Long term behaviour of compost-like-output and its associated soils

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Long term behaviour of Compost-Like-Output and its associated soils

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Abstract

In 2000, the re-interpretation of the Waste Strategy (WS2000) for England and Wales was published. This document clearly laid out the Government's new strategy for managing waste and resources more efficiently, and detailed the transformations required to deliver more sustainable human development. Compost-like-output (CLO), a material derived from optimally composting municipal solid waste (MSW), is one potential avenue through which these targets may be achieved.

When applied to agricultural land, or, as it is currently used, as a topsoil cover for landfill and reclaimed Brownfield sites, the adsorption of inorganic metal ions can involve several processes. The extent to which these processes occur in a soil is difficult to predict, but it is these processes that govern the concentrations of metal ions and complexes in soil solution and therefore ultimately determine the availability to plant root systems, access to groundwaters and thus the success of this waste management practice. To authenticate and potentially improve this procedure, a comprehensive Environmental Impact Assessment (EIA) is needed.

The aim of this study was to identify, quantify and characterise, under specific conditions, the release behaviour of a number of leachate components emanating from CLO and its associated soils, and to compare this performance against those of other waste materials and an agricultural soil. It was found that, although leachates from all treatments were weakly alkaline, substantial metal dissolution had occurred. Numerous heavy metals, nutrients and water-soluble metal salts were identified as being in major breach of landfill and drinking and surface water directives, as well as being significantly higher in concentration than a typical agricultural soil for the Durham region. In particular, extremely high conductivities (> 20mS m^{-1}) were recorded in undiluted and mixed CLO treatment leachates. Poor aesthetic quality and an extremely heterogeneous nature were also highlighted as major detrimental properties.

In view of this, a simple pre-washing procedure using tap-water was devised which showed that significant remediation value would be gained from this economical pre-treatment technique. However, for the most part, active remediation was found to be insignificant, and mixing significantly reduced the favourable high organic matter (OM) content characteristic of CLO. This suggests that the amending materials chosen offer little more amelioration than that achieved by passive dilution.

Further sequential extraction experiments and principal component analyses revealed that prevailing environmental conditions are of central consequence to the levels of contamination incurred. For the CLO-containing treatments, major releases were found to occur under field conditions experienced during the lysimeter trials – an oxic environment. The potential for further substantial contamination has, however, been shown to be immanent if an anaerobic environmental setting prevails. These anoxic releases are also true for sewage sludge, but additionally this material has been shown to intermittently leach components, under the same field conditions and to a significantly greater degree, that are characteristic of acidic, reducing and oxidising environments.

It is imperative, therefore, that if CLO or sewage sludge is to be used in agriculture, either as a basis for bio-fuel production or as a soil amendment, the prevailing conditions should be continuously monitored and any necessary action swiftly taken.

Declaration and Copyright

I confirm that no part of the material presented in this thesis has previously been submitted by me or any other person for a degree in this or any other university. Where relevant, all material which is the work of others has been acknowledged.

Signed:

Date

Acknowledgments

I would firstly like to thank Dr Fred Worrall for his supervision, patience, particularly during times when medication deemed it difficult to identify oneself, and expertise throughout the entirety of this project.

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Now that's the badger…

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Chapter 1

Introduction

1.1 Project Rationale

1.1.1 What is Municipal Solid Waste? The problem defined.

In 2000 the re-interpretation of the Waste Strategy (WS2000) for England and Wales was published. This document clearly laid out the Government's new strategy for managing waste and resources more efficiently, and described the transformations required to deliver more sustainable human development. The key word, then and ever since, has been 'sustainable.' Specific targets were set in view of the vast quantity of waste that was being sent to landfill, and the missed opportunity for recovering energy from this waste. At the time, this figure was around 400 million tonnes per year, around 27% of which was represented by the Municipal Solid Waste (MSW) fraction. As the name suggests, MSW is almost always predominantly household solid waste (domestic waste) which is collected by the municipality for the given area. This collection is normally carried out by the local authority itself, or can be contracted out to companies such as Premierwaste, for whom this PhD was conducted. Of the 28 or so million tonnes of MSW produced by England and Wales in 2000, a mere 17% was recovered (including recycling and composting) leaving 83% (21 million tonnes) to be landfilled.

Seven years on, in May 2007, a new strategy, specifically for England, was produced which addressed the progress made since 2000; based upon this information, a set of more ambitious and extensive aims were proposed for the future. Significant improvements to recycling and composting figures, in particular, have been made with a nearly quadrupled rate of 27% in 2005-6 of that achieved in 1996-7. The attempt at *'breaking the link between economic growth and the environmental impact of waste'* – (WS2000) also appears to have begun, with MSW obligation growth rates diminishing to 0.5% per year, significantly outstripping the average 3% economic growth rate typical of the late 1990's. This progress has been fuelled by the significant changes in policy to the landfill tax scheme, as well as the introduction of the Landfill Allowance Trading Scheme (LATS) in April 2005, which has shaped the future of landfill diversion by offering intelligent and flexible financial incentives to participating bodies. The latter offered Waste Disposal Authorities (WDA) the responsibility for effectively distributing tradeable landfill allowances, in accordance with the UK as a whole in achieving its government targets laid down by the Waste and Emissions Trading Act (2003). Each authority is given the options of trading allowances with other authorities, storing them for future years, or bringing future allowances forward. The scheme is therefore flexible with regard to individual investment strategies and thorough management infrastructures must be planned to ensure that the most effective waste diversion strategy is implemented. As a result of the landfill tax amendments, landfill tax has risen at a rate of £3 per tonne each year since April 2002. This figure currently stands at £32 per tonne. In April 2008, the Landfill Tax for active waste going to landfill was set to rise by £8 per tonne each year for the next three years at least, thus reaching a level of £48 a tonne for the financial year 2010/2011 – a 100% increase over 3 years (WS2007).

The diversion of waste away from landfill into other channels of waste management represents a carbon saving in itself, but of particular interest here is the significant carbon saving represented by the diversion of waste from incineration to aerobic digestion. Figure 1.1 illustrates the equivalent tonnes of carbon dioxide emitted by each waste management practice processing the same weight of MSW (Worrall, 2006 – *pers. comm.*). It clearly shows that, in the long term (>100 years), aerobic digestion produces substantially lower amounts of CO_2 relative to the other two waste management schemes (i.e., incineration and landfilling). After about 25 years and onwards, the process of incineration is shown to be more environmentally effective at lowering carbon emissions relative to landfilling, but aerobically digesting equivalent amounts of MSW over the same time-scale would almost halve the amount of CO_2 released comparative to incineration.

In 1992, the United Nations Framework Conservation on Climate Change (UNFCCC of FCCC) was created as an international environmental treaty at the United Nations Conference on Environment and Development (UNCED), informally known as the Earth Summit. Its stated objective is *"to achieve stabilisation of greenhouse gas concentrations in the atmosphere at a low enough level to prevent dangerous anthropogenic interference with the climate system"* – (UNFCCC). A key component of achieving this goal lies in the creation of the 1997 Kyoto Protocol, which significantly strengthens the convention's purpose by committing signed parties/countries to individual, legally-binding targets to limit or reduce their greenhouse gas emissions. To date, 189 countries have ratified the Protocol, which eventually came into force on the 16th February 2005 (DEFRA, 2008). Under this Protocol, developed or industrialised countries have committed to reduce their green house gas emissions by 8% of that seen in 1990 by a target date of 2012. In the UK this figure is 12.5%. Subsequent to this, the European Union devised The EU Emissions Trading Scheme (Directive 2003/87/EC) which is the world's largest entity-based domestic cap and trade emission allowance scheme. The scheme allows the EU's 15 member states to redistribute their personal allowances (1 allowance equals 1 tonne of CO_2) amongst installations in the scheme based on how much CO_2 each heavy industry emits. Therefore, the trading of carbon credits on the open market designates carbon reservation as a profitable enterprise. If a company exceeds its environmental targets, as set out by the government, the surplus carbon saved is then liable for sale to lesser companies who, for whatever reason, fail to meet this jurisdiction. This monetary inducement not only encourages carbon emitting companies to reduce their overall carbon emissions, but actively promotes their decreasing levels to below that set by the government targets.

Companies such as Premierwaste have also taken advantage of additional funding which was made available for the development of new waste treatment facilities and kerbside recycling schemes. These initiatives have driven the Premier Advanced Recycling Centre (PARC) to become the largest independent waste management company in the North East and one of the largest in the UK. In order to meet and hopefully exceed these government targets, new and existing waste management strategies and technologies need to be further advanced, turning the projection of a sustainable developed future into a reality. The manipulation of the composting process, aerobic digestion in particular, may offer one step toward the prospect of just such an environmental future.

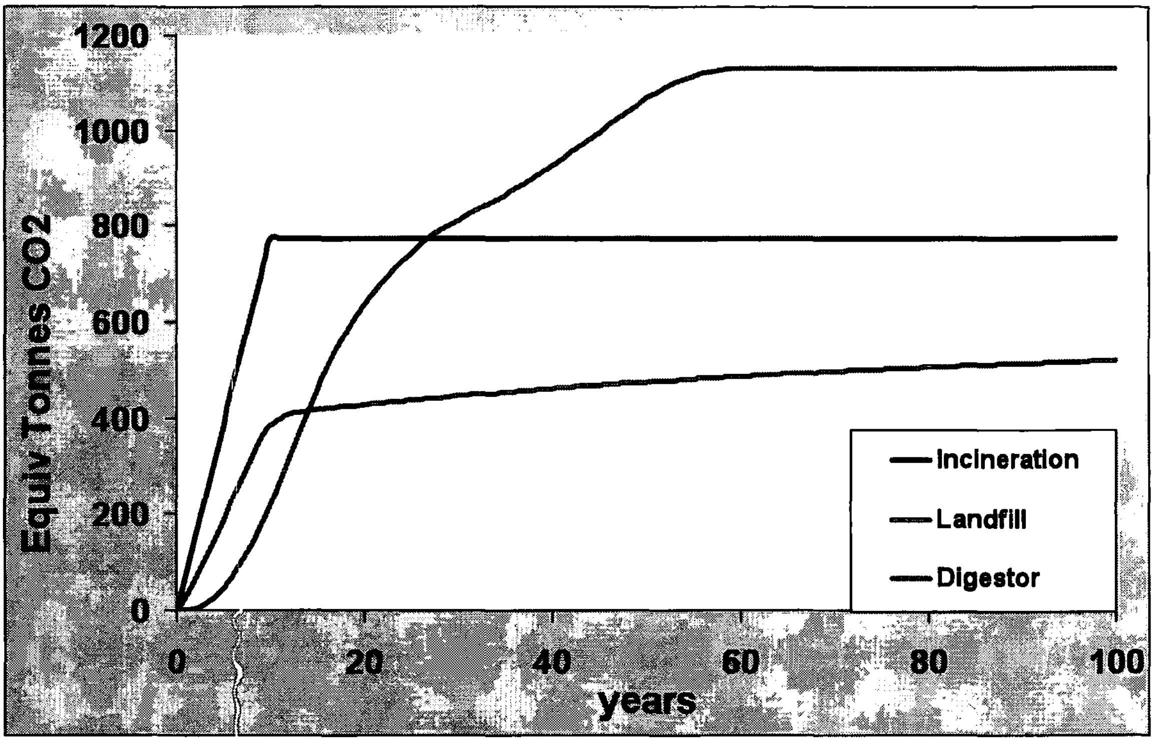


Figure 3.1: Illustrates the equivalent tonnes of CO_2 emitted for the three MSW management practices: incineration, landfill and aerobic digestion. Adapted from Worrall, 2006 (*pers com.*).

1.2 Solutions

1.2.1 Composting and Aerobic digestion of MSW

With the introduction of this new government regime, waste disposal priorities have shifted to focus upon the biodegradable waste fraction and so the significance of composting, in particular, aerobic digestion increases relative to other treatment processes. This form of waste management utilises the natural composting process by optimising exact controlled conditions, such as aeration rate, temperature and water content, to maximise the efficiency at which organic material is decomposed. It is estimated that over 75% of un-segregated MSW can be biologically degraded and further used for compost production (Olsson and Retzner 1998). This figure still remains high at 55-60% if all recyclable paper products are accounted for.

'Composting is an aerobic process, in which a solid organic material is converted to a more stable, humified product' – (Cronje *et al.*, 2003). The principal factor governing the efficiency of a composting body is the temperature accumulation

and distribution within and throughout the composting material. In addition, the temperature of the system influences other variables, such as sufficient nutrient supply, moisture content, pH and, probably most relevant of all, oxygen content (Cronje *et al.,* 2003). Oxygen content, especially in forced systems (in-vessel systems) such as that operated by Premierwaste, reciprocates its value by also monitoring temperature. The effective aeration of the decomposing organic material governs the spatial distribution of gases, moisture and temperature throughout, which in turn determines the supply of oxygen to the heat-generating microbes. Providing this microbial population is supplied with sufficient nutrients, obtained from the organic material itself, and suitable amounts of oxygen from forced airflow inlets, the self-heating/self-insulating arrangement will continue.

In the natural environment, in static-pile systems, it can often take as long as 2 weeks to attain optimum composting conditions owing to the imperfect provision of one or more of the variables described. On reaching this optimum phase the composting body undergoes a number of biological, chemical and physical changes (Sadakar, 2001 and 2003). Initially, the easily decomposable fraction is attacked; this includes sugars and starches, proteins, fats, and some cellulose parts typically found in undigested feedstocks. Here, the temperature resides at around 20-40°C, conditions (mainly the high availability of easily exploitable organic substances) are most suited to mesophilic pathogens (mesophiles). This microbial activity gradually raises the temperature to a maximum of 70°C at which stage the compost heap is said to be in the thermophilic phase and the dominant micro-organisms are now thermophilic pathogens (thermophiles) (Hogland *et al.,* 2003). This is considered to be the most productive stage of the composting process and is referred to as the active stage; the temperature rise can occur over just a few hours owing to the high porosity and self-insulating character of the organic material of which the pile is predominantly composed.

Sustained thermophilic temperatures are crucial in ensuring rapid decomposition of organic matter while simultaneously providing optimal conditions for the effective destruction of most potential human pathogens, as well as most plant pathogens and weed seeds. Periodic mixing of the compost pile is essential for maximum pathogen and seed kill as well as affording additional ventilation by increasing the size and number of pore sites and channels. Without aeration the interior of the compost heap can exceed mesophilic temperatures (70+°C), inhibiting virtually all microbial activity (Turner, 2002). The period, therefore, for which this optimum regime can be sustained is ultimately dependent upon the length of the aerobic phase, i.e., how much available oxygen is contained within the pores and voids of the waste body and how easily oxygen can diffuse into the waste from the surrounding environment (Hogan *et al.*, 1989). Eventually the readily utilisable organic substrates remaining will not be sufficient to support thermophilic microbial activity in which case supplementary feedstock maybe needed to ensure maximal degradation and pathogen removal.

With the return of mesophilic conditions the final curing stage begins, during which fungi and actinomycete populations predominate and the bacterial mass is depleted. Bacteria are considered less adept at metabolising the remaining more resilient compounds, mainly lignins and humic materials (chitin) but also some cellulose too. These water in-soluble recalcitrant compounds, renowned for their chemical complexity, can only be broken down by extracellular enzymes – a component which bacterial cells do not posses (CIWMB Publication #443-00-005 2001). Consequently, microbes capable of manufacturing extracellular enzymes will have a discernable advantage at colonising this stage of the composting process. At this point, humus is formed, which results from the incomplete degradation of the residing organic matter. It is humus, with its natural ability to retain nutrients (nitrogen and phosphorus), micronutrients (copper, zinc, iron, manganese etc.) and water, that this process is accredited to (CIWMB Publication #442-00-013 2001). Organic matter is dissolved and absorbed by various micro-organisms utilizing the nutrients and energy for their own synthesis. Their activities convert most of the organically bound nutrients back into a mineral form which can then be exploited by plants and other microbes. The undigested portion of biologically resistant compounds amasses as various components of humus. This valuable end product effectively stores carbon in more stable, resistant forms; a key principal on which Premierwaste depends.

Thus, materials that contain a large percentage of lignins, cellulose or other biologically resistant components have less to offer plants in the way of recyclable nutrients but contribute significantly to the formation of humus. Different plants have different ratios of these organic components, but variance also appears in the same plants at different stages of their life; green leaves from deciduous trees, for example, do not contribute very much substance for the accumulation of humus but do benefit the immediate needs of micro-organisms and plants more than their dry, fallen counterparts. Humus, however, is not completely immune to decomposition and will eventually be recycled so that all the elements in humus revert back to their initial sources.

This principal is of particular relevance when assessing the causes for the heterogeneous nature displayed by compost-like-output (CLO) itself. In addition to the multiple sources from which household waste is derived, including commercial, industrial and horticultural sources, seasonal variations can also be great. Often, with the green waste fraction, this temporal difference is closely related to a change in organic detritus accumulation, more of which occurs in the autumn period. Much of this compostable material at this time will be ideally suited for humus production, whereas in spring and summer a significantly larger proportion is 'fresh,' colonised almost immediately by micro-organisms. Concurrent to this is a secondary product turned out by Premier: 'Parcgro' has been '*specifically manufactured comprising of three recycled materials blended together: CLO, composted green waste and screened soils and subsoils*'- (Premierwaste, 2008). This synthetic soil mixture is currently being utilised as topsoil on 'Brownfield' sites as a basis for Short Rotation Coppice Willow, and therefore must specifically accommodate the additional needs of plants.

1.2.2 Premierwaste's strategy

Premierwaste's mission is summarised as: *'Priding itself on tackling the core environmental objectives of Government, industry and commerce, through the development of unique recycling, composting and diversion from landfill technologies.'* - (Premierwaste, 2008).

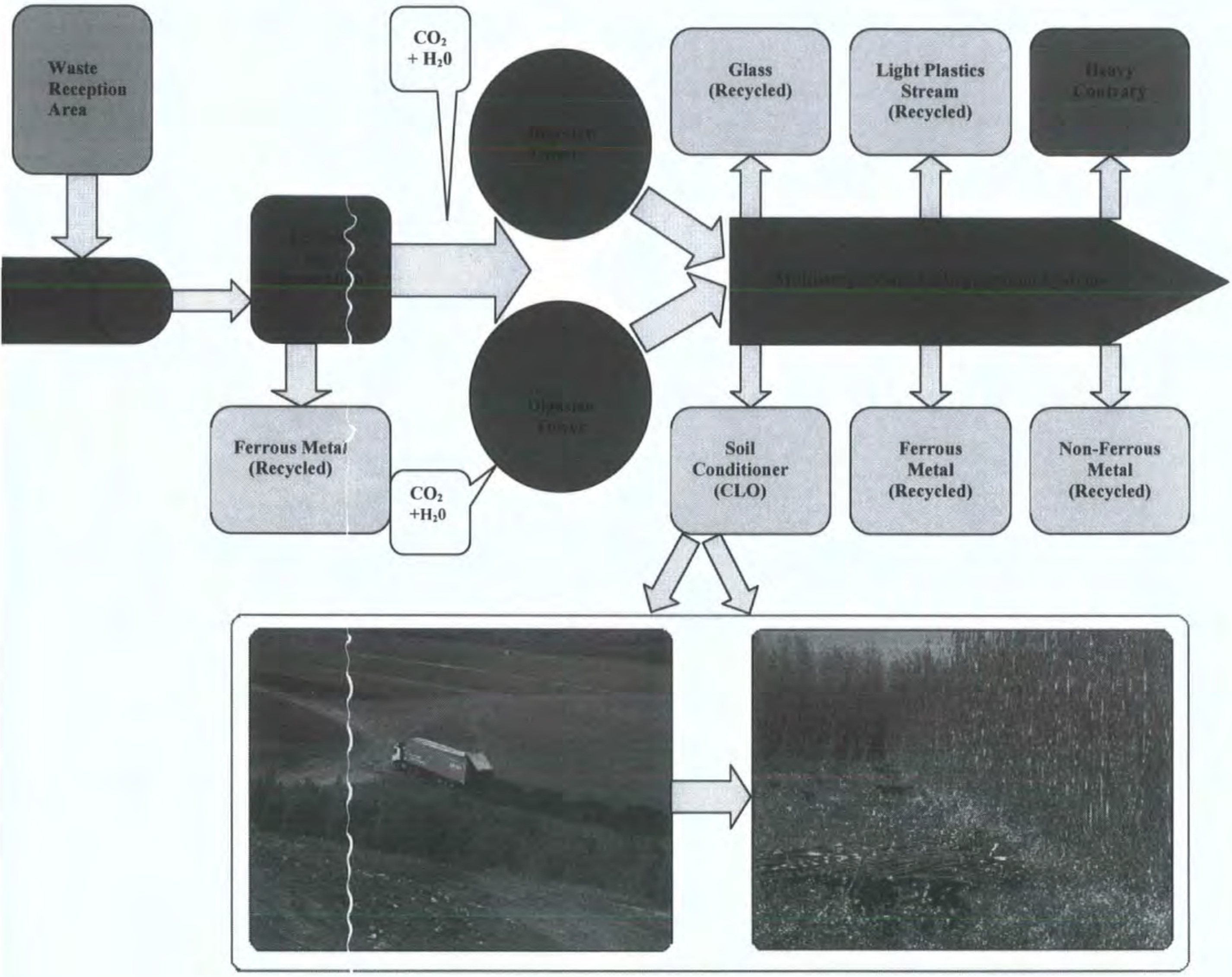


Figure 1.2: Graphically summarises the various processes involved and the waste streams and recyclables generated from the waste management practice conducted Premierwaste.

In addition to recycling the biodegradable fraction of un-segregated municipal solid waste the company boasts an overall diversion from landfill rate of >80% by employing patented technology that can effectively recover glass, light plastics and metals. Figure 1.2 visualises the complete recycling process.

Initial un-segregated household waste is loaded into a low speed, high torque shredder where the waste is shredded into suitably sized pieces for effective processing in the digester vessel. The shredded material is discharged onto a conveyer belt which transports the waste up to the digester vessels. A spinning disk and mechanical arm then evenly distribute the waste over the whole width of the first digester chamber. Once full, the chamber conditions are under computer control which ensures that an optimum processing environment consisting of exact humidity, temperature and aeration conditions is kept constant 24 hours a day. This is paramount to effectively accelerating the natural composting process – which normally takes many months – to 6 to 9 days. Gaseous emissions are constantly monitored and cleaned to remove any traces of particulates, bacteria/fungi and ammonia and to certify environmental compliance.

After 2 to 3 days processing time, dependant on waste specific conditions, namely waste composition, the now partially degraded material is gravitationally discharged into the second processing chamber below. The digester is divided into three chambers so that optimum reactions can be maintained throughout the entire vessel with one chamber being emptied as the next is filled. Agitation of each separate chamber is performed by huge mechanical mixing arms which also act as aeration devices.

On leaving the third chamber, usually after about 6-9 days, the digestion process is said to be complete and the sanitised cured material is discharged via the means of an Archimedes screw and vibrating conveyor belt. This aids the break up of the mixed stabilised waste and facilitates later segregation techniques, the first of which involves a secondary conveyor belt that takes the waste under a magnetic separator, extracting any ferrous material, such as steel cans, and depositing them into a ferrous recycling container to be returned for smelting. Screening of the remaining solid material is carried out using a cylindrical 'Trommel' screen which sorts the digester output into fines (<8mm) and oversize (>8mm) for further segregation. The fines, which now constitute most of what is known as compost-like-output (CLO), are finally processed through a fluidised density separator to remove any remaining glass particles. This soil conditioner is then transported to the aggregates recycling centre at Coxhoe landfill site where it is windrowed, on average, for a further 6 months. Finally, the oversized material undergoes a secondary density separation that further divides un-digested (non-biodegradable) material into light (plastic) and heavy contrary fractions (heavy plastics, textiles etc.). The heavy contrary material is then discharged onto a belt conveyor which first passes under a secondary head-drum magnet to remove any persistent ferrous material, and then through an Eddy current separator which removes non-ferrous metals, such as, aluminium drinks cans. Appreciable amounts of brass, copper and zinc are also extracted during this phase, all of which are sent for recycling. The light plastic stream is dispatched for further refinement, and packed into bales before being sold into extrusion markets.

In all, over 80% of the original un-segregated household waste is either digested down into a further recyclable CLO end product or sent for recycling as glass, metals or plastics. The remaining contrary fraction is sent to landfill.

1.2.2.1 Compost-like-Output: what are its merits?

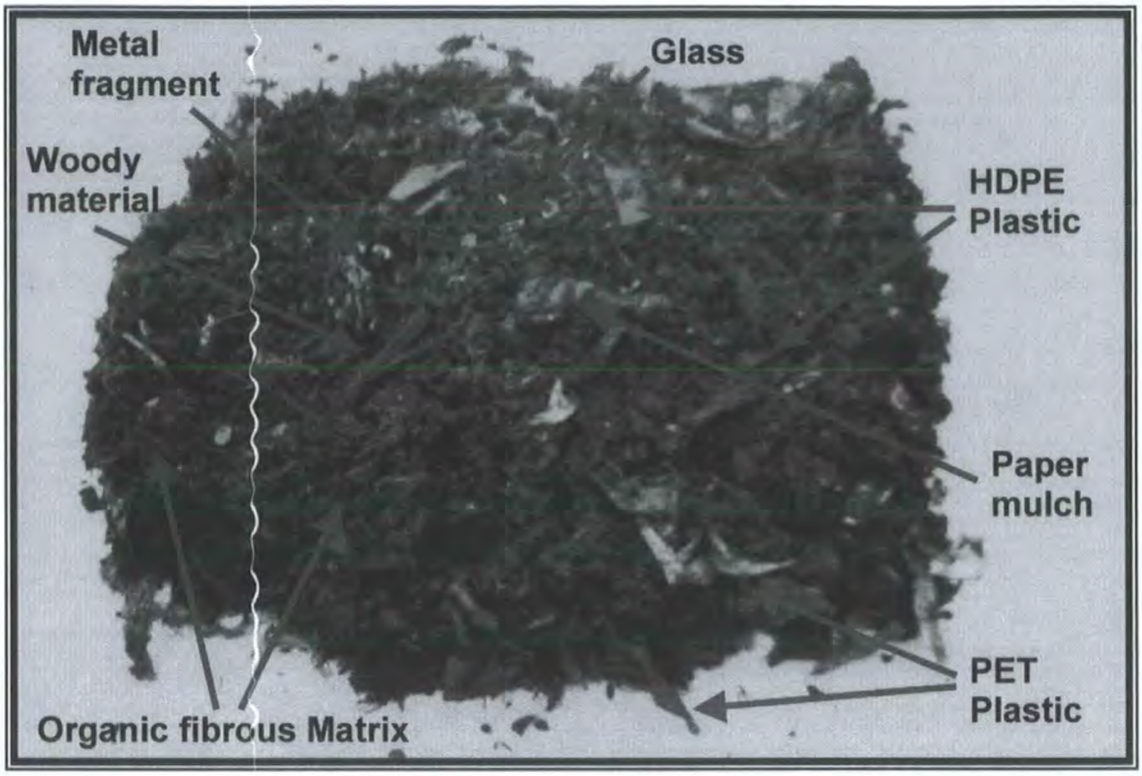
Compost-like-output is an organic rich substance derived from the aerobic digestion of MSW once all recyclable metals, plastics and glass have been removed. The high organic matter content and presence of slow release plant nutrients, in particular nitrogen and phosphorus, provides the potential for it to be used as a sustainable material (e.g. Montemurro *et al.*, 2005, Walter *et al.*, 2006 and Negre *et al.*, 2006). The application of MSW and its associated materials to land, usually as a soil amendment, have been extensively studied in agricultural systems covering a diverse array of physical, biological and chemical properties. Examples include the potential for the remediation of Brownfield sites by either restoring the soil microbial activity in re-establishing a fertile nutrient balance or by the general improvement of the soil's physical properties (Guerrero *et al.*, 2000 and 2001). The effects of adding these organic wastes to varying terrains including grasslands, reclaimed lands, native rangelands (Sort & Alcaniz 1996, Pierce et al., 1998, Jorba & Adres 2000, Ros *et al.*, 2003, Moreno-Penaranda *et al.*, 2004) and scrublands in semiarid Mediterranean environments (Walter *et al.*, 2006) have also been reported. Irrespective of site-specific requirements, the desired effects following correct application of composted MSW usually revolve around the introduction to, and conservation of, organic matter within the soil and the development of a sustainable agroecosystem.

Supplementary to the favourable nutrient content, it has been suggested (Sikora and Yakovchenko, 1996) that plant yields could also be increased according to a general improvement in soil physical structure, brought on by the application of MSW compost to the soil. This improvement in soil properties – specifically increased porosity, water retention capacity and aggregate stability – would act as a positive feedback mechanism with increased crop yields further enhancing the enriched soil, by means of providing additional plant residues. Furthermore, the establishment of well developed plant root systems with greater penetrative power will aid in preventing excessive erosion from run-off water. The land will thus be maintained as an agricultural source, directly enhancing the terrestrial carbon sink as well as indirectly contributing to the fight against rising CO_2 emissions by recycling anthropogenically generated waste as a basis for sustainable re-growth.

1.2.2.2 Compost-like-Output: what are its downfalls?

1.2.2.2.1 Heterogeneous nature

As can be seen (photograph 1.1), compost-like-output can be extremely heterogeneous in physical character.. A careful balance between a representative sample record, both typical and realistic of the physical nature and purpose for which the CLO will be used, and experimental accuracy and precision had to be maintained throughout. Replicates were always performed in triplicate, or more, to enhance the data pool. For example, the field lysimeters were assembled in triplicate and the CLO contained within was obtained directly from the aerobic digester with no post vessel-processing having been carried out. The amending materials (green compost, brick dust aggregate and magnesium limestone) were also kept in their original physical forms, i.e., were not homogenised. In contrast, the solid material under analysis in the laboratories had to be refined; a particle size of <1mm was deemed most suitable, ensuring that >90% of the original material was incorporated. When experimentation could commence upon un-sieved material, however, mainly Loss on Ignition and Tessier's adapted sequential extraction procedure, it was decided it might be beneficial to highlight any discrepancies observed between the screened fine fraction and the residual contrary material.



Photograph 1.1: Undiluted CLO material; highlighting the major constituents of the recycled waste product and its inherent heterogeneous physical nature.

1.2.2.2.2 Inorganic contaminants – heavy metals

The detrimental effects associated with the utilisation of Municipal Solid Waste (MSW) in its various post collection forms have been well documented (e.g. Pinamonti et al., 1997, Esakku et al., 2005 and Gupta and Kawahata et al., 2005). The factors limiting or defining the suitability of aerobically digested MSW as a compost or cover material is greatly affected by an assessment of metal speciation and the subsequent bioavailability of these elements. In order to comprehensively evaluate the environmental impact of a given metal pollutant, the separation of total heavy metals into various environmentally-linked fractions must be calculated, as opposed to merely determining total metal content. The water-soluble, exchangeable and acid extractable fractions are considered to be mobile phases that are easily bioavailable whereas the oxidisable and reducible species will require the onset of much harsher environmental conditions in order to be made available in solution. The residual fraction is almost inert with respect to natural leachability.

This partitioning of trace metallic and metalloid elements in natural aquatic and terrestrial systems is a function of the chemical form of the element, which in turn is controlled by the physico-chemical and biological characteristics of that system (Kersten and Forstner 1986). More specifically, the ability of a sediment affiliating these elements via sorption-desorption and dissolution-precipitation reactions governs dissolved concentrations. The extent to which these processes occur in a soil is difficult to predict but it is these processes that determine the concentrations of metal ions and complexes in soil solution, and therefore ultimately the availability to plant root systems as well as access to groundwaters.

1.2.2.2.3 Inorganic contaminants – metal salts

A specific study by Gros et al (2005) highlighted the adverse effects of mineral contaminants, such as salts, on both physico-chemical and biological soil balances – in particular, how Municipal Solid Waste Incinerator (MSWI) ash derived leachates heavily loaded with base cations may seriously influence a soil's quality via encouraging both soil disaggregation and the migration of colloids. Extensive aggregate slaking could potentially upset the delicate chemical equilibrium that exists between plants and the vital nutrients and water supplies they rely upon for their survival.

Complimentary work, by Abbas et al (2002), assessed the potential for the stabilisation of various ash residues from fluidized bed combustion of MSW using a simple water extraction method. The effects of different parameters, such as washing time, liquid to solid ratio (L/S) and multi-stage washings were optimized during experimentation, were measured by applying a two-stage serial batch-leaching test (CEN 12457-3) on original and washed ashes. With respect to salt leachability, the three ashes under investigation gave mixed results: bottom ashes were considered stable; bag house filter ashes contained a significant soluble portion (up to 50% by weight) and so washing was deemed an inappropriate stabilisation method; for cyclone ashes the process can be considered to be a cheap and simple stabilisation method. In view of these findings, a modified pre-treatment test was devised in an attempt to see whether the washing of CLO could be used as a suitable stabilisation method. The economic viability of this process plays an important role in determining if this method is 'suitable,' so, tap water was used, and washings times and volumes of water (L/S ratio) were kept to a minimum.

Further studies by Kim et al (2005) support water-washing pre-treatment in conjunction with a supplementary carbonation (10% CO_2 and 90% N_2 gas was pumped into the solid material until a constant 9% carbonation saturation was attained) saturation method to be a promising approach to obtaining early waste stabilisation as well as reducing leached heavy metals to minor levels. Of particular interest were the significant reductions observed in both Ca and Pb concentrations which was attributed as being as a direct result of pre-washing the MSW incinerator residues with distilled water.

These findings underline the importance of conducting a complete Environmental Impact Assessment (EIA) which encompasses all major toxicants in their various forms and to what degree site-specific conditions play a role in their existence in a leachable state. Furthermore, the need for experimental controls is supported by the heterogeneous nature of the materials involved so that any between treatment discrepancies can be statistically justified. A sewage sludge treatment was also incorporated from the second year in the hope of relating the performance of the CLO and its associated soils both quantitatively and qualitatively to other waste practices.

1.3 Controls and Comparisons

1.3.1 Agricultural soil control

It was imperative to include a suitable control in all experiments so that treatment specific characteristics could be rationalised against an environmentally accepted reference material. The material of choice was an agricultural soil (characteristic of the soils found around County Durham) collected from Houghall Farm, just outside Durham city centre. The field from which this was excavated was being set-aside as part of a four year crop rotation scheme and was certified organic farmland (Simpson *pers. comm.*). An agricultural under organic farming management soil was deliberately chosen based upon the assumption that a soil of this type and setting would display natural background levels of soil nutrients with minimal or no interference from artificial fertilisers, pesticides and herbicides. Furthermore, it is soils of this series and type that, if a best case scenario is achieved by Premierwaste, will be amended with CLO and potentially used as a basis for bio-fuel production.

The farmland was low-lying, situated within a few hundred meters of the river Wear's floodplain and the soil wass of the Dunkeswick Series, derived mainly from Carboniferous shales and sandstones and developed in a stony till (Jarvis *et al.,* 1984). A top 30cm sample was taken in which the horizons typically contained stones and many rounded and sub-rounded sandstones and grits. Other diagnostic features of this very dark grayish-brown clay loam included extremely abundant medium and fine sized pores as well as a plentiful fine fibrous root system (Hollis, 1975).

1.3.2 Sewage Sludge reference

The application of sewage sludge to agricultural land is a well-established practice. Accordingly, strict guidelines are set out in the Council Directive of 12th June 1986 on the protection of the environment, in particular the soil, where sewage sludge is used in agriculture (86/278/EEC). It is well recognised that municipal sewage sludge contains valuable agronomic properties, such as plant-utilisable nitrogen and phosphorus, as well as providing a valuable source of organic matter and micronutrients, (such as Cu, Mn, Zn) justifying its use as a fertiliser (Chambers *et al.*, 2003; Yuruk and Bozkurt 2006). However, the detrimental effects from toxic heavy metals (Cd, Cr, Cu, Hg, Ni, Pb and Zn) and the risks they pose to human health, animals and plants are also well recognised (Bozkurt and Cimrin 2003, Walter *et al.*, 2006, and Yuruk and Bozkurt 2006). The effects of heavy metal accumulation in soils are long-lasting and often permanent, stressing the importance of a thorough understanding of the concerns associated with the agricultural use of sewage sludge. In addition, appropriate pre-treatment before application to land is required in order to reduce the fermentability of the sludge and ensure effective destruction of pathogens and pests, such as beef tapeworm (*Taenia saginata* and cysticercosis) and Salmonellosis (Bruce *et al.,* 1990). It can therefore be seen that many of the same principal characteristics that relate to the utilisation of CLO as a soil conditioner also read across sewage sludge application, thus providing an alternative, useful organic material for comparison.

1.4 Thesis Objectives

This research seeks to provide information regarding the long-term behaviour of soil products and their leachates from the aerobic digestion of MSW, with relevance to other organic material products (sewage sludge) and legislative constraints. The principal objectives of this thesis are summarised as follows:

- **Objective 1a** - To monitor the long-term physical and chemical quality of leachates exuded from undiluted CLO treatments and its associated artificial soils relative to leachates from an agricultural soil and sewage sludge.

- **Objective 1b** - Relate leachate performance to current Drinking and Surface Water Directive Maximum Admissible Concentrations and Coxhoe landfill discharge consents.

- **Objective 1c** - Determine whether any significant remediation value has been achieved as a result of amending the CLO material.

- **Objective 2** - Characterise each of the materials (from which the field leachates are derived) on an annual basis, identifying any physical or chemical changes and potentially assign these findings to specific environmental conditions.

- **Objective 3** - Formulate a suitable pre-washing strategy for the CLO associated soils and identify whether this pre-treatment method is able to ameliorate against water-soluble metal salt releases.

- **Objective 4** - Perform principal component analyses upon leachate data and characterisation data, as well as, upon a combined dataset to evaluate underlying principals and sources responsible for the component releases recorded.

Chapter 2

Lysimeter Leachate Trials

2.1 Introduction

This chapter describes the main study of the thesis that continuously monitored the long-term behaviour of leachates emanating from CLO and its associated artificial soils. This data, in conjunction with solid material extract data, can be used to formulate an overall organic/inorganic export model for each material, quantitatively identifying the conditions under which, and to what degree, contamination occurs for each material.

The use of lysimeters as both a qualitative and quantitative means of assessing the leaching behaviour from waste products and contaminated soils has become popular in recent years (Nordtest Technical Report 473, 2000). Outdoor lysimeter trials are useful in the context of organic material management (and in particular this thesis) as they allow a large amount of solid material to be studied under field conditions without any damage or interference to the land on which they rest. Lysimeters, using intact soil cores, provide a more realistic means of assessment than laboratory techniques without the complications and uncertainties typical of many field studies (Stegemann *et al,* 1995 and Ludwig *et al*, 2000). They are freely draining apparatus, ideal for leachate studies, and are relatively cost effective when compared to field plot studies and similar large-scale laboratory column experiments.

A key emphasis of this project was to gauge the environmental impact of utilising CLO and its associated artificial soils as a medium for which to grow bio-fuel crops. The success of this hinges upon, among other things, how heavily contaminated the leachate emanated from the material is, and how easily accessible it is to surrounding surface waters and groundwaters. Accordingly, lysimeter trials provide an ideal opportunity to present detailed information concerning both performance of leachates and solids concurrently, including flow dynamics, soil retention properties and individual contaminant flux levels. These criteria can then be further examined in the hope of highlighting whether physical mixing of the CLO with other recyclables offers any form of physical or chemical remediation other than that achieved by dilution.

2.2 Study Site

The civic® Municipal Waste Aerobic Digester is based at The Thornley Recycling Facility in County Durham, at grid reference NY395393 at an altitude of 117m O.D (Figure 2.1). The field site was situated to the rear of the plant on an open grassy area free from shrubbery, trees and obvious sources of contamination that may interfere with the subsequent laboratory analyses or the continuous on-site meteorological readings (air temperature and rainfall). The chosen area was both flat and level to ensure even filtration of rainwater; thus, any discrepancies arising concerning percolation pathways were not a consequence of slope angle. The site-specifics, such as underlying geology and vegetation type are of little relevance here, since the area was chosen mainly for its convenient location to the lysimeter materials (manufactured and stored on site), flat topography and characteristic Durham climate. As can be seen in photograph 2.1, a metal perimeter fence was erected to eliminate any unwanted external interferences from inquisitive animals and humans. The climatic conditions over the three years of study were typical of a temperate environment that was heavily influenced by The North Sea, which consequently keeps North East England relatively mild in winter and cooler in summer. Lying to the east of the Pennines, Thornley lies within the rain shadow, and normal yearly totals of rain are in the region of 650-700 mm. Typical recorded extremes of temperature are -6 °C to 27 °C. The mean monthly averages for the time of study, mainly temperature and rainfall, were typical of those recorded for the region by the meteorological station sited at Durham University Observatory.

Photograph 2.2: Field Lysimeter set up at Thornley

2.2.1 Field Lysimeter Apparatus

Lysimeter studies can be designed around and adjusted to suit individual research requirements and so do not conform to any particular regime of standardised testing (Nordtest Technical report 473, 2000). Therefore, careful design and constant maintenance were carried out to prevent collection of biased data from unexpected experimental conditions which would otherwise be difficult to interpret in number form. Each freely draining lysimeter consisted of a 35cm long upper section in which the desired solid material was contained, a central collar, and a bottom half encasing a two litre collection bottle. The tubing was 15cm in diameter (Figure 2.2). The cores were held in situ by a securely attached, very fine nylon/wire mesh matrix which ensured rainwater could drain freely from the core into the collection funnel beneath, whilst retaining the material in place, without loss of any soil aggregates.

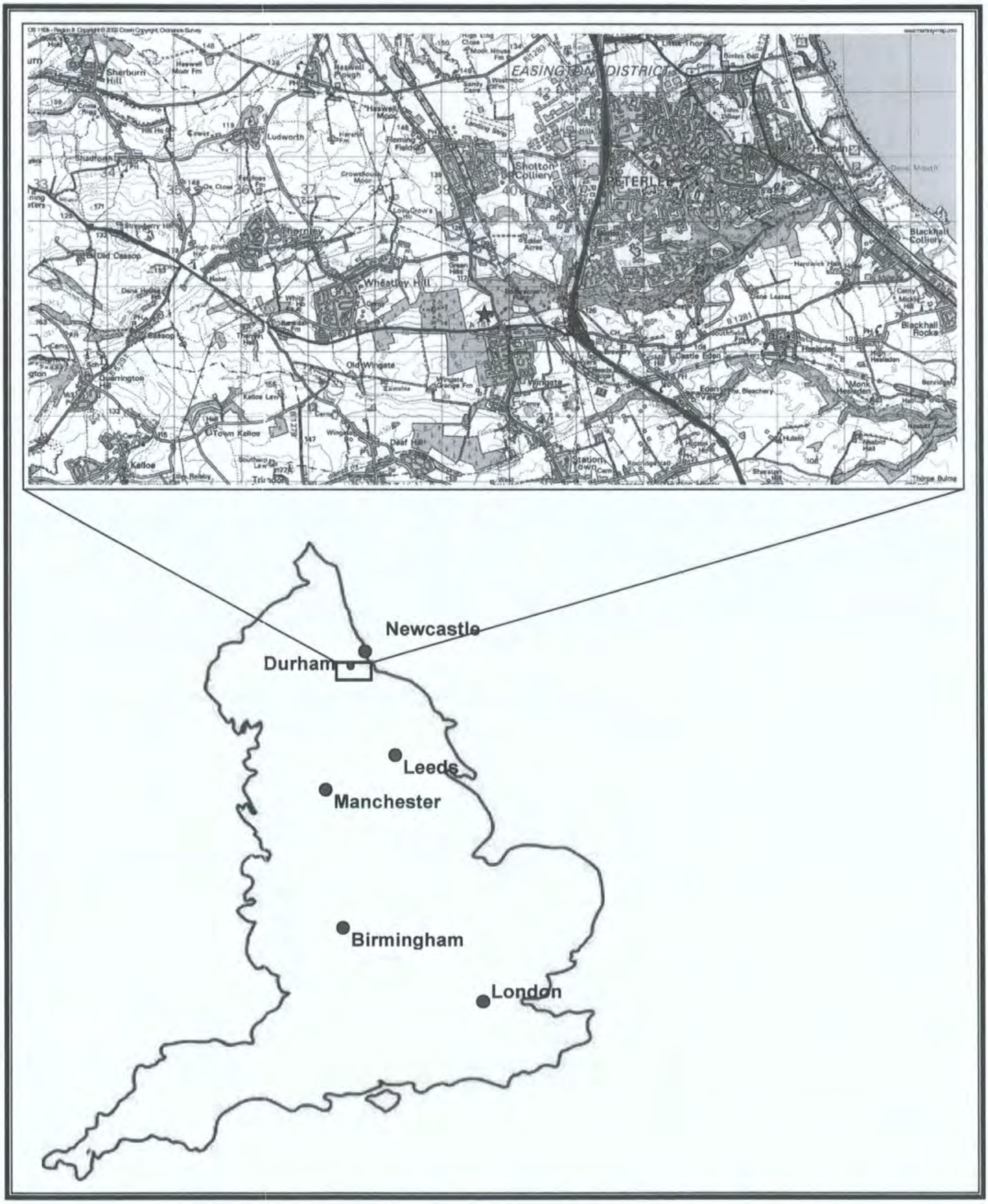


Figure 2.1: Location of field site. Data source © Crown Copyright/database right 2005. An Ordnance Survey/EDINA supplied service.

Fixed within each adjoining collar was a 14 cm diameter glass funnel which ensured that all accumulated leachate was diverted into collection bottles. The glass funnel was to function in the same way as a guard ring at the base of a lysimeter, and thus collected leachates were assumed to be representative of actual field conditions. An impenetrable black plastic sheeting was laid down to prevent any plant growth and subsequent evapotranspiration within the base pipe units. A further addition, difficult to incorporate into the diagram, involved attaching a tight-fitting piece of moulded plastic sheeting that covered the adjoining collar unit. This was to prevent unwanted rainwater from entering the apparatus. Maintenance of the lysimeters usually entailed re-application of an all-purpose weather sealant to the central collar joint to ensure a water-tight fit. In total, 21 full lysimeters over a number of phases, and a further 30 repeat cores, were constructed.

2.2.2 Field Lysimeter materials

All of the CLO used in the lysimeters during the study was incorporated on the same day as it was discharged from the aerobic digester to minimise contamination and degradation losses during the compost's curing phase. Each of the three mixed treatments combined 1 part CLO with 3 parts desired material (w/w). These were acquired from the stock storage piles located at the Joint Stocks Quarry Landfill based in Coxhoe, County Durham. The materials were: green compost waste recycled from County Durham, brick dust and aggregates from construction and demolition waste, and ground (<6 mm) magnesium limestone also acquired from the surrounding area. The 'Parcgro' is a synthetic material comprising of three recycled materials blended together in equal proportions: CLO, composted green waste (as in the (Comp) mixed treatment), and screened soils and sub-soils. A detailed description of the two comparison materials (sewage sludge and agricultural soil) and their origins can be found in chapter 1.

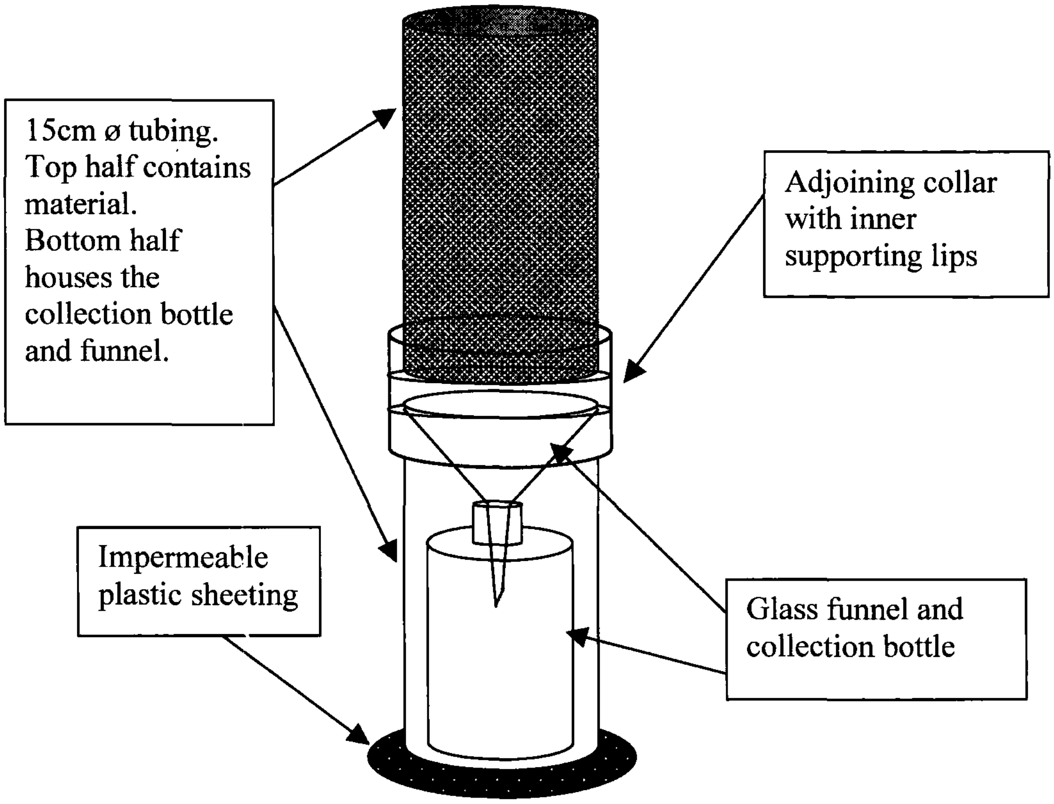


Figure 2.2: Diagrammatic representation of field lysimeter setup

The various materials in the lysimeters were compacted in the same manner (using a ramming device), so that all treatments resembled, as closely as possible, the compaction density of soil. However, owing to the highly variable physical properties of the materials used, each treatment lysimeter inevitably contained different weights. The quantities of material used to fill each lysimeter upper section were as follows:

- Original CLO - 3 kg
- CLO 2005 and 2006 - 5.25 kg
- Parcgro - 5.5 kg
- Comp, BDA and ML - 5 kg
- Agricultural soil - 8 kg
- Sewage sludge - 6.5 kg.

This compaction ratio is indicative of one way in which parameters can be set in an attempt to accurately signify the physical properties displayed by the agricultural soil, as used in the control. It also guaranteed uniformity across all treatments. When studying organic materials in this type of 'filled in lysimeter', the main objective is to try and simulate the scenario in which the materials will be used in the field, rather than concentrating efforts on replicating the conditions typical of an undisturbed soil (Nordtest Technical report 473, 2000). The aerobically digested materials (CLO's) themselves were of a highly disturbed and nonhomogeneous nature and the physical mixing with other products would only enhance these properties further. It must be noted, however, that it was probable that the compaction of the material in this manner was the cause of water-logging seen in the CLO 2006 and sewage sludge treatments. Nevertheless, compaction of the material is inevitable as this is how the CLO is currently incorporated as topsoil in the capping of landfill sites and brownfield sites.

2.2.3 Field work program

In June 2004 a factorial set of lysimeters, comprising three replicates of five treatments were erected at the Thornley Aerobic Digester recycling plant. The fifteen lysimeters were established to assess behaviour of both CLO and CLO amended soils. The lysimeters covered a range of soil treatments, each having three replicates, as well as an agricultural soil control. It was proposed that for each lysimeter the leachate would be monitored on regular basis (every 2 weeks) to assess water balance, metal and nutrient leaching, and carbon loss. Sampling involved exchanging the collection bottles for lysimeters that had produced leachate since the previous sampling event, as well as uploading meteorological data for that period. During periods of increased precipitation sampling frequency increased, as did leachate volumes. It was imperative that leachates were collected immediately to prevent unnecessary deterioration before laboratory analyses could commence. In order to accomplish this, and bearing in mind that different treatments displayed different filtration rates (drainage ratios), leachate production was closely monitored following any rainfall activity and individual treatment leachates were collected once a 40ml threshold had been reached.

After a review with Premierwaste of the leachate performance over the first year of study it was decided that an additional two treatments, each with three replicate lysimeters, would be introduced to the set up in June 2005. These consisted of pure pasteurized sewage sludge, as a comparative waste treatment, and a 'CLO 2005,' typical of the digestate at that time. Sewage sludge, or Environmental Waste Cake as it is sometimes referred to, is currently a widely used agronomic fertiliser, and therefore provides a practical material which can be used to compare specific properties of the CLO and its amended soils against.

In a similar fashion, a further six lysimeters were added the following year (2006), this time replacing the ML mixed treatment and the 'CLO 2005' on the basis of their leachate performance. The 'CLO 2005' was replaced with an up-to-date CLO (referred to as 'CLO 2006' and the ML treatment was substituted for a 'Parcgro' treatment – one of the commercial products currently manufactured by Premierwaste. The replacement of the 'CLO 2005' was to highlight whether ongoing alterations of the aerobic digester waste system were in fact improving or deteriorating the overall environmental quality of, and subsequent leachate performance from, the fresh CLO. In total, over the three year study, seven treatments were assessed:

Three undiluted compost-like-output treatments:

- Original compost-like-output (CLO (2004))
- CLO (2005)
- CLO (2006)

Four mixed treatments:

- CLO (2004) /Green compost blend (Comp)
- CLO (2004) /Brick Dust Aggregate blend (BDA)
- CLO (2004) /Magnesium Limestone blend (ML)
- Parcgro

And two comparison treatments:

- Undiluted agricultural soil control (Soil)
- Undiluted pasteurised sewage sludge.

In addition to these monitored lysimeters, two sets of 15 replicate columns were constructed and placed on an adjacent free-draining wooden pallet (photograph 2.2). These columns comprised only the upper section of the normal lysimeters (shaded section, Figure 2.2) and were exposed to exactly the same conditions as the other lysimeters. At the end of each year, the replicate lysimeter sets were sacrificially sampled to assess: soil development; weathering of particulates; nutrient status; and metal and organic carbon content. Thus, constant, long-term leachate performance and annual characterisations could be assessed.

2.3 Sample Analyses

The analyses of leachate samples were split into two main stages; same day analyses (initial), and post-freezing (secondary).

2.3.1 Initial sampling

The initial phase of sampling involved in-situ measurements (unless insufficient leachate was present): and included pH, leachate volumes, and electrical conductivity (EC). Samples were then decanted and filtered for biological oxygen demand; total suspended solids and dissolved organic carbon assessment.

2.3.1.1 pH

Leachate samples were in liquid form so an electrode method of pH measurement was employed, determining the activity of hydrogen ions within a solution by measuring the potential between a glass and reference electrode. A feature integrated into the electrode probes automatically compensates for any temperature (ATC) variations encountered during analysis. The temperature of a solution is known to affect, both physically and chemically, the pH measurement. Furthermore, as noted by (Clesceri *et al.,* 1998), glass electrodes are not significantly affected by salinity (except at pH>10), colour or redox state which is of paramount importance in this study.

A Hanna instrument HI 9025 microcomputer pH meter was used. This pH meter is designed to be both affordable and produce very precise results (± 0.01 pH at 20°C) under varied conditions. The probe tips were stored in a 0.1M solution of KCl between sampling days to prevent drying-out and mineral build up.

On the day of collection, leachate samples were allowed to equilibrate to room temperature. The pH meter was then rinsed both inside and out with de-ionised water and time was allowed for drip-drying. Calibration of the instrument was then carried out using two standard solutions of known pH (pH 4 and pH 7 ± 0.01 at 25°C). Care was taken not to touch the interior of the pH probes to avoid any damage to the probes themselves and to avoid potential contamination. Each sample was analysed, making sure to leave the probe submerged in the supertinant fluid, until a constant pH was attained. Between each analysis the electrodes were systematically washed and dried as before, thus significantly reducing contamination/dilution from carry-over.

2.3.1.2 Volume/Drainage ratio

The drainage ratio, in this study, can be defined as:

$$\text{Drainage Ratio} = \frac{\text{Total drained water from lysimeter}}{\text{Total water precipitated on lysimeter}}$$

This can be expressed as a percentage of the precipitation that has fallen upon the lysimeter and then leached through the freely draining apparatus over a defined time period. It affords an insight into a material's potential absorbent quality as well as its water retention capacity under normal field conditions.

The calculation used to attain a drainage ratio (DR) is as follows:

$$\mathrm{DR} = \frac{\pi r^2 h}{100\,V}$$

Where:

r = lysimeter radius (cm)
h = rainfall (mm)
V = ml (cm^3)

For each sampling event the leachate volume was measured by weighing the collection vessel full of sample and then reweighing it empty. To attain accurate leachate volumes for each batch, a known amount of leachate from each lysimeter was periodically weighed. The true volume of leachate could then be calculated for each lysimeter in turn as not exactly one litre of leachate from certain treatments weighed as one kilogram. This was because the leachate was seldom pure rainwater since metals, particulate matter, dissolved salts and dissolved organic carbon also present. This was of greater relevance at the beginning of the three year study when initial leachate flushes were heavily laden with such substances.

2.3.1.3 Electrical conductivity (EC)

This is an estimate of the amount of total dissolved salts (TDS), or the amount of dissolved ions in water. The higher the concentrations of dissolved salts present in a water sample, the greater its ability to conduct an electrical signal and subsequently produce a higher value. In this study electrical conductivity (EC) is expressed in micro Siemens per meter (μS/m), unless otherwise stated.

A Hanna Instrument HI 9033 multi-range conductivity meter was employed. The device allows samples, ranging in concentration from de-ionized water to brine (0-35mS/cm), to be measured (to within 1% of the full scale at 20°C) without having to switch or recalibrate the probe, which is ideal considering the quantity and nature of test samples to be analysed over the study period. Measurements are performed with automatic temperature compensation. Prior to each sample being measured the probe was rinsed in de-ionised water. Whenever possible, as with pH measurements, analyses were carried out upon the whole leachate sample in order to minimize any potential contamination and maximize representative values.

2.3.1.4 Total Suspended Solids (TSS)

Total suspended solids (TSS) is the measurement of particulate matter (mineral or organic) suspended in a water sample. It is a simple but useful water quality assessment and can effect the environment in a number of ways if present in large quantities (10,000mg/l upwards). The main detrimental effects, in the context of this project (to drinking waters and surface waters and their extraction) were the effects TSS has on light penetration which may subsequently hinder the ability of algae to oxygenate waters. In addition, the interferences with water treatment processes, including coagulation, flocculation, and disinfection that high TSS loads may instigate, can be financially and environmentally costly – in particular, the need for more chlorine to disinfect turbid waters. Conditions may then be created that favour the onset of anaerobic environments, which has obvious effects on both drinking water and agriculture. Converse to this, are the effects TSS may have on the adsorption or complexation of dissolved metals. This can be argued to be beneficial by rendering the trace metals more insoluble, and therefore theoretically less toxic to plant species or environmentally detrimental by increasing their mobility. It must, however, be remembered that lysimeter studies only assess the total TSS values exuded from a material and do not take into account the potential extent of trace metal mobility.

Although TSS concentrations are generally referred to as a narrative standard in water quality assessments, a quantitative value can be attained from limits set for effluents from municipal wastewater treatment plants. Treatment must be provided so that TSS values meet limits of 30mg/l as a monthly average and 45mg/l as a weekly average. It is against these figures that the treatment eluviations will be compared. It is customary to define this parameter as the residue accumulated on filtration through a 0.45 µm pore size filter paper. However, due to the nature of the leachate, with its extremely fine TSS or suspended particulate matter (SPM), pre dried Whatman FilterCup™ glass microfibre filters (GF/F:0.7µm pore size) were used instead in an attempt to achieve a more representative reading for all treatments. Unlike membrane filters with a comparable retention value, they have a very rapid flow rate and an extremely high loading capacity. After vacuum filtering, the papers were dried to a constant weight at 105°C. The increase in weight of the filter paper over the volume of sample filtered is the TSS. Filtration volumes were adjusted according to the amount of TSS in the samples in an attempt to minimise excessive filtration times (>10mins), which can lead to clogging of the filter papers and subsequent removal of colloidal material. Each sample was thoroughly mixed and large floating particles and submerged agglomerates of materials (e.g. leaves and insects) were removed prior to the vacuum filtration procedure.

All filter papers and residues were dried at 105°C for a minimum of 12 hours and then allowed to cool in a desiccator prior to weighing to 4 decimal places on a Mettler

AJ100 electronic balance. Residues dried at 105°C, as opposed to 180°C, may retain not only water of crystallization but also some mechanically occluded water (Clesceri *et al.*, 1998), the latter of which would be almost completely removed at the upper temperature. However, laboratory limitations suggested drying at 105°C to be most appropriate for this study. Furthermore, post-filtration washing of the filter papers with de-ionised water was not carried out owing to the fact that, for the undiluted CLO samples and initially the mixed treatment leachates, no more fluid would pass through the GF/F: 0.7µm pore size filter papers. Although after the initial flush of heavily laden leachates had passed and subsequent samples became easier to filter, it was known that new undiluted CLO treatments were to be assessed in the coming years. In the interests of consistency, it was decided that TSS calculations would have to include a certain degree of total dissolved solids (TDS).

Milli-RO purified water blanks were undertaken to ensure that the weight of filters did not significantly alter throughout. TSS values are presented as flux values (mg) and in mg/l.

Calculations:

Flux TSS

$$\text{Flux TSS} = \left(\frac{A-B}{1000}\right) \times \left(\frac{V_c}{V_f}\right)$$

And in (mg/l) TSS

$$\text{TSS} = \left(\frac{A-B}{1000}\right) \times \left(\frac{1000}{V_f}\right)$$

Where:

A = weight of dried filter paper and residue (g)
B = weight of dried filter (g)
V_c = volume of total sample collected (ml)
V_f = volume of sample filtered (ml).

2.3.1.5a Dissolved Organic Carbon (DOC)

The relevance of assessing dissolved organic carbon (DOC) concentrations in the context of this mainly inorganic-orientated assessment is first the role of DOC as a water quality parameter and, second, the linked potential importance of its ability to form metal complexes. The prime motivation for measuring DOC (or colour levels) as a water quality tool was concerned with the relative ease with which it can form bonds or chelate with metal species forming organometallic compounds – the properties, and hence toxicity, of which, may be vastly different to that of the metal ions themselves (Connell, 1997). The most important class of complexing agents occurring naturally through the decomposition of organic matter are the humic substances, the most pertinent of which are the insoluble forms known as humin and humic acid. The binding of the metal ions can occur as chelation between a carboxyl group and a phenolic hydroxyl group, as chelation between two carboxyl groups, or as complexation with a carboxyl group. The chelating ligand bonds are usually considered stronger than complexation, since two sites of bonding on the metal ion is involved. In addition, this binding to metals in solution can often induce strong oxidative effects that simultaneously deplete waters of dissolved oxygen and diminishes the dissolved concentration of the metal, as well as providing a food source for oxygen consuming microbes (Manahan, 1991).

Studies by Anderson (*et al.,* 1993), Christensen (*et al.,* 1996) and Toribio (*et al.,* 2006) have evaluated the magnitude of metal complexing properties of DOC in various leachates from landfills and Mediterranean soils treated with sewage sludge. These studies are invaluable in quantifying the potential heavy metal binding effects that DOC has in leachates of a similar nature to those presented here (typically leachates of high ionic strength and high concentrations of competing cations), and with minimal manipulation of organic carbon.

DOC was measured using the colorimetric method described by Bartlett and Ross (1988). It was necessary to dilute the CLO 2005 and 2006 leachates 20 times, the original CLO leachates 10 times and the remaining treatments leachates 5 times, due to their high DOC contents. A set of serially diluted standards were prepared using citric acid for each batch of samples. The following range of standards was prepared: 30mg/l; 15mg/l; 7.5 mg/l; 3.75 mg/l and 1.875mg/l, as well as two milli-RO purified water blanks. Calibration lines were then drawn, from which DOC contents (mg/l) could be obtained for each leachate sample by multiplication with the attained absorbance values, measured at 495nm. All samples had been filtered using 0.45μm pore size Whatman® Cellulose nitrate membrane filters.

2.3.1.5b Absorbance measurement

A spectrophotometer (Camspec Ltd. M100) was used to measure sample absorbance at 400nm. Preliminary trials suggested that there was a greater experimental error incumbent with using individual cuvettes, mainly from scratches, than if the same cuvette was re-used for each sample, providing thorough washing was carried out. Therefore, a single cuvette was used for each treatment type – each sample was pipetted into polystyrene cuvettes, all of which had been calibrated with blank absorbencies of milli-RO purified water. After each absorbance measurement was taken the cuvette was washed at least three times with milli-RO purified water and a further blank absorbance taken to ensure thorough cleaning.

2.3.2 Secondary Analyses

2.3.2.1 ICP-OES

Principle:

Inductively coupled plasma – optical emission spectrometry (ICP-OES) originating from the 1960's (Greenfield *et al.,* 1964) – is now generally considered to be one of the most proficient techniques for elemental analysis. Grounds for its success include the high temperature of the plasma which breaks all chemical bonds, limited background interferences, ability to produce linear calibration curves over a wide range of concentrations and the capacity to measure numerous elements concurrently.

ICP-OES is an emission spectrophotometric technique which exploits the fact that excited electrons emit energy at a given wavelength as they return to their ground state, the fundamental factor being that each element emits energy at specific wavelengths according to its chemical character. Normally, a few wavelengths are chosen for each element and the intensity of the energies emitted is proportional to the concentration of the element being analysed.

The sample in solution is introduced into the system through a peristaltic pump which leads to a nebuliser. Here, the sample, as well as humidified argon gas is injected as a fine aerosol mist into the centre of the plasma flame, housed within the torch assembly unit. This consists of a quartz torch surrounded by an induction coil through which radio frequency (RF) radiation is applied creating an intense oscillating magnetic field which sequentially induces an electrical field. The radio frequency-generated and maintained argon plasma reaches extremely high temperatures (6000 to 10,000K) which simultaneously evaporates and separates the sample into free atoms and ions. The surplus energy, produced from collisions with surrounding free electrons, is then used to excite the now free atoms and ions into higher energy states. After the electrons have returned to ground state at their specific spatial positions within the plasma, the light emitted is focused through a lens via an entrance slit into the spectrometer. Once inside, the light is separated into discrete spectral lines by a diffraction grating. The intensity of these lines can then be calculated to give a quantitative measurement of the elemental composition of the sample relative to a reference standard. Both sequential (monochromator) and simultaneous (polychromator) measurements, capable of analyzing spectral lines individually or several at one time respectively, can be taken.

A list of the elements used, and whether they were considered low or high concentration (all values in (nm)), is shown below (Table1.1). Average values were calculated for those elements sharing more than one wavelength.

Procedure:

A Perkin Elmer Optima 3000 Family Optima 3300RL ICP Emission Spectrometer was used for all ICP-OES work. The Perkin Elmer ICP Winlab™ software was used to undertake all necessary calibration and reprocessing of signals. This system operates using a dual detector: a UV detector measures the ultraviolet wavelengths ranging from 165 to 403nm and a VIS detector covers the visible wavelength range from 404 to 782nm. The plasma is viewed horizontally through an optic channel; the torch assembly is positioned vertically. The diffraction grating is an echelle grating and signal detection is by a polychromator. Due to the large numbers of samples a Perkin Elmer AS90 auto sampler was employed which is connected to the peristaltic pump.

All samples were filtered through 0.45µm Whatman® Cellulose Nitrate Membrane Filters on the same day as collection from the field site. Samples were then transferred to 25ml polystyrene sample vials and acidified to <pH 2 by adding 0.2ml of HNO_3 to each 20ml sample. The samples were then frozen for a maximum of 9 months prior to metal analysis.

On preparation of the samples for analysis a representative 10ml sample of thoroughly mixed leachate was extracted from each vial. Only with the pure CLO 2005 and 2006 leachates was a 10 times dilution factor necessary (i.e. 1ml of sample to 9ml 3.5% HNO_3) to prevent saturation of the detection probe. Yttrium (Y) solution (0.1ml of 100mg/l) was added per 10ml of sample as an internal standard as well as 0.1ml of concentrated HNO_3 (to ensure acidification). Detection trials on a wide selection of samples from all treatments indicated that a large range of standards were required. Standards were split into two groups – low and high. Two stock solutions were prepared from 10000mg/l (high) and 1000mg/l (low) analytical grade standard stock solutions, from which the standards were made. Table 2.2 shows the set of standards and their concentrations used for each element analysed. The concentrations of the base cations (Si, Na, K, Ca and Mg - high) were consequently recorded in mg/l and the remaining elements ('trace metals' - low) in µg/l. Standards were again of 10ml volume, except the larger standards (40ml) which were analysed intermittently throughout the sample queue to verify machine accuracy. Calibration blanks (~ 3.5% HNO_3) were run with every batch of samples. This procedure using calibration blanks and internal sample standards ensured accuracy, precision and reproducibility of the results.

Low Standards			**High Standards**		
Conc.	Stock sol. (ml)	HNO_3(ml)	Conc.	Stock sol.	HNO_3(ml)
1000	5	5	100	5	5
200	1	9	10	0.5	9.5
100*	2*	38*	5*	1*	39*
40	0.2	9.8	1	0.05	9.95
10	0.05	9.95			

Table 2.1: shows the preparation of the two sets of standards (high and low). * refers to large 40ml standard and sc volumes are 4 times larger.

2.3.2.2 Ion Chromatography (IC)

Principle

Ion chromatography provides a means for determining ions in solution carrying one or two charges, both qualitatively and quantitatively. The use of column liquid chromatography (CLC), in particular high-performance liquid chromatography (HPLC) in inorganic analysis, first evolved in the 1970's. Work carried out by Small (cited in Woods *et al.*, 1997) initiated a cohort of scientists studying and progressively developing modern chemically suppressed ion chromatographic techniques. The use of anion exchange chromatography is becoming increasingly popular, mainly due to its simplicity and sensitivity (Metrohm, 2000). When used as a complimentary technique to ICP-OES, a diverse range of common ionic species found in both natural and anthropogenic environments can be rapidly quantified with assured accuracy. However, it has been reported in a critical review of the suppressed ion chromatographic analysis of ions by Singh and Abbas (1996) that this technique may not be as robust as was originally thought when environmental waters contain high salt concentrations. Based on earlier unpublished findings by Johnson and Worrall (2003), it is predicted that aqueous matrices emanated from CLO amended soils will be of a high ionic strength and may contain appreciable amounts of sulphate. Of particular relevance here is the prospect of erroneous results when quantifying low sulphate (SO_4) anion concentrations in the presence of large concentrations of matrix cations, such as sodium (Na^+), and not anions, such as Cl^-, as was previously thought. The large influx of analyte cations introduced into the suppressor system can cause an unusually high build-up of H^+ ions on its surface during the ion-exchange process

(Mercurio-Cason et al, 1986). This build-up allows the formation of anion-proton pairs (HSO_4^-) via configuration with influent SO_4 ions, which reduces the overall ionic charge and produces smaller and broader sulphate peaks. In view of this, preliminary tests were carried out which suggested evidence of some form of sulphate peak widening; the reason behind this, however, is not clear. It must be noted that the high salt concentrations observed in this study are not of the same magnitude (in most cases 3 orders of magnitude lower) as those reported by Singh and Abbas (1996) both in their literature review and their suppressed ion chromatographic analysis of various real waters. In the latter analysis, Singh et al (1996) revealed that soil extracts from sandy soils, produce concentration gradients more fitting to the scale observed in this study.

