a wide variety of plants, Zn deficiency levels are characterised by levels of less than 20-25 mg/l in dry matter, which are ample but not excessive levels in the range 25-150 mg/l. Amounts of greater than 400 mg/l may indicate Zn excess in a variety of plants (Chapman, 1966; Alloway, 1995). Soils showing Zn ranging from 880 to 2130 mg/l were sufficient to be toxic to wheat and clover (Chapman, 1966).

In Irish grass, Rogers and Murphy (2000) state average Zn to be 30.83 mg/kg with analysis of 928 samples giving a range of between 13 mg/kg and 84 mg/kg. According to (Coulter *et al*,. 1999) Zn content of Irish herbage normally ranges from 25 to 45 mg/kg, with levels below 20 mg/kg being undesirable from an animal health point of view.

Excess Zn often produces iron chlorosis (Chapman, 1966). A good indication of a Zn mineral outcrop is the presence of a luxuriantly growing ragweed when other vegetation is stunted. Research shows that zinc readily accumulates in the leaves of many species. Plants of different species show Zn contents in the dry matter of 20 mg/l to 10,200 mg/l. In a study referred to by Chapman (1966) the distribution and growth of 30 plant species growing on a soil where total Zn was 12.5%, Zn content ranged from 39 mg/l in the fruit of False Solomon's seal to 5400 mg/l in Horsetail.

Heavy dosages or prolonged use of P fertilizers have been shown on many soils to decrease Zn uptake, and even to cause Zn deficiency of certain crops (Chapman, 1966). Zinc accumulation is favoured under soil conditions where there is a long-continued build up of organic matter in surface layers. Zinc is brought up from lower horizons by plant roots and held in the organic residue, with much of this Zn being in available form (Chapman, 1966).

Factors affecting the availability and solubility of Zn in soils include total content, pH, organic matter, adsorption site, microbial activity and moisture regime. Availability of Zn decreases at increasing pH values. In soils low in organic matter content, Zn availability is directly affected by the content of organic complexing or chelating ligands, originating from decaying organic matter or root exudates. High soil P levels may decrease Zn availability and uptake by plants, as do interactions with other nutrients. Most common is Zn-Fe antagonism but also Zn-Cu, Zn-N and Zn-Ca interactions are widely known. Zinc absorption and accumulation by plants varies widely between plant species and cultivars. In general, increases in soil Zn concentrations cause increases in plant tissues (Kiekens, 1995).

Although culture of crops in strongly acidic soils allows uptake of increased levels of Cd and Zn, the presence of Zn in the crops reduces the potential for risk of Cd uptake. Zinc phytotoxicity serves as a maximal limit on crop Cd, and plant (intrinsic) Zn inhibits absorption of plant Cd in animals (Chaney, 1994).

At Glendalough, Co. Wicklow, tailings from a long abandoned Zn /Pb mine (ca. 100 years) had the following plant species growing thereon, *Glyceria fluitans, Eriophorum augustifolium* and *Juncus effususlla.* The sediments were found to contain Zn concentrations averaging 7000 mg/kg, with highest values reaching 25,000 mg/kg, indicating that species growing on the tailings pond must be tolerant of high concentrations of Zn and possibly other metals (Beining and Otte, 1996).

In a study by Jeffery *et al.* (1974) using *Festuca rubra* spp. *commutata* and *Trifolium repens* at 4000 mg/l zinc, there was an 80% reduction in dry weight of the clover compared with no reduction to grass dry weight.

2.8.6 Mercury

No essential biological function of Hg is known and it is one of the most toxic elements to man and many higher animals. Mercury does not appear to have the same toxicity problems in relation to plants, levels at which toxicity problems are encountered are far above those encountered under normal conditions. Availability of soil Hg to plants is low, and roots serve as a barrier to Hg uptake. If 50 t/ha of sludge are applied to soil, the added amount of Hg is typically in the order of 50 mg/m^2, a considerable increment with respect to the normal background level (Steinnes, 1995).

2.8.7 Iron

Most soils contain several percent of Fe and plants require concentrations in dry matter in the order of up to 100 mg/l. Iron deficiency results from the low availability of soil Fe (Wallihan, 1966).

Soil Fe is a significant factor in Cd and Zn sorption and fixation, Cu and Pb sorption and Co and Ni fixation and minimization of antimony (Sb) fixation (King, 1988a). These and other cations often interact with both Fe and Mn oxides such that prediction of sorption and subsequent availability to plants becomes complex. Relative aeration and redox potential are also important factors in sorption, fixation and release of not only the redox sensitive elements such as Fe, Mn, Cu etc. but also of the elements that interact with the oxides of these elements (Olness *et al.*, 1998).

Lack of Fe produces, in its moderate and acute stages, a characteristic and easily identifiable type of leaf chlorosis in most plants. The concentration of Fe in the dry matter of leaves is usually of the order of 10^{-2} to 10^{-4} times that in the soil in which the plant grows (Wallihan, 1966).

Other elements known to be essential to plants achieve concentrations in plant tissues that are approximately equal to or greater than those existing in the soil. Soil dust on leaves is considered to be a serious source of contamination in plant Fe analysis (Wallihan, 1966).

The availability of Cu and Zn to plants is reduced by a high concentration of Fe (Coulter *et al,*. 1999); the authors also state that Fe concentration in Irish soils is high although no value is given. High Cu and Zn can reduce the uptake of Fe but the concentration required to cause Cu deficiency is high. Iron chlorosis has been recorded in Irish cereals and Cu and Zn concentrations of 59 mg/kg and 235 mg/kg respectively.

2.8.8 Chromium

Chromium in soils is typically in the range of 5-1000 mg/l and many investigators have found detectable quantities in a wide variety of plants (Pratt, 1966). Average concentration in world soils is 20 mg/kg (Mc Grath, 1995).

Chromium exists in Cr^{3+} and Cr^{6+} oxidation states in the environment. It has been found that Cr is toxic to plants. There is some indication that Cr is accumulated in the roots and that the main toxic effect is exerted in the roots. It has also been found that Cr added at 5 mg/kg to soil increases the rate of combustion of organic matter and the rate of nitrification in soils (Pratt, 1966).

Chromium content of lettuce grown on Serpentine soils (often containing several percent of Cr) was no higher than that of lettuce grown on other soil types. This does not eliminate the risk of Cr toxicity due to a possibility of an effect on the roots without translocation to the aerial portion (Pratt, 1966).

Metals accumulate at high levels in the surface of soils treated with sewage sludge. The depth to which metal contamination occurs is dependent on the depth to which sludge was incorporated. After addition, however, there is little evidence of downward movement of metals in sludged soils, including Ni and Cr, even after long periods of time. The availability of Cr from sludge treated soils appears to be low; uptake of Cr by plants and transport to the aerial tissues is minimal at near neutral soil pH, characteristic of Cr^{6+}. In comparison with Cr, Ni is relatively available, less so than Zn and Cd but more so than Cu which is more strongly complexed by organic matter (Mc Grath, 1995).

2.8.9 Arsenic

The uptake of As by many terrestrial plants is not significant. Even on high As soils, plants will generally not contain dangerous levels of As. In soils, natural As levels are dependant on the source rock type and are normally in the range 1-40 mg/kg, with most soils being in the lower half of this range (O' Neill, 1995).

Arsenic accumulates in much larger amounts in the roots as opposed to the above ground parts of plants. Liebig (1966) reports that As levels in native plants on natural soil did not exceed 10 mg/l. In most cases soils contaminated with As produce vegetation of higher As content than uncontaminated soils (Liebig, 1966). Disposal of sewage sludge on land does not cause significant increase in the As levels of crops grown (O' Neill, 1995).

2.8.10 Boron

The uptake of Bo by plants has been shown to be intimately related to the concentration of other ions in the nutrient substrate. When a plant has a low Ca supply, it will have a low tolerance for Bo, and, when there is an excessive supply of Ca, there will be a high Bo requirement. Grasses are low in Bo. Boron deficiency in a wide variety of plants is characterised by levels less than 15 to 20 mg/l in dry matter. Adequate levels are commonly between 25 and 100 mg/l and amounts over 200 mg/l are often associated with Bo excess (Bradford, 1966).

2.8.11 Manganese

According to Smith and Paterson (1995), Mn is an essential requirement for higher plants. Soils derive all Mn from their parent material therefore soil levels reflect the composition of the relevant parent material. Apart from the natural mineralogical sources, the only other significant source of Mn is the application of the element to deficient crops.

Rogers and Murphy (2000) in a study of metal levels in Irish grass quote Mn levels of between 10 mg/kg and 693 mg/kg, with an average figure of 120 mg/kg Mn.

Uptake of Mn is a function of its concentration in ionic form in the soil solution and the concentration present on the exchange sites of the cation exchange complex. Plants take up Mn as Mn^{2+} and the availability of Mn is largely governed by the supply of H^+ ions and electrons, which reduces the higher valency states of Mn^{2+}.

2.8.12 Cobalt

Cobalt is required by ruminants and N-fixing microorganisms. Total Co content of soils varies widely, from 0.05 to 300 mg/kg, with an average content in the range 10-15 mg/kg. Within a given soil profile, Co is generally concentrated in those horizons rich in organic matter and clays. In alkaline conditions, Co is immobile. In acid conditions dissolution and leaching are more likely to occur. Therefore, total Co concentrations are greater in alkaline than in acidic soils. According to Coulter *et al.* (1999), the mean total Co level in Irish soil is 7.4 mg/kg, with levels ranging from 5.0 mg/kg to 10.4 mg/kg.

As with Mn, Co uptake by plants is a function of the concentration of Co in the soil solution and on the exchangeable sites of the cation exchange complex. Soil drainage therefore, has a major influence on Co availability for plant uptake (Smith and Paterson, 1995). Irish grass contains on average 0.156 mg/kg Co, ranging from 0.06 mg/kg to 0.28 mg/kg (Rogers and Murphy, 2000).

2.9 Positive aspects of land disposal of sewage sludge

According to Chaney (1994) soil and plant chemistry prevent risk to animals from nearly all biosolids-applied trace elements mixed in soil. Adsorption or precipitation of metals in soils or in roots limits uptake and translocation to shoots of most elements, and phytotoxicity from Zn, Cu or Ni limit residues of metals in plant shoots to levels chronically tolerated by livestock and humans. In addition, biosolids are not pure metal salts but are a mixture of metals and adsorbing/ chelating/ precipitating materials. This mixture interacts to reduce metal phytoavailability and bioavailabilty even when biosolids are ingested by grazing livestock or indeed children.

According to a study by Chang *et al.* (1984), crop absorption of heavy metals removes an insignificant amount (<1%) of the heavy metals introduced to the soil through the land application of sludges.

The 'sludge protection hypothesis' supports the idea that plant metal uptake reaches a maximum as sludge application to soil increases, with application over sufficient time converting the surface soil almost completely into sludge residue (Mc Bride, 1995). Frost and Ketchum (2000) have demonstrated that organically bound metals in biosolids are less available than more mobile salts found in commercial fertilizers, leading to the suggestion that the mineralisation of organic matter, over the 20 year storage time of the sludge used, did not result in an increased concentration of bioavailable metals.

Ye *et al.* (2001) found that sludge amendment reduced total Zn, Pb and Cd contents and DPTA-extractable Pb and Cd contents in substrata. They also suggest that a reduction of total and extractable metals in tailings amended with sludge may be due to the role of chelation, complexation and adsorption between metals in tailings and organic matter in sludge, in addition to the dilution effect when sludge is mixed with tailings.

At the Plazo site in southern Illinois, USA, Stucky *et al.* (1980) found that the reason plants survived initially in the presence of large quantities of heavy metals, was, because the metals were still associated with organic compounds in the sewage sludge. At the end of the third growing season, elevated levels of metals were still present. This was as a result of metals being bound in the organic fractions of dead plant material and some metals forming insoluble compounds.

2.10 Negative aspects of land disposal of sewage sludge

Plant yield decreases have been noted by Cunningham *et al.* (1975) in corn with sewage sludge additions, especially at high loading rates. Yield decreases appear to be toxicity reactions incurred as a result of elevated salt and metal concentrations. These authors attributed yield reductions to induced Mn deficiency and elevated concentrations of Ni and Cd in plant tissues. The sludge 'time bomb hypothesis' states that a slow mineralisation of organic matter in sludge releases metals into more soluble forms (Mc Bride, 1995).

Sewage sludge application to a degraded soil under a semi arid environment increased the total soil Cu, Pb and mainly Zn concentrations; soil cadmium increased slightly while soil Ni and Cr concentrations were not affected. The authors concluded that distribution of the heavy metals in the amended soils were in a direct relation to the concentrations and degree of availability of these metals in sludge (Illera *et al.*, 2000). Hooda and Alloway (1994) found elevated concentrations of Cd, Cu, Ni, Pb and Zn in ryegrass compared with controls growing on soil treated with sewage sludge. Increasing plant metal accumulation over successive harvests was observed for all metals except Cu. This coincided with declining pH and organic matter contents over time. The findings are likely to be highly relevant to field situations where sludge application could decrease soil pH and thus require close monitoring and control of soil pH.

Coker and Matthews (1983) stated that there was no clear evidence to support the suggestion that organic matter chelates metals into forms unavailable for plant uptake and that these metals will be released later when the organic matter decays, i.e. the so called "time-bomb effect" and also state that only 20% to 40% of digested sludge organic matter was decomposed over the first 12-18 months.

2.11 Incorporation of sludge into soil

Stucky *et al.* (1980) recommend incorporation of sludge as deep as possible into mine spoil substrate in order to facilitate the deep rooting of plants. Palazzo and Reynolds (1991) recommend incorporation of a sufficient amount such that the pH of the medium is raised to a minimum of 5.5, or tilled to a depth of 20 cm. The depth of soil contamination depends on the depth to which sewage sludge is physically incorporated by ploughing and other cultivations or upon the presence of cracks or channels in the soil at the time of the application of sludge (Mc Grath, 1995). Due to downward movements in soil materials of small colloids in solution, the application of aged sludges as top dressings may eventually weaken the inherent ability to improve the physical condition of mine spoil.

As long ageing periods lead to increased diminution of organic particles in sludge, which increases dispersion, the sooner the application of sludge after completion of its stabilization the more effective a soil physical ameliorant it will be. Thus, it should be spread as quickly as possible after its stabilization has been completed. Losses through volatilization are lower at higher application rates because thicker layers mean smaller sub-aerially exposed surfaces (Harris and Megharaj, 2001). Both digested and undigested dewatered sludges are best applied to cultivated land by being mixed into the topsoil (Coker, 1983).

2.12 Mine Tailings Rehabilitation

Most mining operations involve the extraction and processing of large volumes of earth material. These operations usually result in either the generation of large volumes of waste or the transformation of materials into waste (Myers and Crews, 2002). Mine tailings or mill tailings are the residual solids from mined material after the marketable product has been removed (Strachan, 2002).

The major physical feature of tailings is the small and relatively uniform size of the particles, which generally range from fine sand down to clay. Tailings consist of a structureless matrix, frequently with unsatisfactory porosity, aeration, water infiltration and percolation, with the result that water and wind erosion of the unprotected surface is severe (Williamson *et al.*, 1982). Disturbed lands such as mine tailings are not composed of material that is in equilibrium with its environment. This is particularly the case with freshly disturbed spoils (Berg, 1975).

Mining operations have a finite life and, eventually, facilities must be closed and reclaimed in order to be returned to some beneficial future land use (Myers and Crews, 2002). The requirements for tailings impoundments in the twenty-first century are that they be located, designed, permitted, operated and closed in a manner that is acceptable from operational, environmental, and safety perspectives (Strachan, 2002). Ecological restoration and mine reclamation have become important parts of the sustainable development strategy of many countries (Gao *et al.*, 1998). A fundamental goal of long term closure is to achieve 'walk away' conditions that assure both physical and chemical stability without the need for long term monitoring, maintenance or repair (Vick, 2002).

These environmental concerns now have such prominence that the ultimate fate of mined-out areas and waste disposal facilities is a major consideration on the part of planning authorities when determining applications for new mine sites (Bradshaw and Johnson, 1992), and frequently involves the design and construction of a remedial cover (Myers and Crews, 2002).

The residues from the extraction of Pb/Zn mines are permanently stored in tailings ponds, which require revegetation to reduce their environmental impact (Ye *et al.*, 2002). Processing of mined material is carried out in an aqueous medium, tailings disposal consists of the management of aqueous slurry (Strachan, 2002). Tailings impoundments are unique in that the waste material is hydraulically placed in a reservoir, and closure and reclamation activities usually include conversion to a non-impounding type of reclaimed configuration (Myers and Crews, 2002). There may also be elevated levels of associated non-target metals and metalloids remaining in the waste after beneficiation (Bradshaw and Johnson, 1992).

A vegetation cover represents the more economic and acceptable method of stabilizing mine wastes and reducing pollution (Bradshaw and Johnson, 1992; Johnson *et al.*, 1994). A suitable and adapted vegetation cover is beneficial in the restoration of contaminated land and results in enhanced amenity values as well as prevention of surface soil erosion, which is of particular importance at sulphide bearing facilities (Baker and Senft., 1995; Powell, 1988; Myers and Crews., 2002).

One of the most common cover design objectives is to limit infiltration and water flux across the cover waste interface. Use of vegetation in lieu of rock cover has the added benefit of impacting the water balance and flux rate by encouraging evapotranspiration (Myers and Crews, 2002).

Finely ground tailings can blow or wash into surrounding areas, and, because they are toxic and low in nutrients, can degrade farmland (Bradshaw, 1970). Both contamination routes cause changes in the flora and fauna and may even threaten human health. The waste is an unaesthetic element in the landscape (Bergholm and Steen, 1989). The mining and smelting of Pb and Zn ore often results in contamination of soil with Cd, Pb and Zn. Adverse environmental impacts from contaminated sites includes risk to human health, phytotoxicity, contamination of water and soil, and ecotoxicity (Basta and Gradwohl, 2000).

2.12.1 Acid Mine Drainage

The past two decades have seen heightened awareness of a naturally occurring environmental problem in mining referred to as Acid Mine Drainage. This difficult to predict and quantify problem is associated with sulphide ore bodies mined for Pb, Zn, Cu, gold (Au) and other minerals including coal.

Valuable minerals when extracted leave Fe sulphides. These have no commercial value and are rejected along with other barren particles and disposed of in the tailings impoundment (Vick, 2002). The presence of significant quantities of iron pyrites (FeS_2), which may not be removed during ore beneficiation, often leads to very acidic waste as the mineral is comminuted during processing and then undergoes oxidation and hydrolysis to generate sulphuric acid by a continuous, slow release process (Bradshaw and Johnson, 1992). In this process, they undergo various reactions to produce reduced pH and elevated sulphates, along with metals in solution, some of which may bioaccumulate and biomagnify in the food chain (Vick, 2002).

Secondary contamination occurs in groundwater beneath open pits, ponds, sediments in river channels and reservoirs and floodplain soils impacted by contaminated sediment (Pierzynski *et al.*, 1994).

In principle, a tailings cover provided by a vegetation layer restricts oxygen from the surficial tailings and oxygen diffusion into void spaces thereby reducing reaction rates and acid mine drainage. In addition, the cover acts to prevent ponding and reduce infiltration of surface water, thereby restricting transport of reaction products (Vick, 2002).

Mobilisation of trace metal enriched tailings and drainage waters from the Parc Pb-Zn mine workings in North Wales has had a considerable negative impact on local watercourses and terrestrial ecosystems (Johnson and Eaton, 1980).

2.13 Revegetation of Mine Tailings

The essential aims of revegetation are long term stability of the land surface ensuring no surface erosion by dust or wind and the reduction of leaching throughputs, lessening the amounts of potentially toxic elements released into local watercourses (Bradshaw and Johnson, 1992).

The development of a vegetated landscape or ecosystem in harmony with the surrounding environment, and with some positive value in an aesthetic, productivity or nature conservation context (Johnson *et al.*, 1994) is a natural follow on objective. The degree to which this is met depends on the ambient climate since vegetation will intercept and return rainfall to the atmosphere by evapotranspiration. In temperate climates, the amount intercepted and returned will be up to 50% of the total (Bradshaw and Johnson, 1992; Johnson *et al.*, 1994).

Wastes from metalliferous mines, especially acidic ones, are very difficult materials upon which to establish vegetation (Bradshaw and Johnson, 1992). Remnants of mining activities often have a coarse structure (Ernst, 1996), and these can result in low soil moisture content in sites due to the low water holding capacity (Berg 1975). This keeps metal availability at a low level to plant roots and water. In addition, physical resistance may require such energy that it may hamper penetration of plant roots into deeper soil layers (Ernst, 1996).

Bradshaw (1970) however, claims that although the surface of the mine tailings may become excessively dry, there is usually adequate moisture a few centimeters down. If plants can develop adequate roots, they will not suffer from drought. Clayey and silty materials can result in sites that are both erosive and droughty because of a low water infiltration rate (Berg 1975).

Surface roughening, scarification and mulching will help in obtaining plant establishment on clayey and silty materials (Berg 1975). Vegetative remediation methods for metal contaminated sites can utilise amendments that reduce metal bioavailabilty, as well as metal tolerant plant species, with the goal of establishing a vegetative cover sufficiently dense to prevent wind and water erosion and to remain viable for extended periods (Pierzynski *et al.*, 1994).

Powell (1988) also states that, for reclamation programs to be successful, one must select plant species that are climatically adapted to the region and that are adapted to the soil conditions present. Ye *et al.* (2002) demonstrated that heavy metal toxicity, especially available Pb, low content of nutrient and poor physical structure were major constraints on plant establishment and colonization of Pb/Zn mine tailings in southern China. Berg (1975) cites plant toxicities induced by excess acidity, extremes in texture, excess soluble salts and poor physical condition resulting from excess sodium as additional limiting factors. Excess acidity is primarily due to sulphide weathering (Bradshaw and Johnson, 1992). Pyrite bearing waste that is disposed of at neutral or slightly alkaline pH can degrade within months or years to produce extreme acidity (Johnson *et al.*, 1994). In mining remnants, chemolitho-trophic bacteria may acidify the soil and thus enhance metal mobility or precipitate the metals as sulphides (Ernst, 1996). Soluble salts can be a major problem in seedling establishment and growth. Sodium (Na) has a dispersing effect on soil, and this effect, if strong enough, results in soils becoming almost impermeable to water, forming a dense crust upon drying that interferes with seedling emergence (Berg 1975).

Sludge is often used as a growth medium in mine spoils (Harris and Megharaj, 2001). According to Gallagher and O'Connor (1999), revegetation trials at Avoca, Co. Wicklow, have shown that one waste product i.e. sewage sludge can be used to aid revegetation of Avoca mine spoil, therefore ameliorating the environmental effects of another waste product.

According to Stucky *et al* (1980), sludge applied to low pH medias, has at least three attributes that may affect yields; it increases the pH of the media, provides a source of nutrients and improves the physical condition of the media. Seaker and Sopper (1984) found that microbial processes such as humification, soil aggregation and N cycling are essential in the establishment of productivity in mine soils. The decomposition of plant materials in soil may also be enhanced by microorganisms introduced from sludge that is inherently low in toxic heavy metals.

In a study by Shu *et al.* (2002) a field experiment on Pb/Zn tailings at Lechang, Guangdong Province, China demonstrated that domestic refuse was a very useful ameliorative material for improving edaphic conditions of tailings. Domestic refuse not only contained high levels of N, P and K, but also helped to improve the poor physical properties and microbial activities of the tailings. The application of domestic refuse may provide a cost effective method for tailings rehabilitation and moreover, it provides an alternative for disposal of domestic refuse.

2.14 Revegetation studies and projects

Direct seeded metalliferous ecosystems are likely to have less productivity and faunal diversity than normal soils (Goode, 1999). Stuckey *et al.* (1980) found that in trials on acidic mine spoil amended with sewage sludge in Illinois, USA, after three growing seasons, reed canary grass (*Phalaris arundinacea*), switchgrass (*Panicum vergattum*) and orchardgrass (*Dactylis glomerata*) were the three most successful species planted. The minimum pH tolerated by roots of reed canary grass, switchgrass and orchard grass was 3.5, 3.7 and 4.2, respectively.

Bergholm and Steen (1989), in field trials concerning the establishment of plant cover on a deposit of Zn mine waste in Sweden, found that, over time, the concentration of Zn decreased in the roots and increased in the shoots. Also, Zn concentration decreased with increasing shoot biomass, as did levels of lead and Cd. Therefore, with respect to grazing animals, it is desirable to maintain a high aerial biomass.

Palazzo and Reynolds (1991) found that, after 16 years, the total and DTPA-extractable Cu, Zn, Cr, Pb, Ni and Cd decreased in acidic dredge spoil treated with an application of 100 t/ha sewage sludge, to nearly the levels of the control soils. Concentrations of metals in plants also decreased. Decreases in tissue concentrations ranged from 40-70% for Cu, Cr, Pb, Ni and Cd and up to 90% for Zn. The application of sewage sludge to this substrate increased soil pH, concentration of P, and, exchangeable Ca and Mg in the soil.

Shu *et al.* (2002), found that, in general, all grass species growing on Pb/Zn tailings at Lechang, southern China, amended with domestic refuse had the highest percentage cover, likely due to the high nutrient content of the waste, but also due to the improvement of the physical properties of the tailings.

2.15 Silvermines TMF

The Silvermines area is best known for the major Zn and Pb deposits mined by Mogul from 1968-1982 and the barite deposit, which was operated by Magcobar (Ireland) Ltd between 1963 and 1993. Production between 1968 and 1982 amounted to 10.7 million tonnes at 7.36% Zn and 2.7% Pb (DAFRD, 2000).

Soils of the Silvermines area are devoted to grassland agriculture, predominantly dairying and dry stock (DAFRD, 2000). Goode (1999), states that, in 1997, on the Silvermines Tailings Management Facility, there was good growth and cover of the salt- and metal –tolerant grass *Agrostis stolonifera* cv. 'Seaside'.

In an EPA report (EPA, 1999) on the tailings site, it was estimated that 50% of the tailings had poor growth or no grass cover. However, some of the grass cover indicated a sustainable growth. The Silvermines tailings site, like most modern tailings impoundments, is more exposed to the drying effects of wind than the surrounding countryside (Good, 1999).

According to Steinborn and Breen (1999), metal levels from soil around some of the disused buildings and surrounding area of Shalee mine, Silvermines, were elevated.

Overall Cu levels in soil ranged from 2.45 mg/kg to 96.6-mg/kg dry weight, while overall Cu vegetation levels ranged from non-detectable levels to a maximum of 89.03 mg/kg dry weight. Soil Zn levels were less than or equal to 308 mg/kg, whilst levels as high as 637 mg/kg dry weight were found in vegetation. All soil samples showed extremely high Pb levels ranging from 1,862 mg/kg to 25,539 mg/kg. Lead levels in the vegetation were also high; some species having levels of 800 mg/kg Pb dry weight (Steinborn and Breen, 1999).

2.16 Species selection for revegetation and metal tolerance

Theories of ecological succession can be applied to mine reclamation. When grassland is converted into bare land, natural succession subsequently proceeds from weeds to sparse herbs to dense herb grassland (Gao *et al.*, 1998).

Proper selection of plant material for revegetation of tailings is essential (Bergholm and Steen, 1989). According to Gao *et al* (1998) ecological succession can be hastened by selection of drought resistant, sterility tolerant and fast growing crops or herbage. After stabilization of the substrate is sufficient, planting of several kinds of grasses to quickly cover spoil, or intercropping/rotating grass with leguminous crops, is required in order to combine cultivation with restoration of soil fertility.

For screening vegetation varieties, the properties of strong stress resistance, such as strong metal tolerance, drought resistance lodging-resistance and disease resistance is demanded. High yield and high fertilization rates are considered important, as are developed root systems and high biomass yield (Gao *et al.*, 1998).

The most clear-cut separation between tolerant and non-tolerant individuals is in their ability to establish, survive and reproduce in metal contaminated substrates (Baker and Walker, 1989). The superior ability of individuals from one species to survive may also be linked to tolerance of other factors such as low nutrient availability and drought which are often features of mine spoils (Antonovics *et al.*, 1971)

Relative differences in the uptake of metal ions that varies between plant species and cultivars is genetically controlled (Sterrit and Lester, 1980; Mench and Martin, 1991; Alloway, 1995b). This can be due to various factors, including; surface area of the root, root CEC, root exudates and the rate of evapotranspiration (Alloway, 1995b). However, the metals which, when present in excessive amounts, are most toxic to higher plants and microorganisms are Hg, Cu, Ni, Pb, Co and Cd (Mench and Martin, 1991).

It has been found that populations of species growing on toxic soils (Table 2.2) are able to continue rooting in toxic conditions inhibitory to ordinary species (Bradshaw 1970).

Davies (1987) states that plants which colonize tailings sites, tend to germinate in rabbit or sheep droppings and they are usually metal tolerant ecotypes.

Tolerance appears to be specific to individual metals. Metal tolerant plants must either render the metal innocuous or contain enzyme systems which are unaffected by metals. Mine plant populations are often dwarfed, with smaller leaves and grow more slowly as a result of adaptations to moisture stress (Bradshaw 1970).

Results of field trials concerning the establishment of plant cover on a deposit of Zn mine waste in Sweden demonstrate the usefulness of several grasses with reasonable Zn tolerance, including *Festuca rubra, Agrostis tenuis, Agrostis stolonifera* and *Poa pratensis*. The red fescue (*Festuca rubra*) cv. Merlin preformed very well and dominated plant cover, ten years later (Bergholm and Steen, 1989). Cultivars are now commercially available enabling direct seeding of large toxic areas and include *Festuca rubra* cv. 'Merlin' (Pb - Zn), *Agrostis capillaris* cv. 'Parys' (Cu) and *Agrostis capillaris* cv. 'Goginan' (Pb - Zn) (Bradshaw and Johnson, 1992).

According to Bradshaw (1970) in Britain, species found on soils contaminated with heavy metals are bent grass (*Agrostis*), fescue (*Festuca*), sorrel (*Rumex acetosa*) and plantain (*Plantago lanceata*). Johnson and Eaton (1980), from studies in the vicinity of a derelict Pb - Zn mine in Wales, state that land in the most advanced stage of damage through environmental contamination was derelict, the original ryegrass (*Lolium perenne*)-dominated sward was replaced by *Plantago lanceolata, Rumex acetosa, Deschampsia caespitosa* and *Agrostis tenuis*, all species known to have evolved Pb-Zn tolerant ecotypes.

Johnson and Eaton (1980) observed that trace-metal rich waste dispersed from the tailings dam by gully erosion has led to die-back of the normal ground cover vegetation by flora composed entirely of heavy metal tolerant populations of the grasses *Dechampsia caespitosa, Festuca rubra and Agrostis tenuis*.

Although tolerant plants will survive on ordinary soils, they are at a disadvantage in competitive situations with non tolerant plants (Bradshaw 1970). At Glendalough, Co. Wicklow, drainage from abandoned Zinc/Lead mine flows into a nearby marsh.

Vegetation here is dominated by *Molina caerulea, Holcus lanatus, Juncus acutiflorus, Phragmites australis* and *Potentilla erecta* occurred frequently (Beining and Otte, 1996).

Grasses, fodder and grain crops are particularly suited for utilization of sewage sludges. Most are tolerant of raised conditions of potentially toxic elements than other crop types: for grain crops in particular absorb less Ca than other parts of the plant. Grasses and grain crops are more tolerant of low levels of soil K than others. This makes them suitable since sewage sludge has a low concentration of K (Coker, 1983). Cereals and legumes accumulate lower concentrations of metals than leafy plants such as lettuce and spinach (Sterrit and Lester, 1980).

Gallagher and O'Connor (1999), found that on mine spoil from Cu mining at Avoca, Co. Wicklow, natural colonization of non-phytotoxic spoil by heather and gorse indicated possible long term sustainable ground cover on suitably ameliorated phytotoxic spoil by these species. The authors also state that although natural colonization by pine, birch, heather and gorse was taking place, a lengthy period would pass before an acceptable ground cover by these species would develop.

2.16.1 Legumes

Legumes are ideal for revegetation of metal mined wastelands which lack N (Ye *et al.*, 2001). Long term growth on mine waste depends on an adequate supply of N, therefore legumes such as *Trifolium repens* (white clover) and related species are an important component of the seed mixture, since they have the capacity to supply N by fixation from atmospheric sources (Williamson *et al.*, 1982).

According to Jeffery *et al.* (1974), the presence of legumes in N deficient soils results in greatly increased dry matter production for both their own growth and growth by associated plants. A legume-grass sward serves both as a cover for wastes, and for the accumulation and maintenance of N levels.

Table 2.2 Plant species used in seed mixtures used on Irish mine sites

Tynagh mine tailings-opencast Pb/Zn operations (Jeffrey *et al*., 1974)	**OutokumpuTara Mines Pb/Zn tailings** (Brady, 1993)	**Silvermines Pb/Zn mine tailings** (Tierney, 1998)
Festuca rubra cv. *rubra* (Red fescue)	*Festuca rubra* cv. *merlin* (Red fescue)	*Festuca rubra* cv. *waldorf* (Red fescue)
Festuca rubra cv. *commutata* (Red fescue)	*Festuca rubra* cv. *dawson* (Red fescue)	*Agrostis stolonifera* (Creeping bentgrass)
Festuca ovina (Sheep's fescue)	*Agrostis stolonifera* cv. *emerald* (Creeping bentgrass)	*Lolium perenne* cv. *wendy* (Perennial ryegrass)
Festuca longifolia (Hard fescue)	*Agrostis capillaris* cv. *Goginan*	*Lolium perenne* cv. *vigour* (Perennial ryegrass)
Agrostis tenuis (Bentgrass browntop)	*Poa compressa* cv. *reubens* (Canada bluegrass)	*Pucinellia distans* (European/ Weeping Alkali Grass)
Agrostis stolonifera (Creeping bentgrass)	*Trifolium repens* S184 (White clover)	*Trifolium repens* (White clover)
Poa pratensis (Rough stalked meadow grass)		

(After Jeffrey *et al*., 1974; Brady, 1993; Tierney, 1998)

2.16.1.1 *Trifolium repens*

Ye *et al*, 2001, demonstrated that two legumes, *Sesbania rostrata* and *cannabina* could grow on highly toxic Pb / Zn tailings substrata for at least 80 days. However, continued growth of both species suffered from adverse effects later. These authors state that the legumes suffered from heavy metal toxicity.

An important aspect of reduced microbial biomass on sludge treated soils is that *Rhizobia* species, the symbiotic N fixing bacteria in the roots of legumes, are particularly sensitive to metals, including Zn (Kiekens, 1995). In general, heavy metals in sewage sludge tend to reduce the nodulation rate in alfalfa, white clover (*Trifolium repens*) and red clover (*Trifolium pratense*), especially at low pH (Ibekwe *et al.*, 1997). According to Ibekwe et *al.* (1997), the potential risk to white clover (*Trifolium repens* cv. Regal) from sludge induced heavy metal toxicity is of great concern because of their symbiotic association and capacity for N_2 fixation. They also found few significant effects of sludge borne heavy metals on plants, N_2 fixation and on numbers of *Rhizobium leguminosarum* bv. *Trifolii* at concentrations of metals studied, provided soil pH was maintained near 6.0. Where reductions in rhizobial number and plant parameters were observed, the decrease was primarily attributed to low soil pH and, to a lesser extent heavy metal toxicity from sludge.

Chaudri *et al.* (1992) found that the order of metal toxicity to *Rhizobium leguminosarum* bv. *Trifolii* (white clover) is Cu>Cd>Ni>Zn. Under varying circumstances, red clover (*Trifolium pratense*) and birdsfoot trefoil (*Lotus corniculatus*) were successfully established on the Palzo spoil in southern Illinois (Stucky *et al.*, 1980).

2.16.1.2 Grasses versus Legumes

Alternatively, in a laboratory study by Pallant and Burke (1994), three grasses and two legumes were grown for 8 weeks on acidic mine spoil treated with dolomitic lime and municipal sewage sludge. On average, grasses produced more than triple the aerial biomass, more than double the root length density and double the below ground biomass of the legumes. Legumes, however, had greater root to shoot ratios. They concluded that reclaiming mine spoils treated with sewage sludge may be accomplished more effectively using grass species than legumes.

Grasses survived longer than legumes in Zn sand waste in trials in Sweden. Over the long-term, legumes were more sensitive than grasses to Zn. Only *Trifolium repens* had developed satisfactorily among clover species used in trials (Bergholm and Steen, 1989).

2.16.2 Grasses

2.16.2.1 *Lolium perenne species*

Lolium perenne (perennial ryegrass) was planted in trials on acidic mine spoil amended with sewage sludge in Illinois, USA (Stucky *et al.*, 1980)..

In this experiment, perennial ryegrass was a successful cover crop due to its adaptability. Requirements for a crop cover under the conditions of the Palzo experiment were quick emergence and the ability to provide supplemental cover if the permanent species failed to become established. This would reduce erosion until the following fall/spring when forage could be established. A third requirement was that that cover crop should not be competitive to the extent that the permanent species was suppressed. In most instances, perennial ryegrass met all three requirements (Stucky *et al.*, 1980).

In temperate climates, ryegrass can grow over a wide range of pH if adequate nutrients are available. In situations where erosion must quickly be brought under control, the use of a small percentage of rapid growing forage species such as ryegrass in the seed mixture will act as a nurse crop by assisting stabilisation while slower growing species establish (Williamson *et al.*, 1982).

2.16.2.2 *Festuca* species

The value of *Festuca rubra* (red fescue) and *Agrostis capillaries* (Colonial bentgrass) for seeding unstable and toxic land is considerable since revegetation can be achieved by direct sowing and treatment with simple organic fertilizers. *Festuca rubra* has established a reputation for success in mine waste rehabilitation, however, fescues and bent grasses are slower growing species and do not provide rapid ground cover (Williamson *et al.*, 1982).

Stucky *et al.* (1980) in pre- trials on acidic mine spoil found that *Festuca arundinacea* (Tall fescue) established but did not survive after one growing season. In this study, the authors indicated that under greenhouse conditions vegetation could be established and maintained by incorporating sewage sludge into the Palzo acidic spoils. After three growing seasons on the Palzo site (pH 4.3), the creeping red fescue *Festuca rubra*, had achieved a 34% total ground cover.

2.16.2.3 *Poa* species

According to Chaney (1994), when high sludge rates are applied, uptake can be increased for several years due to formation of biodegradation by-products that increase metal diffusion and convection to the roots. The effect is more significant for *Poaceae* (meadow grass) than other species, perhaps due to the role of phytosiderophores in metal uptake.

2.16.2.4 *Holcus* Species

The rapid reproduction of *Holcus lanatus* (Yorkshire fog) and *Agrostis capillaries / castellena* (Highland bentgrass) grass species makes them very suitable for revegetation purposes (Bleeker *et al*, 2002).

2.16.2.5 *Agrostis* species

Results of field trials concerning the establishment of plant cover on a deposit of Zn mine waste in Sweden indicated that an increase in *Agrostis tenuis* (Browntop bentgrass) species had evolved a local population with zinc tolerance and, in addition, *Agrostis stolonifera* (Creeping bentgrass) may also have developed zinc tolerance (Bergholm and Steen, 1989).

Mine populations of *Agrostis tenuis* are more tolerant of phosphorus deficiencies than are normal populations (Bradshaw 1970).

2.16.3 Seeding rates

Stucky *et al.* (1980) successfully used a seeding rate of 22, 22, 28 and 22 kg/ha for *Festuca arundinacea, Trifolium pratense, Festuca rubra and Poa compressa,* respectively on the Plazo mine spoil.

2.17 Sludge application rates for tailings revegetation

Lower rates of sludge application are environmentally desirable, though less effective at enhancing hydraulic conductivity and aggregation in pyritic mine tailings (Harris and Megharaj, 2001). Sewage sludge was applied to an acidic dredge spoil disposal site at 100 t/ha (Palazzo and Reynolds, 1991). Revegetation trials on the Avoca mine spoil resulting from copper mining in the area incorporated sewage sludge to the top 20cm of spoil at application rates of 138 t/ha to 248 t/ha (dry weight) (Gallagher and O'Connor, 1999).

Fifty percent (v/v) of sludge application rate was found to be the best loading rate for plant growth in the reclamation of Pb /Zn tailings (Ye *et al.*, 2001).

2.18 Greenhouse studies

Ye *et a*l (2001), carried out their investigation of the feasibility of using *Sesbania rostrata* and *S.cannabina* for the reclamation of Pb /Zn tailings by means of a greenhouse study. Both *Sesbania rostrata* and *S.cannabina* show some degree of metal tolerance. Their study also found that application of sewage sludge increased contents of total C, N, P and K, and reduced total Zn, Pb, Cd and DPTA extractable Pb and Cd in tailings substrata. These, in turn, reduced zinc, lead and cadmium uptake and accumulation in shoot and root tissues of both species, and improved plant growth performance, including biomass, growth rates, and stem nodulation.

Chaney (1994) states that metal uptake slopes measured in pot studies are much higher than those found in the field. Thus, greenhouse or growth chamber studies cannot be used to estimate uptake slopes. Alloway (1995b) also states that uptake of metals from soils is greater in plants grown in pots of soil grown in the greenhouse than from the same soil grown in the field. This is possibly due to differences in microclimate and soil moisture, and to the roots of container grown plants growing solely in contaminated soil, whereas those of field grown plants may penetrate to less contaminated soil.

3.0 Materials and Methods

3.0 Materials and Methods

3.1 Experiment Design

3.1.1 Small Pot Screening

A small pot trial was conducted to assess the suitability of grass species to establish and grow on mine tailings.

3.1.2 Mine tailings and sewage sludge

The mine tailings were excavated from the Gortmore Tailings Management Facility located at Silvermines, Co Tipperary in April 2002. Thermally dried primary sludge was collected from Ringsend Sewage Treatment facility at Ringsend, Dublin city in May 2002. Agricultural soil was also collected in May 2002. A control soil, a brown podzol originating in Co. Roscommon, was also used in the study. All tailings and soil samples were air dried and sieved through a 2 mm aperture sieve and mixed thoroughly to a uniform composition.

Plate 3.1 Thermally dried primary sludge from Ringsend Treatment Plant, Dublin

3.1.3 Plant growth experiment

A greenhouse experiment was designed to test the growth of a number of grass species in tailings and in a control soil amended with sewage sludge. The green house was constructed on a concrete surface, standing at 30m by 30m. Venting at either end of the greenhouse controlled ventilation and avoided high humidity.

Unamended tailings and unamended soil were used as a controls. Sieved soil and tailings samples were thoroughly mixed with pre-weighed volumes of sewage sludge, based on t/ha measurements, in plastic basins. Various sludge application rates were used (Table 3.1). Amended tailings and soil were placed in boxes (dimensions 36 x 27.5 x 18 cm height).

Table 3.1 Experimental design for greenhouse trials

Treatment	Original sample mixed with Sludge
Treatment A	Brown podzol control soil
Treatment B	Soil + 2t/ha sewage sludge amendment
Treatment C	Soil + 20t/ha sewage sludge amendment
Treatment D	Tailings + 20t/ha sewage sludge amendment
Treatment E	Tailings + 50t/ha sewage sludge amendment
Treatment F	Tailings control

Each box was sown with grass. Six grass species were sown on each treatment (Table 3.2). Tailings were seeded at an average rate of 200 kg/ha (Table 3.3) whilst agricultural soil was seeded at the recommended rate of 30 kg/ha (Emorsgate seeds, pers comm.). Seeding took place on the 10th May 2002. Three replicates of each treatment were sown.

The boxes were placed in a greenhouse, arranged in a randomised block design as described by Reilly (1997) and watered daily. Temperature varied between 4°C and 38°C and day length varied between 14 and 18 hours during the experimental period. The plants were allowed to grow for a period of 12 weeks under natural light conditions. In August 2002, plants were harvested to approximately 10mm above substrate level.

Table 3.2 Grass species used in greenhouse trials

Grass Species	Cultivar	Common name
Poa pratensis	*sobra*	Smooth meadow grass
Lolium perenne	*danilo*	Perennial ryegrass
Holcus lanatus		Yorkshire Fog
Festuca rubra	*rubra*	Strong creeping red fescue
Agrostis stolonifera	*kromi*	Creeping bent
Trifolium repens	*britta*	White clover

Table 3.3 Seeding rates used in greenhouse trials

Grass Species	Seeding rate on control. soil	Seeding rate on Tailings
Poa pratensis	30 kg/ha	225 kg/ha
Lolium perenne	30 kg/ha	200 kg/ha
Holcus lanatus	30 kg/ha	180 kg/ha
Festuca rubra	30 kg/ha	200 kg/ha
Agrostis stolonifera	30 kg/ha	180 kg/ha
Trifolium repens	30 kg/ha	200 kg/ha

3.2 Sample preparation

3.2.1 Substrate sample preparation

Substrate samples were collected using an auger (20 mm diameter, 100 mm depth) from the root zone of each treatment. Samples were stored in sealed plastic bags and air dried in the laboratory to consistent weight. All substrate samples were ground to pass through a 2 mm aperture sieve before undergoing chemical analysis.

3.2.2 Vegetation sample preparation

Grass samples were initially rinsed with tap water, followed by thorough rinsing with distilled water. Prior to oven drying at 80°C samples were rinsed in ultra pure water.

After drying and reaching a consistent dry weight, grasses were cut into small portions. Samples were then milled in a Tecator 1093 Cyclotec sample mill with a grid fineness of 1.0 mm. Samples were stored in plastic sample bags and analysed within an 8 week period.

3.3 Biological Analysis

3.3.1 Germination percentage and shoot height measurement

A small representative sample of seeds was germinated at approximately room temperature on a water soaked cotton wool base in Petri dishes. This was carried out over a period of approximately 14 days. After this time, seeds displaying germination i.e. emergence of root and shoot, were counted and expressed as a percentage of the total sown.

During pot trials, shoot measurements of each grass were measured by rules and recorded. This was done at a six separate areas of the pot and the average figure recorded. Results were expressed in mm. This was carried out on a weekly basis.

3.3.2 Dry Weight Biomass

Grass samples were oven dried at 80°C until there was no further loss in weight. The final weight was then recorded for biomass determination. Results were expressed as g/m^2.

Plate 3.2 Greenhouse trials June 2002

3.4 Chemical Analysis

3.4.1 Substrate pH

Substrate analysis of pH was carried out on a soil to water ratio of 1:2 (Peech, 1965) method. Ten gram of substrate previously air dried and sieved to <2 mm was placed in a beaker and 20 ml of distilled water added. The beaker was swirled and left to stand for 30 minutes. Using a calibrated pH meter (Orion Model 210A), the electrodes were immersed in the solution and gently stirred using a magnetic stirring bar whilst the pH reading was taken. Thermally dried sludge was similarly analysed for pH using a sludge to water ratio of 5:1.

3.4.2 Exchangeable Potassium

Potassium was extracted using Morgan's extracting reagent (NaOac-HOAc)(Byrne, 1979). Morgan's reagent is made up of NaOAc adjusted to pH 4.8 with acetic acid. Six gram of dried sieved soil are placed in an Erlenmeyer flask, covered with Para-film and shaken on a mechanical shaker for 30 minutes. When extracted from soil, solutions are filtered through glass fibre filter paper and exchangeable K is then determined by flame photometer (Knudsen and Peterson, 1982). A range of standards from 0 to 20 mg/l K are prepared and dilutions of samples, where necessary carried out. A Corning 400 Flame Photometer was used to determine the exchangeable K content and results were expressed in mg/l.

3.4.3. Available Phosphorus

The extraction of P in 6 gram of soil was also carried out in Morgan's extracting reagent (Byrne, 1979). Morgan's extracting reagent which is composed of distilled water, sodium hydroxide and glacial acetic acid, is designed to dissolve an amount of P proportional to the fraction available to plants. Of the total P in soils, less than 1% is available to plants. Six gram of dried sieved soil were placed in an Erlenmeyer flask, covered with Para-film and shaken on a mechanical shaker for 30 minutes. When extracted from soil, solutions were filtered through glass fibre filter paper and available P was analysed colourimetrically using the chemical reaction between P and ammonium molybdate. A characteristic blue colour is produced when either molybdate or its heteropoly complexes are partially reduced. This occurs 10 minutes after the addition of 6 ml of 'AG' reagent to 3 ml of sample and standards. This 'AG' reagent is made using 290.6 ml of distilled water, 3.5 ml of ammonium molybdate, 31.5 ml of 18% (HCl), 10.6 ml of ascorbic acid and 7.9 ml of sodium antimony tartrate added to a pre- acid washed beaker (5% HCl) in the above order. Standards ranging from 0 to 4 mg/l were prepared and treated in the same manner as samples with addition of 'AG' reagent. Following colour development of standards and samples, samples were read on a Ultra Violet Visable (UV-Vis) spectrophotometer, calibrated and set to a wavelength of 880 nanometres (nm). Results are expressed as mg/l available P.

3.4.4 Organic Matter

Organic matter (OM) was determined using the loss on ignition method. In this method OM is destroyed, after which loss of weight in the soil is taken as OM (Broadbent, 1965). This method involved pre treating crucibles by ignition in the muffle furnace at 900°C for fifteen minutes and then leaving them to cool in a dessicator. Crucibles were pre-weighed and 10 g of soil placed in each crucible, weighed to four decimal places. The crucibles were placed in the muffle for fifteen minutes at 950°C. Following this, crucibles were placed in a dessicator to cool and re weighed. Loss of weight can be used in the following formula to calculate % OM (Nelson and Sommers, 1982).

$$\%\ \text{Organic Matter} = \frac{A-B}{W} \times \frac{100}{1}$$

A = Weight of crucible and soil before ignition (gram)
B = Weight of crucible and soil after ignition (gram)
W = weight of air dried soil (gram)

3.4.5 Organic Carbon

The percentage organic carbon content of substrates was analysed using the rapid dichromate oxidation technique (Nelson and Sommers, 1982). A known amount of substrate, not exceeding 0.3g of soil was weighed and transferred to an Erlenmeyer flask and 10ml of 1N (K_2CrO_7) dispensed into the flask. Analysis of thermally dried sludge required a lower sample weight, (0.05g). After soil was dispersed by swirling, 20ml of concentrated (H_2SO_4) was added to the flask. After swirling for 1 minute, the flask was left to stand on aluminium foil for 30 minutes. Two hundred ml of distilled water was then added followed by 10 ml of concentrated phosphoric acid. Diphenylamine indicator was used (1ml) and following this the contents of the flask was titrated with 0.2N ferrous ammonium sulphate. The colour change was black to purple/blue.

$$\% \text{ Organic Carbon} = \frac{(V1 - V2/5)x0.003x100}{W}$$

V1 = Volume of 1N potassium dichromate

V2 = Volume of 0.2 N ferrous ammonium sulphate

W = weight of air dried soil

3.4.6 Nitrogen

Percentage total N in soil was analysed using the Kjeldahl method (Bremner, 1965). In this method, the sample under analysis is converted to ammonium nitrogen (NH_3^+- N) by digestion with concentrated H_2SO_4 containing substances that promote this conversion, and the (NH_3^+- N) is determined from the amount of NH_3 liberated by distillation of the digest with alkali. Seven gram of air dried and sieved soil (<2 mm), or 1 gram of thermally dried sludge, were placed in a dry macro-Kjeldahl flask with two Kjeldahl catalyst tablets and 25 ml of redistilled water used to wash down the walls of the flask. 30 ml of concentrated analar H_2SO_4 was then added dropwise to the flask, in the fumehood. The flask was then cautiously heated in the digestion block. When water was removed and frothing ceased, heat was increased until such time as the digest was clear. The contents were then boiled for 5 hours. After completion of the digestion, the flask was allowed to cool and 50 ml of redistilled water added to the flask. The flask was gently swirled and the cold solution transferred to a 250 ml volumetric flask. Coarser sand grains were left in the flask. The solution was diluted to the mark with redistilled water.

The distillation procedure involved adding 10 ml of 2% boric acid to a 50 ml Erlenmeyer flask and covering with parafilm. The 'Buchi' distillation unit was preheated. Then, 25 ml of digested sample was pipetted into a clean digestion flask and the walls washed down with 25 ml of redistilled water. The digestion flask was attached to the unit, and the Erlenmeyer with boric acid indicator solution placed under the digestion outlet with the tube resting in the 2% boric acid indicator solution. Fifteen ml of 32% (NaOH) was added to the digested sample and a 5 minute distillation commenced. Following distillation, the Erlenmeyer was removed and the contents titrated with 0.02 N HCl until there was a colour change from green to wine red. Blanks containing redistilled water were digested and distilled in the same manner as above. Percentage N in the sample was calculated using the formula:

$$\% \text{ Nitrogen} = x \text{ ml HCl} \times \frac{0.28}{1000} \times \frac{250}{25} \times \frac{100}{W}$$

W = weight of soil sample (gram)

3.4.7 Cation Exchange Capacity

Cation Exchange Capacity was carried out using the method described by Chapman (1965) which involves placing 4g of <2 mm air dried in a 50 ml round bottom, narrow neck centrifuge tube and adding 33 ml of 1M (NaOAc) solution. This solution was then mechanically shaken for 5 minutes and centrifuged until the supernatant was clear. The liquid was decanted and the procedure repeated three times. The sample was then washed in an identical manner with three, 33 ml aliquots, of 99% isopropyl alcohol. Using the shaking and centrifuging procedure employed previously on the sample, adsorbed Na was replaced by means of 33 ml aliquots of 1M NH_4OAc reagent and each decant placed in a 100 ml volumetric flask. The solution was diluted to volume with NH_4OAc reagent. Sodium was determined by a Corning 400 Flame Photometer with a range of prepared standards. Results were expressed in milliequivalents per 100g of air dried soil.

3.4.8 Digestion of substrate samples and vegetation samples for elemental analysis

A known amount, 0.3g (correct to four decimal places on an analytical balance) of air dried <2 mm substrate sample and dried, milled plant material were placed in digestion tubes (three replicates per sample) and 8 ml of concentrated (HNO_3) added. Tubes were placed on a heating block and left to digest at approximately 125°C for 3 hours until evolution of brown NO_2 gas ceased and the solution was a clear straw yellow colour. Depending on the sample, precipitate remained near the bottom of the tubes and settled on cooling. After a sufficient cooling period, samples were filtered through glass fibre filter paper and made up to volume with redistilled or ultra pure water in a 50 ml volumetric flask.

Analysis of digests for total metals following appropriate dilutions, was conducted by PlasmaTech Ltd, Business Innovation Centre, Ballinode, Sligo using Inductively Coupled Plasma-Mass Spectrometry (Varian Plasmaquad). Results were expressed as mg/kg. Total metal concentration in a number of sample digests were determined by a Perkin Elmer 2380 Flame Atomic Absorption Spectrophometer. Iron, Mn and Zn were analysed by this method and results expressed as mg/kg.

3.5 Quality Control

Samples were analysed using appropriate blanks and standard solutions. All blanks and standard solutions were matrix matched with the samples. Calibrations were conducted under the instrumental conditions employed in sample analysis. Linearity of response was considered acceptable by use of R^2 coefficients which was acceptable if >0.995. Calibration graphs were resloped every 15 samples and recalibrated every 15-20 samples depending on sample type. Replicate readings were carried out on a number of samples in each batch and a certified reference material digest was analysed with approximately every 40-50 samples. Additionally, splits (subdivision of original sample material and analytical samples) and spikes (introduction of known amount of analyte at the earliest practicable stage in the analytical sequence) were carried out to verify accuracy. The accuracy and precision of the digest methods and ICP-MS and AAS techniques were checked by analysing certified reference materials (CRM), which contain known concentrations of trace metals.

Reference materials used in this project were as follows;

GBW 07604	Poplar leaves
CRM 029-050. Lot No. JC 029	Sewage Sludge

3.6 Statistical analysis

All data was input to and calculated using Excel (Microsoft XP 2000). Graphs were produced from Excel. Statistical tests were completed using the Sigmastat 2.03 programme for Windows. Both T-test and Analysis of Variance were carried out on data.

3.6.1 Paired T-Test

The Paired t-test examines the changes which occur before and after a single experimental intervention on the same individuals to determine whether or not the treatment had a significant effect. The t-test is commonly used to evaluate if the differences in means between two groups is greater than what may be attributed to random sampling variation. The t-test was used in this study when comparing two treatments (Section 4.9). Differences were regarded as significant if $P < 0.05$.

3.6.2 Analysis of Variance

ANOVA (analysis of variance) is used when comparing two or more different experimental groups to see if they are affected by two different factors which may or may not interact. ANOVA was carried out to test for significant differences between treatments used in this study. One way ANOVA was followed by Tukey's comparison of means test to compare treatments. Differences were regarded as significant if $P < 0.05$.

4.0 RESULTS AND DISCUSSION

4.0 Results and Discussion

4.1 Thermally dried biosolids chemical characteristics

4.1.1 pH and Cation Exchange Capacity

Analysis of the thermally dried biosolids (TDB) used in these trials reflects its slightly acidic pH value of 6.0 (Table 4.1). Cation exchange capacity due to the high organic matter content (Table 4.2) is elevated, 56.28 meq/100g.

Table 4.1 pH and CEC of thermally dried biosolids used in trials

	pH	CEC meq/100g
TDB	6.02 (0.28)	56.28 (0.09)

Values in parentheses are standard deviation of mean of 8 samples

4.1.2 Organic Matter and Organic Carbon

Thermally dried biosolids contained on average 83.61% organic matter. Organic C content of the TDB was 33.75% (Table 4.2). Sommers (1977) quotes a median value of 32% organic C in sludges.

Table 4.2 Organic matter (%) and organic C (%) content of thermally dried biosolids used in trials

	Organic Matter (%)	Organic Carbon (%)
TDB	83.61 (0.69)	33.75 (1.37)

Values in parentheses are standard deviation of mean of 8 samples

4.1.3 Total Kjeldahl Nitrogen, Available Phosphorus and Exchangeable Potassium

Total Kjeldahl N content of TDB was 2.23%, a value less than the Irish mean quoted by O'Riordan *et al.* (1986a). The C:N ratio of TDB was approximately 15:1. Available P was approximately 448.5 mg/l and exchangeable K measured 430.8 mg/l. These figures are slightly less than those available in the literature, however, here we refer to available and exchangeable levels of P and K respectively, as opposed to total values quoted in the literature.

Table 4.3 Total Kjeldahl nitrogen, available phosphorus and exchangeable potassium content of thermally dried biosolids used in trials

	Total Nitrogen (%)	Phosphorus (mg/l)	Potassium (mg/l)
TDB	2.23 (0.27)	448.5 (23.55)	430.8 (30.74)

Values in parentheses are standard deviation of mean of 10 samples

4.1.4 Elemental composition of Ringsend thermally dried biosolids

Irish sewage sludges have always been regarded as having low metal concentrations, making them suitable for a wide range of disposal routes. In a study in 1988, results were obtained for 68 different Irish sewage sludges. A follow up study show a significant reduction over the 12 year period (Table 4.4) (IEI, 2001).

Table 4.4 Elemental concentration (mg/kg) in Irish sewage sludges in the years 1988 and 2001*

Element	1988 study 68 sewage sludges (mg/kg)	2001 study 27 sewage sludges (mg/kg)
Cadmium	2.7	0.93
Zinc	1319	488
Copper	651	365
Lead	228	67
Nickel	852	28

* Taken from IEI, (2001)

According to IEI (2001), Ireland has witnessed a decline in its heavy industry with a growth in its high technology industry sectors. More stringent effluent discharge licences and integrated pollution control legislation have had a major influence on the level of metals discharged in wastewaters and effluents. The 'polluter pays' principal has ensured better industrial practice, with the majority of industrial effluents now being treated at source with appropriate BATNEEC (Best Available Technology Not Entailing Excessive Cost), now referred to as BAT (Best Available Technology).