It is proposed that careful sample preparation, including an appropriate dilution factor for each treatment studied, is the most suitable means of retaining proper quantities for both minor and major ions essential for their accurate IC detection. This statement is only true if each determinant anion peak is of sufficient height and is suitably separated and well resolved down to the baseline, and only really applies to sulphate in this instance. If broadening of the sulphate peak has occurred but there is no overlapping evident then concentration calculations using the entire peak area should suffice. The anions of strong acids – in this case, chloride (Cl^-) and bromide (Br^-) – are not normally affected by this phenomenon and so accurate integration and determination for these two anions can be assured.

The Metrohm 761 Compact IC employs the use of a Metrohm MSM (Metrohm Suppressor Module) which is made up of three separate suppressor units: one for the eluent (1.3mM Na_2CO_3/2M $NaHCO_3$), one associated with the regeneration solution (20mmol/L H_2SO_4), and one cleaned with milli-RO purified water. The three-way suppressor unit successively rotates between these channels so that analysis, regeneration and washing occur simultaneously. A two-channel peristaltic pump transmits the fluids around the compact IC.

The success of this system rests on its ability to concurrently increase analyte anion sensitivity and decrease background conductivity of the eluent. The cation exchange column, or exchanger, removes cations from the influent solution, based on their size and charge, and replaces them with H^+ ions forming strongly ionized acids (e.g. NaCl is converted to HCl) whilst the eluent is reduced to weakly conducting carbonic acid (H_2CO_3).

Procedure

In total, six anions of importance were investigated: fluoride, chloride, bromide, nitrate, phosphate and sulphate. Of particular interest were chloride and sulphate, owing to previous high levels of detection in leachates from aerobically digested CLO. All samples were filtered through 0.45µm Whatman® Cellulose Nitrate Membrane Filters on the day of collection from the field site. Samples were then transferred to 25ml polystyrene vials and frozen for a maximum of 9 months prior to analysis.

On preparation of the samples for analysis, a representative 10ml sample of thoroughly mixed leachate was pipetted from each vial. All samples were diluted 10 times (i.e. 1.0ml sample in 9.0ml milli-RO purified water) except for CLO 2005 and 2006 leachates which required x20 dilution (i.e. 0.5ml sample in 9.5ml milli-RO purified water). In addition, 0.1ml of 100mg/l sodium bromide (NaBr) solution was added per 10ml of sample as an internal standard. Preliminary detection trials on a representative set of samples from all treatments showed a standard range from 0mg/l to 10mg/l was required. Standard linear calibration curves were produced using standard solutions made up from an analytical grade standard stock solution (1000mg/l). The following serially diluted standards were used for all six anions analysed: (10mg/l, 5mg/l, 2.5mg/l, 1.25mg/l and 0mg/l). Blanks of milli-RO purified water as well as two standards (5mg/l and 10mg/l) were run throughout the sample queue to ensure machine sensitivity.

2.4 Statistical Analysis

Two groups of statistical analyses were conducted – one encompassing the three-year study materials, (group 1) and the other the remainder (group 2). The first group compared the original CLO material with the other three-year mixed treatments – Comp, BDA, ML – and the agricultural soil. It was decided to include the sewage sludge treatment data, which was only available for two years, in both groups for performance comparison of an accepted organic fertiliser. The second group incorporated the materials that were introduced to the study at later dates; the CLO 2005 and 2006 treatments, Parcgro and the sewage sludge treatment. In addition, both groups compared theoretical adjusted leached values for equal weights of the mixed treatment materials with their parent undiluted CLO treatment (i.e., group 1 – Comp, BDA and ML with Original CLO and group 2 – Parcgro with CLO 2005 and 2006)). It was hoped that this latter comparison would reveal whether remediation of properties/elemental concentrations under field conditions were a result of passive dilution or active remediation. Finally, an overall statistical comparison, including all treatments over the whole study period, was conducted with the intention of highlighting the overall controls on leachate quality.

All results were analysed statistically using analysis of variance (ANOVA). The chemical parameters were assessed in both concentrations (mg/l) and flux values (mg/kg). Values were tested against treatment type and batch number (time) using a general linear model. The magnitudes of these effects, as well as the power of the analysis, were also considered with a view to determining the overall importance of controlling factors. Tukey's simultaneous pairwise comparisons test was used to distinguish differences between means at $P < 0.05$ as a post hoc-test. Statistical results are included in each section for the readers ease.

2.5 Flux levels

Concentration measurements (μg/l) have an undisputed application in quantifying and comparing data between both treatments and legal limits. Flux values recorded for each treatment type are also useful as they provide a comparative indication of how much material, by weight, is being flushed into the environment. Although time comparisons cannot be accurately conducted (see below), total flux amounts can, which provides a good visual means of assessing, relatively, overall leachate data within and between treatments. Flux values also incorporate the contribution from rainfall and the drainage ratio for each lysimeter. The effects of plants significantly affected drainage ratio calculations (see Chapter 3) but this is ultimately a realistic evaluation of field conditions to which the materials will be exposed and so remains contextually accurate. The flux values (mg/kg) were calculated per kilogram of material that currently defines the quantities of CLO (in the form of Parcgro) required when covering current Brownfield sites with topsoil.

However, the fact that treatments were introduced at different times throughout the study compromised the comparison of group 1 and 2 treatments, with respect to temporal changes within each year. Furthermore, the sewage sludge treatment was studied for two years, beginning in summer of 2005, and so individual batch comparisons with group 1 and 2 treatments proved insignificant. This was due to temporal rainfall pattern and intensity variations over the consecutive years, which produced differing leachate volumes between collection times. However, annual total leached flux measurements could be assessed, although it must be noted that significant differences in annual rainfalls were recorded (year 1 – 866.4mm, year 2 – 665.9mm and year 3 – 548.2mm). Subsequently, 1 and 2 year total fluxes were calculated.

2.6 Legislation

When this project began, Premierwaste were, and currently still are using the CLO as topsoil on the Coxhoe landfill site. However, if utilisation on agricultural (or similar) land was to be the company's way forward, then restructuring of government documentation (as has been produced for sewage sludge recycling) would be necessary. As aerobically digested MSW has not yet been accepted as an appropriate agricultural amendment, and no official government documentation regarding this exists, it is difficult to accurately quantify in an environmental impact assessment (EIA) the actual effects of introducing CLO to agricultural soils. Ideally, a directive on the protection of the environment, particularly the soil, laying out solid characteristic limits as well as leached limit values relating to the protection of groundwaters where CLO is used would suffice. Thus, an amalgamation of the following four government documents, as well as accepted landfill discharge consents, was compiled to provide a realistic but environmentally orientated database for comparison purposes. The four documents, in order of enforcement, are as follows:

1. Council Directive of 16th June 1975 concerning the quality required of surface waters intended for the abstraction of drinking water in the Member States (75/440/EEC).

2. Council Directive of 17th December 1979 on the protection of groundwater against pollution caused by certain dangerous substances (80/68/EEC).

4. Council Directive of 15th July 1980 relating to the quality of water intended for human consumption (80/778/EC).

3. Council Directive of 12th June 1986 on the protection of the environment, and in particular of the soil, when sewage sludge is used in agriculture (86/278/EEC),

2.7 Data handling and quality assurance

Data in the lysimeter trials was initially recorded in 3 ways:

1. Observations and measurements collected in the field were recorded systematically in field notebooks. These include parameters, such as weather conditions, plant status, maintenance requirements, and any unusual circumstances that may interfere with the proper functioning of field equipment or otherwise compromise the trial.
2. Parameters measured manually in the laboratory (initial sampling methods) were recorded systematically on custom laboratory results sheets or in laboratory workbooks.
3. Parameters measured on automated systems in various laboratories (nutrients, metals and non-metals) and meteorological data obtained from an on-site meteorological station, as well as Durham University meteorological observatory, were recorded in computer data files.

Care was taken to avoid transcription errors when transferring data from paper to PC, and outlying values were double checked for any such mistakes. Where possible, particularly with the trace metal data, due to the large quantities of numbers being produced, simple linear graph plots were performed across the entire data spread to identify any obvious systematic (or potentially more serious) errors. Furthermore, where samples were predicted to cause 'complications' with the running of the IC and

ICP-OES machines, a representative selection of samples was run prior to analysis to maximise time and financial efficiency and avoid damaging the equipment. This procedure, as well as regularly analysing the same samples twice and including blank values, rapidly became second nature owing to the nature of the materials from which samples were sourced. These prior analyses enabled quantitative figures to be set, as initially very little was known about how certain properties of CLO would behave and which elements it contained, making it difficult to assign realistic concentration ranges. The resulting spreadsheets for individual sampling periods (batches) were combined to form an overall spreadsheet containing all data collected during the lysimeter trials. This file could then be easily transferred between statistical and analytical software packages (Excel to Minitab).

2.8 Results

2.8.1 pH

pH values, although almost always alkaline, remained within government constraints (6.5 – 9.5). According to EC drinking (80/778/EEC) and surface water (75/440/EEC) Directives, pH levels are only assigned a maximum admissible concentration (MAC) at the upper limit, as the lower limit is a guidance value (GL) only (dashed red lines, Figure 2.3). The pronounced initial increase in pH levels followed by a general decrease in trend for all treatment leachates, and the pH range in which these changes occur over the first year, are consistent with findings by Ishiguki, *et al* (2003) and Biligili, *et al* (2006), who assessed the quality of leachates exuded from aerobic waste landfills. There are only two short-lived episodes throughout the study during which the lower GL are breached: first a minimum pH value of 4.45 reached by leachate emanating from the original CLO treatment; the second unacceptable acidic value was from the sewage sludge comparison treatment. These results were confirmed not to be anomalous as all three repeat lysimeters displayed similar acidic levels concurrently. A further notable observation was the atypical behaviour (relative to other treatments) seen in leachates produced by the CLO 2005, although no infringement of restrictions occured at any time. Equally, this was seen for the sewage sludge treatments soon after field establishment. Figure 2.3 illustrates these points, where the solid red, blue and black lines represent original CLO, CLO 2005 and sewage sludge, respectively.

2.8.1.1 Discussion

From an agricultural perspective, alkalinity possesses less of a threat to trace metal solubility than acidity due to the increased solubility of many contaminants, and subsequent availability for uptake by plants, in low pH environments. Efforts, such as the incorporation of slaked lime (quick lime), are often made to increase a soil's pH owing to favourability for plant growth. The main points for attention are the leachates from the original, undiluted CLO and the sewage sludge treatments; these were the only treatments which (admittedly only on one occasion) breach the lower government GL. These recorded low pH's were probably due to a shift to a temporary anoxic environment. In the case of the CLO, where the material was discharged from a well aerated digestion vessel then compacted into lysimeters, the action of which was to drastically reduce the number of available pore spaces and gaseous voids, owing to its deformable nature under strain (Durmusoglu *et al.*, 2006). This decrease in void space would cause a decrease in the overall permeability of the composted MSW and provide the conditions required for water-logging. Bilgili et al (2006) indicated that during the aerobic digestion of pilot-scale MSW landfill reactors, a critical oxygen concentration of 8% in the effluent gas was required to keep the system in an aerobic state and prevent the production of methane. Water-logging would cause a short-fall from this critical value.

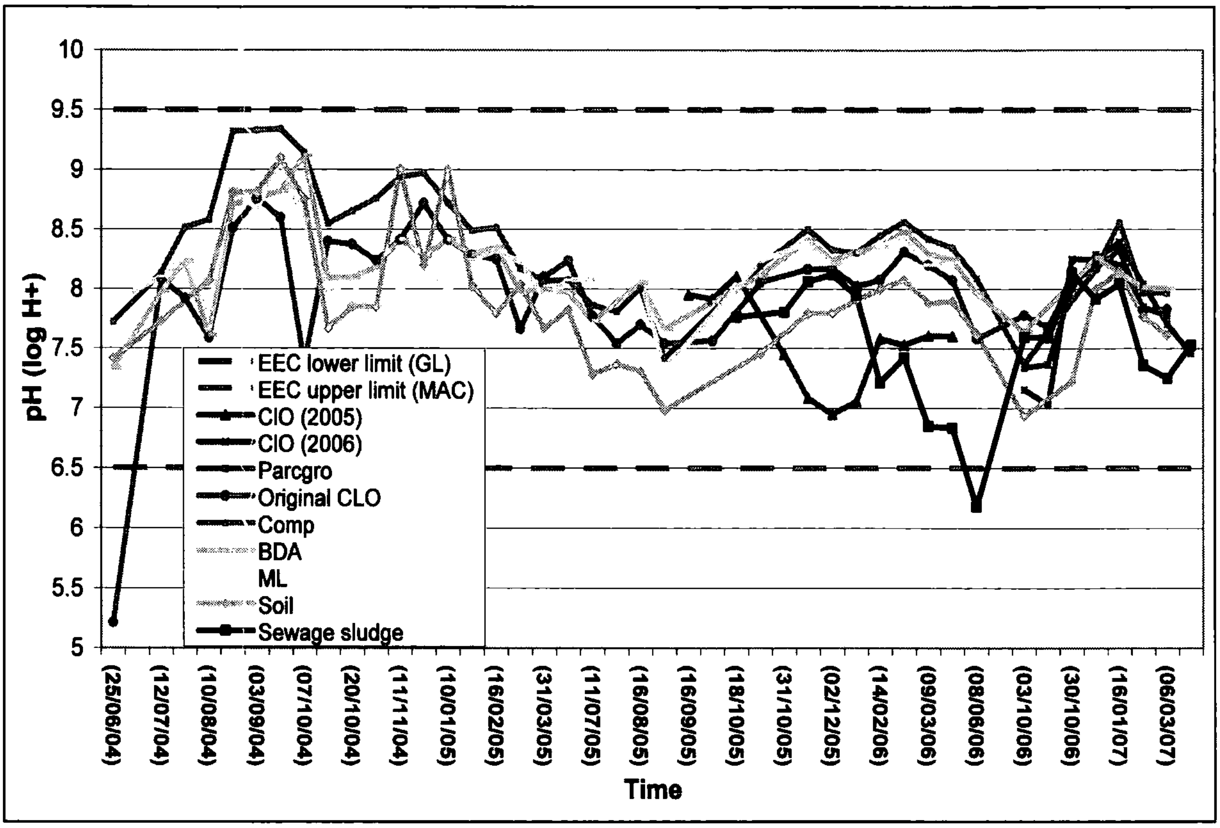


Figure 2.3: Leachate pH fluctuation over time for all treatments.

This phenomenon was also evidenced in the sewage sludge treatment, which had previously been resting in the open air after transportation from the waste water treatment works but after a more prolonged period of time. The CLO 2005 displayed a similar pattern of leachate behaviour analogous to that seen by the sewage sludge. Although CLO 2005 leachates never reached acidic levels, it was thought that similar changes to the aerobic status of the material were the cause of the progressive drop observed in pH levels. These treatments were the only undiluted materials to experience prolonged periods of water-logging (<2 months), most likely a direct result of compaction. Evaporation losses are highly unlikely considering recorded mean temperatures (8.4°C) for the autumn/winter period in which the pH drop occurred.

This highlights two immediate differences between the two waste treatment products. Firstly, the CLO appears to be far more sensitive to the onset of anaerobic conditions, but at the same time demonstrates the ability to suitably aerate itself as it decomposes so that it eventually equilibrates back to a near neutral pH. Presumably this was a direct result of the heterogeneous physical nature of the CLO which lends itself to air entrapment in voids and/or the formation of interlinking conduits along which preferential flow of rainfall may bypass the surrounding matrix (Flury *et al.*, 1994). These voids, following continued decomposition of the organic-rich material, continued wetting-drying periods, and freeze-thaw action will gradually expand, enabling pH equilibration to be achieved. Secondly, the physical nature of sewage sludge appears to enhance the time over which ponding conditions are favoured, which from an agronomic and environmental perspective is unfavourable. The fine textured material with its distinct adhesive properties acts as a water-impermeable substance following slight compression. Furthermore, field observations illustrate that macropores, in the form of multiple moisture and temperature related cracks are easily formed once sewage sludge is dehydrated or frozen; freezing was most probably the reason why ponding was able to finally percolate through for lysimeter 2 of the sewage sludge treatment (corresponding temperatures reached -4 °C over a three day period). In this instance, the fine grain size and cohesive nature of the sewage sludge thus demonstrate adverse physical properties, relative to those of the CLO, which can subsequently affect soil chemistry by encouraging anoxic, low pH conditions.

2.8.2 Volume/Drainage ratio

As will be described later for drainage ratio, the establishment of varying amounts of vegetation and the different introductory times of treatments caused substantial difficulties in assigning any kind of quantitative analyses for this property. Leachate cumulative volume plots over time did not allow scientific justification and so the best way to identify whether any significance lay between treatments was to include the first year data only. This greatly reduced the interference from plants (since they were generally not fully established until the second year of study), as well as averaging out rainfall measurements over an annual period. Statistical significances were found between the larger sewage sludge volumes and those of the BDA ($P<0.05$) and ML ($P<0.01$) treatments. This implies that, relative to sewage sludge, the CLO artificially produced materials appeared to improve water retention properties, but mixing the CLO material with brick dust aggregate and magnesium limestone increased the quantity of leachate exuded into the environment. There was no significant difference from the agricultural soil for any treatment, and so it must be stated that all treatments are no different from a typical Durham soil with regard to this soil moisture retention property.

Treatment	**Year 1**		**Year 2**		**Year 3**	
	% Rainfall Drained	**% st. dev**	**% Rainfall Drained**	**% st. dev**	**% Rainfall Drained**	**% st. dev**
CLO (2005)			102.7	4.5		
CLO (2006)					**86.2**	10.9
Parcgro					**87.8**	9.5
Original CLO	**53.8**	13.0	**62.4**	25.6	**70.3**	13.3
Comp	**53.3**	18.9	**62.5**	39.0	**48.5**	15.9
BDA	**60.7**	7.6	**53.2**	73.6	**34.9**	40.4
ML	**63.2**	13.4	**40.3**	24.0	**85.1**	9.5
Soil	**54.2**	15.5	**82.8**	3.7	**65.9**	6.3
SS			**72.0**	30.8	**83.3**	8.8

Table 2.2: Displays drainage ratios and their respective standard deviations for all treatments over the 1st, 2nd and 3rd years of study. The red value indicates anomalous result.

2.8.2.1 Discussion

The uncontrolled establishment of various naturally occurring plants, either progeny of the materials themselves or from wind germination, greatly influenced the volume of leachate each lysimeter produced (exemplified by the high standard deviations) and thus the drainage ratio.

Water losses via evapotranspiration were also not manageable since Premierwaste wished these species to remain untouched, as this represented, as closely as possible within the scope of the lysimeter trials, the agricultural context for which the materials would ultimately be used. Previous work carried out by Poly et al 2002 revealed the beneficial effects that indigenous plant cover can have in assisting beneficial plant bacteria, and in restoring porosity after a single leachate pulse event. Further findings by Gros et al (2006) provided evidence that both indigenous and dense plant cover was capable of limiting the adverse effects of solid waste leachates on soil physico-chemical properties. These include protection of organic matter inputs, soil moisture contents and aggregate stability, attributed to either a phytoremediation process involving the adsorption of some of the salts (Gros *et al.*, 2006), or the morphological and stability improvements incurred from root systems.

Visual examples of the effect that plant establishment had on the drainage ratio can be seen in the mixed Comp and ML treatments represented by the pink and yellow lines, respectively, in Figure 2.4. Plant establishment began to take hold after the first summer period (03/09/04) and it can be seen that for the first complete rainfall peak (10/08/04) all treatments, apart from the control soil, gave leachate volumes close to precipitation volumes for that period. Broadly speaking, over the autumn/winter months (next two-three main rainfall events), all treatments, but in particular the ML, Comp and CLO (2004) trials, all of which sustained substantial vegetation, give lower leachate volumes. It is difficult to find a good fit for this pattern owing to a number of factors, including imperfect correlation of rainfall peaks with collection times, highly variable plant growth, and also the death of many plants over the summer periods, all of which contributed differently between treatments and with time. An attempt to quantify plant cover over time was carried out initially, but the shear volume of growth on some lysimeters (and not on others), and the variation in plant species and size rendered this unsuccessful. Furthermore, leaf biomass became so large in some cases, that it was thought unlikely, judging from the lack of leachate data over significant periods of time, that any precipitation was reaching the collection vessels. This was either as a result of plant uptake or because the plant-cover was so dense that any water falling on top of the lysimeter was directed elsewhere. The extent and variation in plant cover can be seen in photograph 2.2 and the subsequent effect on drainage ratio was signified by the increased standard deviation values during the second year of study (Table 2.3).

The protocol of this thesis clearly stated that the study was not a plant trial so, unfortunately, the ramifications (both positive and negative) that random establishment of plants brought to the lysimeter soils is an unknown. Statistical analysis revealed that there were no significant differences between treatments, and so it must be concluded that the heterogeneity of each material in conjunction with lysimeter plant cover variation, were together greater than any treatment variation in their ability to absorb or retain moisture.

A further unexplainable error can be clearly seen in the elevated leachate volumes for the CLO (2005 and 2006) treatments (blue line, Figure 2.4): for the most part, they considerably surpass precipitation values (the initial elevated peak after water-logging, however, was caused by the addition of the ponding waters, which was also true for sewage sludge (black line, Figure 2.4)). This behaviour was only seen for one treatment but over a number of sampling periods, eliminating mechanical and anomalous causes. After numerous systematic data checks, as well as correlating the meteorological data from both the field site and Durham University Meteorological Office, the only conceivable explanation was external human intervention. This, unfortunately, was quite plausible since the treatment was situated next to the perimeter fence of the field area and could be easily accessed.

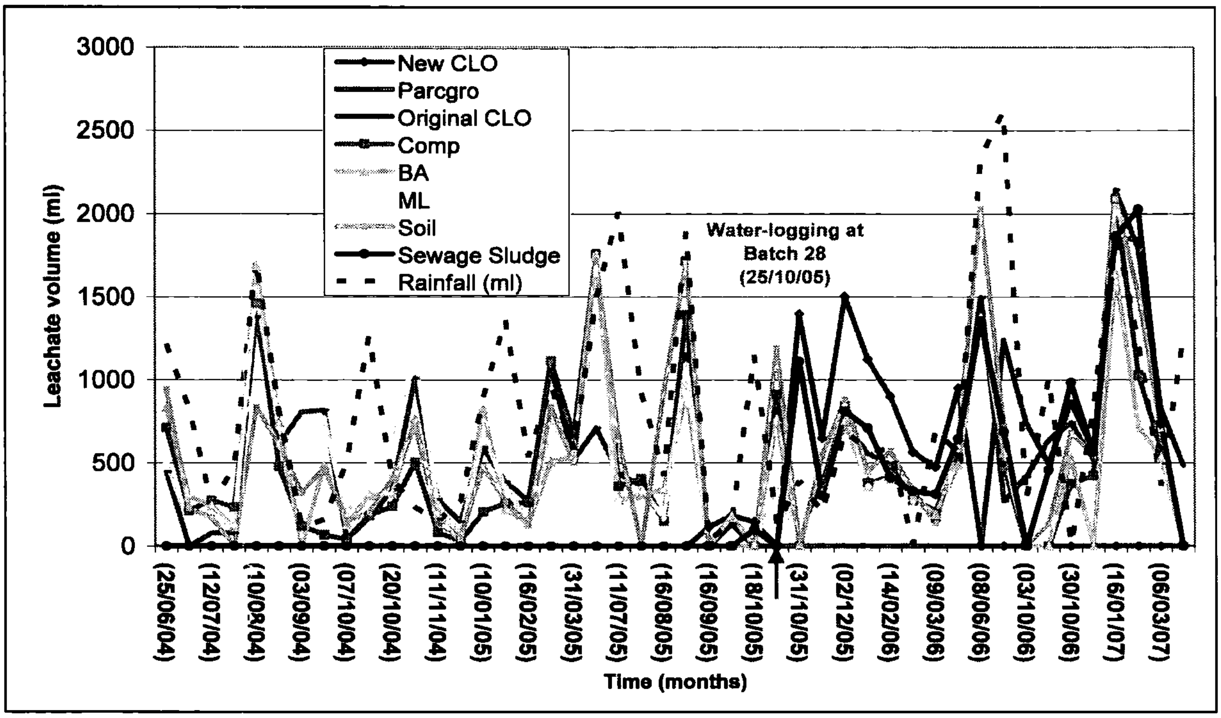


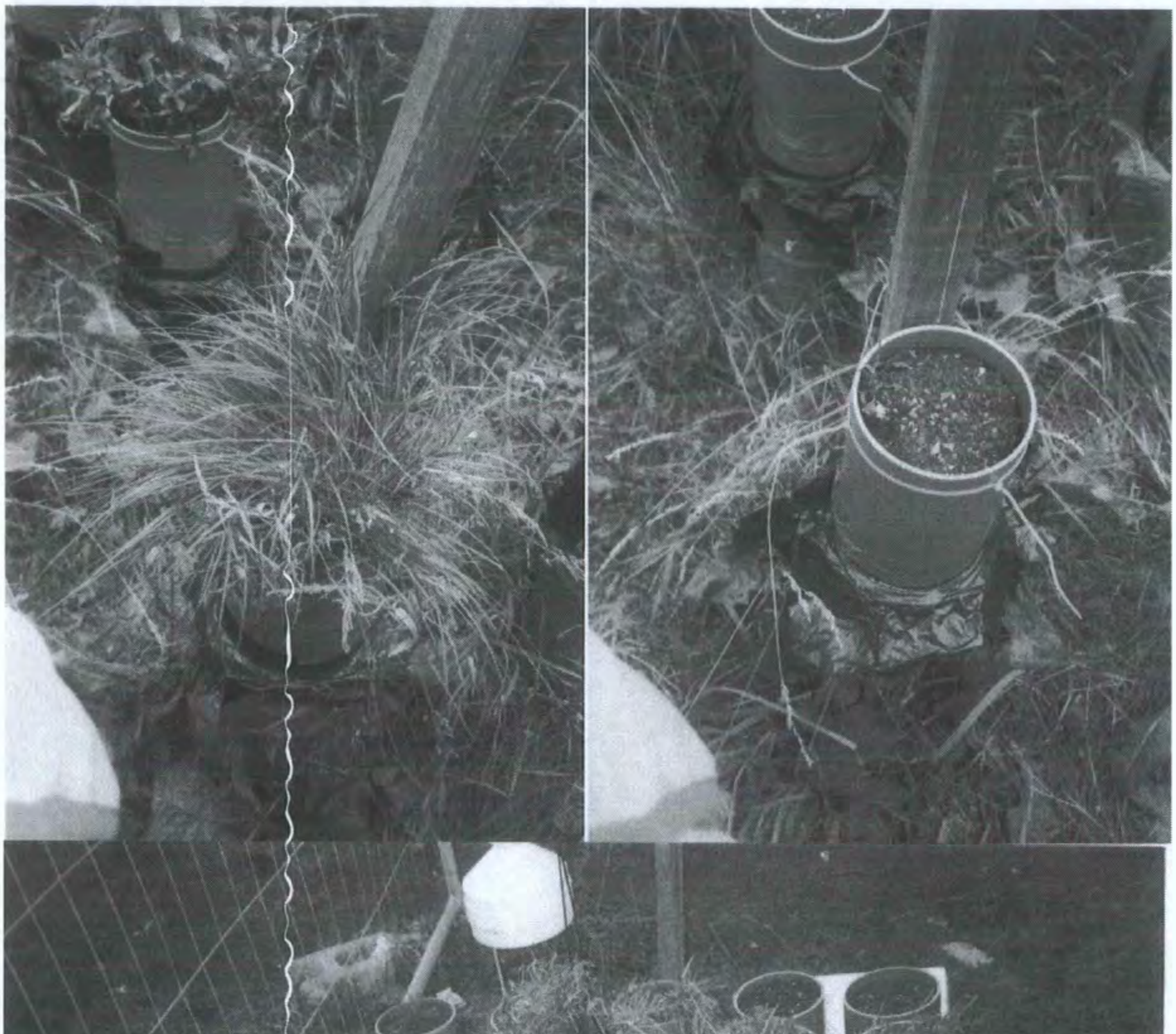
Figure 2.4: Collected leachate volumes (ml) comparison with time. Equivalent values of rainfall (ml) are represented by the dashed blue line.

2.8.3 Electrical conductivity

It must be recognised that the government limit values for electrical conductivity are purely a guidance level (GL) from a legislative perspective as well as an absolute value. Comparison of conductivity levels, although simple enough between lysimeter trials or laboratory studies where controlled conditions are known, prove difficult to manifest relative to recorded groundwater values. Groundwater concentrations will vary depending upon catchment size, precipitation levels, as well as associated temporal and spatial variations. Thus, actual values from the lysimeter trials represent flux values by volume (per lysimeter) and weight (per kilogram) of material used. Specific electrical conductivities seen in leachates emanating from each lysimeter represent field conditions, therefore incorporating a rainfall figure relative to all lysimeters, and so are more suitable for GL (400-1000 μScm^{-1}) and landfill discharge consent (mean maximum – 43.10$mScm^{-1}$) evaluations. Between-treatment comparisons were conducted using specific electrical conductivities corrected for weight allowance.

When measuring electrical conductivity flux values per lysimeter (Figure 2.5) it can be seen that all treatment leachates, including the agricultural soil control, are higher than government conductivity guidance levels (400-1000 μScm^{-1}) at some point over the investigation. Treatments containing CLO as well as the sewage sludge considerably exceeded this level for the entirety of the study (i.e., only the agricultural soil achieves levels suitable for drinking water extraction). This potentially presents a serious problem with respect to dissolved salt concentrations potentially leaching into groundwaters; actual recorded figures are, therefore, not as important – of greater environmental concern are the causes of extreme salinity, the prospect of remediation, and the significant differences between treatments with time. All treatment electrical conductivities, however, were always below that exuded from the Coxhoe landfill site, which was in close proximity to the field site, and so rainfall can be said to be of negligible difference, and so direct comparison of values can be taken.

It can be concluded therefore, that if any of the artificial soils, including sewage sludge, were spread upon agricultural land or land intended for the extraction of water, the conductivity levels in these waters would no longer be acceptable or fit for human consumption. The time in which this would materialise would be governed by catchment specifics and the application rate of the said 'soils.'



Photograph 2.2: showing vegetation cover variation for the: a) Comp, b) CLO 2004 trials and c) repeat lysimeters from left to right: agricultural soil, ML, BDA, Comp, CLO 2004.

When consulting electrical conductivity flux values per kilogram of material (Figure 2.6) it can be seen that conductivity patterns for the three-year treatments show a gradual decrease in concentration from a peak optimum flush appearing early to mid-August in the first study year, depending on treatment; the Comp and BDA treatments peak exactly one month prior. All treatments showed a steady decline in leachate conductivity until half way through the three years (Batch 25, 16/09/05), after which point slight fluctuations in signals were seen until the completion of experimentation in June 2007. The small-scale of these rise and fall events, relative to initial flush concentrations, deems this behaviour less important and was probably due to temporal rainfall and temperature variation. The final recorded concentrations were roughly a tenth of their respective peak values for all treatments, except the Comp treatment where values were twenty times smaller.

The CLO 2005 and 2006 treatments displayed similar trends and time-release patterns to the CLO 2004. In addition, CLO 2005 released salts immediately after establishment in the field without any gradual build-up to the main flush event, unlike its counterparts. Leachates produced by artificial Parcgro soil behaved in a similar fashion to those of CLO 2006, of which they were partially composed. Conductivity levels were around half those of its parent material. Sewage sludge leachates performed considerably better than the undiluted CLO treatments regarding electrical conductivity levels and adjusting for temporal rainfall variations produces leachates of similar quality to those of mixed treatments. Sewage sludge minimum values at the end of the two-year assessment averaged 1660 μScm^{-1}.

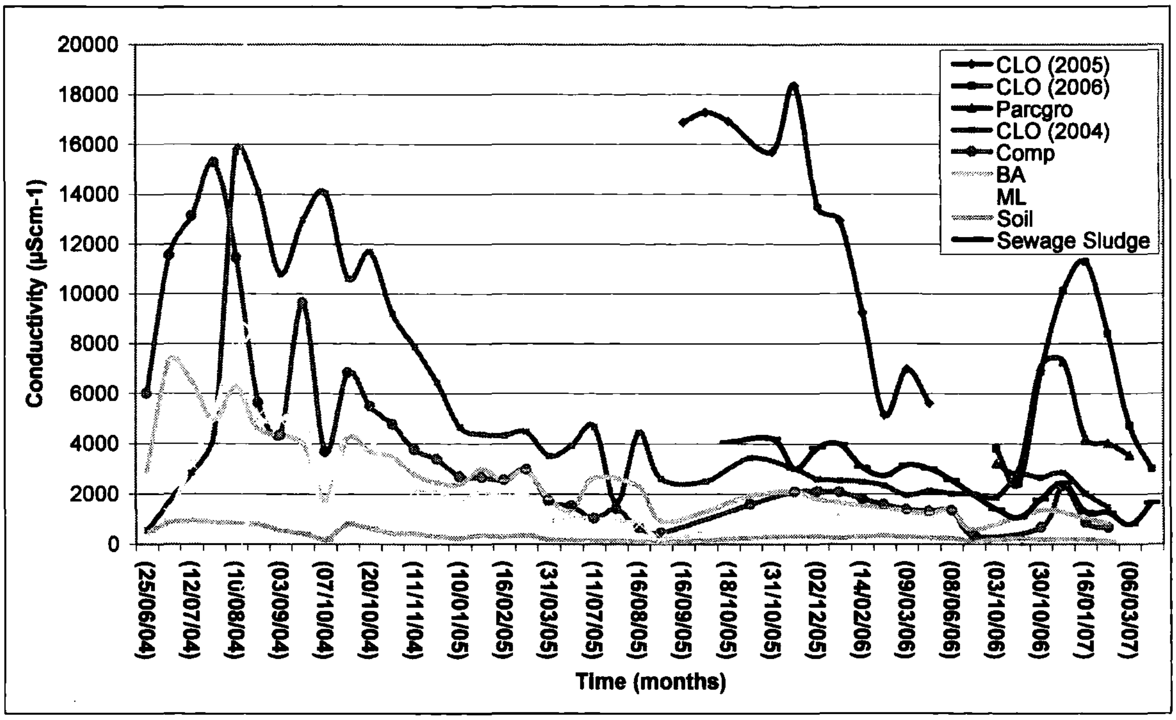


Figure 2.5: Recorded leachate EC levels by volume of material, over time.

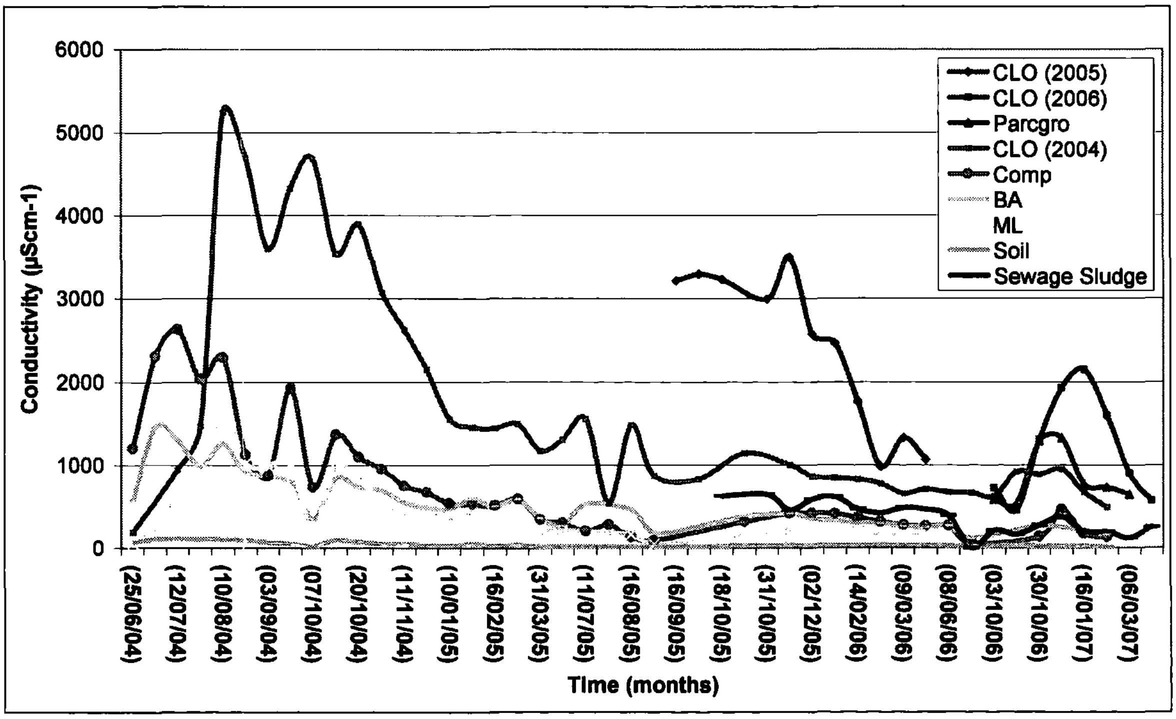


Figure 2.6: Recorded leachate EC levels by weight of material, over time.

2.8.3.1 Components responsible for leachate EC

Matrix plots were computed for all 'base cations' (Si, K, Na, Ca and Mg) as well as for all anions (chloride, nitrate and sulphate) measured in this study. There was no correlation found to exist between 'trace metal' leaching behaviour and pH, conductivity and DOC. Accordingly, statistical relationships are presented and explained in Chapter 5 (by means of the Principal Component Analysis technique). A summarised matrix plot (Figure 2.7, below) shows the relationships between K, Na, Cl and conductivity. These three components were considered to be the major species controlling conductivity levels in all the CLO-containing treatments. However, a cation pattern emerges where Ca becomes more prolific at later dates and, more specifically, with exemption of the Comp and CLO 2005 trials, develops into the dominant cation. This is discussed below.

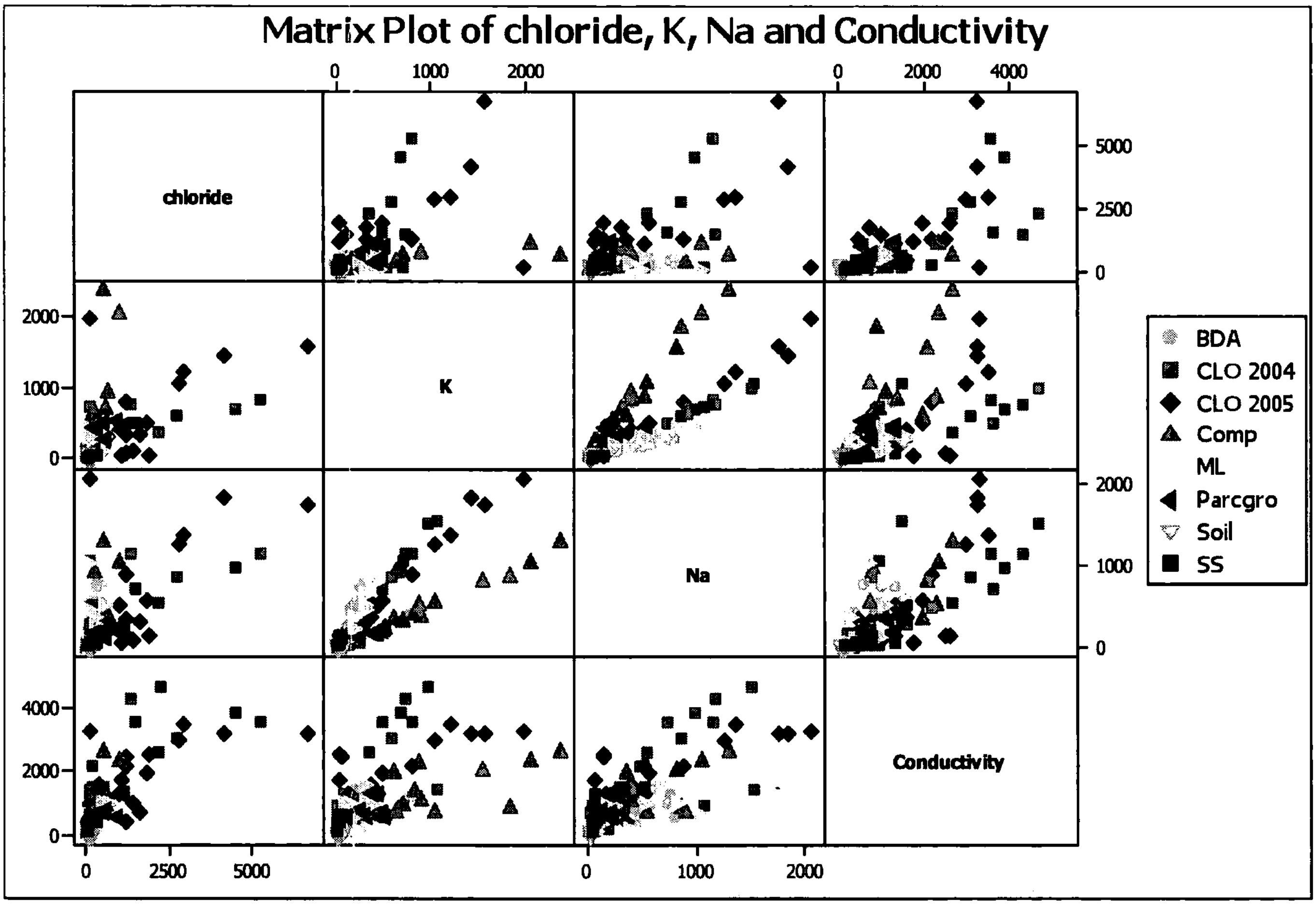


Figure 2.7: Matrix plot showings correlations between Cl, K, Na (mg/l) and conductivity (μScm^{-1}).

A similar trend for all CLO-containing treatments was seen for the anion SO_4, which was more prolific in leachates emanating from the BDA trial. The Comp leachates, and to a lesser effect (owing to limited data for the Parcgro trial) were dominated by K throughout, as opposed to almost equal quantities of both K and Na seen in other CLO-containing treatments, as shown in Figures 2.5 and 2.6. This was expected since both these treatments are largely comprised of green compost; the latter is known to be K rich. NO_3 also plays a larger role in later leachates.

Leachates from the two comparison treatments (sewage sludge and agricultural soil) behaved slightly differently to the other CLO trials. For sewage sludge, the dominant ions throughout were Ca and SO_4 but Mg was a more influential cation and NO_3 appeared intermittently throughout the two years of recording. The CLO characteristic flushing behaviour described for Ca was also observed in sewage sludge leachates but it was apparent that the Ca cation was more prolific from the beginning relative to the other base cations and so was assumed to be a major salinity dictator throughout. However, there were no characteristic high level flushes of dissolved salts shortly after the introduction of sewage sludge into the field, as seen with all CLO-containing treatments. Levels began much lower (about a quarter of that seen for the undiluted CLOs) and remained much lower for the entirety of the study. This was exemplified by significant differences ($P<0.05$) with all CLO associated leachates and levels for the soil control (see below). Agricultural soil displays almost identical traits for each of the five cations under evaluation, which almost perfectly coincide with the conductivity readings, implying better constrained salinity-dependency on these base metals. The foremost differences between the soil and the remainder of the treatments were that Ca began and remained the dominant cationic species, and NO_3 remained the major anion throughout.

These findings would predict the major conductivity controlling soluble salts in leachates from treatments containing CLO to be KCl, NaCl, Na_2SO_4, and, at a later date, gypsum ($CaSO_4.2H_2O$). Findings by Ludwig et al (2000) confirm that conductivity levels in leachates emanating from landfilled municipal solid waste incinerator (MSWI) air pollution control (APC) residues were controlled by these elements. In contrast, the Ca component of the landfill leachates was found not to be controlling conductivity levels, as may be the case here. Ludwig attributed this to the fact that analysed leachates were not sourced solely from the landfill itself and incorporated percolation waters from the landfill cover also.

The additional higher levels of NO_3 found in the agricultural soil leachates, which parallel those seen by Ca and to a lesser extent K, would denote gypsum as well as $Ca(NO_3)_2.4H_2O$ and KNO_3 to be the naturally occurring mineral salts managing electrical conductivity levels in the soil control. The relative elevation in K and NO_3 concentrations in leachates from the Comp and Parcgro treatments would designate KCl as the dominant salt, rather than NaCl as seen with other CLO-containing treatments, but also smaller amounts of KNO_3 may occur, particularly at later stages during leachate evolution. Sewage sludge leachates were dominated by Ca by a factor of 4 and SO_4 by a factor of 2 for the entirety of the study period, suggesting conductivity would be mainly governed by gypsum ($CaSO_4.2H_2O$).

2.8.3.2 EC Statistical analysis

2.8.3.2.1 Group 1 and 2

There were quite distinct trends between treatments seen for both groups. For the three-year study (group 1), the dominant treatment was the original CLO which was significantly higher ($P<0.0001$) than all other treatments. Agricultural soil, on the other hand, was significantly ($P<0.0001$) lower than all other treatments. This draws a distinct line between the undiluted CLO, its mixed treatments, and soil and sewage sludge treatments with regard to the conductivity levels recorded in exuded leachates (Original CLO >> Comp, BDA and ML >> SS and soil). Mixing the CLO with 75% amending material significantly reduced leached salinities, but not enough to equal levels attained by typical agricultural soil. The dilemma therefore was whether the mixed treatment leachate levels are compliant with government GL's and if this amelioration of salinity was due to active remediation or passive dilution.

Comparisons with drinking water regulations may undermine the utilisation of the mixed treatments as a soil replacement on catchments intended for extraction of drinking waters (even after three years of leaching levels are still higher than GL for drinking water), and further statistical analyses revealed no significant beneficial differences against undiluted CLO. Therefore, environmentally unacceptable reduced salinities can only be attributed to passive dilution.

Similar results were attained for the one-year study treatments where the CLO 2005 digestate produced significantly higher ($P<0.0001$) salinity leachates than the rest of the treatments and the sewage sludge ($P<0.05$) the exact opposite. Again, no active remediation resulted from using Parcgro material. An overall view of relative salinity levels reveals the following decreasing pattern, where (>> equals statistical significance to at least $P<0.01$):

2005 CLO >> 2006 CLO > Original CLO >> Parcgro > Comp > BDA > ML > SS > Soil

It was also interesting to note a statistical difference ($P<0.001$) between different batches of the 'same' CLO material.

2.8.3.3 Discussion

The main distinguishing patterns seen in leachates from treatments comprising all or some part CLO, relating to recorded conductivity levels, have been described. An explanation for the temporal coincidence of initial increase of Ca^{2+} and sharp decrease in Na^+ may be similar to that observed for natural sodic (high levels of exchangeable Na) soils (Sumner, 1993; Spark *et al.,* 1995). When the concentration of soluble salts accumulates in a substance, the soil exchanger sites often become loaded with the counterion, in this case Na^+ and K^+. The drying of material over the summer period causes favoured precipitation of the more insoluble Ca salts, such as $CaSO_4$, or, as appears to be the case for the soil control, as $Ca(NO_3)_2$. With the onset of rainfall, preferential adsorption of the more soluble Na^+ and K^+ ions on exchange sites and the subsequent release of Ca^{2+}, and to a lesser extent Mg^{2+}, then occurs. The influential property affording this behaviour is the differing size/charge ratio of the two cations and the consequent varying solubility they display in solution. A similar assumption can be made for the smaller Cl^- being preferentially bonded to the Na^+ and K^+ over that of the larger SO_4^{2-} and NO_3^- ions, depending on treatment type, and thus the later dominance of the latter anions and their association with Ca^{2+} in leachates. This was similar to the findings of Gros et al (2006) where solidified Air Pollution Control residue (SAPCr) leachates were applied to an Alfisol soil. Certain properties, in particular the near neutral pH (7.6) and the extremely high electrical conductivity (11.2 dS m^{-1}), compared well to equivalent values exhibited by CLO and its associated soils.

Although the Comp treatment was governed by K throughout, the preferential adsorption of NaCl and KCl to calcium sulphate/nitrate salts can still be seen in elemental leachate concentration time series of leachates from this treatment. Limited data sets deemed identification of similar trends in CLO 2005 and CLO 2006 treatments and Parcgro treatments unsuccessful, since each of these treatments were only assessed for a one year period. No such relationship appeared to exist between sewage sludge solid /liquid phases as the elemental composition of leachates produced were dictated by $CaSO_4$ throughout. In addition, there was relatively little detected change in elemental concentrations between phase boundaries for the low sodic agricultural soil matrix, with cation concentrations occurring in the following decreasing order: Ca > K > Mg = Na > Si.

In summary, electrical conductivity may present one of the major problems associated with CLO, particularly if CLO and its artificial soils are to be utilised in an agricultural context. The extremely high levels of metal salts that were easily exuded would have detrimental effects on groundwater courses and plant life alike. It has also been shown that mixing the CLO with various amending materials does not offer any overall active remediation of the elements responsible, probably due to the elevated levels involved, making it difficult for any material to adsorb or complex ions. In fact, adjusted weight values reveal that two of the mixed treatments (Comp and Parcgro) actively increased leached concentrations of K which has been shown to be partially responsible for the high conductivities recorded.

2.8.4 Total Suspended Solids (TSS)

It must be noted that TSS analyses did not commence until January 2005 due to complications regarding which quality assessment technique would prove to be most beneficial for this study. Direct temporal comparisons with other leachate parameters can therefore only be undertaken from that time onwards. TSS were included mainly as a soil stability comparative tool, and so relative patterns and figures were subject to a number of varying factors and were not analysed in depth. The main objectives were to attain an overall estimation of TSS values for each treatment, to relate these to that seen in sewage sludge and the agricultural soil, and to determine whether any form of remediation of stability has been achieved from mixing CLO with other recyclable products. Owing to the high numbers and long filtering times required for samples, no repeat recordings were carried out; data was therefore based upon a single lysimeter for each treatment, statistical analyses could therefore not be conducted. Flux readings (mg) for each lysimeter and mg/l values were calculated. Flux values revealed that peak TSS concentrations did not necessarily coincide with periods of increased rainfall; only on one occasion (batch 24 – 12/09/05) did elevated concentrations coincide with a period of increased rainfall for all treatments. Thus, any variations in concentrations were considered to result from instabilities within the soil matrices themselves.

The main points to note concerning TSS concentrations (Table 2.4) were that the CLO 2005 and 2006 trials performed worst relative to the rest of the treatments, with TSS values being highest for all treatments at nearly every sampling point. The CLO 2005 treatment on one occasion was found to have a recorded TSS of 1720mg/l in leachate collected on the 6th October, 2005. The original CLO treatment records the next highest TSS values

No active remediation had been afforded by mixing the original CLO. In fact, all three mixed treatments (Comp, BDA and ML), had caused TSS values to relatively increase at some point. In contrast, the performance or aggregate stability of the Parcgro artificial soil relative to its parent material (CLO 2006) had substantially improved.

Thus, with regard to a TSS remediation treatment, the current mixing regime (1 part CLO: 1 part green compost: 1 part screened soils) appeared to be more effective than amending the CLO with just green compost, brick dust aggregate or magnesium limestone.

Sewage sludge TSS behaviour was analogous to that observed in the CLO 2004 treatment, but concentrations were closer to the region of the Comp, BDA and ML mixed treatments.

Time	**CLO 05,06**	**Parcgro**	**Sewage sludge**	**CLO 2004**	**Comp**	**BDA**	**ML**	**Soil**
Batch 16 (27/01/05)				132.9	43.2	33.4	37.9	82.6
Batch 17 (16/02/05)				68.8	50.8	20.9	17.9	80.4
Batch 18 (09/03/05)				34.2	46.5	83.7	20.8	139.7
Batch 19 (31/03/05)				23.3	19.1	25.9	4.0	36.1
Batch 20 (18/04/05)				67.0	62.3	56.2	20.1	30.0
Batch 21 (11/07/05)				265.5	89.7	502.3	114.1	6.9
Batch 22 (29/07/05)				126.7	13.0	62.9		18.9
Batch 23 (16/08/05)				618.9	84.0	29.8	164.4	19.0
Batch 24 (12/09/05)				571.6	582.8	396.2	192.3	357.9
Batch 25 (16/09/05)	799.4							
Batch 26 (06/10/05)	1720.0			114.5		35.9		
Batch 28 (25/10/05)	280.6			70.9	13.6	36.7	16.0	26.6
Batch 30 (07/11/05)	258.4		87.7	60.4	64.4	47.1	22.9	44.4
Batch 31 (02/12/05)	339.1		82.9	23.3	40.3	16.3	54.2	52.0
Batch 32 (05/01/06)	350.0		154.4	34.1	112.7	23.1	60.2	214.8
Batch 33 (14/02/06)	154.6		152.0	41.4	125.4	16.4	54.4	242.4
Batch 34 (23/02/06)	361.8		250.0	41.6	69.2	15.2	70.9	85.2
Batch 35 (09/03/06)			249.4	37.8	103.5	35.1	40.4	457.7

Batch 37 (08/06/06)			93.7	25.1	43.7	40.7		41.1
Batch 38 (21/09/06)	92.9	115.1	46.1	34.6	30.8	18.4		12.9
Batch 39 (03/10/06)	95.2	67.4	15.5	11.3	23.2			
Batch 40 (24/10/06)	354.3	40.9	12.7	94.5				49.7
Batch 41 (30/10/06)	726.7	20.2	12.4	4.2		7.2		2.7
Batch 42 (27/11/06)	199.7	19.2	27.1	8.4	12.5			11.3
Batch 43 (16/01/07)	328.6	13.4	14.4	4.8	11.7	16.2		14.7
Batch 44 (22/02/07)	146.2	29.3	11.7	7.9	15.4	9.0		90.0
Batch 45 (06/03/07)	93.0	26.9	10.1	7.3	28.7	27.8		52.0
Batch 46 (15/05/07)	72.7		41.6					

Table 2.3: TSS concentrations (mg/l) over time, for each treatment.

With the exception of the CLO 2005 and 2006 treatments, on one occasion for each (1720mg/l and 726mg/l, respectively), typical values for all treatments fluctuated within the range 2-600mg/l. Generally speaking, the agricultural soil performed the best, as expected of an already established soil, but even here fluctuating TSS concentrations exceeded 450mg/l. Coxhoe landfill records suggest a maximum value of 250mg/l was present in landfill leachates, but this figure had an associated 112% standard deviation and so must be viewed with caution. Further comparison with results attained by Ward et al (2005) from typical landfill leachates suggest that aerobic digestion of MSW is capable of reducing TSS values by an order of magnitude. Leachates, on average, contained 2-10,000mg/l TSS for the landfill.

2.8.4.1 Discussion

It was not surprising that mixing the original CLO with brick dust aggregate and magnesium limestone did not significantly reduce TSS values and indeed increased them. Visual observations and sieving studies of both materials indicated that both consisted of appreciable amounts of fine, almost powder-like material. Decomposing green compost can further add to the already significant organic material released from the CLO material; this will be suspended in leachates.

A number of factors could be affecting the release of solids from the parent materials in the lysimeters into percolating rainfall that forms the leachates in which these solids are suspended. These include: the presence of and the degree to which plant life had established on top of each lysimeter core; aggregate stability over time; flow pathways within the soils, and temperature variations. All testify to the difficulty experienced in assigning specific patterns to TSS over time for each treatment. The complexity of these factors, how they relate to one another and ultimately to what degree this affects TSS levels, together with limited data, describes a need for further investigation of this soil characteristic. For example, the existence of plants, as with drainage ratio, would have contributed significantly, helping to bind the soil matrix with their root systems thus limiting leachate TSS levels to some extent. The preservation of plants was, however, purposely incorporated into the experiment design, which was strongly geared around realistic field scenarios and so compromises are always necessary between scientific precision and representative field conditions. Furthermore, it has been assumed that the observed TSS leachate values were indicative of erosion but realistically these suspended solids would not travel far vertically in a field-based situation – a limiting factor of lysimeter trials. This may also account for higher than expected levels flushed from the agricultural soil lysimeters.

The important points to be taken from this section are that, relative to wastewater standards (30mg/l average per month and 45mg/l average per week), TSS levels measured from all treatments, including the agricultural soil, were elevated and that no reduction had been achieved by the mixed treatments relative to original CLO. The term 'reduction' rather than remediation has been used because although decreases in TSS solids are desirable, this is only true to a certain level (which is uncertain and can only be estimated based on municipal wastewater targets). With the data available, it must be concluded that the downward transport of suspended solids recorded in all treatments, and the lack of remediation afforded by mixing the CLO, may be unacceptable for use on agricultural land which may be used for drinking water extraction. TSS can therefore be added to the list of potentially detrimental properties exhibited by CLO and its associated soil mixtures. Contrary, as mentioned earlier, the appearance of TSS levels, particularly in the range detected here, may provide remediation, in itself, of leached metal concentrations, if the CLO and its artificial soils were to be used in a none agricultural context. Additional studies relating to the metal speciation found in dried TSS samples may prove beneficial in quantifying the extent of remediation. However, diminutive residue sample sizes may deem this impractical unless the scale of the lysimeter set-up could be increased.

2.8.5 Dissolved Organic Carbon (DOC)

This section, as well as providing a idea of the DOC contents in leachates, will subsequently quantify each treatment's potential for metal complexation. Figure 2.8 illustrates the calculated DOC concentrations (mg/l) as well as characteristic trends in which this carbon was flushed out over time for all treatment leachates. Coxhoe discharge consents for DOC were unavailable, but relative to values recorded by Ward et al (2005) in landfill leachates in Florida (as with TSS values) where the maximum values ranged from 150mg/l – 1126mg/l and on one occasion reached values as high as 6165mg/l, it can be seen that these are in a comparable range. No reduction in leached water-soluble organic carbon has been achieved by the composting process as would be expected from a process specifically tailored to biodegradation of the organic fraction of a material. Drinking water colour parameter limits are set at 20mg/l and so it is quite clear that recorded DOC levels could be a serious cause for concern if CLO associated soils, in any of the theorized forms, were to be used in drinking water catchments.

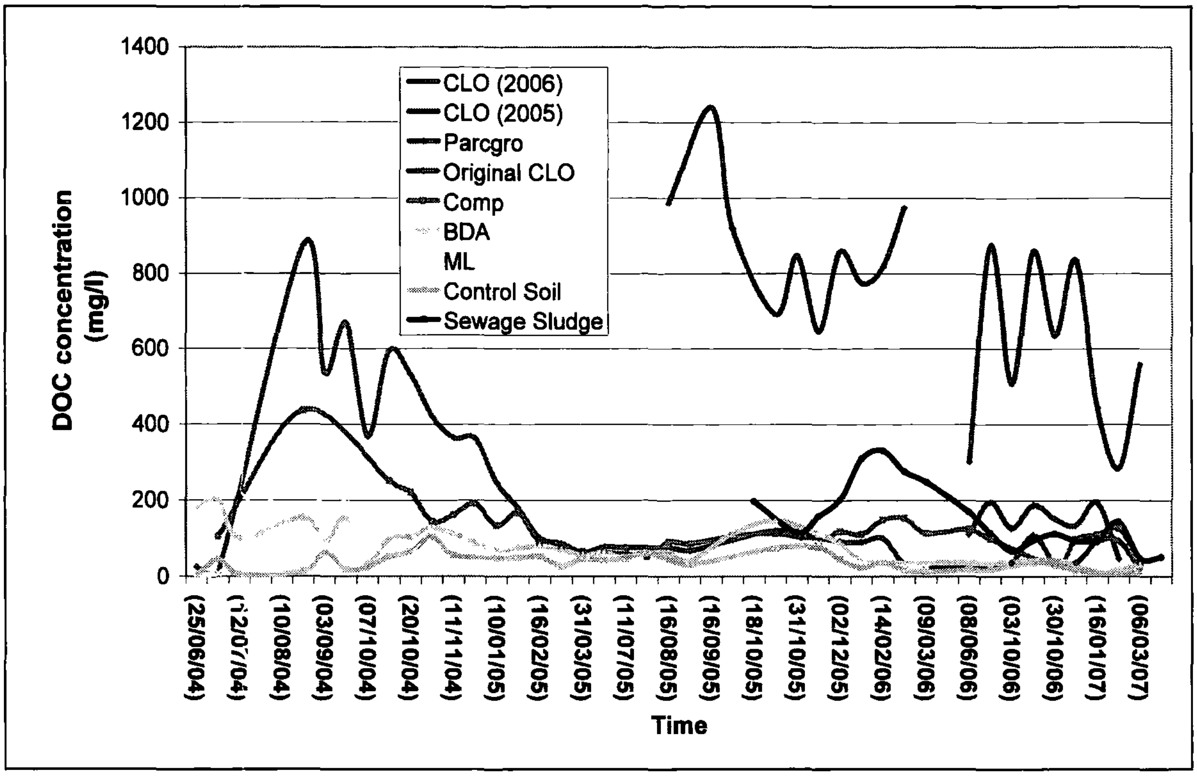


Figure 2.8: Treatment leachate DOC contents over time (mg/l).

All treatments afforded, on average, similar flushing patterns relative to those observed for other leachate parameters analysed, including conductivity, base cations and trace metals. The CLO 2005 and 2006 treatments, however, demonstrated considerable rises and falls in DOC levels with time, with a much less pronounced overall decreasing trend. It can be seen that the highest DOC concentrations were achieved by undiluted CLO treatments, which, considering the TOC contents of the original solid materials before leaching, (ranging from 50.07% to 53.31%) would be expected (Chapter 3). The maximum attained values during their peak flush phases were 874mg/l, 1240mg/l and 874mg/l for the 2004, 2005 and 2006 CLO treatments, respectively. The next CLO-containing treatment, regarding decreasing TOC (33.1%) and DOC (maximum – 437mg/l) levels was the Comp treatment, followed by the BDA and ML treatments, with the agricultural soil – with its relatively low organic values (TOC – 6.5% and DOC – 103mg/l) – exuding the least DOC of any treatment. The order of decreasing recorded levels of DOC in leachates for the three-year study materials was therefore analogous to their respective TOC contents determined by loss on ignition (LOI). The Parcgro treatment, although producing analogous DOC and original TOC values to the BDA and ML treatments (mean TOC values all around

21%), did not display a similar initial flushing of DOC. Presumably this could be attributed to the mixing of the CLO with various soil grades, considering both CLO and green compost organic contents (dissolved and total) were similar for the temporally different mixtures. A final point was that the sewage sludge treatment displayed similar levels and trends of DOC leaching to that of the Comp treatment, despite having an initial mean TOC value of 53.2%, equivalent to that of the undiluted CLO solids. Thus, the organic carbon present in the sewage sludge is not as susceptible to the dissolution process as the organic carbon that comprises significant proportions of the CLO; partially an indication of increased stability.

2.8.5.1 Discussion

The release of water-soluble organic carbon has been shown to be significant, especially from the artificial CLO containing soils, relative to that of an agricultural soil. If these materials, either in their pure form or as amended soils such as Parcgro, are to be used upon land, the effects that these recorded levels of DOC have on the surrounding groundwaters could be extensive. It has been shown (Dekker, 1994) that even after 15 years of percolation, waters containing organic carbon loads of 140kg C_{org} ha^{-1}/y from sewage sludge effluents, still contained an organic carbon fraction that was biodegradable. This, in conjunction with high levels of nitrates and sulphates in the groundwater (similar to leachates from CLO treatments), indicated that the consumption of dissolved oxygen through the biodegradation of water-soluble organic matter is a rate-limiting process with a cumulative effect. Potentially, if higher levels of DOC, caused by CLO application to land, are leached into catchment waters the cumulative effect on dissolved oxygen depletion may be enhanced, both by content and with time. Furthermore, the potential for the increased mobility of complexed metals through transport of DOC-laden leachates could be of concern; additional testing in field/catchment scenarios, as mentioned above, may be of benefit in quantifying the effect these large DOC flushes have on groundwater contamination. Now that distinct DOC concentrations are confirmed to have been leached from these high TOC materials it would be interesting to quantify the effects this may have on the complexing of metals in both the solid state and liquid phase, and thus their bioavailability (similar to TSS). DOC is, however, distinct from TSS, as it will move vertically and laterally through soil mediums potentially making it a greater threat to surface and groundwaters, depending upon the adsorptive abilities of the pathways it encounters.

Statistical analyses reveal that there was a clear distinction between the elevated DOC concentrations found in leachates of the undiluted forms of CLO and its diluted progeny materials, as well as those of sewage sludge and agricultural soil. The decreasing order of DOC is as follows (>> signifies $P<0.05$):

2005 CLO >>2006 CLO >> 2004 CLO >> SS > Parcgro > Comp > ML > BDA > Soil

These findings were correlated with the TOC values described above, except that the CLO 2005 and 2006 treatments, which were all similar in TOC content (50.07 – 53.31%), were significantly different from each other in the DOC order shown here. This suggests, as with many of the measured elemental components of CLO associated leachates, that the alterations made to the aerobic digestion recycling process since 2004 have also enhanced levels of DOC vulnerable to the leaching effects of percolating rainwaters. This could be due to a variation in compost maturity being discharged, subsequent to shifting optimisation conditions over the three years, mainly the manipulation time within the digester ranging from 6-9 days. Results indicate that original CLO composting conditions were either optimised more efficiently or operated for the upper limit of the available time. These scenarios would both manufacture end products that had undergone considerable leaching of salts, metals and organic matter, and so potentially reduce the quantities and toxicities available for field-based leaching. Nevertheless, it remains that even if these observed differences between the three undiluted CLOs do result from varying digester performance, the environmental concerns relating to the elevated leachate concentrations persist.

2.8.6 Leachate Elemental Concentrations over time

In this section leached metal, non-metal and nutrient concentrations were assessed over time. Due to the heterogeneous nature of the CLO materials and the random uncontrollable factors affording preferential flow and vegetation growth the leachates were, physically and chemically, highly variable. Normalising the data relative to the soil control treatment would bias the results – more important was the collection of realistic, representative data for various water quality properties displayed by CLO and its associated soils under field conditions over a long period time. Leachate concentration time series over time were deemed the most appropriate in identifying characteristic trends and comparative concentrations for all treatments simultaneously. Statistical analyses were conducted to identify whether remediation from mixed treatments was of an active or passive (dilutive) nature.

A clear distinction in concentration ranges existed (between Si, K, Na, Ca and Mg, and Ni, Zn, Cu, Cd, Pb, Al, P, Fe, Co, Mn, Ti, Sc, Cr, Li, and V). For ease of analysis, these two groups of elements will be referred to as the 'base cations' and 'trace metals', respectively. Consequently, actual values are presented as (mg/l) and (µg/l), and flux values as (mg/kg) and (µg/kg) for base cations and trace metals, respectively. All anions (F^-, Cl^-, Br^-, HPO_4^{2-} and SO_4^{2-}) are recorded in (mg/l and mg/kg). Graph data used mean incremental concentrations (mg/l) of the three repeat lysimeters for each treatment and sometimes logarithmic scales have been used to visualise data. Coxhoe Landfill discharge consents and EC Drinking water constraints are both graphically represented by maximum values. Maximum recorded values for all treatment leachates are referred to throughout to be in accordance with government legislative constraints, as well as being the most appropriate representation for a comprehensive Environmental Impact Assessment (raw data per treatment lysimeter is in Appendix 1 on the attached data cd).

2.8.6.1 'Base Cations'

It must be remembered that cation concentrations are presented in mg/l and so mean values seen graphically for the original 2004 treatment would be roughly double that if they had been adjusted by weight (mg/kg). This is why care needs to be taken if comparison with conductivity patterns is to be carried out.

It is apparent that over the entire study no beneficial active alleviation of any base cation had occurred relative to the pure CLO treatment. In fact, in a number of cases, mixing the CLO with the supposed remediation material had actually increased concentrations of certain elements, at some point in time, above that of pure CLO. This was the case for K in the Comp treatment, Si in BDA, Ca for both BDA and ML treatments, and all three remediation treatments showed increased Mg and Na concentrations. However, passive remediation or effective dilution can occur if elemental concentrations are reduced to below the maximum admissible concentration (MACs) set out by the EC Surface and Drinking Water Directives. This passive dilution of the CLO, although not environmentally substantial, may offer the reduction necessary to legalise leachates exuded from the various treatments. Passive remediation values were also compared to levels found in discharge consents from the Coxhoe landfill site. Base cation mean leachate concentrations over time can be seen below in Figure 2.9 for K, Na and Ca.

Despite the fact that no mixed treatment offered an amelioration of Si, with BDA worsening the situation, the general low levels detected for all treatments relative to other base cations are noteworthy. Furthermore, there is no legislative limit incumbent to Si, concentrations displayed by sewage sludge were on average at least two times higher than any other treatment, and the agricultural soil control exhibited higher levels than all treatments at some point. However, the CLO 2005 and 2006 treatments leached higher levels of Si which was further evidence for the heterogeneous nature of the CLO, particularly between batches (i.e., temporal variation). Detected Si concentrations were not necessarily environmentally acceptable, but were not in breach of any legislation concerning the quality or protection of soils relating to, and waters intended for, human consumption.

Conversely, concentrations of K that breach legal limits have been found in leachates from all treatments but especially in the Comp treatment, where initial maximum concentrations climbed to almost 2800 mg/l, which exceeds both EC Drinking Water MACs (12mg/l) and landfill maximum values (1400mg/l). After the initial flush, however (around mid October, 2004), K levels in the compost and CLO leachates have diminished sufficiently to below mean concentrations found in runoff from the Coxhoe landfill site (where they reside for the remainder of the study period, well above EC MACs). BDA and ML values, although in permanent breach of EC Drinking Water restrictions, show promise relative to landfill values being lower throughout the study. It must also be noted that both the sewage sludge and the agricultural soil treatments displayed levels of K that continuously breached Drinking Water legislation, but never reached landfill intensities. As with the dissolution of Si, the CLO 2005 treatment exhibited extremely high leached concentrations (2296mg/l) in the same region as the Comp treatment.

A similar, but slower, leachate concentration time series was seen for Na. Maximum values being leached from any treatment, except CLO 2005 (2534mg/l), remained below that leached from the landfill site (2240mg/l). Nevertheless, it took at least a year for the three remediation trials and a further 8 months for the original CLO to attain drinking water MACs. Limited available data, together with its highly variable nature, prevent meaningful interpretation that the Na concentration leached from CLO 2005 will remain below acceptable levels. However, statistical analyses revealed that for the data attained there was a significant difference ($P<0.001$) between Parcgro artificial soil and 2005 CLO but not 2006 CLO.