Table 4.5 Elemental composition of thermally dried biosolids

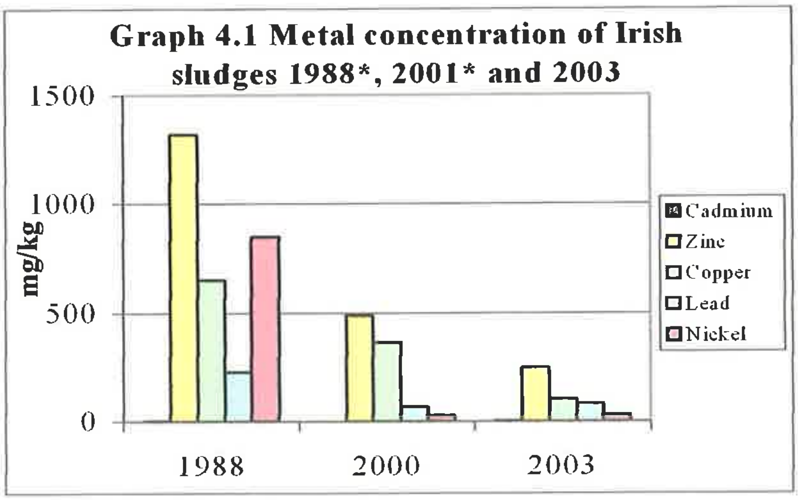
Element	Concentration (mg/kg)	S. I. 148 of 1998 Regulation Limits (mg/kg)
Arsenic	< 30	
Boron	< 55.5	
Cadmium	3.39 (0.32)	20
Chromium	< 75	
Cobalt	1.64 (0.21)	
Copper	105.06 (3.74)	1000
Iron	2597.0 (112.87)	
Lead	83.54 (4.02)	750
Manganese	110.22 (8.33)	
Mercury	< 3	16
Molybdenum	7.13 (0.32)	
Nickel	31.94 (6.42)	300
Selenium	< 9	
Zinc	245.83 (3.47)	2500

Values in parentheses are standard deviation of mean of 12 samples

Results obtained for metal levels in TDB (Table 4.5) displayed levels below the current mandatory limit values set out in the EU Direcive concerning sewage sludge disposal to agricultural land (86/278/EEC) enacted in Ireland as SI 148 of 1998. Results less than a stated value refer to samples that have been screened for the particular element and were

found to be below the limit of detection when analysed by ICP-MS analysis. All key metal levels were significantly lower than limit values in the legislation.
A comparison of metal levels from 1988 to 2003 is presented in Graph 4.1. In Ireland, domestic sources of metals, primarily copper and zinc but also cadmium and lead, are the main source of these metals in sludge. These low levels from domestic sources, as opposed to other sources, may limit the use of sewage sludge in agriculture (IEI, 2001). Mean Cu levels found in TDB were 105.06 mg/kg, and a separate study in 2002 found mean concentration of 118.67 mg/kg (Lehany, 2003). Both figures are substantially lower than national averages in 2000 and 1988. Up to 80% of the Cu discharged from households originates from corrosion of domestic plumbing (IEI, 2001).

A similar trend was observed with Zn values. TDB displayed mean Zn concentration of 246 mg/kg in this study, a figure also significantly lower than those quoted for 1988 and 2000. Zinc levels of 284 mg/kg were obtained for Ringsend TDB in a separate study in 2002 (Lehany, 2003). Zinc arises mainly from the use of detergents and body care products, with losses from plumbing being an increasingly rare source (IEI, 2001).



* Taken from IEI, (2001)

The elevated level of Cd contained in TDB in this study is of concern. Although the level remains less than the limit values cited in 'Use of Sewage Sludge in Agriculture Regulations', 148 of 1988, it is greater than that of previous years and greater than the value obtained for TDB quoted by Lehany (2003). In the 2001 study, Cd was found to be <3.67 mg/kg. However, Alloway (1995a) states that, in the past, Cd levels in UK sludges have ranged from 17 to 23mg/kg DM. Therefore, Ringsend TDB cadmium levels would appear to be lower than those of UK sludges. Pb levels were slightly greater than those for Irish sludges in 2000. TDB displayed mean lead level of 83.54 mg/kg. Concentration of Fe in TDB was 2597 mg/kg. Lehany (2003) found Fe levels in Ringsend TDB between 2303 mg/kg and 2779 mg/kg.

4.2 Agricultural soil chemical characteristics

4.2.1 pH

According to Coulter *et al.* (1999) the target pH for Irish agricultural grassland soil should be approximately 6.5, and Olness *et al.* (1998) state that an optimal pH of 6.7 is required to attain a maximal rate of nitrification. Gardiner and Radford (1980) state that soil with pH values between 6.6 and 6.9 are nearly neutral, and that a soil with a pH between 6.0 and 6.5 is slightly acidic.

From Table 4.6, it can be observed that the pH of the agricultural brown podzol soil used in trials was on average 6.42, therefore slightly acid. Addition of TDB to the soil at a rate of 2 t/ha increased pH slightly to 6.62. This increase was significant ($P<0.05$). No statistical difference ($P<0.05$) was observed between B and C. Although at 20 t/ha remained significantly different to unamended soil. Addition of TDB had the effect of increasing the brown podsol to a near neutral pH. Increasing soil from a very acidic condition to near neutrality often results in favourable growth response of plants (Olness *et al.*, 1998). Giordano *et al.* (1975) increased soil pH from 4.9 to 6.3 by applying garbage compost to soil which in turn increased corn yield.

Table 4.6 Average pH of agricultural soil under different treatments

Treatments	A	B	C
pH	6.42 (0.32)	6.62 (0.20)	6.68 (0.30)

Treatment A- Agricultural soil, no amendment
Treatment B- Agricultural soil + TDB at 2 t/ha
Treatment C- Agricultural soil + TDB at 20 t/ha
Values in parentheses are standard deviation of mean of 18 samples

Hooda and Alloway (1994) found sludge addition to sandy loam soil resulted in a pH increase from 5.4 to 6.8 initially, but shortly afterwards decreased to 5.45. The initial rise was likely to have been due to the presence of NH_3-N in the sludge, and the decrease likely to have been the result of nitrification and synthesis of acidic products of sludge decomposition. They also found an increase from pH 6.6 to 7.0 in a sandy soil as a result of sludge treatment.

4.2.2 Organic matter

Within the soil profile, organic matter content is always highest in the surface horizon, but podzols and vertisols may have some translocated humic material further down the profile (Alloway, 1995a).

The brown podsol used in this study had on average 5.01% organic matter. Addition of TDB at 2 t/ha increased organic matter to 5.93%, although not significantly ($P>0.05$) and at 20 t/ha the increase to 7.02% was more notable (Table 4.7). At this rate, organic matter was significantly increased ($P<0.05$). The high cation exchange capacity of organic matter enables it to act as an ideal reservoir of plant nutrients (Gardiner and Radford, 1980). Therefore. the increase in organic matter through the addition of TDB increases the availability of essential nutrients to plants grown thereon.

Organic matter creates favourable physical conditions for crop growth (Gardiner and Radford, 1980). In addition, Coker (1983) states that organic matter, especially the humic acids, adsorb metal ions, particularly in the middle and upper parts of the pH range of agricultural soils.

Application of organic matter, such as sludge, serves as a granulating agent and can be used to produce a friable and easily cultivated loam soil. This effect is most pronounced on sandy soils of low clay content (Epstein *et al.*, 1976).

After one day, Hooda and Alloway (1994), observed an increase in soil organic matter from 3.55% to 5.65% in a sandy loam soil with addition of anaerobically digested sludge at 50 t/ha, and a further increase to 8.40% at an application rate of 150 t/ha. However, this sludge added organic matter appeared quite resistant to decomposition, with soil organic matter contents decreasing by only 3% in the control to 16% in the 150 t/ha treatment after one year. In addition, the authors noted the trend of decreasing organic matter over the residual period occurred at a faster rate in soils kept at 25°C than those at 15°C.

In contrast, Illera (2000) observed only a slight increase in soil organic matter after application of 80 t/ha digested biosolid, from 3.4% to 3.8%. The increase was not significant (P<0.05) compared to the control soil. The effect of biowaste application on soil organic matter must extend beyond 4-5 years.

Table 4.7 Organic matter (%) in agricultural soil under different treatments

Treatments	A	B	C
% Organic Matter	5.01 (0.86)	5.93 (0.91)	7.02 (1.01)

Treatment A- Agricultural soil, no amendment
Treatment B- Agricultural soil + TDB at 2 t/ha
Treatment C- Agricultural soil + TDB at 20 t/ha
Values in parentheses are standard deviation of mean of 18 samples

4.2.3 Organic Carbon

Table 4.8 exhibits organic carbon levels in the brown podsol used in this study before and after the addition of TDB. Soil with no amendment contains on average 1.6% organic carbon, which increased to 1.66% on addition of 2 t/ha of TDB. Application of 20 t/ha TDB increased organic carbon to 1.87%. Increases in organic carbon were not statistically significant. The level of organic carbon indicates the amount of organic matter in the soil. The surface horizon of mineral soils in Ireland normally contains 3% to 6% organic carbon (Gardiner and Radford, 1980).

Table 4.8 Organic carbon (%) in agricultural soil under different treatments

Treatments	A	B	C
% Organic Carbon	1.60 (0.21)	1.66 (0.19)	1.87 (0.35)

Treatment A- Agricultural soil, no amendment
Treatment B- Agricultural soil + TDB at 2 t/ha
Treatment C- Agricultural soil + TDB at 20 t/ha
Values in parentheses are standard deviation of mean of 18 samples

4.2.4 Cation Exchange Capacity

As can be observed from Table 4.9 the addition of TDB had the effect of increasing the CEC of the soil. Application of 2 t/ha increased TDB from 20.44 meq/100g to 22.20

meq/100g. A further increase to 24.74 meq/100g was noted with addition of 20 t/ha TDB, only at this sludge application rate was the increase in CEC significant ($P<0.05$). Soils with high organic matter content usually have high CEC (25-40 meq/100g of soil). The CEC of a soil low or devoid of, organic matter is generally less than 12 meq/100g (Gardiner and Radford, 1980).

Soil values for CEC change with soil pH level because the CEC of the organic fraction increases with rise in soil pH (Coker, 1980). According to Sterrit and Lester (1980) the CEC of a soil may increase on application of sludge. The ability of a soil to retain nutrients such as Ca, Mg and K is largely dependant on CEC. Cation exchange capacity of a silt loam soil increased from 5-6 meq/100g to 15 meq/100g by the application of dried sewage sludge compost at rates approaching 240 t/ha (Epstein *et al.*, 1976).

Table 4.9 CEC (milli equivalents/100g) of agricultural soil under different treatments

Treatments	**A**	**B**	**C**
CEC meq/100g	20.44 (1.06)	22.20 (0.71)	24.74 (0.70)

Treatment A- Agricultural soil, no amendment
Treatment B- Agricultural soil + TDB at 2 t/ha
Treatment C- Agricultural soil + TDB at 20 t/ha
Values in parentheses are standard deviation of mean of 18 samples

4.2.5 Total Nitrogen

The increase in total N for treatment A, B and C with addition of TDB at 2 t/ha, and 20 t/ha, can be observed in Table 4.10. Percentage total N in the brown podsol soil used in these trials is 0.18%, increasing to 0.19% with addition of 2t/ha TDB, and to 0.2% with the addition of 20 t/ha. The C:N ratio in treatment A is 8.9:1, in treatment B C:N ratio is 8.7:1. Treatment C, with sludge addition of 20 t/ha has a C:N ratio of 9.4:1. The C:N ratio indicates generally the degree of decomposition of organic matter; a ratio between 8 and 15 is considered satisfactory and indicates conditions favourable to microbial activity (Gardiner and Radford, 1980). The N in sludge becomes available for the process of nitrification, denitrification, immobilization, volatilization and mineralisation in the soil N cycle after sludge has been applied (Pierzynki, 1994).

Table 4.10 Total Kjeldahl nitrogen (%) in agricultural soil under different treatments

Treatments	A	B	C
% Total Nitrogen	0.18 (0.007)	0.19 (0.008)	0.20 (0.007)

Treatment A- Agricultural soil, no amendment
Treatment B- Agricultural soil + TDB at 2 t/ha
Treatment C- Agricultural soil + TDB at 20 t/ha
Values in parentheses are standard deviation of mean of 18 samples

4.2.6 Available Phosphorus

Soil P, like N, increased with addition of TDB. Unamended soil contained on average 1.32 mg/l available P. This figure is low by Irish standards. Coulter *et* al. (1999) state that Irish soils contain, on average, contain 7.7 mg/l P. Available P in these trials increased to 1.73 mg/l with the addition of 2 t/ha TDB, and further increased to 4.56 mg/l on addition of 20 t/ha TDB. The increase from treatment A to B was not significant ($P>0.05$), however treatment C was significantly higher ($P<0.05$) in P than treatment B and C. Pierzynski (1994), shows that, when 200 kg/ha equivalent of available N in sludge was applied to soil, extractable P increased from 35 mg/kg in the control to almost twice that, 68 mg/kg, with sludge addition. The author states that the imbalance between N and P in sludges can cause soil P to increase substantially, in some cases to the point of potential for loss of P through leaching or runoff.

Table 4.11 Available phosphorus (mg/l) in agricultural soil under different treatments

Treatments	A	B	C
Phosphorus (mg/l)	1.32 (0.24)	1.73 (0.18)	4.56 (1.29)

Treatment A- Agricultural soil, no amendment
Treatment B- Agricultural soil + TDB at 2 t/ha
Treatment C- Agricultural soil + TDB at 20 t/ha
Values in parentheses are standard deviation of mean of 18 samples

4.2.7 Exchangeable Potassium

Potassium in sludges is normally assumed to be 100% available for uptake (Pierzynski, 1994). The addition of TDB increased exchangeable levels of K in the brown podsol soil used in these trials. Control soil contained on average 82 mg/l K, increasing to 89.4 mg/l on addition of 2 t/ha of TDB and to 98.7 mg/l on addition of 20 t/ha TDB. As was the case with P, addition of sludge to soil at 2t/ha did not significantly increase (P>0.05) K in comparison with treatment A. However, K levels in treatment C were significantly higher (P<0.05) than both treatment A and treatment B.

Table 4.12 Exchangeable potassium (mg/l) in agricultural soil under different treatments

Treatments	A	B	C
Potassium (mg/l)	82.0 (3.5)	89.4 (7.9)	98.7 (7.0)

Treatment A- Agricultural soil, no amendment
Treatment B- Agricultural soil + TDB at 2 t/ha
Treatment C- Agricultural soil + TDB at 20 t/ha
Values in parentheses are standard deviation of mean of 18 samples

4.3 Mine tailings chemical characteristics

4.3.1 *pH*

The addition of sewage sludge to soil can decrease, increase or have no effect on soil pH. The mineralisation of organic C, and N, nitrification of ammoniacal nitrogen forms, the hydrolysis of Fe and Al compounds and the oxidation of sulphides can all act to decrease soil pH (Pierzynski, 1994).

According to Williamson *et al.* (1982) pH values of mine tailings and waste rock range from below 2 to above 8, depending on the nature of the gangue material, pyrite content and the chemicals added during processing. The pH of Silvermines tailings is slightly above the normal plant growth range of 5-7 (Williamson *et al*, 1982), unamended tailings exhibits a pH of on average 7.73. Tierney (1998) found pH on five sites on rehabilitated areas of Silvermines tailings site to be within the range 7.2 to 7.7.

Table 4.13 Average pH of mine tailings under different treatments

Treatments	F	D	E
pH	7.73 (0.18)	7.61 (0.21)	7.40 (0.19)

Treatment F- Tailings, no amendment
Treatment D- Tailings + TDB at 20 t/ha
Treatment E- Tailings + TDB at 50 t/ha
Values in parentheses are standard deviation of mean of 18 samples

The addition of TDB to mine tailings had the effect of lowering its pH. At a rate of 2 t/ha, pH was lowered to 7.61, an increased rate of 20 t/ha further decreased tailings pH to 7.4 (Table 4.13). Williamson *et al.* (1982) give data on the increase of pH of fine uranium tailings with the addition of sewage sludge. At 5 t/ha, the pH of the tailings was 3.6, however at 52 t/ha the pH had increased to 4.8.

In a greenhouse study by Ye *et al.* (2001) to evaluate the effects of sewage sludge for the reclamation of mine tailings, the authors show a decrease in pH with increasing sludge application. In their study, tailings alone, had a pH of 7.53 and was lowered to a pH of 5.61 with 75% sludge and 25% tailings (v/v) mix. McNearney and Belyaeva (1998) observed an increase in pH from 6.8 to 7.1 one year after the application of biosolids to metal mine tailings.

4.3.2 Organic Matter

Analysis of Silvermines tailings shows that average organic matter content on unamended tailings is 4.9%. Tierney (1998) found organic matter levels in the range 5.47% to 8.97%; however, his samples were taken from rehabilitated/revegetated area of the tailings site.

Table 4.14 Organic matter (%) content of mine tailings under different treatments

Treatments	F	D	E
% Organic Matter	4.9 (0.03)	6.01 (1.08)	8.36 (1.07)

Treatment F- Tailings, no amendment
Treatment D- Tailings + TDB at 20 t/ha
Treatment E- Tailings + TDB at 50 t/ha
Values in parentheses are standard deviation of mean of 18 samples

The addition of 20 t/ha of TDB increased percentage organic matter to levels of 6.01% on average. At an application rate of 50 t/ha organic matter in tailings, biosolids mix was on average 8.36% (Table 4.14). Williamson *et al.* (1982) state that 100 t/ha or more of organic matter incorporated into 15 cm depth of tailings provides approximately 5% organic matter. This is the case for field conditions. It is considered in this study that the slightly elevated organic matter levels are as result of the size restriction of trial boxes and the inability to mix biosolids to the depth possible in the field. McNearney and Belyaeva (1998) observed an increase in organic matter from 0.23 to 0.83 % with the addition of biosolids.

4.3.3 Organic Carbon

Silvermines tailings exhibited organic C levels of, on average, 2.16%. Addition of 20 t/ha of TDB increased organic C to 2.52% and to 2.82% with TDB at 50 t/ha (Table

4.15). Tierney (1998) found an average of 2.21% within a range of 1.63% and 3.36% organic C on rehabilitated areas on the Silvermines tailings site.

In a greenhouse study by Ye *et al.* (2001) to evaluate the effects of sewage sludge for the reclamation of mine tailings, the authors also observed a gradual increase in total C (%) with increasing sludge application rates. Tailings alone contained 0.7% carbon with 25% tailings plus 75% sludge mixture increasing total carbon to 2.44%. The increase in organic matter will subsequently increase organic matter in tailings.

Table 4.15 Organic carbon content (%) of mine tailings under different treatments

Treatments	F	D	E
% Organic Carbon	2.16 (0.29)	2.52 (0.26)	2.82 (0.33)

Treatment F- Tailings, no amendment
Treatment D- Tailings + TDB at 20 t/ha
Treatment E- Tailings + TDB at 50 t/ha
Values in parentheses are standard deviation of mean of 18 samples

4.3.4 Cation Exchange Capacity

Cation exchange capacity of typical mine tailings can be as low as 1-2 meq/100g (Williamson et al., 1982) and lack of organic matter and clay minerals result in a low ability to retain and supply nutrients for plant growth. Cation exchange capacity of a soil low or devoid of organic matter is usually less than 12 meq/100g. Silvermines mine tailings therefore falls into this category.

Silvermines tailings exhibited CEC values of 9.4 meq/100g on average. Addition of biosolids at 20 t/ha increased CEC to 12.14 meq/100g, and to 16.7 meq/100g with an addition rate of 50 t/ha (Table 4.16). A low CEC is undesirable in a substrate material as it limits the availability of essential plant nutrients (Sterrit and Lester, 1980), therefore, low CEC, such as in Silvermines tailings, is undesirable from a plant growth perspective. Therefore the increased organic matter in tailings as a result of biosolids application (Sterrit and Lester, 1980) improves tailings CEC. Stuckey *et al.* (1980) found cation exchange capacity of Palzo acidic strip mine spoil to be 11.7 meq/100g.

Table 4.16 CEC (%) of mine tailings under different treatments

Treatments	F	D	E
CEC meq/100g	9.4 (0.69)	12.14 (0.80)	16.7 (0.73)

Treatment F- Tailings, no amendment

Treatment D- Tailings + TDB at 20 t/ha

Treatment E- Tailings + TDB at 50 t/ha

Values in parentheses are standard deviation of mean of 18 samples

4.3.5 Total Kjeldahl Nitrogen

Total N in Silvermines tailings was found to be 0.08%. Tierney (1998) found N levels of on average 0.061% in 1990/91. The addition of TDB was found to increase total N, 20 t/ha causing an increase to 0.12% N and 50 t/ha increasing total N to 0.23% nitrogen (Table 4.17). This increase in total N is desirable as it is the plant nutrient which favours growth response.

Increases in total N usually result in increased herbage yields where sludge is applied to land (Olness *et al.*, 1998). Ye *et al.* (2001) observed a gradual increase in total N in Pb/Zn tailings with increased on sludge application rate to tailings. Most sewage sludge contains greater than 1% total N (Barnhisel, 1988), and this can compensate for the N deficiency in tailings (Ye *et al.*, 2001).

The C:N ratio of unamended tailings was found to be 39:1, an extremely high ratio. This agrees with Berg (1975) who states that the C:N ratio of geological materials is greater than that for surface soils. The C:N ratio decreased to 21:1 with the addition of 20 t/ha TDB and further decreased to 12:1 with 50 t/ha TDB addition. Ratios higher than 15 are associated with a slower decomposition rate and with the accumulation of raw organic matter, in more extreme cases, indicative of unfavorable conditions for microbial activity (Gardiner and Radford, 1980). The C:N ratio of TDB was approximately 15:1, therefore causing a reduction in C:N ratio of mine tailings.

Table 4.17 Total Kjeldahl nitrogen (%) of mine tailings under different treatments

Treatments	F	D	E
% Total Nitrogen	0.08 (0.005)	0.12 (0.007)	0.23 (0.008)

Treatment F- Tailings, no amendment

Treatment D- Tailings + TDB at 20 t/ha

Treatment E- Tailings + TDB at 50 t/ha

Values in parentheses are standard deviation of mean of 18 samples

4.3.6 Available Phosphorus

Tierney (1998) found average levels of 0.516 mg/l P in Silvermines, although levels of 0 mg/l and as high as 8.1 mg/l were found. Ye *et al.* (2001) found that, as with total N and total K, total P in tailings amended with sludge increased with increasing application rate. As is the case with N, mine tailings are deficient in most plant nutrients (Williamson *et al.*, 1982) and application of sludge will greatly enhance P levels and subsequently have desired effects on growth productivity (Sterrit and Lester, 1908).

Results in this study saw an increase in available P from 0.87 mg/l to 1.2 mg/l on application of TDB at 20 t/ha and a further increase to 1.91 mg/l on application of a higher TDB rate of 50 t/ha (Table 4.18). It can be observed therefore that Silvermines tailings were low in P prior to the application of TDB.

Table 4.18 Available phosphorus (mg/l) of mine tailings under different treatments

Treatments	F	D	E
Phosphorus (mg/l)	0.87 (0.17)	1.2 (0.26)	1.91 (0.12)

Treatment F- Tailings, no amendment

Treatment D- Tailings + TDB at 20 t/ha

Treatment E- Tailings + TDB at 50 t/ha

Values in parentheses are standard deviation of mean of 18 samples

4.4 Agricultural soil elemental composition

Trace or minor elements are found in varying amounts in most soils. Soils can contain different levels some of these elements. The 'term trace' element is usually taken to include any element whose content in soils lies below 1% (10,000 ppm) and whose content in agricultural crops is usually not greater than 100 ppm (Gardiner and Radford, 1980).

Results for a number of elements analysed were less than a stated figure when analysed by ICP-MS. Those below the detection limit can be stated as being screened for a particular element and have been found to be below the limit stated.

4.4.1 Arsenic

Arsenic in agricultural soil was found to be less than 16.5 mg/kg in all samples analysed. Although the free element arsenic is not considered poisonous, many of its compounds are extremely toxic (Liebig, 1966). In soils, the natural levels of As range from 1-40 mg/kg, most levels falling in the lower range (O Neill, 1995). Results from this study conclude that As levels in agricultural soil with and without biosolids are below the limit of detection which is within the lower range for As in soils.

4.4.2 Boron

Boron levels in agricultural soil under different treatments are displayed in Table 4.19. Boron is an essential plant nutrient, however, analysis of soils for total Bo is of little use in determining the availability of Bo in the soil (Bradford, 1966). From the results in Table 4.14 it can be observed that addition of TDB did not have a noticeable effect on total Bo levels in the soil. In addition, Bo in TDB was below the limit of detection (Table 4.5). Boron levels in agricultural soil were below the limit of detection in all unamended soil samples, two values were obtainable with treatment B, 40.64 mg/kg and 41.31 mg/kg and all samples were below the limit of detection in treatment C.

Table 4.19 Boron levels (mg/kg) in agricultural soil under different treatments

Treatment	A (mg/kg)	B (mg/kg)	C (mg/kg)
Holcus lanatus Trial pots	<30.52	40.64**	<30.52
Festuca rubra Trial pots	42.62**	41.31**	<30.52
Agrostis stolonifera Trial pots	<30.52	<30.52	<30.52

Treatment A- Agricultural soil, no amendment
Treatment B- Agricultural soil + TDB at 2 t/ha
Treatment C- Agricultural soil + TDB at 20 t/ha

Values in parentheses are standard deviation of mean of 9 samples
** two levels below 30.52 mg/kg

4.4.3 Cadmium

Cadmium levels in agricultural soil under different treatments are displayed in Table 4.20. Background levels of Cd in soils lie in the range 0.06 to 1.1 mg/kg, with a calculated worldwide mean of 0.53 mg/kg (Alloway, 1995a). According to a study by Mc Grath (1998) surface soils, totaling 295 and sampled on a grid basis, representing 22% of the land base of the Republic of Ireland, mean Cd content was 0.52 ± 0.46 mg/kg. In addition, it was found that 30 soil samples exceeded the threshold value for sewage sludge addition, 1.0 mg/kg (SI 148 of 1998). In a soil heavy metal survey of an area on the western perimeter of Dublin city, Fleming and Parle (1977) found Cd levels ranged from <3 to a maximum of 3.5 mg/kg.

Alloway (1995a), states mean Cd concentrations in topsoils to be 0.8 mg/kg with a median of 0.7 mg/kg and a range of 0.2 to 40.9 mg/kg. In addition, the author states that the median (50 percentile) values for sewage sludges used on agricultural land in the UK have decreased from 9 mg Cd /kg DM in 1980 to 3.2 mg Cd /kg in 1991. The upper levels (90 percentile) values have decreased from 33 mg Cd /kg in 1980 to 12.0 mg Cd / kg in 1991. From these figures, it would appear that values obtained in the study are below UK values for Cd in agricultural land to which sewage sludge was applied.

Cadmium in TDB used in this study was on average 3.39 mg/kg (Table 4.5). In treatment A, agricultural soil with no amendment, all soil samples analysed exhibited

Cd levels below the limit of detection of <1.65 mg/kg. Treatment B, soil with TDB addition of 2 t/ha again, exhibited no values above the limit of detection. Treatment C representing agricultural soil with TDB addition of 20 t/ha exhibited no Cd levels above the detection limit. From these results it can be concluded that Cd levels in an agricultural brown podsol were <1.65 mg/kg and that the effect of TDB was unquantifiable, save for the fact that addition of TDB does not elevate Cd levels above the limit of detection. It cannot be deduced whether this soil is within the Irish Regulations for use of sludge on land (SI 148 of 1998).

Illera *et al.* (2000) found that sewage sludge application increased Cd concentration in soils. This increase is due to the increase of extracted Cd in the first three chemical fractions (extractable, acid soluble and Fe/Mn oxide-carbonated).

Hooda and Alloway (1994) found that addition of sludge application containing 40 mg/kg Cd increased cad Cd levels in a sandy loam from 0.45 mg/kg to 2.05 at 50 t/ha sludge application, and to 5.66 mg/kg at 150 t/ha. They also found that addition of sludge application increased Cd levels in a Breckland sand from 0.12 mg/kg to 2.00 at 50 t/ha sludge application, and to 5.62 mg/kg at 150 t/ha.

Antoniadis and Alloway (2002) observed Cd increase from 0.37 mg/kg in a control soil to 0.44 mg/kg with 10t/ha addition of sewage sludge containing 0.32 mg/kg Cd, and a further increase to 0.69 mg/kg Cd with sludge application of 50 t/ha. From these figures, it can be observed that an elevated Cd level in sludge will result directly in an increased Cd level in soil, and that the increase will be proportional to the amount of Cd in the sludge. This author concludes that, even at 20 t/ha TDB application rate, this would not greatly increase Cd levels in the soil as levels within the biosolids are quite low.

Although various soil parameters can affect the availability of Cd, the total amount of the element present in the soil is one of the major factors affecting the Cd contents of plants. Sewage sludge is the most common source of relatively high concentrations of Cd in soils. The organic matter applied in the sewage sludge increases the metal absorbing capacity of the amended soil (Alloway, 1995a).

Table 4.20 Cadmium levels (mg/kg) in agricultural soil under different treatments

Treatment	A (mg/kg)	B (mg/kg)	C (mg/kg)
Holcus lanatus Trial pots	<1.65	<1.65	<1.65
Festuca rubra Trial pots	<1.65	<1.65	<1.65
Agrostis stolonifera Trial pots	<1.65	<1.65	<1.65

Treatment A- Agricultural soil, no amendment
Treatment B- Agricultural soil + TDB at 2 t/ha
Treatment C- Agricultural soil + TDB at 20 t/ha

Values in parentheses are standard deviation of mean of 9 samples

4.4.4. Chromium

Mean concentration of chromium in UK soils is approximately 34 mg/kg (Mc Grath, 1995). Agricultural soil concentrations of Cr with and without TDB addition were all below the limit of detection, < 41.3 mg/kg, and also below values quoted in the literature. Mc Grath (1998) found that mean Cr content in 295 Irish soil samples was 49.5 ± 26.7 mg/kg. The author found that 2 soil samples exhibited values above that stated in Irish law, 150 mg/kg (SI 148 of 1998) prohibiting application of sewage sludge.

Chromium in its trivalent state is stable in soils and has low availability (Illera *et al.*, 2000). In a study by this author, the application of sewage sludge, and municipal solid waste had no effect on total Cr content. The author concluded that this may be a result of low Cr availability in the wastes or application of the waste to soil surface, resulting in insufficient time passed for Cr to pass into the soil. Chromium in TDB was below the limit of detection for TDB samples <75 mg/kg.

4.4.5 Cobalt

Cobalt levels in agricultural soil under different treatments are displayed in Table 4.21. Cobalt content of soils varies considerably with an average content of between 10 mg/kg and 15 mg/kg (Smith and Paterson, 1995). Results obtained for unamended agricultural soil used in this study exhibit Co levels of on average 6.48 ± 1.3 mg/kg.

This result is slightly less than the national average quoted by Coulter *et al* (1999) of 7.4 mg/kg, although this source states that results ranged from 5.0 mg/kg to 10.4 mg/kg.

Average Co concentration in treatment B, TDB application at 2 t/ha, was 6.5 ± 0.9 mg/kg. The increase was not significantly different ($P>0.05$) from treatment A, and it can therefore be concluded that addition of TDB at 2 t/ha does not significantly increase Co concentration in agricultural soil.

However, average Co concentration in treatment C is 9.3 ± 3.5 mg/kg, resulting in treatment C being significantly different ($P<0.05$) from both treatment A and treatment B. Treatment C represents application of TDB at 20 t/ha and resulted in elevated levels of Co in agricultural soil.

Table 4.21 Cobalt levels (mg/kg) in agricultural soil under different treatments

Treatment	**A** (mg/kg)	**B** (mg/kg)	**C** (mg/kg)
Holcus lanatus Trial pots	7.12 (1.32)	6.18 (1.17)	6.01 (0.49)
Festuca rubra Trial pots	5.73 (1.68)	6.29 (0.84)	9.63 (4.1)
Agrostis stolonifera Trial pots	6.58 (0.08)	6.26 (0.98)	12.27 (1.6)

Treatment A- Agricultural soil, no amendment
Treatment B- Agricultural soil + TDB at 2 t/ha
Treatment C- Agricultural soil + TDB at 20 t/ha
Values in parentheses are standard deviation of mean of 9 samples

Cobalt is primarily required for the synthesis of vitamin B12 in the rumen of animals and deficiency is mainly a problem with sheep with cattle also being affected (Coulter *et al*., 1999).

4.4.6 Copper

Copper levels in agricultural soil under different treatments are displayed in Table 4.22. According to Mc Grath (1998), mean Cu in 295 Irish soil samples was 16.9 ± 9.6

mg/kg. Two of the samples analysed exceeded 50 mg/kg, the limit for Cu in soils which permits sewage sludge application.

TDB displayed values of 105 mg/kg DM, (Table 4.5). This figure is significantly lower than previous levels obtained in Irish sludges (Table 4.5). Total Cu in unamended agricultural soil in this study was below the national average of 16.9 mg/kg (Coulter *et al*, 1999). This source states that Irish soil values range between 3.8 mg/kg and 10.7 mg/kg Cu. Baker and Senft (1995) quote average Cu range for soils as between 20 mg/kg and 30 mg/kg. Copper concentration in treatment A, unamended soil was 22.3 ± 6.2 mg/kg. Fleming and Parle (1977) found Cu levels in an urban area ranging from 19 mg/kg to 145 mg/kg, with the normal range 5 to 60 mg/kg, the range into which the soil in this study falls. In contrast average Cu concentration, when TDB is applied at 2 t/ha in treatment B, was 19.9 ± 3.1 mg/kg, decreased from treatment A. Treatment C, application of TDB at 20 t/ha, exhibited Cu concentration greater than that of treatments A and B. Mean Cu concentration within this treatment was 25.8 ± 6.9 mg/kg. Although Cu concentration in agricultural soil under different treatments fluctuated slightly, however, it did not vary significantly ($P>0.05$) between the three treatments. As a result of the heterogeneous nature of the biosolids-soil mixture, fluctuations between samples and treatments will arise.

Hooda and Alloway (1994) found that Cu concentration in a sandy loam soil increased from 16.2 mg/kg to 60 mg/kg with the addition of 50 t/ha sludge containing 1031 mg/kg Cu to 132.5 m/kg with 150 t/ha of sludge. This trend has not been observed to the same extent in this study, although Cu levels in TDB were lower by a factor of ten than sludge used in the 1994 study containing mean Cu concentration of 1031 mg/kg. In addition, sludge application rates were greater in the study by Hooda and Alloway.

Illera *et al.* (2000) found the application of 80 t/ha of digested sewage sludge significantly increased the total Cu content in the soil, and also changed Cu distribution in the soil. It can be deduced from these results that at application rates of 2t/ha and 20 t/ha Cu levels in soil did not significantly ($P>0.05$) differ with application of biosolids containing 105 mg/kg Cu.

Table 4.22 Copper levels (mg/kg) in agricultural soil under different treatments

Treatment	**A** (mg/kg)	**B** (mg/kg)	**C** (mg/kg)
Holcus lanatus Trial pots	22.53 (5.03)	20.56 (2.29)	23.30 (9.16)
Festuca rubra Trial pots	19.76 (8.47)	19.43 (3.92)	23.80 (5.35)
Agrostis stolonifera Trial pots	24.53 (6.27)	19.61 (3.99)	30.22 (5.55)

Treatment A- Agricultural soil, no amendment
Treatment B- Agricultural soil + TDB at 2 t/ha
Treatment C- Agricultural soil + TDB at 20 t/ha
Values in parentheses are standard deviation of mean of 9 samples

4.4.7 Lead

Lead levels in agricultural soil under different treatments are displayed in Table 4.23. Mc Grath (1998) analysed 295 Irish soil samples and found mean Pb concentration of 30.4 ± 15.2 mg/kg. The author also found 30 samples exceeding 50 mg/kg Pb, the maximum allowable for application of sewage sludge.

Lead concentration in uncontaminated soils varies considerably although Davies (1995) states that in England and Wales, normal surface concentration varies between 15 and 106 mg/kg with mean of a 42 mg/kg. TDB used in this study contained on average 84 mg/kg Pb (Table 4.5).

Treatment A, unamended soil, exhibited Pb concentrations of 20 ± 3.5 mg/kg. This falls within the normal range for soils in an Irish urban area of 10 mg/kg to 70 mg/kg quoted by Fleming and Parle (1977), but slightly lower than the national average of 30 mg/kg found by McGrath (1998). The addition of TDB resulted overall in only a slight increase in Pb concentration, which was not significantly different ($P>0.05$) to that of treatment A. Mean Pb concentration in treatment B was 20.3 ± 2.02 mg/kg. In contrast, with the application of 20 t/ha TDB in treatment C, Pb concentration increased to 23.7 ± 3.3 mg/kg and was significantly greater ($P<0.05$) than treatment A and treatment B.

Hooda and Alloway (1995) found that the application of sludge containing on average 706 mg/kg Pb increased Pb levels in a sandy loam soil containing 53.1 mg/kg prior to sludge application. Addition of 50 t/ha increased Pb concentration to 77.1 mg/kg and to 131.8 mg/kg with addition of 150t/ha.

Illera *et al.* (2000) found that one year after 80 t/ha sewage sludge application, total Pb concentration in soil increased by 37%. This study found application of TDB containing only 84 mg/kg Pb did not significantly ($P>0.05$) increase Pb levels in soil at 2 t/ha, however a significant increase ($P<0.05$) was noted with an application rate of 20 t/ha.

Table 4.23 Lead levels (mg/kg) in agricultural soil under different treatments

Treatment	**A** (mg/kg)	**B** (mg/kg)	**C** (mg/kg)
Holcus lanatus Trial pots	19.35 (0.88)	21.62 (2.05)	26.80 (3.47)
Festuca rubra Trial pots	17.26 (3.51)	19.01 (1.29)	21.94 (0.41)
Agrostis stolonifera Trial pots	23.42 (2.85)	20.23 (2.3)	22.33 (2.85)

Treatment A- Agricultural soil, no amendment
Treatment B- Agricultural soil + TDB at 2 t/ha
Treatment C- Agricultural soil + TDB at 20 t/ha
Values in parentheses are standard deviation of mean of 9 samples

4.4.8 Manganese

Manganese levels in agricultural soil under different treatments are displayed in Table 4.24. Total Mn concentration in the unamended agricultural soil used in this study ranged from 684 mg/kg to 754 mg/kg, averaging 709.9 mg/kg. According to Smith and Paterson (1995), the normal range of Mn in soils is 20 mg/kg to 10,000 mg/kg, with critical concentrations between 1500 and 3000 mg/kg. The addition of 2 t/ha of TDB to the substrate increased total Mn in the soil (Table 4.24). Total Mn concentration at 2 t/ha was significantly higher ($P<0.05$) than the control soil with levels ranging from 695 mg/kg to 748 mg/kg. Significantly higher ($P<0.05$) Mn levels were observed when sludge addition rate was 20 t/ha in comparison with the control and with the 2 t/ha treatments. At the 20 t/ha application rate, total Mn levels of 736 mg/kg to 763 mg/kg were recorded.

Table 4.24 Manganese levels (mg/kg) in agricultural soil under different treatments

Treatment	A (mg/kg)	B (mg/kg)	C (mg/kg)
P.pratensis Trial pots	715.53 (33.67)	739.90 (24.60)	754.47 (34.39)
L.perenne Trial pots	692.54 (4.66)	694.88 (16.37)	736.22 (17.03)
H.lanatus Trial pots	705.30 (9.04)	733.61 (15.55)	740.76 (24.05)
F.rubra Trial pots	745.49 (17.74)	748.14 (20.36)	763.63 (29.50)
A.stolonifera Trial pots	716.33 (1.23)	720.32 (45.85)	743.41 (20.95)
T. repens Trial pots	684.00 (17.35)	716.30 (15.45)	736.36 (12.48)

Treatment A- Agricultural soil, no amendment
Treatment B- Agricultural soil + TDB at 2 t/ha
Treatment C- Agricultural soil + TDB at 20 t/ha

Values in parentheses are standard deviation of mean of 9 samples

In some Irish soils, herbage levels of Co may be low as a result of high Mn levels, and a substantial quantity of Irish soils have Mn levels greater than 500 mg/kg (Coulter *et al.*, 1999). Walker *et al.* (2003) found total Mn levels of 1600mg/kg in a 'murcia' soil close to an old Pb/Zn mine in the Spanish province of Murcia. In the same study, an agricultural soil from the Valencia region, high in both Cu and Pb exhibited levels of 341 mg/kg Mn.

4.4.9 Mercury

All agricultural soil samples analysed for Hg in this study were below the determination limit of 1.32 mg/kg for soil samples. The normal range for mercury in soils is 0.01 to 0.5 mg/kg, with critical soil levels of 0.3 to 5 mg/kg (Steinnes, 1995).

4.4.10 Molybdenum

Molybdenum levels in agricultural soil under different treatments are displayed in Table 4.25. Molybdenum concentration in TDB was 7.13 mg/kg.

Table 4.25 Molybdenum levels (mg/kg) levels in agricultural soil under different treatments

Treatment	**A** (mg/kg)	**B** (mg/kg)	**C** (mg/kg)
Holcus lanatus	2.36 (0.73)	4.28 (0.9)	3.6 (0.33)
Festuca rubra	2.88 (0.56)	3.89 (0.60)	3.76 (0.79)
Agrostis stolonifera	3.94 (0.63)	4.18 (0.61)	3.54 (0.93)

Treatment A- Agricultural soil, no amendment
Treatment B- Agricultural soil + TDB at 2 t/ha
Treatment C- Agricultural soil + TDB at 20 t/ha
Values in parentheses are standard deviation of mean of 9 samples

Unamended soil in treatment A contained mean Mo concentration of 2.94 ± 0.98 mg/kg. With the addition of TDB at 2 t/ha in treatment B this increased to 4.12 ± 0.65 mg/kg. Therefore, Mo concentration was significantly greater ($P<0.05$) in soil when TDB was applied at 2t/ha. Treatment C, however, had a lower mean Mo concentration, 3.6 ± 0.64 mg/kg, than treatment B. This value was not statistically different ($P>0.05$) to treatment, A or B.

4.4.11 Nickel

Nickel levels in agricultural soil under different treatments are displayed in Table 4.26. Average Ni concentration in world soils is approximately 20 mg/kg but varies widely with soil type (Mc Grath, 1995). Mc Grath (1998) found mean Ni concentration in Irish soils of 13.5 ± 12.5 mg/kg. Fourteen samples had values greater than 30 mg/kg, prohibiting the use of sewage sludge on such soils. Nickel concentration in unamended agricultural soil was on average 29.8 ± 5.25 mg/kg. This represented treatment A, a slightly higher concentration than that stated by Mc Grath (1998) in Irish soils. A number of soil samples analysed were above the limit set in SI 148 of 1998 prohibiting use of sludge on land. Treatment B, addition of TDB at 2t/ha increased mean Ni concentration to 30.6 ± 5.1 mg/kg, this increase however, was not significant ($P>0.05$). Application of 20 t/ha TDB increased mean soil concentration of Ni to 40.3 ± 13.8 mg/kg. Therefore, the application of 20 t/ha TDB significantly increased ($P<0.05$) Ni concentration in a brown podsol. Nickel concentration in TDB was 32 mg/kg.

Table 4.26 Nickel levels (mg/kg) in agricultural soil under different treatments

Treatment	**A** (mg/kg)	**B** (mg/kg)	**C** (mg/kg)
Holcus lanatus	29.56 (2.18)	30.32 (3.72)	29.24 (4.05)
Festuca rubra	26.99 (8.74)	32.98 (7.99)	44.31 (20.31)
Agrostis stolonifera	33.00 (1.28)	28.49 (3.23)	47.24 (6.92)

Treatment A- Agricultural soil, no amendment
Treatment B- Agricultural soil + TDB at 2 t/ha
Treatment C- Agricultural soil + TDB at 20 t/ha
Values in parentheses are standard deviation of mean of 9 samples

Antoniadis and Alloway (2002) observed an increase in Ni concentration from 12.47 mg/kg in a control soil to 13.01 mg/kg with 10 t/ha addition of sewage sludge containing 30.56 mg/kg Ni, and an increase of 15.05 mg/kg Ni with sludge application of 50 t/ha. These increases were significantly ($P<0.05$) higher in the sludge amended soils. These results are similar to those found in this study where Ni concentration in TDB was 31.94 mg/kg. On application of 50 t/ha of sludge to a sandy loam soil, Hooda and Alloway (1994) observed an increase in Ni concentration from 16.7 mg/kg to 27.0 mg/kg. Application of 150 t/ha resulted in a further increase to 45.2 mg/kg. Similar increases were noted on a breckland soil by the same authors, however in this case, Ni concentration in sludge was 259 mg/kg.

Illera *et al.* (2000) states that waste material application, did not affect significantly the total Ni concentration of soil, and that this confirms the low availability of Ni in waste materials (sewage sludge and municipal solid waste) in the short term. This was also observed for Cr.

4.4.12 Selenium

All agricultural soil samples analysed were below the limit of determination for the element Se which was <6.58 mg/kg. Consequently, differences, if any between treatments cannot be determined. It is also impossible to determine from these results if Se concentration is within the normal range for soils 0.01 to 5 mg/kg (Alloway, 1995b).

4.4.13 Zinc

Zinc levels in agricultural soil under different treatments are displayed in Table 4.27. Total elemental Zn content of the brown podsol used in this study ranged from 72.27 mg/kg to 74.48 mg/kg without any amendment. These figures fall within the normal range of 25 mg/kg to 200 mg/kg Zn levels in an Irish urban environment stated by Fleming and Parle (1977). Mc Grath (1998) quotes average Zn concentration in 295 Irish soil samples of 70.3 ± 35.6 mg/kg, of which 4 samples are greater than 150 mg/kg, prohibiting the use of sewage sludge on these soils. Bhogal *et al.* (2003) found levels of 86 mg/kg Zn in a sandy loam textured soil at Rosemaund, Herefordshire. Hooda and Alloway (1994) found total Zn concentration of 58.2 mg/kg of a sandy loam agricultural soil from south eastern England.

Addition of TDB at 2 t/ha increased total Zn levels in all trials. Zinc content of agricultural soil plus amendments is displayed in Table 4.27. Zinc levels in the substrate amended with 2 t/ha of TDB were significantly higher ($P>0.05$) than those of the control soil and ranged from 75.8 to 79.7 mg/kg Zn.

Antoniadis and Alloway (2002) found Zn concentration to be significantly higher ($P<0.05$) in the soil treated with sludge. The control soil exhibited Zn concentration of 32.08 mg/kg. This increased to 39.15 on addition of 10 t/ha sewage sludge, and to 66.75 on addition of sludge at 50 t/ha. Zinc concentration in sludge was 512.28 mg/kg, which was high in comparison with TDB containing 245 mg/kg Zn.

Table 4.27 Zinc levels (mg/kg) in agricultural soil under different treatments

Treatment	A (mg/kg)	B (mg/kg)	C (mg/kg)
P.pratensis	73.67 (3.86)	77.58 (1.13)	88.06 (6.84)
L.perenne	73.24 (2.17)	77.86 (7.55)	83.94 (5.00)
H.lanatus	72.27 (3.71)	75.80 (3.36)	82.89 (6.45)
F.rubra	73.75 (8.78)	77.85 (3.96)	79.62 (1.02)
A.stolonifera	72.66 (0.87)	79.72 (3.61)	80.12 (2.10)
T. repens	74.48 (0.67)	77.32 (2.9)	85.80 (0.91)

Treatment A- Agricultural soil, no amendment
Treatment B- Agricultural soil + TDB at 2 t/ha
Treatment C- Agricultural soil + TDB at 20 t/ha
Values in parentheses are standard deviation of mean of 9 samples

Addition of TDB to the agricultural brown podsol at 20 t/ha resulted in elevated Zn concentrations that were statistically higher ($P>0.05$) than both the control soil and the 2 t/ha treatment. Zinc levels in soil with 20 t/ha TDB incorporated ranged from 79.6 mg/kg to 88.1 mg/kg. It can therefore be stated that addition of TDB with Zn concentration of 245 mg/kg significantly increased Zn levels in an agricultural soil at both 2t/ha and 20 t/ha.

Illera *et al.* (2000) found that total Zn concentration in soils increased from 91.5 mg/kg in the control soil to 121.8 mg/kg in soil treated with 80 t/ha of digested sewage sludge. Hooda and Alloway (1994) observed an increase in total Zn concentration from 59.7 mg/kg in a sandy loam soil, to 117.2 with addition of anerobically digested sludge at 50 t/ha and a further increase to 226.4 mg/kg at an application rate of 150 t/ha.

4.5 Mine tailings elemental composition

4.5.1 Arsenic

Arsenic levels in Silvermines tailings under different treatments are displayed in Table 4.38. DAFRD (2000) report a mean As value in Silvermines tailings of 503 mg/kg. However, in a later report SRK (2002) state that As in tailings is on average 733 mg/kg. DAFRD (2000) also state that As in mine tailings is in the range 110 to 1,060 mg/kg. This study obtained As values of on average 640.66 ± 14.56 mg/kg. Addition of TDB to mine tailings caused a significant ($P<0.05$) decrease in As concentration in tailings. Addition of 20 t/ha caused As levels to decrease to 417.7 mg/kg, and to 389.33 mg/kg on addition of TDB at 50 t/ha (Graph 4.25). Soil As toxicity threshold concentration to crop plants is 40 mg/kg in sandy soils (Visoothiviseth *et al.*, 2002), compared to 400 mg/kg for clays (O'Neill, 1995). These levels are exceeded in Silvermines tailings. This source also states that in soils with As concentrations exceeding normal background levels the As availability is more influenced by soil texture and pH rather than total As concentration. In addition, Fe content is said to have a strong negative influence on As availability as it strongly adsorbs As. This may have an effect on As availability in this study, as total Fe content in unamended tailings is on average 97,102 ± 4409 mg/kg.

Table 4.28 Metal levels (mg/kg) in un-amended mine tailings, treatment F.

Element	mg/kg
Arsenic	640.66 (14.56)
Cadmium	33.74 (4.09)
Cobalt	7.75 (1.21)
Copper	260.0 (38.6)
Lead	10,484 (494)
Nickel	65.96 (3.26)
Zinc	7499.9 (727.4)

Values in parenthesis are the standard deviation of the mean of 18 samples

Table 4.29 Arsenic content (mg/kg) of mine tailings under different treatments

Treatment	D	E
Holcus lanatus	408.35 (227.33)	376.47 (208.16)
Festuca rubra	373.52 (216.04)	387.50 (160.99)
Agrostis stolonifera	469.56 (182.86)	404.03 (172.38)

Treatment D Tailings + TDB at 20 t/ha
Treatment E- Tailings + TDB at 50 t/ha
Values in parentheses are standard deviation from mean of 9 samples

4.5.2 Boron

All tailings samples analysed for boron were below the limit of detection, 61.1 mg/kg. Due to this, comparison of unamended and TDB treated tailings for Bo concentration cannot be made. Boron levels in agricultural soil were also below this limit of 61 mg/kg, although it cannot be determined if elevated Bo levels exist on tailings compared with agricultural soil.

4.5.3 Cadmium

Cadmium levels in Silvermines tailings under different treatments are displayed in Table 4.30 and Graph 4.2. The Cd concentration in mine tailings from Silvermines tailings contained on average 33.74 ± 3.7 mg/kg in treatment F, no amendment. This value is greater than that obtained by DAFRD (2000) who noted that Cd content of Silvermines tailings is on average 22.5 mg/kg. This value is again higher than that stated by SRK (2002), 17 mg/kg Cd in the tailings.

Table 4.30 Cadmium content of mine tailings (mg/kg)

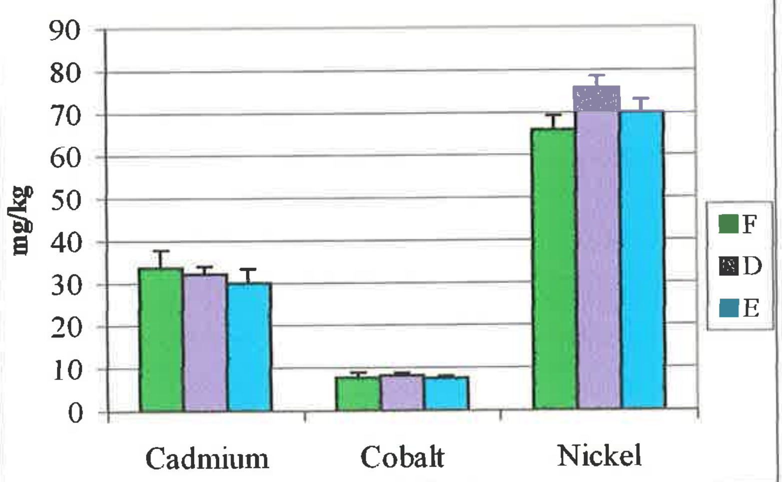
Treatment	D	E
Holcus lanatus	33.18 (1.50)	29.71 (4.26)
Festuca rubra	30.52 (0.43)	29.55 (1.94)
Agrostis stolonifera	32.82 (1.99)	32.17 (0.15)

Treatment D- Tailings + TDB at 20 t/ha
Treatment E- Tailings + TDB at 50 t/ha
Values in parentheses are standard deviation from mean of 9 samples

Addition of TDB at 20 t/ha decreased Cd levels to 32.17 ± 1.8 mg/kg. However, this decrease was not statistically significant (P>0.05). Further TDB application at 50 t/ha caused Cd levels to decrease to 30.16 ± 2.9 mg/kg. Again, this decrease was not significant (P>0.05).

Interestingly, Ye *et al.* (2001) observed similar decreases in tailings Cd concentration with the addition of sludge on addition of 25% (V/V) from 35 mg/kg to 31 mg/kg. Further decreases noted on addition of 50% and 75% sludge to 19 mg/kg and 14 mg/kg Cd respectively. Therefore, total Cd in tailings substrate was decreased with increased sludge application rate both in this study and the greenhouse study by Ye *et al.* (2001).

Graph 4.2. Mean cadmium, cobalt and nickel concentration in mine tailings substrate



Treatment F – unamended tailings
Treatment D Tailings + TDB at 20 t/ha
Treatment E- Tailings + TDB at 50 t/ha

4.5.4 Chromium

All tailings samples analysed for Cr were below the limit of detection, 82.56 mg/kg. Therefore, no comparison of Cr levels in tailings and its amendments were carried out.

4.5.5 Cobalt

Cobalt levels in Silvermines tailings under different treatments are displayed in Table 4.31. Average Co concentration in Silvermines tailings without amendment was found to be 7.75 ± 1.21 mg/kg. This increased slightly to 8.2 mg/kg on addition of 20 t/ha TDB, and decreased below the unamended concentration on addition of 50 t/ha to 7.56

mg/kg. Differences in Co concentration between treatments were slight and not statistically significant ($P>0.05$). Although a soil may be relatively high in total Co, fixation by Mn oxides may result in poor availability of the element to plants. Manganese concentration in unamended Silvermines tailings is on average 2259 ± 187.1 mg/kg.

Table 4.31 Cobalt content (mg/kg) of mine tailings under different treatments

Treatment	D	E
Holcus lanatus	8.75 (0.14)	7.78 (0.63)
Festuca rubra	8.13 (0.18)	7.45 (0.37)
Agrostis stolonifera	7.71 (0.77)	7.50 (0.3)

Treatment D-Tailings + TDB at 20 t/ha
Treatment E- Tailings + TDB at 50 t/ha
Values in parentheses are standard deviation from mean of 9 samples

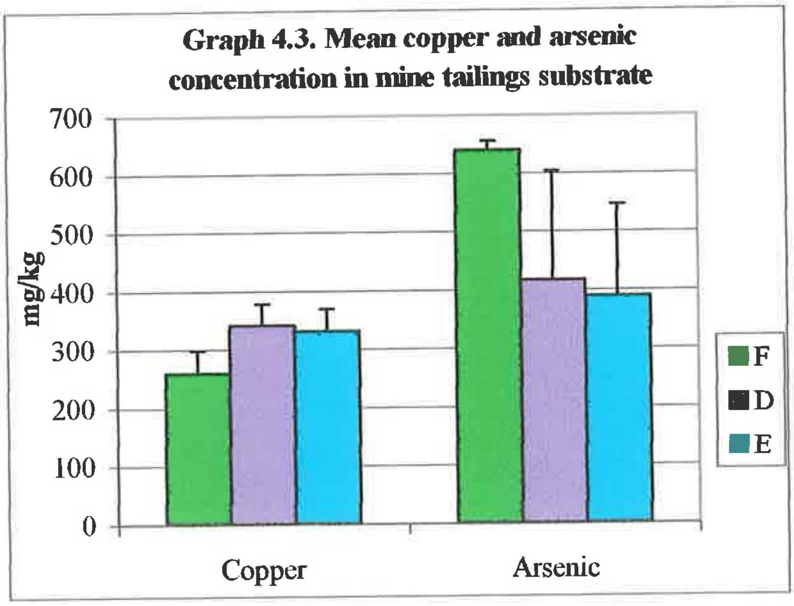
4.5.6 Copper

Copper levels in Silvermines tailings under different treatments are displayed in Table 4.32. The chemistry of Cu in soils is similar to that of Pb in that they are both specifically adsorbed or fixed in soils (Baker and Senft, 1995). Copper levels of 259.96 ± 35.6 mg/kg found in unamended mine tailings in this study were similar to those found elsewhere in the literature. Levels of Cu were found in tailings in this study are similar to those found by DAFRD (2000) who report an average figure 272 mg/kg within a range of 150.3 mg/kg and 395.6 mg/kg. However, SRK (2002), claim levels of only 143 mg/kg Cu were found in Silvermines tailings. It can be stated, however, that the Silvermines Tailings Management Facility does not contain tailings of uniform composition or characteristics, therefore, element concentrations will vary depending on where samples are obtained on the tailings. Addition of TDB at 20 t/ha increased Cu concentration in the substrate to 332.32 ± 36.9 mg/kg. However, at 50t/ha no further increase was noted. Copper concentration in this treatment was 331.39 ± 35.31 mg/kg. Whilst the addition of TDB did significantly increase ($P<0.05$) Cu concentration in the substrate (Graph 4.3), no significant difference was noted with the increased biosolids application rate. The concentration of Cu in TDB was 105.6 mg/kg. This result exhibits a similar trend to that found by Ye *et al.* (2001) where total Cu concentration increased in mine tailings substrata with the addition of sludge, containing 607 mg/kg Cu, although they found further increases with increasing sludge addition.