Based on the time of mixing, it is likely (although it cannot be certain) that the Parcgro material was composed from the 2006 batch of CLO. That said, with the characteristic heterogeneity of the CLO batches over the years, it is highly possible that active remediation may have occurred. Supplementary material would be necessary to confirm this either way as will be discussed below. Therefore, with regard to recorded leached Na concentrations, despite providing passive remediation, the three mixed trials as well as the pure CLO, pose an environmental threat at the concentrations recorded. Although the Parcgro treatment generally demonstrates lower, legally abiding concentrations, the limit was still breached on occasion and active remediation cannot be statistically confirmed. The sewage sludge and agricultural soil leached Na concentrations raise no concerns.

The opposing behaviour of Ca ions has previously been described when explaining conductivity relations. In relation to directive guidance levels (since no MAC is defined) set at 100mg/l, it can be seen that all treatments including the agricultural soil breach this. Again, CLO 2005 gives the highest leached concentration (1333mg/l). No remediation, active or passive, could be statistically proven. Furthermore, BDA and ML trials prolong the time over which GLs are breached before the summer low. It may be stated that similar patterns to that of Ca were seen for the dissolution of Mg over time for all treatments. The only difference being that agricultural soil never breached the MAC (50mg/l); all other treatments fall foul of drinking and surface water limits even at the end of the 3 year study period. Concentrations found in leachates exuded from the CLO 2005 and 2006 treatments (867mg/l) were more than 17-fold larger than the legal limit permitted in waters intended for human consumption. The fall and rise of Mg was not so prominent, partially masked by the heterogeneity of the CLO, and also probably due to the preferential release of the slightly larger Ca ion into solution. Nevertheless, maximum measured concentrations of Mg in any treatment were at least five times lower than the equivalent found in leachates from the landfill site, with the sewage sludge values residing near the upper limit of the treatments.

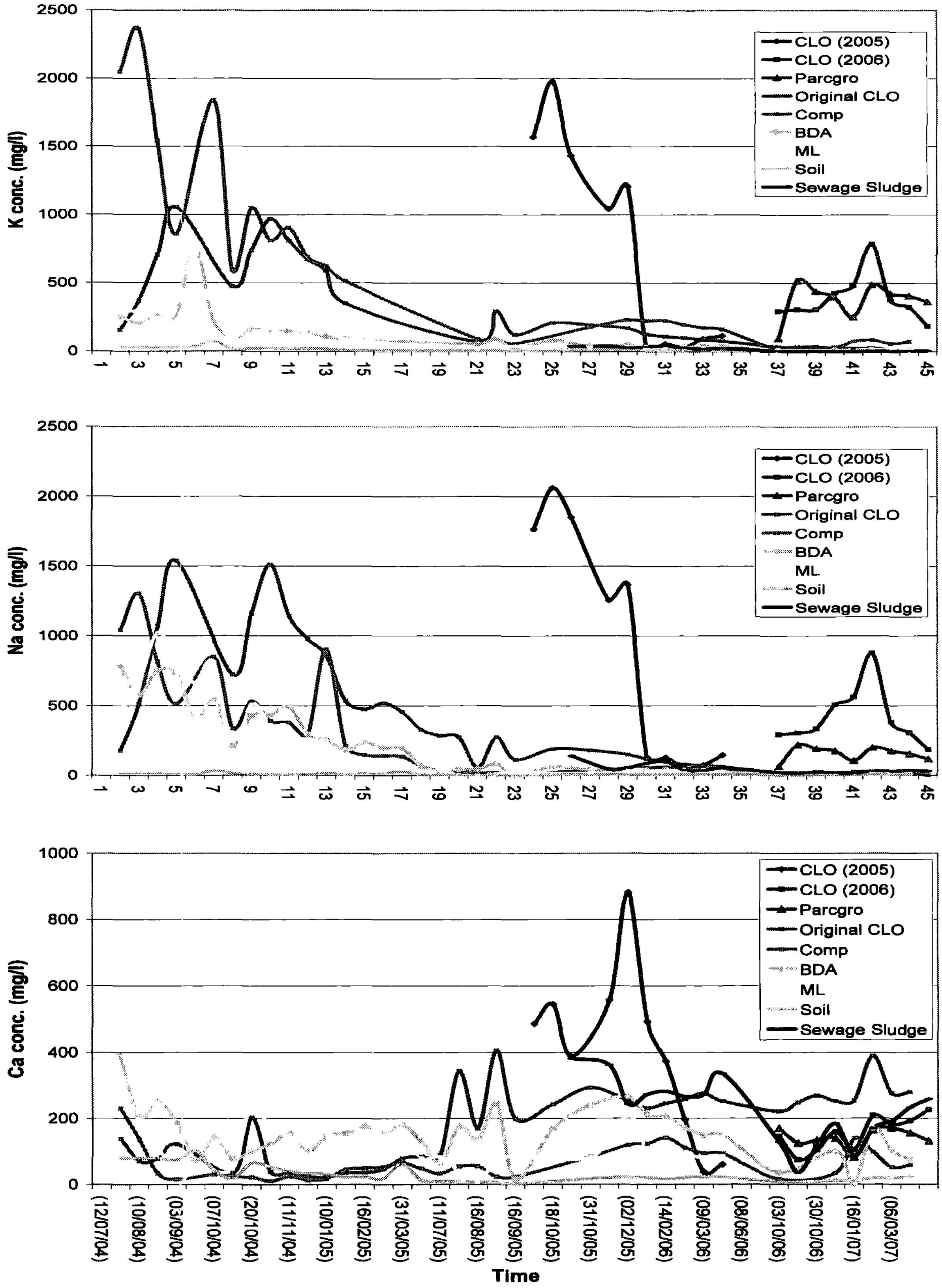


Figure 2.9: Treatment leachate concentration time series over time for a) K b) Na and c) Ca.

2.8.6.2 Base cation statistical analyses and discussion

2.8.6.2.1 Group 1

Significant differences

All five base cation (Si, K, Na, Ca and Mg) leachate concentrations exhibited statistical differences ($P < 0.05$) between treatments. Post-hoc test results can be seen in Table 2.5. Unlike group 2 treatments there was no individual treatment which consistently produced higher concentrations of leached base cations than the others, but the agricultural soil did exude significantly lower levels for four out of the five elements (K, Na, Ca and Mg). For Si, sewage sludge leachates dominate over all treatments ($P<0.0001$) and the BDA treatment significantly outstripped the ML and soil treatments, but was not significantly different to leachates from the Comp treatment. Dissolved K concentrations were significantly higher ($P<0.0001$) in the Comp treatment relative to all other treatments, but the original CLO leaches enough K to produce a significant difference between itself and the soil control and sewage sludge treatments. In each case, a three tiered concentration range was produced. With Na release there was no significant difference between the Na depleted soil and sewage sludge treatments but leached concentrations are low enough to divide them from the rest of the field; this was also true for Mg. Finally, Ca concentrations decreased between treatment in the following order (>> indicating ($P<0.0001$)):

CLO > SS >> ML > BDA >> Comp >> Soil.

Four statistically different concentration ranges were produced, at the head of which were undiluted original CLO and sewage sludge.

Based on these findings the main environmental concern is that none of the treatments, save largely undiluted CLO, may be suitable to be used on agricultural land where catchment waters are intended for human consumption. Furthermore, the high levels of metal salts could seriously damage plant life and any organisms associated with surface and groundwaters that leachates may have contaminated.

Si	**CLO**	**Comp**	**BDA**	**ML**	**Soil**	**SS**
CLO	-	NS	0.05	NS	NS	0.0001
Comp		-	NS	NS	NS	0.0001
BDA			-	0.05	0.05	0.0001
ML				-	NS	0.0001
Soil					-	0.0001
SS						-

K	**CLO**	**Comp**	**BDA**	**ML**	**Soil**	**SS**
CLO	-	0.0001	NS	NS	0.000	0.0001
Comp		-	0.0001	0.0001	0.000	0.0001
BDA			-	NS	NS	NS
ML				-	NS	NS
Soil					-	NS
SS						-

Na	**CLO**	**Comp**	**BDA**	**ML**	**Soil**	**SS**
CLO	-	NS	NS	NS	0.001	0.001
Comp		-	NS	NS	0.001	0.001
BDA			-	NS	0.001	0.001
ML				-	0.001	0.001
Soil					-	NS
SS						-

Ca	**CLO**	**Comp**	**BDA**	**ML**	**Soil**	**SS**
CLO	-	0.0001	0.0001	0.0001	0.000	NS
Comp		-	0.0001	0.0001	0.000	NS
BDA			-	NS	0.000	0.0001
ML				-	0.000	NS
Soil					-	0.0001
SS						-

Mg	**CLO**	**Comp**	**BDA**	**ML**	**Soil**	**SS**
CLO	-	NS	NS	NS	0.000	NS
Comp		-	NS	NS	0.000	NS
BDA			-	NS	0.000	NS
ML				-	0.000	NS
Soil					-	0.0001
SS						-

Table 2.4: Significant differences found between treatments for the 'base cations'. NS = not significant.

2.8.6.2.1.1 Active remediation

It is understandable that mixing the CLO with the three remediation materials may afford a simple dilution of toxic elements when values were not adjusted to the mass of CLO. Any significant difference between treatments can then be identified and attributed to *passive* dilution. Weight-adjusted leached concentrations (not shown here) showed that there has been no *active* remediation for any base cation relative to leached concentrations exhibited by the original CLO with which the amended treatments were mixed. Thus, any significant differences that exist between the original CLO and its associated mixed treatments result from the mixing materials themselves, or from enhancing base cation release from the CLO, elevating relative levels of leached concentrations found in undiluted CLO. This was the case for Si in the BDA treatment giving leachates significantly higher ($P<0.05$) than the rest of the field, and for K in the Comp treatment ($P<0.0001$). As highlighted above, the release of Ca into solution were more complicated than for the other base cations showing, after an initial flush, a gradual increase over time as they were preferentially de-adsorbed from the solid phase.

The decreasing order of leached concentrations between treatments was as follows (>> relates to significant difference ($P<0.001$):

BDA > ML >> CLO > Comp

It is clear therefore that statistical differences between the BDA and ML treatments and the CLO and Comp treatments.

2.8.6.2.2 Group 2

Significance differences

Again, all of the five base cation (Si, K, Na, Ca and Mg) leached concentrations exhibited significant statistical differences ($P< 0.05$) between treatments. The majority of statistical differences in this group were due to elevated concentrations, sometimes by orders of magnitude, of elements being leached from the undiluted CLOs, particularly CLO 2005.

2.8.6.2.2.1 Active remediation

As mentioned above, the success of active remediation hinges upon whether the parent material with which Parcgro was mixed (1 part CLO: 1 part green compost: 1 part screened soils and sub-soils) was sourced from a CLO batch typical of 2005 or 2006. If from 2005, then significant active remediation is evident for all base cations analysed, apart from K - the reason why no amelioration is offered for K by the

Parcgro material is the same reason why K levels are elevated in the Comp treatment in group 1, i.e., the green compost portion contains high levels of K from plant tissues that is in a water soluble form. Based on the time of discharge of CLO 2006 and the time of preparation of the Parcgro soil at the Coxhoe landfill station, the 2006 CLO *was* more likely the material used to produce Parcgro. With there being no statistical evidence to support that active remediation had occurred from the original three year treatments, it is unlikely that mixing a more heavily contaminant-laden CLO with less diluent would initiate active remediation. The representative content of the lysimeter core (i.e., whether it was more characteristic of CLO 2006 or CLO 2005) was beyond the control of the experiment's design. Every precaution was taken to minimise external contamination and to eliminate internal experiment errors, but nothing could (or ultimately should) be done to homogenise the characteristic variation between different CLO batches. The heterogeneous nature epitomises aerobically composted MSW and therefore needs to remain as such to ascertain closely representative data ranges. This is not to imply that it will not complicate statistical analyses (as evidenced), but is worth keeping in mind. Thus, the Parcgro parent material must, on the body of evidence, be concluded to be characteristic of the CLO 2006, and that no beneficial active remediation ($P<0.05$) was achieved for any base cation by mixing.

In addition, significance tests were performed over time to determine whether significant flushing events had occurred. Contrary to what would be assumed from the leachate concentration time series (based on mean average values), the raw data used for statistical analysis showed considerable variation between consecutive sampling events when compared to differences over the entire study period. These large amounts of experimental variation were either a result of the heterogeneous chemical nature of CLO materials and sewage sludges, or due to other random factors (such as, plant growth or preferential flow). Either way, very few significant flush events ($P<0.05$) existed for the parameters analysed (trace metals, non metal, TSS and DOC). The significant flushes that did exist were mainly for the base cations, which readily demonstrated their water soluble nature and potential for removal by a pre-treatment washing method (Chapter 4). These significant differences were proven for CLO and sewage sludge treatments alike. A further point, as can also be seen in the individual elemental leachate concentration time series (Figure 2.9 above), was that CLO-containing materials, particularly undiluted CLO's, can demonstrate larger and more prolonged flushing events comparative to those seen in sewage sludge. Supporting evidence lies in the significant flush events ($P<0.05$) found for Zn, Mn and Fe in sewage sludge leachates that continued for only one or two sampling events soon after their introduction into the field. CLO on the other hand, with its extremely high metal/salt content, particularly Na and K, maintained this significant flushing event for up to six months. This was also true for Ni, Al and Fe dissolutions and is discussed below.

2.8.6.3 Base cation fluxes

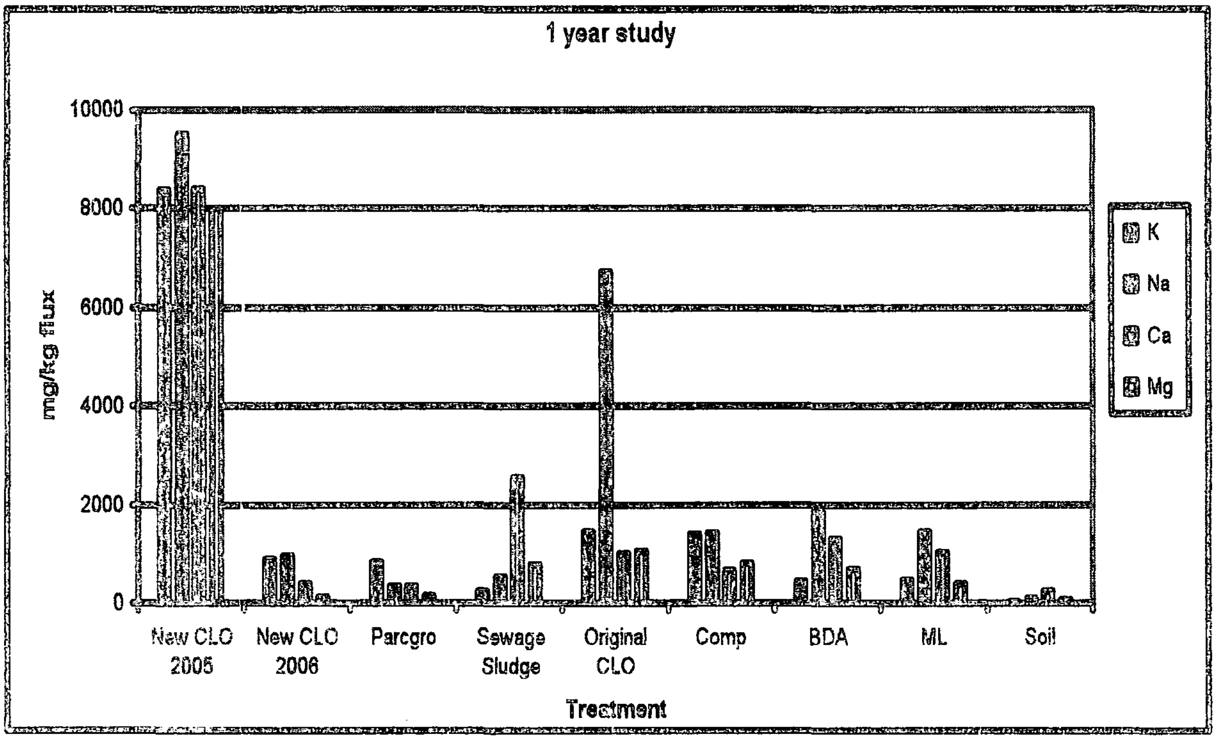
2.8.6.3.1 1 Year study

The main point in evidence in Figure 2.10a is, again, that CLO 2005 dominates flux values with concentrations of base cations up to 8-fold those flushed into the environment from any other treatment, bar Na and Ca from the original CLO and sewage sludge treatments, respectively. The original CLO and sewage sludge treatments both leach larger than normal concentrations of Na and Ca; as expected, agricultural soil performed best, remaining below maximum fluxes of 300mg/kg, compared to 9500mg/kg seen in 2005 CLO leachates. Additional points of interest were the relative performances of CLO 2005 and Parcgro leachates to original CLO and its mixed treatments (Comp, BDA and ML). Newer CLO-containing products appeared to flush out lesser amounts of all base cations over their first year of leaching. Even with a correctional increase in rainfall of 37%, the original mixed treatments still produced Na, Ca and Mg levels higher than the CLO 2006, and in particular the Parcgro treatment. Leachate concentration time series (previously presented) confirm this flux observation and any interference from plants can be ruled out since significant establishment of such species had not yet occurred. Even if plants were a factor, active uptake from their root systems would favour the original CLO and mixed treatments since these treatments increased relative plant growth.

2.8.6.3.2 2 Year Study

When evaluating the second year of the study it can be seen, in Figure 2.10b that leached Ca ions had either become the dominant flushed ion or had significantly increased in concentration relative to other base cations, as this cation was preferentially released into solution over time. All other elemental patterns (relative to each other) remained the same for all treatments and agricultural soil produced by far the lowest concentration leachates with respect to base metal contamination. The sewage sludge treatment was the only treatment to demonstrate concentration increases from 1 year to 2 year fluxes, as this treatment was not characterised by large initial flushes of elements on establishment of the study. Elemental fluxes for the 2 year study were almost exactly double those recorded for the 1 year leachates. This behaviour may, in the long term, be detrimental to the use of sewage sludge in agriculture as it displays a persistent contaminating nature which can be seen, for example, in leached Mg concentrations. For the first year, roughly equal levels of Mg are seen in leachates from the sewage sludge, Comp and BDA treatments. However, second year sewage sludge flux values increased relative to the other two mixed treatments, as a larger proportion of the Comp and BDA treatments' initial available Mg contents has already been flushed.

a)



b)

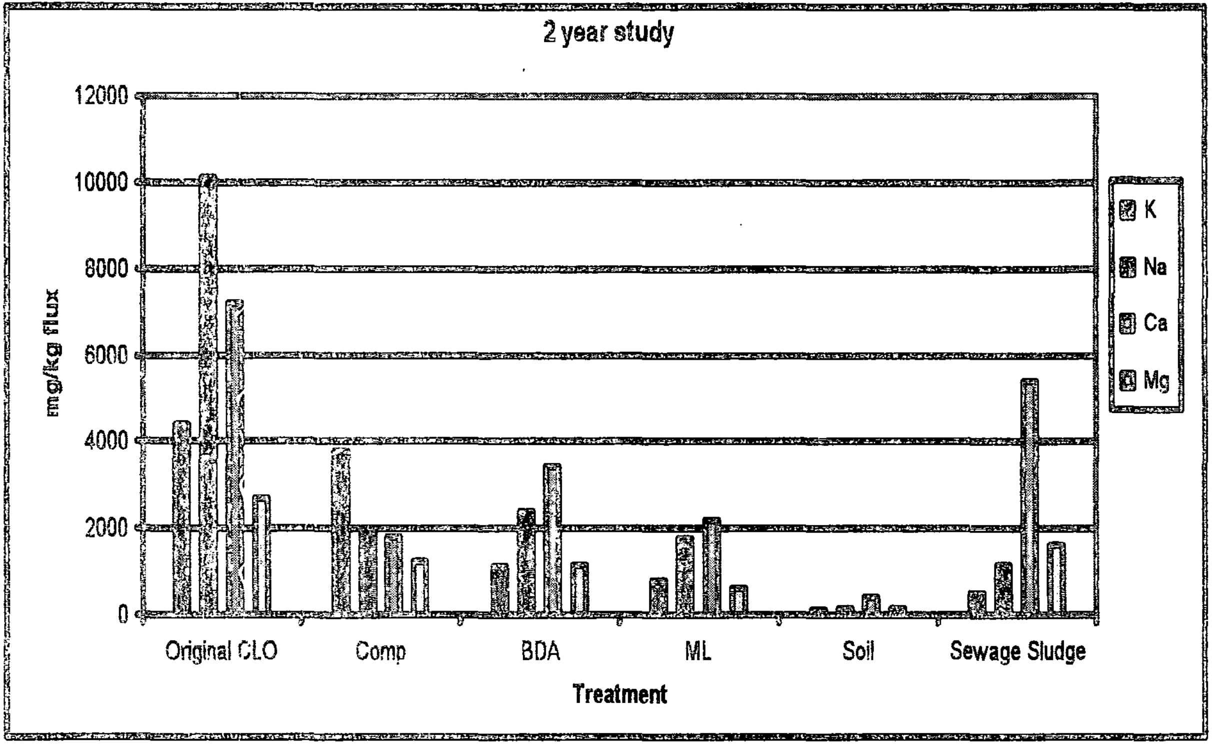


Figure 2.10: Treatment total leachate base-cation fluxes (mg/kg) for a) 1 year of study and b) 2 years of study.

In summary, regarding total leached amounts of base cations and not legislative impeachment, the CLO 2006 and Parcgro products performed well in comparison with their older, CLO 2004 and mixed counterparts. However, the intermediate CLO 2005 highlights some cause for concern. Agricultural soil was by far the most environmentally sound and stable material of the nine examined, followed by Parcgro and, surprisingly, the undiluted CLO 2006. The sewage sludge treatment, although achieving improved K and Na leached levels, did exhibit significantly lower water qualities for Ca and Mg. The three original mixed treatments were inferior to the current Parcgro soil, and thus amending the current CLO with a mixture of green compost, screened soils and sub-soils appears to be of greater benefit to the environment, than amendment with magnesium limestone, brick dust aggregates or just green compost.

2.8.6.4 'Trace Metals'

All metal leachate concentration time series are tabulated in Appendix 1, but mean graphs have been included below for elements highlighted in drinking and surface water directives. Some graphs have been plotted using a logarithmic scale for easier interpretation, and where a secondary *y* axis is used; it is the **bold** treatment in the legend box to which this axis refers. Statistical analyses were performed on all 'trace metals' and again the results are tabulated in Table 2.6 in Appendix 1 on the attached data cd.

Nickel (Ni)

The irregular nature in which Ni was released into solution (Figure 2.11) must be noted as being particularly important when comparing mean graph leachate values with legislative and landfill constraints, as well as in performing statistical analyses on the raw data. Regarding landfill discharge consents (550µg/l), passive remediation of Ni concentrations cannot be implied until commencement of the second year, by which time all three mixed treatments exhibited accepted values. The original undiluted CLO treatment leachates demonstrated a similar behaviour. However, the only treatments certain to achieve EC Drinking water accepted levels were the agricultural soil, which was in permanent agreement, and the Comp trial from 2005 onwards. Concentrations of Ni found in sewage sludge leachates breached drinking water directive limits on a comparable scale to that described above for the Comp treatment, but maximum levels never reach those leached from landfill. Relative to undiluted CLO 2005 and 2006 treatment leachates, Parcgro artificial soil was always in beneficial agreement with maximum landfill consents and, by the end of the 1 year study, was in compliance with drinking water limits (more data however, would be required to statistically prove this). CLO 2005 and 2006 treatment leachates showed very high levels of dissolved Ni – giving maximum values of 9886µg/l and 3575 µg/l, respectively.

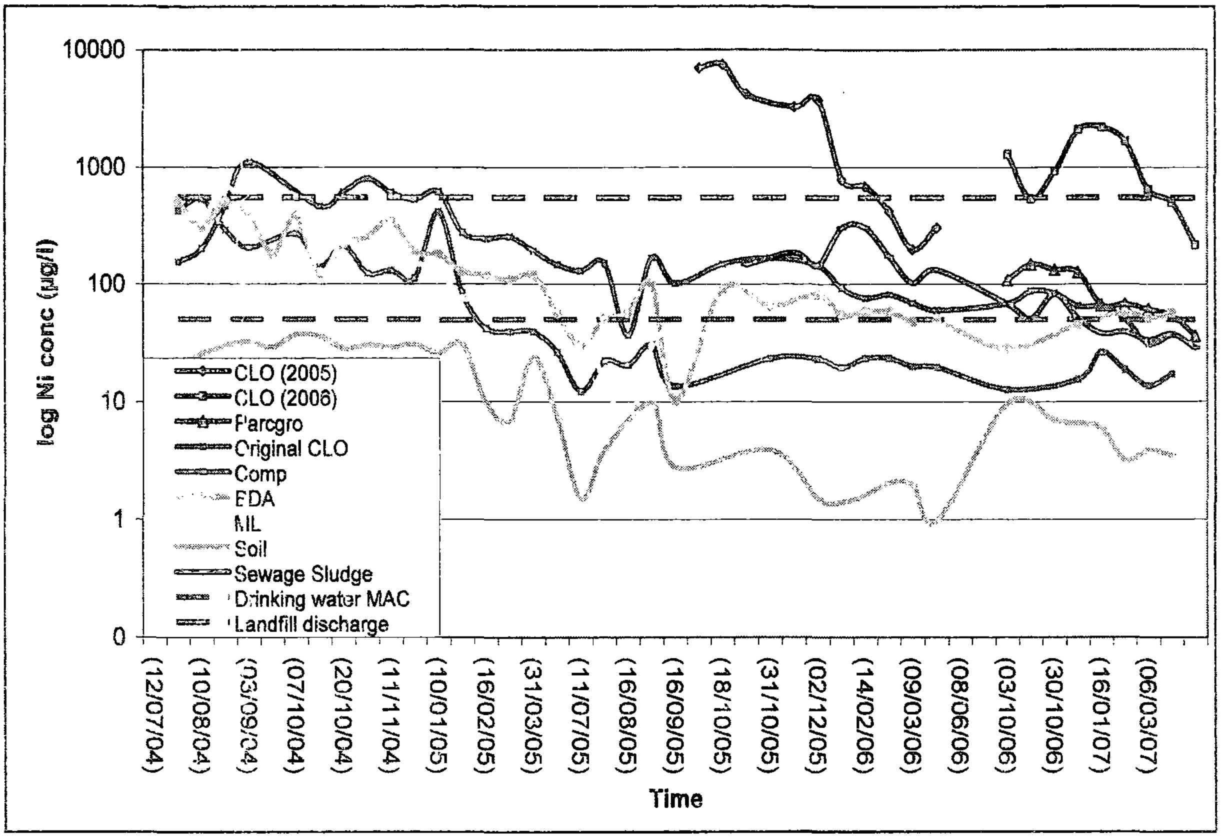


Figure 2.11: Treatment dissolution curves over time for Ni (µg/l). The *y* axis is plotted on a logarithmic scale.

Recorded levels of Ni would pose a serious threat to the environment if leachates were not contained; the extremely high levels of Ni that were flushed during the first year of study for all treatments (except the agricultural soil control) deemed succeeding passive remediation ineffective. The lack of active remediation for Ni could be explained by its dominance in the soluble phase, and its inability to readily form insoluble carbonate, hydroxide, phosphate and sulphide complexes that would remove it from solution (Smith *et al.*, 1976). The hydroxyl-complex $Ni(OH)^+$ and Ni^{2+} free ions are most likely to dominate in solutions above pH 8 (Alloway, 1990). $NiCO_3$ and $NiHCO_3^+$ may also occur (Sposito and Page, 1984), particularly in the mixed treatments, ML and BDA.

Zinc (Zn)

The EC Surface and Drinking Water Directives place the MAC for Zn at 5000µg/l; notably maximum landfill consents are already below this level at 1500µg/l. This level of contamination (Figure 2.12) was not exceeded by all of the 3 year treatments for the entirety of the experiment. Therefore, no passive remediation was required and no active remediation was found; in fact, all 3 year treatments displayed similar leached concentrations throughout. The group 2 treatments, however, all breached the drinking water constraint, but CLO 2006 and sewage sludge were the main offenders, giving maximum values more than 10-fold the legal limit (66425µg/l and 55885µg/l, respectively). CLO 2005 had a lower peak average, with values around 3000µg/l and, atypically, Parcgro leachates peaked high at around 10,000µg/l. Nevertheless, all four treatments breach drinking water constraints and, equally importantly it was evident from these temporal analyses that something serious relative to the availability of leached zinc, had occurred.

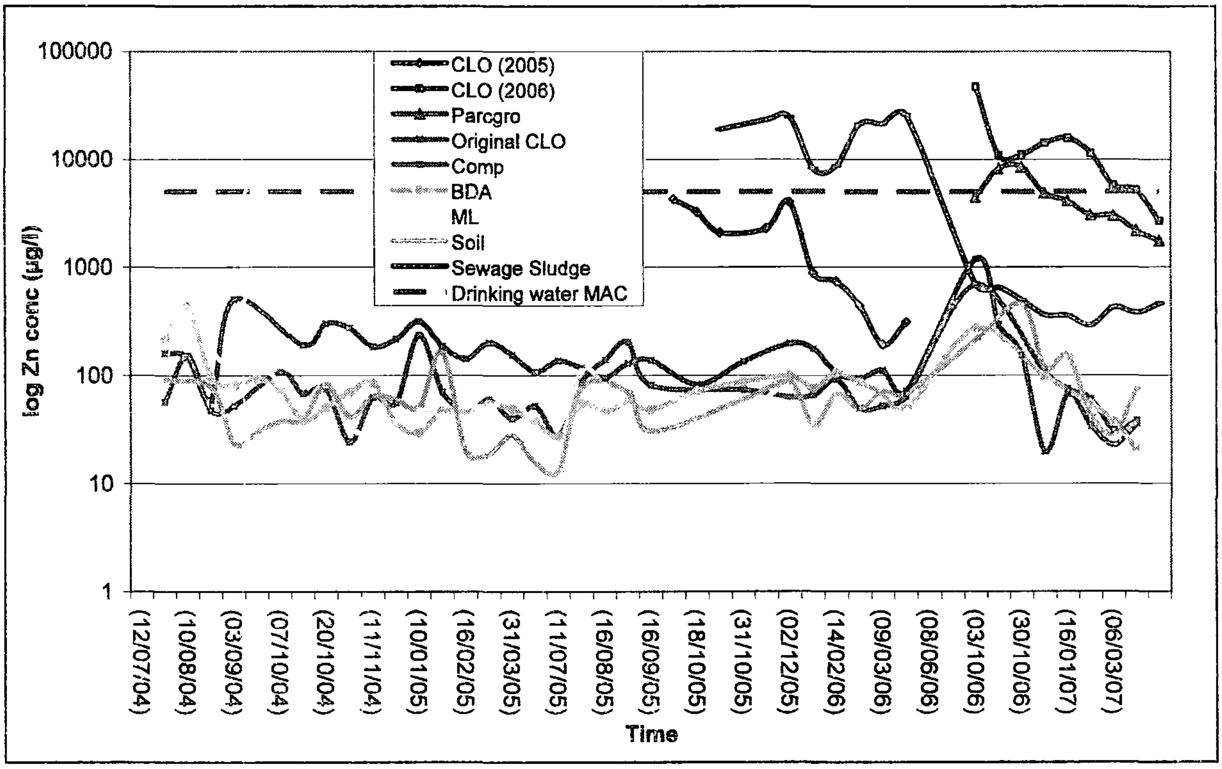


Figure 2.42: Treatment dissolution curves over time for Zn (µg/l). The *y* axis is plotted on a logarithmic scale.

Copper (Cu)

Regarding EC drinking water guidance levels (100/3000µg/l – no MAC is given), all treatments, including CLO 2005 and 2006 leachates, were well below the upper guidance boundary and the 3 year treatments were mainly in accordance with the lower. It can be seen (Figure 2.13) that all group 1 treatments (except BDA on its initial leachate), and the Parcgro and sewage sludge treatments, were significant improvements on maximum levels leached from the Coxhoe landfill site, the level(s) at which MSW waste would reside if it were not aerobically digested into CLO. Leachates from the mixed BDA treatment exceed levels from the original CLO, with which it was mixed, and so it was assumed that the BDA either contained elevated Cu concentrations relative to CLO 2004, or has exacerbated its release. It was evident that, although CLO 2005 and 2006 treatments meet government guidance levels, the release behaviour of Cu into solution was inconsistent, and average leached concentrations were around 8-fold higher than the of original CLO. Additionally, it can be seen that Cu leaching follows a flushing pattern analogous to that seen for the base cation, Ca, in that once the initial contaminant release into solution has taken place, a steady rise in overall leached levels occurs. The sewage sludge treatment also demonstrated this behaviour. It is clear that, of the three amended treatments, BDA had continuously increased leached Cu concentrations relative to pure CLO, and the Comp and ML have offered no Cu amelioration with time.

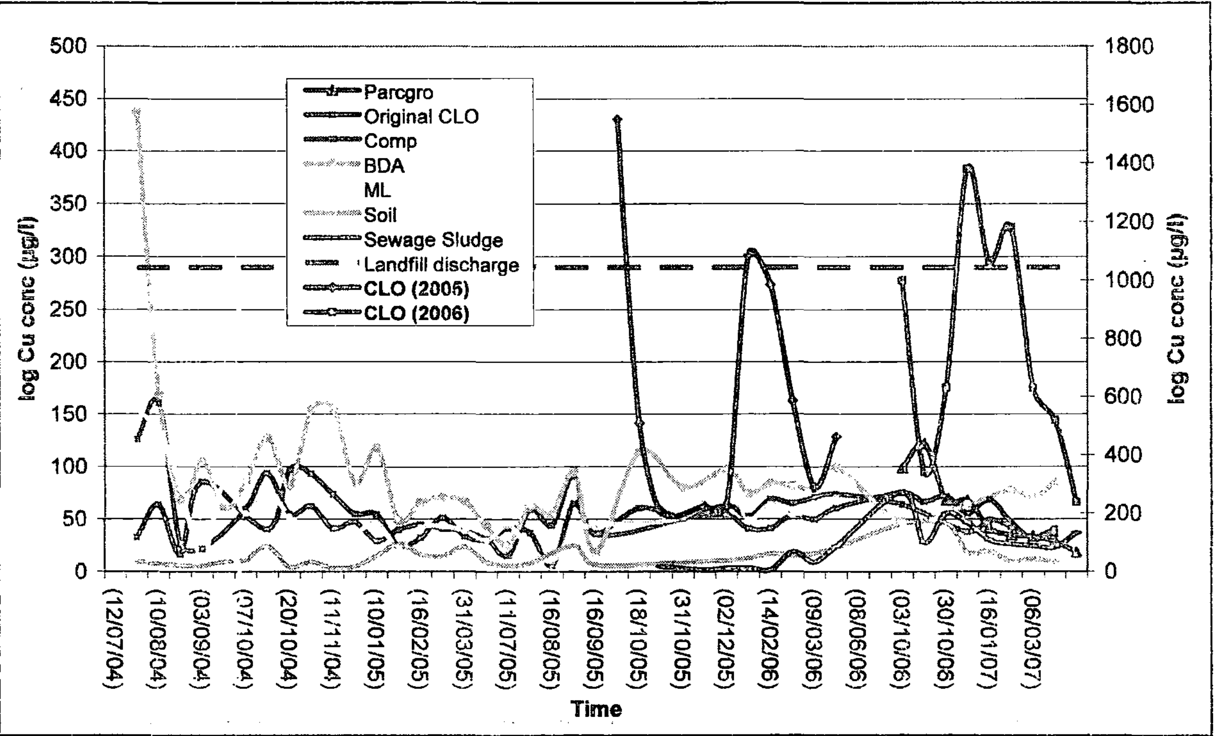


Figure 5.13: Treatment dissolution curves over time for Cu (µg/l). *y* axes are plotted on logarithmic scales and the secondary *y* axis refers to the CLO 2005 and CLO 2006 treatments.

Cadmium (Cd)

Measured Cd levels were close to detection limits (~ 2μg/l). Thus, the irregular pattern exhibited by all treatments (except CLO 2005 which surpassed 1000 μg/l), was most probably a consequence of this, as were the actual recorded concentrations themselves (Figure 2.14). Regardless of this, the extremely low concentrations detected indicate that Cd levels for all treatments, apart from CLO 2005, were certain to be lower than those recorded in leachates from the landfill site (maximum value of 6520μg/l ± 2910μg/l). However, it must be noted that, as with much of the data acquired for the Coxhoe landfill site, a relatively large standard deviation of the mean was evident (44.6% for the batch of samples from which this maximum figure was attained). If all sample batches were included, the standard deviation dropped to 16.9% due to increased sample number (30). This behaviour further exemplifies the persistent heterogeneity between both batches of CLO and raw, untreated, landfilled MSW. Relative to drinking and surface water directive MACs of 5μg/l, most treatments, even with the associated uncertain, performed well apart from the undiluted CLO treatments.

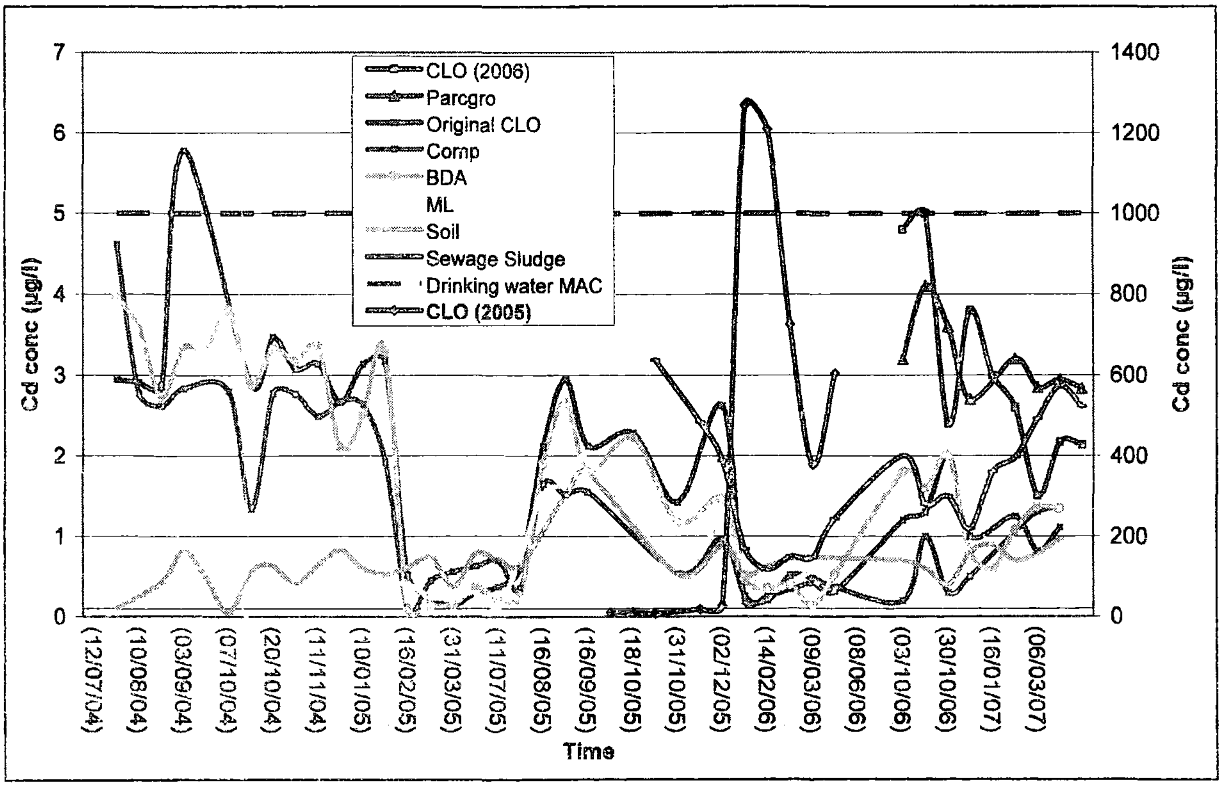


Figure 2.14: Treatment dissolution curves over time for Cd (μg/l). The secondary *y* axis refers to the CLO 2005 treatment.

Studies by Sposito et al (1984) and Alloway (1990) showed that in oxic solutions from alkaline soils, Cd^{2+} was predominantly the free ion. However, neutral species, such as $CdSO_4$ and $CdCl_2$, have been shown to increase where pH levels were above 6.5. As can be seen later, in leachates from treatments containing CLO, the dominant anions available for complexation with metal species were Cl^- and SO_4^{2-}. It is therefore likely that the free ion, as well as the neutral forms of Cd speciation, contributed to the total.

Lead (Pb)

Good remediation, with regard to original CLO, landfill concentrations (290µg/l), and the EC MAC (50µg/l) were evidenced for all three mixed treatments for the entirety of the study, and the Parcgro and sewage sludge treatment leachates were found to have similar concentrations (Figure 2.15). Although mixing CLO with the remediation materials appeared to have benefited leached concentrations of Pb, the undiluted CLO 2005 and 2006 treatments, as well as the original CLO produced maximum flush values of 878.9µg/l, 351.0µg/l and 438.2µg/l, respectively. All three considerably exceeded drinking water targets and would further contaminate landfill discharge levels. Under the current dilution ratio of 1 part CLO to 3 parts remediation material, no measured concentration of Pb was attained that, under current government law, would threaten either the environment or human health. Undiluted CLO would, however, introduce high levels of Pb into an environmental setting.

It was apparent that, during the initial dissolution of Pb, a substantial degree of remediation could be attributed to the materials used. Undiluted original CLO exhibited maximum concentrations at least 18-fold higher than the three diluted treatments (Comp, BDA and ML). Bearing in mind that each of the mixed treatments comprised only ¼ soil conditioner, initial remediation, using maximum values, appeared not only to be active but also exceeding levels of 97%. Moreover, statistical analysis revealed that although a large ($P<0.0001$) difference existed between pure CLO and the other treatments, this amelioration could not be accredited to an active process, because of the heterogeneity of CLO and its associated soils. This supports evidence that the irregular physical and chemical nature of the materials can act as the major controlling factor, above treatment type and time, for certain elements.

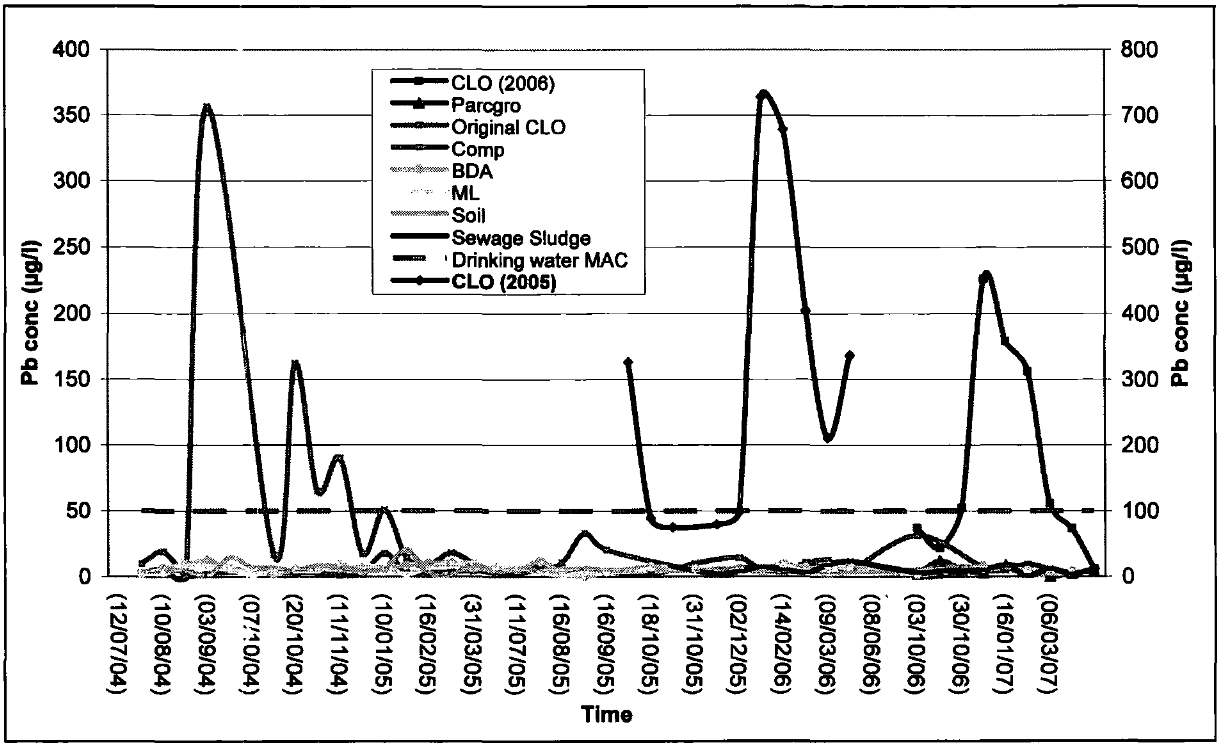


Figure 2.15: Treatment dissolution curves over time for Pb (µg/l). The secondary *y* axis refers to the CLO 2005 treatment.

Cobalt (Co)

As no data exist for landfill or water directive constraints, no direct assessment of passive remediation can be undertaken for Co. Moreover, no significant remediation relative to pure CLO existed, with ML and BDA, and to a lesser extent Comp treatments, introducing elevated irregular levels of Co into initial leachates. Meanwhile, sewage sludge appeared at the upper end of the scale, with values comparable to those found in initial flushes from the ML and BDA treatments.

Relatively unstable ferromagnesian minerals found in abundance in naturally occurring basic and ultrabasic igneous rocks contain appreciable amounts of Co. These rocks, used in the construction industry, could explain why mixing CLO with brick dust aggregate increased the occurrence of this element. The lack of any remediation may be due to the fact that, under alkaline conditions in particular, oxide, hydroxide and carbonate forms of Co are highly insoluble and would be immobilised.

Aluminium (Al)

A logarithmic scale has been used to graphically highlight the split data ranges recorded between treatment leachates (Figure 2.16): the decreasing concentration gradient was (CLO 2005 and 2006) > (Original CLO, Comp, BDA, ML and sewage sludge) > (Parcgro and agricultural soil). All treatments in the middle group breached drinking water constraints at some point during the study – with the original CLO more than the others in both concentration and time. Although for most part the three amended treatments had concentrations below those required by drinking water legislation, the limit was still infringed, either during the initial wash-out period (as with ML and BDA) or sometime later (as with Comp). The CLO treatments (2005 and 2006) illustrate that if this material was left undiluted, contaminant levels can climb as high as 46,583µg/l and 16,460µg/l, respectively, which in the former case, is more than 3-fold the EC water directive value. Only on one occasion did the agricultural soil breach this limit producing leachate with an Al concentration of 1681µg/l.

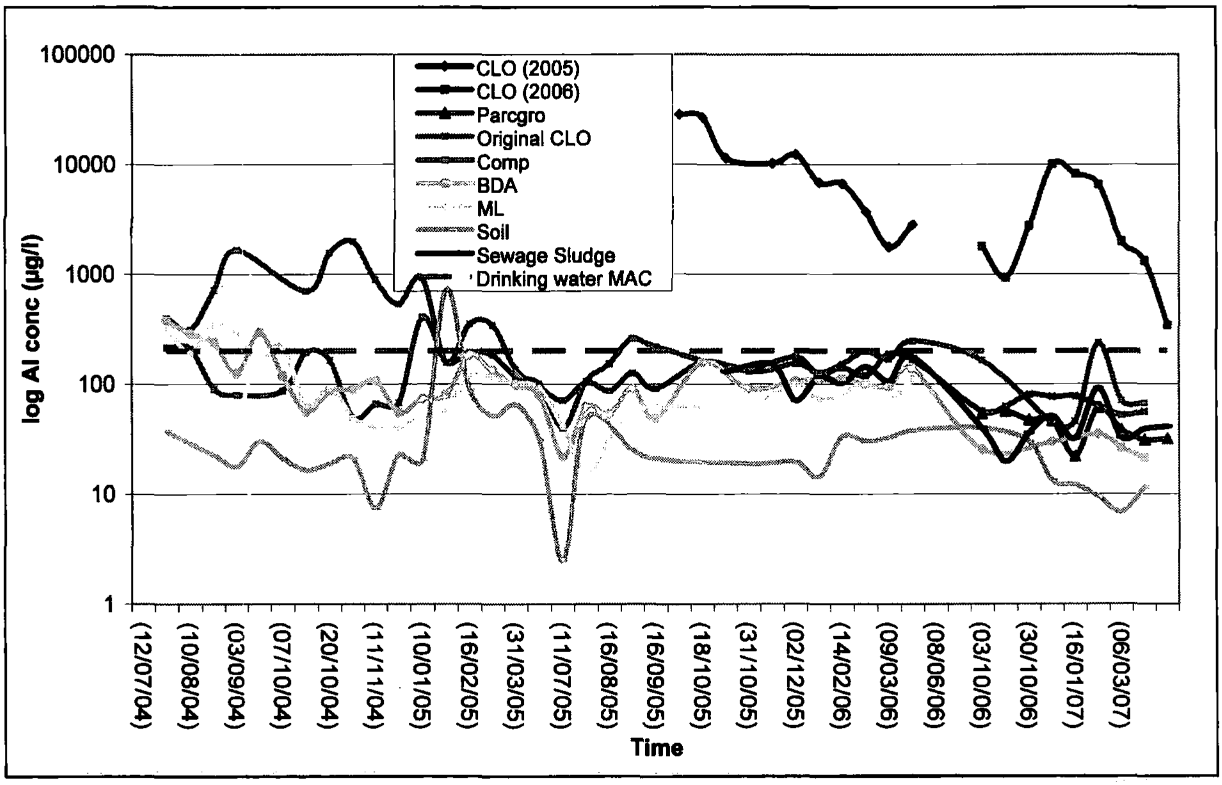


Figure 2.16: Treatment dissolution curves over time for Al (µg/l). The *y* axis is on a logarithmic scale.

Statistically, there were significant differences ($P<0.0001$) between pure CLO leachates and the mixed treatments as represented by the Al leachate concentration time series. However, no statistically significant active remediation existed with time or treatment type, so any differences can only be attributed to passive dilution. It must also be noted that, on one occasion, the agricultural soil control attained a concentration nearly 4-fold that of the legislative limit – a value higher than that attained by any of the mixed treatments.

Iron (Fe)

Sewage sludge, currently accepted as an agricultural fertiliser, gave maximum values of 3000µg/l, which was 15-fold greater than the EC MAC (200µg/l). Similarly, the three mixed treatments – Comp, BDA and ML – gave the following maximum Fe leachate concentrations: 1234µg/l, 1896µg/l and 6485µg/l, respectively. The undiluted original CLO exhibited a maximum concentration over 40mg/l and its counterparts, CLO 2005 and 2006, gave concentrations over 10 and 8-fold that value (450mg/l) and (350mg/l) respectively (more than 2000-fold the legislative limit permitted in drinking and surface waters). Parcgro and agricultural soils were the only treatments not in breach of water regulations. Nevertheless, with regard to leachate from the Coxhoe landfill, where maximum concentrations reach nearly 100 mg/l, pure original CLO offered a 60% reduction in concentration for Fe in solution. This reduction was increased by the amended treatments with Comp giving a 98.8%, BDA a 98.1% and ML a 93.5% lowering in Fe concentration. This suggests a significant improvement has been made relative to landfilling raw MSW, but dilution of original CLO would have to be greater for no or limited detriment to the environment if the materials were to be used in agriculture. That said, Parcgro artificial soil performed well regarding leached Fe content. Considering its parent CLO portion (⅓) was sourced from the 2006 CLO period of production, it is fair to assume that some active remediation, on behalf of the green compost and sub-soils used to make up the remaining two thirds, had occurred. Statistical analyses will be discussed below. Average treatment dissolution curves over time for Fe can be seen in Figure 2.17 below.

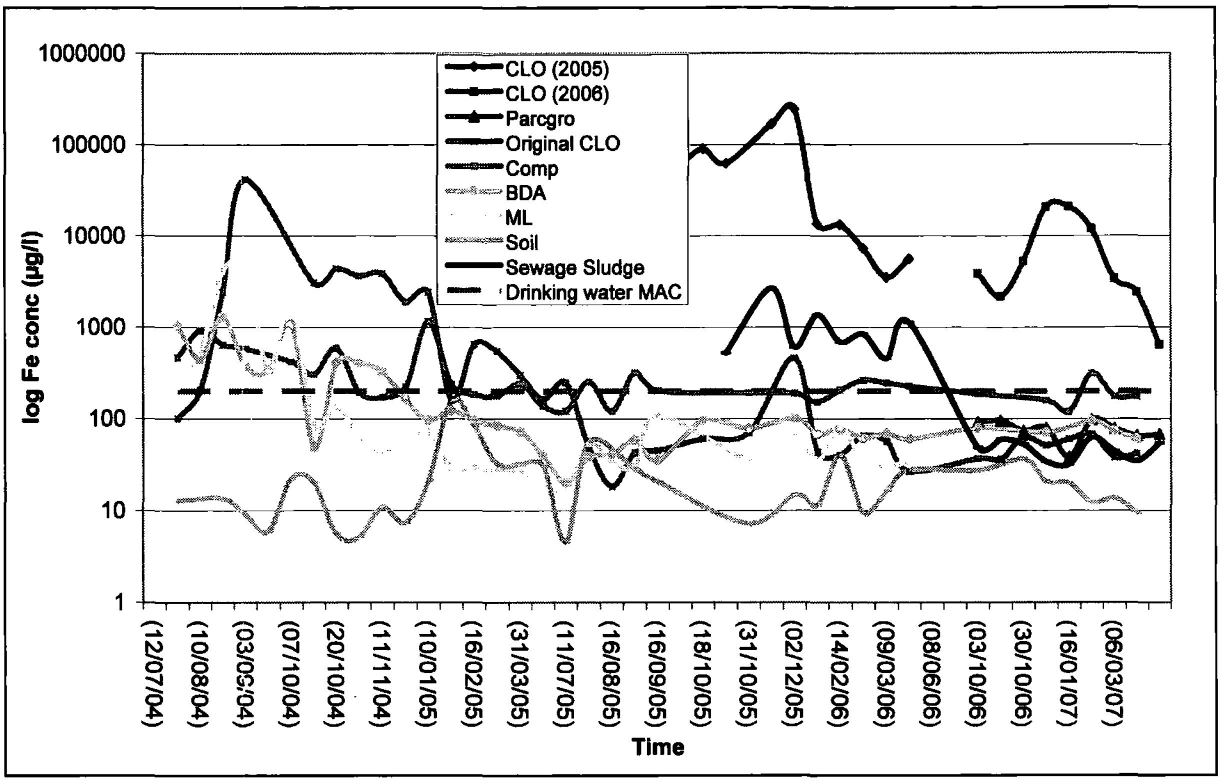


Figure 2.17: Treatment dissolution curves over time for Fe (µg/l). The *y* axis is on a logarithmic scale.

Manganese (Mn)

All treatments, including the soil control, exceeded EC legislation values for surface and drinking waters throughout the whole experiment, and not just during the initial flush as was the case with most other metals (Figure 2.18). For the group 1 treatments, the release of Mn into solution occurred in irregular peaks for the entirety of the study with no apparent relationship with time or treatment (although a slight distancing of the mixed treatments from their parent CLO 2004 occured in the second and third years of study). Relatively, group 2 treatments performed worse, particularly the CLO 2005 and sewage sludge treatments, with maximum concentrations of 29,334µg/l and 2857µg/l, respectively. No remediation, passive or active, was achieved by mixing the CLO with the various materials for either group 1 or group 2 treatments. Nonetheless, it was only the leachates from the CLO 2005 and sewage sludge treatments that exceeded maximum values approved by Coxhoe landfill discharge consents (2580µg/l).

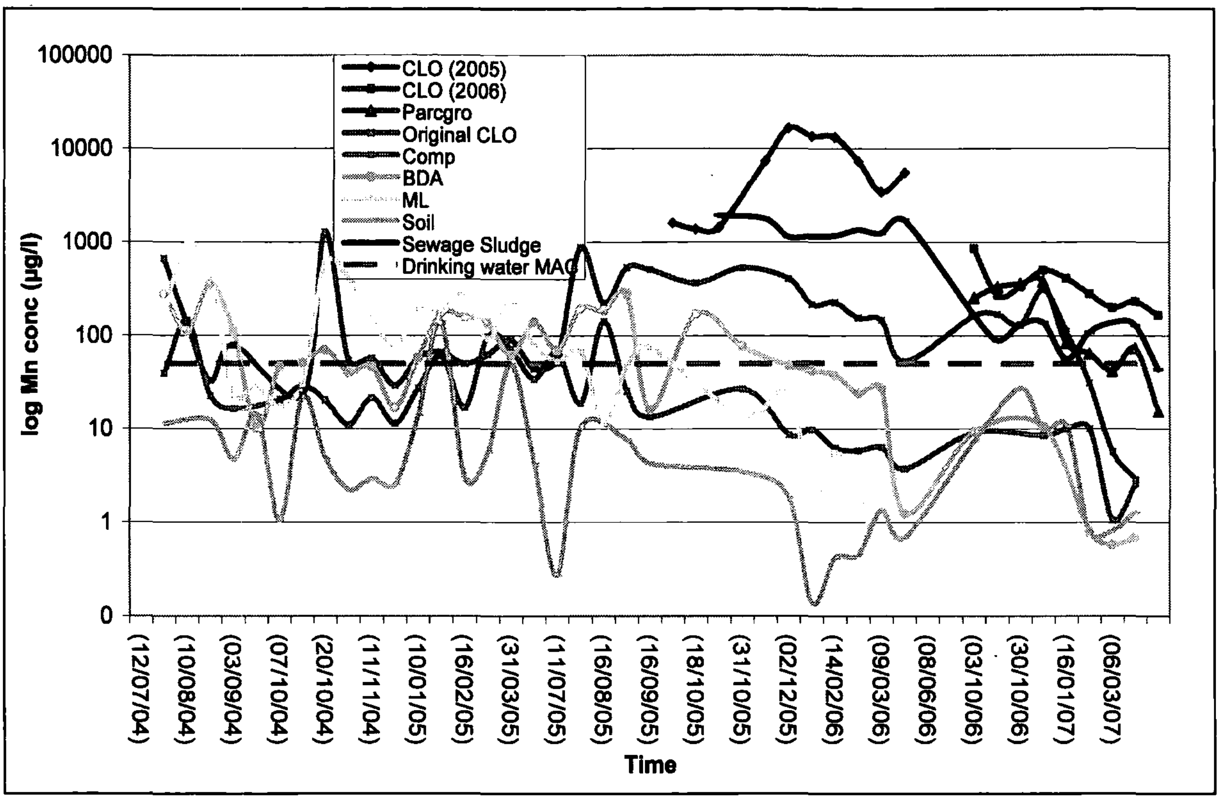


Figure 2.18: Treatment dissolution curves over time for Fe (µg/l). The *y* axis is on a logarithmic scale.

Chromium (Cr)

As there are no limits set by the drinking and surface water directives, comparison of collated data can only be undertaken between treatments and against landfill discharge consents. All group 1 treatments, as well as the sewage sludge and Parcgro treatments, fell well below landfill discharge values (410 µg/l), and so sufficient passive remediation had been achieved from aerobically digesting the MSW, and this was furthered by mixing the resultant CLO with green compost, BDA, ML and sub-soils. However, with newer forms of the undiluted CLO, landfill levels were exceeded, with the 2005 material producing leachates with maximum Cr concentrations of 1302µg/l and the 2006, 623µg/l. A dissolution curve over time has not been included for Cr.

The chemical behaviour of Cr in soil is complex and so a similar situation is likely to present itself in CLO-associated soils due to the complex nature and assortment of inherent elements. The chemical properties and conditions of primary importance concerning Cr leachability are pH levels, the presence of soil organic matter, and the interchangeable aerobic and anaerobic conditions. Kim et al (2005) and Gupta et al (2005) in their studies into MSWI residues and ash leachates discovered that the Cr (VI) ion was released into solution far more readily under aerobic conditions, due to its oxidation related instability. Under anaerobic conditions, the reduced Cr (III) and more stable form is more likely. Similar total Cr concentrations to those described above were also found for the CLO 2005 and 2006 treatments (0.01-0.1mg/l). Therefore, although drinking water legislation is absent, the bioavailability of this soluble metal-organic matter complex, as well as the consequent increased mobility of the metal should be given careful attention under alkaline and aerobic conditions (such as those in this study).

2.8.6.5 Non-metals

Phosphorus (P)

Measured levels of total phosphorus, or organic P, which under alkaline conditions are mostly likely to occur as HPO_4^-, were below the limits set by the drinking water directive (5000 µg/l) for all three amended treatments. In contrast, maximum values attained by the undiluted CLO (CLO 2005 - 29000µg/l, CLO 2006 - 6975µg/l and original CLO - 7347µg/l) and sewage sludge treatments (7000µg/l) reached concentrations well in excess of this, the first of which surpassing water regulations by nearly 6-fold. Successful passive remediation with respect to the original CLO was therefore achieved and, for the most part, P levels in BDA and ML treatment leachates lie below those of the agricultural soil. The Parcgro mixture had also succeeded in the passive amelioration of leachate P concentrations relative to CLO 2006. Data was not available for Coxhoe landfill discharge consents.

2.8.6.6 Trace metal and non-metal statistical analyses

2.8.6.6.1 Group 1

Statistical significance

The main characteristics governing statistical significance between treatments were the high elemental flushes from the CLO and sewage sludge treatments, and the low concentrations found in leachates emanating from the agricultural soil control. Trace metal concentrations in leachates collected from the CLO treatment that significantly ($P<0.001$) exceed those found for the rest of the treatments, included: Pb, Al, Fe, Ti, Cr and V. Those dominant in the sewage sludge treatment were: Mn, Co, P, Zn and Cd ($P<0.05$). Thus, the majority of relative heavy metal contamination, if all treatments were used in the field, would come from these two materials. Considering the toxicity, associated government restraints, and the number and level to which these restraints were exceeded suggests that these two materials represent a similar environmental hazard. A final point concerning the mixed BDA treatment is that this material released significantly ($P<0.001$) higher levels of Co, Li and Ti. These elevated trace metal concentrations were not seen for the other remediation treatments and so, in this context, as well as its limited and often detrimental active remediation characteristics (seen below), the BDA trial was considered an unsuccessful amendment to CLO. However, it must be noted that, Si, Co, Ti, Li and Sc, for which BDA was significant in elevating leached levels, were not included in drinking and surface water regulations. Post hoc statistical results for all treatments can be seen in Table 2.6 in Appendix 1 on the attached data cd.

2.8.6.6.1.1 Active remediation

After weight adjustment, the only metal ions for which there were no significant differences between treatments were Pb, Fe and V, so it must be assumed that variations within treatment were greater than any found between treatments. For the remaining elements, as with the base cations, no beneficial statistically significant active remediation had been achieved over the three years of study. Comparative elemental performances revealed that there was much variation between the three remediation treatments. As mentioned previously, BDA performs poorly with respect to Ni ($P<0.05$), Cu, Co, Li (all $P<0.0001$) and Ti ($P<0.05$) being significant to the other mixed treatments in all cases. The Comp treatment, relative to leached trace metals, was the next worse material with which to amend the CLO. P concentrations were significantly higher ($P<0.0001$) in Comp leachates than all other treatments; in addition, the Comp leached trace metal levels greater than those seen for the undiluted CLO. These included: Al and Ti ($P<0.05$), Cd ($P<0.0001$) and Sc ($P<0.001$). Of these, Cd and Sc levels were also higher than those recorded in ML leachates. Finally, the ML treatment was significantly detrimental regarding leached Ni, Mn ($P<0.0001$) and Cr ($P<0.01$) concentrations. This last mixed treatment although performing worse than undiluted CLO for the three elements mentioned, produces leachates which were significantly less contaminated than the other remediation treatments. Thus, it can be stated that for the 3 year study the order of decreasing leachate performance was:

Soil > ML > Comp > BDA > SS > CLO.

2.8.6.6.2 Group 2

Statistical significance

A similar pattern to that described for the base cations was exhibited for the leached concentrations of trace metals and P. The CLO 2005 treatment dominates every elemental significance test, demonstrating the contaminated nature of material that can be produced by aerobic digestion of MSW. Occasionally CLO 2006 was also statistically significant with reference to sewage sludge, Parcgro, or both, but was always of higher concentration. For example, leached Ni and Al concentrations were significantly higher ($P<0.05$) in CLO 2006 than sewage sludge samples, Zn was significantly higher ($P<0.05$) than in the Parcgro treatment and Cr higher ($P<0.05$) than in both the sewage sludge and Parcgro treatments. The decreasing order of performance was:

CLO 2005 > CLO 2006 > SS = Parcgro

In light of this, further statistical analysis was conducted to compare leachate performances of the sewage sludge treatment against those from the Parcgro treatment. The test revealed that the sewage sludge treatment leachates were higher in concentration for 7 elements, and Parcgro leachates significantly higher in 8 elements

(Table 2.7, below). However, highlighted elements (those elements for which there are government constraints) totalled 5 and 3 for the sewage sludge and Parcgro treatments, respectively. Thus, from a purely legislative perspective, Parcgro performs slightly better (Zn levels found in sewage sludge leachates were considerably higher than those found in any other treatment but are not statistically significant owing to heterogeneity between samples). In practice, a number of other factors, such as total leachable quantities, individual elemental toxicities, adsorption availabilities (and mobility), and to what degree the legal limits are surpassed must be considered to assess the full environmental impact of each material. This will be discussed in greater depth later.

Parcgro treatment	**Sewage sludge treatment**
K (0.00001)	**Mn** (0.0016)
Na (0.00001)	**Ca** (0.00001)
Cu (0.0001)	**P** (0.0003)
Ti (0.0172)	**Al** (0.0064)
Sc (0.0115)	**Fe** (0.0083)
Cr (0.0471)	Si (0.00001)
Li (0.00001)	Co (0.0004)
V (0.0001)	

Table 2.6: Elements for which the treatments are statistically significantly (numbers shown) higher than the other treatment. Bold letters indicate Drinking/Surface water directive MAC or GL constraints are in place for that element.

2.8.6.6.2.1 Active remediation

A statistically significant ($P<0.0001$) active remediation can be attributed to the Parcgro treatment concerning the adsorption of Cu in the solid phase, therefore reducing leached concentrations. However, although this was the only significant active remediation observed for any treatment for the entire study, in the search for an ideal mixing agent for CLO, this finding is deemed of minor importance. Cu was also the only example where leached levels from CLO 2006 were higher than that seen in CLO 2005 material.

2.8.6.7 Overall statistical comparisons (Groups 1 and 2)

As expected from the findings described, when the CLO 2005 and 2006 treatments were incorporated into the whole model, there were statistical significances between them and the rest of the treatments. The CLO 2005 showed statistically higher leached concentrations for every one of the 20 elements analysed, relative to the rest of the treatments. Unfortunately, no other statistical significances were revealed that had not already been discussed above, such as significant beneficial differences between the Parcgro treatment and its predecessors (Comp, BDA and ML). The only significant findings involving the Parcgro leachates placed it higher than all 3 mixed treatments for Sc, in the same region as CLO 2006 and sewage sludge for Zn, and predictably of similar properties to the mixed Comp treatment with respect to leached K levels. However, the mixed treatments BDA (Li) and Comp (K), in particular, displayed high concentrations relative to the CLO 2005 and 2006 treatments but this could not be statistically proven. This was also true for sewage sludge leachates and their characteristic high levels of Si. This gives us a further insight into how some of the remediation materials have introduced certain elements at levels high enough to rival even the undiluted, contaminated CLO treatments.

2.8.6.8 Flux levels

Based on findings from the leaching behaviour of base cations, both between treatment and between years, were assessed for trace metals. Maximum flux concentrations were measured in μg/kg and logarithmic scales have sometimes been used for effective visualisation of the data.

2.8.6.8.1 1 year study

Immediately, for all elements, except Zn in the sewage sludge treatment, it could be seen that the CLO 2005 material produced leachates saturated with extremely high levels of toxic heavy metals (Figure 2.19). Maximum levels were normally in the range of 50-500mg/kg but, as for Fe, reach nearly 1000mg/kg. Again, relative to a typical agricultural soil for the Durham region where levels average around 0.01-

0.1mg/kg and for P peaked at 1mg/kg, the extent to which aerobically digested MSW could potentially be of detriment to the environment is clearly highlighted.

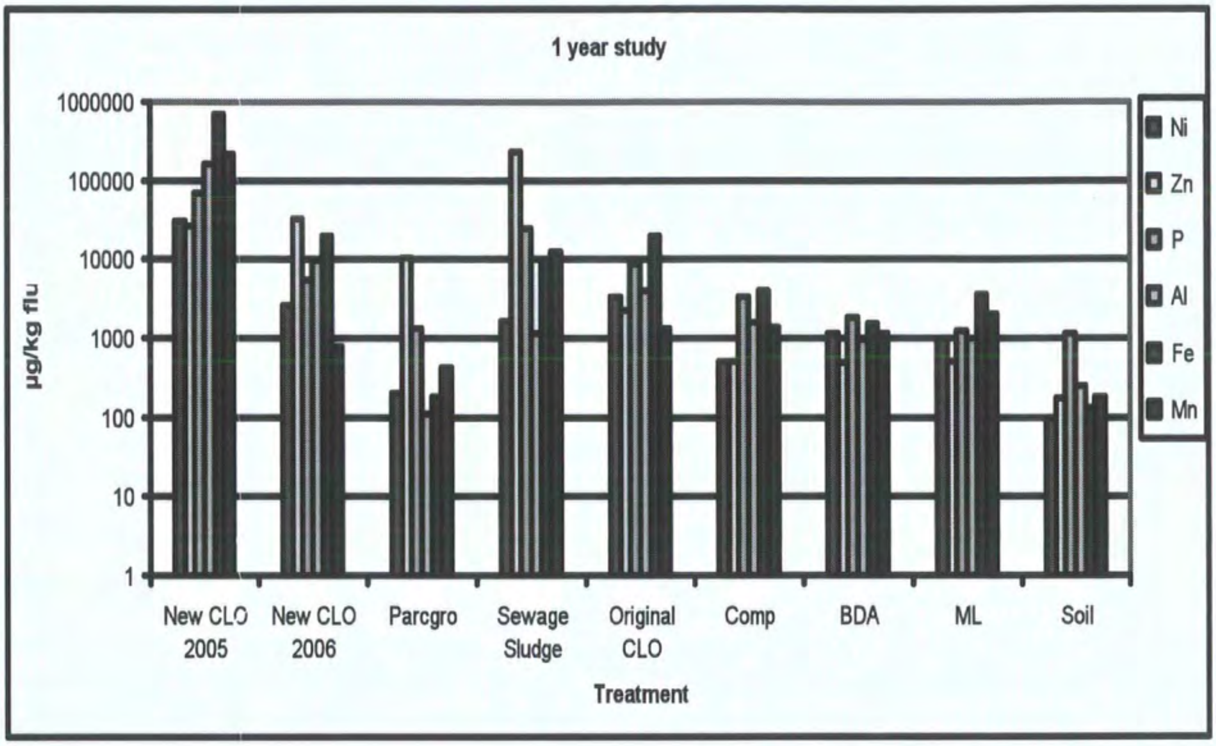
A closer look at Figure 2.19a, reveals that the sewage sludge treatment, in addition to leaching the highest levels of Zn for any treatment, performed on a similar scale to that of CLO 2004 and 2006 – Zn and Mn levels being an order of magnitude higher than levels seen in said CLO leachates. Conversely, levels of Cr, Cu and Pb (Figure 2.19b) were an order of magnitude less than those found in CLO leachates, displaying some form of remediation relative to undiluted CLO's. There was no overall significant difference between the three mixed trials (Comp, BDA and ML).

It must be finally noted that for all trace metal concentrations (in addition to base cation concentrations covered earlier), with the exception of Zn, levels similar to those leached from an agricultural soil were achieved, and in the case of Pb, Cr and Al have actually been improved by the Parcgro treatment. Furthermore, comparative to the rest of the treatments, Parcgro was the only treatment where Pb and Cr concentrations were substantially lower than Zn concentrations, and in the case of Pb, levels fell below those of Cd. However, owing to the small concentration differences between the two treatments, if a rainfall correction was included into the flux calculations for the first year results, Pb was alone in its relative bettering. This adjustment would also place the CLO 2006 treatment above that of CLO 2004, but would remain similar in performance to sewage sludge treatment. In order of increasing total flux trace metal leachate concentrations, the order of preferred treatment was:

Soil > Parcgro > BDA > ML > Comp > SS > original CLO > CLO 2006 > CLO 2005.

The reason for the lowering of the position of the BDA treatment (in comparison with the mg/l ordering) was due to a lower cumulative leachate concentration over time due to the relatively lower volumes of leachate available for this treatment.

a)



b)

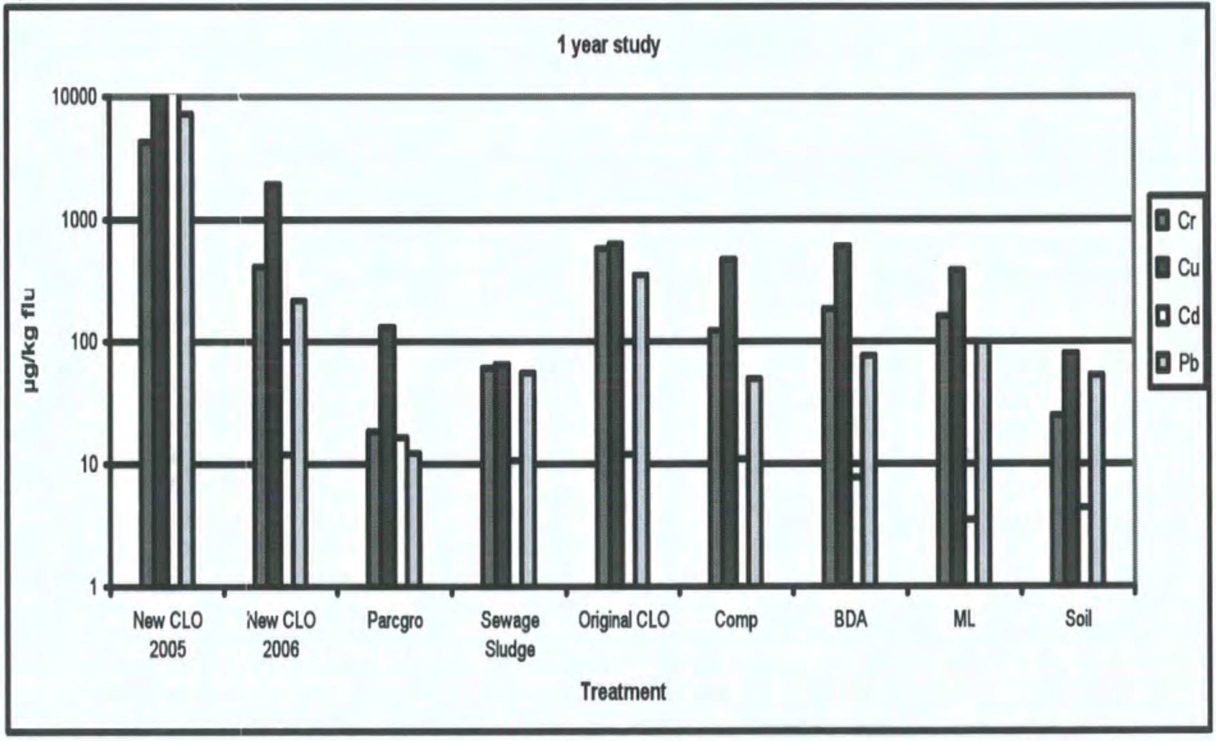


Figure 2.19: Treatment leachate total fluxes over one year of study for a) Ni, Zn, P, Al, Fe and Mn b) Cr, Cu, Cd and Pb.

2.8.6.8.2 2 year study

As with the base cation flushing patterns found for sewage sludge, it can be seen that concentrations for all elements were roughly double those seen for the first, supporting the sewage sludge stability theory respecting leached metal and non-metal ions (the implications of this have already been discussed). The CLO-containing materials again demonstrated a more varied flushing behaviour with the main differences being for the undiluted CLO 2004 treatment giving an early flush of Al in the first year, and the order of magnitude difference seen in the later release of Mn from the solid phase.

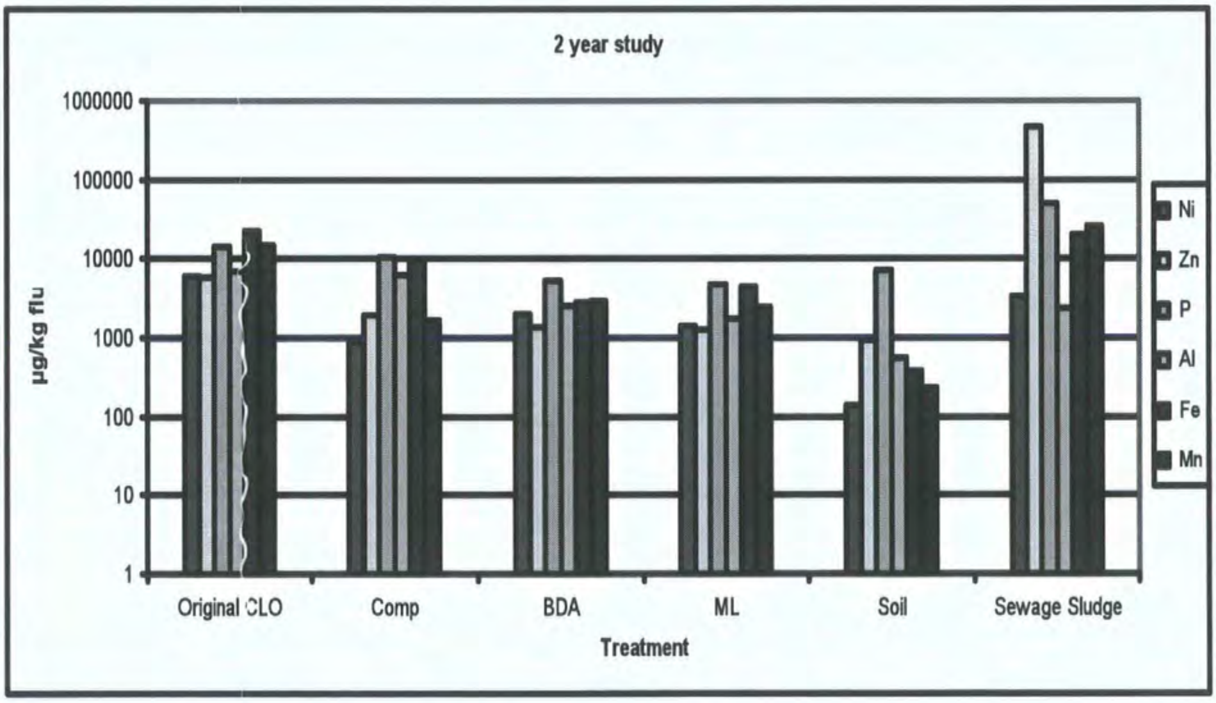
It can be seen from Figure 2.20 (a and b) that, of all treatments, sewage sludge leachates perform least favourably for Zn, P, Fe and Mn, but most favourably (except for the soil treatment) for Cr, Cu and Pb. Although sewage sludge may display a relatively stable approach to the release of elements over time, it does not perform any more creditably, and in a number of cases worse, than all CLO associated soils. Thus, for trace metals and P for the two year comparisons, the order of decreasing environmental favourability was:

Soil > ML > BDA ≥ Comp > original CLO ≥ SS

Again, the reason for the lowering of BDA's position in comparison with the order determined on the basis of leachate concentrations (mg/l) over time (see statistical section) was due to lower cumulative leachate volumes.

In summary, it was evident that there was a comprehensive difference between leachates exuded from CLO 2005 and that of the remaining treatments, in particular the agricultural soil control. The sewage sludge leachate performance although mostly consistent in its release of metal species over time, and therefore affording it some form of relative stability regarding CLO associated soils, exhibited varied behaviour between elements. A number of these trace metals, as well as Ca concentrations, were either comparable with or surpass those emanated from undiluted forms of CLO. With this knowledge, in conjunction with the heterogeneous nature of leachates exhibited by various CLO digestates, it was difficult to assign an accurate order of leachate performances relating to the nine treatments studied – specifically between the sewage sludge and CLO 2006 treatments, as well as between the three original remediation trials (Comp, BDA and ML). Once trace metal sequential extraction data and pre-washing data were obtained from chapters 3 and 4 respectively, a more precise evaluation of each material and its relative properties to various forms of leaching could be compiled. There have also been considerable favourable amendments made to the current CLO material (by mixing green compost and soils) with respect to leachable trace metal behaviour. The Parcgro artificial soil performed best, overall, of the CLO-containing treatments and, considering it comprises ⅓ CLO and the mixed 3 year treatments only ¼, it is evident that progress was being made toward maintaining and bettering the quality of aerobically digested MSW. If efforts can be concentrated on pre-sorting the waste, potentially removing contaminant laden waste streams before it is composted, rather than post-processing mixing in the hope that base metals and trace metals alike will be adsorbed and retained within the solid phase, the development of an agricultural (law-abiding) material may be possible.

a)



b)

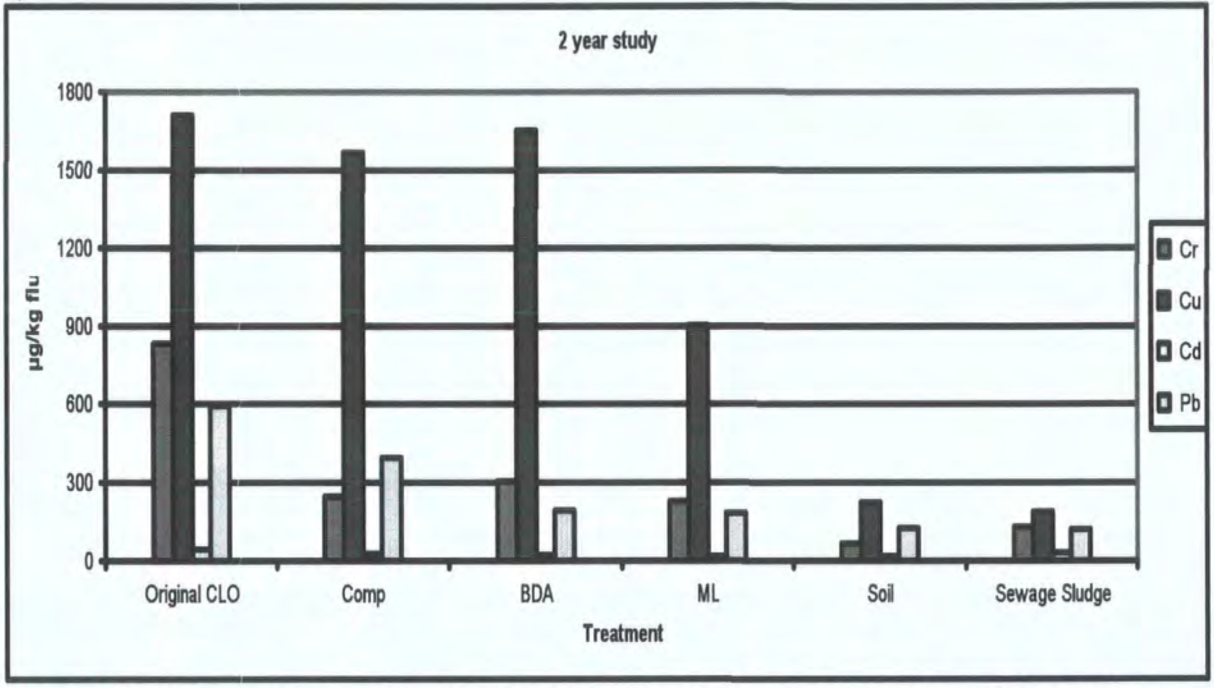


Figure 2.20: Illustrates treatment leachate total fluxes over two years of study for a) Ni, Zn, P, Al, Fe and Mn and b) Cr, Cu, Cd and Pb.

2.8.6.9 Anions

After reviewing anion incremental (mg/l) leachate concentration time series, two things became apparent. First, the release of anions into solution, particularly NO_3 and SO_4, occurred irregularly making it difficult to decipher trends either with time or between treatments. Typical Cl concentrations range between 8000mg/l in undiluted CLO materials, to below 10mg/l in all treatments. NO_3 and SO_4 peak flushes, although lower at 400mg/l and 1400mg/l displayed a high degree of variation with time and treatment type. Logarithmic scales did not produce any bettering of the data. Secondly and more importantly, from a contamination angle, all treatments, including the agricultural soil control intermittently breached EC surface and drinking water regulations (chloride – 25mg/l GL, NO_3 – 50mg/l MAC and SO_4 – 250mg/l MAC) throughout the trials. Coxhoe landfill discharge consents were only attainable for Cl (2,800mg/l) and SO_4 (67mg/l); the latter of which was already below the drinking water MAC. Leachate performances for all treatments were inferior to leachates found in landfill, with respect to exuded SO_4 concentrations, but Cl levels were found to be higher only for undiluted CLO treatments. These absolute comparisons underline the persistent problem of how, or if, remediation of anion contaminants to legislatively accepted levels is possible. Cl was the only counterion to illustrate any initial flushing trend with time (as described with conductivity readings).

It may be the case that, in terms of detecting a relationship between time, treatment and NO_3 and SO_4 flushing behaviour, similar pH related behaviour to that seen by Stegemann et al (1995) was the governing factor. Stegemann observed similar analytical irregularities, as well as an absence of prominent trends for leached SO_4 concentrations over time. He proposed that this behaviour could be a direct result of leachates being saturated with calcium sulphate salts. With increasing pH, the precipitation, and thus removal from solution of Ca ions was encouraged, which in turn would cause a shift in equilibrium supporting the dissolution of SO_4 into the leachate. As can be seen from Figure 2.21, the same is true for calcium sulphate. A similar pattern was also observed for calcium nitrate species. In this study, however, the pH rises and falls over time as do the relative concentrations of Ca and SO_4 found in solution. A decrease in pH coincides with an increase in Ca concentration in solution and the SO_4 level was depleted as it is precipitated. Only the original undiluted CLO treatment results have been plotted as this treatment displayed the strongest Ca and SO_4 trends.

These findings, together with the fact that only three of the six anion concentrations analysed (fluoride, bromide and phosphate concentrations were all negligible) lay within the detectable range provided by the Metrohm Compact IC (see method), meant that cumulative contaminant concentrations (mg/kg) as a function of time were the best way to graphically express the data. Figure 2.22 displays this information for Cl, NO_3 and SO_4. In an attempt to compensate for reduced amount of leachates available for collection for some treatments (due to the decreasing trend in annual rainfall), scatter plots were used where cumulative leachate volumes (ml) represented x axes and flux concentrations (mg/kg) y axes.

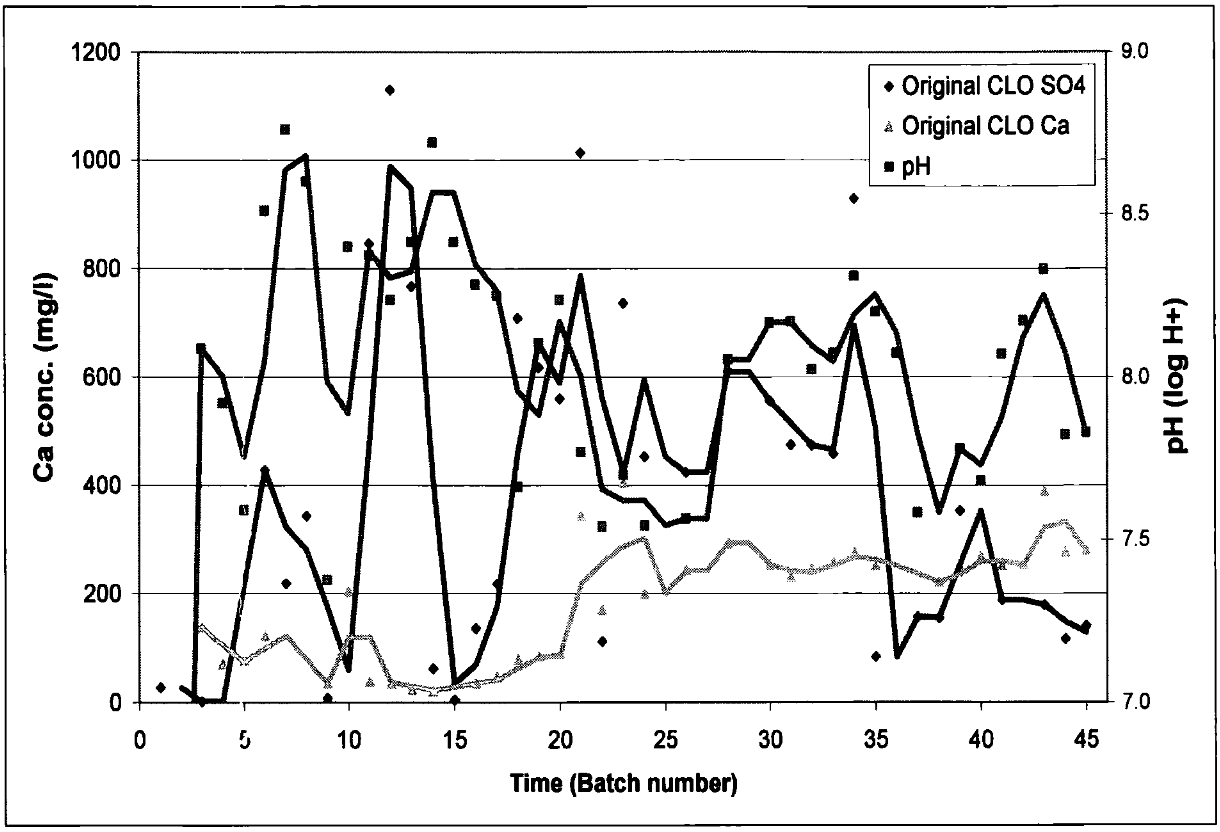


Figure 2.21: Relationship between pH and Ca and SO_4 dissolved concentrations in leachates exuded from the CLO 2004.

Chloride (Cl)

There was a clear distinction between undiluted CLO treatments, particularly CLO 2005 and original CLO, and the remainder of the treatments. The agricultural soil and sewage sludge treatment leachates perform well throughout, producing leachates relatively depleted in dissolved Cl ions. Typical concentrations ranged from 0-6mg/kg and 1-22mg/kg for soil and sewage sludge treatments, respectively. The three original mixed treatments (Comp, BDA and ML) all exuded leachates of similar quality with slight differences – in decreasing quality: Comp < ML < BDA with respective average concentration of 300 mg/kg, 380mg/kg and 480mg/kg. The next level of Cl leaching was illustrated by Parcgro and its associated parent material, CLO 2006. Here, concentrations rose to over 1000mg/kg for undiluted CLO and 850mg/kg for the Parcgro remediation product. These concentrations had been reached after only one year of field leaching; equivalent values reached by this stage for the mixed 3 year trials were: 260mg/kg, 360mg/kg and 350mg/kg for Comp, ML and BDA, respectively. This placed the Parcgro modern equivalent 2.5 to 3-fold worse, and the 2006 CLO 3 to 4-fold worse, than the original mixed CLO treatments (Comp, BDA and ML). This is also true for CLO 2005, which demonstrated the highest (per batch) and most rapid Cl flushes seen by any treatment. That stated, original CLO, though rather slower at reaching the peak Cl flush, exuded the greatest quantity of chloride species for equivalent amounts of leachate. Peak relative Cl fluxes for CLO 2005 and CLO 2004 were: 2500mg/kg and 3400mg/kg. The levels achieved by the original CLO were 10 and 13 times higher than those of its daughter mixed treatments (Comp, and ML and BDA) which were statistically significant to ($P<0.00001$). Thus, with respect to leachable Cl concentrations under field conditions, any amendments that may have been made to the CLO recycling procedure over the years have proved beneficial. However, the mixing regime appears to favour the original trials.

Nitrate (NO_3)

A completely different set of trends and flux values can be seen for the leaching of NO_3 species as a function of cumulative leachate volume relative to that seen above for Cl. Firstly, it appears that for most treatments the initial flush rates were much lower than those seen for SO_4, and thus the time at which steady state equilibrium was attained, if at all, is less obvious. Also, flux values were on average 10-fold lower than those seen for SO_4. Sewage sludge, the mixed treatments BDA and ML, and the soil control, although varying greatly in their total fluxes (193mg/kg, 114mg/kg and 34mg/kg, respectively) appeared to reach a steady state phase. The sewage sludge treatment attained this stage more rapidly with regard to volume of leachate flushed, as was the case seen for numerous trace metal leaching behaviours, but this initial higher flush of NO_3 was not always seen to be 'typical'.

The original CLO and compost trials were analogous in that they both displayed irregular flushes of NO_3 that do not always correlate to increased volumes of leachate, making it more difficult to determine whether steady state conditions had been attained. Furthermore, this irregular release of NO_3, also seen in the sewage sludge treatment on a smaller scale, was reason to suggest that these treatments were particularly unstable and environmentally unsound with regard to NO_3 dissolution.

The Parcgro treatment displays, by far, the highest immediate release rate of NO_3 and, second to original CLO, leached the most NO_3 per sampling event, but consistently unlike the other three high fluxing treatments (Comp, SS and original CLO). Total NO_3 flux for the one year of study was 354mg/kg which was almost equal to 394mg/kg seen for original CLO for three years of study.

A clear distinction lies between the lower BDA and ML treatment leachates and those of the Comp treatment. This was probably due to the high NO_3 levels contained within the green compost relative to the other two mixing agents. This would be analogous to the high levels recorded for leachates from the Parcgro treatment, but it was evident that further mixing of CLO/green compost with screened soils and sub-soils renders NO_3 even more susceptible to leaching. Finally, the low leachate concentrations recorded (<10mg/kg) for the CLOs (2005 and 2006) could be considered atypical behaviour; normally high component levels are observed. It must be noted, therefore, that these treatments' cumulative leachate volumes totalled at 8100ml and 8660ml. The equivalent flushing stage for original CLO was when the irregular behaviour described above first occurred, from which point significant increases in fluxes also were recorded. Elevated NO_3 measurements recorded in the last batch of leachate for CLO 2006 may suggest a similar trend may occur but further long term investigation would be needed to confirm that this would be the case for 2005 and 2006 undiluted forms of CLO.

Sulphate (SO_4)

SO_4 trends and recorded fluxes were similar to those for Cl, the main difference being that the undiluted CLO products and the Parcgro treatment leachates fell into the same general concentration bracket rather than being distinctly higher than the rest of the treatments. This observation does not apply for the original CLO treatment, which illustrates similar large incremental increases in concentration to that seen for Cl and NO_3 dissolution. Again, the soil control performs best of all treatments, followed by the three mixed treatments. This time, however, the Comp trial performs the best with total flux values taken at 16000ml cumulative volume (so to be comparative with ML) to be 410mg/kg. Respective values for BDA and ML were 751mg/kg and 662mg/kg.

Parcgro, CLO 2005 and 2006 and sewage sludge SO_4 dissolutions can be seen to perform similarly with respect to recorded trends and flux values.

2.8.6.9.1 Anion statistical analyses

Statistical significance tests were performed on incremental flux values (mg/kg) and incremental concentration values (mg/l), both of which gave similar results. Flux values have been assessed here. Analyses were conducted in the same manner as for the base cations and trace metal groups.

2.8.6.9.1.1 Group 1

For the three year study, the undiluted CLO 2004 dominated all other treatments displaying a significant difference of $P<0.0001$ for both Cl and SO_4 leached concentrations from all other treatments. Sewage sludge was also significantly higher in dissolved SO_4 ions than agricultural soil ($P<0.001$). Leached NO_3 concentrations were significantly higher ($P<0.05$) in the Comp trial than BDA, ML and soil treatment, but no difference lies between the CLO 2004.

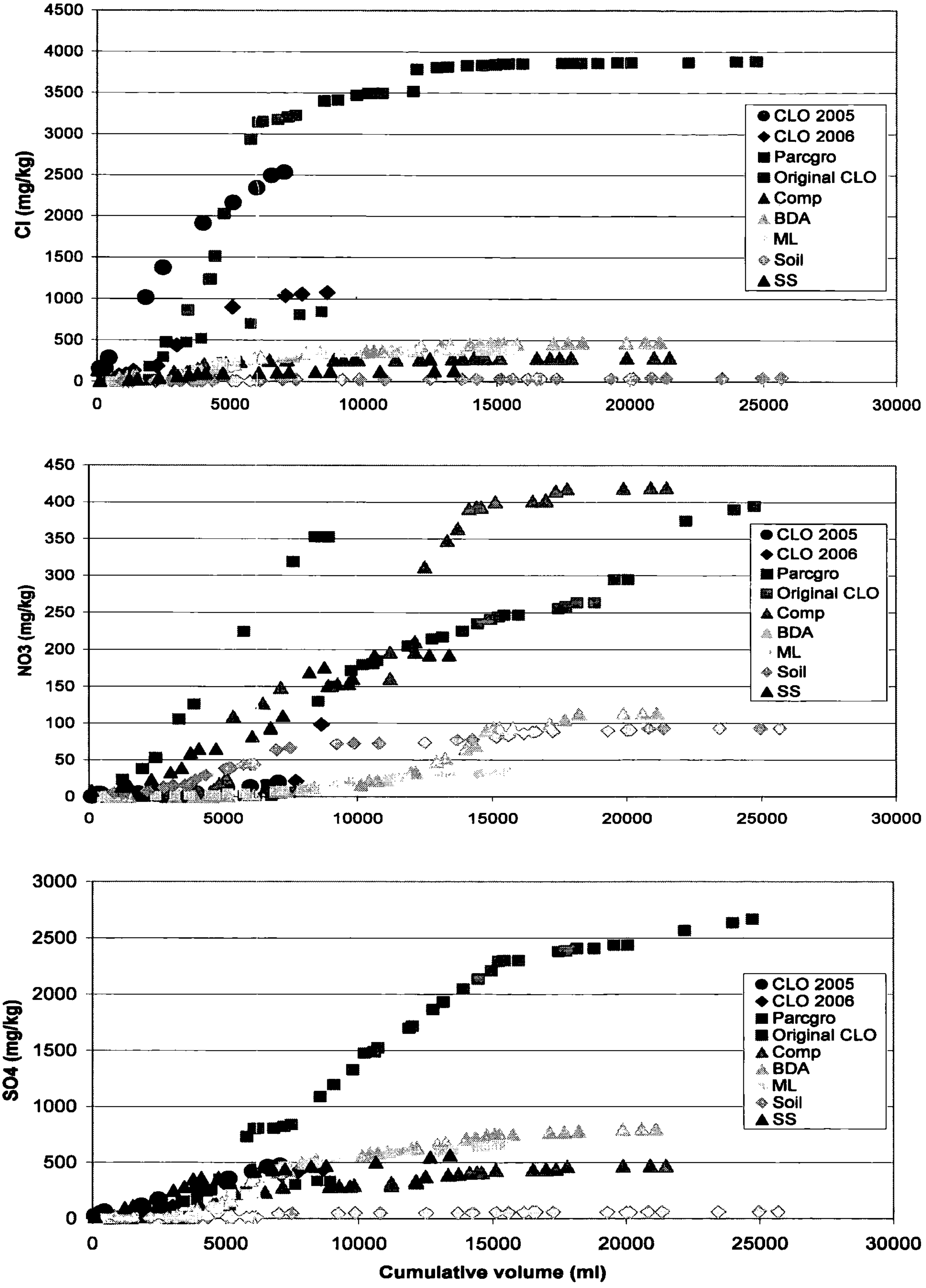


Figure 2.22: Treatment releases for Cl, NO_3 and SO_4 recorded in lysimeter leachates.

Active remediation

There had been an active remediation ($P<0.01$) of Cl leaching produced by mixing the original CLO material with 3 parts green compost. Nevertheless, green compost resulted in significantly higher leachable concentrations of NO_3. Sulphate showed no significant difference between treatments, so it was assumed that differences within treatment were greater than those posed by mixing.

In summary, the three year trial study revealed that, with respect to anion flushing, CLO 2004 leachates were significantly more contaminated with both Cl and SO_4 ions. The Comp trial did offer substantial remediation of Cl that could otherwise pose a serious threat to vegetation and groundwaters, but it must be remembered that concentrations found emanating from all treatments exceeded levels laid down in drinking water and surface water legislation. Together with the increased levels of NO_3 that were flushed from the Comp trial, it can be said that no environmentally-sound remediation, passive or active, had been attained by any of the artificial three year trials.

2.8.6.9.1.2 Group 2

Similar results were seen for the 1 year trials which, considering the Comp trial and Parcgro treatment were derived partly from the same basic materials, would be expected. Cl leaching was significantly ($P<0.05$) higher in the undiluted CLO trials, particularly the 2005 CLO, comparative to sewage sludge. The Parcgro material exuded significantly ($P<0.0001$) higher levels of NO_3 and SO_4 relative to all other treatments.

Active remediation

Statistical testing revealed that no active remediation has occurred for any anion. Consequently, Parcgro, unlike its predecessor, was shown not to offer any active remediation against Cl, exhibiting significantly ($P<0.01$) higher levels than its parent material (CLO 2006), but at the same time incurs significantly more environmental contamination from both NO_3 and SO_4 (both $P<0.0001$).

2.8.6.9.1.3 Overall statistical analysis

The following orders of decreasing leachability, with respect to Cl, NO_3 and SO_4, have been found from statistical analyses (significant differences ($P<0.05$) are represented by (>>):

Chloride

CLO 2005 > CLO 2006 > Parcgro > CLO 2004 >> ML > BDA > SS > Comp > Soil

Nitrate

Parcgro >> SS > CLO 2004 > Comp > CLO 2006 > Soil > BDA > CLO 2005 > ML

Sulphate

CLO 2004 > CLO 2006 > CLO 2005 > Parcgro >> SS > ML > BDA > Comp > Soil

In addition for SO_4, a significant difference lies between the original CLO 2004 and sewage sludge (and thus all the treatments to the right of this in the analysis order above). No other significant differences existed for this anion.

In conclusion, considering incremental leached levels as well as statistical findings, it can be asserted that none of the newer artificially manufactured products are close to the standard acceptable for use on catchments from which waters are extracted for human consumption.

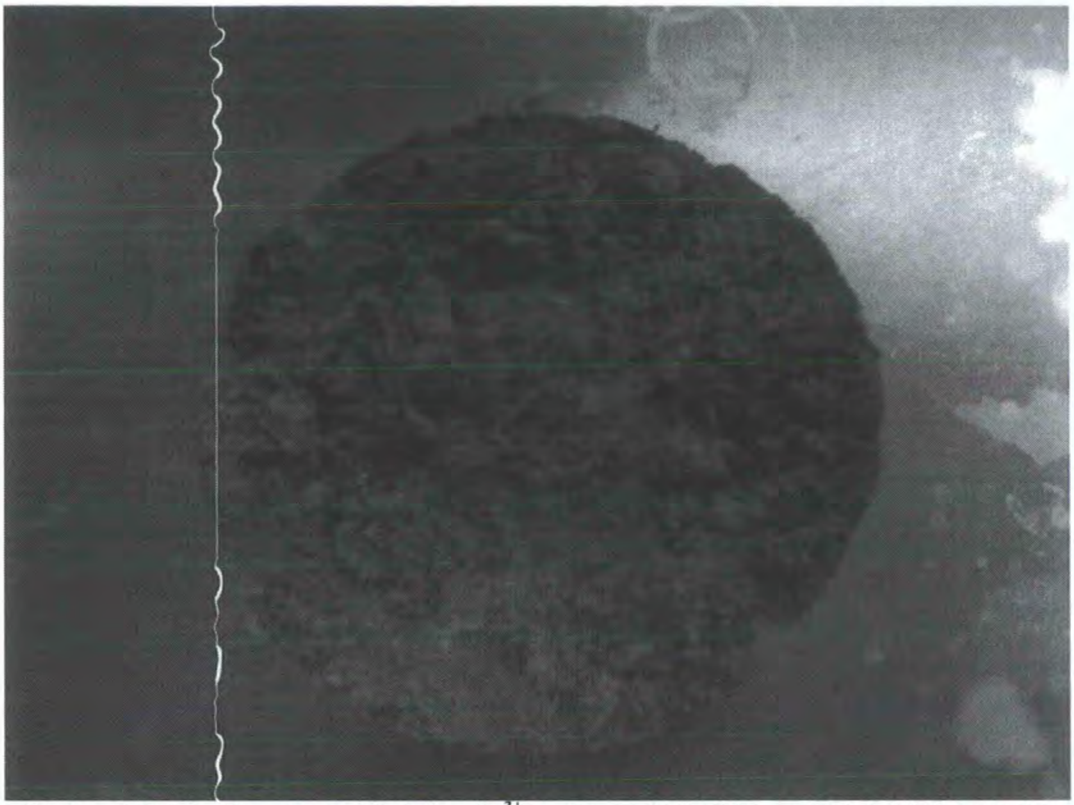
2.9 Chapter Discussion

One of the major environmental concerns associated with CLO is the extremely high levels of alkali and alkaline earth metals found in leachates from all treatments containing CLO. In the cases of Ca and K, concentrations have been recorded in leachates of Comp and CLO 2005, which were more than 125 times and 250 times the level permitted in waters intended for human consumption. These salinity levels (> 26 g/l) equate to levels ¾ of those typically found in sea water (~35 g/l). All four base cations (K, Na, Ca and Mg) were greatly in breach of either maximum admissible concentrations or guidance levels set out by government water directives. The vast amounts of soluble salts flushed from the CLO, even after dilution with amending materials, underlines one of the major problems, but also the potential for remediation. If this material was to be used under acid rain field conditions, some form of economic pre-treatment water-washing method would be imperative to its future. This process's advantages, disadvantages and potential will be assessed in chapter 4.

The trace metals may present a more pressing issue, since the simple flushing of heavy metals using water as the washing medium has previously been shown to be unproductive (Wang *et al.,* 2001). Results from the lysimeter trials raise concerns considering the concentrations and fluxes leached under the influence of percolating rainwaters. For all CLO containing treatments, except CLO 2005 and 2006, the element concentrations breaching landfill discharge consents, and drinking and surface water directive MACs (or GL's where no MACs are set) were: Al, Ca, Cd, Mn and Mg. The elements for which passive remediation to said levels have been achieved by mixing CLO were: Al, Cr, Fe and Ni; those leached elements that comply with both were: Cu, P and Zn. Leachates from New CLO 2005 and 2006 treatments breach drinking water legislation for all elements except Cu. There were only two further improvements, the first of which was applicable only to 2006 CLO, when comparing leached Fe and Cd concentrations to discharge consents from the Coxhoe landfill. Leachates from sewage sludges parallel the exact pattern seen for the 3 year treatments (group 1), with the exception of Al that does not exceed the legislative MAC for waters intended for human consumption. On the whole, there was no real difference, from a legal perspective, between sewage sludge treatments and mixed treatments. The extents to which the government levels were exceeded, and for what length of time this would occur, as well as leached volumes flushed, were of greater environmental concern. Finally, an additional consideration which has been addressed using Principal Component Analysis (PCA) in Chapter 5, is that of the actual raised concentrations of certain elements (Ca, Cu, K, Fe, Ni, Pb and Zn) leached from the newer undiluted CLO treatments, particularly CLO 2005, relative to untreated landfill wastes, with exception of Cu and Zn (which were below drinking water limits). This highlights how the accelerated composting process, although proven to beneficially optimise the microbial decomposition of the organic rich materials held in the MSW stream, is simultaneously capable of prematurely mobilising certain contaminants that may otherwise leach over longer time frames. Employing the Principal Component Analysis tool may also uncover the extent of metal leaching under specific environmental conditions and so provide common sources for the release of said trace metals.

The high detected level of soluble Fe in all treatments, except the control, potentially poses a threat to the environment. In particular, the extremely high levels in leachates emanating from all of the undiluted CLO treatments. As mentioned earlier it is likely that the extreme Fe values, relative to mixed treatment leachates, are not due solely to active remediation processes. Of key significance may be the exchange from a controlled aerobic environment (in the aerobic digester at the Thornley recycling plant) to a temporary anaerobic phase due to initial water-logging of the pure CLO lysimeters. Under well aerated conditions, insoluble Fe^{3+} is likely to be the dominant species but when the pure CLO material was compacted into the field lysimeters it took some time (1-2 months) for free drainage to be attained. It was decided that this phenomenon should be left to itself as it would if it occurred naturally. Therefore, anaerobic conditions prevailed which may have encouraged the reduction of the insoluble Fe (III) to soluble Fe (II), which after establishment of a freely drained system would be released for collection around the periods of elevated Fe concentrations. Oxidation accomplished by subsequent aeration, as well as being favoured by the alkaline conditions, would rapidly encourage the formation of Fe^{3+} precipitates. This scenario was seen in additional laboratory lysimeters that had become water-logged and were later aerated causing a distinct layer of insoluble Fe precipitate to form on the material surface (photograph 2.3, below).

The pattern in which species have been shown to be released into solution was irregular for almost all elements/parameters analysed. When comparing values both within and between treatments it proved difficult to decipher any significant remediation due to the heterogeneous nature of CLO, and to an extent the sewage sludge. This is an innate problem incurred with these materials and can cause a lack of within-treatment repeatability, which in some instances may govern statistical outcomes. It must be recognised that flux calculations incorporate additional leachate volumes which may further exaggerate exposed dissimilarities. The effects of plants on the physical parameters, such as flow pathways, aggregate stability and soil moisture retention, have been shown to be great but the indirect effect on chemical parameters resulting from reduced leachate volumes is difficult to quantify. The effects can be seen in the high standard deviations experienced in all leachates as well as in Coxhoe landfill discharge consent records. A greater display of positive active remediation may have been revealed were it not for the centrality of the heterogeneous nature of materials used. Although every possible measure was taken to maximise the production of scientifically accurate and precise results, physical heterogeneity is characteristic of these materials and so it was imperative that this representative trait was not compromised.



Photograph 2.3: Showing precipitation Fe^{3+} on the surface of the undiluted CLO material.

The incorporation of a further comparative treatment was employed in the form of a pure sewage sludge (biosolids) treatment at the beginning of the second year of study. Sewage sludge provided a further means of establishing additional relative constraints for the concentrations of specific elements and properties under investigation, which might have otherwise been difficult to place given only landfill and directive restrictions. This waste product, currently applied to agricultural land, is acknowledged as an environmentally accepted form of soil amendment. Thus, leachate performance of CLO associated soils and typical agricultural soil for the region was directly compared. It has been highlighted that both sewage sludge and CLO product treatment leachates are capable of significantly underperforming relative to those exuded from the soil control for nearly all parameters investigated. Furthermore, the Parcgro artificial soil and sewage sludge have been shown to perform similarly with respect to infringing legislatively controlled elements. Incorporating the additional properties of conductivity, TSS and DOC, affords slightly less detrimental unfavorable characteristics, to those of the Parcgro product. In this case TSS and DOC, levels have been evaluated with relevance to water quality (as an indication of colour) rather than their potential for heavy metal removal. The latter has not yet been quantified for this study and, according to Christensen et al (1996), the effect of DOC on the mobility of certain heavy metals may only be of minor environmental importance when dissolved concentrations are in the µg/l concentration range and if increased into the mg/l range, as in this study, effects become negligible.

In contrast, ascertaining the extent of heavy metal binding capacity with DOC and the associated effects on metal mobility and bioavailability would be interesting based on the findings (Chirenje and Ma, 1999, Apul *et al.*, 2005, Kumpiene *et al.*, 2006 and Lo *et al.,* 2007). Kumpiene et al (2006) investigated the effects of organic-rich peat on the retention of heavy metals induced from MSWI bottom ashes. They found that, in descending order of complexation strength relative to pH decrease (Cu > Cr > Pb > Zn), substantial proportions of these metals were retained by the peat emphasizing the importance of solid metal-organic complexes. Additionally, they found that contrary to prior findings, Cu leaching increased with increased DOC (a scenario also seen in this investigation), the elevation in DOC levels lead to increased retention of Cu levels in the solid phase which exemplifies the dual effect that elevated OM contents may have on soil matrix mass balance interactions. These findings were proposed to be a result of the high ionic strength of the leachates, caused by major cations, particularly Ca, and their subsequent effect on the flocculation and precipitation of humic-acids-metal complexes. Therefore, in conjunction with the possible associations and subsequent effects theorized between Ca, SO_4 and NO_3 ions, the extremely high levels of Ca (which in themselves pose huge cation competition) recorded in leachates exuded from CLO treatments may be at least partially responsible, for a number of chemical characteristics observed.

Irrespective of these findings, when sewage sludge and CLO were evaluated in their undiluted form, there was no question of which material would contaminate catchment groundwaters to a greater degree if the field conditions experienced here prevailed. In particular, the newer CLO materials (2005 and 2006) were shown to produce substandard leachates for every parameter assessed, and quite commonly (Cr, Al, Fe and Ni) of levels that are an order of magnitude, or more, of inferior quality to those of the sewage sludge. Thus, it has been shown and quantified that with the desired effects of additional high organic matter content and the presence of slow release plant nutrients that CLO materials can introduce to a soil medium, some detrimental aspects. Of particular concern are the total generated amounts of leached contaminants and the long term persistence of these various organic and inorganic species within the environment. An overall elemental comparison with sewage sludge for all treatments can be seen in Table 2.8 below.

The original expectation of finding materials that provided an active remedy for the various parameters analysed has been limited. Active remediation, in an environmental context, can be defined as a beneficial change in the concentration of an element/property in either the solid or liquid phase resulting from interactive processes within the soil matrix above and beyond that due to dilution. With respect to leachates, this normally concerns the reduction in concentration of an element held in solution (trace metals or base cations and associated conductivities) or its bioavailability (TSS or DOC bound metal species). From a solid phase interaction aspect, the amending material's contaminant concentration should increase as the mass balance transfer of solutes is altered by sorption processes such as complexation or chelation. It has become apparent therefore, that active remediation of elements and properties found in remediation treatment leachates has not been significant relative to the undiluted CLO levels recorded; only occurring statistically for Cu relative to the Parcgro treatment and Cl for the Comp trial.

The sheer mass of competing cations for exchanger/complex sites found in the matrices of leachates from CLO containing materials could be said to be one of the main controlling factors responsible for the lack of active remediation observed. Another possible reason for a general absence of active remediation maybe due to the high pH values of the amending materials themselves, in particular; green compost – 8.26, BDA - 10.70 and ML – 9.20. These materials were mixed with 25% CLO (w/w) with a near neutral pH (7.49) and so alkaline conditions prevailed throughout. Under alkaline conditions the immobilisation of several metals from the liquid phase are known to occur (Gupta *et al.*, 2005) and so the amendments offer no scope for overall pH related amelioration. Gupta et al (2005) showed that, in particular, concentrations of the following metals (Al, Cd, Co, Cu, Fe, Mg, Mn, Ni, Pb, Si and Zn) in leachates from MSWI ashes were susceptible to more than two orders of change as pH decreased from alkaline to acidic values. Thus pH may also play an important role in controlling leaching of elements from CLO containing materials, particularly in long term scenarios. Furthermore the precipitation of Ca ions with increasing pH has been theorized prior (Stegemann *et al,* 1995) and associated with that of the SO_4 counterion, thus demonstrating system sensitivity to slight changes in pH.

	Passive remediation relative to Sewage Sludge - (mg/l)						
Element/ property	**Passive Remediation**						
	CLO 2005	**Original CLO**	**Parcgro**	**Comp**	**BDA**	**ML**	**Soil control**
Si	✓	✓	✓	✓	✓	✓	✓
Ca	✗	✓	✓	✓	✓	✓	✓
Mg	✗	✗	✗	✓	✗	✓	✓
Ni	✗	✗	✗	✗	✗	✓	✓
Zn	✓ **	✓ ***	✓	✓ ***	✓ ***	✓ ***	✓ ***
Co	✗	✗	✓	✓	✗	✓	✓
Cd	✗	✗	✗	✓	✗	✓	✓
P	✗	✓	✓	✓	✓	✓	✓
Al	✗	✗	✓	✓	✓	✓	✓
Fe	✗	✗	✓	✓	✓	✗	✓
Mn	✗	✓	✓	✓ **	✓ *	✓	✓

Table 2.7: Remediation relative to that of sewage sludge leachates. *, **, * = recorded concentrations are 5 fold, 10 fold, 100 fold less than sewage sludge concentrations, respectively. ✓ defines passive remediation relative to sewage sludge and ✗ defines no remediation.**

So although, pH levels in all recorded leachates were alkaline over the three years of study, in the long term this buffering capacity of the system may well be tipped the other way and acidic, conditions may thereon prevail. The addition of tonnes of undiluted or mixed CLO to the land will permit the long term exposure to rain waters, uptake of CO_2 from the atmosphere and the release of decomposition acids from the breakdown of the vast quantities of organic matter held within; all of which will contribute to the overall lowering in pH. In addition, if the pre-treatment water-washing of the CLO proved successful, from a total leached salinity point of view, this may well considerably diminish the buffering power of undiluted CLO's; mixing with alkaline amendments will then be of paramount importance in substantiating its utilisation as an artificial soil. However, it must be noted that from an environmental standpoint the current observed behaviours and theorized immobilisation of metals under alkaline conditions is considered to be a major beneficial characteristic of the CLO and amendments used; leaching of potential trace metal contaminants to groundwaters has been limited by these processes.

The worse case scenarios have been calculated where pure CLO and its associated soil leachates have been investigated. Theoretically and realistically however, if applied to agricultural land, or as it is currently being used, as a topsoil cover for landfill and reclaimed Brownfield sites, a proportion of the contaminants would inevitably be adsorbed, complexed or up taken by other diluent pathways. Several different mechanisms can be involved in the adsorption of metal ions, including cation exchange, specific adsorption, organic complexation and co-precipitation. These chemical processes are associated with the adsorption of metals from the liquid phase; say a leachate solution on to the solid phase, be it the soil and its constituents or an amending material as used in this study. The extent to which these processes occur in a soil is difficult to predict but it is these processes that govern the concentrations of metal ions and complexes in soil solution and therefore ultimately determine the availability to plant root systems and access to groundwaters; thus defining a metals 'toxicity'. The presence of large quantities of organic colloids, which provide adsorption sites for the potentially toxic metals (PTM) highlighted here and alkaline conditions are both strong influential factors on increasing adsorption potential. However, there is a finite capacity of sorbents to store a contaminant under favoured conditions, and when this capacity is exceeded the contamination will diffuse into the surrounding medium, in leachates (Gordan and Breach, 1998). As will be revealed from Tessier characterisations and PCA (Chapter 3 and 5) the conditions under which the materials are exposed are central to the overall solubility and mobility of the PTM's. The lysimeter leachate trials have therefore shown that, despite favourable adsorption conditions, the extent to which PTM's have been leached from the CLO containing and sewage sludge materials implies the adsorption capacity has been reached. This in conjunction with the prevailing conditions is thought to govern leachate component solubilities.

Passive remediation, based upon findings in this chapter, would seem to be a more effective means of diluting the detrimental effects that high levels of leachate components may incur on the environment. In this context the process relates more to the reduction in leached concentration of a particular element/property to levels below that fixed by government legislation or that consented in landfill discharges to be acceptable. In a number of cases the concentrations of contaminants being flushed in leachates containing only 25% (w/w) CLO, proves still to be too high for passive remediation according to either landfill discharge consents or drinking water regulations. Nevertheless, a considerable proportion of the elements and compounds which afforded this material dilution and illustrated that passive remediation can be an effective method for reducing leached contaminant concentrations (Tables 2.9a and 2.9b). This was true for Al, Fe and P; the time over which acceptable levels regarding drinking water directives were quite variable but relative to landfill records a distinct improvement has been accomplished. The latter was also true for the base cations, which were shown to be easily dissolved into solution, and so the 6-9 day optimised composting process undertaken by Premierwaste on raw MSW has proven to be of an environmentally beneficial standard. Furthermore, there were elements, such as Cu, Pb and Zn that were leached from all treatments, except the undiluted 2005 and 2006 CLOs, whose concentrations already resided below both landfill discharges and MACs laid out in drinking and surface water directives. This may be due to the pH-dependant release into solution of these metals, as described above.

a)

	Infringement of EC Drinking and Surface Water Directive MACs - (mg/l)							
Element/ property	**Infringement**							
	CLO 2005	**Sewage Sludge**	**Original CLO**	**Parcgro**	**Comp**	**BDA**	**ML**	**Soil Control**
K	✓	✓	✓	✓	✓	✓	✓	✓
Na	✓	✓	✓	✓	✓	✓	✓	✓
Mg	✓	✓	✓	✓	✓	✓	✓	✓
Ni	✓	✓	✓	✓	✓	✓	✓	✓
Zn	✓	✓	✗	✗	✗	✗	✗	✗
Cu	✗	✗	✗	✗	✗	✗	✗	✗
Cd	✓	✗	✓	✓	✗	✗	✗	✗
Pb	✓	✗	✓	✗	✗	✗	✗	✗
Al	✓	✗	✓	✗	✓	✓	✓	✗
Fe	✓	✓	✓	✗	✓	✓	✓	✗
Mn	✓	✓	✓	✓	✓	✓	✓	✓

b)

Infringement of Coxhoe Landfill emissions - (mg/l)								
Element/ property	**CLO 2005**	**Sewage Sludge**	**Original CLO**	**Infringement Parcgro**	**Comp**	**BDA**	**ML**	**Soil Control**
K	✓	✗	✗	✗	✓	✗	✗	✗
Ca	✓	✗	✗	✗	✗	✗	✗	✗
Ni	✓	✓	✓	✗	✓	✓	✓	✗
Zn	✓	✓	✗	✓	✗	✗	✗	✗
Cu	✓	✗	✗	✗	✗	✗	✗	✗
Pb	✓	✗	✓	✗	✗	✗	✗	✗
Fe	✓	✗	✗	✗	✗	✗	✗	✗

Table 2.8: Leachate components in breach of a) EC Drinking and Surface water directive MACs and b) Coxhoe landfill discharge consents. ✓ defines legislative infringement and ✗ defines no infringement.

Nevertheless, it was quite clear that there were certainly many profound physio-chemical improvements that would be absolute necessities if the CLO, even in its 3:1 diluted form or in its current Parcgro form, were to be utilised as a basis for bio-fuel production. Much research is still required into the cumulative effects that a potentially pre-treated, more stabilised, diluted CLO product will have on the surrounding environment when applied at a catchment level for agricultural use, as has been the case for numerous sewage sludges (Casado-Vela *et al.*, 2006, Horswell *et al.*, 2006 and Pigozza *et al.*, 2006). Further experimentation involving the pre-washing of the materials (similar to that employed by Abbas *et al.*, 2003) with de-ionised water may help distinguish those metals occurring as water soluble salts and those that are pH dependant. This, in conjunction with data attained from a modified Tessier sequential extraction procedure will prove information on the elements of the CLO amended soils which are in water-soluble, exchangeable, acid-soluble, reducible and oxidisable fractions (Chang *et al.*, 2005). A comprehensive account of the elemental dissolution, speciation and release patterns, together with PCA results, can then be collated in an attempt to identify the maximum impact that CLO amended soils can invoke on the environment.

2.10 Conclusion

The aim of this study was to identify release patterns and concentrations for specific elements and compounds under field conditions (i.e., on exposure to acid rain waters) and compare these against leachates exuded from a typical agricultural soil for the Durham region, and an agriculturally accepted fertiliser; sewage sludge.

Although leachates from all treatments were found to be consistently weakly alkaline, substantial metal leachate concentrations were detected. A number of heavy metals, nutrients and easily soluble salts were measured in the leachates flushed from CLO and its associated soils. Major breaching of both landfill discharge consents and drinking and surface water directives were observed by all of the treatments containing CLO. In particular, it was highlighted that if pure CLO were to be utilised in its current state as an undiluted agricultural fertiliser, much like sewage sludge currently is, this would be of risk to the environment. Soil instabilities, phytotoxicity in plants, groundwater contamination and their related issues concerning human health could all potentially be as a direct consequence of using this aerobically digested soil conditioner on farm land.

The new 'improved' CLO's (2005 and 2006) were in fact, from an environmental aspect, of an inferior quality for every element and property analysed relative to all other treatments, and in particular to its earlier counterpart; CLO 2004. Whatever mechanical and structural alterations or physiobiochemical processes that were undertaken in an attempt to manufacture a more environmentally durable and versatile artificial CLO product should be rigorously reconsidered. The case may have been that substantial economic benefits were reaped but, environmentally, the changes made were of serious detriment to the performance of both leachate quantity and quality.

A certain level of passive remediation by mixing the CLO with various amending materials was achieved but this was not yet of an environmentally accepted standard for either the 3:1 (Comp, BDA and ML) or currently used method of 1:1:1 (Parcgro) ratio mixtures for utilisation on agricultural land. Active remediation of leachate components has proven to be limited for the concentrations of species being released over the time scale studied here.

Recorded leachate performances for the CLO containing treatments, in particular for the remediation treatments (Comp, BDA, ML and Parcgro), relative to levels seen leached from sewage sludges were both environmentally concerning and to some degree encouraging for MSW aerobic digestion. Sewage sludge field releases have been shown to be inferior to both undiluted and diluted CLO treatments for a number of concerning elements, particularly Mn, P and Zn. No CLO containing treatment or sewage sludge performed to a standard characteristic of an agricultural soil.

These findings have been crucial in identifying the problem components associated with aerobically digested municipal solid waste. A combination of this knowledge together with sequential extraction data, water soluble salts flushes and principle component analyses will provide a more detailed account of whether any remediation value can be secured for these materials and under what conditions contaminant releases are of most environmental concern. This will ultimately determine the potential future of this waste management practice.

Chapter 3

Characterisation of CLO and its associated soils

3.1 Introduction

A great deal of knowledge exists concerning the character and leaching behaviour of various soils (e.g., Bernard *et al.,* 2005, Sposito *et al.,* 1989 and Sposito *et al.,*, 1984,) but it is only in recent years that solid wastes and contaminated soils, in particular the assessment of heavy metal speciation, have been investigated in great depth. For example, evaluations of the retention and leaching behaviour of metals have been carried out upon Municipal Solid Waste Incinerator (MSWI) bottom ash (Kumpiene *et al.,* 2006) and fly ashes (Chang *et al.,* 2005), as well as in decomposed MSW (Esakku *et al.,* 2005). Previous work has also been carried out upon the aerobically digested MSW discharged at the Thornley based recycling plant itself (*pers comm.* - Johnson and Worrall, 2003). This unpublished work, carried out in 2002 and 2003 when CLO was referred to as a 'soil conditioner,' focused upon the water retention and soil improvement properties of the material, as well as the occurrence and nature of metals held in various physical and chemical fractions of the soil conditioner. Particle size distribution, microscopic analyses and a sequential extraction procedure (similar to that to be described later) were used to partition certain heavy metals (copper, cadmium, lead, nickel and zinc) in the 16 mm graded digestate. Currently, the CLO is graded to 6mm and so it is important to identify any physical or chemical improvements, or detriments, that may have resulted from the refining of the material or as a result of ongoing alterations to the waste management practise.

This part of the thesis focuses specifically on these aspects and attempts to ascertain the physical and chemical characteristics of both products of aerobically digested MSW, and the degree of contamination that would result from the use of CLO as some form of artificial soil (i.e., the Parcgro artificial soil currently being manufactured). This will be addressed using a number of varying experimental techniques, concentrating on two main areas – the organic and inorganic phases. Temporal changes in property behaviour have also been incorporated via annual sacrificial sampling of the artificial soils which have been under constant exposure to the environment. Parallel to the CLO associated soils are a sewage sludge treatment and an agricultural soil control for comparison. In addition, comparison of treatment component releases relative to government limit values for concentrations of heavy metals in soil, as well as in sludge for use in agriculture has been undertaken. This detailed data provides a solid basis from which future examination can develop and, hopefully, fuel the establishment of an aerobically digested, environmentally sound waste product that can be effectively recycled and used for bio-fuel production.

3.2 Sample Analyses

3.2.1 Preparation of samples for analysis

All solid samples were collected from the field lysimeters themselves or, as for the original analyses, directly from the materials used to fill the lysimeters and placed into polythene air-tight bags. A Dutch auger was the method of sampling used to ensure a complete soil profile representative of the depth of each lysimeter top. The variation in contaminant concentration down the profile, if any, would have been an interesting characteristic to study but time and financial constraints unfortunately ruled this out. The well-mixed samples were then oven dried at 105°C until constant weight to ensure removal of all free water that may interfere with experimentation. They were then ground with an agate mortar and pestle until >90% of the original dry sample weight could be passed through a 1mm sieve. The homogenised samples obtained were stored in air tight polythene bags in the dark at room temperature until extraction. Although every effort was made to incorporate equal proportions of the screened out material, the majority of the residing material was from the light plastic fraction. However, the environmental ramifications of this, with respect to the component leaching carried out in this study, are considered minor as plastic is considered a non-biodegradable, inert substance with a very small heavy metal binding capacity. Statistical analyses were carried out nonetheless to determine the extent of contamination in the un-sieved material relative to levels attained in sieved samples and the affects this may have on carbon contents.

3.2.2 Moisture content

The moisture content of each material originally used in the field lysimeters was calculated by weighing, in triplicate, a representative amount of solid and then drying at 105°C until constant weight. The difference in weight (x100) was said to be the percentage moisture content.

3.2.3 Pore Volume

The maximum water-pore volumes for each material, as well as for each lysimeter, were calculated. This was done by oven baking at 105°C (as above) to attain the moisture contents and then individual lysimeter field capacities were measured for each material. The latter was achieved by filling a large sealed container with water and immersing each lysimeter column within, so that the water level was above the level of the material held inside the lysimeter column itself. The head gradient created caused a gradual wetting-up of the column from the base upwards. The sealed container was topped up with water if necessary until the water level diminished no further and the core was fully saturated. The lysimeter core was then removed from the apparatus and gently watered from above to ensure complete saturation of the material within. It was then allowed to rest upon a freely draining pallet until all gravity drainage had ceased; this was said to be field capacity. The maximum or total water-pore volumes for each lysimeter, as well as per kilogram of material (w/w), could then be measured.

The total porosity of a material includes both the mobile and immobile waters, for which field capacity values are required to distinguish this difference (immobile waters). Thus, the calculation of both moisture content and field condition absorption volumes or field capacity was necessary to obtain an idea of overall treatment 'effective water-accessible porosity.' Effective porosity alone does not account for the immobile waters held within a material. The inclusion of 'water-accessible' in the effective porosity definition relates to the field conditions experienced by the lysimeters and incorporates the field capacity, or retainable, immobile waters. The field capacity is important when assessing the moisture retention properties of a material of this nature, as it is in the field that this material will hopefully be used. It is theorised that these two parameters will highlight any advantageous soil moisture retention properties, as a result of mixing CLO with other recyclable materials, relative to an agricultural soil. In addition, pore volume calculations can provide a quantitative evaluation of the performance of each treatment under field conditions.

3.2.4 pH

Unlike leachate pH, the procedure for soil pH measurement required a reagent as the material under investigation is in the solid phase. It was decided that the soil suspension would be made with (0.01M $CaCl_2$) owing to its additional buffering capacity of impurities in comparison with de-ionised water. A Hanna instrument HI 9025 microcomputer pH meter was used. Calibration of the instrument was carried out using two standard solutions of known pH (pH 4 and pH 7). Determination of pH in 0.01 M $CaCl_2$ was as follows:

Approximately 2g of air-dried amended soil was placed into a 100ml beaker; to this was added 20ml of 0.01 M $CaCl_2$ which was then mixed, via rotation, using an IKA labortechnik® KS 125 basic shaker table. The electrodes were placed directly into the soil sediment which was continuously agitated throughout. Continuous agitation was chosen as the means for pH determination because this proved most effective at steadying pH fluctuation of the meter within an appropriate timescale. Every measurement was carried out in a consistent manner.

3.2.5 Loss on Ignition (LOI)

Principle:

Sequential loss on ignition (LOI) is a rapid and inexpensive means of quantitatively estimating a solid's various carbon contents. Relative to dichromate oxidation, this practice is 'safe,' providing the correct safety precautions are intact and appropriate safety equipment worn. It eliminates the hazards associated with the use of chromate ($Cr_2O_7^{2-}$) which in a strong acid medium is a powerful oxidant with the potential to cause corrosive damage to the skin as well as respiratory-related areas. Chromate is also carcinogenic, so discharge constraints into sewage systems are in place. Dean (1974) evaluated a method to determine soil organic matter (SOM) and carbonate contents at 500-550 °C and 900-1000 °C, respectively. However, it may also be interesting to distinguish between SOM and refractory or elemental carbons, particularly in the area of waste management, where the various forms of carbon are often sourced from numerous locations, the nature of which can differ biologically, physically and chemically. Thus a three step LOI method was devised, based on previous work carried out by Johnson and Worrall (2003), as mentioned above, who used a thermal gravimetric analyser to accurately detect very small (mg) weight changes with increasing temperature to over 1000 °C. This research, carried out upon various carbon rich materials including cements and aerobically digested household waste, suggested the following temperatures should be used for LOI: organic matter at 375 °C, refractory carbons at 600 °C and carbonates at 900 °C. Furthermore, work carried out by Heiri *et al.,* (2001), in particular the exposure time, temperature and character of the solids used, support the possibility of using a lower temperature (than 500-550 °C) to determine a more accurate estimation of organic matter content, especially for mixed samples.

Procedure:

All porcelain crucibles were dried at 105°C for a minimum of 12 hours then allowed to cool in a dessicator prior to weighing to 4 decimal places on a Mettler AJ100 electronic balance. Air dried samples were then transferred to the crucibles so that around 75% of each crucible was filled. This ensured a representative sample quantity but also prevented any potential loss of 'lighter lengthy materials,' such as threads of plastics or fibrous matter, that otherwise may not have been entirely contained within the crucible sides if fully filled. The Carbolite furnace CSF 1100 was then set and allowed to equilibrate to 105 °C before placing the samples directly onto the oven floor. The samples were left undisturbed for 24hrs then transferred to a dessicator as before. This guaranteed all water had been removed and so was taken to be the initial dry weight of the sample. The furnace temperature was then raised to 375 °C and, once a constant temperature had been reached, the next LOI commenced for 24hrs. At higher temperatures (600 °C and 900 °C), samples were first allowed to cool within the furnace itself until they were safe to be handled with heat protective gloves, transferred to a dessicator and weighed as before. In an attempt to obtain a more representative account, the technique's rapidity and relative inexpense was exploited through carrying out six replicates for each treatment, rather than the usual three or four used in other techniques.

Calculations:

At 375 °C:

$$LOI_{375} = ((DW_{105} - DW_{375})/DW_{105})*100$$

Where: LOI_{375} represents LOI at 375 °C (%); DW_{105} represents the dry weight of the sample before combustion (g), and DW_{375} the dry weight of the sample after heating for 24hrs at 375 °C (g). The weight loss should then be proportional to the organic carbon contained in the sample.

At 600 °C

$$LOI_{600} = ((DW_{375} - DW_{600})/DW_{105})*100$$

Where LOI_{600} represents LOI at 600 °C (%); DW_{375} is the dry weight of the sample after combustion of organic matter at 375 °C (g); DW_{600} represents the dry weight of the sample after heating to 600 °C (g), and DW_{105} is again the dry weight of the sample before the organic combustion (g).

At 900 °C

$$LOI_{900} = (((DW_{600} - DW_{900})/DW_{105})*100)$$

Where LOI_{900} represents LOI at 900 °C (%); DW_{600} is the dry weight of the sample after combustion of organic matter at 600 °C (g); DW_{900} represents the dry weight of the sample after heating to 900 °C (g), and DW_{105} is again the dry weight of the sample before the organic combustion (g).

3.2.6 Dichromate Oxidation

Principle:

The standard wet chemistry technique for determining the total organic carbon content of sediment is usually carried out by means of titration. This method involves the rapid dichromate oxidation of the organic matter within a solid sample. The Walkley-Black method (1934) is a widely used technique which employs the aforementioned oxidation process and has grown in popularity owing to its simplicity and rapid repeatability. In this procedure, potassium dichromate ($K_2Cr_2O_2$), in the presence of concentrated sulphuric acid, is added to the sample producing an exothermic reaction which rapidly oxidises any organic C present. The digestate is then titrated against a ferrous ammonium sulphate solution, reaching a 1 drop end point with a distinct colour change, to remove the excess $K_2Cr_2O_2$. Although studies have shown this technique can lead to the incomplete oxidation of organic C and is particularly ineffective at assimilating elemental C forms, overall the merits (specifically, the speed and relative accuracy to which organic C content estimations could be reproduced for a number of highly variable materials) greatly outweighed discrepancies for this particular study. Furthermore, the familiar correction factor of 1.33 was applied in an attempt compensate for this inefficient (77%) organic carbon recovery. Therefore, a modified version of the Walkley-Black (1934) method was used to determine organic carbon contents of the solid materials on an annual basis throughout the study period.

Procedure:

The determination of total organic C content was as follows:

A measured (0.2g) quantity of air dried sample was placed into a 500ml conical flask and 20ml of 0.167M $K_2Cr_2O_2$ (49.04g of $K_2Cr_2O_2$ in 1 litre Milli-RO purified water) solution was added. The vessel was then mixed by carefully swirling the solution, avoiding throwing the sample onto the sides of the flask. A 20ml volume of H_2SO_4 was immediately added and the resulting exothermic solution was mixed by gentle rotation for about 60 seconds to ensure thorough incorporation of the sulphuric acid. The conical flasks were allowed to stand and cool for 30 minutes. Two reagent blanks (as standards) were run alongside each processing batch. These contained no solid sample.

After resting, the solution was diluted up to 200ml with milli-RO purified water. To the mixture was added 10ml of 85% H_3PO_4 and 0.2g of NaF. This was to complex Fe^{3+} which would interfere with the titration endpoint. Approximately 10 drops of diphenylamine indicator (0.5g of reagent grade diphenylamine in 20ml of milli-RO purified water and 100ml concentrated H_2SO_4) were then added. From this point, continuous agitation (swirling) occurred until the end point was reached. Back titration was performed using 0.5M ferrous ammonium sulphate (196.1g of $Fe(NH_4)_2(SO_4)_2.H_2O$ dissolved in 800ml of Milli-RO purified water containing 20ml of concentrated H_2SO_4 and then diluted with to 1 litre) solution. The solution gradually changed from a bluish-grey colour to a deepening reddish-brown before reaching a 1 drop end point on which the solution turned bright green. Employment of a desk lamp placed under the conical flask significantly improved the accurate detection of this end point.

Calculation:

$$\% \text{ Organic Carbon} = 20\left(1 - \frac{T}{S}\right)\left(\frac{1.0N \times 12 \times 100}{W \times 4000}\right)$$

Where: 1.0N is the normality of $K_2Cr_2O_2$, T (ml) and S (ml) are the ferrous solution titration volumes for sample and blank, respectively, and W (g) is the weight of sediment sample. The millequivalent weight of carbon is represented by 12/4000.

3.2.7 Sequential Extraction procedure for the Speciation of Particulate Trace Metals

Justification:

'The use of total concentration as a criterion to assess the potential effects of sediment contamination implies that all forms of a given metal have equal impact on the environment; such an assumption is clearly untenable' – Tessier et al (1979). This statement advocates the use of a sequential extraction protocol over total metal analysis for metals held within wastes, as a preferred means of attaining a more complete understanding of trace metal mobility, and thus their potential as environmental pollutants. Tessier et al (1979) devised a sequential extraction procedure that provides a solid method for selectively extracting trace metals and partitioning them into chemical forms liable for release under progressively harsher environmental conditions. This appraisal of particulate metal speciation is particularly relevant when assessing the potential impact of wastes since a wide variety of environmental conditions may be encountered depending on how, where and in what quantities the end product is eventually utilised. It is, however, these changing conditions, such as shifting from an oxic to anoxic setting, in conjunction with the heterogeneous physical and chemical nature associated with these wastes that further complicates partitioning studies of trace metals. Kersten and Förstner (1991) undertook a valuable evaluation of the available sequential extraction techniques for cohesive sediments. This study highlighted a number of key issues, such as the degree of fractionation required for the study which relates to the specificity of the individual steps themselves, and the appropriate selection of extractant needed. With particular relevance to this study is the positioning of the 'organic matter fraction' within the scheme (Tessier *et al.,* 1979 and Towner, 1984), the incorporation of a reagent effect which can limit quantitative comparisons of metal partitioning relationships from separate studies (Robinson, 1984), and the inter-stage extractability of sulphide metals in anoxic sediments based upon their solubility (Kersten and Förstner, 1991). Unsurprisingly, there is much discrepancy between researchers and many of the findings have been intensely debated, often to unsatisfactory conclusions, and so little uniformity has been achieved regarding the order of extraction and suitable reagents.