Table 4.32 Copper content (mg/kg) of mine tailings under different treatments

Treatment	D	E
Holcus lanatus	334.79 (35.10)	319.05 (51.09)
Festuca rubra	367.64 (31.58)	340.72 (28.96)
Agrostis stolonifera	314.57 (29.51)	343.91 (35.92)

Treatment D- Tailings + TDB at 20 t/ha
Treatment E- Tailings + TDB at 50 t/ha
Values in parentheses are standard deviation from mean of 9 samples



Treatment F – unamended tailings
Treatment D Tailings + TDB at 20 t/ha
Treatment E- Tailings + TDB at 50 t/ha

4.5.7 Lead

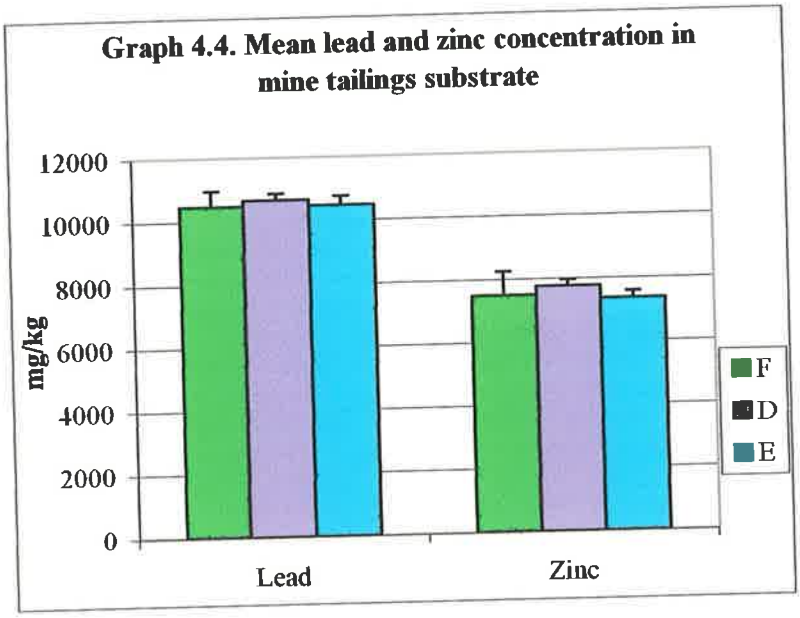
Lead levels in Silvermines tailings under different treatments are displayed in Table 4.33. As with Cu, Pb levels vary in Silvermines tailings, resulting in many different values quoted in the literature. Average Pb concentration found in Silvermines tailings in this study was 10,484 ± 275 mg/kg. DAFRD (2000), state that Pb levels in Silvermines tailings is on average 9924 mg/kg ranging from 8154 to 11,694 mg/kg, whilst SRK (2002) state a higher Pb concentration of on average 11,642 mg/kg. Given that Silvermines was a Pb/Zn mine and that the grade of metallurgical ore varied between 1% and 20% Pb, and that recovery rates varied from 50% to 95% then the Pb content in the tailings should vary widely (Grennan, 2003).

Table 4.33 Lead (mg/kg) content of mine tailings under different treatments

Treatment	D	E
P.pratensis	10,612 (317)	10,545 (917)
L.perenne	10,588 (191)	10,616 (296)
H.lanatus	10,698 (108)	10,273 (947)
F.rubra	10,935 (240)	10,505 (647)
A.stolonifera	10,797 (160)	10,875 (431)
T. repens	10,345 (384.0)	10,085 (387)

Treatment D- Tailings + TDB at 20 t/ha
Treatment E- Tailings + TDB at 50 t/ha
Values in parentheses are standard deviation from mean of 9 samples

The application of TDB at 20 t/ha in treatment D resulted in an increase in Pb concentration to 10,663 ± 184 mg/kg, although this increase was not statistically significant ($P>0.05$). Application of TDB at 50 t/ha resulted in a lower Pb level, similar to that of unamended tailings in treatment F, 10,483 ± 251 mg/kg. Again, this was not a significant difference from either Treatments F or D. It is suggested that Pb concentration initially increased as a result of biosolids addition. However, on a higher rate of addition, the dilution effect (Ye *et al.*, 2001) when sludge was mixed with tailings caused a reduction in the inherently high Pb content in the tailings (Graph 4.4). Ye *et al.* (2001) found that sludge amendment reduced total Pb, Cd and Zn contents in tailings. These authors attribute this reduction to the role of chelation, complexation, and adsorption between metals in tailings and organic matter in sludge, in addition to a dilution effect.



Treatment F – unamended tailings
Treatment D Tailings + TDB at 20 t/ha
Treatment E- Tailings + TDB at 50 t/ha

4.5.8 Mercury

All tailings samples analysed for Hg were below the limit of detection, 8.26 mg/kg. Critical soil concentration of Hg is 0.3 to 5 mg/kg (Alloway, 1995b), therefore, it is impossible to determine if tailings levels of Hg are within normal or critical range. Results do not allow a comparison of Hg levels between treatments to be made.

4.5.9 Molybdenum

All tailings samples analysed for Mo were below the limit of detection 8.26 mg/kg. As with Hg, one cannot determine whether Mo in tailings is within a normal or critical range or what fluctuations if any exist between treatments.

4.5.10 Nickel

Nickel levels in Silvermines tailings under different treatments are displayed in Table 4.34. Nickel concentration in unamended Silvermines tailings was found to be 65.96 ± 3.26 mg/kg. On addition of 20 t/ha TDB, this increased to 75.65 ± 2.5 mg/kg, a significant increase ($P<0.05$) on the unamended tailings. With the addition of 50 t/ha, as for the other metals analysed, Ni concentration was significantly greater than for treatment F, unamended tailings, although not significantly different from the 20 t/ha treatment. In the case of Ni, this was displayed by a reduction in Ni concentration in Treatment E, although a greater concentration of Ni was maintained for the tailings control. As was the case with Pb, this could possibly be attributed either to the dilution effect of TDB, or to the complexing effect of TDB on Ni. Concentration of Ni in TDB was 31.94 mg/kg. Walter *et al.* (2002) observed total Ni concentration increase from 13.0 mg/kg to 16.7 mg/kg after initial application of biosolids at 50 t/ha. However, following this, they observed a decrease in Ni concentration during subsequent years. Although Silvermines tailings are primarily Pb/Zn tailings, according to Mc Grath (1995), a soil with Ni or Cr concentration > 70 mg/kg can be deemed as contaminated by these elements. Therefore, Silvermines tailings can be included in this category.

Table 4.34 Nickel content (mg/kg) of mine tailings under different treatments

Treatment	D	E
Holcus lanatus	76.73 (3.32)	70.08 (4.26)
Festuca rubra	76.94 (1.42)	71.57 (3.46)
Agrostis stolonifera	73.27 (1.16)	70.28 (2.83)

Treatment D Tailings + TDB at 20 t/ha
Treatment E- Tailings + TDB at 50 t/ha
Values in parentheses are standard deviation from mean of 9 samples

4.5.11 Selenium

All tailings samples analysed for Se were below the limit of detection 33.03 mg/kg. As results were less than the limit of detection, no comparisons could be drawn from results of different treatments. It could not be determined if Se levels in tailings were within the normal range in soil of 0.1 to 5 mg/kg (Alloway, 1995b).

4.5.12 Zinc

Zinc levels in Silvermines tailings under different treatments are displayed in Table 4.35. Total Zn in unamended mine tailings measured on average, 7499.9 ± 727 mg/kg. Mine tailings Zn levels are displayed in Table 4.44. DAFRD (2000) quote a mean Zn level of 7459 mg/kg in Silvermines tailings. The range of Zn levels quoted by this source is between 7046 mg/kg and 7872 mg/kg. According to SRK (2000), mean total

Zn concentration in Silvermines tailings is 4563 mg/kg, which is notably lower than the values obtained in this study.

Table 4.35 Zinc content (mg/kg) of mine tailings under different treatments

Treatment	D	E
P.Pratensis	7913 (502)	7470 (1009)
L.perenne	7684 (140)	7342 (480)
H.lanatus	8018 (259)	7183 (574)
F.rubra	7573 (110)	7198 (368)
A.stolonifera	7789 (102)	7726 (288)
T. repens	7521 (231)	7144 (907)

Treatment D- Tailings + TDB at 20 t/ha
Treatment E- Tailings + TDB at 50 t/ha
Values in parentheses are standard deviation from mean of 9 samples

Application of TDB to mine tailings at a rate of 20 t/ha increased total Zn levels in all trials. Zinc levels at this application rate were on average 7749.4 ± 193.89 mg/kg. However, as with Pb, these were not significantly ($P>0.05$) higher than the control levels. TDB was also applied at a rate of 50 t/ha. Total Zn levels in this treatment were 7343.6 ± 223.09 mg/kg, slightly less than in treatment D. This figure was not significantly higher ($P>0.05$) than in unamended tailings. Again, this is being attributed to the dilution effect and, therefore, to a reduction in toxicity as described by Ye *et al.* (1999; 2001). Bergholm and Steen (1989) also observed a decrease in Pb and Zn concentration following the addition of sludge to Zn tailings. Studies have found that although total metals levels of Zn (Mc Nearny and Belyaeva, 1998), Pb, Cd and Cu initially increased following sewage sludge application (Seaker, 1991; Walter *et al.*, 2002), they declined over time, usually within the 5 years following biosolids application (Walter *et al.*, 2002).

4.6 Shoot height

4.6.1 Shoot height of species on agricultural soil

The addition of TDB at 2 t/ha did not result in any significant difference ($P>0.05$) in the shoot height of grasses compared with treatment A. However, a significant increase was observed at 20 t/ha ($P<0.05$), when compared with shoot height of grass species on the control soil. This was the case for all grass species. The clover species *Trifolium repens* did not display any significant differences in shoot height among treatments.

Growth of *Poa pratensis* on agricultural soil was enhanced by the addition of TDB at 2 t/ha (treatment B), and greatly enhanced by the addition of TDB at 20 t/ha (treatment C) (Graph 4.5). Maximum shoot height was achieved by treatment C. *Poa pratensis* grown on agricultural soil without amendment (treatment A) reached an average maximum height of 127 mm. This compared with 132 mm and 243 mm on average for TDB additions of 2 t/ha and 20 t/ha respectively. Shoot height was significantly higher ($P<0.05$) in treatment C than in both A and B, however A and B were not significantly different ($P>0.05$).

Shoot height of *Lolium perenne* on agricultural soil was lower over the growth period than *Poa pratensis* (Graph 4.6). Addition of TDB at 2 t/ha increased shoot height from 92 mm to 110 mm after 12 weeks, although not significantly ($P>0.05$), however the effect of 20 t/ha TDB addition was greater, with shoot height 165 mm after 12 weeks. Shoot height was significantly higher ($P<0.05$) than both A and B at this application rate.

Graph 4.7 shows growth rate for *Holcus lanatus* growing on agricultural soil when TDB was applied at both application rates (Plate 4.1), the increase was only significant ($P<0.05$) at 20 t/ha compared with the other treatments. Average shoot height was 138 mm, 167 mm and 235 mm for agricultural soil alone, with TDB at 2 t/ha and with TDB at 20 t/ha respectively.

Plate 4.1 *Holcus lanatus* on agricultural soil treatments A, B and C.

Festuca rubra exhibited a similar trend to *Poa pratensis* when grown on agricultural soil alone and with TDB additions. Shoot height was 132 mm, 150 mm and 247 mm for agricultural soil alone, with 2 t/ha TDB and with 20 t/ha TDB addition respectively (Graph 4.8). Treatment C was significantly higher ($P<0.05$) than treatment A, no other statistical differences were found. When grown on agricultural soil alone and soil treated with 2 t/ha TDB *A. stolonifera* displayed a similar growth pattern and shoot height throughout (Graph 4.9). Application of 20 t/ha TDB however, significantly increased ($P<0.05$) shoot height in comparison with both treatment A and B (Plate 4.2). Shoot height was on average 203 mm in treatment C, compared with 115 mm in treatment A and 118 mm in treatment B.

Plate 4.2 *Agrostis stolonifera* on agricultural soil treatment A, B and C.

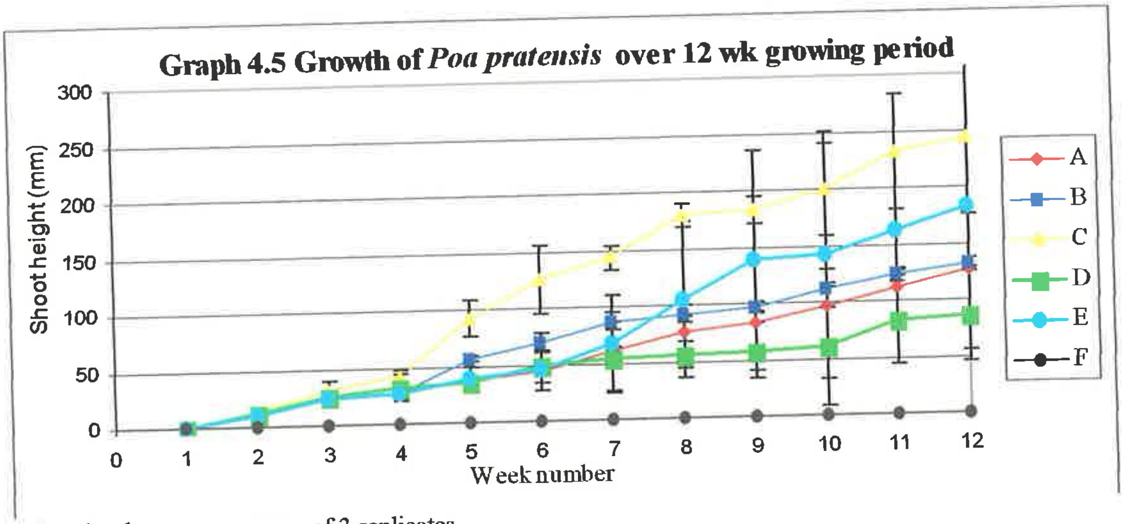
Trifolium repens displayed good growth on the control with 20 t/ha TDB application, similar results were obtained from agricultural soil alone, and with 2 t/ha TDB. Maximum shoot height of 177 mm was obtained at the 20 t/ha application, compared with 122 mm at 2 t/ha and 117 mm in the control (Graph 4.10). Addition of TDB did not result in any significant difference (P>0.05) of *Trifolium repens* on agricultural soil.

4.6.2 Shoot height of species on mine tailings

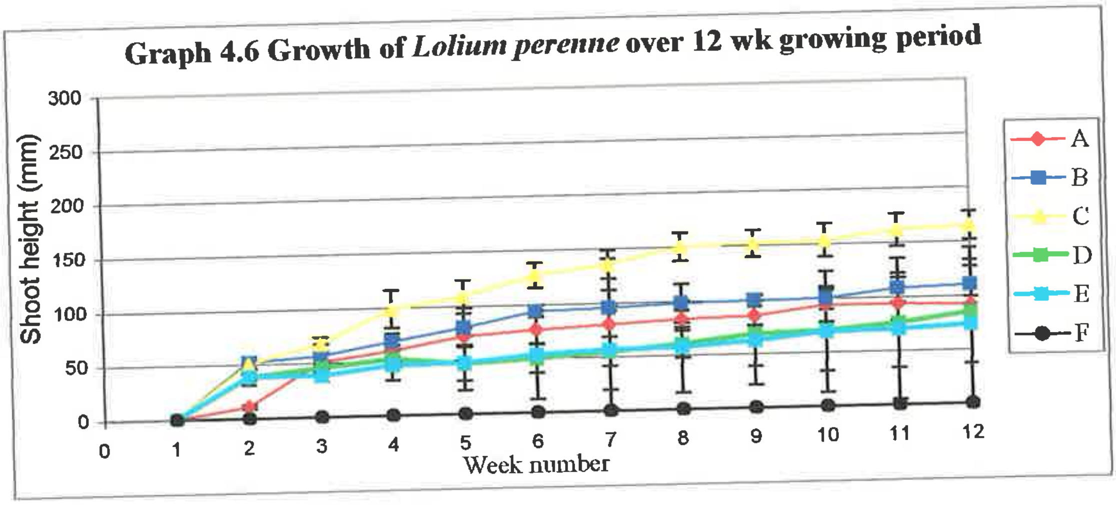
Statistical analysis on mine tailings treatments concluded that differences between treatment E and F were not significant (P>0.05). Therefore although application of TDB resulted in the establishment of grass on tailings, an increased rate of TDB application did not significantly increase shoot height in any species over the growth period.

Graph 4.5 also displays growth measurements of *Poa pratensis* on mine tailings. No seedling emergence took place on mine tailings alone: treatment F (Plate 4.3). It is thought that germination of seeds on tailings was prevented by the poor physical structure of the tailings. Johnson *et al.* (1994) state that vegetation establishment on mine waste is always difficult. Mine wastes lack organic matter and suitable micro-organisms, therefore minimal aggregation of particles occurs and the material lacks structure. Also, optimum plant growth medium contains a mixture of particle sizes (Williamson *et al.*, 1982), not coherent with mine tailings. In addition, the inability of tailings to retain moisture was a major factor in the non-emergence of seedlings.

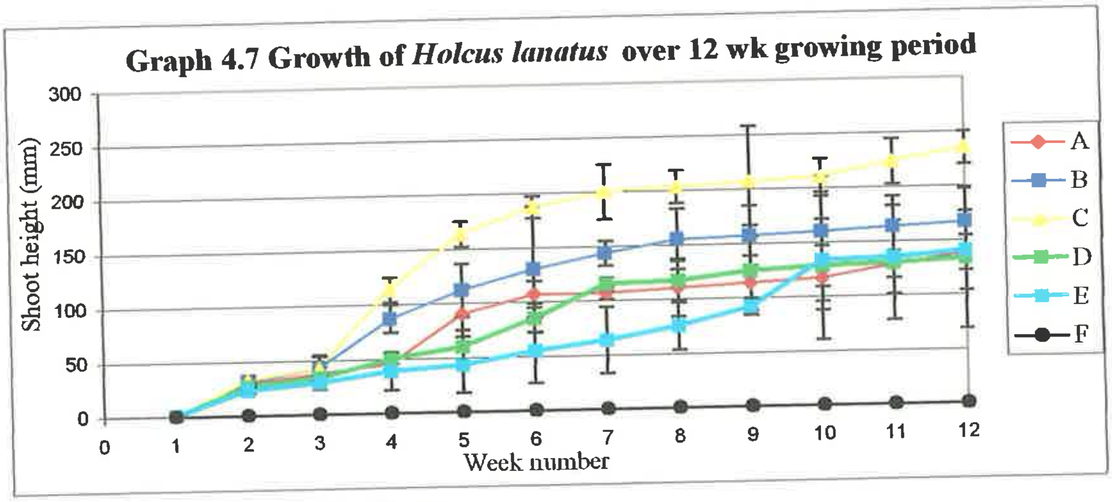
Plate 4.3 Poor germination of seeds on treatment F, tailings alone.



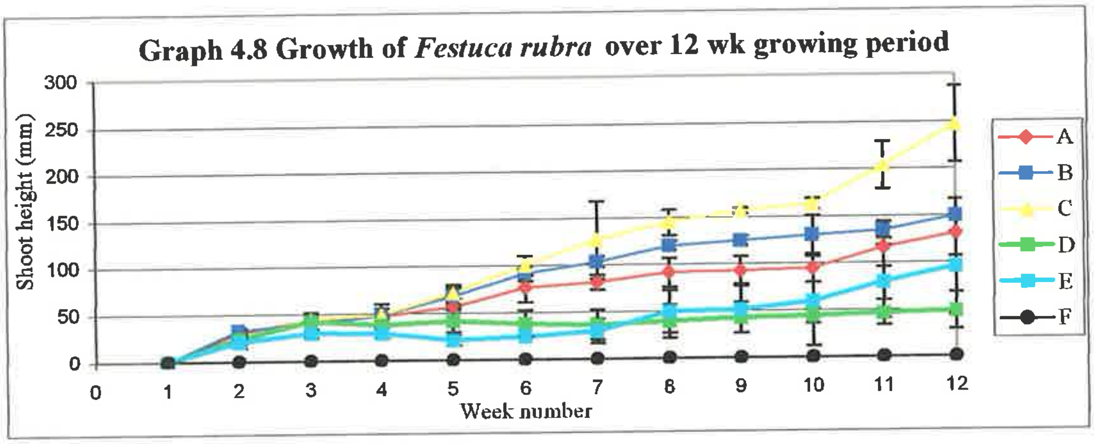
* Results shown are average of 3 replicates.



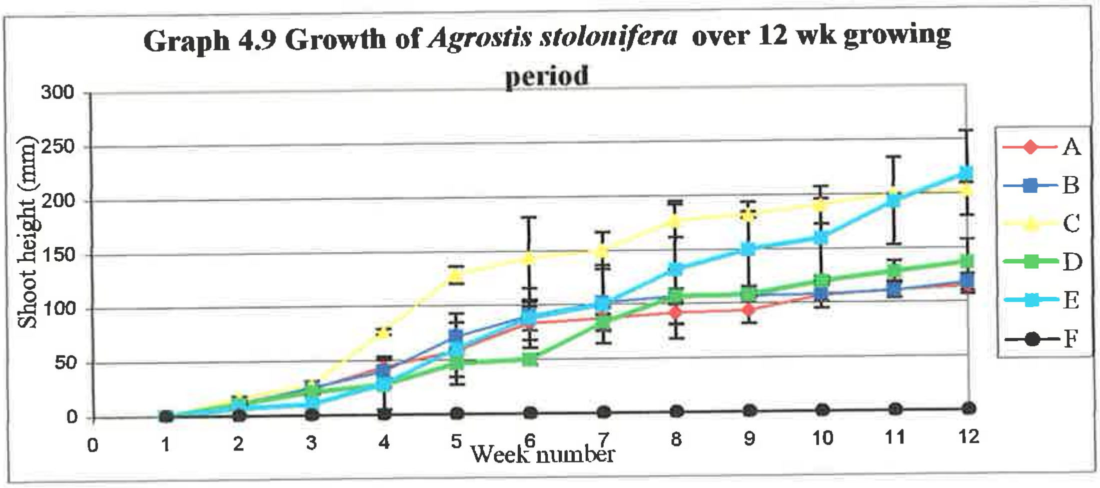
* Results shown are average of 3 replicates.



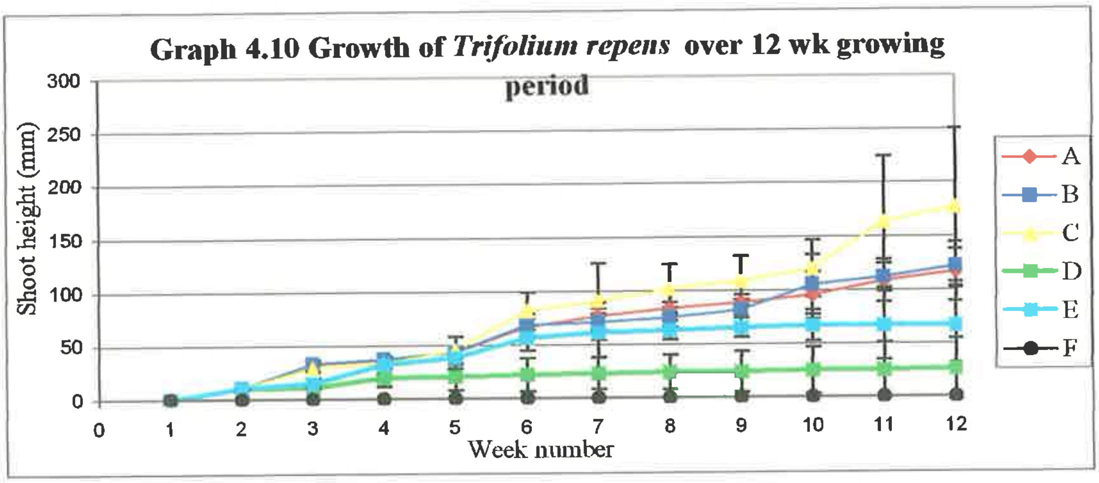
* Results shown are average of 3 replicates.



* Results shown are average of 3 replicates.



* Results shown are average of 3 replicates.



* Results shown are average of 3 replicates.

The amendment of the mine tailings substrate with TDB at an application rate of 20 t/ha (Treatment D) improved the establishment and growth of *Poa pratensis*. However, a higher application rate of 50 t/ha (Treatment E) resulted in significant increase in shoot heights per week (Graph 4.5). At week 12, average shoot height at the 50 t/ha rate was 183 mm, greater than that of treatments A and B. Overall *Poa pratensis* was a fairly quickly growing species, enhanced by the addition of TDB at all application rates used.

As with *Poa pratensis*, *Lolium perenne* seeds did not germinate on unamended mine tailings. Although addition of TDB to the substrate did aid the establishment and the growth of *L. perenne*, little difference occurred with the higher application rate. Average shoot height was 85 mm for 20 t/ha TDB treatment and only 84 mm for the higher application rate of 50 t/ha, biomass however, was greater at this application rate on mine tailings. Hooda and Alloway (1994) observed that addition of sewage sludge to sandy loam soil visibly enhanced growth of *Lolium perenne* relative to the controls although no figures were provided.

Twenty t/ha TDB accelerated growth of *Holcus lanatus* although by the end of the 12 week growing period, shoot height was 133 mm and 140 mm for 20 t/ha and 50 t/ha respectively. This indicates that a TDB application rate of 20 t/ha is sufficient to establish and maintain the growth of a *Holcus lanatus* sward. In Table 4.36 *Holcus lanatus* species, did not display the elevated biomass levels observed with shoot height increases. Biomass decreased with increasing TDB application on mine tailings.

Festuca rubra, like Holcus lanatus had better growth with TDB addition although no major difference was noted with the higher application rate until week 10. Shoot height was 49 mm and 96 mm for the 20 t/ha and 50 t/ha TDB application rate. This species demonstrated the lowest shoot height of the grass species used in trials.

Graph 4.9 shows growth rate of *Agrostis stolonifera* on mine tailings. Amendment of the tailings improved the growth environment for *A. stolonifera* (Plate 4.4). Results for *A. stolonifera* displaying greater shoot height when grown on tailings than that achieved when grown on agricultural soil. Average shoot height of *A. stolonifera* on mine tailings with 20 t/ha TDB was 137 mm after the 12 week growing period and 218 mm with TDB application rate of 50 t/ha.

Plate 4.4 *Agrostis stolonifera* on mine tailings treatment D and E.

Graph 4.10 displays the poor growth of *Trifolium repens* on tailings in comparison with growth on agricultural soil (Plate 4.5). Although greater shoot height was obtained with the higher application rate of 50 t/ha, maximum height was only 67 mm after 12 weeks, in comparison with 26 mm at the 20 t/ha application rate. Ye *et al* (1999) found that seedlings of *Trifolium repens* growing in lead/zinc tailings with lime plus fertilizer amendments were seriously affected and died after two weeks.

Plate 4.5 *Trifolium repens* on agricultural soil treatments A, B and C.

4.7 Dry matter yield

4.7.1 Dry matter yield of species on agricultural soil

Statistical analysis, by means of ANOVA tests, carried out on dry matter yield figures gave the following results. On agricultural soil, *P. pratensis, L. perenne, H. lanatus, F. rubra* and *A. stolonifera* displayed an increase with the addition of 2t/ha of TDB. This increase however, was not statistically significant with any grass species (P>0.05) between treatments A and B. The application of 20 t/ha in treatment C however, did result in a statistically significant increase in yield (P<0.05). The increase was significant in comparison with both treatment A and treatment B. The clover species used, *Trifolium repens* did display yield increase with increasing sludge application rate, however, the increases were not statistically significant (P>0.05).

Table 4.36 Dry matter yield of grass species under different treatments

	Average dry weight biomass g/m^2				
Treatment	**A**	**B**	**C**	**D**	**E**
P.pratensis	63.3 (21.1)	85.3 (28.1)	250.2 (127.9)	53.6 (51.6)	97.8 (92.1)
L.perenne	79.2 (9.4)	87.8 (9.8)	232.1 (32.4)	39.8 (25.4)	85.1 (46.2)
H.lanatus	92.7 (6.8)	121.5 (6.1)	123.4 (55.1)	114.7 (54.2)	90.0 (66.2)
F.rubra	99.8 (35.8)	106.2 (12.2)	233.3 (73.5)	13.1 (5.1)	29.5 (10.0)
A.stolonifera	114.0 (17.1)	142.7 (13.3)	341.1 (25.4)	161.9 (14.2)	193.3 (146.2)
T. repens	131.2 (40.8)	165.0 (57.9)	230.6 (87.7)	17.3 (14.3)	10.6 (3.1)

Values in parenthesis are the standard deviation of three replicates.