However, there is one technique that appears to offer some regularity, and is thus one of the most commonly employed sequential extraction protocols – that devised by Tessier et al (1979). Tessier introduced the concept that reducible phases could be separated in subsequent stages after the displacement of the exchangeable and carbonate fractions has occurred. Consequently, the latter steps, in various proposals, differ only slightly, in a functional context (e.g. L/S ratio, reaction time and post-reaction step sediment washings), as most succeeding protocols have sourced their modifications on Tessier's original findings. This lack of standardization originating from the problems identified above has initiated a shift toward an operationally defined labelling system, based on the extractants chosen, rather than the true speciation trace metal associations within sediments and wastes. In this way, misinterpretation of sequential extraction data can be avoided, allowing for a conventional means of enhancing our understanding of trace metal partitioning by simplifying the natural environmental system. This is the reason for including both the reagent and principle extracted fraction in the methodology description below.

That said, however, there are still certain limitations in using this technique. As highlighted by Tessier et al (1979), these include accuracy and precision, both of which may be compromised by the inherent heterogeneity of the solid materials under analysis. This inhomogeneity is not specific to the procedure, however; CLO and its associated artificial soils are highly assorted in their physical nature which has proved problematic throughout the study. More explicit to the actual selective character of the method is the need to further develop a better defined and purposely constrained set of reagents unique to material of this nature, as opposed to using those that are most applicable to naturally occurring sediment types.

Principle:

An operationally adapted version of Tessier et al (1979) sequential extraction procedure integrated the following five fractions: exchangeable; bound to carbonates; bound to iron and manganese oxides; bound to organic matter and residual. The last of which (residual), could theoretically be split into two; a plastic and glass fraction. This additional phase separation was based upon previous work carried out for

Premierwaste by Johnson and Worrall (2003) on the occurrence and nature of metals in what was then referred to as 'soil conditioner' from the Thornley aerobic digester. By this stage, any remaining trace metals will be chiefly made up of those incorporated into the internal crystal structures of the minerals themselves – essentially, silicate minerals, resistant sulphides and some refractory carbons. Typically, glass, plastics and native metals, as well as any remaining, more robust organic material are broken down during this phase. The CLO intrinsically contains significant quantities of glass (5%) and plastics (11.7%), which together constitute almost 17% of the CLO material, the presence of which contributes significantly to the undesirable aesthetic quality of the CLO. The data from this stage of the sequential procedure could provide useful information regarding both the identity and concentrations of the end member species.

However, conditions typically found in nature would not normally leach the residual metals contained within the plastic and glass fraction into the environment and so are considered 'inert' with respect to leachability under field conditions. It was therefore considered, after preliminary analyses, that the extremely harsh nature of the reagents required to dissolve the residual material, together with the time available for completion of the project that the sequential extraction procedure would be terminated at this point. The residual plastic fraction dissolution procedure has been included below to show how preliminary experiments were conducted.

The only other alteration made to the Tessier scheme was replacing 1M sodium acetate solution (NaOAc) with 1M Ammonium acetate solution in steps one and two.

Fraction 1:- 'Exchangeable' – ***salt-displaceable.*** Changes in ionic strength are likely to affect the sorption-desorption processes that govern the fixation of numerous trace metals to the sediment. This step will remove all metals lightly bound or in ion exchangeable sites, adsorbed onto surfaces or dissolved in adsorbed water. These metals can also be found in precipitated salts.

Fraction 2:- 'Bound to carbonates' – ***acid-soluble.*** Considerable trace metal concentrations can be associated with carbonate minerals which are susceptible to pH changes and mild acid attack.

Fraction 3:- 'Bound to Iron and Manganese oxides' - ***reducible.*** Iron and manganese oxides can exist in a number of forms, all of which can be chemically reduced to their ferrous and manganous forms due to their thermodynamic instability under anoxic conditions. In addition, a reagent proficient at retaining the large quantities of newly stripped metals in solution is required.

Fraction 4:- 'Bound to organics' - ***oxidisable.*** Light organics, such as composted food wastes and garden wastes, contain large amounts of trace metals which are frequently found bound to the living organisms and partially degraded matter, and as coatings on mineral particles held within. This extraction phase involves the complete oxidation of most forms of organic matter while simultaneously avoiding the partial attack of silicate lattices associated with the residual primary and secondary minerals.

Procedure:

The sequential extractions set out below refer to 2.5g sediment samples (dried weight of the original sample used for the initial extraction).

Reagents:

(i) Salt-displaceable: - 1M Ammonium Acetate solution ($NH_4C_2H_3O_2$). The sediment was extracted at room temperature for 1 hour with 25ml of 1M $NH_4C_2H_3O_2$ with continuous agitation. Analysis tubes were centrifuged at 2500 rpm for 2 minutes and the filtrate collected and transferred to 25ml polystyrene vials ready for ICP-OES analysis. The residue was then rinsed by centrifugation with 25ml of milli-RO purified water at least two times. The rinsings were discarded.

(ii) Bound to carbonates: - 1M Ammonium Acetate solution ($NH_4C_2H_3O_2$) adjusted to pH 5.0 with 0.55M acetic acid (HOAc). The residue from (i) was leached at room temperature for 12 hours with 25ml of the reagent solution. Continuous agitation was maintained throughout. This process was repeated if a reaction was still evident after 12 hours. Frequent pH adjustment was necessary throughout in order to maintain the pH 5 buffer due to the high ionic strength of the materials. Analysis tubes were centrifuged at 2500 rpm for 2 minutes and the filtrate collected and transferred to 25ml polystyrene vials ready for ICP-OES analysis. The residue was then rinsed by centrifugation with 25ml of milli-RO purified water at least two times and washings discarded.

(iii) Bound to Fe – Mn Oxides. 0.3M Sodium Thiosulphate ($Na_2S_2O_3$) in 0.175M sodium citrate ($Na_3C_6H_5O_7$) and 0.025M citric acid ($C_6H_8O_7$). The residue from (ii) was extracted at room temperature with 25ml of the reagent solution. The period of experimentation was 6 hours. Analysis tubes were centrifuged at 2500 rpm for 2 minutes and the filtrate collected and transferred to 25ml polystyrene vials ready for ICP-OES analysis. The residue was then rinsed by centrifugation with 25ml of milli-RO purified water at least a further 2 times and the supernatant discarded.

(iv) Bound to organic matter. 0.02M HNO_3 and 30% H_2O_2. The residue from (iii) was transferred to 250ml glass vessels and 15ml of 0.02M HNO_3 and 25ml of 30% H_2O_2 (adjusted to pH 2 with HNO_3) added. The mixture was heated to 85 ± 2°C for 3 hours with intermittent agitation. A second 25ml of 30% H_2O_2 was added after 3 hours and again the sample was heated to 85 ± 2°C for 3 hrs with occasional agitation. After cooling, 25ml of 3.2 M NH_4OAc in 20% (v/v) HNO_3 was added and the sample diluted to 130ml and agitated continuously for 30 minutes. The addition of the NH_4OAc is designed to prevent adsorption of extracted metals onto the oxidised sediment. A 20ml proportion of the supernatant was pipetted into 25ml polystyrene vials ready for ICP-OES analysis. The remaining mixture was then dried at 105 ± 2°C until constant weight and the residue collected for the final sequential extraction.

(v) Residual – a) Plastic. 69% HNO_3 and 70% perchloric acid ($HClO_4$). The residue (~0.5g, depending on treatment) from (iv) was transferred and digested in sealed teflon containers with 2ml of 69% HNO_3 on a hot plate set to 150 ± 2°C overnight. Perchloric acid (2ml) was then added to the mixture and again left overnight on a hot plate set to 150 ± 2°C. The mixture was then transferred to 25ml polystyrene vials and diluted to 10ml with milli-RO purified water ready for ICP-AES analysis.

All glassware used for the experiment was soaked and washed in 14% HNO_3 (v/v) and thoroughly rinsed with milli-RO purified water. All reagents used were of analytical grade and blanks were run for each batch of samples analysed. Samples were weighed and transferred to specially designed, fritted centrifuge tubes (glass, 30ml). Each tube was fitted with a filter or frit secured in the centre so that samples were retained within the apparatus therefore minimising solid material losses and also could be filtered by centrifuging. All centrifuging was carried out using an ALC multi-speed PK® 121 centrifuge with Annita II processing and control interface. The use of rinse water (50ml) was reserved to a minimum to evade unnecessary solubilisation of solid material, particularly organic matter. Trace metal analyses were carried out by ICP-OES and anion (fluoride, chloride, bromide, nitrate, phosphate and sulphate) identification by IC (see Chapter 2 analyses).

3.3 Results

Experimentation was initially conducted for the original amended treatments (Compost, BDA and ML), in their mixed states (1 part CLO to 3 parts amending material), but the relative standard deviations were found to be considerable. This was particularly true for the dichromate oxidation and sequential extraction procedures where smaller sample sizes were used (as can be seen below with BDA and ML treatments). Accordingly, characterisations of initial year samples were carried out on the raw materials in their original pre-mixed states. Calculations of mixed treatment (Comp, BDA and ML) values were then conducted using a correction ratio (mixer to CLO ratio of 3). Green compost refers to the raw materials of the Comp trial, and brick dust aggregate and magnesium limestone the BDA and ML treatments, respectively. The Parcgro treatment was the only material not requiring a correction ratio as this material was acquired already mixed (1 part CLO, to 1 part green compost and 1 part screened soils). Statistical analyses have been included in each section for ease of reading and are carried out as described previously in Chapter 2.

3.3.1 Moisture content

As can be seen in Table 3.1, the moisture contents of the raw materials varied greatly. The sewage sludge material contained the highest percentage, with 66.7% of the material (by weight) made up of water. The fresh CLO materials (CLO 2004, 2005 and 2006) and green compost all contained significantly higher proportions of water than a typical agricultural soil for the Durham region. Thus, it could be considered that amending an agricultural soil typical of that used here, with these materials would actively increase its moisture content. However, amending CLO with green compost, BDA and ML to make the mixed treatments (Comp, BDA and ML as described for the lysimeter trials in Chapter 2) would incur a reduction of this moisture content. In the case of the BDA and ML treatments, the overall moisture contents would be reduced to levels lower than that seen in the agricultural soil control (BDA – 14.5% and ML – 10%), and subsequently be considered unfavourable remediation materials. The extent of this is furthered by the relatively high standard deviation values recorded for these materials (0.7 and 0.4 which equate to 10.4% and 34.8% of the mean for BDA and ML, respectively). The Parcgro material displayed moisture contents analogous to that of the agricultural soil. It is also interesting to note that the mean moisture content of stock CLO samples collected in 2006 were roughly a third of those recorded for the fresh 2006 CLO. This demonstrates that, under field conditions (as stock CLO is windrowed outside at the Coxhoe landfill site), moisture is easily lost from CLO even at a depth of up to 3 meters. Stock samples were purposely collected from the surface (0-1m), mid region (1-2m) and base (2-3m) of the windrow pile in an attempt to minimise any surface effects, such as enhanced evaporation, as well as ensuring representative samples.

As mentioned above, amending an agricultural soil typical of that used for comparison here with any fresh CLO or Comp would initially increase overall moisture contents. However, field observations during lysimeter trials (Chapter 2) have shown that behaviour of the soil moisture retention properties over time and subsequent macropore cracking of CLO may potentially be detrimental.

Treatment/ raw material	Mean moisture content	Standard deviation
CLO 2004	36.6	2.0
CLO 2005	53.3	2.1
CLO 2006	37.2	1.2
Stock CLO 2006	12.9	1.3
Parcgro	19.2	1.4
Sewage sludge	66.7	1.4
Green compost	35.4	3.1
BDA	6.7	0.7
ML	1.1	0.4
Agricultural soil	16.6	1.6

Table 3.1: Mean moisture contents with standard deviations values for all treatments.

3.3.2 Water-pore volume calculations

Table 3.2 shows relative values by lysimeter and weight. The relative maximum pore volume estimation is based on material weight held in each lysimeter and is of most use in terms of comparing treatment values as it can be easily converted to a percentage value. The other columns have been included to illustrate the breakdown of the contributing factors and to gauge an idea of the extent of variation introduced by assessing material as a function of volume rather than weight.

The results show that there is a significant degree of variation between treatments ($P<0.01$) regarding relative maximum pore volumes, particularly between the mixed BDA and ML treatments and undiluted New CLO materials. The Comp treatment, due to its high absorbance levels in the field as well as its natural retainable moisture content, equates this material to pure CLO and sewage sludge treatments with respect to its overall water-accessible porosity.

It is also interesting to note the variation in moisture contents (above) reached by pure CLO treatments over the six hour period after being discharged from the aerobic digester to compaction into the lysimeters. Although CLO samples were obtained at similar times each year (first week of June), and compacting times and any other systematic and mechanical factors that could be, were controlled, moisture differences of 53.3%, 37.2% and 36.6% for CLO (2005), (2006) and (2004), respectively, were still evident. This exemplifies the inherent heterogeneous nature of CLO.

Treatment	**Lysimeter water-pore volume (ml)**	**Lysimeter moisture content (ml)**	**Maximum water-pore volume (ml)**	**Relative Maximum water- pore volume**
CLO (2005)	890	2798	3688	**0.69**
CLO (2006)	935	2522	3457	**0.65**
CLO (2004)	980	1148	2128	**0.40**
Parcgro	1270	1011	2281	**0.43**
Comp	1640	1807	3447	**0.65**
BDA	1110	726	1836	**0.34**
ML	1120	518	1638	**0.30**
Soil	1020	1328	2348	**0.44**
Sewage Sludge	480	4337	4780	**0.79**

Table 3.2: Lysimeter pore volumes (field capacity), moisture contents, maximum pore volumes and relative maximum water-pore volume by lysimeter weight.

Of most interest, however, was how treatment-related maximum pore volumes performed relative to the agricultural soil. The two New CLO treatments together with the Comp and sewage sludge treatments all gave considerably higher values (0.69, 0.65, 0.65 and 0.79, respectively) than the soil (0.44). The BDA (0.34) and ML (0.30) treatments were lower relative to the control; Parcgro (0.43) and original CLO (0.40) both compared similarly. The advantages and disadvantages of these results are discussed below. These three pore volume divisions were all statistically different ($P < 0.01$).

3.3.2.1 Discussion

Owing to interference from plant activity in attaining quantitative results for drainage ratio (Chapter 2), pore volume calculations were most likely to prove to be of relevance when examining soil retention properties. The maximum water pore volume is of particular relevance when examining water retention properties of CLO-containing treatments owing to its tendency to dry out quickly relative to normal soil. Field observations indicated that the occurrence of prolonged periods of dry field conditions, which caused both initial (because the lysimeters were all erected in warm June weather) and inter-dispersed dehydration to below original moisture levels held by the materials, when the lysimeters were first established. Accordingly, moisture contents at the time of mixing for the materials, as well as the proportions used for the remediation trials were taken into consideration when calculating maximum pore volumes to accurately represent the actual field conditions experienced.

The relative differences seen between the BDA and ML treatments and the remainder of the treatments can be explained by the very low moisture contents of the mixing materials; magnesium limestone (1.05%) and brick dust aggregate (6.66%). Even after mixing with CLO (2004), whose moisture content was 36.6%, the estimated maximum pore volumes still remained the lowest. This was most likely caused by the physical nature of the brick dust aggregate and magnesium limestone, both of which had a compact granular make up evidently not capable of absorbing or retaining a great deal of moisture, be it percolating rainfall or surrounding air moisture. However, by mixing 1 part CLO with 3 parts green compost the maximum pore volume is equal to values attained by undiluted CLO treatments. This was expected due to the fact that the compost proportion of the lysimeter core (75% by weight) was composed entirely of green compost rich in plant waters. These waters, once dehydrated, would not necessarily be able to absorb infiltrating rain waters, which in the context of effective porosity would be deemed immobile or dead-end pores. Thus, although initially improving the moisture retention properties, relative to an agricultural soil, the beneficial effects may not be long-lived after a number of wetting/drying phases have occurred, a parameter which could have been quantified if plant species had not proved such a complication in measuring drainage ratios. In hindsight, a possible better way to measure pore volume may be to have dried out the material completely before putting it into the lysimeters and then wetting-up to field capacity. This method would not be problem free, however, since the volume changes for certain treatments, in particular, CLO and sewage sludge treatments would be large. Furthermore, sewage sludge turns extremely hard and brittle once dried, and so compaction would cause considerable aggregate slaking, thus no longer accurately signifying its natural form in which it would be spread on agricultural land.

Both of the New CLO treatments, as well as the sewage sludge treatment showed a considerable increase in estimated pore spaces relative to the agricultural soil; this was assessed in two ways. Firstly, this could be seen to increase the potential for retaining soil moisture and thus offer vegetation a prolonged supply of water during warmer/drier times. Or secondly, and the more likely, based upon field observations and extensive handling of the materials, that during the onset of warmer/drier periods both materials lose any extra moisture they have retained to the atmosphere relatively quickly. This material drying encourages the formation of multiple cracks or fissures. The presence of cracks and extensive pore spaces has, on a number of occasions, been shown to both act and facilitate in the bypassing of water and contaminants through preferential flow pathways. Chemical tracers (Jury *et al.*, 1986 and Ritsema *et al.*, 1993) and dye tracers (Bouma *et al.,* 1977 and Flury *et al.,* 1994 and 1995) have experimentally shown that preferential or bypass flow is common place in a number of soil types, particularly in well-structured loamy to clayey soils. Furthermore, these studies highlighted how this phenomenon can lead to the efficient transport of pesticides and chemicals from the surface to groundwaters and corresponding depths (up to 0.9meters) below the root zone in loamy soils over a shorter time span than priori expected (Flury *et al.,* 1994 and 1995). Thus, this second scenario was detrimental from a soil moisture retention point of view, as water is lost quicker to the atmosphere as well as potentially bypassing the soil matrix (Edwards *et al.,* 1993) and plants roots, but also from a pollutant dispersal standpoint, with particular concern to groundwater contamination. Therefore, undiluted forms of CLO and sewage sludge alike have been shown to share similar susceptibilities to preferential flow and the detrimental effects this may bring, despite being almost completely physically unrepresentative of each other.

Limited evidence to support these observations was provided by preliminary dye-tracer experiments carried out using both the anionic dye Azo Geranine 2G (C.I. Acid Red 1) and Brilliant Blue FCF (C.I. Food Blue 2; C.I. 42090;N-Ethyl-N-[4-[[4-[ethyl[(3-sulfophenyl) methyl]amino]phenyl](2-sulfophenyl) methylene]-2,5-cyclohexadien-1-ylidene]-3-sulfobezenemethanaminium hydroxide inner salt, disodium salt; $C_{37}H_{34}N_2Na_2O_9\text{-}S_3$). These experiments, which were subsequently replaced by the pre-washing assessment, indicated that preferential flow patterns did indeed exist for both the undiluted CLO and sewage sludge treatments. Several cores were filled in the same manner to that carried out for the field lysimeters, brought to field capacity and then the dye was allowed to infiltrate freely until flushed out at the base of the lysimeter. Each dye tracer was carried out using both dyes on separate replicate lysimeters. The cores were then frozen to below -10°C and cross sections were cut every five centimetres along the entire length. Both matrix flow and preferential flow paths were identified for both treatments but the extent to which this occurred was not quantified. Further analyses involving chloride and pollutant break through curves would be required to confirm the effectiveness of preferential flow paths at transferring potential contaminants through these artificial soil mediums.

A final point relating to pore volume comparisons was that the CLO 2004, although displaying a similar susceptibility to preferential flow formation, provided an example of how the various batches of CLO produced by MSW aerobic digestion was ever changing and inherently heterogeneous in nature. The reason why the CLO 2004 had a relatively much lower estimated pore volume was because only 3 kilograms were able to be compacted into the lysimeters on their construction, whereas 5.25 kilograms each of the CLO 2005 and 2006 filled the 30cm length of tubing that made up the top half of the lysimeter. If equal amounts were used then the CLO 2004 maximum pore volume value would be calculated at 0.70, which would be analogous to the 0.65 and 0.69 figures achieved by the 2005 and 2006 digestates. The variation in these bulk densities can partly be explained by inevitable human error, but mainly by the fact that during the time of discharge of the original CLO Premierwaste were in the midst of improving from a 12mm screening regime to that of a 6mm one. Subsequently, the CLO 2005 and 2006 materials were both attained from a 6mm screened discharge.

3.3.3 Lysimeter pore volume flushes

A number of factors have been identified within this study that can affect the accuracy, and therefore the premise of using pore volume as a means of assessing dissolution behaviour over time. Stegemann et al (1995) showed, in a similar investigation into the leaching behaviour and performance of washing municipal solid waste incinerator (MSWI) bottom ashes, that pore volumes can be an effective tool for comparative analysis of two filled-in field based lysimeters. However, in this study the employment of nine different lysimeters, introduced at varying times, each comprising different weights of material, demonstrating very different pore volumes, and the significant presence of cracks and fissures, as well as the presence of varying vegetation cover, deemed pore volume relations over time unbeneficial. Furthermore, if maximum pore volumes for each lysimeter were to be used, then as little as 1-2 pore volumes could be assessed for a number of treatments (undiluted CLO's and sewage sludge). The existence of a number of cracks in all of the undiluted materials indicated bypassing of soil matrices, via preferential macro-porous pathways, would also suggest that pore volume relations may not be of as much relevance as collecting all available leachates and interpolating that data for periods when none had been leached. Thus, the evaluation of *incremental* leachate fluxes over time as a function of the leachate volumes collected, as opposed to just time proved to be uninformative.

a)

Treatment	Cumulative leachate	Maximum pore volume	No. of pore volumes
New CLO 2005	8011.3	3688	2.2
New CLO 2006	8663.7	3457	2.5
Parcgro	8923.2	2281	3.9
Sewage Sludge	4733.8	4780	1.0
Original CLO	9783.3	2128	4.6
Comp	8913.3	3447	2.6
BDA	10146.9	1836	5.5
ML	11143.9	1638	6.8
Soil	9238.9	2348	3.9

b)

Treatment	Cumulative leachate	Maximum pore volume	No. of pore volumes
Original CLO	17466.2	2128	8.2
Comp	16505.0	3447	4.8
BDA	17126.5	1836	9.3
ML	17194.3	1638	10.5
Soil	19286.8	2348	8.2
Sewage Sludge	13408.6	4780	2.8

Table 3.3: Compares numbers of total lysimeter pore flushes experienced over a) 1 year study and b) 2 year study.

However, in relation to *yearly* comparisons between treatments the number of pore volume flushes each lysimeter experienced proved more useful. The field lysimeter trials demonstrated practically the flushing behaviour that would occur if the materials were utilised in agriculture. Therefore, as the number of pore volumes varies greatly for each respective material (Table 3.3) the theoretical volumes of rainwater that are required to flush equal amounts of solutes and contaminants, also varies.

For example, the base cation Mg, takes roughly a year to meet MAC's allowed for drinking water extraction (50mg/l) in the three mixed treatments (Comp, BDA, ML) and the sewage sludge. To reach this point, 2.5, 5.5 and 7 pore volumes for the mixed treatments, respectively were leached, but only 1 pore volume flush was needed to reduce sewage sludge leachates to the same level. These equate to 8913, 10146, 11143 and 4733ml of leachate, respectively. Thus, in itself the sewage sludge produced far less leachate comparative to the CLO associated soils is an environmentally beneficial property. However, this does not take into account the relative initial leached concentrations of Mg for each treatment. In this case the mixed CLO treatments initial flushes were 2 to 2.5-fold higher than that of the sewage sludge, and so for Mg, greater concern should be placed on the CLO containing treatments as opposed to the sewage sludge. Theoretically, however, for elements with similar initial contamination levels for all treatments, the time necessary to attain an environmentally accepted leachate standard could be much greater for the sewage sludge. The time over which this occurred would depend on a number of factors, such as elemental solubility, adsorption strength and initial concentration, but leachate volumes would inevitably increase, thus compromising the aforementioned benefit. These findings will not be true for all elements; for example Zn, where levels already reside below the maximum level enforced by the government for the original CLO and its mixed associates, but proved to be a persistent problem for sewage sludge irrespective of the time/flush volumes used.

Generally, however, the inherent inability of the CLO associated soils to retain moisture or encourage macropore flow via physical cracking or the sewage sludge's capability to effectively absorb rainfall and thus produce less leachate, clearly underlines a treatment difference. Whether this difference in behaviour is deemed environmentally favourable or not, depends upon a number of factors, including the initial dissolved concentrations and adsorption properties of both contaminants and solid materials from which the various leachate components were sourced. As it turns out, at the levels of contamination seen in all CLO leachates, active adsorption had been shown to be a relatively ineffective process at suitably reducing contamination levels. As a result of these findings an experiment was devised in the hope of reproducing better quality CLO materials with respect to their leachability, after they had been washed with tap water. This could prove to be an important remediating factor if efforts concentrate on the pre-washing of the CLO before it was utilised on the field. Because the contaminants that have been seen to be leached from the composted MSW products have little or no value, the development of a cost effective extraction method may be useful. This entailed the use of as little water as possible and was reason for the use of tap water as opposed to purified water. From an environmental standpoint, the CLO containing treatments with their relatively lower pore volumes, display the potential to be 'stabilised' by using a lower liquid/solid (L/S) than would be the case for sewage sludge. A lower total volume of water necessary to achieve the same standard of solid material component leachability, would also prove beneficial. When considering the annual cumulative quantities of waste processed by the aerobic digesters a saving of up to 60,000 litres of water could be achieved if an L/S 2 was attained rather than L/S 3. Therefore, this practice could selectively remove the contaminant fractions of environmental concern; both salt and metal species, as well as minimise relative leachate consumption. The same natural leaching process that is so detrimental in the field could therefore be manipulated, potentially reducing certain contaminant levels sufficiently so that CLO can then be diluted in the same way that has been seen here but with little of the environmental risk (Chapter 4).

3.3.4 pH

Mean pH values were attained from 4 replicate readings for the original year samples and 9 replicates for consecutive years (i.e., 3 replicates per treatment lysimeter); the results of which together with their standard deviations are shown in Table 3.4 below. pH readings were undertaken on the mixed treatments as opposed to the raw materials and so no correction ratio was needed. Here, years refer to lengths of time under field conditions, as opposed to actual study years themselves for comparison purposes. The results are also illustrated graphically in Figure 3.1. It can be seen that all CLO containing materials display alkaline values throughout. In contrast, the agricultural soil and sewage sludge materials remain weakly acidic over the 3 years of study. Unlike observations during the field lysimeter studies (Chapter 2) it is the upper pH drinking water maximum admissible concentration ((MAC) - pH 9.5) that is exceeded, and this is by the remediation treatment BDA. A maximum pH level of 10.09 (±0.22) was attained for this material in its original pre-experimentation state. It must be noted that this material displayed the largest standard deviation of any treatment (±0.48), but this was still within 5% variation of the mean. The only other treatment to breech drinking water guideline levels (GL) was the sewage sludge after 2 years in the field, which attained an acidic pH level of 6.38 (±0.16) which falls below the lower GL of pH 6.5.

Treatment	Original pH	St. dev.	1st year pH	St. dev.	2nd year pH	St. dev.	3rd year pH	St. dev.
CLO 2004	7.46	0.01	8.10	0.05	7.71	0.02	7.48	0.03
Comp	7.59	0.01	7.79	0.06	7.49	0.03	7.25	0.03
BDA	10.09	0.22	8.65	0.02	8.91	0.20	9.25	0.48
ML	7.70	0.01	8.21	0.04	7.94	0.02	7.75	0.10
Soil	6.90	0.11	6.97	0.08	6.63	0.11	6.86	0.01
CLO 2005	7.52	0.12	7.76	0.35				
CLO 2006	7.39	0.19	7.61	0.09				
Parcgro	7.75	0.12	7.67	0.08				
Sewage sludge	6.72	0.11			6.38	0.16		
Blank	5.80	0.02	5.75	0.04	5.80	0.03	5.87	0.13

Table 3.4: Mean pH values and their relative standard deviations for all treatments.

Meaningful comparisons over time can only be performed for the 3 year study treatments: CLO 2004, Comp, BDA, ML and agricultural soil, as only one year of pH values (i.e., 2 recordings) were obtained for the remaining treatment materials. It can be seen from Figure 3.1 that similar behaviours existed with time for the CLO 2004, Comp and ML treatments. The agricultural soil's pH behaviour also followed this decreasing trend for the first two years of study, but unlike CLO containing materials, 3rd year levels are elevated relative to 2nd year levels. In contrast, the BDA treatment exhibits an opposing behaviour, with 1st year pH levels being reduced relative to initial levels followed by a gradual rise in pH from thereon. It is worth mentioning that although care was taken in replicating representative samples of the mixed treatments (with particular relevance, BDA and ML) the relatively high alkaline pH's of the raw materials used as amendments (BDA – 10.70 ±0.02 and ML - 9.21 ±0.01, not shown here) may in themselves increase potential error. The high pH's seen for these mixer materials in conjunction with their fine grained nature, both proved limiting in attaining representative treatment samples.

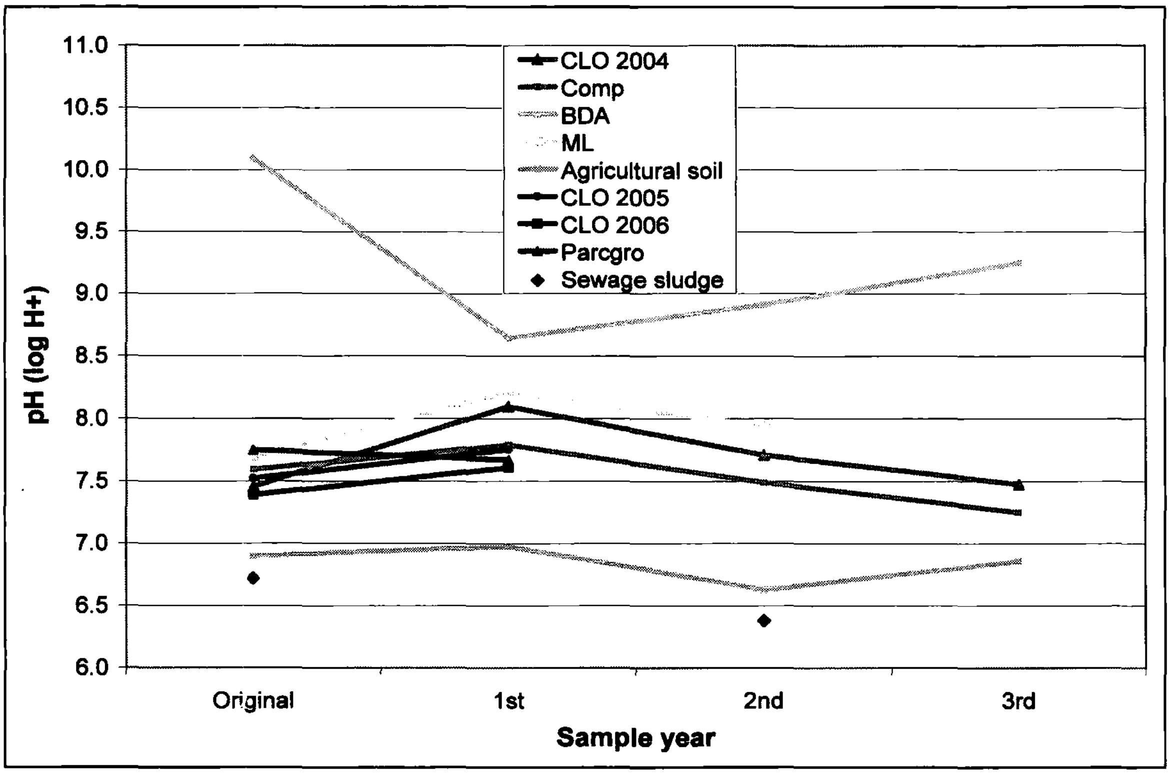


Figure 3.1: Mean treatment pH fluctuations over time.

Table 3.5 summarises significant differences between yearly samplings, and to what degrees of confidence (p-value) these differences can be statistically proven (tick colour). With respect to treatment analysis of variance the BDA and sewage sludge treatments are significantly different to the other treatments over all years. This was also true for the agricultural soil treatment except that no significant difference lies with the compost treatment in the 3rd year of study. BDA values were always significantly more alkaline and sewage sludge and soil values were acidic. The only other relevant significant differences were those seen for the ML treatment which displayed significantly higher pH values than both Comp and CLO 2004 treatments after the 2nd year of study.

With respect to between year variations it can be seen from Table 3.5 that the CLO 2004 and Comp treatments were both statistically different for each year of study ($P < 0.00001$). BDA and ML treatment pHs were predominantly variable with time except for between year 1 and 2, and 2 and 3 for the BDA trial and between initial and final pH's for the ML trial. Although pH levels were only measured for initial and 2 year old sewage sludges, a significant difference ($P<0.006$) was found between these two sets of readings. The New CLO's (2005 and 2006), Parcgro and agricultural soil treatments did not show any statistical significance between years.

Treatment	Year					
	Orig - 1st	Orig - 2nd	Orig - 3rd	1st - 2nd	1st - 3rd	2nd - 3rd
CLO 2004	✓	✓	✓	✓	✓	✓
Comp	✓	✓	✓	✓	✓	✓
BDA	✓	✔	✔		✔	
ML	✓	✔		✔	✓	✔
SS		✔				

Table 3.5: pH significant differences between treatment and year. ✓ - (P<0.00001) ✔ - (P<0.0001), ✓ - (P<0.001) and ✓ - (P<0.01).

3.3.4.1 Discussion

The results presented here indicate CLO materials of this nature (limited data for CLO 2005 and 2006 and Parcgro trials cannot statistically confirm this) have alkaline pH values, which, when exposed to acid rainwaters, persist for up to 3 years after exposure. These levels are in agreement with drinking water guidelines and are therefore considered to be of environmental importance. Dilution of the CLO with BDA or ML increased overall solid pH status, particularly for BDA, but despite an initial increase in pH mixing the CLO with green compost decreased overall pH. Determination of pH on fresh green compost waste (pH 8.26 ±0.03) indicated higher alkalinity levels than in the fresh CLO. These observations suggest that (from a purely remediation of pH point of view) mixing the CLO with green compost wastes will neutralise the material more effectively than amending it with BDA or ML. This is thought to be as a result of the break down of OM held within the green compost and the subsequent production of decomposition acids and thus reduction in overall buffering capacity. Whether this is beneficial relative to the release behaviours and concentrations of metal species, and other potential contaminants or whether alkaline conditions would be more favourable, as experienced for BDA and ML treatments, has been assessed in Chapter 2. Weakly alkaline pH levels in both solids and in leachates are considered to be environmentally favourable. It must be noted however, that amending the CLO with BDA does generate initial alkaline pH values that contravene MACs for drinking and surface waters as set out in government legislation. Sewage sludge materials raised similar concerns at the other end of the pH spectrum by exhibiting acidic pH's (< pH 5.5) that are below government GLs for drinking and surface water and so would not be suitable for extraction for human consumption.

Finally, although weakly acidic pH levels have been recorded for the agricultural soil throughout the 3 years of study, the pattern in which these levels have been achieved is different from those exhibited by the CLO containing treatments. The CLO 2004, Comp and ML trials showed gradual decrease in pH over the last 2 years of the study which would be in agreement with the addition of H^+ from acid rainwaters. This behaviour may therefore indicate that these mixed treatments, together with the undiluted CLO, have a lower buffering capacity than if the aerobically digested MSW is amended with brick dust aggregates. Furthermore the mixing of the CLO with BDA appears to actively increase the pH of the overall material for the last 2 years of the study. In contrast, the agricultural soil's behaviour displays a fluctuation in pH rather than a consistent increase or decrease; the overall scale of which is much smaller (±0.34). pH level fluctuations shown for the CLO containing treatments are nearly double this.

3.3.5 Carbon characterisation

The following results characterise the various carbon contents of each treatment (as well as the raw materials in the mixed treatments) by using the LOI and titration procedures described above. The results vary greatly between treatment, sieved and un-sieved samples and with time (years). The significant differences found with time however, could not be directly attributed to bulk carbon losses owing to the fact that the weight of each lysimeter core material was not known after the termination of each study year. The weight reductions, as a result of the large amounts of metal salts leached from each lysimeter system (for example, up to 3.69% (w/w) of the CLO 2005 treatment can be accounted for by metal salt flushes) resulted in higher recorded carbon percentages. This was particularly relevant for between year percentage changes in black/refractory carbon at LOI temperature 600 °C, where recorded values were substantially lower than for OM at LOI 375 °C and so the effect was enhanced giving elevated carbon contents for subsequent years. Accordingly, a separate section concerning mass balance carbon storage is included after the initial stage carbon characterisations (i.e., materials in their original state before transferral into the lysimeters).

3.3.5.1 LOI

Figure 3.2 illustrates the raw percentage weight losses (carbon) for all treatments at LOI $_{375}$, LOI$_{600}$ and LOI$_{900}$ °C. For the mixed treatments, Comp, BDA and ML the raw mixer material (green compost, brick dust aggregate and magnesium limestone) carbon percentages have also been included. Un-sieved samples have been removed from Figure 3.2 but mean values along with their standard deviations for all treatment percentage weight losses can be seen in Table 3.7, below. Table 3.7 highlights the heterogeneity of the CLO containing materials, particularly for the un-sieved samples, comparative to the agricultural soil control and the sewage sludge material. However, the maximum standard deviation for the sieved samples, seen for the CLO 2006 material, was still relatively low, lying at 2.17, which equates to a 3.66% deviation about the mean value recorded at LOI $_{375}$ °C. Sieved/un-sieved samples were further assessed later. The undiluted CLO materials can be seen to contain similar amounts of organic matter (~50-60%) to that of the sewage sludge material (~53%) - the sewage sludge treatment OM values are not significantly different from the CLO 2004 and 2005 (Table 3.6).

It is worth noting, however, that the CLO 2006 material contained a markedly higher amount of OM ($P< 0.0001$); containing on average, 8%, 7% and 6% more than the CLO 2004, CLO 2005 and sewage sludge materials, respectively. The mixed CLO containing treatments had significantly lower OM ($P< 0.00001$) values than the pure CLO's they were formed from giving mean contents decreasing in the following order: Comp (26.70%) >> BDA (22.56%) >> ML (21.47%) > Parcgro (21.17%). The raw mixer materials, which were used in an attempt to remediate the CLO, have in fact decreased its favourable high OM content, and in the case of BDA, ML and Parcgro mixed treatments the amendments were less than half the CLO's value. However, in comparison with the agricultural soil (mean OM content of 6.5%), the organic matter contents of all other treatments were significantly higher ($P< 0.00001$).

Significance values at LOI_{375}, LOI_{600} and LOI_{900} °C can be seen respectively in tables 3.6, 3.8 and 3.9, below.

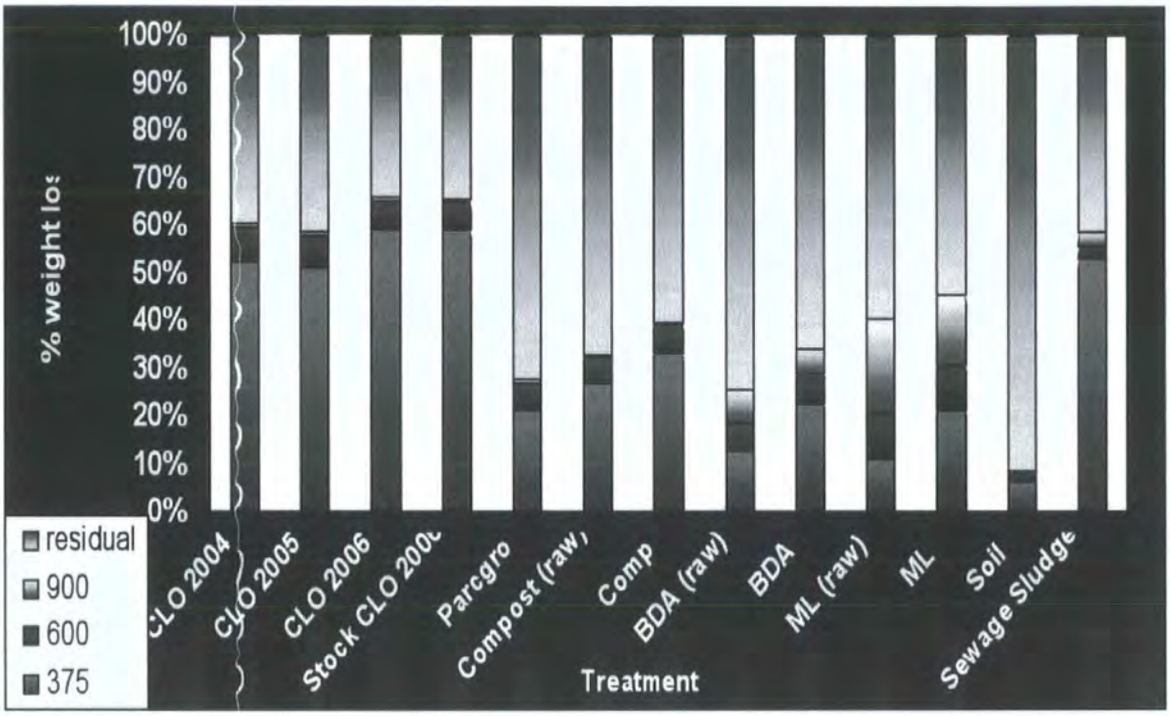


Figure 3.2: Percentage weight loss at LOI_{375}, LOI_{600} and LOI_{900} for each treatment, as well as for raw materials used in the mixed trials.

375 °C	CLO 2004	CLO 2005	CLO 2006	St.CLO 2006	Parcgro	Comp	BDA	ML	Soil	Sewage Sludge
CLO 2004	-	NS	0.00001	0.00001	0.00001	0.00001	0.00001	0.00001	0.00001	NS
CLO 2005		-	0.00001	0.00001	0.00001	0.00001	0.00001	0.00001	0.00001	NS
CLO 2006			-	NS	0.00001	0.00001	0.00001	0.00001	0.00001	0.00001
Stock				-	NS	0.00001	0.00001	0.00001	0.00001	0.00001
Parcgro					-	0.00001	0.00001	0.00001	0.00001	0.00001
Comp						-	0.00001	0.00001	0.00001	0.00001
BDA							-	NS	0.00001	0.00001
ML								-	0.00001	0.00001
Soil									-	0.00001
SS										-

Table 3.6: Treatment significance values at LOI temperature 375 °C. NS = not significant.

At LOI_{600} °C (Figure 3.2 and Table 3.7) the pattern between treatments changed. The amount of carbon, by weight, associated as being black or refractory, as calculated at 600 °C, is below 12% for all treatments. The calculation of percentage black carbon (BC) as a function of sample weight has been used instead of presenting values as a percentage of TOC (as calculated from titration experiments) because, as can be seen from Figure 3.3 the BDA and ML treatment BC levels exceed TOC values. This maybe as a direct result of using a LOI temperature of 600 °C to determine BC contents; partial breakdown of less stable carbonate minerals or more thermally stable macromolecular organic matter (Schmidt *et al.*, 2000) may also have occurred at this temperature, thus artificially increasing the BC values. Alternatively, BC may be considered a separate form of carbon, elemental, and so should not be taken as a proportion of TOC but in fact of total carbon (TC).

The largest standard deviations (>1-2%) at LOI_{600} were recorded for the BDA and ML treatments; both in their mixed and raw states. The occurrence of these higher standard deviations in both raw and mixed materials eliminates the process of mixing to be the source of error and so it is more likely to be as a result of the LOI temperature of 600 °C allowing some form of inorganic carbon to be uncontrollably demineralised. Hieri et al (2001) stressed that at a LOI temperature of 550 °C the loss of inorganic carbon from minerals such as siderite, magnesite and rhodochrosite can occur causing greater estimations of BC to be recorded. Subsequently, the ML treatment BC mean percentage (both raw material (9.51%) and as a mixed treatment (9.00%) was significantly higher ($P< 0.012$) than all other CLO containing treatments (and the raw BDA and Comp materials) (~5.5-7%), as well as that of the sewage sludge (2.47%) and agricultural soil (1.83%). The percentage BC contents calculated for the soil ($P< 0.00001$) and sewage sludge ($P< 0.0003$) were statistically lower than all other treatments but were not significant from each other.

The undiluted 2004 and 2005 CLO's displayed marginally elevated refractory carbon percentage values (mean values of 7.46% and 7.00%, respectively) relative to that seen in the 2006 digestate (4.71%). This, in conjunction with the findings at LOI_{375} °C, indicate that the newer CLO (2006) comprised greater OM contents but smaller percentages of refractory/black carbons relative to its predecessors (CLO 2004 and 2005). Unlike with OM records therefore, there was little difference seen at LOI_{600} between undiluted and mixed CLO treatments (except ML) and similarly between the original mixed treatments (Comp, BDA and ML) and their raw amending constituents.

Treatment / raw material	% loss at 375	St. dev.	% loss at 600	St. dev.	% loss at 900	St. dev.	Titration TOC %	St. dev.
CLO 2004	52.16	1.13	7.46	0.30	0.62	0.11	17.29	1.87
CLO 2005	50.91	1.07	7.00	0.17	0.95	0.08	17.42	0.59
CLO 2006 (un-sieved)	60.54	4.59	4.71	0.53	0.65	0.16	NA	NA
CLO 2006	59.06	2.17	6.10	0.24	0.75	0.15	19.13	1.65
Stock CLO 2006 (un-sieved)	65.70	2.88	4.08	0.69	0.74	0.03	NA	NA
Stock CLO 2006	59.02	1.62	5.99	0.31	0.69	0.03	NA	NA
Parcgro (un-sieved)	25.24	5.41	3.43	0.09	0.78	0.61	NA	NA
Parcgro	21.17	0.87	5.67	0.20	0.65	0.04	6.22	0.15
Compost (raw)	26.70	1.46	5.72	0.26	0.53	0.20	8.08	0.55
Comp	33.07	1.09	6.16	0.19	0.55	0.15	10.59	0.07
BDA (raw)	12.69	1.41	6.00	1.52	6.81	1.76	0.57	0.06
BDA	22.56	1.06	6.36	1.14	5.26	1.32	4.95	0.09
ML (raw)	11.24	0.28	9.51	1.77	19.66	1.92	0.55	0.07
ML	21.47	0.21	9.00	1.33	14.90	1.44	4.94	0.06
Soil	6.49	0.16	1.83	0.05	0.33	0.05	1.85	0.13
Sewage Sludge	53.17	0.29	2.47	0.08	2.97	0.13	16.06	0.12

Table 3.7: Treatment mean values, with standard deviations, for LOI and titration results for materials in their initial states.

Original	CLO 2004	CLO 2005	CLO 2006	Stock CLO	Parcgro	Comp	BDA	ML	Soil	Sewage Sludge
CLO	-	NS	NS	NS	NS	NS	NS	0.012	0.00001	0.00001
CLO		-	NS	NS	NS	NS	NS	0.001	0.00001	0.00001
CLO			-	NS	NS	NS	NS	NS	0.00001	0.00001
Stock				-	NS	NS	NS	0.0001	0.00001	0.00001
Parcgro					-	NS	NS	0.00001	0.00001	0.0003
Comp						-	NS	0.00001	0.00001	0.00001
BDA							-	0.00001	0.00001	0.00001
ML								-	0.00001	0.00001
Soil									-	NS
SS										-

Table 3.8: Treatment significance values at LOI temperature 600 °C. NS = not significant.

When considering the results found at LOI_{900} °C (Figure 3.2 and Table 3.7) it was clear that the primary observation was the elevated carbonate contents of the raw magnesium limestone, both in its raw (mean - 19.66%) and mixed states (ML mean – 14.90%). The raw brick dust aggregate and mixed treatment (BDA) also showed values elevated relative to the other treatments (mean values of 6.81% and 5.26%, respectively). These concentrations were both statistically significant from the other treatments ($P< 0.00001$) and understandably the raw results gave higher inorganic C percentages than when they were mixed with the more inorganic carbon-depleted CLO. Secondly, it can be seen that there was a lack of variation between the undiluted CLO treatments and the Comp (and its raw green compost constituent) and Parcgro treatments. All these treatments have been shown to comprise less than 1% inorganic carbon. The agricultural soil displayed similar low carbonate contents, averaging at 0.33%. Sewage sludge samples were statistically different ($P < 0.03$) from all other treatments, displaying carbonate contents close to 3%.

Original	CLO 2004	CLO 2005	CLO 2006	Stock CLO	Parcgro	Comp	BDA	ML	Soil	SS
CLO	-	NS	NS	NS	NS	NS	0.00001	0.00001	NS	0.0074
CLO		-	NS	NS	NS	NS	0.00001	0.00001	NS	0.033
CLO			-	NS	NS	NS	0.00001	0.00001	NS	0.049
Stock				-	NS	NS	0.00001	0.00001	NS	0.039
Parcgro					-	NS	0.00001	0.00001	NS	0.03
Comp						-	0.00001	0.00001	NS	0.0047
BDA							-	0.00001	0.00001	0.00001
ML								-	0.00001	0.00001
Soil									-	0.0018
SS										-

Table 3.9: Treatment significance values at LOI temperature 900 °C. NS = not significant.

3.3.5.2 Carbon storage

As mentioned above the assessment of carbon losses over time required a weight adjustment based on total component (metal salts) fluxes per field lysimeter. Over each year the total fluxes of elemental and anion leachates (mg/kg) were calculated for each lysimeter; this derived a percentage correction factor which could then be applied to the respective LOI value for each year of study, in turn. The calculated weight losses during the LOI experiments could then be related over time. Table 3.10 shows the mean corrected data for each treatment over time (years) at LOI temperatures; 375 °C, 600 °C and 900 °C. Statistically significant differences between years as a function of treatment have been summarised below in Table 3.11.

The primary findings of interest here were concerned with the losses of OM content recorded at LOI_{375} °C for the treatments containing CLO. These treatments have been shown above to contain significantly greater quantities of organic material relative to an agricultural soil typical of the Durham region, but were not significantly different in content from the sewage sludge material. It can be seen here that for the undiluted CLO treatments (2004, 2005 and 2006), a significant ($P<0.01$) proportion of this organic matter was lost during the first year (either as CO_2 or as DOC); 65.04%, 73.83% and 66.49% of the OM originally present has been stored, respectively. The

Comp and Parcgro trials; both of which contain at least 33% green compost waste and in the case of the Parcgro soil product, screened soils also, both give stored OM percentages, after the first year of study, analogous the undiluted CLO's; Comp – 69.55% and Parcgro – 72.84%. The Parcgro losses were indeed significant ($P<0.00001$) but the Comp trial losses between initial OM status and that seen after 1 year of exposure were not. So, although initial OM contents were significantly lower than undiluted CLO contents (as shown above) the relative percentage losses were of comparable amounts. However, when the CLO was diluted with brick dust aggregate and magnesium limestone (BDA, ML), not only were the initial OM contents significantly reduced relative to undiluted CLO but the percentages stored were also significantly ($P<0.00001$) decreased over the first year of exposure; BDA – 31.38% and ML – 29.90%.

Treatment	Year	LOI$_{375}$ °C	St. dev.	LOI$_{600}$ °C	St. dev.	LOI$_{900}$ °C	St. dev.
CLO 2004	**Orig**	52.16	1.13	7.46	0.30	0.62	0.11
CLO 2004	**1st**	33.93	0.38	9.32	0.30	1.51	0.19
CLO 2004	**2nd**	32.83	1.68	11.17	0.40	1.97	0.15
CLO 2004	**3rd**	29.79	0.96	8.64	0.40	2.59	0.17
Comp	**Orig**	33.07	1.09	6.16	0.19	0.55	0.15
Comp	**1st**	23.00	0.92	5.42	0.22	0.99	0.12
Comp	**2nd**	21.91	0.99	6.64	0.35	1.41	0.12
Comp	**3rd**	20.26	0.48	6.24	1.49	2.47	0.33
BDA	**Orig**	22.56	1.06	6.36	1.14	5.26	1.32
BDA	**1st**	7.08	0.59	5.35	0.22	7.95	0.79
BDA	**2nd**	6.92	0.72	6.18	0.65	8.25	0.53
BDA	**3rd**	6.12	0.97	4.28	0.27	9.99	0.76
ML	**Orig**	21.47	0.21	9.00	1.33	14.90	1.44
ML	**1st**	6.42	0.51	5.01	0.08	27.10	0.70
ML	**2nd**	6.87	0.52	8.86	0.74	20.47	1.28
Soil	**Orig**	6.49	0.16	1.83	0.05	0.33	0.05
Soil	**1st**	6.88	0.12	1.68	0.03	0.39	0.02
Soil	**2nd**	6.01	0.35	3.01	0.47	0.36	0.03
Soil	**3rd**	5.59	0.14	2.51	0.05	0.33	0.02
SS	**Orig**	53.17	0.29	2.47	0.08	2.97	0.13
SS	**2nd**	46.92	2.81	3.70	0.19	1.87	0.08
CLO 2005	**Orig**	50.91	1.07	7.00	0.17	0.95	0.08
CLO 2005	**1st**	37.59	2.49	6.89	0.26	2.00	0.45
CLO 2006	**Orig**	59.06	2.17	6.10	0.24	0.75	0.15
CLO 2006	**1st**	39.27	1.82	8.23	0.67	3.11	0.17
Parcgro	**Orig**	21.17	0.87	5.67	0.20	0.65	0.04
Parcgro	**1st**	15.42	0.75	6.34	0.41	4.32	0.93

Table 3.10: Mean adjusted LOI percentage weight losses together with their respective standard deviations for all treatments over time (years).

The sewage sludge retained, on average, 88.24% of its initially high OM content (53.17%); this being over a two year period of exposure. Losses after 1 year of exposure were not available for sewage sludge but it can clearly be seen that, although a significant difference ($P<0.0001$) existed between initial year and 2 year OM contents, the rate at which OM was lost from sewage sludge relative to CLO containing treatments is significantly ($P<0.00001$) lower. The agricultural soil actually displayed a carbon increase over the first year of study but from then on a gradual decrease averaging at 10% OM loss per annum was established. The sewage sludge treatment has been shown therefore to be extremely favourable with respect to its carbon storage over time, relative to all CLO-containing treatments, and the agricultural soil itself.

Treatment	**Year**					
375°C	**Orig - 1st**	**Orig - 2nd**	**Orig - 3rd**	**1st – 2nd**	**1st - 3rd**	**2nd - 3rd**
CLO 2006	✓	NA	NA	NA	NA	NA
CLO 2005	✓	NA	NA	NA	NA	NA
CLO 2004	✓	✓	✓			✓
Parcgro	✓	NA	NA	NA	NA	NA
Comp		✓	✓		✓	✓
BDA	✓	✓	✓			
ML	✓	✓	NA		NA	NA
Soil		✓	✓	✓	✓	✓
SS	NA	✓	NA	NA	NA	NA
600°C						
CLO 2006	✓	NA	NA	NA	NA	NA
CLO 2005	✓	NA	NA	NA	NA	NA
CLO 2004	✓	✓	✓	✓	✓	✓
Parcgro	✓	NA	NA	NA	NA	NA
Comp		✓		✓		✓
BDA			✓		✓	✓
ML	✓		NA	✓	NA	NA
Soil		✓	✓	✓	✓	✓
SS	NA	✓	NA	NA	NA	NA
900°C						
CLO 2006	✓	NA	NA	NA	NA	NA
CLO 2005	✓	NA	NA	NA	NA	NA
CLO 2004	✓	✓	✓	✓	✓	✓
Parcgro	✓	NA	NA	NA	NA	NA
Comp	✓	✓	✓	✓	✓	✓
BDA		✓	✓		✓	✓
ML	✓		NA	✓	NA	NA
Soil	✓				✓	
SS	NA	✓	NA	NA	NA	NA

Table 3.11: Summary of significant differences found between treatments over time (years) for LOI temperature 375°C, 600°C and 900°C. ✓ - ($P< 0.00001$), ✓ - ($P<0.0001$), ✓ - ($P<0.001$) and ✓ - ($P<0.01$). NA = Not applicable.

3.3.5.2.1 Discussion

Characterisation of the carbon contents of the various treatment materials in this way has revealed a number of key points. Firstly, the high organic matter contents (50-60%) of the undiluted CLO's are of central environmental importance, particularly for the interests of utilising the CLO as a basis for bio-fuel production. The presence of organic matter not only acts as a vital supply of nutrients to plants but it is known to complex a number of metal contaminants, rendering them insoluble and bio-unavailable. Undiluted CLO organic matter contents were of a similar value to the sewage sludge treatment, and were both significantly higher than levels found in the soil control. Thus, with respect to a typical agricultural soil for the Durham region, the CLO materials (and mixed treatments) would favourably increase the overall SOM content but this increase was not significantly different from that achieved by sewage sludge, and in the case of the mixed treatments, detrimental.

In terms of the storage of carbon over time the CLO, and particularly its associated soil products (BDA and ML), do not perform as favourably as sewage sludge. Firstly, it appears that the CLO material is particularly unstable with respect to OM, typically losing 25%-35% of its OM content after one year of weathering. This would suggest that complete curing of the composted MSW (CLO) has not occurred and indeed in-situ curing may well have taken place after the establishment of freshly discharged CLO in the field lysimeters.

Secondly, mixing the CLO material with 3 parts BDA or ML has significantly decreased the overall OM content, as well as significantly increasing carbon losses over time. The green compost waste amending material (used in the Comp and Parcgro treatments) appeared to perform the best out of the mixed treatments with respect to overall OM content but the percentage reduction on mixing relative to pure CLO was still around 20% for the Comp trial and 30% for the Parcgro material. The BDA and ML mixed treatments reduced the overall OM content by more than 50% deeming them unfavourable amending materials with regard to soil organic matter contents. Amending the CLO in this way was therefore considered to be of detriment with respect to carbon storage. In contrast, the sewage sludge appeared as stable, if not more stable, than the agricultural soil with respect to temporal carbon losses. These findings highlight a distinct difference between the CLO material and the sewage sludge, which, from an agronomic and environmental point of view, favours that of the sewage sludge material.

It must be remembered, however, that the CLO is relatively immature with respect to OM and the lysimeter trials themselves are likely to encompass a large degree of disturbance, therefore enhancing carbon losses. This will be particularly relevant with the mixed treatments (Comp, BDA, ML and Parcgro) which were not only compacted into the lysimeters like all treatments but in addition underwent substantial agitation during the mixing process. Efforts to minimise this mechanical error were undertaken by using similar compaction regimes but inevitable variation between treatments was unavoidable.

The BDA, and particularly the ML treatments, contained significantly higher amounts of carbonates than all other treatments, but of specific importance were the higher values comparative to the undiluted CLO treatments and the sewage sludge. The presence of carbonates is considered to be a favourable characteristic owing to their ability to act as an effective pH buffer; elevating both leachate (Chapter 2) and solid pH's (above) to weakly alkaline levels. By maintaining these alkaline conditions, the release of significant quantities of potential metal contaminants into the soluble phase has been prevented. In the following chapter, comparison of pre-washing metal releases with those observed from steps 1 and 2 of the sequential extraction procedure showed that substantial amounts of metal species are released into solution under acidic conditions (step 2), especially for the BDA treatment (this will be assessed later). Thus, a compromise is paradoxically induced by mixing the CLO with brick dust aggregate or magnesium limestone; in order to achieve elevated pH levels of satisfactory alkalinity the OM matter content is diminished.

Finally, with regard to refractory/black carbons, all of the CLO containing treatments, as well as the raw amending materials, contained significantly higher percentages than both the agricultural soil ($P< 0.00001$) and sewage sludge ($P<0.0003$). Bio-mass derived black carbon (BC) may play an important role in adsorption reactions and with particular relevance to this study, the adsorption of base cations from solution onto the solid phase (Schmidt *et al.,* 2000 and Lehmann *et al.,* 2003). Lehmann showed that for Brazilian Anthrosols, containing higher proportions (up to 51% of the TOC) of BC's relative to adjacent non-rich BC soils, the oxidation of surface functional groups, such as carboxyl organic ligands (i.e., COO^-) on BC particles caused a net negative charge across the soil surface. This accommodated a higher CEC per unit C as well as a higher charge density in the BC-rich Anthrosols compared to the BC-poor adjacent soils. The BC also increased the surface area and so the presence of BC was considered to be an efficient means of providing CEC and cation retention in the studied soils. Czimezik and Masiello (2007) have recently further hypothesized that it was the presence of these reactive carboxyl functionalities in conjunction with the unique refractory aromatic cores that allowed the BC to be stabilised by interaction with the mineral phases of soils. Scanning electron microscope analyses by Brodowski et al (2005) were in agreement with this partially oxidised BC-mineral surface interaction. Metal cations on surface minerals include Ca^{2+}, and Al and Fe oxyhydroxides (Czimezik and Masiello, 2007).

Thus, the 3-fold elevated BC contents found at LOI 600 °C for all CLO associated treatments, and the 5-fold percentage increases for ML (both raw and mixed materials), compared to soil and sewage sludge BC contents were considered to be a positive characteristic. However, elevated standard deviations described above as well as the limited agreement to the TOC/SOM regression (see below) indicate that the brick dust aggregate and magnesium limestone materials perform inconsistently to the other treatments with respect to the carbon characterisation methods used here. A reduction in LOI temperature from 600 °C to 550 °C (as recommended by numerous authors including Schulte *et al.*,1991 and Heiri *et al.*, 2001) when estimating BC contents may have improved both the repeatability and accuracy of the experimental data. It was difficult however; to assign a 'true' thermal-operationally defined temperature for BC, simply because it comprised a continuum of compounds making it a heterogeneous material.

3.3.5.3 Titration

The results attained from the dichromate oxidation titrations can be seen in Table 3.7 above and are also represented graphically in Figure 3.3 below. It can be seen that treatment differences were analogous to those illustrated in Figure 3.2 at LOI_{375} °C. The main dissimilarity being the relatively lower titration values attained for the raw brick dust aggregate and magnesium limestone materials which were used in the BDA and ML mixed treatments, respectively. The undiluted CLO treatments (2004, 2005 and 2006) give mean TOC values of 17.29 ±1.87%, 17.43 ±0.59% and 19.13 ±1.65% respectively which again were similar to mean values achieved by the sewage sludge treatment (16.06 ±0.12%). The CLO treatments once more displayed a greater degree of heterogeneity relative to the other treatments; exemplified by their higher standard deviation values. Mixing the CLO with the various amendments produces TOC values that were proportionally similar to those found after combustion at 375 °C except that the Parcgro trial mixture displayed average values (6.22 ±0.15%), which were slightly higher than the BDA (4.95 ±0.09%) and ML (4.94 ±0.06%) treatments. The agricultural soil remained relatively low giving a mean TOC of 1.85 ±0.13%, but was not the lowest value like with LOI at 375 °C. The raw BDA and raw ML materials display the lowest TOC values with mean values respectively of 0.57 ±0.06% and 0.55 ±0.07%.

In view of the similar patterns observed for LOI at 375 °C and titration results, regression lines were drawn relating the two different carbon characterisation methods. Initial year data, as used above, was plotted as well as all 3 year sacrificial data (initial, 1st, 2nd and 3rd years). The latter was included to increase *n* (sample size) from 40 (initial year only) to 138 (all years), which produced a better fit of the data giving an R^2 value of 0.9647.

A common equation can be used to convert dichromate oxidation titration TOC into a % OM, which is as follows (Aleksandrova and Naidenova, 1976 cited in Jankauskas, 2006 and Schulte *et al.*, 1991):

$$\%\text{ Organic Matter} = \%\,TOC \times 1.72$$

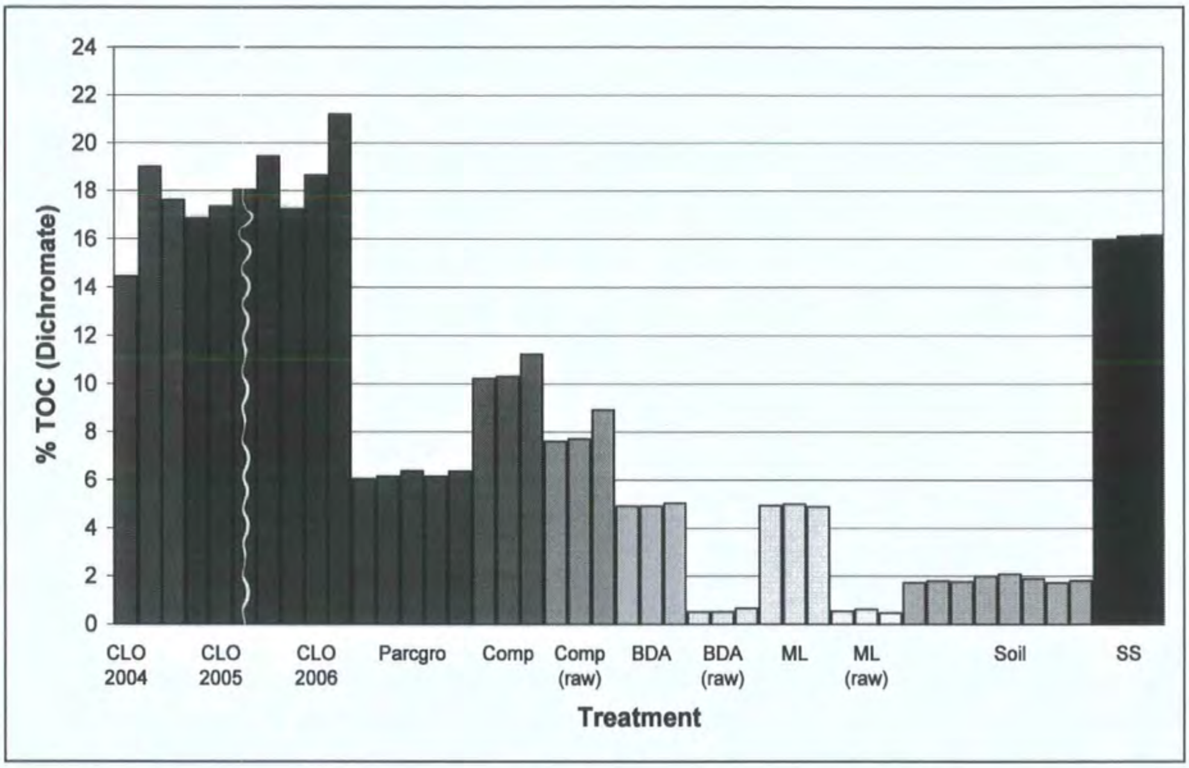


Figure 3.3: Percentage oxidisable carbon (TOC) for each treatment as well as for raw materials used in the mixed trials.

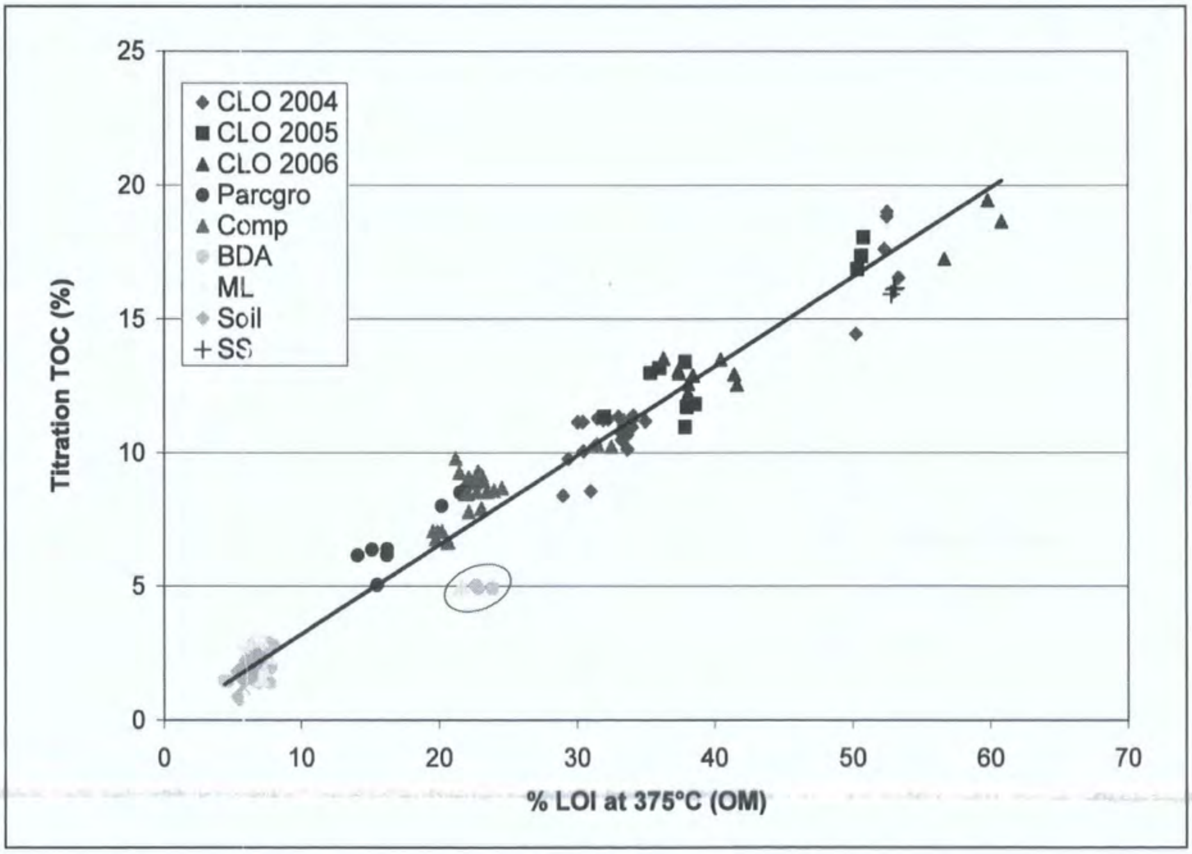


Figure 3.4: Regression fit between treatment OM at LOI_{375} and titration TOC.

When applied to the measured titration TOC values the resulting theoretical OM contents correlated well (>98% of the data displayed a standard deviation <5%) with LOI data at 375 °C for all CLO containing treatments, as well as for the agricultural soil. The only results to incur standard deviations greater than 5% were those of the original year BDA and ML treatments; the blue and yellow outliers circled in red on Figure 3.4 (these values represent the ready mixed samples and not the post experimentally corrected values for the raw materials). Thus, it can be stated that the literature OM conversion equation performs well for CLO containing treatments, except for original year BDA and ML treatments, as well as for the agricultural soil and sewage sludge and so may be considered a reliable alternative to conducting both LOI and titration experiments.

The estimation of organic carbon contents of original year BDA and ML treatments using the aforementioned transfer coefficient appears to introduce complications. A possible simple explanation for the limited correlation observed between titration TOC and LOI OM estimations for the BDA and ML treatment original year materials may lie in the different sample weights used for the respective chemical and thermal methods. Loss on ignition involved sample weights close to 10 grams whereas the titration method was optimised using sample weights around 0.2 grams. This has been shown not to be a problem for other samples (indicated by the good linear correlation coefficients achieved, Figure 3.4), including BDA and ML treatment materials which have weathered for over a year and consequently have substantially homogenised in physical nature. However, it was noted at the time of sample preparation for dichromate titration experiments that for the original year BDA and ML mixed treatments it was difficult to accurately obtain representative samples owing to the varying physical grain sizes of the materials that comprised these two treatments (CLO, brick dust aggregate and magnesium limestone). It was likely therefore that the titration method underestimated the TOC contents of the ML and BDA mixed treatments as more brick dust aggregate and magnesium limestone, having much finer particle sizes may have been used. This exemplifies the problem associated with carrying out experimentation directly upon the ready mixed materials and thus supports the added accuracy in applying a correction factor (mixer to CLO ratio of 3) to the raw material results themselves. Emission of these ML and BDA initial year discrepancies raise the regression coefficient to 0.9741.

3.3.5.4 Un-sieved/sieved analyses

Statistical analyses were performed on LOI results at the three temperatures described for treatments, which after separation through a 1mm sieve, still contained residual material. In addition, analysis of variance was carried out on 'stock' CLO, which was collected in 2006 from the aggregates recycling centre at Coxhoe landfill site where the freshly discharged CLO was windrowed, on average, for 3-6 months. This stock CLO 2006 was tested against the fresh CLO 2006 digestate. Titration experiments could not be performed upon the un-sieved materials due to the low sample size (~0.2g) required.

Statistical results showed that although the un-sieved stock CLO 2006 was significantly different ($P<0.0002$) from the sieved stock CLO 2006 at LOI 600 °C, there was no significant variation found at 375 °C or 900 °C. Furthermore, no significant variations were found in carbon characterisation at any LOI temperature between the stock CLO 2006 and the fresh CLO 2006 from which it had matured. The remaining statistical analyses are presented in Table 3.12. It can be seen that there were significant differences between the un-sieved and sieved amounts of the 3 fresh undiluted CLO's at all LOI temperatures, but the Parcgro mixture only gave a significant variation at 600 °C.

°C	CLO 2004	CLO 2005	CLO 2006	Parcgro	Stock CLO
375	0.00001	0.00001	0.0001	NS	NS
600	0.036	0.011	0.00001	0.0001	0.0002
900	0.036	0.0002	0.00001	NS	NS

Table 3.12: Analysis of variance results comparing un-sieved/ sieved samples. Statistical differences ($P<0.05$). NS =Not significant.

The findings tell us that the windrowed CLO material (stock CLO 2006) does not appear to lose any significant amount of carbon whilst it is left curing at the Coxhoe recycling facility. This was contrary to the annual carbon losses seen above for fresh CLO samples used in the field lysimeters. Secondly, any differences seen in Table 3.7, between the stock CLO 2006 and its fresh counterpart (CLO 2006), were not significantly different from the within batch differences incurred by the inherent heterogeneity of the material in question; which is signified by the significant difference (P<0.0002) found between un-sieved and sieved samples.

The remaining results indicate that the annual fresh CLO samples consistently produce sieved material that was significantly different from the material unable to be passed through a 1mm screen. These differences are seen at all LOI temperatures, in which case the un-sieved material was always higher in OM content at 375 °C but lower in refractory carbons and inorganic carbon at 600 °C and 900 °C, respectively. The Parcgro artificial soil product was blended with green compost and screened soils and so was less heterogeneous in its physical appearance, which is displayed by there being only one significant difference between un-sieved and sieved samples at 600 °C. This again highlights the heterogeneity of the undiluted CLO materials but also gives an indication of the degree to which characterisation experiments undertaken in the laboratory may not be entirely representative of the material that was being discharged from the aerobic digester at Thornley.

3.3.6 'Component' speciation

The metals, non metal (phosphorus) and anion mean data were assessed, both by component and by treatment in an attempt to identify relationships between certain treatments or elements/complexes. As with the lysimeter trials (Chapter 2), a clear distinction between leached concentrations of 'base cations' (Si, K, Na, Ca and Mg) and the remaining 'trace metals' existed, and so a similar division was included below. The release of anions (chloride, nitrate and sulphate) was only detected for the original solid materials and this was limited to the first two steps of the sequential extraction procedure and so percentage comparisons between fractions and time (years) could not be included for these anion species. It was assumed therefore that all major anions were associated with readily exchangeable metal-salt complexes capable of being leached under neutral conditions.

The data have been plotted by element for the 'base cations' (Si, K, Ca and Mg), due to the relatively consistent behaviour and low number of elements, and by treatment for the 'trace metals' for the opposite reasons. A brief description of individual trace metal speciations has also included in an attempt to generalise the findings by element as well as by treatment. What were considered to be the more important elemental and treatment plots have been included in the text but all raw data releases can be seen tabulated in Appendix 2 (attached data cd). It was intended that by plotting the data in this way would assist interpretation for the reader but also facilitate the identification of common elemental partitionings, which ultimately would be of more use to Premierwaste.

Generally speaking, there was little or no significant change with time (i.e., between annual sampling events), in elemental extraction patterns and so for ease of reading any significant differences with time have been included in the elemental and treatment breakdowns that follow. The data below have been presented as mean percentages of the total amounts (µg/kg) extracted during the four sequential extractions described above (analyses). Statistical summary tables have also been included at the end of each sub section, grouped by similar treatment, for easier review. These tables have been colour co-ordinated. An additional statistical section is also included concerning significant differences found between sieved/un-sieved samples and released amounts (fluxes) for each element over time and between treatments. Throughout this section the individual fractions have been referred to using an operationally defined labelling system based on the extractants chosen, rather than the assumed target speciation trace metal associations (see methodology).

3.3.6.1 'Base cations'

Statistical results used in this section for the 'base cation' releases during the sequential extraction procedure have been included below by fraction step (Table 3.13) and by treatment (tables 3.14a, b and c). Anion releases could only be undertaken by treatment as only exchangeable releases for the initial year of analysis were detected; statistical results are based upon original year findings alone. The treatment results have been grouped according to 'similar' treatment releases (see below) and have been compared in each case to the sewage sludge treatment and the agricultural soil control. A further point to note is that even after blank corrections, levels of Na found in step 3 extraction solutions dominated this elements analysis throughout. This was due to the presence of Na in the reagents used for sequential step 3 (sodium thiosulphate ($Na_2S_2O_3$) and sodium citrate ($Na_3C_6H_5O_7$)). Relative amounts of Na therefore, cannot be accurately quantified and so have not been reviewed.

Element	Step					
	1 – 2	1 – 3	1 – 4	2 – 3	2 – 4	3 – 4
Si	✖	✔	✓	✖	✓	✓
K	✓	✓	✓	✖	✖	✖
Ca	✓	✔	✔	✓	✓	✖
Mg	✖	✖	✓	✖	✓	✓

Table 3.13: Elemental significant differences between extracted fractions. ✓ - (P<0.00001), ✔ - (P<0.0001), ✔ - (P<0.001), ✔ - (P<0.01) and ✖ - Not significant.

Element	Treatment differences									
	CLO 05 – CLO 06	CLO 05 -- Parc	CLO 05 – Soil	CLO 05 – SS	CLO 06 – Parc	CLO 06 – Soil	CLO 06 – SS	Parc – Soil	Parc – SS	Soil – SS
Si	✖	✖	✖	✓	✖	✔	✓	✓	✔	✓
K	✖	✖	✔	✖	✖	✓	✓	✔	✖	✖
Ca	✖	✖	✓	✖	✖	✓	✖	✓	✖	✓
Mg	✖	✖	✖	✖	✖	✖	✖	✔	✖	✖
Cl	✖	NA	NA	✓	NA	NA	✓	NA	NA	NA
NO_3	✖	NA	✓	✓	NA	✓	✓	NA	NA	✓
SO_4	✓	NA	✓	✔	NA	✖	✖	NA	NA	✔

Table 3.14a: Elemental significant differences between treatments for CLO 2005, CLO 2006 and Parcgro and the sewage sludge and soil control. ✓ - (P<0.00001), ✔ - (P<0.0001), ✔ - (P<0.001), ✔ - (P<0.01) and ✖ - Not significant. NA – Not applicable.

Element	Treatment differences					
	CLO 04 -- Comp	CLO 04 – Soil	CLO 04 – SS	Comp – Soil	Comp – SS	Soil – SS
Si	✖	✖	✖	✖	✓	✓
K	✖	✖	✖	✔	✖	✖
Ca	✖	✓	✖	✓	✔	✖
Mg	✖	✖	✖	✖	✖	✖
Cl	✖	NA	✔	NA	✓	NA
NO_3	✔	✓	✖	✔	✖	✓
SO_4	✖	✔	✖	✖	✓	✔

Table 3.14b: Elemental significant differences between treatments for CLO 2004 and Comp, and the sewage sludge and soil control. ✓ - (P<0.00001), ✔ - (P<0.0001), ✔ - (P<0.001), ✔ - (P<0.01) and ✖ - Not significant. NA – Not applicable.

Element	**Treatment differences**					
	BDA – ML	**BDA – Soil**	**BDA – SS**	**ML – Soil**	**ML – SS**	**Soil – SS**
Si	✓	✓	✓	✗	✓	✓
K	✗	✗	✗	✗	✗	✗
Ca	✗	✓	✓	✓	✗	✓
Mg	✓	✗	✗	✓	✓	✗
Cl	✗	NA	✗	NA	✗	NA
NO_3	✗	✓	✗	✓	✗	✓
SO_4	✗	✗	✓	✗	✓	✓

Table 3.14c: Elemental significant differences between treatments for BDA and ML, and the sewage sludge and soil control. ✓ - ($P<0.00001$), ✓ - ($P<0.0001$), ✓ - ($P<0.001$), ✓ - ($P<0.01$) and ✗ - Not significant. NA – Not applicable.

The major portion of Si can be attributed to the oxidisable fraction for all treatments (Figure 3.5) and this can be statistically proven ($P<0.00001$). For the CLO 2004, Comp and agricultural soil treatments, more than 90% of the total leached Si was shown to be bound to organic matter/sulphides. However, there was considerable variation between the undiluted CLO materials (2004, 2005 and 2006) where the acid-soluble phase was more prolific in the CLO 2005 (22.4%) and CLO 2006 (28.1%) digestates, in comparison with that observed for the CLO 2004 (4.3%). It can be seen that by mixing the CLO 2004 with brick dust aggregate (BDA treatment) and green waste and screened soils (Parcgro treatment), the reducible (i.e., Si bound to Fe and Mn oxides) fraction has increased.

The release of K into solution (Figure 3.5) was dominated by the exchangeable fraction, with CLO containing treatments possessing more than 70% exchangeable K. The BDA, ML, sewage sludge and agricultural soil treatments showed increased amounts of reducible K ranging from 18.8% in the BDA treatment to 30.6% in the soil control. The agricultural soil also showed similar percentages of oxidisable K (28.6%). Acid reducible phase percentages for all treatments were below 10%.

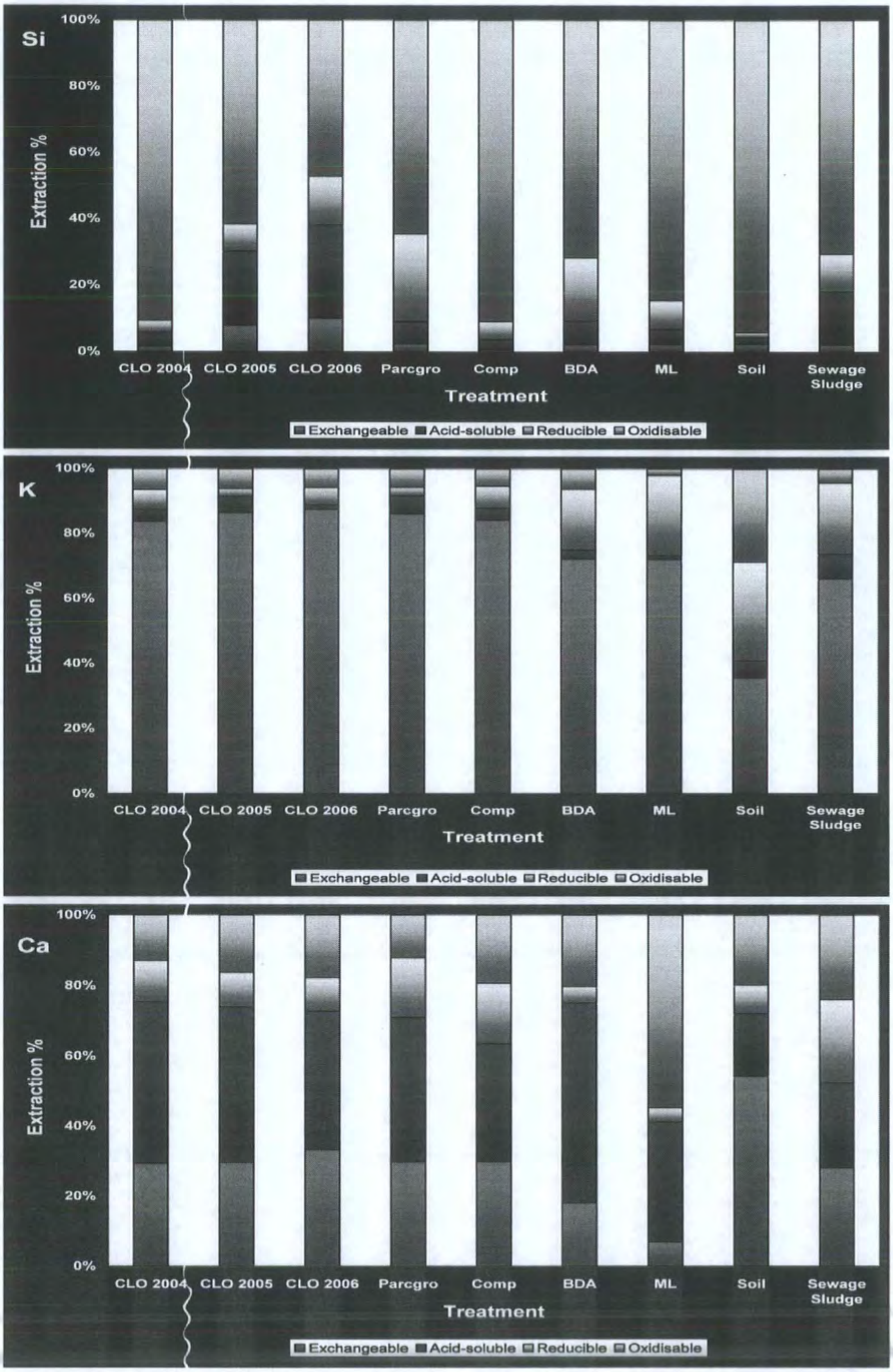


Figure 3.5: Percentage extractions for the exchangeable, acid-soluble, reducible and oxidisable fractions between treatments for Si, K and Ca.

The release patterns of Ca and Mg were overall analogous to one another and so the Ca plot in Figure 3.5 was taken to represent the main behavioural patterns also seen for Mg. The main difference being that Ca releases display a more prolific acid-soluble phase and Mg releases a more prolific oxidisable phase for all treatments (~40% in both cases). The elevated partitioning of Mg within the oxidisable fraction was especially true for the ML treatment. The distribution of Ca and Mg between the four extraction phases was again similar for the undiluted CLO's, Parcgro and Comp treatments. The exchangeable and acid-soluble fractions accounted for more than 70% of the total Ca released, except for the Comp (63.6%), sewage sludge (52.3%) and ML (41.1%). The remaining 30% of extractable Ca were divided roughly equally between the remaining reducible and oxidisable phases, except for the ML treatment which displayed an elevated oxidisable fraction (54.7%). Exchangeable amounts of Ca and Mg also played a substantial role for all treatments, particularly for the agricultural soil where levels were elevated to 54.3% and 37.5%, respectively ($P<0.00001$). Sewage sludge materials showed evenly distributed quantities of Ca for each of the four steps, but elevated levels of exchangeable and oxidisable fractions are seen for Mg; this was comparable to Ca releases seen for the agricultural soil.

3.3.6.1.1 Base cation discussion

In general it can be seen that the release pattern, and thus partitioning of the 'base cations', for any treatment, is strongly influenced by the valency state of that element. Silicon, having a valency of four and considered as a center matrix element (Wang *et al.,* 2001), is primarily bound to organic matter ($P<0.00001$) and as will become apparent behaves like the 'trace metals' and not a base cation, as the grouping of it in this way would suggest. As explained above the grouping of the 'trace metals' and 'base cations' was based upon lysimeter study findings and leached concentrations. It has also been highlighted that the undiluted CLO fractionation patterns for the 'base cations' have been shown to closely correlate with the Parcgro and Comp treatments but be significantly different from the agricultural soil. A similar correlation has been shown to exist between the BDA and ML treatments but statistical differences with the soil control are more varied. This will be discussed further once 'trace metal' fractionation patterns have been evaluated.

The bivalent Mg^{2+} is bonded mainly to the organic fraction ($P<0.00001$) but considerable proportions have been found complexed to easily exchangeable surface minerals for all treatments except BDA and ML ($P<0.02$). This suggests that the major leaching of Mg is likely to occur on initial contact with percolating rainwaters, particularly in the agricultural soil but also if the materials are well drained and aerated with little or no OM replacement. If a fertile vegetation cover could be maintained providing a constant supply of OM, then much Mg leaching may be avoided. Maintaining a fertile environment will be of particular importance if the CLO material is amended with magnesium limestone where 78.4% of the leachable Mg is released during extreme oxidising conditions.

Ca is significantly partitioned between all four of the leaching stages tested ($P<0.01$) except that there was no statistical difference found between the two redox fractions (reducible and oxidisable). This was because the majority of leachable Ca occurs during the mobile fraction (exchangeable and acid-soluble phases) implying, and which has been shown in Chapter 2, that major Ca releases will occur over a short period of time after being exposed to acid rainwaters. The extent of this, however, will be lessened if the CLO is amended, in a manner similar to that involved for the ML treatment. The oxidisable fraction is subsequently of greater environmental importance for this treatment. The soil control, although displaying a similar mobile fractionation pattern to that of the undiluted CLO, BDA and Parcgro treatments, the extent to which Ca release was dependant upon acid rainfall supplying the levels of protonation required to unhinge the acid-soluble fraction, is reduced. Conversely, the BDA treatment appears more reliant upon a certain level of acidification in order to release substantial bound Ca. As will be seen in the following chapter, however, the flux releases for the agricultural soil are insignificant in comparison to those experienced for the remaining treatments.

Finally, the monovalent K^+ appears to be weakly bound in easily displaceable metal-salts and so can be strongly associated with the exchangeable fraction ($P<0.00001$). This significance is limited to the original year of sampling only and so K comprised one of the few limited elements that displayed any statistical variation between annual sampling events ($P<0.0001$), as the majority of K is readily flushed after lysimeter establishment. This will be highlighted later during flux comparisons. The undiluted

CLO's, Parcgro and Comp treatments released >80% of their leachable K under neutral conditions; a significant issue when considering all three of the detectable anions tested (chloride, nitrate and sulphate) were also leached during this highly mobile phase. The presence of KCl, KNO_3 and K_2SO_4, as base cations salts are therefore likely to be a major problem related to the utilisation of CLO in any environmental setting; the problems associated with which have been assessed previously (Chapter 2). The remaining treatments (BDA, ML and sewage sludge) still partition the majority (>70%) of K leaching to the mobile phase (exchangeable and acid-soluble). The agricultural soil, however, would release just over half of the total considered leachable K if a change in redox conditions occurred. This underlines a clear distinction between the agricultural soil and the rest of the treatments.

The behaviour of the agricultural soil and sewage sludge treatments, with respect to base cation speciation patterns, were shown to vary depending on individual elemental releases but the main valency relations described above still apply. Both treatments have been shown to be significantly different (soil – $P<0.049$ and sewage sludge – $P<0.027$) from at least three of the CLO containing treatments but also from each other for varying components. The exception to this was for Mg where all treatments displayed a significant difference ($P<0.00001$) to that of the ML treatment. Statistical analyses undertaken on treatment fluxes described later in the chapter explain the significance of these findings.

3.3.6.2 'Trace metals'

After analysis of graphical data plots relating to the partitioning of the trace metals into the four sequential extraction steps it was decided that relationships existed between certain treatments and so five treatment groups were assigned as follows:

1) **CLO 2005, CLO 2006 and Parcgro**
2) **CLO 2004 and Comp**
3) **BDA and ML**
4) **Sewage Sludge**
5) **Agricultural soil**

Similarities between groups 1 and 2 were also found between annual sampling events which will be discussed later. Each of these groups will now be discussed in turn. Treatment fractionation graphs along with statistical summary tables have been included below, in each group section.

1) CLO 2005, CLO 2006 and Parcgro

This treatment group can be broken down into three assemblages of elements, each of which is based on the major partitioning of the said elements into certain fractions; oxidisable dominated, reducible dominated and acid prolific. The first two element assemblages contain oxidisable and reducible metals, respectively, as their major components and the third assemblage is formed from trace metals that have an elevated acid-soluble fraction, but this acid fraction is not necessarily the dominant fraction overall. These various metal assemblages for the three treatments can be seen in Figure 3.6. The organically bound or more accurately termed oxidisable fraction (as can also include species bound to sulphides) includes the following trace metals: Ni, Sc, Cr, Li and V. Where, in decreasing fraction amounts the following is always true:

Oxidisable > reducible > exchangeable > acid-soluble.

The reducible dominated assemblage metal components are: Cu, Pb, P, Al, Fe, Ti and Co. Where, in decreasing fraction amounts the following is always true:

Reducible > oxidisable > acid-soluble > exchangeable.

It is worth noting that these two assemblages of trace metals (oxidisable and reducible) are more pronounced in the Parcgro treatment relative to the CLO 2005 and 2006.

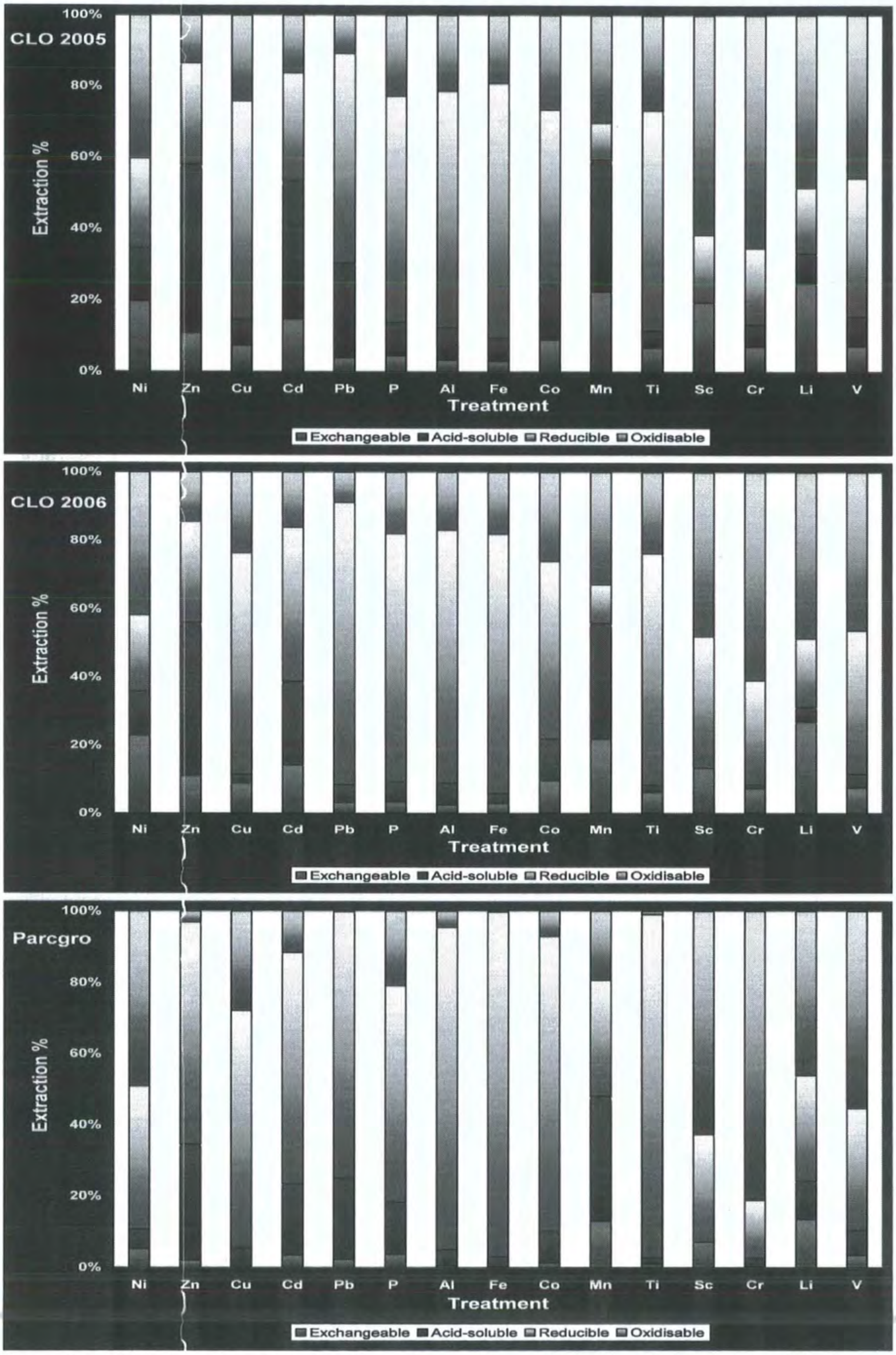


Figure 3.6: Percentage extractions for the exchangeable, acid-soluble, reducible and oxidisable fractions for all 'trace metals' in CLO 2005, CLO 2006 and Parcgro treatments.

The acid prolific assemblage contains Cd, Mn and Zn, in which case the acid-soluble fraction was of greater importance relative to the other trace metal recorded percentages. The only notable variations from this were the increased acid-soluble levels of Pb in the CLO 2005 and Parcgro treatments but not in the CLO 2006. However, the partitioning of Pb was still dominated by reducing conditions.

Finally, the CLO 2005 and 2006 and Parcgro treatments had the largest proportion of exchangeable metals of any treatment. The trace metals for which this fraction was more prolific were Ni, Cd (but to a lesser extent in Parcgro extractions), Mn, Sc and Li but all trace metals show some exchangeable component. After a year of exposure to field conditions the exchangeable fraction diminished and only the named trace metals above remained complexed to surface minerals.

With respect to changes with time (yearly sample events) there were no significant alterations seen for the CLO 2005 and 2006 digestates but it is worth mentioning that after one year of lysimeter weathering the Parcgro treatment had a greater partitioning of all trace metals in the oxidisable fraction. This increase in organically bound trace metals introduced a proportional decrease of partitioning of trace metals in the reducible fraction, and in doing so shifted towards a metal fractionation pattern similar to that observed for the group 2 treatments, as described below.

Statistically, as can be seen below (Table 3.15), most trace metal releases in this group of CLO containing treatments were significantly different from that of the soil and sewage sludge materials. Having said that, the Parcgro treatment was statistically indistinguishable from the agricultural soil for all elements tested. There was no statistical difference found between the two undiluted CLO treatments (2005 and 2006). It is also worth noting that, for the CLO containing treatments, the trace metals that were dominantly partitioned in the reducible phase appear to show more closely related releases than for those metals partitioned to the other fractions. This was due to a change in metal fractionation between annual sampling events. All statistical analyses were performed upon extraction data attained for all sample years so as to greatly increase the power of analysis, but also due to the relatively small differences observed for most treatments over time.

A statistical summary for this treatment group can be seen below in Table 3.15.

Element	Treatment differences									
	CLO 05 – CLO 06	CLO 05 – Parc	CLO 05 – Soil	CLO 05 – SS	CLO 06 – Parc	CLO 06 – Soil	CLO 06 – SS	Parc – Soil	Parc – SS	Soil – SS
Ni	✗	✓	✓	✗	✓	✓	✓	✗	✓	✓
Co	✗	✗	✗	✓	✗	✗	✓	✗	✓	✓
Sc	✗	✓	✓	✓	✓	✓	✓	✗	✗	✗
Cr	✗	✓	✓	✗	✓	✓	✗	✗	✓	✓
Li	✗	✗	✓	✗	✗	✓	✗	✗	✓	✗
V	✗	✓	✓	✓	✓	✓	✓	✗	✗	✗
Cu	✗	✗	✓	✓	✗	✓	✓	✗	✓	✓
Pb	✗	✓	✓	✓	✓	✓	✓	✗	✗	✗
P	✗	✗	✗	✓	✗	✓	✓	✗	✓	✓
Al	✗	✗	✓	✓	✗	✓	✓	✗	✓	✓
Fe	✗	✗	✗	✓	✗	✗	✓	✗	✓	✓
Ti	✗	✗	✗	✓	✗	✗	✓	✗	✓	✓
Zn	✗	✓	✓	✓	✓	✓	✓	✗	✓	✓
Cd	✗	✓	✓	✓	✓	✓	✓	✗	✗	✓
Mn	✗	✓	✓	✓	✓	✓	✓	✗	✗	✗

Table 3.15: Elemental significant differences between treatments for CLO 2005, CLO 2006 and Parcgro and the sewage sludge and soil control. ✓ - ($P<0.00001$), ✓ - ($P<0.0001$), ✓ - ($P<0.001$), ✓ - ($P<0.01$) and ✗ - Not significant. NA – Not applicable. Elements are coloured by dominant fractionation: black – oxidisable, blue – reducible and red – acid-soluble.

2) CLO 2004 and Comp

These two treatments have been grouped together owing to the large number of metals that were dominated by the oxidisable fraction. The exceptions to this rule were Ti in the CLO 2004, and Cd and Mn in the Comp trial but still a significant proportion of the total metal speciation was oxidisable. Furthermore, it can be said that, with a couple of exceptions, the partitioning of trace metals into the various fractions decreased in the following order: Oxidisable > reducible > acid-soluble > exchangeable.

Cadmium and Zn in the CLO 2004 and Mn in both the CLO 2004 and Comp treatments displayed elevated acid-soluble releases, and Ni, again for both treatments, exhibited increased percentage releases for the exchangeable fraction.

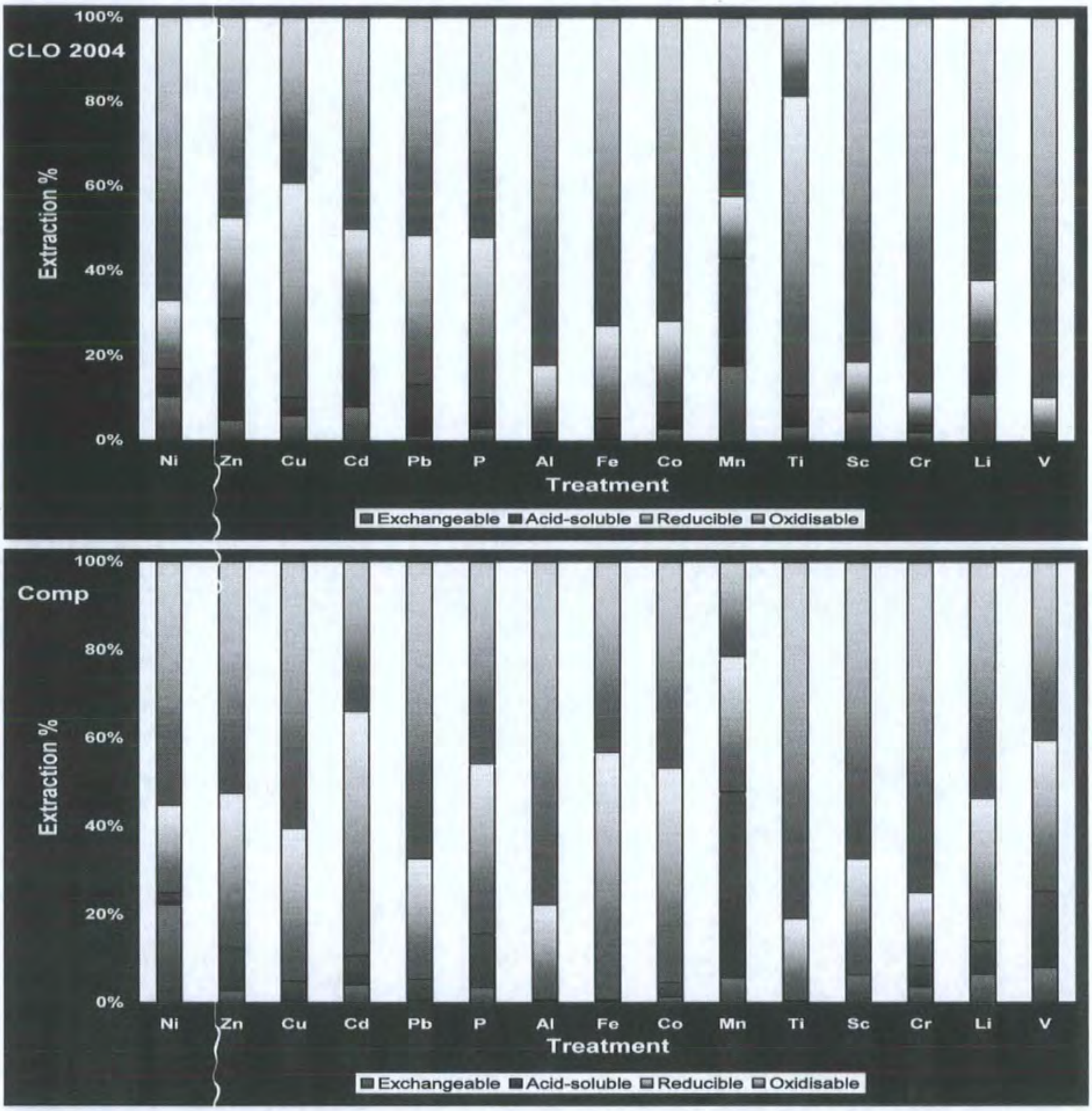


Figure 3.7: Percentage extractions for the exchangeable, acid-soluble, reducible and oxidisable fractions for all 'trace metals' in CLO 2004 and Comp treatments.

Although in separate groups the CLO 2005, 2006 and Parcgro treatments (group 1) exhibited some similarities to the CLO 2004 and Comp treatments (group 2), as has been seen with base cations releases above. Here, the similarity lies with the oxidisable fraction, where Ni, Sc, Cr, V and Li were all dominantly partitioned. Also, there was significant partitioning of most trace metals in the reducible fraction, as seen for group 1 treatments. The extent to which this trace metal reducible partitioning occurs, as can be seen in Figure 3.7, was however more limited and the oxidisable fraction remained as the dominant fraction for nearly all metals in the CLO 2004 and Comp treatments.

Element	Treatment differences					
	CLO 04 – Comp	CLO 04 – Soil	CLO 04 – SS	Comp – Soil	Comp – SS	Soil – SS
Ni	✓	✓	✓	✓	✓	✓
Zn	✓	✓	✓	✖	✓	✓
Cu	✓	✓	✓	✖	✓	✓
Pb	✓	✓	✓	✓	✖	✖
P	✖	✖	✓	✖	✓	✓
Al	✓	✓	✓	✖	✓	✓
Fe	✖	✓	✓	✓	✓	✓
Co	✖	✓	✓	✖	✓	✓
Sc	✖	✖	✓	✖	✓	
Cr	✓	✓	✖	✖	✓	✓
Li	✓	✓	✓	✓	✖	✖
V	✓	✓	✓	✖	✖	✖
Ti	✖	✖	✓	✖	✓	✓
Cd	✓	✓	✓	✖	✓	✓
Mn	✖	✖	✖	✖	✖	✖

Table 3.16: Elemental significant differences between treatments for CLO 2004 and Comp, and the sewage sludge and soil control. ✓ - ($P<0.00001$), ✓ - ($P<0.0001$), ✓ - ($P<0.001$), ✓ - ($P<0.01$) and ✖ - Not significant. NA – Not applicable. Elements are coloured by dominant fractionation: black – oxidisable, blue – reducible and red – acid-soluble.

After the first year of weathering, the Comp trial moved toward a trace metal partitioning pattern similar to that described for the initial year group 1 treatments (i.e., most trace metals had increased reducible fractions) and the Parcgro material mirrored the initial year group 2 treatments (i.e., increased oxidisable fraction). The same is also true for the CLO 2004 treatment which had shifted toward a trace metal speciation indicative of that seen by the CLO 2005 and 2006 in their initial sampling (increased reducible phase) but in this case it is not reciprocated (insignificant change was seen with time for the CLO 2005 and 2006). The controlling fractions determining these interchanges were the oxidisable and reducible phases, as the acid-soluble and exchangeable fractions did not significantly change in value with time. This behaviour will be discussed later. A statistical summary for this treatment group can be seen above in Table 3.16.

3) BDA and ML

These two mixed treatments showed similar properties throughout this investigation and the partitioning of trace metals was no exception (Figure 3.8). The behaviour of most metal releases under the various experimental conditions were similar, except that the BDA treatment almost always displayed a more pronounced partitioning of trace metals in the acid-soluble phase (P and Ti being the exceptions). Both treatments displayed similar proportions of oxidisable and exchangeable metals and so the higher attained percentages of acid-soluble metals in the BDA extraction solutions were typically in place of the reducible metal fraction. This group was therefore not characterised by one particular dominant fraction like with groups 1 and 2 but instead by the similar pattern in which the BDA and ML treatment trace metals were released.

In relation to the parent material (CLO 2004), from which the BDA and ML treatments were partially made, the main differences were in the significantly reduced proportions of the following metals; Li, Fe, Co, Al, Pb, Zn and Ni that were bound to the organic matter and thus were susceptible to oxidation. Ni and Zn can also be seen in appreciable amounts in the exchangeable fraction for the BDA and ML treatments, relative to levels extracted from the CLO 2004. In addition, for the BDA alone, the higher percentage values achieved for the acid-soluble phase distinguishes this treatment yet further, from the CLO 2004.

Again, the elemental partitioning with time was limited to a small number of metals and each change relating to an individual fraction only. The relatively high Ni and Zn exchangeable levels were flushed-out after the first year of weathering, as were Sc and Cr. Cu and Ti reducible fractions were considerably increased as were the acid-soluble and reducible fractions of the total leachable amounts of P, once exposure to field conditions had commenced. No other significant changes with annual sampling appear to have occurred. A statistical summary for treatment group 3 can be seen below (Table 3.17).

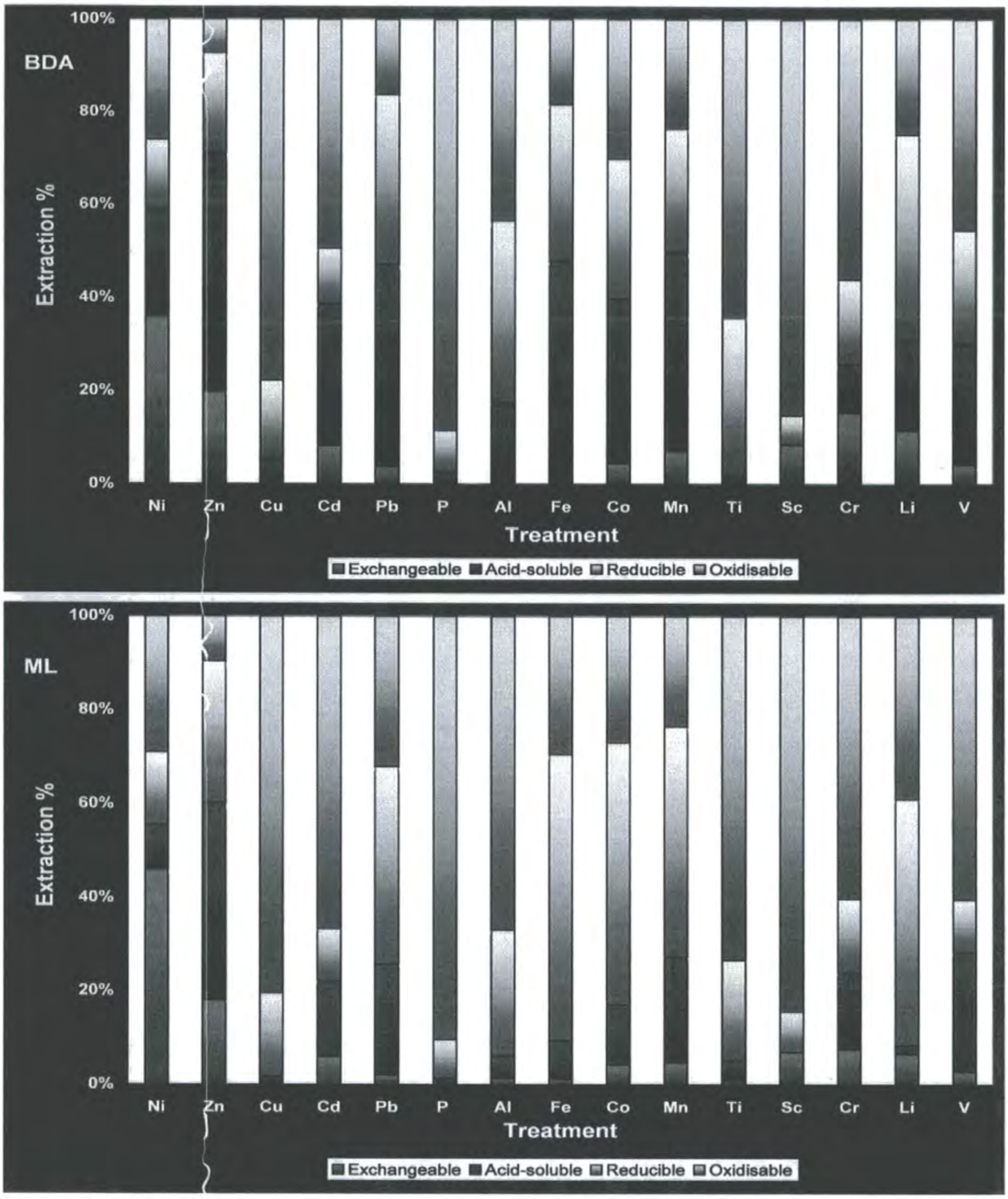


Figure 3.8: Percentage extractions for the exchangeable, acid-soluble, reducible and oxidisable fractions for all 'trace metals' in BDA and ML treatments.

Element	Treatment differences					
	BDA – ML	BDA – Soil	BDA – SS	ML – Soil	ML – SS	Soil – SS
Ni	✖	✖	✓	✓	✓	✓
Zn	✖	✖	✓	✓	✓	✓
Cu	✖	✖	✓	✖	✓	✓
Cd	✖	✖	✓	✖	✓	✓
Pb	✖	✖	✖	✖	✖	✖
P	✖	✖	✓	✖	✓	✓
Al	✖	✖	✓	✖	✓	✓
Fe	✖	✖	✓	✖	✓	✓
Co	✖	✖	✓	✖	✓	✓
Mn	✓	✓	✓	✖	✖	✖
Ti	✓	✓	✖	✖	✓	✓
Sc	✖	✖	✓	✖	✓	
Cr	✖	✖	✖	✖	✓	✓
Li	✓	✓	✓	✖	✖	✖
V	✖	✖	✖	✖	✖	✖

Table 3.17: Elemental significant differences between treatments for CLO 2004 and Comp, and the sewage sludge and soil control. ✓ - (P<0.00001), ✓ - (P<0.0001), ✓ - (P<0.001), ✓ - (P<0.01) and ✖ - Not significant. Elements are not coloured coded as BDA and ML dominant fractions do not correlate.

4) Sewage Sludge

The sewage sludge and agricultural soil treatment sequential extraction trace metal speciation results (Figure 3.9) were very similar in fractionation pattern, making sewage sludge characteristically the closest related material of the 10 studied, to that of a typical Durham region soil. Moreover, both treatments displayed very little metal salt complexes comparative to the CLO containing treatments and also displayed very little change in metal speciation over time. Having said that, significant differences to the soil in extracted amounts (μg/kg) for most trace metals (Ni, Zn, Cu, Cd, P, Al, Fe, Co, Ti and Cr) were evident; with sewage sludge always having higher levels than the soil (flux values will be evaluated later). Subsequently, sewage sludge and agricultural soil trace metal speciation results have been kept separate despite their percentage fractionation similarities.

As with group 1 treatments (CLO 2005, 2006 and Parcgro) the sewage sludge material could be characterised into three main elemental assemblages. The first two assemblages contain oxidisable and reducible dominated trace metals, and the third consists of elements that were almost totally partitioned to these two fractions and thus show proportionally very little acid-soluble or exchangeable behaviour. The trace metals that were significantly (>50%) bound to organic matter and thus considered to be susceptible to mobilisation after oxidisation were Ni, Zn, Cu, Sc, Cr and V. Of these, V was also substantially characterised by the reducible fraction (34.5%) and shares the remaining leachable 20% equally between exchangeable and acid-soluble fractions. The elements dominated by the reducible fraction were Li, Ti, Fe Pb and Cd. As with V, Cd also partitioned significantly with the oxidisable (25.5%) and acid-soluble (18.6%) fractions. Al, Co and P were the trace metals that almost totally (>90%) partitioned between the oxidisable and reducible fractions. Mn was similar to Cd and V in that it was mostly speciated between the oxidisable (31.5%), reducible (37.2%) and acid-soluble (22.8%) but no one fraction significantly dominates Mn speciation.

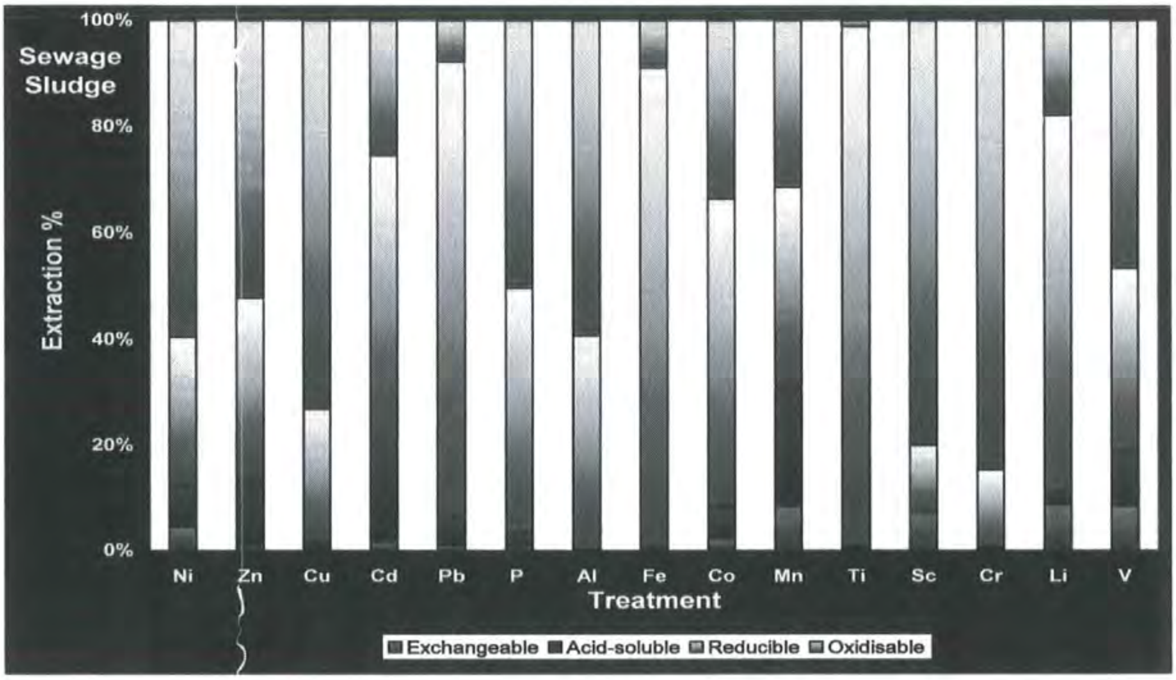


Figure 3.9: Percentage extractions for the exchangeable, acid-soluble, reducible and oxidisable fractions for all 'trace metals' in sewage sludge.

Statistical results (Tables 3.15, 3.16, and 3.17) illustrate that sewage sludge, although seeming relatively similar in fractionation pattern to all other CLO containing materials and the agricultural soil, was significantly different in actual fluxed concentrations, for trace metals in particular. This important finding will be discussed below in the flux section.

5) Agricultural soil

The agricultural soil, although showing similar fractionation patterns to the group 1 (initial year analyses) and group 2 (1st year analyses) CLO treatments for the reducible dominated trace metals, displayed significantly lower extractable amounts (µg/kg) than these treatments. These significantly lower measured fluxes as a function of treatment and time constitute reason enough for it to be assessed separately. However, it must be noted, relative to BDA and ML treatments, flux values were leached to a similar degree.

The main characteristic feature of the agricultural soil was that the majority of the trace metal (Zn, Cu, Cd, Pb, P, Al, Fe, Co, Mn and Ti) partitioning could be attributed to the reducible fraction (>50%). Additionally Pb (19.4%) and Zn (36.0%) displayed larger acid-soluble fractions and thus negligible exchangeable and oxidisable fractions. Subsequently, there were only 3 trace metals (Ni, Sc and Cr) that were dominated (>70%) by the oxidisable fraction. Li and V both displayed large oxidisable speciations (~50%) but Li also displayed similar proportions for the reducible fraction and V was more substantially partitioned into the acid-soluble phase speciating equally between the acid-soluble and reducible fractions (21.1% and 21.4%, respectively). The agricultural soil was also characterised by low percentages of exchangeable metals present.

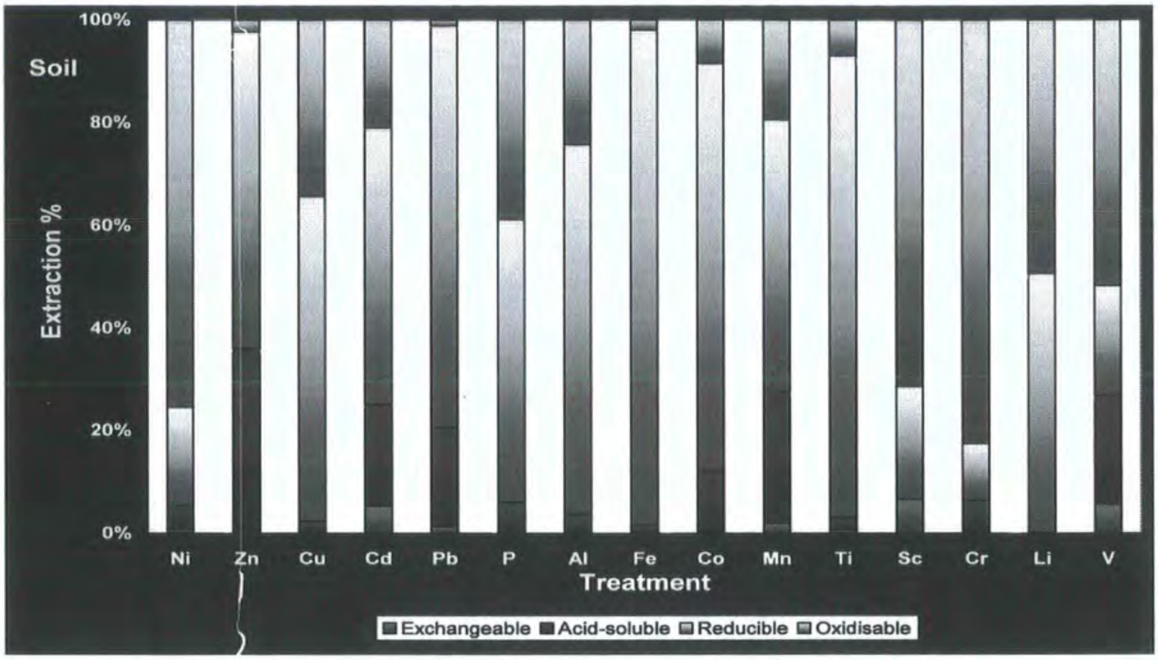


Figure 3.10: Percentage extractions for the exchangeable, acid-soluble, reducible and oxidisable fractions for all 'trace metals' in the agricultural soil control.

3.3.6.2.1 Discussion

In view of these speciation results a few generalised points can also be made to compliment the treatment findings described above, concerning individual elemental fractionation patterns, irrespective of treatment. Cd, Mn, Pb, Zn and Co to a lesser extent, all demonstrated a greater affiliation, relative to the other elements, to the acid extractable fraction. V also displayed this behaviour but it was limited to the mixed treatments (Comp, BDA and ML) and the agricultural soil. It can be said that Ni was largely partitioned to the oxidisable fraction with BDA and ML treatments having >25% and the remaining treatments >40% of their total leachable Ni extracted during step 4 of the sequential extraction procedure. In addition, Ni was speciated considerably in salt displaceable (exchangeable phase) complexes (except in the soil and sewage sludge treatments), especially for the mixed treatments BDA and ML (~35% and ~45%). Li was dominated (>65%) by the reducible and oxidisable fractions for all treatments but was also present (~20%) as displaceable salts in the undiluted CLO treatments.

Similar findings by Esakku et al (2005) and Kumpiene et al (2006) are mirrored here in that over 80% of the total leachable amounts of Cu were associated with the reducible and oxidisable phases (Figures 3.7 and 3.8). In addition, there was a distinct increase in oxidisable Cu contents (>60%) for the mixed treatments (Comp, BDA and ML) and the sewage sludge treatments (Figures 3.7, 3.8 and 3.9) relative to the >60% reducible Cu displayed by the remaining treatments (Figures 3.7 and 3.10), except CLO 2004 (>50%). Al, Fe and P also displayed similar reducible/oxidisable fractionation partitionings. For all four of these elements <20% of the total calculated leachable amounts are partitioned in the exchangeable and acid-soluble phases. Finally, it can be noted that significant amounts of Cr (>56%) and V (>40%) were bound to organic matter (oxidisable fraction – Figures 3.7, 3.8, 3.9 and 3.10).

It has been shown that elemental partitioning varies considerably between trace metals and treatments but speciation patterns do not significantly alter over time. The aforementioned exceptions to this were the mixed treatments containing green waste (Comp and Parcgro) and the undiluted CLO 2004 treatment. The two fractions that proportionally altered with time were the reducible and oxidisable phases; the reducible partition increased for most trace metals for the CLO 2004 and Comp trials and oxidisable proportions became more prolific for the Parcgro treatment with time. The latter shift toward a greater partitioning of trace metals that were associated with organic matter/sulphides may be as a result of the improved mixing of the Parcgro constituents with time. The artificial Parcgro product consists of 1 part CLO 2006: 1 part green waste: 1 part screened soils and was blended on the day of collection. This recent mixing and immediate laboratory testing would not allow trace metals to be released into solution and subsequently be adsorbed by the organic rich CLO component. After a years exposure, percolating waters may have redistributed dissolved trace metal species throughout the whole material allowing more efficient adsorption complexes to occur with the organic matter fraction.

The above theory does not however explain the relocation of trace metal partitioning toward Fe-Mn oxide associations (reducible fraction) seen in the CLO 2004 and Comp trials. It is likely that the changes seen for these two treatments were related to a shift in equilibrium position brought on by a change in environmental conditions on establishment of the lysimeter experiments. Ultimately, a repositioning of trace metal equilibrium may have been initiated due to variations in aerobic digester controlled conditions and MSW characterisation. The heterogeneous nature of the CLO digestates has been well documented throughout this study and so a change in source components between 2004 and consecutive years, will also effect the initial characterisation of the CLO and its associated soils. This transformation in digester output is also likely to be as a result of ongoing alterations to the overall recycling process and thus its efficiency at removing particularly troublesome waste streams (such as the introduction of a secondary eddy current metal separation unit). Actual in vessel digester conditions, although constantly computer controlled, are modified to best suit the state and efficient decomposition of the individual waste batches. It is an alteration in these conditions, and thus the reducing/oxidising environment that is most expected to cause trace metal instability and need for re-equilibration on exposure to external surroundings. The CLO that was discharged in 2004, and thus that used in the Comp trial, was noticeably of a 'superior' quality to that of later digestates, with regard to aesthetic criteria, leaching behaviour and various water quality determinative properties (Chapter 2). To achieve this, it is fair to say that a more efficient oxygen-water-temperature balance was necessary for the aerobic microbes to function optimally. Under these conditions the oxidisable fraction (organic matter and sulphides) would therefore be efficient metal scavengers but on compaction and subsequent water-logging (as experienced for both CLO 2004 and Comp trials) in the field lysimeters the redox potential would alter in favour of reducing conditions. An imperfect in-vessel digester environment would facilitate the initial elevated reducible trace metal associations seen in the CLO 2005 and CLO 2006.

The mixed treatments (BDA and ML), as well as the agricultural soil control and the sewage sludge did not show any significant change in trace metal partitioning patterns with annual sampling events. This suggests that the partially self enhanced field conditions experienced for these treatments were relatively constant and thus the chemical nature of the materials did not significantly alter since their establishment. This may also be testament to the lysimeter set-up which operationally attenuate aeration and free drainage of the materials contained within, therefore discouraging water-logged anaerobic conditions necessary for reducible conditions. However, the sequential extraction data presented here has shown that if more extreme conditions than experienced in the field are endured then substantial amounts of potentially leachable trace metals could be released.

Tables 3.18 and 3.19 below summarise the base cation/anion and trace metal desorption percentages recorded for the sequential experimental data. The four fractions (exchangeable, acid-soluble, reducible and oxidisable) have been grouped into a mobile fraction (exchangeable and acid-soluble) and a redox released fraction (reducible and oxidisable).

3.3.6.2.2 Mobile fraction

The first two sequential extraction steps (representing the exchangeable and acid-soluble fractions) are of greatest immediate environmental concern. The conditions under which these releases occur are easily favoured and both of these fractions are highly mobile and therefore more easily bio-available (Esakku *et al.,* 2005). The proportion of a trace metal that is available in soluble or exchangeable forms can indicate the propensity for uptake of metal cations by plants or for leaching. The reducible and oxidisable metal forms associated with Fe-Mn oxides and organic materials alike, are considered to be less of a threat with respect to their leachability under normal environmental conditions as they are more strongly bound and only likely to be leached out under extreme conditions (Esakku *et al.,* 2005). Indeed, metal cations may be complexed or chelated to organic matter by metal-organic ligands. Organic matter, for example, is known to be the main solid-phase component capable of retaining trace metal cations, even at lower pH's, decreasing their soluble and exchangeable forms, thus reducing the potential risk of contaminating various waterways (Gerritse *et al.,* 1984; Mann *et al.,* 1993). However, as will be seen in Chapter 5, this is not necessarily the case as significant contamination has be recorded in the field lysimeter studies which has been shown to be strongly correlated with the oxidisable release.

As stated previously, the first two steps, representing the mobile fraction are of immediate concern with respect to metal leaching as acid rain percolation is capable of affecting both the ionic strength and carbonate components (Kumpiene *et al.,* 2006). Furthermore, the effects of weathering of the CLO, in particular, have been shown to produce alkaline leachates, which although is favourable from a trace metal-acid-soluble standpoint, will again affect the ionic balance of the 'soil' solution and thus exchangeable fraction releases. This is particularly pertinent when assessing the release of base cation salts into solution, as demonstrated by the high percentage extractions achieved in Table 3.18a, especially the anions (chloride, nitrate and sulphate), K and Ca. Elevated mobile fraction Ni values for the CLO 2004 and 2005, and even more so for the BDA and ML treatments indicate that this transition metal is also closely affiliated with displaceable metal salts. This finding is supported by work carried out by Flyhammar (1997) who reported that the exchangeable phase was important for Ni in fresh and shredded MSW. Similar affiliations but to lesser extents, can be said to exist for Li and Mn, in all CLO-containing treatments.

Treatment	Si	K	Ca	Mg	Cl	NO_3	SO_4
CLO 2004	5.8	87.4	75.4	38.7	100	100	100
CLO 2005	30.3	91.4	74.0	44.2	100	100	100
CLO 2006	38.2	88.9	72.8	48.5	100	100	100
Parcgro	9.2	91.7	71.0	28.4	100	100	100
Comp	3.8	87.8	63.6	39.6	100	100	100
BDA	9.3	75.0	75.1	33.0	100	100	100
ML	6.8	73.2	41.1	16.5	100	100	100
Soil	4.4	40.8	72.0	54.2	ND	100	100
SS	18.2	73.8	52.3	44.8	100	100	100

Treatment	Ni	Zn	Cu	Cd	Pb	P	Al	Fe	Co	Mn	Ti	Cr	Li	V
CLO 2004	16.9	28.7	10.2	29.7	13.3	10.2	2.1	5.4	9.1	43.2	10.9	4.1	23.4	2.0
CLO 2005	34.8	58.0	14.6	53.5	30.5	13.8	12.4	9.4	24.5	59.3	11.4	13.1	33.2	15.5
CLO 2006	35.8	56.1	11.5	38.7	8.4	9.4	8.9	5.7	21.8	55.9	8.4	8.5	31.3	11.5
Parcgro	10.8	34.7	5.7	23.5	25.2	18.4	5.1	3.1	10.3	48.0	2.8	2.6	24.3	10.5
Comp	24.9	12.4	4.9	10.8	5.4	15.6	0.7	0.7	4.6	47.9	0.4	8.5	13.9	25.3
BDA	59.1	71.4	5.5	38.8	47.0	2.6	17.5	47.9	39.7	49.9	1.9	25.9	31.4	30.3
ML	55.5	60.2	1.8	22.0	25.7	1.2	6.2	9.3	16.9	27.2	5.0	23.9	8.4	28.3
Soil	5.4	36.0	2.3	25.1	20.7	6.1	3.8	1.8	12.4	27.7	3.1	6.4	0.2	26.8
SS	12.7	13.6	1.5	20.4	6.5	3.4	0.2	0.5	8.6	31.2	0.7	0.6	10.9	18.8

Table 3.18: Treatment percentage releases associated with the 'mobile' phase for a) 'base cation' salt components and for b) 'trace metals'. ND = Not Detected.

The acid-soluble fraction has been shown, for most elements/anions, to be of relatively minor importance with regard to proportional releases. This in part could be testament to the large buffering capacity of the CLO itself, as well as the amending materials chosen (brick dust aggregate and magnesium limestone). Alkaline pH levels in leachates and solids, even after 3 years of extended periods of acid rain, continuous weathering and interaction with atmospheric CO_2, demonstrate that acid-soluble leaching is unlikely. However, the higher percentage releases shown by all treatments for: Cd, Mn, Pb, Zn, and Co to a lesser extent, and in addition for the BDA treatment;

Al, Fe, Li, Ni and V, could cause significant contamination if acidic conditions were favoured. The elevated acid-soluble partitioning of many trace metals seen for BDA, relative to the other treatments implies that carbonates present in the brick dust aggregate are good scavengers. This explains the high mobile fraction desorptions observed for the BDA treatment in Table 3.18.

In particular, the high percentage acid-soluble speciations observed for Mn and Zn were of most concern as these releases occur over all treatments, except in the ML and sewage sludge treatments for Zn. It is worth mentioning that acid-soluble Mn speciation proportionally increased also with yearly extractions for all treatments but especially the for CLO containing materials; a similar observation to that of Flyhammar (1997), who found higher Mn concentrations in acidic extractions from degraded MSW than fresh MSW. The release of Ca was also strongly affiliated with this phase, further increasing the proportion of this base cation found in the mobile fraction. Wan et al (2006) stressed a dependency relationship of the leaching behaviour of certain heavy metals (Zn, Pb, Cd and Cu) from MSWI fly ashes during the mobile phase with that of Ca components, such as aphthitalite and calcite and anyhydrite by ordinary physical and chemical adsorption. The similar extraction efficiencies seen here for Zn, Pb, Cd and that of Ca under neutral conditions may also suggest a similar relationship exists during leaching from CLO.

3.3.6.2.3 Reducible/oxidisable fractions

As can be seen from Table 3.19 below, the main risk for release of the retained metals was associated with changes in redox status. Sequential extraction studies carried out by Chang et al (2005) and Wan et al (2005) on MSWI fly ashes, Kumpiene et al (2006) on MSWI bottom ashes, Esakku et al (2005) on decomposed MSW and Flyhammar (1997, 1998, *et al.,* 1999) all reported similar findings. The exceptions to this have already been discussed above and are largely governed by the base cation salt components, Mn, Ni and Zn partitioning in the mobile fraction. The combination of the sequential extraction data for steps 3 and 4 in Table 3.19 may well resolve discrepancies seen above between the CLO 2004 and Comp trials and that of the CLO 2004, 2005 and Parcgro treatments for initial and one year analyses. Flyhammar et al

(1999) reported that the reagents used during step 3 of the amended Tessier extraction procedure performed here may attack metals/compounds that are strongly adsorbed to organic matter, as well as Fe-Mn oxides. In there procedure a clear distinction is drawn between the 'easily' reducible (metals strongly adsorbed to OM and/ or bound to Mn-oxides, amorphous Fe-oxides) and 'moderately' reducible (bound to Fe-(hydr)oxides and Zn-acid volatile sulphides) fractions. Mn-oxides are more easily reduced than amorphous Fe-oxides owing to the larger redox potential. This more definitive operationally defined criteria may also elucidate the high (>60% in the case of undiluted CLO and soil treatments) presence of Cu (as well as other metals) observed in the 'reducible' fraction in addition to the 'oxidisable' fraction in this study. Cu speciation has explicitly been confined to the oxidisable fraction by the authors cited above. These findings stress the importance of further developing a better defined and purposely constrained set of reagents unique to material of this nature and using both an operationally defined and target species labelling system.

Treatment	Si	K	Ca	Mg	Cl	NO_3	SO_4
CLO 2004	94.2	12.6	24.6	61.3	0	0	0
CLO 2005	69.7	8.6	26.0	55.8	0	0	0
CLO 2006	61.8	11.1	27.2	51.5	0	0	0
Parcgro	90.8	8.3	29.0	71.6	0	0	0
Comp	96.2	12.2	36.4	60.4	0	0	0
BDA	90.7	25.0	24.9	67.0	0	0	0
ML	93.2	26.8	58.9	83.5	0	0	0
Soil	95.6	59.2	28.0	45.8	NA	0	0
SS	81.8	26.2	47.7	55.2	0	0	0

Treatment	Ni	Zn	Cu	Cd	Pb	P	Al	Fe	Co	Mn	Ti	Cr	Li	V
CLO 2004	83.1	71.3	89.8	70.3	86.7	89.8	97.9	94.6	90.9	56.8	89.1	95.9	76.6	98.0
CLO 2005	65.2	42.0	85.4	46.5	69.5	86.2	87.6	90.6	75.5	40.7	88.6	86.9	66.8	84.5
CLO 2006	64.2	43.9	88.5	61.3	91.6	90.6	91.1	94.3	78.2	44.1	91.6	91.5	68.7	88.5
Parcgro	89.2	65.3	94.3	76.5	74.8	81.6	94.9	96.9	89.7	52.0	97.2	97.4	75.7	89.5
Comp	75.1	87.6	95.1	89.2	94.6	84.4	99.3	99.3	95.4	52.1	99.6	91.5	86.1	74.7
BDA	40.9	28.6	94.5	61.2	53.0	97.4	82.5	52.1	60.3	50.1	98.1	74.1	68.6	69.7
ML	44.5	39.8	98.2	78.0	74.3	98.8	93.8	90.7	83.1	72.8	95.0	76.1	91.6	71.7
Soil	94.6	64.0	97.7	74.9	79.3	93.9	96.2	98.2	87.6	72.3	96.9	93.6	99.8	73.2
SS	87.3	86.4	98.5	79.6	93.5	96.6	99.8	99.5	91.4	68.8	99.3	99.4	89.1	81.2

Table 3.19: Treatment percentage releases associated with the 'redox' phase for a) 'base cation' salt components and for b) 'trace metals'. NA = Not Applicable.

Nonetheless, it has been shown that the reducible-oxidisable fractions dominate the majority of trace metal releases relative to the total amount of leaching possible (all four phases). The reasons for this are due to the complex nature, solid-aqueous interactions and sensitivity to changing environmental conditions of the CLO and agricultural soil materials involved. Indeed, Flyhammar (1997) showed that oxic sediments from various environments behaved similarly with respect to metal leaching as fresh and shredded MSW, and fractionation patterns seen in sewage sludges are very similar to anoxic sediments. Metals in MSW can exist in a number of varying forms including elemental forms, additives (organic and inorganic salts), polymers (such as plastics, leathers, rubbers and papers) as well as in complex solid phase matrices (Flyhammar, 1998). As these various materials decompose a mixture of resistant primary substances, degradation products and synthesised fractions of both organic and inorganic matter (secondary minerals) will be established. These minerals often exist as particle coatings, co-existing alongside stabilised OM and play an important role in scavenging for metals due to their large surface area and active adsorption sites (Flyhammar *et al.,* 1999). Furthermore, the high OM content of the MSW and the interactions of the various metals with it can greatly influence trace metal solubilities in leachates depending on whether the organic compounds are mobile (i.e., dissolved organic matter).

Kumpiene et al (2006) highlighted the importance of OM at retaining Pb, Cr and Cu in studies where MSWI Bottom ashes were mixed with peat. In this study over 85% of Cu and 70% of Pb, with the exception of the BDA treatment (>50%) and Cr were extracted under redox conditions for all treatments. Ti, Al, Fe (with the exception of the BDA treatment - >50%) and P show redox partitioning levels for all treatments over 80% and Co, Li and V displays levels over 60%. An interesting relationship was discovered by Kumpiene et al (2006) that showed an increase in retained Cu concentrations with increased DOC levels. This is contrary to results obtained previously which determined that under alkaline conditions the dissolution of soluble organics occurs and subsequent formation of soluble metal-OM complexes occurs (Hsu and Lo, 2000 and Chirenje and Ma, 1999). Kumpiene et al (2006) attributed these findings to the possible flocculation of humic acid-metal complexes and their subsequent precipitation out of solution as a result of an increase in ionic strength of the leachates caused by the abundance of major cations, such as Ca. These findings are of particular relevance to this study owing to the fact that the potential negative effects of increased metal mobility brought on by alkaline conditions in leachates may have been ameliorated; paradoxically for the same reason the DOC may have originally become mobile.

The minerals or compounds that are often associated with the reducible-oxidisable fraction trace metals are often reactive, amorphous and metastable phases and so are highly susceptible to pH and redox potential changes as a result of shifting environmental conditions (Flyhammar *et al.,* 1999). In turn, this can increase the solubility, mobility and bioavailability of the trace metals that are subsequently released. Calmano et al (1993) showed that binding forms of heavy metals (Zn, Cd, Pb and Cu) can change significantly by the periodic redox changes in sediments with a low buffering capacity. The same may be true in this study, shown by the large proportions of redox dependant releases of many trace metals. It must be noted, that a large buffering capacity to pH has been found for the CLO and its associated soils but not necessarily Eh.