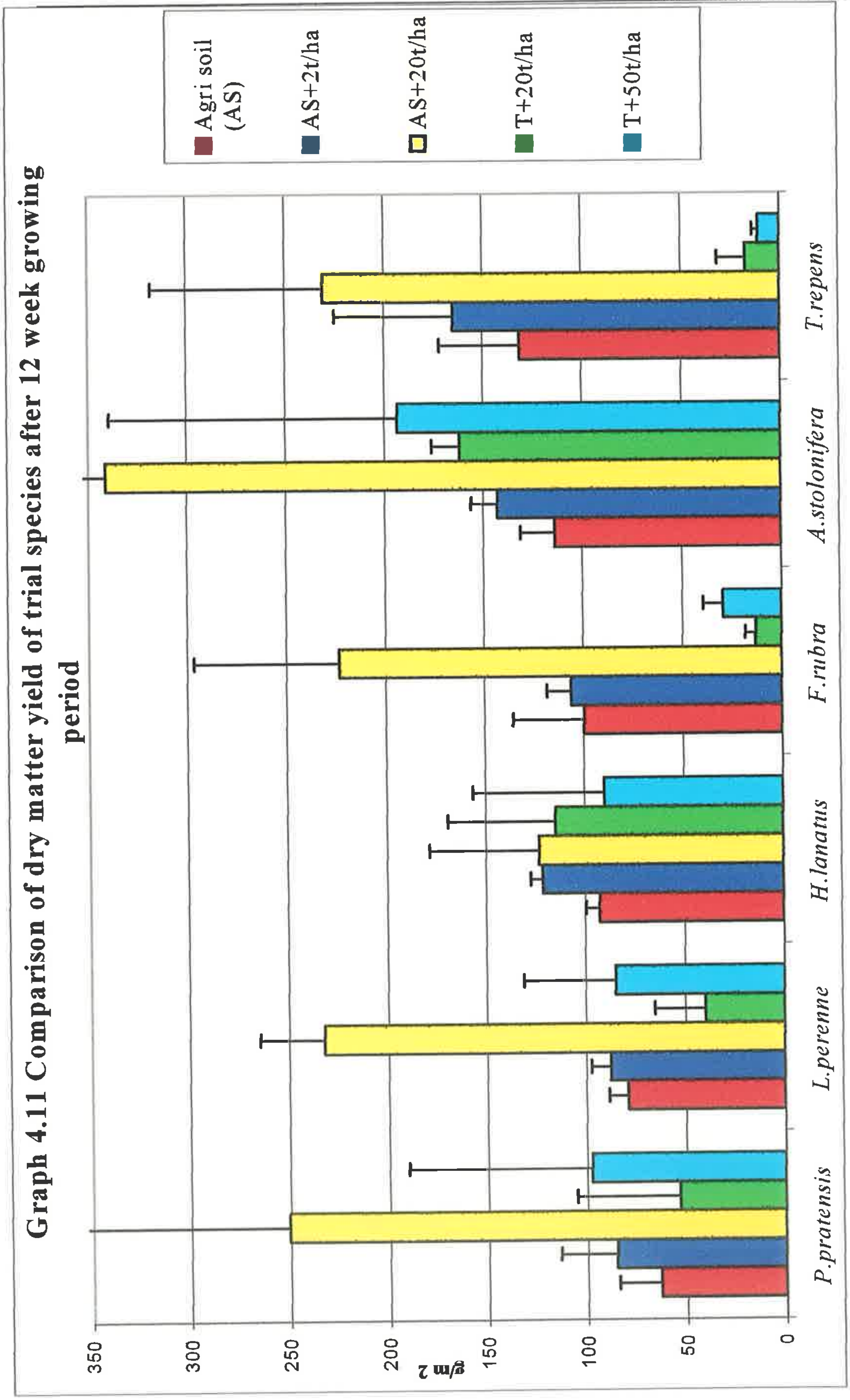
Treatment A- Agricultural soil, no amendment

Treatment B- Agricultural soil + TDB at 2 t/ha

Treatment C- Agricultural soil + TDB at 20 t/ha

Treatment D- Mine tailings + TDB at 20 t/ha

Treatment E- Mine tailings + TDB at 50 t/ha



Graph 4.11 Comparison of dry matter yield of trial species after 12 week growing period

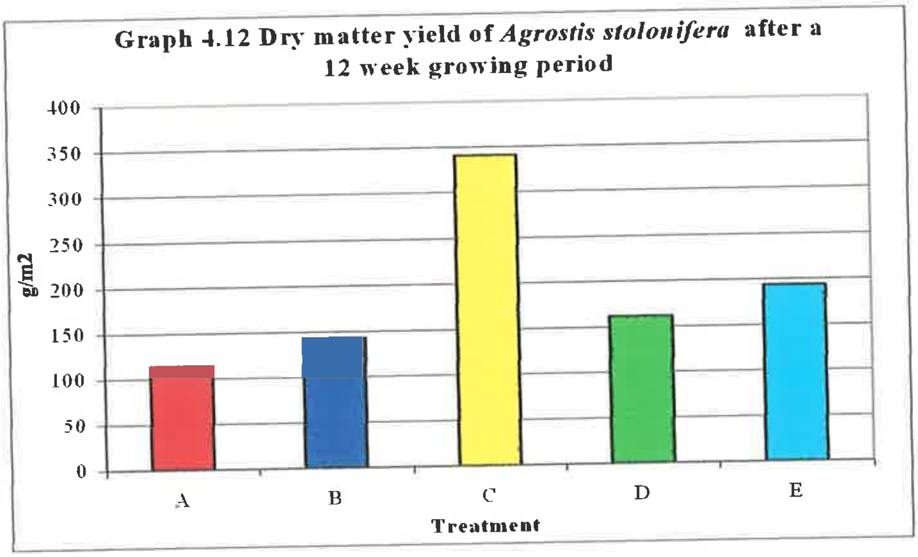
Dry matter yield of all species grown on each treatment is displayed in Graph 4.11. On agricultural soil, optimum yield was achieved with treatment C, application of TDB at 20 t/ha. *P. pratensis, L. perenne, F. rubra* and *A. stolonifera* produced, on average, 250.2 g/m^2, 232.1 g/m^2, 223.3 g/m^2 and 341.1 g/m^2 with this treatment after 12 weeks, over twice the yield produced by treatment B, TDB at 2 t/ha. Table 4.1 displays the average yield achieved for each species under each different treatment.

On agricultural soil, both *A. stolonifera* and *T. repens* had high dry matter yield compared with other species, with *P. pratensis* and *L. perenne* displaying lower dry weight yield for treatment A and B on agricultural soil. Application of TDB improved yield on agricultural soil, with greater yield observed where an application rate of 20 t/ha was used.

Yield responses of bluegrass (*Poa pratensis*) (Olness *et al.*, 1998) and corn (*Zea mays*) (Giordano *et al.*,1975) increased as sewage sludge application to soil increased According to Olness *et* al. (1998) much of the yield increase for many crops has stemmed from the large additions of N, P and K contained in the biosolids applied to the soil.

Holcus lanatus exhibited least response to TDB input, although yield did increase with treatments B and C, the increase was only slight in comparison with that from other grasses.

Agrostis stolonifera grass generated highest yields in all treatments. It can also be observed in Graph 4.12 that it responded favourably to TDB addition, both on agricultural soil and mine tailings. It can be concluded that yield of *A. stolonifera* was greatest at highest application rates in this study. Coker (1983) states that N in sludges is the primary factor determining yield increases.

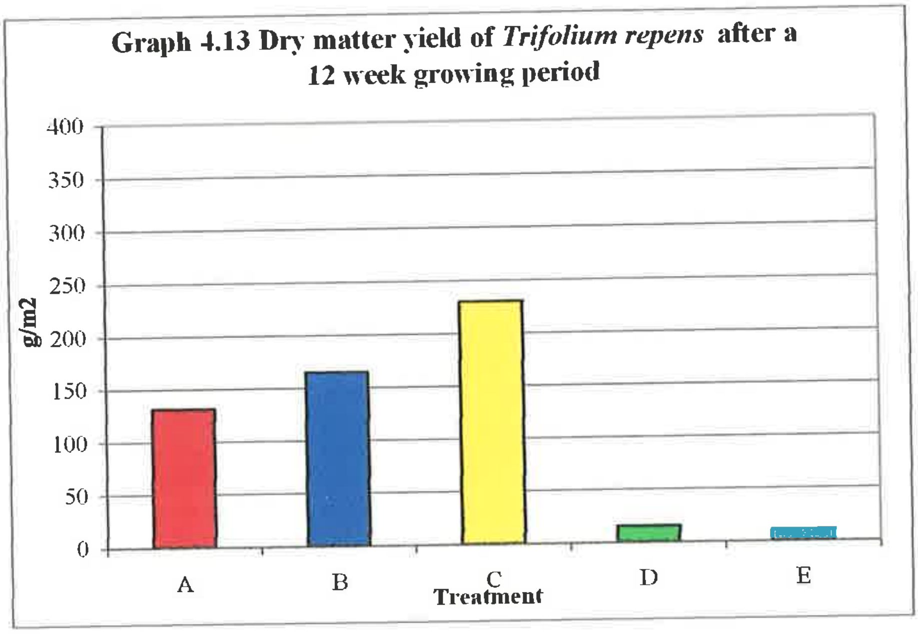


Treatment A- Agricultural soil, no amendment
Treatment B- Agricultural soil + TDB at 2 t/ha
Treatment C- Agricultural soil + TDB at 20 t/ha
Treatment D- Mine tailings + TDB at 20 t/ha
Treatment E- Mine tailings + TDB at 50 t/ha

From Graph 4.13, the poor growth of *Trifolium repens* on mine tailings can be observed. Although response to increased levels of TDB was good on agricultural soil, the result was the opposite for tailings. Dry matter yield after 12 weeks was on average 17.3 g/m^2 with treatment D and 10.6 g/m^2 with treatment E.

Yield decreases in corn have been studied (Cunningham *et al.*, 1975; Mench *et al.*, 1994) where sewage sludge has been added to soil, particularly at high loading rates. Yield decreases appear to be toxicity reactions incurred as result of elevated salt and metal concentrations. Mench *et al.* (1994) noted a 27% decrease in vegetative yield with sludge loading of $\geq$300 t/ha on sandy soil with mildly acidic pH.

Poor dry matter yield of *Trifolium repens* on mine tailings can be attributed to metal toxicity described by Chaudri *et al.* (1992) as levels of the most toxic metals to clover; Cu>Cd>Ni and Zn are high in Silvermines tailings. Results in this study are similar to those found by Pallant and Burke (1994) who found that grasses are more suitable for mine waste reclamation than legume species.



Treatment A- Agricultural soil, no amendment
Treatment B- Agricultural soil + TDB at 2 t/ha
Treatment C- Agricultural soil + TDB at 20 t/ha
Treatment D- Mine tailings + TDB at 20 t/ha
Treatment E- Mine tailings + TDB at 50 t/ha

4.7.2 Dry weight yield of species on mine tailings

Dry matter yield on mine tailings was lower than that on agricultural soil. Paired t-test results show that only *F. rubra* and *L. perenne* had a significantly higher ($P<0.05$) yield with the higher TDB application rate of 50 t/ha. *L. perenne* and *A. stolonifera* also displayed increased yield with this treatment, however, not statistically higher ($P>0.05$). *Holcus lanatus* and *Trifolium repens* produced lower yield with the higher sludge addition rate of 50 t/ha, the decrease was not statistically significant.

Graph 4.11 displays the dry matter yield of all species used in the trials. Due to failure of seeds to germinate on tailings without amendment, no yield results for this treatment (F) were obtained.

Festuca rubra also exhibited poor dry matter yield on mine tailings, although unlike *Trifolium repens,* had increased yield with increased application of TDB. Dry matter yield for *Festuca rubra* was 13.1 g/m^2 with 20 t/ha TDB and 29.5 g/m^2 with 50 t/ha. As documented earlier (section 2.16.2) both fescues and bent grasses such as *Festuca rubra* and *Agrostis stolonifera* although suitable for mine waste rehabilitation, are slow growing and do not provide rapid ground cover (Bradshaw, 1970; Williamson *et al.*, 1982).

Plate 4.6 Poor growth of *Trifolium repens* on treatment D, mine tailings compared with treatment E where improved growth was observed.

Both *Festuca rubra* and *Trifolium repens* (Plate 4.6) displayed lowest yield on tailings, a result also found by Jeffery *et al.* (1974) who claim an 80% yield reduction of these species when grown when grown on mining waste compared with normal soil. They state this yield reduction to be a direct result of Cu toxicity.

Overall, *Agrostis stolonifera* displayed the highest yield on both substrates. Whilst all species grew on agricultural soil, and had increased yield with increasing TDB application, only *P. pratensis, L. perenne, H. lanatus* and *A. stolonifera* had elevated yield when grown on mine tailings in comparison with low yield in the other two species. *Holcus lanatus and Agrostis species* were found by Bleeker *et al.* (2002) to grow rapidly on arsenic tailings. This was also found to be the case in the current study.

McNearney and Belyaeva (1998) state that although biosolids generally enhanced plant growth capability of tailings during the first growing season, the highest biosolids application rate of 67.2 t/h caused the greatest growth in terms of aboveground biomass production and increase in percent cover. Results of this study were similar in that all grass species, save for *Holcus lanatus*, responded better in terms of dry matter yield and growth rate to the increased TDB application of 50 t/ha on mine tailings.

4.8 Elemental composition of herbage grown on agricultural soil

4.8.1 Arsenic

Analysis of herbage grown on an agricultural brown podsol soil exhibited As levels below the limit of determination <6.58 mg/kg for herbage samples. The disposal of sewage sludge on land is not thought to cause a significant increase in As in crops at a typical addition rate of 5 t/ha sludge, the rate of As addition being 4 mg/m^3 (O'Neill, 1995). This author states that levels of As in plants are generally low, often being close to the limit of detection, even when the crops are grown on contaminated land. In addition, as with most trace elements, uptake varies widely from species to species. Liebig (1966) states that As levels in native plants on natural soil did not exceed 10 mg/kg, in vegetables and other plants As concentration varied from 0 to 10 mg/kg.

4.8.2 Boron

As can be observed in Table 4.37, the uptake of Bo by plants has been shown to be intimately related to the concentration of other ions in the nutrient substrate. Boron deficiency is characterised by levels less than 15 ppm to 20 ppm. Adequate, but not excessive, levels are commonly between 25 ppm and 100 ppm (Bradford, 1966), however, Reuter and Robinson (1986) state that > 15 mg/kg Bo is high and < 3 mg/kg is deficient.

Boron uptake by *Lolium perenne* was below 12.17 mg/kg, which was the limit of detection in all three treatments. *Holcus lanatus* Bo levels were lowest in treatment A, the unamended soil with only one value, 17.01 mg/kg detectable. Only one value 22.49 mg/kg was detectable in treatment B, and was substantially higher than the other two which were below the limit of detection. Treatment C *Holcus lanatus* samples were below the limit of detection except for one value of 13.53 mg/kg.

Agrostis stolonifera in treatment A, agricultural soil with no amendment had two Bo levels below 12.17 mg/kg, the third level was 29.77 mg/kg. With the addition of 2 t/ha, Bo levels in this grass species were below the limit of detection. Treatment C resulted in Bo levels in *Agrostis stolonifera* of on average 23.29 ± 9.17 mg/kg.

Trifolium repens displayed levels on average of 19.77 ± 6.51 mg/kg. This decreased slightly in treatm ent B to 18.61 mg/kg ± 3.37. Treatment C, displayed greatest Bo levels in *Trifolium repens* 23.29 ± 8.83 mg/kg. Statistical analysis shows these values are not significantly different ($P>0.05$).

Festuca rubra displayed average levels of 23 mg/kg approximately, throughout treatments, although one replicate in treatment A was < 12.17 mg/kg. *Festuca rubra* accumulated greatest levels of Bo from soil in this study.

Table 4.37 Boron levels (mg/kg) in herbage grown on agricultural soil

	Treatment		
	A	**B**	**C**
P.pratensis	26.06* (6.39)	30.34 (14.09)	22.98**
L.perenne	< 12.17	< 12.17	< 12.17
H.lanatus	17.01**	22.49**	13.53**
F.rubra	23.92* (9.91)	23.09 (8.63)	23.29 (8.83)
A.stolonifera	29.77**	< 12.17	23.0 (9.17)
T. repens	19.77 (6.51)	18.61 (3.37)	21.22 (9.69)

Treatment A- Agricultural soil, no amendment

Treatment B- Agricultural soil + TDB at 2 t/ha

Treatment C- Agricultural soil + TDB at 20 t/ha

Values in parentheses are standard deviation of mean of 3 samples

*** 1 value under < 12.17 mg/kg lowest detectable level**

**** 2 values under < 12.17 mg/kg lowest detectable level**

4.8.3 Cadmium

Cadmium levels in herbage grown in agricultural soil under different treatments are displayed in Table 4.38. In one of the few Irish papers available relating to Irish herbage elemental content, Fleming and Parle (1977) found Cd levels in the range of <0.02 to 0.9 mg/kg in herbage in an Irish urban area. They also found that Cd levels in both grass and clover grown on garden soils from an urban area were non-detectable.

Poa pratensis displayed on average 0.60 mg/kg Cd when grown on agricultural soil alone in treatment A (Table 4.24). Treatment B exhibited Cd levels in *P.pratensis* of on average 1.13 ± 0.33 mg/kg. Two replicates in treatment C displayed non detectable levels, i.e. 0.66 mg/kg and one level of 2.88 mg/kg were found.

Table 4.38 Cadmium levels (mg/kg) in herbage grown on agricultural soil

	Treatment		
	A	B	C
P.pratensis	0.60 (0.12)	1.13 (0.33)	2.88**
L.perenne	0.58**	< 0.66	1.07**
H.lanatus	< 0.66	0.73**	< 0.66
F.rubra	1.04 (0.35)	< 0.66	1.08 (0.18)
A.stolonifera	0.57 (0.19)	< 0.66	< 0.66
T. repens	0.45**	< 0.66	< 0.66

Treatment A- Agricultural soil, no amendment

Treatment B- Agricultural soil + TDB at 2 t/ha

Treatment C- Agricultural soil + TDB at 20 t/ha

Values in parentheses are standard deviation of mean of 3 samples

* 1 value under < 0.66 mg/kg lowest detectable level

* 2 values under < 0.66 mg/kg lowest detectable level

As with Bo uptake, uptake of Cd by *Lolium perenne* in treatment A was below the limit of detection, 0.66 mg/kg in two replicates. In treatment B Cd concentration was below 0.66 mg/kg in all samples. Treatment C exhibited one value above the limit of detection of 1.07 mg/kg. Similarly, *Holcus lanatus* was low in uptake of Cd, as was the case with Bo. In treatment A, all Cd levels were below 0.66 mg/kg. With TDB application in treatment B, one replicate displayed a level of 0.73 mg/kg, with two further replicates displaying less than 0.66 mg/kg. All three replicates in treatment C were below the limit of detection 0.66 mg/kg. Antoniadis and Alloway (2002) found 0.03 mg/kg Cd in *Lolium perenne* grown on a loamy sand soil. This increased to 0.075 mg/kg on addition of 10 t/ha of sludge and to 0.073 mg/kg on addition of 50 t/ha. In the same study on a sandy loam soil, Cd increased from 0.015 mg/kg, increasing to 0.021 mg/kg and 0.026 mg/kg on addition of 10 t/ha and 50 t/ha of sewage sludge respectively. This sludge contained 0.31 mg/kg Cd. These increases, however, were not significant (P>0.05). The authors state that concentrations of Cd at 50 t/ha, which were slightly lower than at 10 t/ha, were likely to be due to a 'dilution effect'. This suggests that the plant dry matter production at 50 t/ha was higher, and the quantities of Cd absorbed from the soil were lower, than the 10 t/ha treatment in terms of µg per g of plant.

Plant concentration of Cd in *Trifolium repens* was low, as a likely result of low dry matter yield in this species. Vasseur *et al.* (1998) found that Cd was more concentrated in the roots of plants exposed to sewage sludge. Aitken and Cummins (1997) found plant Cd levels unaffected by sludge application. Analysis of data for Cd levels in vegetation is difficult as most levels are below the limit of detection. This however, may be a positive result in that effects of biosolids addition on herbage levels of Cd, if any, are low.

4.8.4 Chromium

Herbage samples grown on agricultural soil with, and without sewage TDB amendment, contained Cr levels which were below the limit of detection 16.44 mg/kg. However, Pratt (1966) suggests that Cr is accumulated in roots of plants. This study focused on analysis of the aerial portions of grass and clover. Uncontaminated or background concentrations of Cr in plants are of the order of 0.23 mg/kg, and are generally les than 1 mg/kg across a wide range of soil Cr values (Mc Grath, 1995). Therefore, it is impossible from results obtained in this study to determine if Cr levels are within levels stated in the literature, although Mc Grath (1995) states that Cr in crop plants grown on sludge treated soils containing elevated Cr levels are barely above background levels; therefore Cr toxicity is not thought to be of concern in this study.

4.8.5 Cobalt

Cobalt levels in herbage grown in agricultural soil under different treatments are displayed in Table 4.39. Uptake of Co by plants is a function of the concentration of Co in the soil solution and on the exchange sites of the cation exchange complex i.e. the 'available' or labile pool (Smith and Paterson, 1995). Cobalt concentration in herbage grown on agricultural soil with no amendment ranged from <0.07 mg/kg to 0.21 mg/kg. Coulter *et al.* (1999) state that the aim of soil treatment with Co is to raise Co herbage levels to between 0.1 and 0.15 mg/kg Co. Results in this study indicate 'adequate Co concentration in herbage' grown on agricultural soil according to the range stated by Coulter *et al.* (1999). Rogers and Murphy (2000) quote average Co levels in Irish grass of 0.156 mg/kg Co ranging from 0.06 to 0.28 mg/kg.

Table 4.39 Cobalt levels (mg/kg) in herbage grown on agricultural soil

	Treatment		
	A	B	C
P.pratensis	0.14* (0.08)	0.10 (0.02)	0.13 (0.02)
L.perenne	0.13* (0.03)	0.26 (0.17)	0.20 (0.12)
H.lanatus	0.12 (0.02)	0.15* (0.00)	0.17 (0.13)
F.rubra	0.09 (0.01)	0.09**	0.13**
A.stolonifera	< 0.07	0.15 (0.04)	< 0.07
T. repens	0.11 (0.00)	0.20 (0.07)	< 0.07

Treatment A- Agricultural soil, no amendment

Treatment B- Agricultural soil + TDB at 2 t/ha

Treatment C- Agricultural soil + TDB at 20 t/ha

Values in parentheses are standard deviation of mean of 3 samples

* 1 value under < 0.07 mg/kg lowest detectable level

* 2 values under < 0.07 mg/kg lowest detectable level

From Table 4.39 it can be observed that *Poa pratensis* accumulated on average 0.14 mg/kg Co, with one value less than the limit of detection of 0.07 mg/kg in treatment A. The addition of TDB in treatment B decreased the average Co accumulation to 0.1 mg/kg. Treatment C resulted in 0.13 mg/kg Co accumulated by *Poa pratensis*.

Evidence has suggested increased Co uptake occurs as soil pH decreases (Smith and Paterson, 1995), therefore low Co uptake in species used in trials may be attributed to a near neutral pH in agricultural soil, particularly on addition of TDB.

Vanselow (1966) found levels of 0.20 mg/kg in *Poa pratensis* in early bloom. *Lolium perenne* accumulated highest levels of Co. Average Co concentration in *Lolium perenne* grown within treatment A was 0.13 mg/kg, with one value below the limit of detection. In treatment B, this increased to 0.26 ± 0.17 mg/kg. In treatment C, however, average Co concentration was 0.20 mg/kg ± 0.12 mg/kg. *Festuca rubra* accumulated a lower level of Co. Treatment A displayed average Co concentration of 0.09 mg/kg ± 0.01 mg/kg. In treatment B, only one value of 0.09 mg/kg was detectable. Within treatment C, again, only one value was detectable. This value was 0.13 mg/kg Co in *Festuca rubra.*

An increase of Co concentration in *Holcus lanatus* was observed with increasing TDB application. Treatment A had a mean Co concentration of 0.12 ± 0.02 mg/kg, increasing to 0.15 ± 0.00 mg/kg, with one value less than the limit of detection in treatment B. Application of 50 t/ha of TDB in treatment C resulted in average Co concentration of 0.17 ± 0.13 mg/kg.

Similar trends were observed with both *Agrostis stolonifera* and *Trifolium repens.* Both had low concentrations in treatment A, increasing to, on average, 0.15 mg/kg and 0.20 mg/kg. However, Co concentration decreased with treatment C to less than the limit of determination for both species. Vanselow (1966) found levels of 0.17 to 0.20 mg/kg in blooming *Trifolium repens* and 4.6 mg/kg in mature species.

4.8.6 Copper

Copper levels in herbage grown in agricultural soil under different treatments are displayed in Table 4.40. According to Coulter *et al.* (1999), Cu contents of <5 mg/kg in herbage dry matter are undesirable, and in a good pasture the aim should be to ensure contents of around 10 mg/kg are present. Copper in herbage grown on agricultural soil in this study ranged from 5.23 mg/kg to 19.40 mg/kg among species. Fleming and Parle (1977) found that normal range of Cu in herbage from an Irish urban area was 3-20 mg/kg whilst Rogers and Murphy (2000) found Irish grass Cu levels of on average 9.22 mg/kg ranging from 1.6 mg/kg to 23.7 mg/kg.

Uptake of Cu by all grass species displayed the general trend of decreasing on addition of 2 t/ha of TDB in comparison with the control, whilst increasing, in most cases, above that of the control with 20 t/ha TDB addition. This reduced uptake in treatment B is likely to be as a result of complexing of Cu to the organic matter in the soil, which is documented by many authors (Hooda and Alloway, 1994; McGrath, 1995).

Poa pratensis accumulated on average 12.5 ± 5.1 mg Cu/kg in treatment A. The addition of TDB in treatment B resulted in a lower uptake of 7.98 ± 0.97 mg/kg. This level of uptake was significantly lower ($P<0.05$) than treatment A, and also significantly lower than treatment C, 13.01 ± 3.43 mg/kg. However, the addition of 20 t/ha of TDB did not significantly ($P>0.05$) increase Cu levels in *Poa pratensis* in comparison with the same grass on control soil.

Lolium perenne displayed a similar trend, treatment A yielding herbage with Cu levels of 13.26 ± 8.7 mg/kg. Reuter (1986) states 6-7 mg/kg Cu to be adequate for both *Lolium perenne* and *Trifolium repens*. Therefore, both species accumulated Cu levels above what is deemed adequate. This accumulation decreased to 10.36 ± 3.6 mg/kg in treatment B. Addition of 20 t/ha of TDB increased Cu levels in *Lolium perenne* to 13.43 ± 2.4 mg/kg, although differences between Cu uptake in treatments were not ($P>0.05$) statistically different. Hooda and Alloway (1994) observed an increase from 12.55 mg/kg Cu in *Lolium perenne* to 16.05 mg/kg on addition of 50 t/ha biosolids and to 18.55 mg/kg Cu on addition of 150 t/ha. The maximum concentration of Cu accumulated by *Lolium perenne* from the biosolids application in the 1994 study was 20 mg/kg. All results for herbage on agricultural soil with no amendment in this study were within this range. Greater than 7 mg/kg in *Lolium perenne* is considered high (Reuter, 1986).

Uptake of Cu by *Holcus lanatus* on treatment A was on average 7.67 ± 2.3 mg/kg. This decreased on addition of TDB in treatment B to 6.83 ± 1.16 mg/kg, although this decrease was not significant ($P>0.05$). In treatment C, Cu uptake by *Holcus lanatus* was 8.58 ± 0.76 mg/kg. This was higher than uptake in both treatments A and B, however not statistically different ($P>0.05$) from either.

Again it was found that *Agrostis stolonifera* accumulated lower metal levels than other grass species. Copper concentration in *Agrostis stolonifera* as grown with treatment A was 7.77 ± 2.46 mg/kg, decreasing to 6.76 ± 0.65 mg/kg in treatment B. Treatment C exhibited, the greatest accumulation, 11.32 ± 4.82 mg Cu/kg. It was found, however, that Cu accumulation between treatments was not significantly different ($P>0.05$). Fleming and Parle (1977) found Cu levels of 13.2 mg/kg and 11.8 mg/kg in grass grown in a greenhouse trial. The soil had a pH of 7.7 and the authors claim results represent 'true plant uptake'. It could therefore be deduced that Cu levels in grass were similar to those of Fleming and Parle (1977), and that application of sludge at 2 t/ha reduced availability of Cu in soil.

Table 4.40 Copper levels (mg/kg) in herbage grown on agricultural soil

	Treatment		
	A	B	C
P.pratensis	12.50 (5.1)	7.98 (0.97)	13.01 (3.43)
L.perenne	13.26 (8.69)	10.36 (3.63)	16.43 (2.43)
H.lanatus	7.67 (2.3)	6.83 (1.16)	8.53 (0.76)
F.rubra	8.17 (0.16)	6.37 (1.06)	7.63 (1.38)
A.stolonifera	7.77 (2.46)	6.76 (0.65)	11.32 (4.84)
T. repens	10.25 (1.33)	11.75 (0.20)	11.62 (2.61)

Treatment A- Agricultural soil, no amendment

Treatment B- Agricultural soil + TDB at 2 t/ha

Treatment C- Agricultural soil + TDB at 20 t/ha

Values in parentheses are standard deviation of mean of 3 samples

Trifolium repens displayed a different trend with maximum Cu accumulation in treatment B. As can be observed in Table 4.26, accumulation of Cu increased with TDB application. However, this was at its highest in treatment B, 11.75 ± 0.20 mg/kg. No significant difference (P>0.05) was recorded between treatments. In their greenhouse trial, Fleming and Parle (1977) recorded Cu uptake in clover of 7.8 mg/kg and 8.1 mg/kg. These values were lower than those of grass in this study and contrast to results in Table 4.40. However, Fleming and Parle (1977) do not state what clover species was analysed. In addition, elevated Cu levels in the clover used in this study may result from the lower dry matter yield of this species compared with those of the grasses, therefore, reducing or eliminating the 'dilution effect' of high dry matter yield. Reuther and Labanauskas (1966) claim that *Trifolium pratense* with Cu levels between 7 and 16.4 mg/kg are in the intermediate range. This would suggest that grass and clover species analysed in this study are within an intermediate range of Cu uptake. According to Mc Grath (1995), Cu is less readily available to plants in sludged soils as it is complexed by organic matter. Mc Grath (1995) also suggests that availability of Cu and resulting uptake by plants would decrease in the months/years following application. Additionally, low Cu uptake may be attributed to enhanced uptake of P (Bingham, 1966) which would be greater in sludged soils.

4.8.7 Lead

Lead levels in herbage grown in agricultural soil under different treatments are displayed in Table 4.41. Fleming and Parle (1977), state that normal range of Pb in herbage in an Irish urban area is 1 – 20 mg/kg. All Pb levels in this study were within this range. Only a small proportion of the Pb in soil is available for uptake by plants. In addition, uptake is likely to be greater in the winter months, as opposed to the period of active growth in summer (Davies, 1995).