Thus, it has been shown that if water-logged, anoxic conditions prevail in artificial soils that have either been 'amended' with >25% CLO or consist purely of CLO, typical of those tested here, major trace metal releases are likely to occur. Proportional amounts of trace metals are also expected to be leachable from the agricultural soil and sewage sludge treatments if similar redox conditions are favoured. If an aerobic, well drained soil medium with a well established vegetation cover (retaining a high OM content) can be retained which remains weakly alkaline in pH, then trace metal releases will be more limited and base cation salts will be the major environmental concern. This is ultimately governed by the fractionation of the majority of trace metals within the redox-dependant phase and the majority of base cation salt components being affiliated with either exchangeable or acid-soluble species, such as carbonates.

3.3.6.3 Flux releases

Although fractionation patterns are of paramount importance when evaluating and predicting the potential risk to the environment of a particular material, the actual extracted amounts between treatments and their relation with time and individual elements are also important. A comparison of released amounts (fluxes -µg/kg) exuded by each treatment is key to the understanding and extent to which the potential contamination of water-ways may occur. It was decided that this was best assessed statistically and the results have been represented graphically by treatment, fractionation step and year where possible, for each element in turn. The main effects plots can be seen below in Figures 3.11 to 3.17. These plots illustrate the findings that are summarised in significance Tables 3.13 to 3.17 (above). In addition, comparison of the flux releases have been undertaken relative to government limit values for concentrations of heavy metals in soil and sludge for use in agriculture as set out by Council Directive (86/278/EEC).

The main points of interest highlighted by these plots were the fluxed amounts released between treatments. It has been shown that there was little change over the 3 years of sampling; the only significant differences being found for K, Li and V. K (exchangeable fraction) being exuded in larger amounts in the first year and in contrast Li and V (redox fractions) were released in progressively significantly smaller concentrations in consecutive years.

The primary observation between treatments was the higher extraction levels achieved by the sewage sludge treatment compared to all other treatments for the following elements: (Si, Cu, Zn, Cd, Co, P, Al, Fe, Mn and Ti). The latter two elements still demonstrate the highest released amounts of any treatment but are not significantly different from the mixed treatments (Comp, Parcgro and ML), as with Mn or from BDA with Ti. All of these elements were strongly associated with the reducible and oxidisable fractions which may explain why similar releases were not observed in the field lysimeter leachates as described in Chapter 2. A comparison of leachate flux behaviour with fluxes extracted during the modified Tessier sequential extraction procedure will be assessed further in Chapter 5. The elements/anions that displayed extracted amounts that were either the lowest, or considered low, relative to the CLO containing treatments, and to a certain degree with the soil control were: Cl, NO_3, K, Mg, Pb, Li and V. The first four of these elements have been shown to be strongly affiliated with the mobile phase, in particular existing as easily displaceable complexes. Pb, Li and V sewage sludge extractions were predominantly dominated by the reducible phase but V also showed a large oxidisable fraction. The remaining elements/anion tested, (Ca, SO_4, Ni and Cr) were found in similar quantities to those exuded from the undiluted CLO's which in the case of Ni and Cr were also significantly higher than levels exhibited by the mixed treatments. Ca and SO_4 are considered highly mobile whereas Ni and Cr species are dominated by the oxidisable fraction (although Ni has shown significant exchangeable characterisation for CLO treatments).

The agricultural soil control, with the exception of Mn where levels were of a similar level to that of the mixed treatments (Comp, Parcgro and ML) and the undiluted CLO 2004, always displayed extracted levels of the lowest, or within the lowest bracket of any treatment. The undiluted CLO treatments underperform relative to their intended remediation mixed treatment materials (Comp, Parcgro, BDA and ML) for the following elements: Ni, Zn, Pb, Cu, Al, P - CLO 2005 and 2005 only, Cd, Cr and V, as well as all anions (Cl, NO_3 and SO_4). This apparent amelioration of elemental fluxes, as illustrated in Chapter 2, is nothing more than a dilution effect and so little or no active remediation has been achieved by amending the CLO with the chosen mixer materials. In fact, for a number of elements the mixed treatments actually increase or exude similar extraction concentrations relative to their undiluted parent CLO's; summarised as follows. The Comp and Parcgro treatments displayed above-dilution extraction levels for K, Fe, Co and Mn. Similar differences existed for BDA for Si, Ca, Li and Ti and for ML for Mg and Mn.

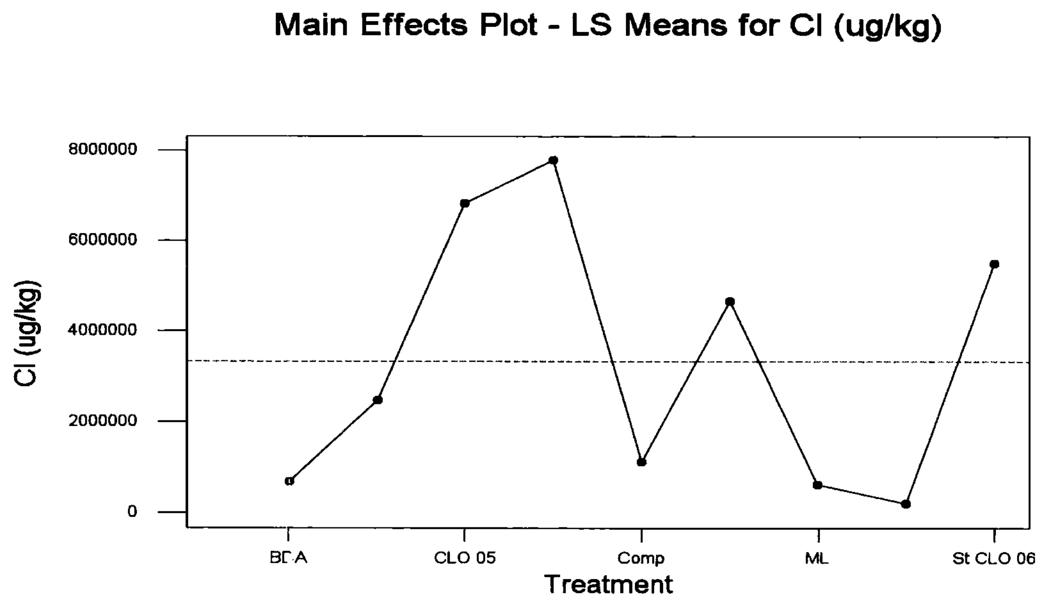
A further comparison was made between a fresh CLO 2006 digestate and an equivalent stock CLO 2006 which had been windrowed for around 3 months post discharge from the aerobic digester at Thornley. This comparison was included to determine whether any potential natural remediation had been achieved in elemental/anion leachable concentrations whilst the CLO was curing at the Coxhoe landfill site. No statistical differences were found between these two treatments but a statistical difference ($P<0.001$) existed for Cl between the other CLO 2006 batch and the stock CLO 2006. In addition a significant difference ($P<0.0002$) was also found between the two CLO 2006 batches (CLO 2006 and Fresh CLO 2006). These flux releases indicate that there was little change in the chemical nature, with respect to leachable concentrations during the windrowed curing-stage at Coxhoe. Statistically therefore, the differences between similar batches for released amounts of Cl were as important or greater than between the fresh and windrowed CLO 2006 material. Furthermore, the Cl fluxes were always higher in the stock CLO suggesting that this highly mobile metal salt component may have been flushed by rainwaters to greater depths where it was then re-adsorbed or co-precipitated in the decomposing CLO. It is therefore concluded that no significant naturally occurring remediation with respect to contaminant leachability can be attributed to the windrowing process that the CLO undergoes at Coxhoe landfill site.

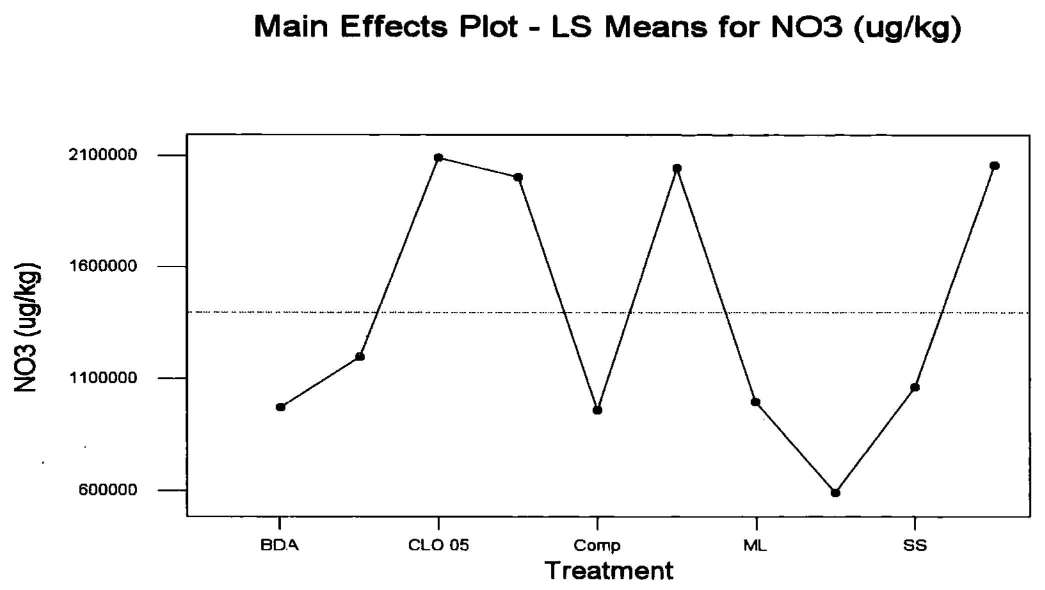
In summary, based purely on the results found during the characterisation analyses described here, the following decreasing order of potential contamination associated with each treatment was follows (>> indicates a significant ($P<0.05$):

SS >> undiluted CLOs >> Comp and Parcgro > BDA > ML > Soil

It must be stated though that firstly, owing to the variable nature of the undiluted CLO tested, they have all been grouped together as no one yearly batch demonstrated consistently higher extraction values. Secondly, that the distinctions between the mixed treatments were based upon numbers of elements that appear in the drinking and surface water legislation GL's and MAC's for each treatment. The degree to which government law is infringed cannot be assessed here as flux values are considered only. Thirdly, the placement of BDA may well be easily interchanged with that of the Parcgro and Comp treatments owing to this treatments higher partitioning of trace metals to the acid-soluble phase, as may have been the case in field based leachate studies in Chapter 2 (this will be assessed in Chapter 5). The re-positioning of this treatment in the scale above would be based upon the immediate availability of the increased levels of mobile contamination and the greater partitioning of trace metals in the 'more resilient' reducible and oxidisable fractions for the Comp and Parcgro trials. These assumptions are therefore condition based and so the preference of one amendment material over another must be strongly related to the likely conditions under which it will be utilised.

The only real solid statements that can be made are that the sewage sludge extractions were significantly higher than the CLO containing treatments and the soil control, and that the soil control had potential contamination levels were significantly lower than any other treatment. Furthermore, the major trace metal releases have been shown to be governed by redox-dependant conditions irrespective of treatment, which is evidence to support the previous statement.





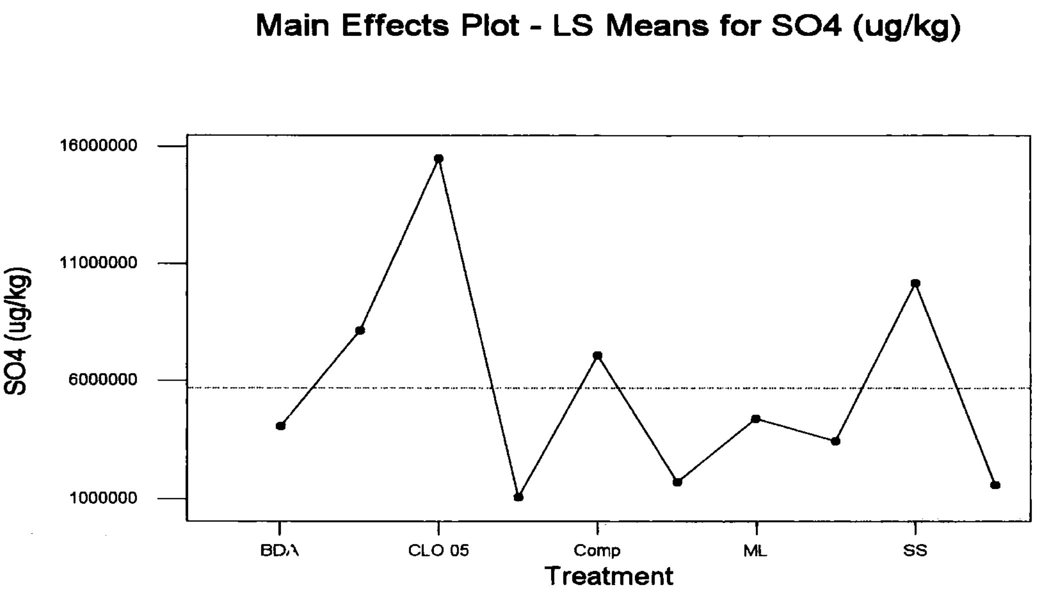
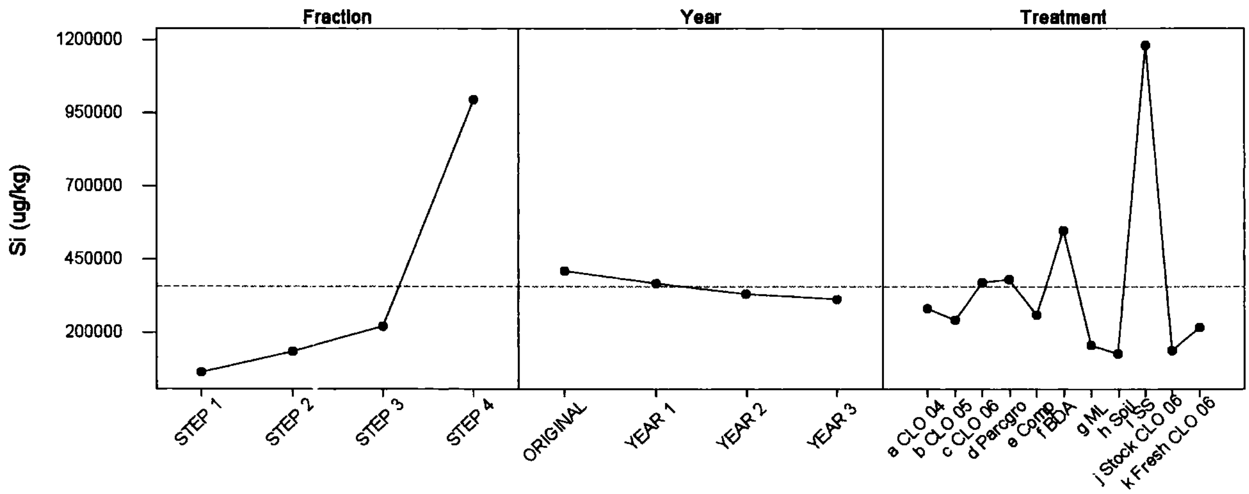
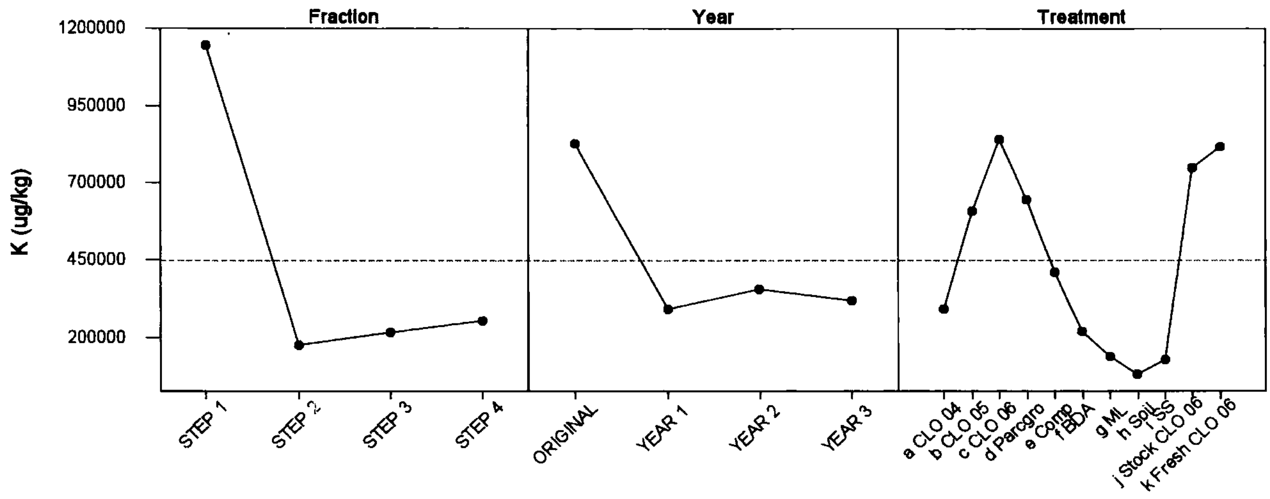


Figure 3.11: Main effects plots for Cl, NO_3 and SO_4.

Main Effects Plot - LS Means for Si (ug/kg)



Main Effects Plot - LS Means for K (ug/kg)



Main Effects Plot - LS Means for Ca (ug/kg)

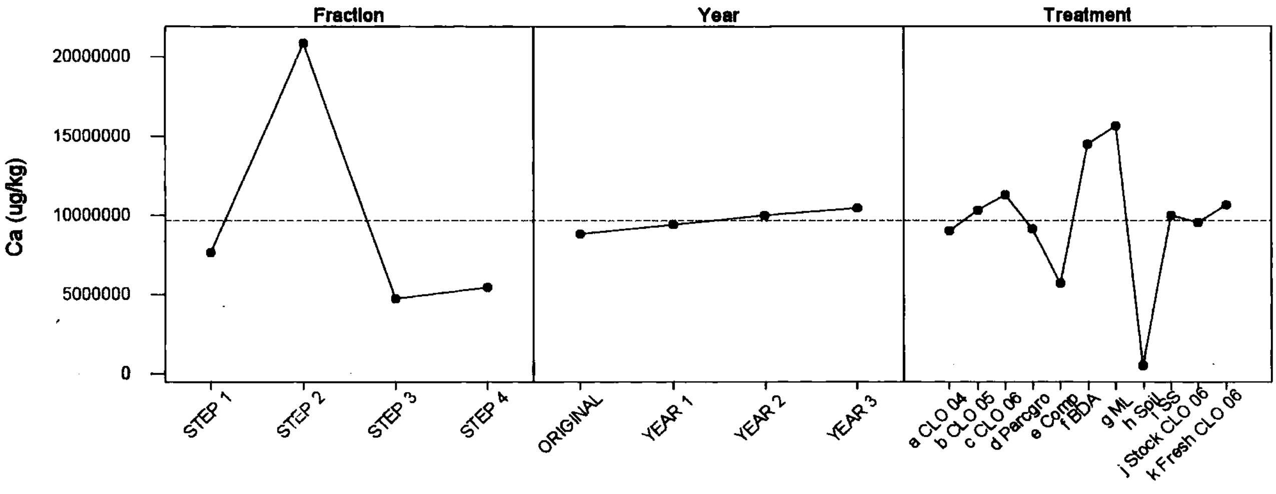
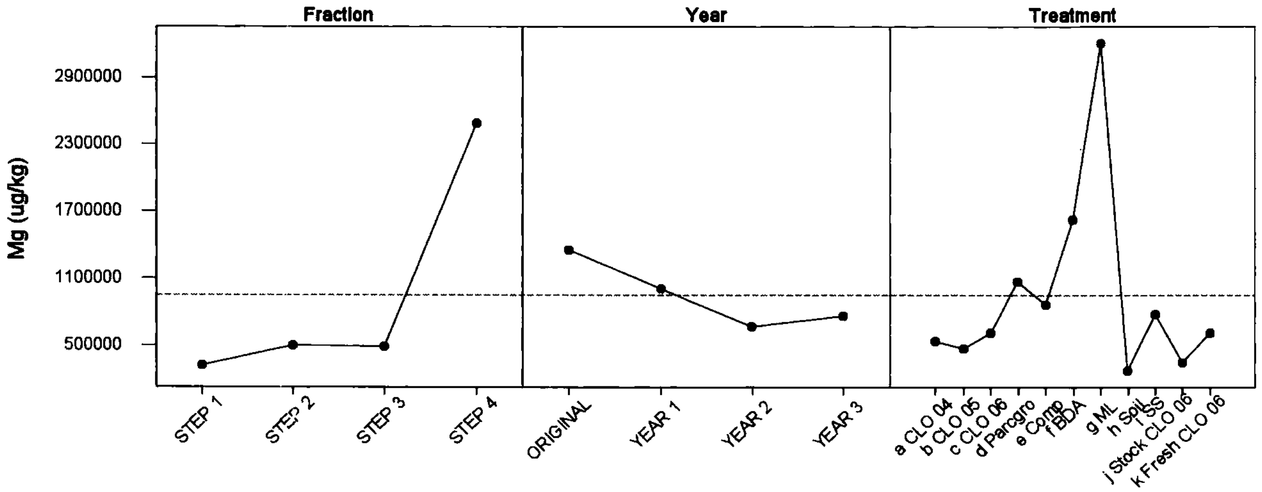
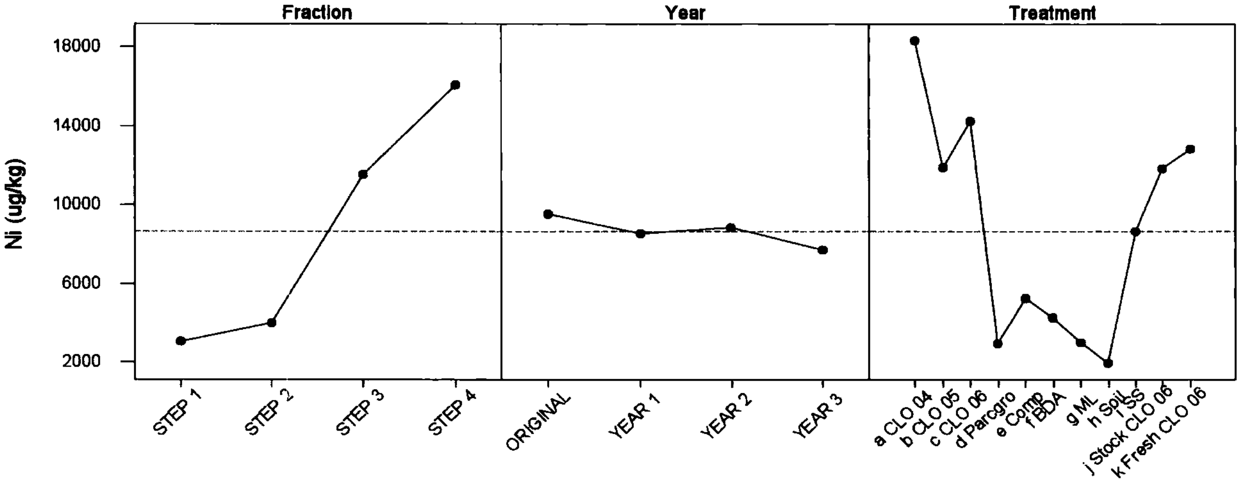


Figure 3.12: Main effects plots for Si, K and Ca.

Main Effects Plot - LS Means for Mg (ug/kg)



Main Effects Plot - LS Means for Ni (ug/kg)



Main Effects Plot - LS Means for Zn (ug/kg)

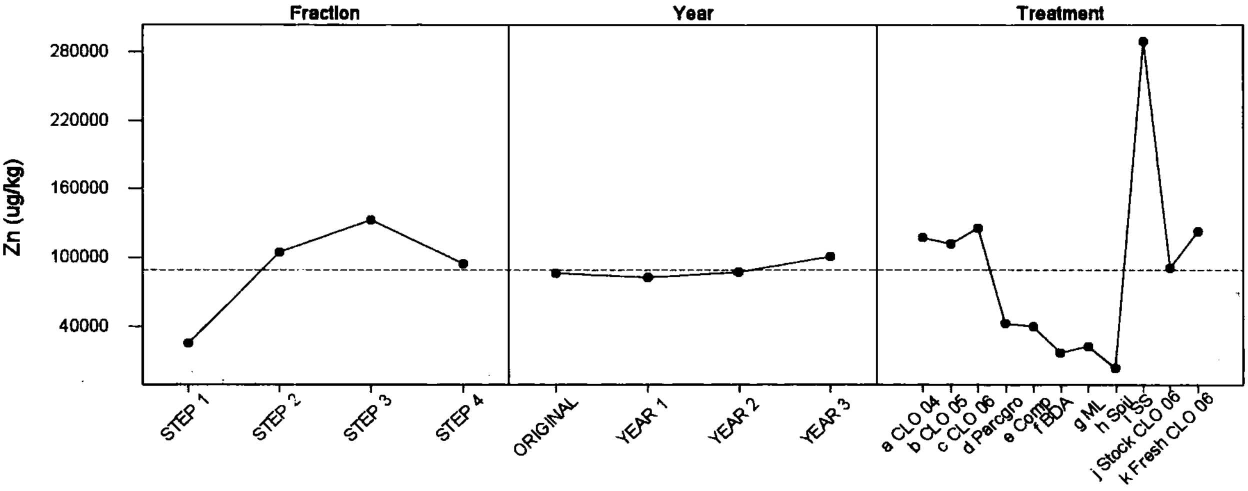
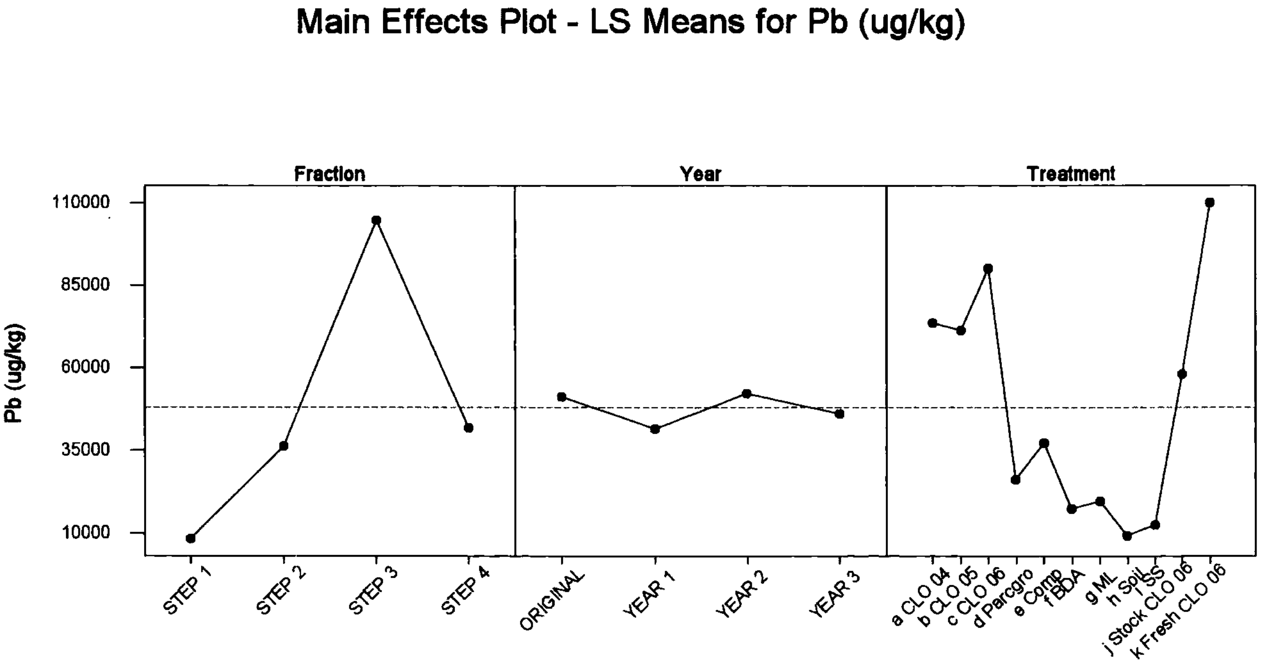
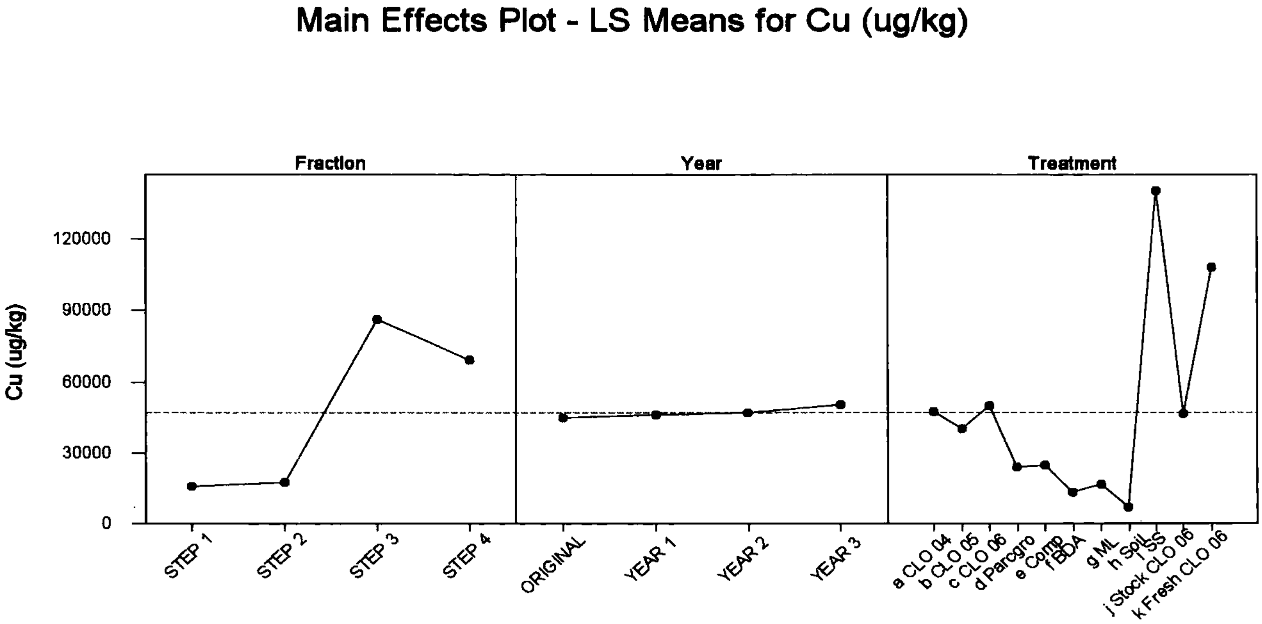


Figure 3.13: Main effects plots for Mg, Ni and Zn.





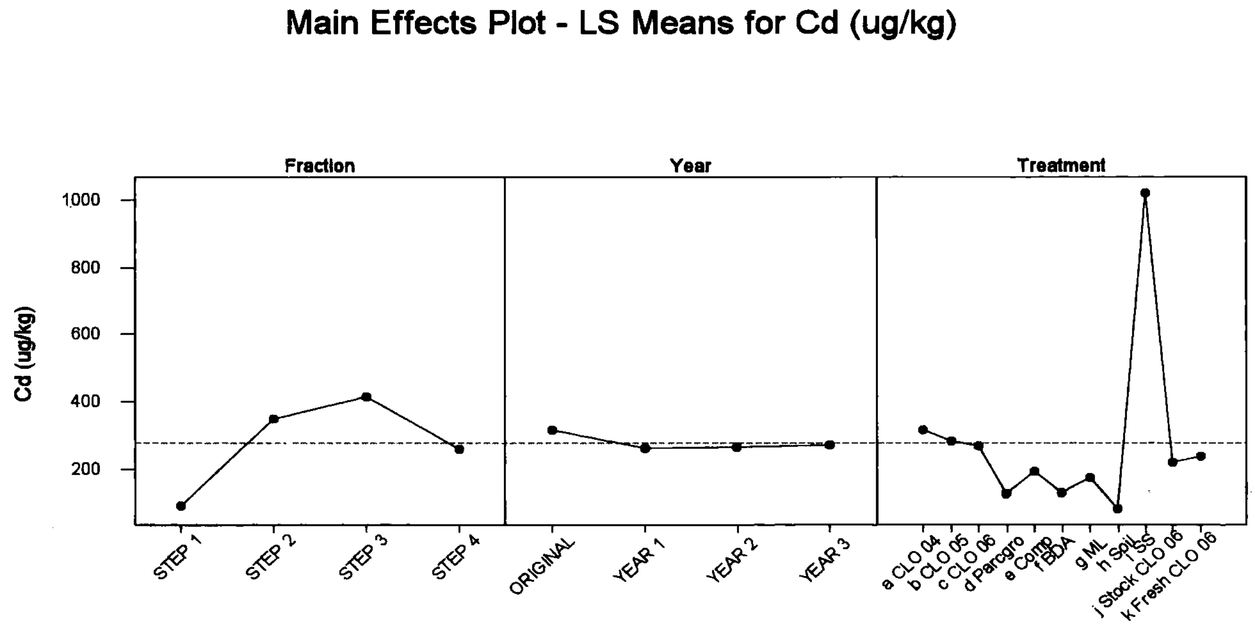
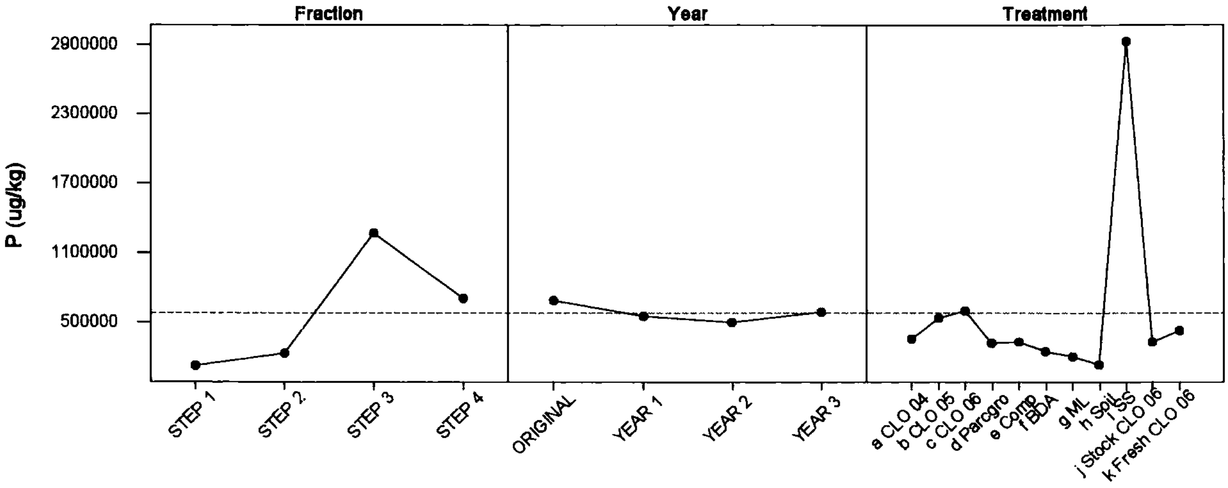
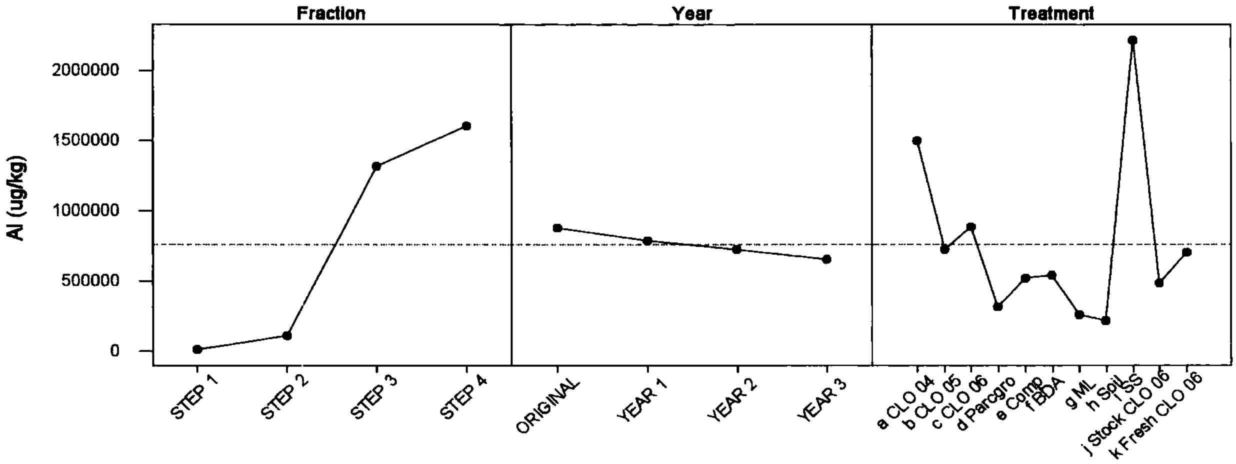


Figure 3.14: Main effects plots for Pb, Cu and Cd.

Main Effects Plot - LS Means for P (ug/kg)



Main Effects Plot - LS Means for Al (ug/kg)



Main Effects Plot - LS Means for Fe (ug/kg)

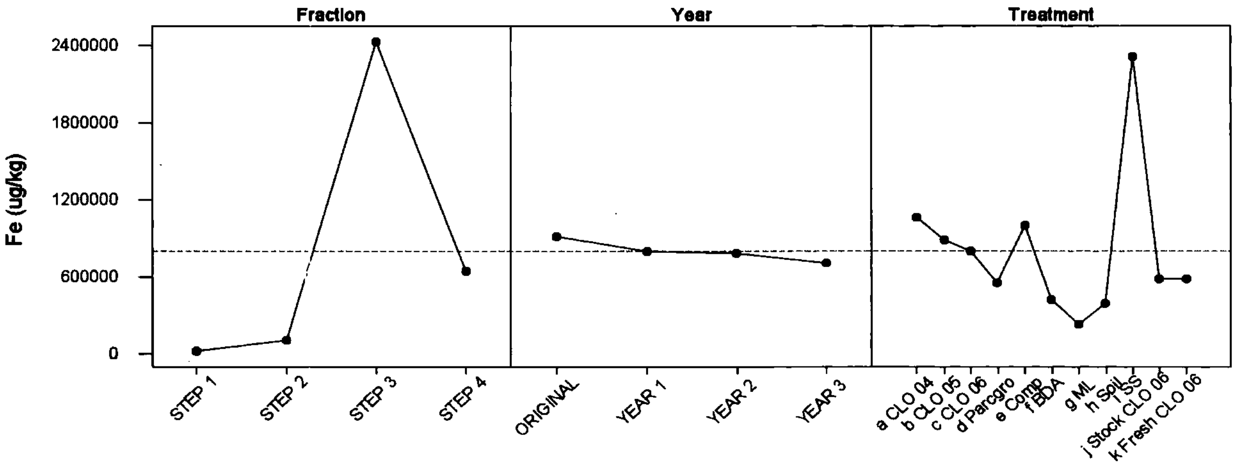
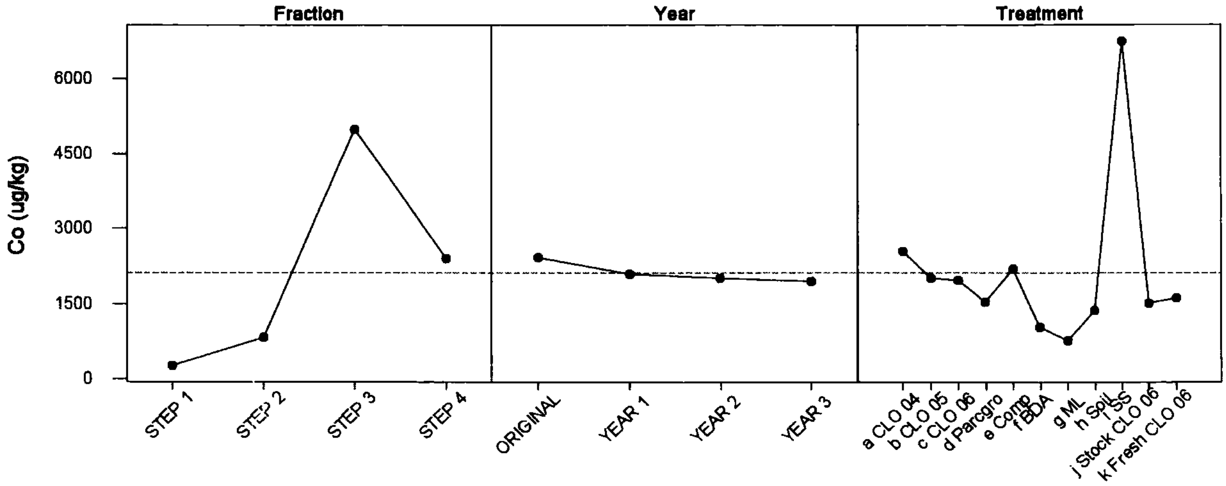
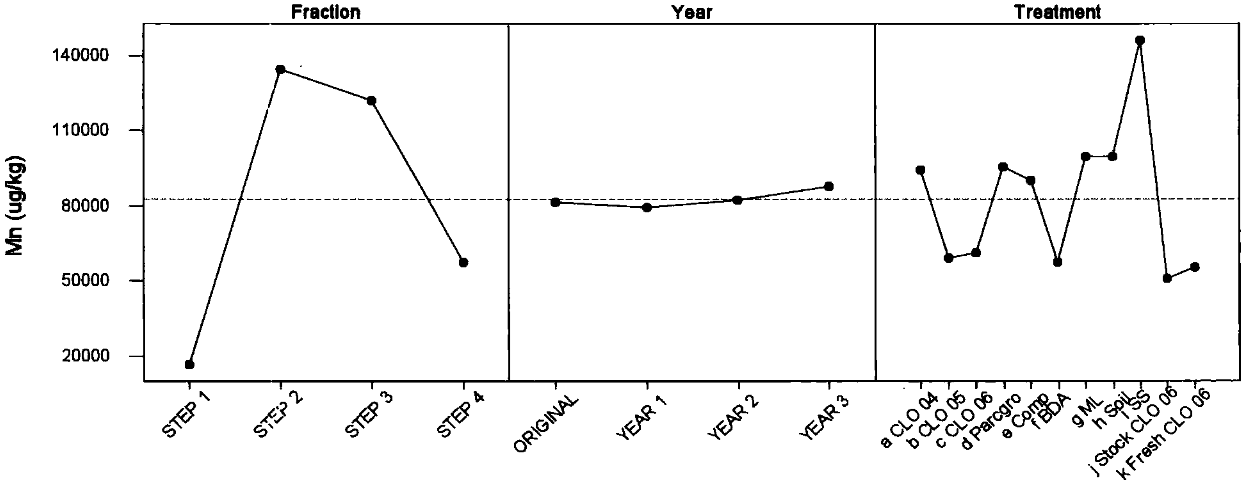


Figure 3.15: Main effects plots for P, Al and Fe.

Main Effects Plot - LS Means for Co (ug/kg)



Main Effects Plot - LS Means for Mn (ug/kg)



Main Effects Plot - LS Means for Ti (ug/kg)

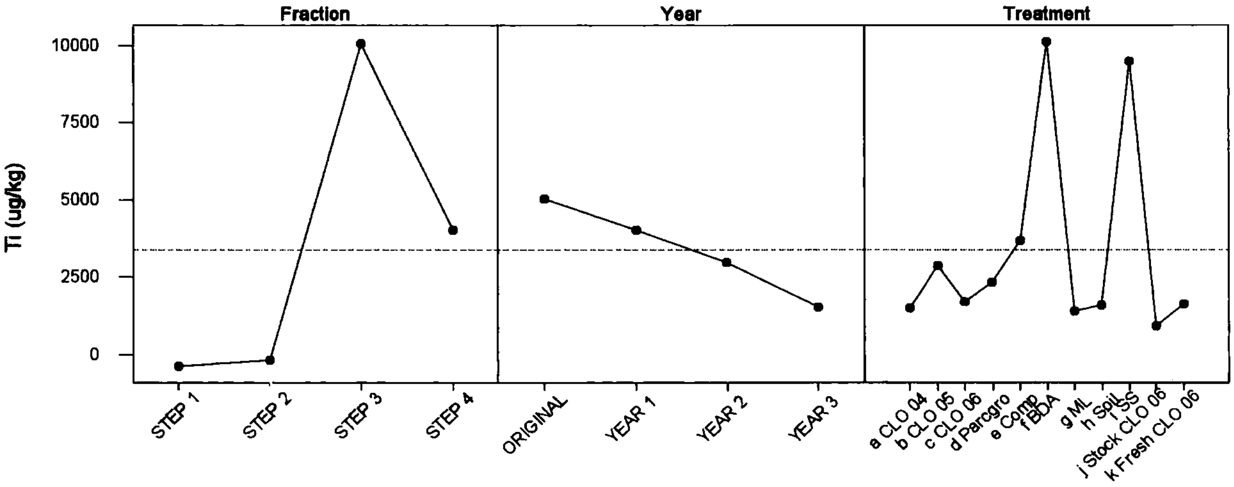
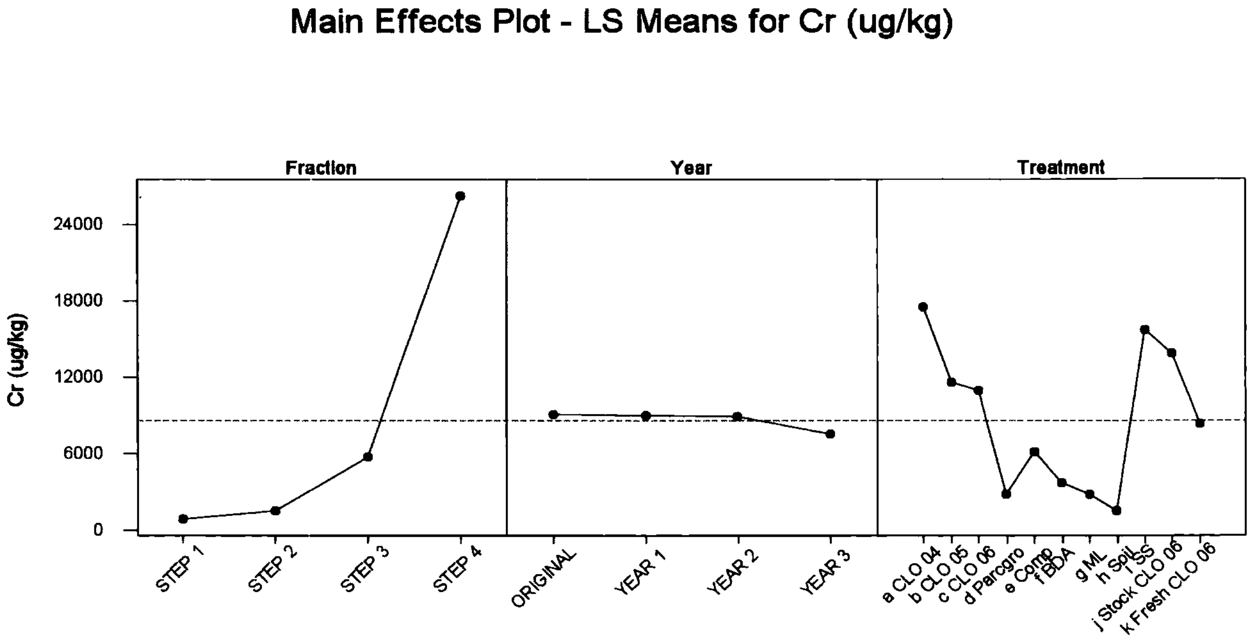
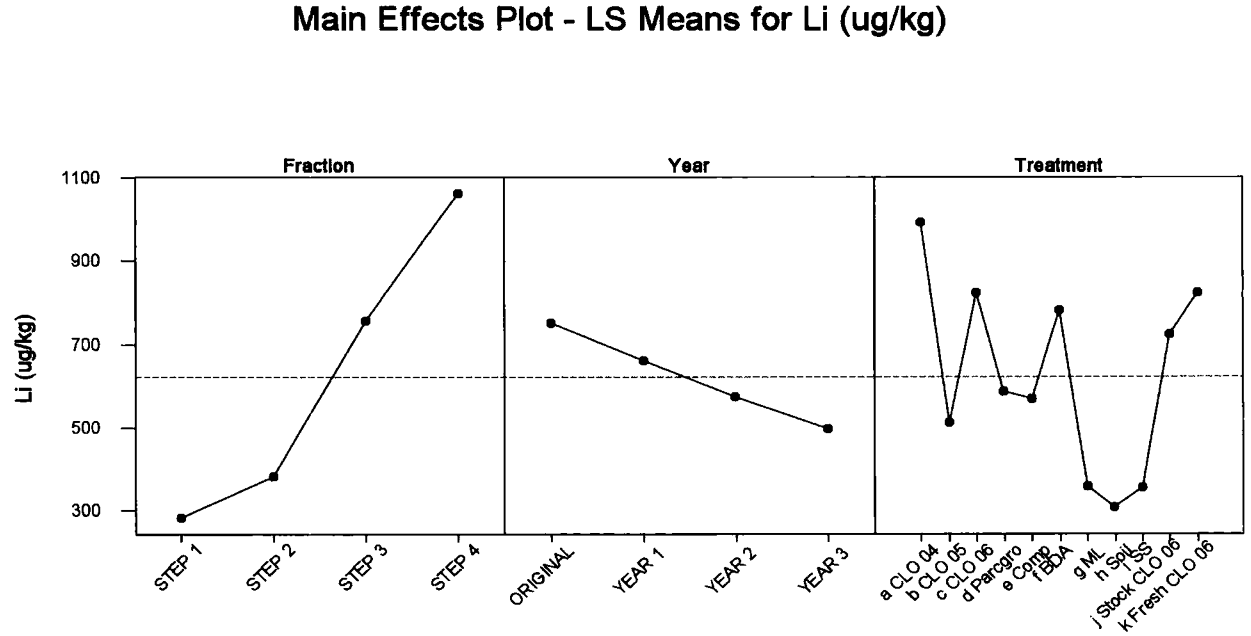


Figure 3.16: Main effects plots for Co, Mn and Ti.





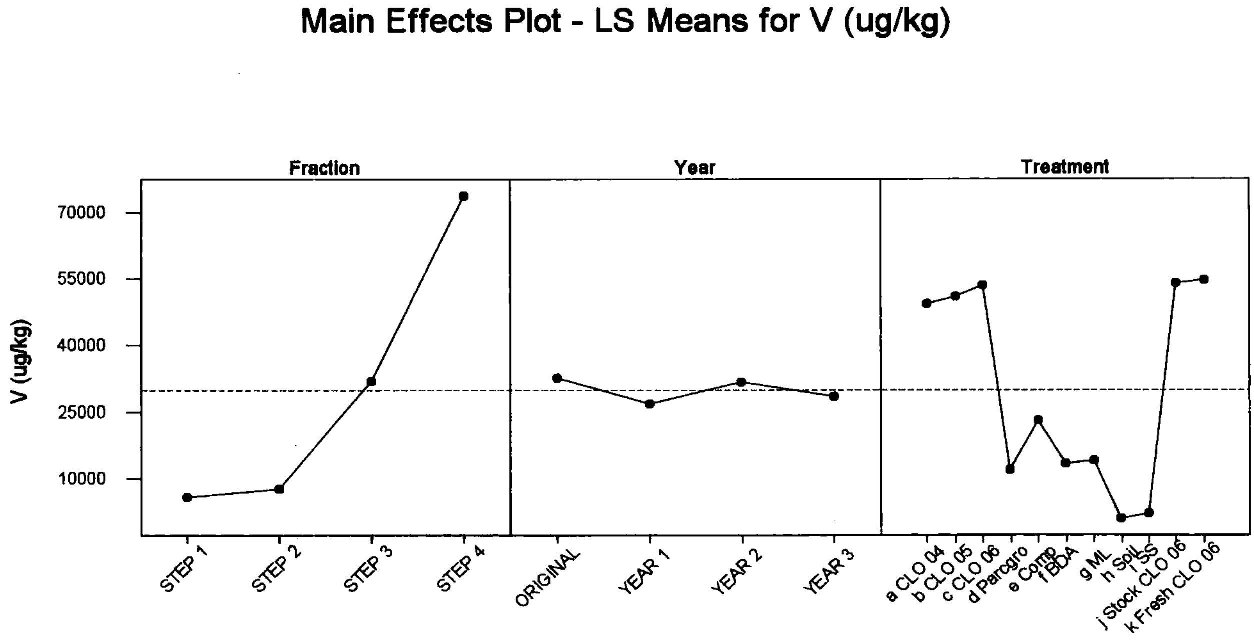


Figure 3.17: Main effects plots for Cr, Li and V.

3.3.6.4 Un-sieved/sieved analyses

The un-sieved/ sieved analyses, as with the carbon characterisation results, illustrate that significant differences existed between the CLO treatments. This therefore reveals that the heterogeneous nature of the CLO material is not just of a physical nature but also a chemical speciation one. However, this is limited to the undiluted CLO 2006 digestate for the following elements: Si ($P<0.05$), Zn ($P<0.003$), Cd ($P<0.003$), Co ($P<0.48$), Mn ($P<0.002$) and for CLO 2005 with Mn ($P<0.004$). All other analyses proved insignificant (Stock CLO 2006, Parcgro and CLO 2004) with respect to elemental/anion extracted amounts between sieved and un-sieved samples.

Thus, although differences have been shown between undiluted CLO samples that were acquired in 2006, as the other year CLO samples did not display the same variation it cannot be assumed that these differences were as a direct result of the 1mm sieving grading used. However, the one thing that was certain as a result of these analyses was the scale of heterogeneity displayed by the undiluted CLO materials, and to a lesser degree in the Parcgro material, prior to any laboratory refining necessary for experimentation.

3.3.6.5 Legislation

Table 3.20, below, shows the maximum cumulative levels of heavy metals attained in sequential extracts (for all 4 fractions), by treatment. These leached values have been compared against government recommended and mandatory set limits for both soil and sludge intended for use in agriculture, as depicted by Council Directive of 12th June 1986 on the protection of the environment, and in particular of the soil, when sewage sludge is used in agriculture (86/278/EEC). The limit values for concentrations of heavy metals in soil have not just been included for direct comparison but more so to gain an understanding of the concentration levels ultimately required if the CLO and its associated soils were to be utilised with or as a soil replacement. It must be remembered that the cumulative sequential extraction results presented here do not incorporate residual material phase concentrations and so extract concentrations/government limits are not necessarily transferable. The Council

Directive (86278/EEC) states that the analysis (atomic absorption spectrometry) for heavy metals must be carried out following 'strong acid digestion'. Concentrated hydrogen peroxide was the 'strongest' reagent used in this study as dilute nitric acid was only incorporated as a means of adjusting the extraction pH. Step 5 of the modified Tessier sequential extraction procedure used satisfies this requirement but as already mentioned it was decided that, for the main part, releases from the residual phase were surplus to requirement and so not included. Care must therefore be taken when undertaking direct comparison of cumulative extraction releases with government limits as perchloric and hydrofluoric acid digestion would significantly increase overall heavy metal extraction fluxes. An overall performance of each treatment can still be evaluated based on the assumption that the majority of potentially toxic metals (PTM) capable of being leached under environmental conditions have been extracted during the 4 step sequential extraction procedure used in this study.

It can be seen, from Table 3.20, that none of the treatments exceed either the recommended or mandatory limits set for sludge intended for agricultural use. This is likely to be as a result of the 'incomplete' sequential extraction method used which did not include a strong acid digestion. Comparison of the results against set limits for soil proves to be of greater environmental concern considering heavy metal limit values have been substantially exceeded by a number of treatments; this being without a 'strong acid digest'. The original intention of this thesis was to highlight whether the CLO and/or its associated products (Comp, BDA, ML and Parcgro) could be utilised as soil mediums themselves. The results presented here strongly oppose this. Where heavy metal soil limits are defined the undiluted CLO digestates (2004, 2005 and 2005) exceed not only recommended limit values but for the main part (both with reference to time and element breaching) mandatory limits also. If the CLO material was diluted (1part CLO: 3 parts mixer (Comp, BDA and ML) or 1 part CLO: 1 part green compost waste: 1 part screened soils (Parcgro)) the situation improves for Ni, Zn and Cd where contamination fluxes are brought below recommended soil limits. In the case of Zn, however, the Comp trial material breaches recommended levels for the entirety of the 3 year study. Cu and Pb releases were still in breach of recommended soil limits after dilution of the CLO, and in the case of the Comp treatment also breaches mandatory levels. The ML treatment in its 2nd and final year of study, before it was abolished, infringed upon mandatory levels set for Cu concentrations. It is worth noting that the agricultural soil itself breaches recommended levels for Pb contents.

Year	Treatment	Ni	Zn	Cu	Cd	Pb	Cr
Original	CLO 2005	52.3	395.1	144.9	1.0	286.2	49.6
Year 1	CLO 2005	55.6	486.7	217.3	1.3	308.3	56.8
Original	CLO 2006	56.6	369.2	242.0	1.1	479.4	47.0
Year 1	CLO 2006	73.5	618.7	221.8	1.3	383.7	54.7
Original	St CLO 2006	60.8	350.9	167.9	1.0	243.6	59.2
Original	Fresh CLO 2006	36.4	366.2	472.5	0.9	414.9	10.0
Original	Parcgro	26.1	138.9	69.2	0.5	68.9	19.5
Year 1	Parcgro	12.9	214.3	126.3	0.6	102.9	13.5
Original	CLO 2004	79.8	449.0	170.8	1.5	315.1	70.7
Year 1	CLO 2004	83.2	439.2	239.5	1.1	331.7	72.9
Year 2	CLO 2004	92.2	445.6	213.5	1.5	629.4	93.8
Year 3	CLO 2004	69.1	996.1	270.6	2.1	316.1	69.9
Original	Comp	26.2	195.5	99.7	1.0	431.5	23.3
Year 1	Comp	25.8	161.6	174.4	0.9	214.4	35.1
Year 2	Comp	26.4	222.8	107.4	0.8	160.7	32.5
Year 3	Comp	19.4	162.6	131.6	0.8	132.6	23.2
Original	BDA	23.4	109.7	51.8	0.7	81.2	18.6
Year 1	BDA	27.9	97.9	56.1	0.5	82.7	17.9
Year 2	BDA	14.3	94.8	109.2	0.5	103.7	16.8
Year 3	BDA	20.6	75.3	64.1	0.5	74.6	11.7
Original	ML	22.1	112.8	65.1	0.9	96.2	18.7
Year 1	ML	14.3	108.3	57.1	0.8	95.0	16.0
Year 2	ML	10.9	76.1	140.4	0.7	81.3	13.3
Original	Soil	9.9	19.6	30.3	0.3	37.6	10.3
Year 2	Soil	19.2	57.5	32.4	0.4	57.7	6.3
Year 3	Soil	11.2	46.2	45.2	0.4	61.0	5.6
Original	Sewage sludge	43.1	1273.1	643.8	5.2	72.4	85.4
Year 2	Sewage sludge	39.9	1306.3	821.1	4.4	151.0	61.4
Soil limit	Recommended	30	150	50	1	50	ND
Soil limit	Mandatory	75	300	140	3	300	ND
Sludge limit	Recommended	300	2500	1000	20	750	750
Sludge limit	Mandatory	400	4000	1750	40	1200	ND

Table 1.20: Maximum cumulative sequential extraction (all 4 fractions) levels of heavy metals leached from treatment materials compared with suggested limit values in soil and in sludge intended for use on agricultural land.

Finally, the sewage sludge is analogous to the undiluted CLO treatments in terms of infringement of government limits but the flux concentrations exuded were considerably larger for Zn, Cu and Cd. The difference between these treatments (sewage sludge and the undiluted CLO's) is that the sewage sludge is only permitted to be *applied* to agricultural land rather than being intended to act as a new soil medium. The same therefore (application of rather than replacement of), based on the findings presented here, would be appropriate for the CLO material, and this should only be in a diluted state, and at the very least in the proportions described above.

3.4 Conclusion

The characterisation of moisture content, pH and carbon, as well as metal and anion releases were carried out upon undiluted and amended CLO and alongside that of sewage sludge and an agricultural soil typical of the Durham region. The following conclusions can be drawn from these experiments:

- The moisture content although initially higher relative to the soil control does display significant dependability upon CLO output and retains less moisture than that of sewage sludge. Evidence to support formation of preferential pathways through substantial cracking of the CLO products has also been observed but further experimentation would be necessary to confirm this.

- pH levels in the solid CLO containing materials appear to be of little environmental concern, displaying weakly alkaline levels for the entirety of the three year study. The CLO and its associated products were therefore considered to display favourable pH levels relative to the sewage sludge.

- High (>50%) organic matter contents of the undiluted CLO digestates were of significant importance, both from a nutrient supply and potential metal adsorption point of view. These OM contents were not significantly different from those seen for sewage sludge.

- Mixing the CLO with the chosen amendments significantly reduced overall OM contents (<33%) which raises the issue of whether any amelioration is being afforded, other than that achieved by dilution, by mixing the CLO. Any remediation value affiliated with the attained alkaline pH's cannot be attributed directly to the amending materials and in the case of BDA the proportion of acid-soluble trace metals was increased.

- Further experimentation is required to confirm whether the observed elevated BDA and ML treatment black carbon contents relative to that seen for the sewage sludge and soil control are beneficial with respect to trace metal retardation. Undiluted CLO materials however contained significantly higher percentages of BC than the sewage sludge and soil control.

- Trace metal and anion speciations reveal that the majority of immediately mobile (exchangeable and acid-soluble) contamination from all treatments would originate as base metal salts, in particular, those containing K, Ca, Cl and SO_4 components. Ni has also been identified to be associated with this fraction for the CLO containing treatments, particularly BDA and ML.

- Major environmental concerns should focus upon the likelihood of major trace metals being released from undiluted CLO's and Comp and Parcgro treatments if anoxic reducing conditions prevail. The significance of oxidisable releases are still important, and increasingly so for the BDA (as are acid-soluble phase releases) and ML treatments.

- The aeration and prevention of water-logging, as well as, a constant supply of fresh OM, possibly via an extensive vegetation cover, is therefore imperative.

- Sewage sludge releases for a number of redox-dominated trace metals (Si, Cu, Zn, Cd, Co, P, Al, Fe, Mn and Ti) were shown to be significantly higher than all other treatment releases. The mobile phase controlling base cation salt components appears to be relatively less of a concern, being released in similar amounts to that of the other treatments.

- The agricultural soil elemental releases are almost always, except for Mn, of a low level relative to CLO containing treatments and sewage sludge.

- Finally, un-sieved contributions to elemental (both carbon and metal) and anion releases were considered to be relatively insignificant as this fraction attributed <10% (w/w) of the solid materials. Un-sieved significant differences do however support the need for a more efficient pre-treatment separation procedure.

Chapter 4

Pre-washing pre-treatment of CLO

4.1 Introduction

Technological advances in the waste management sector are ongoing, especially with the topicality of global warming and the landfilling of waste, and its consequences upon the environment. Therefore, company aims and objectives change. Ongoing discussions with Premierwaste indicated a need for this change to be incorporated into aspects of the project. In particular, in view of findings relating to the presence of dangerously high levels of metal-salt complexes flushed out of all CLO-containing treatments, it was proposed that some form of action should be taken to address this. Thus, in place of soil lysimeter behavioural experiments intended to provide information concerning flow pathways through artificial soils, a factorial pre-washing experiment was devised which was considered a more valuable means of assessing, and potentially remediating, detrimental characteristics of CLO. This is not to say that the presence of preferential flow pathways within CLO associated soils in unimportant; simply that, with the time available, remediation efforts were considered of more value in addressing a potential environmental problem concerning CLO, as opposed to quantifying another potential problem.

Numerous laboratory and field-based studies, focusing on the release of alkali and alkaline earth metals (Abbas *et al.,* 2002 and Gros *et al.,* 2003 and 2006) and heavy metals (Wang *et al.,* 2001, Kim *et al.,* 2001, 2003 and 2005, Ludwig *et al.,* 2005 and Izquierdo *et al.,* 2007), from various MSWI ashes and residues under leaching conditions have been conducted. These data highlighted the detriment that leached mineral contaminants can inflict upon the environment, and also proposed a suitable means of amelioration, once the MSW had been incinerated. The release of metals from ash deposits is reliant upon their form and the relative solubility of those metals under pH-dependent conditions (Ludwig *et al.*, 2005). These authors showed that the release of water-soluble base cations into solution was governed by dilution, with no acclaimed dependency on H^+ concentration. However, heavy metals may be present as carbonates or oxides, or be contained in moderately soluble phases trapped with these carbonates or oxide complexes – both of which require protonation for their dissolution and release. Little, however, is known about the possible effects that aerobic digestion of MSW may have on the availability of these metals under neutral conditions. Long term lysimeter trials (Chapter 2) have shown that extremely large quantities of dissolved metals have been found in leachates exuded from a number of treatments containing CLO which, from recorded leachate pH levels, are not of an acidic nature. Therefore, it is important to provide some quantification concerning the release of water-soluble salts and the extent to which the composting process may actively increase heavy metal leachability under the washing medium of water. A simple pre-washing step may, then, become an environmentally important and economically viable stage in Premierwaste's MSW recycling process.

4.2 Sample Analyses

4.2.1 Materials

In this study temporal variations of the compost-like-output (CLO 2006 and a 2006 derivative batch which had been left outside at the Coxhoe landfill station to cure for an additional 5 months) were investigated as well as an agricultural loamy soil (agricultural soil) and sewage sludge. All materials used, except the stock CLO were identical to those used in the lysimeter trials in Chapter 2.

4.2.2 Pre-washing with tap water

Principle:

The use of a modified Tessier's sequential extraction (Chapter 3) provides a good overall picture of the partitioning of metals and anions which could be released under a number of chemical and environmental conditions. However, the impending risk to the environment from highly mobile contaminants, such as metal salts, presents one of the major drawbacks of using aerobically digested household waste as a soil amendment. Gros et al 2005 *'stressed the importance of accounting for mineral contaminants, such as salts, when conducting an assessment of waste reuse* *scenarios'*; therefore, additional information specifically relating to water-soluble contaminant release patterns, the timescales on which this can occur, and the potential for 'stabilisation' of CLO could also prove extremely beneficial.

An experiment was devised in which solid samples were washed with tap water under controlled conditions to further the understanding of anion and metal release patterns relating to the water-soluble phase. The relatively simple procedure was based on recent work carried out by Abbas et al (2002) who specifically looked at the potential stabilisation of MSW combustion residues by washing them with de-ionised water. For this study, tap water was used, since treated waters would prove economically unviable in a commercial context (dealing with over 100,000 tonnes of waste per year), despite the likelihood of treated water being a more efficient contaminant removal medium. It must be remembered that CLO is a commercial product, sourced from household waste, and so any means of remediating pollutants must suit both its environmental and its industrial brief.

In addition, as stated by Abbas et al (2002) *'for a full scale water extraction process to be economically feasible the amount of water should be low and the extraction time should be as short as possible without seriously lowering the efficiency.'* This was certainly true if the substrates which, like the ashes from combusted MSW, were machine washed with various waters in a controlled environment. However, in this study, the potential also arose to investigate whether washing composted MSW in the field via natural filtration of rainwaters through the material provides a means of stabilisation. It is common practise for the freshly discharged CLO to be laid to rest for up to 5 months at Coxhoe landfill site before it is used further. It has been noted by Castaldi et al (2006) that within the initial composting mass, labile and soluble forms of certain heavy metals were transformed to more stabilised species. This phenomenon may be further promoted as rainwater flushes through composted MSW, taking with it the more mobile and easily dissolved species. If the alleviation of any contaminants from CLO can be deemed a result of this windrowed curing stage, and the degree to which this has occurred quantified, then a still more cost-effective method may be available.

Comparisons of water-leachable concentrations from undiluted, freshly discharged CLO, a 5 month old curing undiluted CLO, sewage sludge, and an agricultural soil with recorded concentrations for these treatments from a 2 year period under field conditions (Chapter 2) were made. The basis of these temporal comparisons was the considerable lowering of (most) mineral and trace metal contaminants to levels suitable for drinking water extraction achieved after 2 years of rainwater leaching. These values were not taken to be the total water-extractable contents, but rather representative evaluations of in-situ leachable measurements for the solid materials in scenarios characteristic of their potential and current utilisation.

Abbas et al (2002) calculated the extraction efficiency of the washing process by giving the extracted amounts as percentages of that released under total water-extractable conditions, which involved dilution of solid samples to a high liquid solid ratio (L/S), at which point the concentration of the species under investigation became independent of the L/S ratio. On average, this ratio was 200 which, when attaining a representative 50 gram sample for the CLO treatment, meant that liquid volumes in excess of 10 litres would be necessary. This was impractical in the laboratories available and so field lysimeter cumulative component leachate fluxes (mg/kg) after 2 years were used, as mentioned above.

Under the typical conditions experienced for County Durham, and temperate climates in general, it is highly unlikely that total amounts of water-extractable contents will ever be reached. Furthermore, even in undiluted form, which would seriously damage the environment, the CLO, based on field studies, would require around 80 years to reach the stage where total leached amounts could potentially have exuded. A more realistic estimation of the leaching behaviour of each material can be evaluated using a 2-step batch-leaching test (CEN 12457-3), recommended by the European Union as the standard leaching test for granular wastes. The justifications behind using this method are its simplicity, rapid repeatability, and its recommendation by the EU, as well as others (Izquierdo *et al.,* 2007 and Abbas *et al.*, 2002), as a rapid means of assessing the environmental impact of a granular waste material. This test replicates the conditions for both short-term (L/S = 2 or L/S 2 as will be referred to throughout) and long-term (cumulative L/S 2 and L/S 8) leaching behaviour. The long-term behaviours at L/S 10 for CLO, sewage sludge and agricultural soil equated to 2.1

years, 4.8 years and 6.2 years, respectively under the conditions experienced for the lysimeter trials (Chapter 2). Including the CEN 2-step batch-leaching test into this study therefore allows assessment of its appropriateness for quantifying the leaching behaviour for these materials and highlights the large bulk density differences displayed by CLO and sewage sludge compared to agricultural soil.

It must be noted, however, that the L/S ratios of 9, 4.2 and 3.3 for the field lysimeter treatments – CLO, sewage sludge and soil (calculated from lysimeter core weights and a cumulative 2 year rainfall of ~27 litres), respectively – were considerably lower than the aforementioned L/S ratios attained by Abbas et al (2002) for the total water extractable and are quite variable in value owing to these respective bulk densities. However, as already illustrated in Chapter 2, by this point, the majority of contaminant levels had diminished sufficiently to place them in agreement with drinking and surface water government MACs (Mn and Ni being the exceptions for both CLO and SS treatments). It is these reduced levels, in conjunction with the orientation of this study toward the collection of field-based component behaviour of leachates that provide representative levels against which tap water extraction data can be compared.