Poa pratensis on agricultural soil with no amendment (Treatment A) displayed 5.71 mg/kg Pb after a 12 week period. This decreased in treatment B, and although remaining less than the control, increased slightly in treatment C (Table 4.27). Values in treatments B and C were both significantly ($P<0.05$) less than the control, but not statistically different from each other. These results were elevated compared to Pb levels found in grass grown in greenhouse trials by Fleming and Parle (1977). They found Pb levels of 1.3 mg/kg and 0.85 mg/kg in grass grown on soil of pH 7.7. Soil pH in this study was one unit lower, this may have resulted in a slightly elevated uptake. From the results of other grass species in Table 4.41, it can be observed that *Festuca rubra* followed a similar trend to *Poa pratensis*. However, although treatment B was significantly lower ($P<0.05$) in Pb uptake than treatment A, treatment C was not significantly different ($P>0.05$) than treatment A or treatment B. Although Pb levels decreased with TDB application, Stuckey *et al.* (1980) would consider the levels in Table 4.41 to be harmful.

Lolium perenne accumulated 5.2 ± 0.24 mg/kg Pb in treatment A, whilst this decreased to 4.65 ± 1.88 mg/kg in treatment B, and further decreased to 3.38 ± 0.57 mg/kg in treatment C. No statistical difference ($P>0.05$) was found between treatments. Hooda and Alloway (1994) observed an increase in Pb accumulation in *Lolium perenne* from

0.193 mg/kg to 0.273 mg/kg on application of 50 t/ha sludge containing 706 mg/kg Pb. However, on addition of 150 t/ha, only 0.218 mg/kg was accumulated when grown on a sandy loam soil. A similar trend was observed by the authors on a breckland soil. It is generally considered that total soil concentration of Pb is not reflected in herbage as Pb is not readily available for plant uptake.

As was the case with other metals, lowest Pb accumulation was observed in the grass *Agrostis stolonifera* and the clover *T. repens*. In the case of *Agrostis stolonifera*, treatment A resulted in Pb accumulation of 2.8 ± 0.97 mg/kg, decreasing to 1.98 ± 0.86 mg/kg in treatment B. Treatment C resulted in accumulation of 2.01 ± 0.81 mg/kg. No significant difference ($P>0.05$) was recorded between treatments.

Table 4.41 Lead levels (mg/kg) in herbage grown on agricultural soil

	Treatment		
	A	**B**	**C**
P.pratensis	5.71 (0.30)	1.70 (0.22)	2.30 (0.92)
L.perenne	5.20 (0.24)	4.65 (1.88)	3.38 (0.57)
H.lanatus	3.76 (5.09)	2.51 (0.51)	5.3 (2.26)
F.rubra	5.38 (0.63)	2.16 (1.06)	4.10 (2.92)
A.stolonifera	2.8 (0.97)	1.98 (0.86)	2.01 (0.81)
T. repens	2.26 (0.31)	1.77 (0.33)	2.06 (0.81)

Treatment A- Agricultural soil, no amendment

Treatment B- Agricultural soil + TDB at 2 t/ha

Treatment C- Agricultural soil + TDB at 20 t/ha

Values in parentheses are standard deviation of mean of 3 samples

As can be observed in Table 4.41, a similar trend in uptake of Pb was observed in *Trifolium repens* species. Again, differences between treatments were not statistically significant ($P>0.05$). Fleming and Parle (1977) found Pb levels in clover grown on soil of pH 7.7 of 0.73 mg/kg and 0.52 mg/kg. Lead levels in this study are above most levels found in literature. Aitken and Cummins (1997) found that plant Pb levels were unaffected by sludge application. Explanation for the decrease in Pb uptake with sludge application can be attributed to the fact that metals in sludge are generally organically bound therefore, less available to plants as documented by Frost and Ketchum (2000). Additionally uptake is greater in winter months as opposed to the period of active growth in summer (Davies, 1995) when these trials were undertaken. However, reduced Pb uptake in this study is likely to be as a result of the mutual antagonism between phosphate and Pb; phosphate addition reducing Pb toxicity described by Jeffery *et al.* (1974).

4.8.8 Mercury

All herbage samples grown in agricultural soil with, and without TDB amendment, contained Hg levels which were below the limit of detection 0.66 mg/kg. In general Hg does not pose a serious problem with phytotoxicity; levels at which toxicity symptoms are apparent are far above those encountered under normal conditions (Steinnes, 1995). This author also states that availability of soil Hg to plants is low, and roots serve as a barrier to Hg uptake. Alloway (1995b) states that normal range of Hg in plants is 0.005 to 0.17 mg/kg. From results presented in this study it is impossible to state if Hg in grasses and clover are within the normal range for soil or indeed whether Hg levels are affected by Biosolids application. It can be stated however, that values are below the critical concentration (1 mg/kg) where toxicity to plants is possible (Alloway, 1995b).

4.8.9 Molybdenum

Molybdenum levels in herbage grown in agricultural soil under different treatments are displayed in Table 4.42. Rogers and Murphy (2000) found on average 2.49 mg/kg Mo in Irish grass, with values ranging from 0.1 mg/kg to 52.0 mg/kg. Molybdenum in grasses grown on agricultural soil with no amendment ranged from <0.66 mg/kg to 3.16 mg/kg, as can be observed in Table 4.42 and therefore, can be considered normal for grass compared with figures from Rogers and Murphy (2000). Addition of TDB in treatment B increased Mo concentration in all grass species. In all grass species, save for *Lolium perenne*, application of 20 t/ha TDB in treatment C, Mo accumulation was less than grown on treatment B. As described previously, *Agrostis stolonifera* displayed lowest metal accumulation among the grasses, whilst the clover species *Trifolium* *repens*, exhibited lowest overall accumulation of Mo although elevated content was observed on treatment C.

Table 4.42 Molybdenum levels (mg/kg) in herbage grown on agricultural soil

	Treatment		
	A	B	C
P.pratensis	2.31 (0.73)	2.60 (0.39)	1.40 (0.50)
L.perenne	1.84 (0.18)	1.92 (0.25)	2.67 (1.05)
H.lanatus	3.17 (0.10)	3.59 (1.41)	3.56 (0.44)
F.rubra	2.09 (0.03)	2.62 (1.34)	1.86 (0.32)
A.stolonifera	1.31 (0.03)	1.90 (0.94)	1.66 (0.15)
T. repens	0.95**	< 0.66	1.20 (0.10)

Treatment A- Agricultural soil, no amendment

Treatment B- Agricultural soil + TDB at 2 t/ha

Treatment C- Agricultural soil + TDB at 20 t/ha

Values in parentheses are standard deviation of mean of 3 samples

* *2 values under < 0.66 mg/kg lowest detectable level

Reuter (1986) states that adequate Mo values for *Trifolium repens* are within the range 0.15 to 0.2 mg/kg, therefore, Mo levels in this study are elevated according to this source. Molybdenum, like Se and Cr are more available to plants under alkaline conditions (Fleming and Parle, 1977).

4.8.10 Nickel

Nickel levels in herbage grown in agricultural soil under different treatments are displayed in Table 4.43.Uptake of Ni by *Poa pratensis* in Treatment A was on average 4.24 mg/kg. Treatment B increased uptake in this grass to 5.19 mg/kg, although the increase was not significant (P>0.05). Thermally dried biosolids application of 20 t/ha in treatment C resulted in a substantially lower level of Ni in *Poa pratensis* of on average 2.78 mg/kg. This result was significantly lower (P<0.05) than in treatment B, but not significantly different to metal levels in *Poa pratensis* in treatment A.

This trend was also observed with *Lolium perenne* and *Holcus lanatus* although differences between treatments did not display any statistical difference in either case. Hooda and Alloway (1994) noted a maximum Ni concentration in *Lolium perenne* of 30.7 mg/kg. These authors observed an increase from 2.94 to 12.72 mg/kg with the addition of 50 t/ha sewage sludge containing 259 mg/kg Ni. A further increase to 19.07 mg/kg was observed on application of 50 t/ha to the sandy loam soil.

Antoniadis and Alloway (2002) observed Ni increases from 2.18 mg/kg to 6.52 mg/kg with 10 t/ha sludge application and to 6.60 mg/kg with 50 t/ha of sludge containing 30.56 mg/kg on a loamy sand soil. From Table 4.43, it can be observed that Ni levels appear slightly greater than those found in the literature, although McGrath (1997) states that Ni in sludge treated soils is readily available.

Table 4.43 Nickel levels (mg/kg) in herbage grown on agricultural soil

	Treatment		
	A	**B**	**C**
P.pratensis	4.24 (0.39)	5.19 (1.32)	2.78 (0.48)
L.perenne	4.91 (1.01)	5.05 (1.29)	3.75 (1.44)
H.lanatus	4.50 (0.87)	3.64 (0.56)	3.99 (1.76)
F.rubra	3.91 (0.18)	3.25 (0.61)	1.98**
A.stolonifera	2.54 (1.02)	2.9 (1.09)	< 1.65
T. repens	5.25 (0.72)	8.01 (2.99)	2.24 (0.17)

Treatment A- Agricultural soil, no amendment

Treatment B- Agricultural soil + TDB at 2 t/ha

Treatment C- Agricultural soil + TDB at 20 t/ha

Values in parentheses are standard deviation of mean of 3 samples

* 2 values under < 0.66 mg/kg lowest detectable level

Festuca rubra accumulated Ni concentrations of 3.91 ± 0.18 mg/kg in treatment A, agricultural soil with no amendment. In treatment B, Ni accumulation decreased to 3.25 ± 0.61 mg/kg. Only one value was obtained for Ni concentration in *Festuca rubra* in treatment C. Nickel concentration therefore significantly decreased ($P<0.05$) with increased TDB application in *Festuca rubra*.

Trifolium repens exhibited highest levels of Ni accumulation, on average 5.25 ± 0.72 mg/kg within treatment A. Accumulation increased slightly in treatment B, although not significantly ($P>0.05$). Treatment C resulted in lowest accumulation of Ni although this level was not significantly lower ($P>0.05$) than that of the control treatment A.

4.8.11 Selenium

Herbage samples grown on agricultural soil with, and without TDB amendment, contained Se levels below the limit of detection 6.58 mg/kg. According to Rogers and Murphy (2000) Irish grass contains on average 0.093 mg/kg with values ranging from 0.01 to 2.5 mg/kg, therefore, it cannot be deduced from these figures whether herbage in this study contained Se concentrations in the range normal for Irish grasses or indeed whether the addition of TDB to soil on which herbage was grown contributed to any changes in Se levels in herbage.

4.8.12 Zinc

Zinc levels in herbage grown in agricultural soil under different treatments are displayed in Table 4.44. Coulter *et al.* (1999), state that the Zn content of Irish herbage normally ranges from 25 to 45 mg/kg. However, Fleming and Parle (1977) found, in Irish greenhouse trials, that grass accumulated 81 mg/kg and 57 mg/kg Zn on a soil of pH 7.7. This source also quotes normal range of Zn in herbage to be in the range of 10 to 50 mg/kg. Results in this study fall within this range in all cases where herbage is grown on agricultural soil with no amendment. Rogers and Murphy (2000) found average Zn concentration in Irish grass of 30.83 mg/kg, slightly lower than the average in this study, with values ranging from as low as 13 mg/kg to 84 mg/kg. *Poa pratensis*, which accumulated highest levels of metals, in Treatment A displayed average metal concentration of 37.51 ± 4.20 mg/kg. On application of TDB in treatment B, Zn content of *Poa pratensis* was found to be slightly higher 48.43 ± 8.78 mg/kg. Highest application of TDB in treatment C resulted in the highest level of accumulation at 64.48 ± 13.39 mg/kg. However, increases in Zn concentration between treatments were not found to be significant ($P>0.05$).

Uptake of Zn by *Lolium perenne* was slightly higher in Treatment A, displaying levels of 47.77 ± 7.24 mg/kg. Treatment B resulted in Zn levels in this grass to be slightly lower, although not significantly (P>0.05) than treatment A. However, Zn levels increased substantially with the application of 20 t/ha TDB in treatment C to 68.58 ± 3.86 mg/kg. The increase observed in Zn concentration in *Lolium perenne* in treatment C was significantly higher (P<0.05) than both treatment A and treatment B. Therefore, application of TDB at 20 t/ha significantly increases Zn concentration in *Lolium perenne* compared to a control. As with other metals, *Holcus lanatus* followed a similar trend to *Poa pratensis* (Table 4.44), although in this case differences between treatments were not found to be significant (P>0.05). These findings agree with those of Hooda and Alloway (1994). These authors observed an increase in Zn concentration in *Lolium perenne* from 41.15 mg/kg to 95.01 mg/kg on addition of 50 t/ha of sludge containing 1408 mg/kg Zn to a sandy loam soil. This further increased to 98.83 mg/kg with a higher application rate of 150 t/ha. On a breckland soil, Zn concentration in *Lolium perenne* increased from 35.44 mg/kg to 102.49 mg/kg and 116.12 mg/kg on application of 50 and 150 t/ha sludge respectively. The authors observed a maximum Zn concentration in this grass of 116 mg/kg.

Antoniadis and Alloway (2002) observed an increase in Zn concentration *Lolium perenne* from 2.64 mg/kg to 7.72 mg/kg Zn on addition of 10 t/ha sludge containing 512.3 mg/kg Zn. A further increase to 18.05 mg/kg was observed on addition of 50 t/ha. Increase of Zn levels in both studies results from the high concentration of Zn in the sludge applied and in some cases the higher application rates used.

Agrostis stolonifera again, accumulated lowest levels of Zn, increasing slightly in treatment B and C. These increases were not significant (P<0.05). Fleming and Parle (1977) found Zn concentrations of 47 mg/kg and 43 mg/kg in clover in Irish pot trials. Results in Table 4.3 show Zn concentration in *T.repens* to be slightly greater than those found by the 1977 study. Application of TDB did not appear to affect Zn concentration in *T.repens* greatly and no significant differences (P>0.05) between treatments were observed. These results generally agree with Coulter *et al.* (1999) that enhanced N causes increased levels of Zn, observed in all grasses save for *Festuca rubra* when the highest TDB application and subsequently, N application was applied.

Table 4.44 Zinc levels (mg/kg) in herbage grown on agricultural soil

	Treatment		
	A	B	C
P.pratensis	37.51 (4.20)	48.43 (8.78)	64.48 (13.39)
L.perenne	49.77 (7.24)	42.79 (2.98)	68.58 (3.86)
H.lanatus	39.07 (8.67)	31.80 (14.38)	51.06 (5.6)
F.rubra	57.19 (12.82)	32.53 (4.81)	46.60 (5.6)
A.stolonifera	37.03 (18.23)	37.29 (3.91)	47.53 (5.63)
T. repens	47.00 (3.4)	71.57 (15.49)	48.00 (8.03)

Treatment A- Agricultural soil, no amendment

Treatment B- Agricultural soil + TDB at 2 t/ha

Treatment C- Agricultural soil + TDB at 20 t/ha

Values in parentheses are standard deviation of mean of 3 samples

4.8.13 Summary

The order of metal concentrations in TDB was Zn>Cu>Ni>Pb>Cd, and subsequently the order of relative concentration in *Lolium perenne* grown on TDB amended soil was identical, Zn>Cu>Ni>Pb>Cd. This was the order of metal concentration in all species used in trials, although in the case of *Festuca rubra* Pb concentration was greater than Ni concentration at 2 t/ha. *Agrostis stolonifera* also exhibited Pb concentration greater than Ni concentration but at 20 t/ha TDB. Apart from these exceptions, the order of metal concentration was identical for TDB, for herbage grown on soil amended with 2 t/ha and soil amended with 20 t/ha TDB.

Mc Grath (1977) states that Ni is less readily available in soil than Zn, but moreso than Cu, which is strongly complexed by organic matter. This may be the case generally but in this 12 week trial Cu was found at higher concentrations in herbage than Ni. The plant abundance of essential micronutrients ranks as follows Fe>Mn>B>Zn>Cu>Mo>Cl.

It should be noted within the results for elemental composition of herbage grown in these trials, that levels of many metals such as Cu, Zn, Pb and Ni are higher than the figures quoted in literature for Irish herbage. This, however, can be attributed to the fact that previous studies have also found metal uptake levels in greenhouse and pot trials to be greater than outdoor or field trials (Chaney, 1994; Alloway, 1995b).

4.9 Elemental composition of herbage grown on mine tailings

Greenhouse trials of herbage growth on Silvermines mine tailings substrate resulted in a failure of all grass species to establish on unamended tailings substrate. Due to this failure, no dry weight yield was obtained in treatment F. Therefore, no herbage analysis for this treatment was undertaken, however, literature obtained (DAFRD, 2000; SRK, 2002) provides guideline values for a number of metals in herbage grown in the field from Silvermines and Tara mine tailings. In addition, *Trifolium repens* provided extremely low yield on tailings and much of the aerial portions were dead and decaying. This author felt that the analysis of this material was unsuccessful and that it resulted in erroneous and inconsistent results. Many authors have found that legume species do not perform well on mine tailings substrate (Ye *et al.*, 2001) and suggest that high N and Cu contents in the substrate decreased nodulation and N_2 fixation in roots. Ibekwe *et al.* (1997) state that there was potential risk to white clover (*Trifolium repens*) from biosolids induced heavy metal toxicity.

4.9.1 Arsenic

Arsenic levels in herbage grown on tailings are higher than herbage grown on agricultural soil. On agricultural soil values are all less than 6.58 mg/kg, whereas on tailings values as high as 11.72 mg/kg were obtained. O Neill (1995) states that As levels of 3460 mg/kg were found growing on spoil heaps containing As levels of 26530 mg/kg, and that grasses in urban soil containing 20 mg/kg As were found to have a maximum of 3 mg/kg As. O'Neill (1995) states that grasses growing on spoil tips from mining can have elevated As concentration. Also, DAFRD obtained values of 0.81 mg/kg As on herbage from Silvermines tailings facility, substantially lower than figures obtained in this study.

Arsenic levels in Silvermines tailings are high (Table 4.28). However, this author suggests that As uptake by grasses may have been reduced or ameliorated as a result of the neutral pH of the tailings, the effect of organic matter addition (O'Neill, 1995) and the Fe content in the tailings, which has a strong negative influence on As availability (Visoothiviseth *et al.*,2002).

In As contaminated land and tailings in Thailand, Visoothiviseth *et al.* (2002), found As levels in grass species ranging from 6 to 40 mg/kg. These authors also found two fern species to be hyper accumulators of As with levels of 3860 mg/kg to 6380 mg/kg in their fronds.

Table 4.45 Arsenic levels (mg/kg) in herbage grown on mine tailings

	D	E
P.pratensis	11.20 (0.53)	<6.63
L.perenne	7.36**	<6.63
H.lanatus	11.72**	10.22**
F.rubra	10.63 (0.24)	9.12**
A.stolonifera	<6.63	<6.63

*** 1 value under < 6.63 mg/kg lowest detectable level**
****2 values under < 6.63 mg/kg lowest detectable level**
Treatment D- Tailings + TDB at 20 t/ha
Treatment E- Tailings + TDB at 50 t/ha
Values in parentheses are standard deviation of mean of 3 samples

Grass species in treatment D contained higher concentrations of As than in treatment E (Table 4.45). However, this author suggests increased metal binding to organic matter and reduced As concentration in treatment E substrata is a result of the dilution effect of TDB application.

Arsenic concentration in herbage grown on tailings in this study range from <6.63 mg/kg to 11.72 mg/kg. This is within a range of 5-50 mg/kg, where, according to Alloway (1995), toxicity effects are likely to occur (Alloway, 1995). It should be noted that there is a lower As accumulation in *Agrostis stolonifera* in this study, as Visoothiviseth *et al.* (2002) state that the *Agrostis* species are reported to be As hyper accumulators. They also state that mechanisms of arsenate tolerance have been noted in *Holcus lanatus.*

Arsenic concentration of herbage grown on agricultural soil in this study was undetermined as values were less than the limit of detection 6.65 mg/kg. Many values above this were obtained in herbage grown on Silvermines tailings; therefore, As in herbage grown on tailings accumulated greater concentrations of As than those grown on agricultural soil.

4.9.2 Boron

Boron in Silvermines tailings was below the limit of detection for mine tailings, 61.1 mg/kg. No data has been found in the literature regarding Bo levels in Silvermines tailings. Although Bo levels in herbage grown on Silvermines tailings are slightly greater than herbage grown on agricultural soil, these values are not excessive (Bradford, 1966) and neither is there a statistically significant difference ($P>0.05$) between the two. This author states that adequate levels of Bo lie in the range 25 to 100 mg/kg. Mc Grath *et al.* (2001) state that the typical range of Bo in unpolluted Irish pastures was 1 to 20 mg/kg, therefore, some values obtained in the current study are over this range.

The general trend of Bo uptake in herbage grown on tailings observed in this study is increased uptake with increased TDB application (Table 4.46). *Poa pratensis* concentration increased from 14.37 mg/kg and two values less than 12.25 mg/kg in treatment D to 20.89 ± 2.44 mg/kg. *Lolium perenne* Bo concentration increased from less than 12.25 mg/kg to 17.94 ± 1.91 mg/ka. *Holcus lanatus* displayed elevated Bo content increasing from 17.85 ± 0.59 in treatment D to 26.89 ± 2.11 mg/kg.

Festuca rubra accumulated highest Bo concentration in treatment D, this decreased to 17.39 ± 3.02 mg/kg with one value less than the limit of detection in treatment E. As was frequently observed throughout this study, *Agrostis stolonifera* displayed lower uptake than other grass species. In treatment D, Bo concentration was 17.65 ± 3.43, with one level less than the limit of detection. A slight decrease was observed in treatment E to 17.21 ± 4.8 mg/kg

Table 4.46 Boron levels (mg/kg) in herbage grown on mine tailings

	D	E
P.pratensis	14.37**	20.89 (2.44)
L.perenne	< 12.25	17.94 (1.91)
H.lanatus	17.85 (0.59)	26.89 (2.11)
F.rubra	26.46 (1.36)	17.39* (3.02)
A.stolonifera	17.65* (3.43)	17.21 (4.8)

* 1 value < 12.25mg/kg lowest detectable level

**2 values < 12.25mg/kg lowest detectable level

Treatment D- Tailings + TDB at 20 t/ha

Treatment E- Tailings + TDB at 50 t/ha

Values in parentheses are standard deviation of mean of 3 samples

4.9.3 Cadmium

DAFRD (2000) obtained Cd values of 1.03 mg/kg in herbage consisting of *Agrostis, Holcus and Poa* species from Silvermines Tailings Management Facility. They also quote Cd levels in *Agrostis* grown on Tara mines of only 0.37 mg/kg. Results from herbage analysis in this study for Cd can be observed in Table 4.47. All grasses displayed slightly elevated Cd levels in comparison with grass grown on agricultural soil and figures quoted in the literature. However, Jackson and Alloway (1991) state that enhanced uptake of Cd by plants occurs when grown in a greenhouse. Normal Cd concentration in herbage is 0.1 – 2.4 mg/kg, with toxicity effects likely between 5 mg/kg and 30 mg/kg (Alloway, 1995). Therefore, Cd levels grown on tailings are not likely to cause phytotoxicity as Cd levels found in this study were within a range of <1.38 to 2.06 mg/kg, with many values less than the limit of detection.

As can be noted in Table 4.39, Cd concentration decreased with increasing TDB application in the tailings substrate. As a direct result of this, herbage Cd levels in most cases decreased from treatment D to treatment E. *Poa pratensis* Cd concentration decreased from 1.93 mg/kg to 1.65 with two values < 1.38 mg/kg. *Holcus lanatus, Agrostis stolonifera, Lolium perenne* and *Festuca rubra* all decreased slightly in treatment E, with many values below the limit of detection.

Ye *et al.* (2001) found that Cd concentration in plant tissue, as with tailings substrate, tended to decrease with increased sludge application. In addition, they observed greater concentration of Cd in roots of plants as opposed to the aerial portions.

Herbage grown on agricultural soil was generally lower in Cd concentration than that grown on tailings. Many values of treatments A, B and C were below the limit of detection of 0.66 mg/kg. In contrast, on mine tailings, many values were recorded and those that were undetectable were less than 1.38 mg/kg. Statistical analysis could not be carried out to compare Cd uptake in agricultural soil and tailings as a result of many values being undetectable.

Table 4.47 Cadmium levels (mg/kg) in herbage grown on mine tailings

	D	E
P.pratensis	1.93 (0.05)	1.65**
L.perenne	1.40**	< 1.38
H.lanatus	1.41 (0.08)	1.40**
F.rubra	2.06 (0.02)	1.73**
A.stolonifera	1.79*	1.62**

*1 value under < 1.38 mg/kg lowest detectable level

Treatment D- Tailings + TDB at 20 t/ha

Treatment E- Tailings + TDB at 50 t/ha

Values in parentheses are standard deviation of mean of 3 samples

4.9.4 Chromium

Herbage growing on Silvermines tailings exhibited Cr levels of less than the limit of detection 16.66 mg/kg. Therefore a comparison of tailings herbage and agricultural soil herbage could not be made. Additionally, it was not possible to observe any fluctuations in Cr concentration between treatment D and E. In addition, Cr in Irish pastures is generally within the range 0.1 to 0.3 mg/kg (McGrath, 2001), therefore, it cannot be deduced from these results if values are within this range.

4.9.5 Cobalt

Cobalt concentration in tailings was an average of 1.83 mg/kg in treatment D and decreased slightly to 1.48 mg/kg in treatment E. These figures are substantially higher than those quoted by Mc Grath *et al.* (2001) for normal herbage content of Coin Irish non polluted pastures; 0.03 to 0.2 mg/kg. Uptake by *Festuca* and *Agrostis* species was reflected by this slightly lower Co levels herbage from treatment E, a similar trend observed by these species in Table 4.39 on agricultural soil. The remaining grass species increased uptake with higher TDB application.

Table 4.48 Cobalt levels (mg/kg) in herbage grown on mine tailings

	D	E
P.pratensis	2.11 (0.24)	2.32 (0.15)
L.perenne	1.07 (0.46)	1.77 (0.19)
H.lanatus	2.88 (0.08)	1.65 (0.29)
F.rubra	1.30 (0.19)	0.77 (0.19)
A.stolonifera	1.78 (0.46)	0.89 (0.24)

Treatment D- Tailings + TDB at 20 t/ha
Treatment E- Tailings + TDB at 50 t/ha
Values in parentheses are standard deviation of mean of 3 samples

Cobalt levels in herbage on agricultural soil are less than those grown on tailings, in some cases by a factor of ten. Therefore there is a significant difference ($P<0.05$) in uptake of Co by herbage grown on agricultural soil compared with that grown on tailings. Vanselow (1966) states that values exceeding 1 mg/kg in herbage are rare, and toxicity symptoms have been recorded in citrus species at 11 mg/kg. Although Co levels in herbage on tailings are above normal concentration, they are not toxic. Alloway (1995b) states that values between 15 and 50 mg/kg are phytotoxic. *Poa pratensis* and *Lolium perenne* increased Co concentration, but only marginally in treatment E.

4.9.6 Copper

Copper in forage crops and pasture crops depends on soil availability of Cu, plant species, stage of growth, time of year and lime and fertiliser applications (Baker and Senft, 1995). Copper uptake was increased when grown on mine tailings in comparison with an uncontaminated agricultural soil. According to Alloway (1995), normal Cu range in herbage is 5-20 mg/kg and toxicity effects likely to occur between 20 and 100 mg/kg. Copper in herbage grown in tailings ranged from 23.11 mg/kg to 34.68 mg/kg, therefore, within the range for phytotoxicity.

Copper content in herbage growing on Silvermines tailings was found by DAFRD (2000) to be between 7.1 mg/kg and 8.2 mg/kg. This source also states that Cu concentration of herbage growing on Tara mine tailings was 13.5 mg/kg Cu. Figures from this study indicated elevated Cu levels compared with values cited for Silvermines tailings vegetation in the literature. However, in a greenhouse study carried out by Ye *et al.* (2001) in tailings containing 91 mg/kg Cu, herbage accumulated 10 and 25 mg/kg Cu in stem and roots, respectively. This increased to 34 and 47 mg/kg in stem and roots respectively on application of 25 % sludge. Both of these species were legumes and Baker and Senft (1995) state that legumes accumulate larger amounts of Cu than grasses.

A similar trend can be observed in this study. Copper concentration in herbage increased with increasing Biosolids application. Again, it was noted that *Agrostis* accumulated slightly lower levels than other grass species (Table 4.49). On tailings containing 99 mg/kg and 198 mg/kg, Shu *et al.* (2002b) found Cu levels in grass species of 32.27 and 22.26 mg/kg Cu. These authors state that different levels of metal accumulation by these grasses on different substrata reflected both the edaphic conditions and the difference between populations and species in terms of metal accumulation. Copper levels in tailings herbage in this study (Table 4.49) should be looked on with suspicion of Cu toxicity (Reuter and Labanauskas, 1966), although no visible signs of phytotoxicity were observed, except in case of *Trifolium repens* which is particularly susceptible to Cu toxicity (Jeffery *et al.*, 1974; Chaudri *et al.*, 1992). Copper causes reduced growth of both *Trifolium repens* and *Festuca rubra*.

Uptake of Cu by herbage was found by this study to be significantly higher ($P<0.001$) when grown on Silvermines tailings than when grown on an agricultural brown podsol soil.

Table 4.49 Copper levels (mg/kg) in herbage grown on mine tailings

	D	E
P.pratensis	25.34 (1.98)	33.41 (0.76)
L.perenne	28.12 (0.45)	32.19 (2.3)
H.lanatus	23.11 (1.81)	34.68 (1.02)
F.rubra	27.80 (0.26)	32.37 (1.64)
A.stolonifera	24.14 (0.67)	29.59 (0.89)

Treatment D- Tailings + TDB at 20 t/ha

Treatment E- Tailings + TDB at 50 t/ha

Values in parentheses are standard deviation of mean of 3 samples

4.9.7 Lead

Lead in herbage grown on Silvermines tailings was stated to be on average 29.2 mg/kg (DAFRD, 2000), whilst SRK (2002) report Pb concentrations in Tara Mines herbage of on average 16.3 mg/kg. According to Davies (1995), only a small proportion of the Pb in soil is available for uptake and translocation of Pb to the shoot of plants is low. This source states that high substrate conditions result in stunted growth or death and that some plants can evolve a tolerance to Pb. This is perhaps why substantially lower Pb levels were recorded on herbage growing naturally on Silvermines Tailings Management Facility. In accumulator species, uptake becomes less at high concentrations. On the other hand, these species may be excluders, since metal concentrations in shoots are kept low and constant over a range of soil concentrations until a threshold value is reached when uptake becomes unrestricted (Davies, 1995).

Ye *et al.* (2001) observed a reduction in Pb concentration in substrate and subsequently herbage grown thereon after addition of sludge to Pb/Zn tailings. These authors noted a reduction of Pb concentration in leaves of *Sesbania roatrata* on addition of sludge from 67 mg/kg to 37 mg/kg, 34 mg/kg and 25 mg/kg on addition of 25%, 50 % and 75% sludge, respectively. Another legume, *Sesbania cannabina* showed decreases in Pb concentration from 94 mg/kg to 77 mg/kg, 76 mg/kg and 60 mg/kg on addition of the same sludge applications.

Table 4.50 Lead levels (mg/kg) in herbage grown on mine tailings

	D	E
P.pratensis	87.1 (4.93)	78.42 (1.65)
L.perenne	78.38 (1.47)	57.01 (6.94)
H.lanatus	81.74 (3.1)	68.61 (2.84)
F.rubra	79.64 (1.54)	54.39 (3.72)
A.stolonifera	75.54 (1.83)	59.71 (4.46)

Treatment D- Tailings + TDB at 20 t/ha
Treatment E- Tailings + TDB at 50 t/ha
Values in parentheses are standard deviation of mean of 3 samples

Similar decreases in Pb concentration were noted in this study (Table 4.50). Additionally, Davies (1995) states that Pb remains in an insoluble or stable form in surface layers of soil after application of sewage sludge. Lead levels recorded in this study were in the range of 30 – 300 mg/kg; at which toxicity occurs. Normal Pb concentration in herbage is 0.2 – 20 mg/kg (Alloway, 1995). *Poa pratensis* displayed a decrease from 87.1 ± 4.93 mg/kg to 78.42 ± 1.65, *Lolium perenne* from 78.38 ± 1.47 mg/kg and *Holcus lanatus* from 81.74 ± 3.1 mg/kg to 68.61 ± 2.84 mg/kg. The other grass species used in trials also displayed a decrease in Pb concentration in treatment E, *Festuca rubra* from 79.64 ± 1.54 mg/kg to 54.39 ± 4.46 mg/kg and *Agrostis stolonifera* from 75.54 ± 1.83 mg/kg to 59.71 ± 4.46 mg/kg. *Agrostis stolonifera* also displayed lower uptake in treatment D than other grasses, although in treatment E this was not the case.

As with other metals, *Agrostis stolonifera* accumulated a lower concentration of Pb, while *Poa pratensis* and *Holcus lanatus* displayed slightly elevated levels. Ye *et al.* (1999; 2001) state that both pig manure and sewage sludge was found to be effective in reducing Pb availability to plants, leading to lower uptake. It is likely Pb levels in the herbage grown on tailings were reduced due to the dilution effect of TDB on tailings, and the availability of Pb becoming reduced by organic matter in TDB.

Accumulation of Pb by herbage was greatly elevated when grown on mine tailings in comparison to herbage grown on agricultural soil (Table 4.41) The difference in uptake was statistically different ($P<0.05$).

4.9.8 Mercury

Herbage growing on Silvermines tailings exhibited Hg levels of less than the limit of detection 1.33 mg/kg. As a result of this no comparison of Hg levels in herbage among different treatments could be observed. Additionally it is impossible to determine if Hg levels in herbage grown on tailings are above typical in Irish unpolluted pastures; 0.01 to 0.05 mg/kg (McGrath *et al.*, 2001).

4.9.9 Molybdenum

All tailings samples analysed for Mo displayed levels less than 8.26 mg/kg. Although a number of values were elevated, most were similar to those of herbage grown on an uncontaminated agricultural soil and no significant difference ($P<0.001$) was recorded between Mo levels grown on the two different substrates. Alloway (1995) states that the normal range of Mo in plants is from 0.03 to 5 mg/kg and toxic effects are likely between 10 and 50 mg/kg. *P.pratensis, H.lanatus, F.rubra* displayed increased Mo concentration with the higher TDB application. Grasses increased from 1.51 ± 0.43 mg/kg, 2.84 ± 1.31 mg/kg and 1.49 ± 0.56 mg/kg to 1.87 ± 1.09 mg/kg, 4.00 ± 0.96 mg/kg and 3.21 ± 0.93 mg/kg respectively from treatment D to treatment E. *A.stolonifera* and *L.perenne* had lower concentration of Mo in treatment E, decreasing from 1.72 ± 0.05 mg/kg and 4.83 mg/kg to 1.68 ± 0.18 mg/kg and 3.87 respectively. Some values observed were above the range of typical concentration of Mo in unpolluted Irish pastures; 0.05 to 2.0 mg/kg Mo (McGrath *et al.*, 2001).

4.51 Molybdenum levels (mg/kg) in herbage grown on mine tailings

	D	E
P.pratensis	1.51 (0.43)	1.87 (1.09)
L.perenne	1.72 (0.05)	1.68 (0.18)
H.lanatus	2.84 (1.31)	4.00 (0.96)
F.rubra	1.49 (0.56)	3.21 (0.93)
A.stolonifera	4.83 (0.85)	3.87 (0.62)

Treatment D- Tailings + TDB at 20 t/ha
Treatment E- Tailings + TDB at 50 t/ha
Values in parentheses are standard deviation of mean of 3 samples

4.9.10 Nickel

Nickel concentration in herbage is normally in the range 0.1 to 5 mg/kg (Mc Grath, 1995), and phytotoxicity is likely to occur between 10 and 100 mg/kg (Alloway, 1995). Herbage Ni levels found in this study were above the normal range, and some within the range where toxic effects are likely, when grown on mine tailings. It is also generally found that Ni concentration in herbage reflects that in the soil (Mc Grath, 1995). It was found that *Holcus lanatus* accumulated the greatest level of Ni 12.21 ± 1.85 mg/kg in treatment D decreasing to 11.51 ± 0.15 mg/kg in treatment E, followed closely by *Poa pratensis* which had levels of 11.82 ± 2.78 mg/kg in treatment D decreasing to 10.80 ± 3.84 mg/kg in treatment E. It was found in all grass species that Ni concentration was reduced with increasing TDB application (Table 4.52). *Lolium perenne* and *Festuca rubra* had lower Ni uptake than other species displaying levels of 5.39 ± 0.31 mg/kg and 6.45 ± 0.52 mg/kg in treatment D. *Lolium perenne* increased to 5.55 ± 0.23 mg/kg and *Festuca rubra* conversely decreased to 6.29 ± 1.04 mg/kg. Surprisingly, *Agrostis stolonifera* displayed a high concentration of Ni in treatment D; 13.27 ± 1.93 mg/kg. However, this decreased to 8.9 ± 0.3 mg/kg in Treatment E. This decrease can be attributed to the increase in soil organic matter that reduced the availability of Ni as a result of the binding of the metal in the organic complexes described by Mc Grath (1995).

Nickel concentration of herbage is significantly higher ($P<0.001$) when grown on Silvermines tailings than when herbage is grown on an uncontaminated agricultural soil. All values obtained in herbage grown on agricultural soil had elevated Ni content compared with typical ranges in unpolluted Irish pastures of 0.5 to 3 mg/kg (McGrath, 2001).

Table 4.52 Nickel levels (mg/kg) in herbage grown on mine tailings

	D	E
P.pratensis	11.82 (2.78)	10.80 (3.84)
L.perenne	5.39 (0.31)	5.55 (0.23)
H.lanatus	12.21 (1.85)	11.51 (0.15)
F.rubra	6.45 (0.52)	6.29 (1.04)
A.stolonifera	13.27 (1.93)	8.90 (0.30)

Treatment D- Tailings + TDB at 20 t/ha
Treatment E- Tailings + TDB at 50 t/ha
Values in parentheses are standard deviation of mean of 3 samples

4.9.11 Selenium

Herbage growing on Silvermines tailings exhibited Se levels of less than the limit of detection 6.66 mg/kg. Selenium concentration in unpolluted Irish pastures is in the range 0.03 to 0.5 mg/kg (McGrath, 2001), therefore, it is not possible to determine if Se values were within this range or indeed if fluctuations existed in herbage concentrations of Se between different treatments.

4.9.12 Zinc

DAFRD (2000) found herbage growing on Silvermines tailings to contain Zn levels of 191 mg/kg. SRK (2002) quote levels of 378 mg/kg Zn in herbage on Tara Mines tailings. Levels of 816.58 mg/kg and 688.76 mg/kg were found in two grass species growing on tailings containing on average 7607 mg/kg and 3562 mg/kg Zn (Shu *et al*, 2002).

In the current study, Zn concentration was greatly elevated in herbage grown on Silvermines tailings compared with Zn levels in herbage grown on agricultural soil and was statistically different ($P<0.001$) between the two substrates.

Table 4.53 Zinc levels (mg/kg) in herbage grown on mine tailings

	D	E
P.pratensis	732.15 (19.39)	705.31 (43.56)
L.perenne	505.93 (144.42)	472.02 (21.23)
H.lanatus	508.94 (36.93)	448.92 (11.22)
F.rubra	604.01 (51.84)	443.12 (170.13)
A.stolonifera	686.34 (86.51)	436.49 (34.73)

Treatment D- Tailings + TDB at 20 t/ha
Treatment E- Tailings + TDB at 50 t/ha
Values in parentheses are standard deviation of mean of 3 samples

Results in Table 4.53, show a similar trend to results from a greenhouse trial carried out by Ye *et al.* (2001). In both cases a reduction in Zn concentration in substrate and subsequently herbage grown thereon occurred on addition of sludge to Pb/Zn tailings. These authors noted a reduction of Zn concentration in leaves of *S. roatrata* on addition of sludge from 522 mg/kg to 455 mg/kg, 202 mg/kg and 129 mg/kg on addition of 25%, 50 % and 75% sludge respectively. Another legume *S. cannabina* showed decreases in Zn concentration from 447 mg/kg to 312 mg/kg, 226 mg/kg and 221 mg/kg on addition of the same sludge applications.

Zinc levels in herbage grown on mine tailings in this study ranged from 436 mg/kg to 732 mg/kg. These levels were above the range of 100-400 mg/kg where toxicity effects are likely to occur (A lloway, 1995). This study observed a reduced Zn concentration with the higher TDB application rate of 50t/ha in treatment F. *Poa pratensis* displayed highest Zn accumulation, on average 732 mg/kg in treatment E and 705 mg/kg in treatment F. *Lolium perenne* and *Holcus lanatus* displayed lowest Zn levels, although in treatment F, *Agrostis* accumulated lowest Zn concentration. Similarly, on agricultural soil, *Agrostis stolonifera* accumulation was lowest among the species at the highest TDB application. Zinc absorption and accumulation by plants vary widely between plants and species (Kiekens, 1995).

4.9.13 Summary

The order of total metal concentration in TDB was Zn>Cu>Ni>Pb>Cd. Results from this study showed the order of total metal concentration in Silvermines mine tailings was Pb>Zn>As>Cu>Ni>Cd (Section 4.1). Tailings vegetation displayed different levels of uptake among species. However, in general, the order of total metal concentration in herbage grown on Silvermines tailings is Zn>Pb>Cu>Ni>As>Cd. This concludes that metal uptake by grass species is not directly related to levels of all metals in the soil. Despite the extremely high Pb concentration in tailings, Pb was not accumulated as readily was Zn in the plant species used in these trials. Although Ni, As and Cd are at the lower end of the scale in relation to uptake by grass species, the concentration of these elements in herbage may be potentially hazardous.

5.0 Conclusions and Recommendations

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The addition of TDB, from Ringsend sludge treatment facility in Dublin to agricultural soil enhanced the soil as a growth medium. An increase in pH, to a near neutral pH (Gardiner and Radford, 1980), optimal for plant growth (Olness *et al.*, 1988), as well as increases in organic matter, organic C, CEC, total N, available P and exchangeable K were recorded. Increase of each of the above parameters improved soil in relation to plant growth (Gardiner and Radford, 1980; Epstein *et al.*, 1976). The improvement of soil as a plant growth medium, through the use of sludge as a soil conditioner has been shown also by Olness *et al* (1998).

Application of TDB enhanced shoot height and dry matter yield of five grass species and one clover species which were grown on agricultural soil. On agricultural soil, the yield of all grass species was significantly higher than both the control and 2 t/ha treatment when a TDB application rate of 20 t/ha was used. At an application rate of 2 t/ha, yield was greater in all grass species than the control, although not significantly. The application of TDB to soil increased growth of the clover species *Trifolium repens* although these increases were not significant. A visible difference in shoot height was clearly noted whilst trials were in operation and the growth rate of all species was enhanced with the addition of TDB, in particular at the higher application rate of 20 t/ha. The use of an application rate higher than 2 t/ha is recommended from a plant yield perspective. However it is also important to note that biosolids application to agricultural land must reflect the nutrient requirements of the crop as determined by a soil test. Although the higher rate of 20 t/ha did increase yield and growth rate, it was not proportional to the factor of ten fold increase in application rate. Therefore, in order to identify the best application rate, a further series of pot trials at 2, 6, 10, 14 and 18 t/ha are required. This should be followed by a series of field trials.

Some metals in agricultural soil were below the limit of detection when analysed by ICP-MS. These metals were As, Se, Cd, Hg and Cr. Therefore, this study did not deduce if these metals are within the limits set in the 'Waste Management (Use of Sewage Sludge in Agriculture) Regulations, 1998' (SI 148 of 1998) to allow use of sludge on agricultural soil. Adequate levels of Bo, Co, Mn and Mo were found and slight increases were noted with the addition of TDB. Copper, Pb and Zn were within limits set in SI 148 of 1998 for use of sludge on land, however, they were slightly greater than Irish figures quoted by Mc Grath (1998) except in the case of Pb. Increases in the concentration of these metals in soil increased on addition of TDB. In most cases, the increase was only significant in Treatment C, 20 t/ha. However, this would not be of concern as the 'Waste Management (Use of Sewage Sludge in Agriculture) Regulations, 1998' (SI 148 of 1998), state that only 2 t/ha of treated sludge may be applied to agricultural land in Ireland per annum. Nickel concentration in the agricultural soil used in this study was above the Irish average quoted by Mc Grath (1998) and, would be a limiting factor in the application of TDB as the levels exceed those cited in the Regulations (SI 148 of 1998). Application of TDB significantly increased Zn concentration in the soil in both treatments.

Herbage grown on agricultural soil exhibited levels of metals below the limit of detection. Due to this, one cannot state if harmful levels of As, Cr, Hg and Se were present in herbage from results obtained, although this seems unlikely. Cadmium levels were below the limit of detection. Adequate levels of Bo (Bradford, 1966), Co (Coulter *et al.*, 1999; Rogers and Murphy, 2000), and Mo (Rogers and Murphy, 2000) were obtained. Although increases in these metals were noted in some species, generally these fluctuations were not elevated and not significantly different from the control.

Copper levels in herbage were within normal ranges found in Irish herbage (Coulter *et al.*, 1999; Rogers and Murphy, 2000). Uptake of Cu by all species decreased slightly in Treatment B, and then, increased above control levels in Treatment C. This decrease is attributed to the complexing action of sludge organic matter, making Cu less available for plant uptake (Hooda and Alloway, 1994). Uptake of Pb was also lower in Treatment B in all species. This is likely to be a result of the same scenario, documented by Baker and Senft (1995). Generally, Pb concentration increased in Treatment C, although it still remained less than the control. Lead levels were within normal range for an urban soil but slightly elevated compared with other greenhouse trials (Fleming and Parle, 1977). Therefore, Pb levels were affected by TDB application, and, disagreed with the findings of Aitkin and Cummins (1997). Lead in herbage is generally unrelated to soil concentration and not readily accumulated by herbage (Davies, 1995). An unusual trend was noted with Ni concentration in herbage. Uptake in some grasses increased in Treatment B and decreased in Treatment C in comparison with the control soil. This is unusual as Ni is normally readily available in soil (Mc Grath, 1995). Other authors (Hooda and Alloway, 1994; Antoniadis and Alloway, 2000), also observed increased herbage levels of Ni when sludge was applied to soil.

Zinc herbage levels were slightly higher than mean values for Irish grassland (Coulter *et al*., 1999; Rogers and Murphy, 2000), but were within the range for Irish urban soil (Fleming and Parle, 1977) even though the soil used was sourced rurally. Although Zn values did fluctuate between treatments, generally, the uptake was greatest in Treatment C and a significant difference were recorded only once. No major significant differences were observed between Treatment A and B. Although Zn only increased to a small degree in Treatment C, results are comparable to those found by Hooda and Alloway (1994) and Antoniadis and Alloway (2000). In all but one grass species the order of metal concentration in grass grown on TDB amended soil was identical to the order of metal concentration in TDB. This disagreed with the finding of Mc Grath (1995) that Cu is more available than Zn, although this trend may differ in full scale trials implemented for a longer period of time. Overall metal levels in herbage in this trial were higher than levels found in the literature, this is more than likely to be as a result of enhanced uptake often observed in greenhouse trials (Alloway, 1995b; Chaney, 1994). Soil metal levels were not greatly affected by application of TDB to soil, and subsequently herbage metal levels were not significantly elevated as a result of TDB application to soil.

Thermally dried biosolids improved the chemical characteristics of an agricultural brown podsol and resulted in little change to the total metal levels in the soil. The application of TDB at 2 t/ha to agricultural soil resulted in no significant increases in metal levels, therefore, the use of a higher rate of TDB application may be beneficial. A rate of 5 t/ha or 10 t/ha, whilst less than the 20 t/ha application rate used in these trials, is not likely to cause adverse effects on soil metal or herbage metal concentrations. This of course, is only provided that over the long term metal levels in both soil and herbage are frequently monitored. Application of biosolids also requires monitoring as it may result in excessive loading of N and P to soil, therefore posing a water pollution risk. *Agrostis stolonifera*, although not frequently found growing in Irish pastures accumulated lowest concentration of most elements on agricultural soil. Normal pasture species such as *Holcus lanatus, Lolium perenne, Poa pratensis* and *Trifolium repens* had similar results and accumulated higher levels of metals.

The chemical properties of mine tailings were found to be quite different from the agricultural soil and were generally unfavourable for plant establishment and growth (Williamson *et al.*, 1982). Amendment of tailings with TDB caused a number of chemical changes within the substrate. A decrease in pH was achieved by addition of TDB, although still remained slightly higher than the pH range optimal for plant growth (Williamson *et al.*, 1982). Favourable increases, also documented by Ye *et al.* (2001) in organic matter, organic C, total N and available P resulted from TDB addition tailings. Additionally, CEC was increased favourably.

A preliminary finding of the study was the inability of grass to establish on Silvermines tailings without an ameliorant. No germination of seeds took place where the substrate was unamended. The lack of establishment of vegetation on tailings alone is attributed to the physical limitations of the substrate as a growth medium. The lack of moisture holding capacity within the tailings in the greenhouse trials and the poor physical structure of the substrate was responsible for this occurrence. Grass species did establish and prevail on mine tailings which were amended with TDB. Although increases in dry matter yield were observed on addition of TDB at 50 t/ha in four of the grass species, only *Poa pratensis* and *Festuca rubra* displayed significantly higher yield at this application rate as opposed to the 20 t/ha application rate. *Holcus lanatus* and *Trifolium repens* exhibited decreased yield on addition of a higher TDB application rate of 50 t/ha and, in general, yield of both these species was poor. *Trifolium repens* when grown on mine tailings displayed severe phytotoxicity directly resulting from the inherently high concentration of Cu and Zn in the substrate. This phytotoxicity has been documented elsewhere (Ibekwe *et al.*, 1997).

Metal levels, particularly those cited in the 'Waste Management (Use of Sewage Sludge in Agriculture) Regulations, 1998' (148 of 1998), have a higher concentration in tailings than in agricultural soil. Levels of Bo, Cr, Hg, Mo and Se in mine tailings were below the limit of detection. Arsenic concentration in Silvermines tailings was extremely high, however it was reduced on addition of TDB, and further reduction occurred at the higher application rate. Cadmium levels in tailings also followed this trend which has also been found by Ye *et al.* (2001). These authors also noted the same result as this study in relation to Cu. Copper levels in this greenhouse study, however, increased with the addition of sludge although the effect was greater at the higher application rate. Levels of Cd, Pb and Zn were substantially higher than levels cited by SRK (2001).

Nickel, Pb and Zn followed a different trend when amended with TDB. Levels of these metals increased in Treatment D, 20t/ha, however on addition of the higher TDB application rate to 50 t/ha levels decreased. Other authors who have observed similar results (Bergholm and Steen, 1989), state the reduction to be resulting from complexing of these metals to metal binding sites on the organic matter matrix (Baker and Senft, 1995), and the dilution effect caused by the introduction of a less toxic material (Ye *et al.*, 2001).

Unamended mine tailings was unable to promote, establish or sustain plant growth of any kind. The application of TDB enhanced the physical structure of the tailings. This was exhibited by the ability of the tailings to retain moisture and, the increased porosity that its previously uniform particle structure lacked. *Trifolium repens,* which was planted alone failed on tailings. This has been documented elsewhere (Ye *et al.*, 2001; Pallant and Burke, 1994) and is likely to be caused by elevated Cu and Zn levels in the substrate (Ibekwe, 1997). A seed mixture consisting of *Agrostis stolonifera, Holcus lanatus* and *Trifolium repens* is likely to perform well on tailings. The latter is likely to survive and grow better in a seed mixture than when grown alone. *Agrostis stolonifera* and *Holcus lanatus* showed highest yield response on tailings, whilst *Agrostis stolonifera* accumulated lower levels of metals than other grass species used.

Arsenic in herbage grown on tailings was elevated compared with normal herbage levels and the levels found in herbage grown on Silvermines Tailings Management Facility (DAFRD, 2000; SRK, 2002) decreased with the higher TDB application rate, however, substrate levels were also lower in this treatment. At this concentration of As in herbage, toxic effects are likely (Alloway, 1995a). Boron levels in herbage on tailings are slightly higher than those on agricultural soil, although these levels are not excessive (Bradford, 1966).

Cadmium concentration in herbage decreased with increasing concentration in the substrate. Ye *et al.* (2001) also observed this trend. Cadmium concentration was generally lower when grown on agricultural soil. Cobalt concentration in herbage grown on tailings was slightly elevated, with slight fluctuations resulting from TDB addition. Copper displayed a different uptake pattern to other metals on tailings. It differed in both substrate and herbage, this was also observed by another author (Ye *et al.*, 2001). Copper levels in herbage grown on tailings were above levels in literature (DAFRD, 2000; SRK, 2002), and also above agricultural soil herbage levels. Copper concentrations found were within a range for phytotoxicity (Alloway, 1995a) and increased with increasing TDB application rate.

Copper, Pb, Ni and Zn all displayed values above those found in herbage on Silvermines tailings (DAFRD, 2000; SRK, 2002) and within a range likely to be phytotoxic (Alloway, 1995a). However, unlike Cu, concentration of Pb, Zn and Ni decreased with increasing TDB application. A trend also noted by Ye *et al.* (2001) for Pb and Zn. In the case of Pb and Ni this can be attributed to Pb being in a stable or insoluble form following sludge addition (Davies, 1995); or the complexing of Ni with the organic matter matrix, thus rendering it less available to plants (Baker and Senft, 1995; Mc Grath, 1995). Additionally, the 'dilution effect' reduced metal levels in the immediate vicinity of plant growth by mixing with sludge (Ye *et al.*, 2001).

Metal uptake by grass species on tailings was not directly affected by levels in the soil, demonstrating the ability of certain metals, such as Zn, to be more readily accumulated than other elements that may have a higher concentration in the substrate. Significantly higher concentrations of Co, Cu, Pb, Ni and Zn were noted when herbage was grown on mine tailings in comparison with herbage grown on agricultural soil. Cadmium levels were generally higher but due to some levels being undetectable, the difference may not be significant.

Although most herbage growing on tailings exhibited metal levels exceeding values in the literature (DAFRD, 2000; SRK, 2002); and within ranges stated to be phytotoxic (Alloway, 1995a), no visible signs of stunted growth or toxicity were observed amongst the grasses. This was not the case with *Trifolium repens* however, where plant mortality and decay were evident after a number of weeks. The grass species *Agrostis stolonifera* which has evolved metal tolerant ecotypes (Williamson *et al.*, 1980), frequently displayed lowest uptake of metals. This may be due to its high dry matter yield in comparison with other species, thus, providing a dilution effect of high growth also documented by Antoniadis and Alloway (2002).

The Silvermines Pb/Zn tailings, which, prior to TDB application was too hostile to plant establishment, was successfully vegetated in this study. The effect of TDB on the chemical characteristics of the tailings was favourable, resulting in increase levels of essential plant nutrients and CEC, thereby aiding the establishment and growth of a number of grass species. *Holcus lanatus* and *Agrostis stolonifera* performed best in relation to yield response to TDB addition. Although metal levels in tailings were extremely elevated only *Trifolium repens* displayed any signs of toxicity or mortality. Herbage metal levels were within ranges stated by some authors to be toxic, the application of TDB caused a reduction in herbage metal levels in most cases. Application of TDB at 50 t/ha was not as successful as at the lower rate of 20 t/ha in terms of yield response, it is recommended that rates of 25, 30, 35 and 40 t/ha be investigated prior to extensive use. In addition the use of a number of applications over time, using the lower application rate is likely to be more beneficial in the long term than for example one application of 50 t/ha.

Overall to note in this study was the elevated levels of metals in herbage in comparison with levels quoted in the literature. This study agrees with findings of other authors (Chaney *et al.*, 2000; Alloway, 1995b), that enhanced uptake or accumulation of metals occurs in greenhouse or pot trials as opposed to field trials. Additionally elevated temperatures in the greenhouse may enhance uptake and this may be responsible for elevated metal levels. Hooda and Alloway (1994), demonstrated this when they found higher levels of all metals when grown at 25°C as opposed to 15°C.

The use of TDB as a soil ameliorant and mine tailings substrate amendment was extremely successful. The chemical properties from a plant growth perspective, and plant yield on both substrates were improved. The metal levels on both substrates in some cases were changed slightly and no unfavourable or damaging effects were noted as a result of TDB application.

5.2 Recommendations

From the results of this study, the author proposes the following recommendations for any further research in relation to this type of project;

The results of this study conclude that TDB application to agricultural soil did not result in excessive metal levels in herbage. Long term analysis of herbage grown on biosolids amended soil should be carried out, in order to asses the effect of biosolids application in subsequent years.

Whilst greenhouse trials are an extremely valuable exercise in revegetation studies and provide essential information regarding species selection and biosolids application rates, this author recommends implementation of full scale field trials. Long term field trials on Silvermines Tailings Management Facility would give an exact representation of substrate metal levels and more importantly exact herbage uptake levels and trends. Unfortunately due to the Foot and Mouth epidemic and access issues, that part of the project could not be completed within the project time frame. This author recommends repeated biosolids application over a period of time and the use of a seed mixture. Based on the results of this project, the mixture should consist mainly of *Agrostis stolonifera, Holcus lanatus* and *Trifolium repens.* This should enhance the growth of the sward and reduce toxicity effects suffered by clover species when grown alone.

Further studies on Silvermines Tailings Management Facility should involve assessment of bioavailable levels of metals and leachate analysis from the tailings. The effect on biosolids application, if any, on these aspects may be a useful line of investigation.

Due to concerns over the heavy metal content of the of tailings herbage, the use of Silvermines Tailings Management Facility for the prolonged grazing of animals of any kind should be prohibited.

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APPENDIX 1

Appendix A

Herbage reference material Poplar leaves GBW07604

	Certified value	Range	Avg value obtained from analysis	% Recovery
Arsenic	0.37	0.31 - 0.43	<6.61	
Boron	53	49 - 57	45.26	85
Cadmium	0.32	0.27 - 0.37	<0.33	
Cobalt	0.42	0.4 - 0.44	0.37	88
Chromium	0.55	0.5 – 0.6	<16.52	
Copper	9.3	8.8 – 9.8	9.27	100
Mercury	0.026	0.023 - 0.029	<1.65	
Molybdenum	0.18	0.17 – 0.19	0.17	94
Nickel	1.9	1.7 – 2.1	1.89	99
Lead	1.5	1.3 – 1.7	1.46	97
Selenium	0.14	0.13 – 0.15	<6.61	
Zinc	37	36 – 38	34.59	93

** average figure minus digest blank (high values for blanks)

Sewage sludge reference material CRM 029-050

	Certified value	Range	Avg value obtained from analysis	% Recovery
Arsenic	26.5	7.7 – 45.4	<32.88	
Boron	16.6	14.3-18.9	<60.84	99
Cadmium	537	376 – 698	528.97	
Cobalt	3.07	0.550 – 5.58	<2.47	
Chromium	325	261 – 390	No value	
Copper	665	569 – 760	549.21	83
Mercury	4.17	1.68 – 6.65	<3.29	
Molybdenum	8.77	5.3 – 12.2	8.21	94
Nickel	150	112 - 188	140.73	94
Lead	227	208 – 346	198.78	88
Selenium	19	0.00 – 39.6	<32.88	
Zinc	847	587 – 1,110	824.65	97