Procedure:

A factorial design, measuring dissolved elemental concentrations and conductivity levels exuded from solid waste samples (CLO 2006, curing stage CLO 2006, and sewage sludge), as well as from agricultural soil, were compared. The factors considered were contact time, number of extraction steps, and liquid to solid ratio (L/S). Contact or mixing times were 5, 10, 15, 20, 30 minutes and 1 hour; the number of washing steps were, one, two and three (after each washing step, conductivity and dissolved elemental concentrations were taken); L/S ratios were 2, 3 and 5. Initially, L/S 1 was included, based on its economic value, but insufficient leachate was available, post-reaction, for CLO treatments owing to their high absorbance levels.

A 50 gram sample of dried solid was weighed into a 250ml glass beaker. Larger 500ml glass beakers were employed for the L/S 5 washing step, ensuring complete mixing of solid and liquid phases. The appropriate volume of tap water was added to the beaker and an IKA labortechnik® KS 125 basic shaker table was employed to ensure effective agitation of samples during analysis. Conductivity measurements were taken in-situ immediately after each time interval, and all leachate samples were decanted and stored in 25ml vials for immediate metal (ICP-OES) and anion (IC) analyses (as described in Chapter 2). For the 2 and 3 step washings, excess leachates were removed using vacuum filtration after which the next step commenced on the same sample. All experiments were carried out in duplicate and blanks were run throughout to assess contamination from laboratory glassware. It was important that all apparatus had been thoroughly washed with milli-RO purified water and dried to ensure removal of any residual nitric acid wash that may interfere with IC analysis or L/S ratios.

4.2.3 CEN leaching test

This is a 2-stage serial batch-leaching test. The CLO materials were milled using a pestle and mortar until >90% (w/w) of the material had a particle size <4mm (the sewage sludge and agricultural soils were already in this desired state). A representative 50g sample was then mixed with 100ml of tap-water to attain an L/S 2, and the mixture was then agitated continuously for 6 hours. In-situ conductivity values were taken immediately after this time had passed, and samples were then decanted and stored in 25ml vials for immediate ICP-OES and IC analyses. In the second step, the materials remaining from the first step were leached for a further 18 hours at L/S 8, with fresh tap water. The results of the CEN tests are presented as released amounts based on dry material weight (mg/kg) at L/S 2 and at accumulated L/S 10.

The decisions not to incorporate filter papers when conducting vacuum filtration and to use tap water rather than de-ionised water, were both in order of attaining actual leached characteristic component concentrations. Tap water, de-ionised, and rain-water blanks were also run to calculate the extent to which tap water may affect leachate component concentrations and to identify any discrepancies between laboratory results and field data resulting from the varying water types. It was ensured that the exact same conditions were adhered to for the CEN testing as for the pre-washing experiments to avoid experimental bias.

4.3 Results

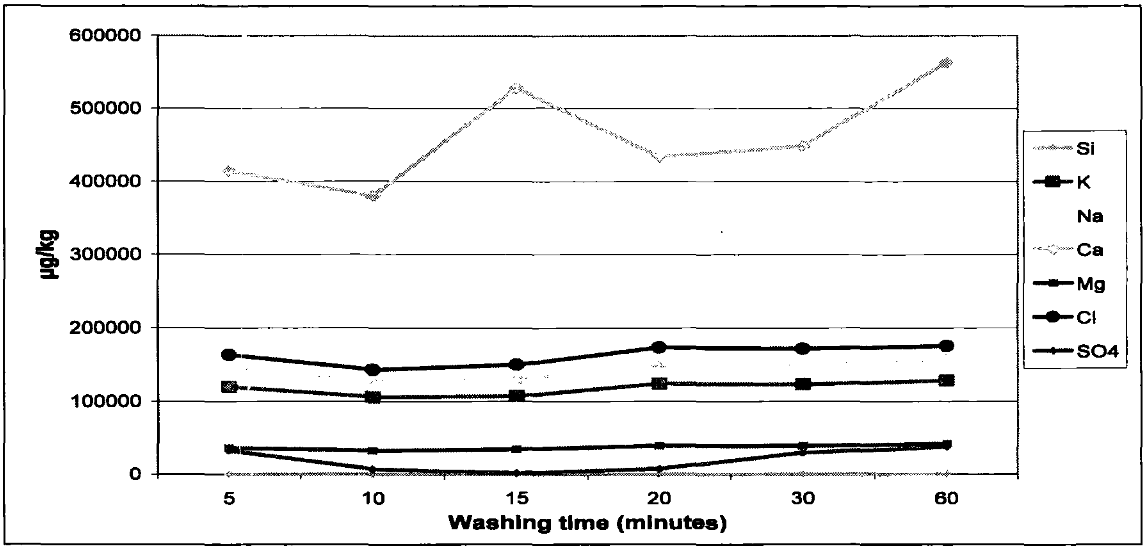
The results described below have been grouped by treatment to obtain a representative account of flushing behaviour and component extraction efficiency for each of the materials analysed. However, a brief overview of treatment findings regarding their behaviour as a function of contact/reaction time has also been included below since little relationship was found between contact time and treatment component releases (and so has not been included in the main breakdown). All flux comparisons are displayed in µg/kg and electrical conductivity values in either microseimens (µS/cm^{-1}) per kilogram of material or (µS/cm^{-1}/kg) per litre of water for comparison purposes between different L/S ratios. An overall comparison between treatment findings has been carried out in the discussion.

4.3.1 Contact/reaction time

Little relationship was found between contact/reaction time and component release concentrations for sewage sludge and CLO treatments. Conversely, the agricultural soil treatment showed an inverse relationship between contact time and component released concentration for a number of trace metals including: Ni, Zn, Cu, Pb, Al, Fe, Mn, Ti and V as well as for NO_3. The scale over which this occurred (for the soil treatment) was < 250µg/kg, which, together with the fact that this treatment was incorporated as a comparison treatment, meant that the findings were considered no further. An example of this lack of component relationship with reaction time can be seen in Figure 4.1 which shows the comparison between CLO component releases at L/S 2 and contact time. This is also indicative of the behaviour displayed by the sewage sludge.

This overall lack of relationship between reaction time and released amounts was also observed by Ludwig et al (2005). Ludwig, however, did find a positive relationship with increasing reaction time (1, 24 and 72 hours) for Cr and Ni releases, and to some extent Cu from MSW ashes. In this study, assessing the behaviour of releases from aerobically digested MSW on much shorter time scales (5-60 minutes), did not reveal similar relationships. Any differences observed with time were due primarily to the heterogeneity of the samples. In view of these findings, time variations have only been included for conductivity measurements and not for elemental analyses.

a)



b)

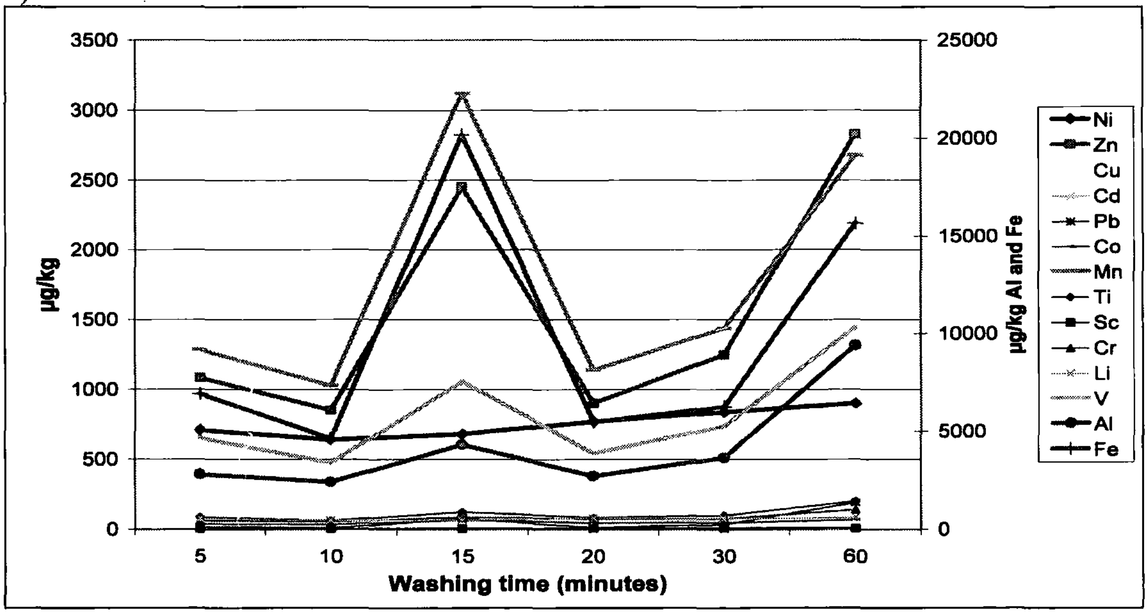


Figure 4.1: Comparisons of a) base cation salt component and b) trace metal extraction concentrations of CLO with tap water at L/S 2 for different time periods. At each interval new CLO material was used. Al and Fe have been plotted on the secondary y axis on Figure 4.1b

4.3.2 Sewage Sludge

4.3.2.1 Conductivity

The time of extraction, as well as the number of extraction steps, influenced the ionic strength of sewage sludge leachates. Furthermore, sewage sludge displayed a good homogenous release of salts with both time and extraction steps – gradually increasing with both. The number of extraction steps appeared to have a greater governing effect on the ionic strength; the main benefit (i.e., the release of most metal salts) was achieved within the first washing step for both time periods (5 and 10 minutes). Table 4.1 shows the influence that changing L/S ratio had on the ionic strength of leachates. As with the other 2 factors (contact time and extraction steps), increasing the L/S ratio from 2 to 5 increased relative conductivities but to a lesser extent. This was especially true after step 1 had commenced, as the differences in recorded EC levels became less pronounced. The accumulated L/S 10 conductivities achieved after the 24 hour CEN test were not exceeded at any stage, although washing the sewage sludge 3 times for 10 minutes each at L/S 5 did produce levels close to this. If L/S ratio was the main governing factor, then the cumulative 3 step washing levels at L/S 3 (accumulated L/S 9) for both time periods would be close to the CEN test leached levels (L/S 10), and the L/S 5 (accumulated L/S 15) totals would exceed this level. This was not the case, and the staggered appearance of the total 3 step washings at all L/S ratios, as well as the lower respective levels for the 5 minute washings, further indicated that all 3 factors were controlling leached conductivity levels.

Conductivity levels in sewage sludge leachates have thus been shown to be dependent on all 3 factors, with time and washing steps being of greater influence than L/S ratio. The question therefore arises whether increasing the number of washing steps or the extraction time would be beneficial relative to the levels achieved after each stage/time period with respect to drinking water regulations. If sufficient quantities of conductivity-controlling components had been leached after the first washing step, or after 5 minutes, then would it be environmentally necessary to further extract components, if this were economically viable (i.e., using more water, increase extraction times or number of extraction steps)? This will be discussed later.

µS/kg/litre	1 of 3x5	2 of 3x5	3 of 3x5	Total 3x5	1 of 3x10	2 of 3x10	3 of 3x10	Total 3x10
L/S2	3982	2390	1663	8035	5600	3066	2213	10879
L/S3	4524	3255	2012	9791	5295	3825	3060	12180
L/S5	6758	3500	2128	12385	7925	3925	2915	14765
CEN L/S 10				15616				15616
µS/kg								
L/S2	39820	23900	16630	80350	56000	30660	22130	108790
L/S3	30160	21700	13410	65270	35300	25500	20400	81200
L/S5	27030	14000	8510	49540	31700	15700	11660	59060
CEN L/S 10				89890				89890

Table 4.1: Mean conductivity values for a multi-stage multi L/S washing procedure for leachates of sewage sludge. Cumulative (3 washing step totals) levels are also included and compared against cumulative CEN L/S 10 conductivities. Both actual (µS/kg) and relative (µS/kg/litre) values are shown.

4.3.2.2 Base metal salts

The main elements controlling conductivity levels in decreasing order were: NO_3 > SO_4 > Ca > Cl > Mg > Na (Figure 4.2). Si and K leached concentrations were relatively very low, typically in the region of 5000µg/kg for a cumulative 3 step total flush. Levels of Mg and Na were below 40,000µg/kg for all 3 L/S ratios. There was some heterogeneity displayed between L/S ratios, particularly for Cl, NO_3 and SO_4 at L/S 2 with respect to washing step release behaviours but, for the majority of leachates, the first stage exuded the greatest concentrations, followed by the second and then third steps. Anion concentrations actually diminished with increasing water content, with NO_3 levels for the 3 step washing total decreasing from 364,000µg/kg for L/S 2 to 104,000µg/kg for L/S 5, SO_4 levels decreasing from 225,000µg/kg to 40,000µg/kg and Cl levels decreasing from 40,000µg/kg to 14,000µg/kg for the same. Conversely, the base cations all increase with increased levels of tap water – Ca showing the greatest relative concentration elevation from 9,000µg/kg to 22,000µg/kg.

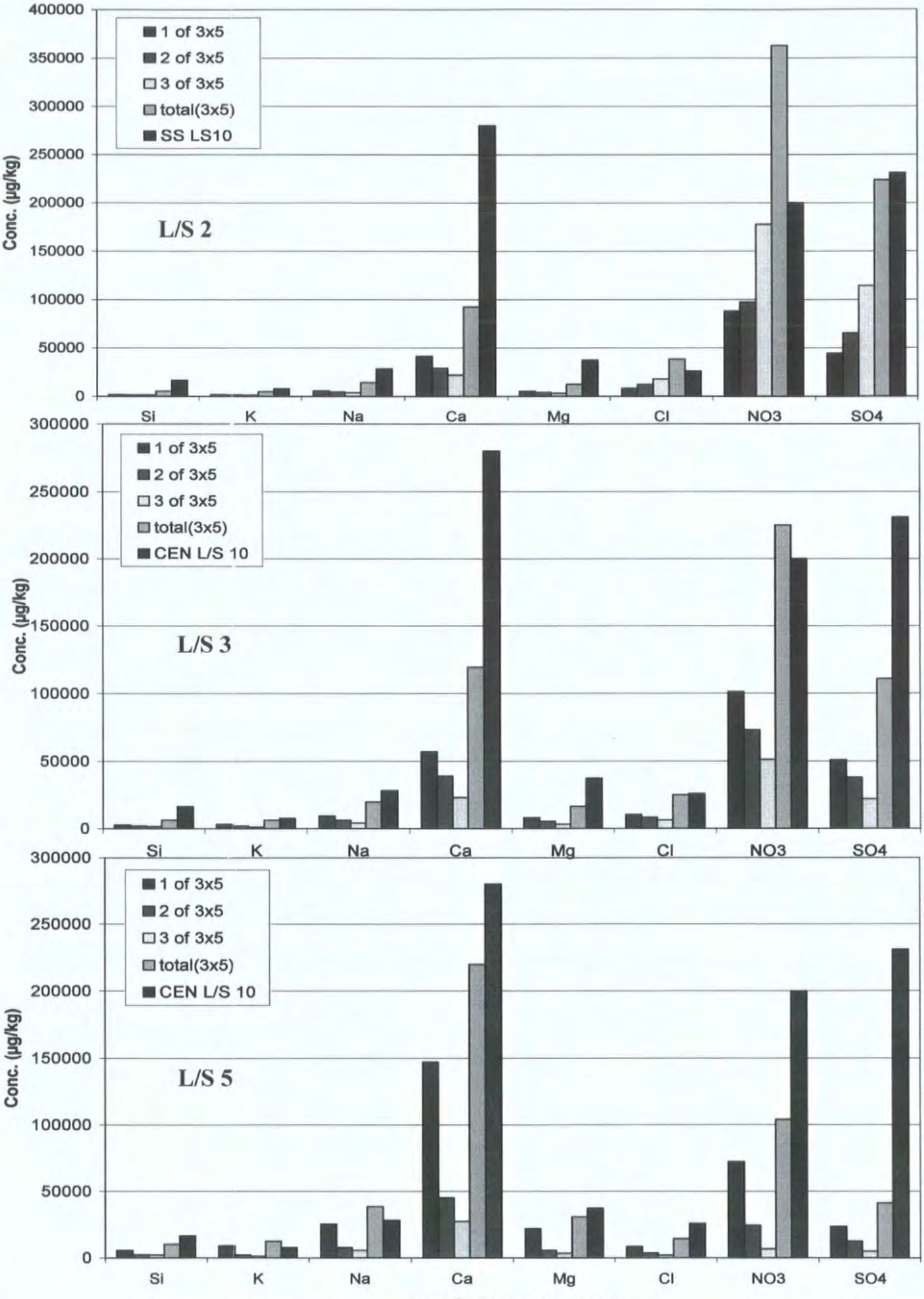


Figure 4.2: Mean base cation/anion released concentrations (µg/kg) for a multi-stage multi L/S washing procedure for leachates of sewage sludge. Cumulative (3 washing step totals) levels are also included and compared against cumulative CEN L/S 10 concentrations.

Release patterns for the L/S 5 experiment suggest that total leached concentrations described were controlled by the first washing step release of metal salts, with all component concentrations considerably higher relative to releases occurring during the second and third steps. This may be due partly to sample heterogeneity, but also the effect that increasing the L/S ratio can have upon increased and decreased levels of leached base cations and anions. With this behaviour came relatively higher flushing of the said components on the first washing step. This implies (legislative limits aside) that for sewage sludge, with respect to metal salt extraction amounts, the most beneficial pre-treatment method would be a 3 step washing for 10 minutes each at L/S 5. Realistically, however, considering the substantial releases after the first stage only, a more economic method may involve a single stage washing for 10 minutes at L/S 5. The compromise of using an L/S ratio of 5 rather than 2 was based on the extra costs this would entail and on the benefits of increased base cation extraction efficiency and the disadvantageous higher retained levels, in the solid phase of anions.

4.3.2.3 Trace metals

For the main elements of interest, the order of their release concentrations, was: Mn > Fe > Zn > Al > Ni (Figure 4.3). The dissolution of Mn was characterised by a steady increase with increasing L/S ratio and a steady decrease with increasing number of washings. This homogenous trend was also seen throughout by Ni but the steady decrease in concentration with increasing washing step was limited to L/S 5 for Fe. The remaining release patterns for Al, Fe and Zn were all heterogeneous with respect to L/S ratios and washings steps. Al and Zn can be twinned regarding the importance of a second flush over all L/S ratios but, respecting total dissolved levels over 3 washing steps, Zn displays a gradual increase from 85µg/kg to 205µg/kg from L/S 2 to L/S 5 and Al maintains levels around 30µg/kg for L/S 2 and 3 but then quadruples in concentration at L/S 5. Furthermore, Zn was the only trace element to be released into solution in greater quantities over the 3 step washing method than seen in the accumulated CEN L/S 10 leaching test. Total dissolved Fe concentrations began and finished around 300µg/kg for LS/ 2 and L/S 5, respectively, with a relatively depleted value of 175µg/kg recorded in leachates exuded at L/S 3. Total 3 step concentrations released into solution for Mn, Ni and Zn, irrespective of individual step behaviour, show a strong positive correlation to L/S ratio. Fe, on the other hand, and to some extent Al, appeared to be governed more by sample heterogeneity, represented by the varied total, and between step, leached concentrations recorded at changing L/S ratios. Finally, with respect to individual washing step behaviour, the importance of a second washing for additional element release was seen for Al, Fe and Zn. All remaining elements were of minor importance, exemplifying concentrations below 20µg/kg for all L/S ratios.

Thus, as seen for base metal salt releases, L/S ratio plays a significant role in determining certain trace metal dissolution concentrations (Mn, Ni and Zn) but, additionally, sample heterogeneity (Al and Fe) and multistage washings (Al, Fe and Zn) are also important.

4.3.2.4 Total 2 year flushes

The total flux of an element/component from the washing experiments can be compared to the total 2 year flux observed in the field lysimeter trials. It became apparent that the variations in concentrations observed, as a result of changes in both L/S ratio and multistage washings, when compared to the total flux concentrations measured in the 2 year lysimeter trials, changed little and so only L/S 2 values have been included. Extraction efficiency comparisons at L/S 2 can be seen in Table 4.2 (below).

It is clear that the extraction efficiency of NO_3 is much greater than for the other base metal salts, with steps 1, 2 and 3 each releasing 45.5%, 50.3% and 92.1% of the total flux recorded over a two year period under field conditions (193,110µg/kg). A substantial amount of NO_3 is therefore still readily available for release during the third washing step, even after considerable amounts have been released during steps 1 and 2. In total around 188% of NO_3 levels observed exuding from the lysimeter trials over a 2 year period were released during a cumulative 3 stage washing procedure. NO_3 is the only component which the CEN test accurately predicts (103.6%); all other component extraction efficiencies are below 40%. Thus, it can be seen that although the CEN batch leaching test equates well, the 2 year field leached levels of NO_3 were not characteristic of levels extracted systematically under laboratory controlled conditions. Depending on the amount of NO_3 still available for leaching (further testing of total extractable contents would be necessary), the simple 3 stage tap washing of sewage sludge may prove extremely valuable in minimising leachable NO_3 levels. This, however, is the only component effectively extracted by the washing process. Cl and SO_4 cumulative leached levels (after a 3 step washing process) were substantially lower at 28.5% and 38.5%, respectively. The individual washing steps afforded no particular preference to released concentrations so, unlike with NO_3, a 3 step washing procedure would have to be employed to gain any significant environmental remediation for both Cl and SO_4.

The base cation concentrations all displayed extraction efficiencies below 5% of that attained after 2 years of leaching in the field. It must be stated, therefore, that the pre-treatment of sewage sludge by this method showed little effect on the release of base cations from the solid phase and so is not recommended as a possible stabilisation method for these metals. Conversely, the same method was shown to extract large amounts of anions, particularly after a 3 step washing procedure.

With regard to trace metal releases, the benefits were limited due to the water-insoluble form in which the metals were evidently retained. Relative concentrations were all around or below 10%, with Pb and Cd displaying the most soluble characteristics, releasing 10.2% and 9.4% of the 2 year field based leached level after a 3 stage washing procedure. Zinc concentrations were negligible at 0.1% extraction efficiency.

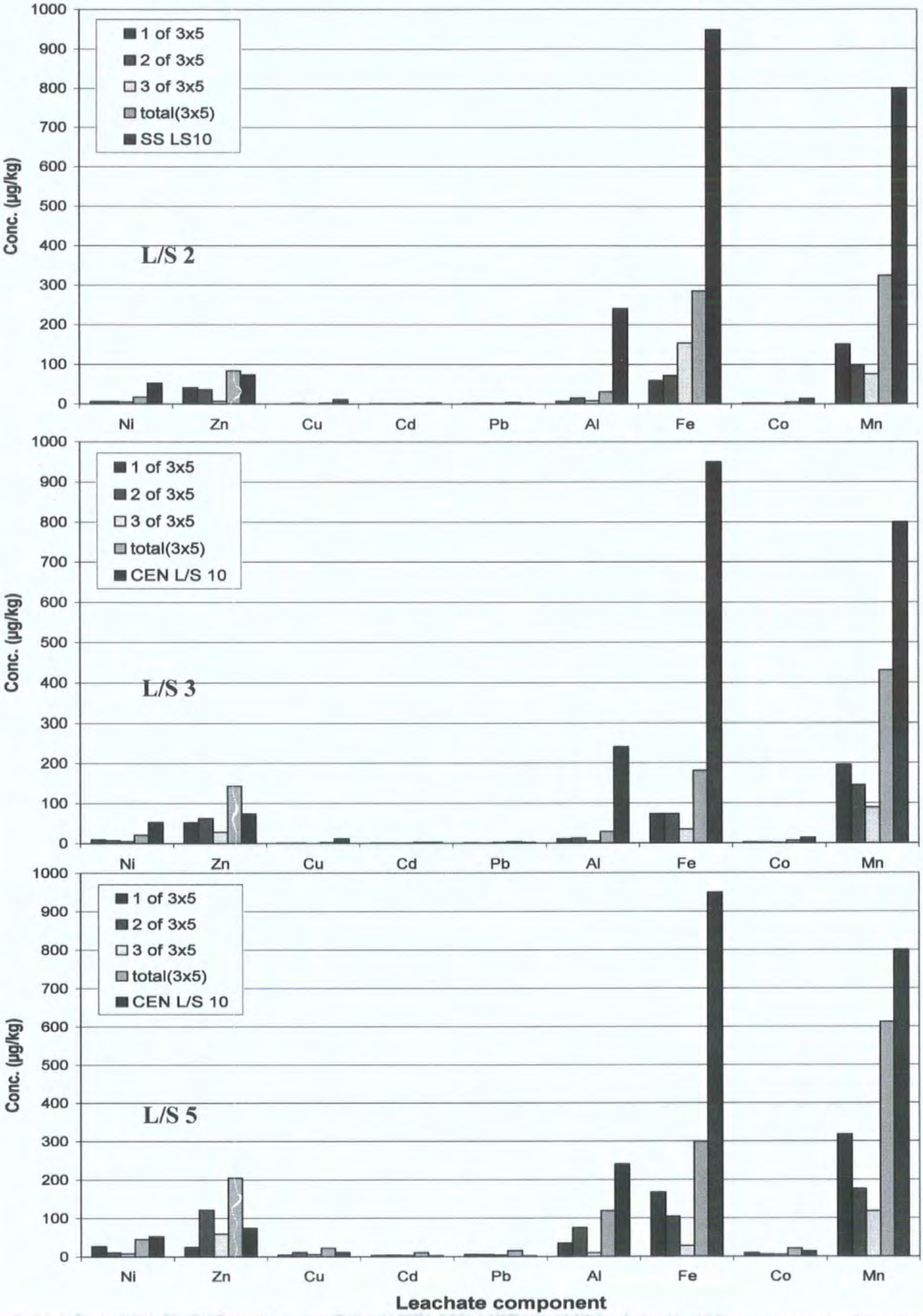


Figure 4.3: Mean trace metal released concentrations (µg/kg) for a multi-stage multi L/S washing procedure for leachates of sewage sludge. Cumulative (3 washing step totals) levels are also included and compared against cumulative CEN L/S 10 concentrations.

L/S 2	1 of 3x5	2 of 3x5	3 of 3x5	Total (3x5)	CEN L/S 10
Si	2.1	1.8	1.7	5.6	17.4
K	0.9	0.8	0.6	2.3	3.7
Na	1.4	1.2	1.0	3.6	7.1
Ca	2.0	1.4	1.0	4.4	13.3
Mg	0.8	0.6	0.5	2.0	5.9
Cl	6.2	9.0	13.3	28.5	19.3
NO_3	45.5	50.3	92.1	187.9	103.6
SO_4	7.6	11.3	19.7	38.6	39.9
Ni	0.5	0.5	0.4	1.3	4.0
Zn	0.0	0.0	0.0	0.1	0.1
Cu	0.4	2.0	0.4	2.7	14.6
Cd	3.1	2.7	3.5	9.4	17.2
Pb	2.7	4.8	2.7	10.2	5.7
Al	0.8	1.8	1.0	3.5	27.9
Fe	0.7	0.9	1.9	3.5	11.5
Co	1.5	1.3	1.1	4.0	10.4
Mn	1.6	1.0	0.8	3.5	8.7

Table 4.2: Extraction efficiencies relative to 2 year field releases for a multi-stage washing procedure at 5 minute washing times for sewage sludge at L/S 2.

4.3.3 CLO

4.3.3.1 Conductivity

The multi-stage washing procedure revealed large differences in recorded conductivity levels between steps 1 and 2 but, after a third washing step, the change in conductivity diminished (Table 4.3). This indicated that a large proportion of conductivity controlling components of CLO were readily available and highly labile in a water-based medium. When comparison of conductivity levels per litre of leachate (relative comparison for L/S – Table 4.3) was carried out there was an overall reduced increase, and sometimes a decrease, in relative conductivity levels with an increase in L/S ratio. This suggested that the release of base cation salt components from CLO was less reliant upon the addition of extra wash water. Furthermore, for both 5 and 10 minute contact times, the cumulative L/S 10 CEN test conductivities were not exceeded by the total 3 step washing results at L/S 5 (accumulated L/S 15), again indicating that L/S ratio was not a major governing factor. The main difference observed for CLO, with respect to ionic strength of leachates, therefore related to the number of washing stages.

However, it must be noted that sample heterogeneity was likely to play a role. This was exemplified by the varying conductivity results for the total flushes for both 5 minute and 10 minute washing times at various L/S ratios. For the 5 minute total flushes, there was a small increase in ionic strength from L/S 2 to L/S 3 and a drop from L/S 3 to L/S 5 but, for the 10 minute wash results, a staggered increase within increasing L/S ratio was adhered to. Care must be taken, therefore, not to misinterpret the effects of sample heterogeneity when assigning certain observed release patterns to be a result of the experimentally controlled factors.

µS/kg/litre	1 of 3x5	2 of 3x5	3 of 3x5	Total 3x5	1 of 3x10	2 of 3x10	3 of 3x10	Total 3x10
L/S2	23400	8860	4250	36510	16260	6310	3492	26062
L/S3	26205	8685	4125	39015	19320	6420	3602	29342
L/S5	17275	8550	5050	30875	20550	8570	5573	34693
CEN L/S 10				41020				41020
µS/kg								
L/S2	234000	88600	42500	365100	162600	63100	34920	260620
L/S3	174700	57900	27500	260100	128800	42800	24010	195610
L/S5	69100	34200	20200	123500	82200	34280	22290	138770
CEN L/S 10				242200				242200

Table 4.3: Mean conductivity values for a multi-stage multi L/S washing procedure for leachates of CLO. Cumulative (3 washing step totals) levels are also included and compared against cumulative CEN L/S 10 conductivities. Both actual (µS/kg) and relative (µS/kg/litre) values are shown.

4.3.3.2 Base metal salts

There was an immediate distinction between both maximum attained concentrations and the major elemental release comparative to that seen in sewage sludge leachates. The maximum concentration of Ca from CLO material (Figure 4.4) was nearly double that attained for leached NO_3 levels from the sewage sludge treatment (Figure 4.2). In addition, there were no detectable concentrations of NO_3 leached from CLO for the entirety of the study. For all metal salt component elements the release patterns with changing L/S ratio and multistage washings was extremely homogenous. SO_4 and Ca aside (at L/S 5), there was a gradual increase in leached element concentrations with increasing L/S ratio and also a typical behaviour of substantial release on the first stage of washing followed by progressively diminished levels for steps 2 and 3. Sulphate release was affected at an L/S of 5, elevating its concentrations (L/S 2 and 3 ~ 15,000µg/kg and L/S 5 – 110,000µg/kg) to levels above that seen for Mg (45,000µg/kg for all L/S ratios) but for L/S ratios of 2 and 3 leached SO_4 values were below that of Mg. This behaviour of increased dissolved SO_4 concentrations with increasing L/S ratio was contrary to that found with sewage sludge recordings. Detected Ca concentrations were also affected at L/S 5 displaying relatively lower 3 step washing totals due to a diminished release on the initial step at L/S 5. This, again, was converse to elevated Ca levels recorded during the first washing step at L/S 5 for sewage sludge. As mentioned above, Mg dissolution behaviour remains relatively constant throughout with respect to L/S ratios and multi-step washings. The remaining 2 base cation release patterns parallel one another with Na levels being slightly higher than those recorded for K. Total released Na concentrations for a 3 step washing procedure at L/S 2, 3 and 5 respectively, were: 184,000µg/kg, 192,000µg/kg and 240,000µg/kg. The only other anion detected was Cl which showed little correlation to L/S change; total 3 step washing levels resided just above 200,000µg/kg at L/S 2 and 3 and only increased to 270,000µg/kg at L/S 5. The decreasing order of exuded base cation and anion concentrations, not accounting for SO_4 levels at L/S 5, from the CLO were as follows: Ca > Cl > Na > K > Mg > SO_4. Maximum attained concentrations for Si, achieved after the 3 step washing procedure, were distinctly lower at 6,000µg/kg and are considered of minor importance.

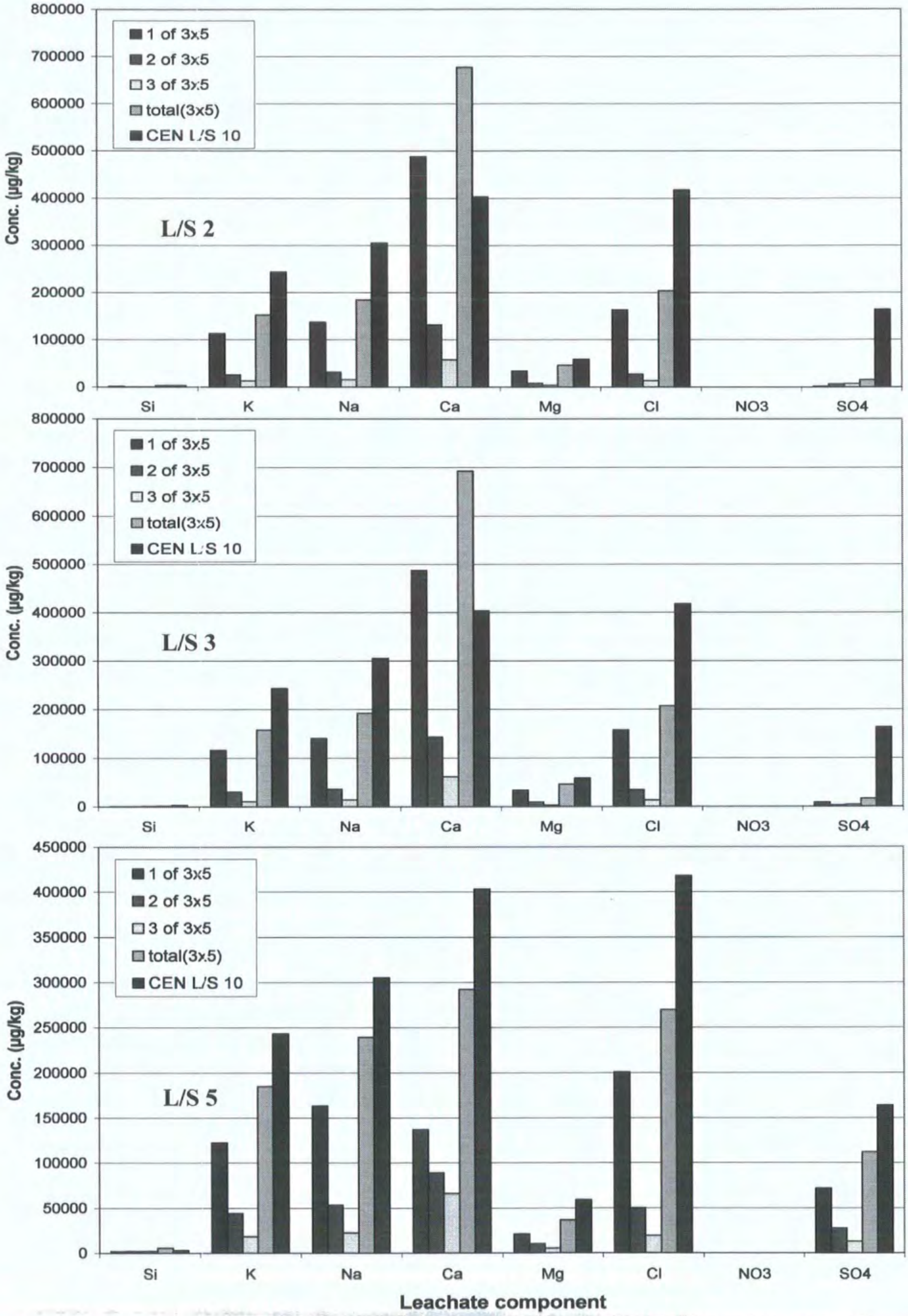


Figure 4.4: Mean base cation/anion released concentrations (µg/kg) for a multi-stage multi L/S washing procedure for leachates of CLO. Cumulative (3 washing step totals) levels are also included and compared against cumulative CEN L/S 10 conductivities.

4.3.3.3 Trace metals

As with base cation salt releases the main factor controlling the release of trace metals into solution was washing step. Leached trace metal levels were higher during the initial washing phase for all metals at all L/S's. Step 2 releases always surpassed those seen during step 3. At L/S 5 Mn releases were similar for all three washing steps. Differences between elemental released concentrations were also substantial, with Fe exuded at levels (total 3 stage flushes at L/S 2 and L/S 3 of 106,000µg/kg and 130,000µg/kg respectively) significantly higher than the rest of the elements. The order of decreasing elemental concentrations was as follows: Fe > Al > Mn > Zn > Ni. Initial step flushes for these 4 trace metals diminished slightly with progression from an L/S ratio of 2 to 3. Al decreases from 4,600µg/kg to 4,000µg/kg, Mn from 3000µg/kg to 2,800µg/kg, Zn from 1,900µg/kg to 1,600µg/kg and Ni from 746µg/kg to 700µg/kg. These relatively small changes in concentration demonstrate the minor affect that L/S ratio had on extraction efficiency for the trace metals examined. Of more importance was the multistage washing behaviour; this will be discussed in further detail later.

A clear distinction can be seen between the varying levels recorded at L/S 2 and 3 and those at L/S 5 (Figure 4.5). In particular, the trace metal concentrations for a cumulative 3 step washing procedure, resultant of lower initial step flushes were significantly decreased at L/S 5, whereas levels released at L/S 2 and 3 were similar in both nature and actual concentration. As this behaviour, to a lesser extent, was seen in the results attained for metal salt releases it is unlikely that the controlling factor was sample heterogeneity rather than a change in L/S.

In addition, it should be noted that Al, Mn and Zn total concentrations after the 3 step washing process at L/S 2 and 3 considerably surpassed levels determined by the accumulated L/S 10 CEN test. Furthermore, released Mn levels even surpassed CEN values at L/S 5 but Fe only exceeded CEN levels at L/S 3. This further (in addition to exceeding Ca concentrations) casts in doubt the appropriateness of using the 2-stage serial batch-leaching CEN test as a representative means for determining long term leaching behaviour of components from CLO.

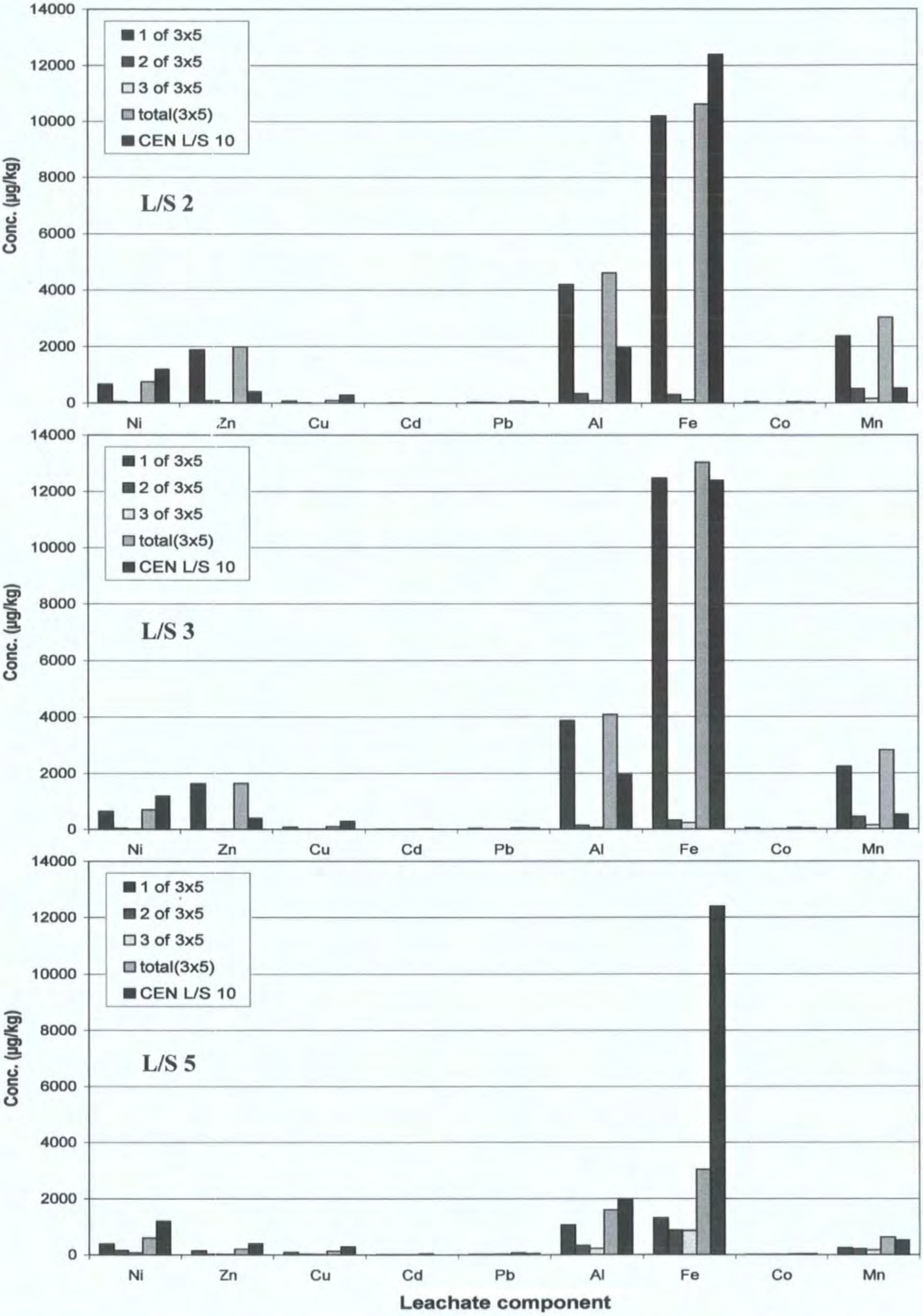


Figure 4.5: Mean trace metal released concentrations (µg/kg) for a multi-stage multi L/S washing procedure for leachates of CLO. Cumulative (3 washing step totals) levels are also included and compared against cumulative CEN L/S 10 conductivities.

4.3.3.4 Total 2 year flushes

As seen for sewage sludge, the increase in L/S ratio had little benefit on the extraction efficiency for each component in comparison with the amount flushed over a 2 year period and so only L/S 2 values have been included (Table 4.4). Similar levels of base cation extraction to sewage sludge were seen but the main difference was in the substantially lower values attained for anion extraction efficiencies (Table 4.2). Maximum Cl and SO_4 releases for a cumulative 3 step washing procedure were 5.3% and 0.6%, respectively. Equivalent values for the base cations are as follows: Ca – 12%, Si – 8.2%, K – 4% and Na and Mg, 2.2% and 2.1%, respectively. No comparison data was available for NO_3.

As already mentioned, the release patterns between washing steps for almost all alkaline earth and alkali metal salt components (SO_4 having a diminished initial flush) were significantly governed by the initial flushing step, so involving second and third stage washings would not necessarily be economical. This was also true when increasing the L/S >2. The significant differences in flushes experienced between washing phases was much greater than any change incurred by altering the L/S ratio. The levels achieved after 2 and 3 step washings, however, would have to be assessed relative to government drinking water and surface water limits to assess whether levels have been diminished enough to deem them environmentally sound. Based on leached levels recorded in the field after 2 years of study, as well as the relatively low (<10%) extraction efficiencies observed for the metal salts, it would appear that pre-washing CLO in this way has not afforded any significant remediation.

Of greater importance were the extraction efficiencies observed for the trace metals (Table 4.4). It can be seen that the percentages of Al and Fe extracted after a 3 step washing process, relative to the amounts released into solution after 2 years in the field, were 83.8% and 61.5%, respectively. Arguably, of even greater importance, as for all trace metals (Cd and Pb to a lesser extent), were the levels exuded after only 1 washing of the CLO with tap water at L/S 2 for 5 minutes. For Al and Fe these values were 76.3% and 59%, which equate to 91% and 96% of the total amount released after a 3 step washing process and so present both an economic and environmentally beneficial method for remediating leached trace metal concentrations from freshly digested CLO. Extraction efficiencies were also substantial for other trace metals giving values after 1 washing at L/S 2 for 5 minutes of: Co – 48.7%, Zn – 45.5%, Mn – 28.7%, Ni – 13.9%, Cd – 13.4%, Pb – 10.9% and Cu – 6.1%. Cd and Pb release was not exclusive to the initial washing phase, but after a 3 step washing procedure the percentages released rose to 43.5% and 21.0%, respectively. All in all, tap water washing proved to be extremely efficient at removing substantial amounts of trace metal concentrations most economically. It must also be remembered that these washing experiments and subsequent comparisons have been undertaken on undiluted CLO only; therefore, after dilution with amending soils and compost (as in the current Parcgro), any additional remediation properties would decrease trace metal contamination levels further.

L/S 2	1 of 3x5	2 of 3x5	3 of 3x5	Total (3x5)	CEN L/S 10
Si	4.6	1.5	2.1	8.2	8.5
K	3.2	0.7	0.4	4.3	6.8
Na	1.7	0.4	0.2	2.2	3.7
Ca	8.7	2.3	1.0	12.0	7.2
Mg	1.6	0.4	0.2	2.1	2.7
Cl	4.2	0.7	0.3	5.3	10.8
SO_4	0.1	0.3	0.3	0.6	6.9
Ni	13.9	1.1	0.6	15.6	25.0
Zn	45.5	2.1	0.4	47.9	9.6
Cu	6.1	0.9	0.4	7.4	22.6
Cd	13.4	15.7	14.4	43.5	9.9
Pb	10.9	7.1	3.0	21.0	13.9
Al	76.3	6.0	1.5	83.8	35.4
Fe	59.0	1.8	0.7	61.5	71.7
Co	48.7	1.3	2.3	52.4	40.8
Mn	28.7	6.1	1.9	36.7	6.3

Table 4.4: Extraction efficiencies relative to 2 year field releases for a multi-stage washing procedure at 5 minute washing times for CLO at L/S 2.

Ni and Mn may, however, prove more difficult to stabilise regarding their leachability. Their recorded leached concentrations after 2 years were still in breach of drinking and surface water directives, and also their relatively lower recorded extraction efficiencies of 13.9% (Ni) and 28.7% (Mn) after 1 washing indicated that these levels cannot be effectively reduced by simple tap water washing. These values increased to 15.6% and 36.7%, respectively, after 3 washing steps.

4.3.4 Agricultural soil

4.3.4.1 Conductivity

Table 4.5 shows that washing length/reaction time has had very little effect on the levels of conductivity displayed in leachates exuded from agricultural soil. All results for 5 and 10 minute washings for each individual washing step, as well as cumulative 3 step washings, gave electrical conductivities just under 4000μScm^{-1} and ~11,000μScm^{-1}, respectively. However, when consulting relative ionic strengths with changing L/S ratio, it can be seen that values were perfectly proportional to the increase in water over the material weight. This explained the relative positioning of the accumulated L/S 10 CEN test results between those of the cumulative 3 stage washings at L/S 3 and at L/S 5. Recorded values were an order of magnitude lower than those for sewage sludge, and 1.5 orders lower than levels seen in CLO sample solutions.

μS/kg/litre	1 of 3x5	2 of 3x5	3 of 3x5	Total 3x5	1 of 3x10	2 of 3x10	3 of 3x10	Total 3x10
L/S2	404	365	357	1126	396	356	359	1111
L/S3	557	527	518	1601	563	533	518	1613
L/S5	908	923	870	2700	928	895	863	2685
CEN L/S 10				2213				2213
μS/kg								
L/S2	4040	3650	3570	11260	3960	3560	3590	11110
L/S3	3710	3510	3450	10670	3750	3550	3450	10750
L/S5	3630	3690	3480	10800	3710	3580	3450	10740
CEN L/S 10				7790				7790

Table 4.5: Mean conductivity values for a multi-stage multi L/S washing procedure for leachates of the agricultural soil. Cumulative (3 washing step totals) levels are also included and compared against cumulative CEN L/S 10 conductivities. Both actual (μS/kg) and relative (μS/kg/litre) values are shown.

4.3.4.2 Base cation salts

The decreasing order of released base cation salt components (Figure 4.6) was as follows: NO_3 > Cl > Ca > SO_4. The remaining base cation accumulated concentrations for a 3 stage washing procedure were all below 7mg/kg and considered negligible.

The recorded behaviour for all cations and anions, with regard to number of washing stages, was similar to that recorded for conductivity values in that very little variation was seen between washing step released concentrations. Any differences that do occur are relatively minor and only really noteworthy for NO_3 release, and so were likely to be caused by sample heterogeneity. In contrast, as highlighted with conductivity values, there does seem to be a positive relationship for all base cation salt components with L/S ratio. These differences were, however, small relative to sewage sludge and CLO typically, being substantially lower (>1 order of magnitude), but a relationship with L/S ratio was still apparent. The larger of these differences were experienced for NO_3, then Cl and Ca giving respective values at L/S 2, 3 and 5 for initial step releases as follows: NO_3 - 48,500μg/kg, 68,000μg/kg and 108,000μg/kg, Cl – 7,600μg/kg, 11,000μg/kg and 18,000μg/kg and Ca – 4,300μg/kg, 5,770μg/kg and 9,100μg/kg. In fact, for all component concentrations, except Si, for a 3 step washing process at L/S 5 CEN test measured values were exceeded. This was analogous to the ionic strength behaviour.

4.3.4.3 Trace metals

The behaviour of trace metals (Figure 4.7), with regard to their relationship between separate washing steps, was similar to that described for the conductivity controlling base cation salt components. Al and Fe were the only two trace metals that showed any significant deviation from this, both releasing greater quantities on their third washing step. This, in turn, causes a rise in the total 3 step flushes to levels above those expected for constant release over each step, as well as above that based on the remaining trace metal release patterns. Three step washing totals for Al and Fe at L/S 2, 3 and 5 were as follows: Al – 922μg/kg, 664μg/kg and 762μg/kg and Fe - 646μg/kg, 455μg/kg and 524μg/kg, respectively. The decreasing order of trace metal released concentrations was: Fe >> Al > Cu > Zn > Mn > Pb. There was a significant difference (>>) within this ordering, being between Fe and Al and the rest of the elements. The 3 step total flush releases at L/S 2, 3 and 5 for Cu were: 49 μg/kg, 71μg/kg and 113μg/kg which were an order of magnitude lower than levels seen in solution for Fe. The remaining elements all exhibited total 3 step releases below 30μg/kg.

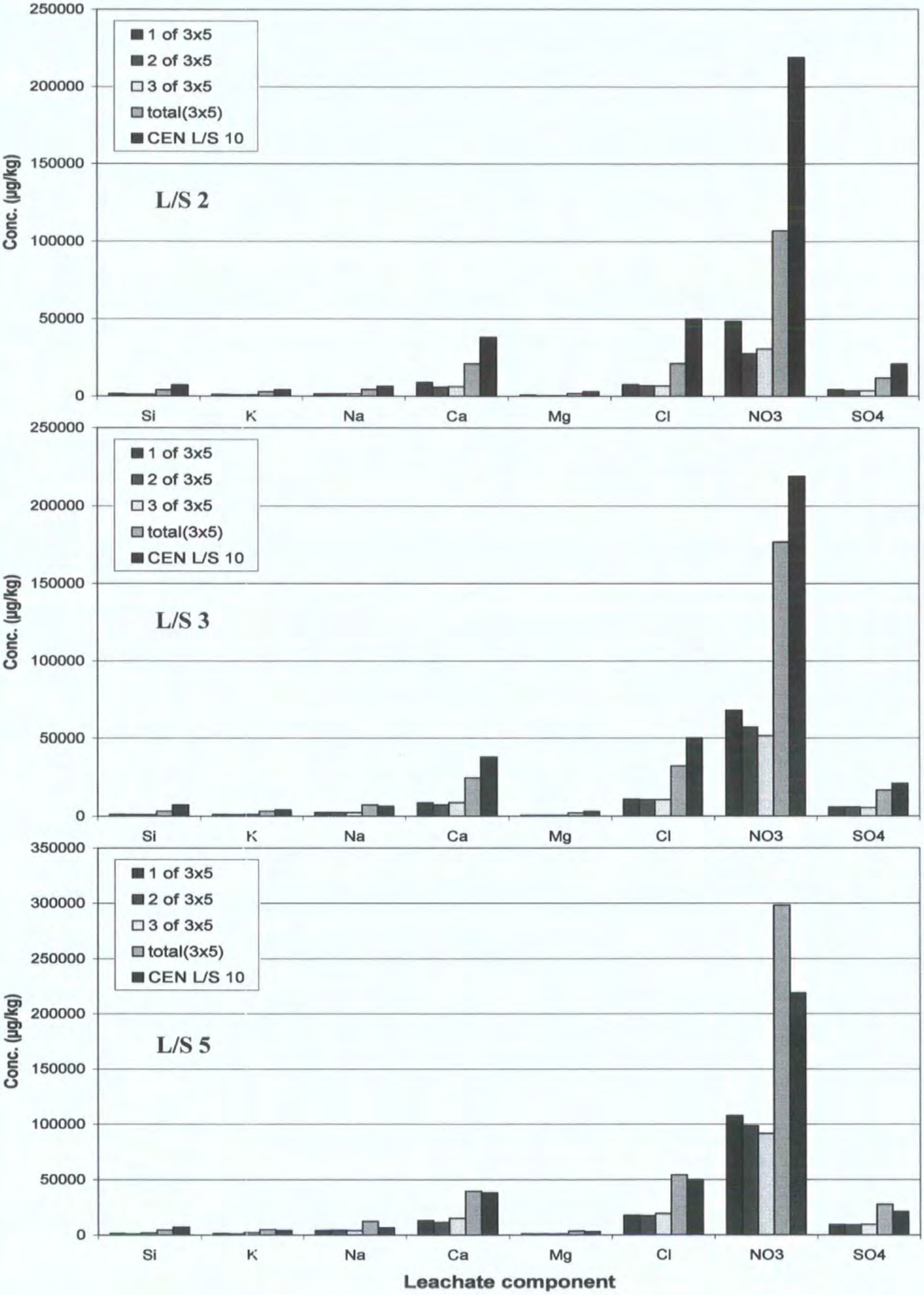


Figure 4.6: Mean base cation/anion released concentrations (µg/kg) for a multi-stage multi L/S washing procedure for leachates of the agricultural soil. Cumulative (3 washing step totals) levels are also included and compared against cumulative CEN L/S 10 conductivities.

The actual concentration differences found in amounts released, comparative to sewage sludge and CLO, were at least 2 orders of magnitude lower. In addition, the positive correlation observed above with increasing L/S ratio was only apparent for Cu which, incidentally, was the only element that exceeded CEN levels (at all 3 L/S ratios). All other trace elements were released, for each consecutive washing, was in their greatest quantities at L/S 2. L/S 3 concentrations were generally comparable to those attained at L/S 5. Thus, for soil, the volume of contact water used did not appear to determine the amounts of trace metals in solution and neither did contact time or number of washings. Recorded concentrations were therefore consistent irrespective of the experimentally controlled conditions.

4.3.4.4 Total 2 year flush

The base cation salt component extraction efficiencies for agricultural soil (Table 4.6) were analogous to those leached from sewage sludge, in that anion concentrations were generally exuded in greater concentrations to that of the base cations. The order of decreasing extraction efficiency was: NO_3 > Cl > Si > SO_4. All remaining base cation extractions, relative to the amounts leached after 2 years in the field, were below 10%. Leached percentages at L/S 2 were: for NO_3 – 121.0%, Cl – 61.2%, silicon – 28.9% and SO_4 – 20.7%. These results indicate that even for a well established, stabilised agricultural soil large amounts of base cation salt components, in particular the anions NO_3 and Cl, are capable of being released as a result of agitation with water. Pre-washing results indicate that substantial amounts of these two anions, especially at higher L/S ratios, have been released after 3 washes at 5 minutes each, which exceed levels exuded after 2 years of field-based leaching.

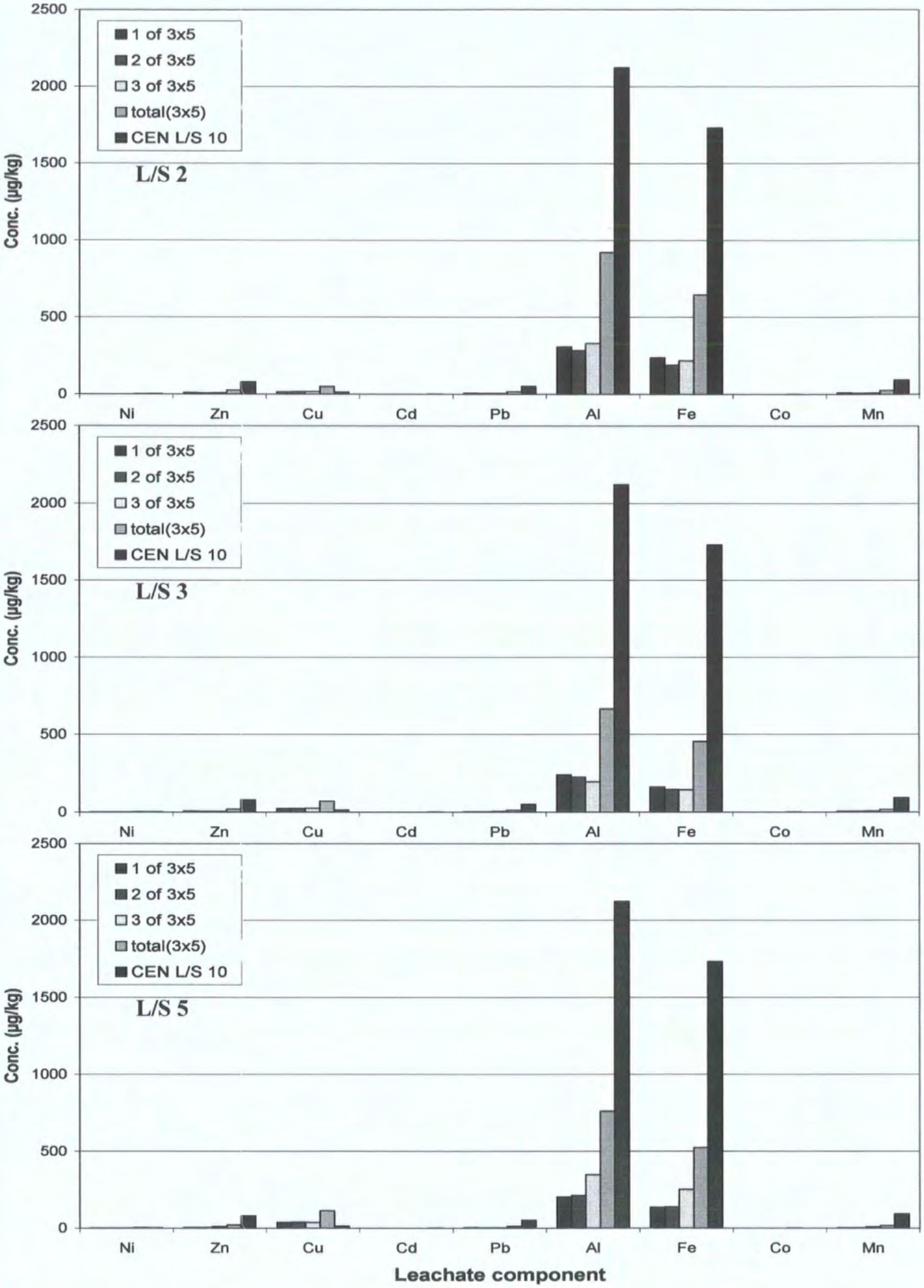


Figure 4.7: Mean trace metal released concentrations (µg/kg) for a multi-stage multi L/S washing procedure for leachates of the agricultural soil. Cumulative (3 washing step totals) levels are also included and compared against cumulative CEN L/S 10 conductivities.

Also evident were the leached levels relative to those after the CEN test had been performed. Generally, for all base cation salt components, Si and Na being the main exceptions, the release after a cumulative 3 stage washing procedure at L/S 2 was around 50% of that released during the accumulated L/S 10 CEN test. For L/S 3 the figure increased but remained below that of the CEN test, and at L/S 5 the level was exceeded. Levels attained after 3 stage leaching were lower than this stated pattern for Si and higher for Na, the latter of which surpassed CEN accumulated levels at L/S 3. This revealed 2 things: again, the relationship between the increased releases of base cation salt components with increasing water-washing volumes, but also what would appear to be a relatively good long-term prediction of released concentrations by the CEN test for soils of this nature. Conversely, an L/S ratio of 3.3 was observed in the field lysimeter trials (Chapter 2) after 2 years for the agricultural soil, and so, in order for the CEN test to accurately predict field-based released concentrations accumulated, LS 10 results should be theoretically 3 times this value. Clearly this was not the case (the only exception being for NO_3)). Therefore, actual measured long-term levels of base cations and anions released into the environment were greatly underestimated by the accumulated CEN L/S 10 batch leaching test. This was also true for all trace metals, analysed.

Substantial extraction efficiencies were found for specific trace metals (Table 4.6), particularly Al and Fe, each having 195% and 183% of the 2 year total flush released after 3 step washings at L/S 2. Copper also showed a significant equivalent release of 68% but was the only trace element analysed, as highlighted earlier, that showed any relation to increasing L/S ratio and exceeded CEN released concentrations at all L/S ratios. Mn and Pb both demonstrated similar extraction efficiencies at 23% and 21% respectively, and Co was 7.3%. All other trace metal removals were below 5%.

L/S 2	1 of 3x5	2 of 3x5	3 of 3x5	total(3x5)	CEN L/S 10
Si	11.7	8.3	8.8	28.9	51.8
K	1.3	1.0	0.9	3.2	4.5
Na	1.7	1.7	1.8	5.2	7.6
Ca	3.4	2.3	2.4	8.1	14.6
Mg	0.8	0.5	0.6	1.9	3.2
Cl	22.0	19.7	19.5	61.2	143.5
NO_3	54.9	31.3	34.8	121.0	247.9
SO_4	7.6	6.6	6.5	20.7	37.0
Ni	0.6	0.6	0.7	1.9	4.5
Zn	1.6	1.2	1.4	4.2	12.7
Cu	9.4	10.3	9.7	29.4	8.2
Cd	0.7	0.8	1.0	2.5	19.0
Pb	9.1	6.2	6.1	21.4	66.4
Al	78.7	72.7	84.5	235.9	542.7
Fe	83.0	66.6	76.6	226.2	605.7
Co	2.8	1.7	2.8	7.3	6.4
Mn	9.1	6.7	7.6	23.4	87.1

Table 4.6: Extraction efficiencies relative to 2 year field releases for a multi-stage washing procedure at 5 minute washing times for the agricultural soil at L/S 2.

4.3.5 Results summary

In summary, component releases during the pre-washing methods described have highlighted a clear distinction between the potential application of this pre-treatment technique as an effective amelioration process for CLO but not for sewage sludge. In addition, subsequent extraction efficiencies relative to 2 year field releases have proved a useful comparative means for resolving variable representative estimates of extraction efficiencies.

The benefits of pre-washing sewage sludge have been limited to NO_3, with ~45% of the amount released from the field lysimeters being leached in a single 5 minute washing of the material with tap water at L/S 2. This component was, however, alone since the majority of component releases, even after a 3 step washing procedure, displayed insubstantial cumulative extraction efficiencies. The environmental benefits gained from a pre-treatment method of this kind for the components analysed were considered negligible for sewage sludge. This was likely to be due to the fact that major component field releases were primarily exuded under anaerobic conditions (Chapter 5).

Conversely, pre-washing CLO was shown to be an effective removal method for substantial quantities of water-extractable trace metals, particularly species of Al and Fe. As the major benefits were associated with the first washing step and for a 5 minute contact time, this simple pre-treatment method could prove economically viable. If CLO could be pre-treated in this manner, and then well aerated on application to land (as experienced in the field lysimeters), the threat of environmental contamination would be significantly reduced. The pre-washing method appeared, contrary to predictions based upon findings from field leachate data (Chapter 2), to be less effective at removing base metal salt components. The extraction efficiencies after a cumulative 3 stage washing scenario, comparative to 2 year field fluxes, remained below 12% for all base cations and anions analysed. This (shown in Chapters 3 and 5) may be a result of the strongly oxidising conditions that prevailed for the main part of the field lysimeter experiments, which facilitated the release of base cation salt components into leachates.

The agricultural soil component releases showed a clear positive relationship between L/S ratio and released quantities of base cation salt components, as well as Cu, but all other trace metal concentrations in solution were released irrespective of contact time, L/S ratio or number of washings.

4.3.6 Tessier comparisons

It has been shown that, for all 3 treatments, the 2-stage serial batch-leaching CEN test results have, for a number of components, been exceeded by pre-washing releases. For the CLO material, a single 5 minute washing proved sufficient in elevating dissolved trace metal concentrations to levels higher than those exuded by the CEN test. In addition, NO_3 levels in solutions emanated from sewage sludge and agricultural soil treatments, as well as Al and Fe levels from the soil, have surpassed 2 year field fluxes. These findings indicate that, in this instance, the CEN leaching test was capable of underestimating the environmental consequences of given trace elements and anions found in leachates, based on both tap water washings and long-term levels in the field. The latter is cause for concern considering that all 3 materials were intended for use either as a base medium or as a fertiliser in agricultural settings. Ludwig et al (2005) stated, based on findings of heavy metals releases using water and acid reagents, that the long-term effects of heavy metal releases from ashes should only be predicted by pH-dependant tests. They demonstrated that less than 0.2% of the total amounts (pressure digestion in concentrated HNO_3) of Cd, Cr, Cu and Ni were released via water extraction methods, as most heavy metals were released into solution from their parent pH-dependant salts that become soluble with the addition of H^+. In view of this, comparison of the pre-washing experiment data was made against results obtained from a modified Tessier's sequential extraction procedure (Chapter 3). These comparisons supplement those carried out against the 2 year field fluxes; it was hoped they would provide a more detailed information on component releases under various chemical, environmentally analogous conditions.

However, it was revealed that the pre-washing component releases, for any scenario, were considerably less than those exuded during each sequential extraction step, even under neutral conditions as signified by step 1 (Chapter 3). This showed that the pre-washing releases although not proportional to the various Tessier extraction step releases may still prove beneficial in helping to explain the low base cation releases from CLO. Moreover, the sensitivity of component releases for all 3 treatments toward a lowering of pH to acidic conditions (pH ~ 4, step 2) was, as theorised by Ludwig et al (2005), substantially increased. This resulted in extraction efficiencies, comparative to each fractionation step, below 10% for the majority of component releases, the main exceptions being sewage sludge, Cl (17.4%) and NO_3 (34.0%), and CLO, Al (20.2%) and Fe (37.0%) for a cumulative 3 stage washing procedure. As seen with field release extraction comparisons, the major releases for Al and Fe species from CLO were also observed during the first washing step: 18.4% and 35.5%, respectively. This suggests that the character in which components are released in both pre-washing and Tessier laboratory experiments to some extent were comparable to that seen in the field, but the chemical conditions simulated by the Tessier procedure were significantly harsher, causing greater quantities to be exuded.

Direct comparison of pre-washing component releases with those exuded during individual and cumulative sequential extraction phases was informative only on the basis of relative levels achieved, rather than actual behavioural patterns observed. Thus, owing to the fact that the majority of extraction efficiencies relative to Tessier step extractions were well below 10%, the results have not been included here. The important point to take from this observation was that (as shown in Chapter 3) the level of component release correlated strongly with prevailing environmental conditions (as theorised by the various sequential extraction phases), but these conditions were not singularly analogous to those experienced in the field or with tap water washings. Principal component analysis, similar to that described in Chapter 5 where field leachate component releases were compared to sequential extracts, would be a more informative tool in deciphering and constraining individual treatment component behaviours. With this statistical analysis technique, similar component release patterns and relationships between pre-washing, Tessier extracts and field lysimeter releases may then become more discernible. Furthermore, PCA may shed some light on why pre-washing trace metal extraction efficiencies from CLO were higher than expected, and the base cation salt components lower. Given more time, this information, in conjunction with post pre-washing stability washing experiments could be used to further understanding and efficacy of pre-washing's potential remediation value for CLO.

4.4 Statistical Analyses

The ANOVA statistical general linear model, described in Chapter 2, was employed to determine the extent of variation between leached component concentrations and the controlled factors – contact time, L/S ratio, and multistage washings. The sizes of these effects, as well as the power of the analysis, were also considered in an attempt to determine an overall controlling factor. Tukey's simultaneous pairwise comparison test was used to distinguish differences between treatment means at $P < 0.05$. Statistical analyses revealed that material heterogeneities played a significant role in the repeatability of results for sewage sludge and CLO. In addition, duplication rather than multiple repeats due to time constraints limited statistical validation of the washing procedure. In order to statistically authenticate the use of a pre-washing method for the removal of water-extractable contaminants from CLO, further replicate data would be recommended, as well as increased sample sizes where possible.

4.4.1 Conductivity

Table 4.7 shows the statistical significances found between recorded conductivity levels and treatment, L/S, and washing step. No significant differences were found to be a function of increasing reaction time; with treatment type and increasing L/S overall governing the conductivity levels measured. The number of washing steps incorporated into the pre-washing stage was also significant in controlling conductivity, but this was between initial and consecutive washing steps. A statistical significance was not found between steps 2 and 3, indicating that the major conductivity controlling species were sufficiently extracted/dissolved after a single 5 minute agitated washing period.

Treatment	**SS**	**CLO**	**Soil**
SS	–	0.00001	0.0065
CLO		–	0.00001
Soil			–
Step	**Step 1**	**Step 2**	**Step 3**
Step 1	–	0.00001	0.00001
Step 2		–	NS
Step 3			–
L/S	**L/2 2**	**L/S 3**	**L/S 5**
L/S 2	–	0.00001	0.00001
L/S 3		–	0.0004
L/S 5			–

Table 4.7: Statistical differences for conductivity levels as a function of treatment, L/S ratio and washing step. NS – Not significant.

4.4.2 Component releases

When analysing treatment component releases, statistical differences ($P< 0.05$) were limited to sewage sludge with changing L/S ratio and CLO with number of washing steps. It is worth mentioning that statistical differences were found for most component releases over all treatments (sewage sludge, CLO and soil) with changing L/S (summarised by Table 4.8). Post-hoc testing, however, revealed that the only treatment exhibiting a true correlation with L/S was sewage sludge, since the significant CLO component releases occurred sporadically and was thought to be more a result of sample heterogeneity. The statistical differences ($P < 0.05$) highlighted in Table 4.8 concerning the agricultural soil component releases were found (after post-hoc testing), for most elements (Si, K, Ca, Mg, Zn, Cu, Pb, Al, Fe, Mn, Ti, Sc and Cr) to coincide with increased washing/reaction time. These differences all lay between the 1 hour washing time and those of 10 and 15 minutes. As mentioned above, this finding was insubstantial owing to the fact that an inverse relationship was shown to exist between released component amounts and contact time. This behaviour was only evident for the agricultural soil control.

Component	**Soil**	**Sewage Sludge**	**CLO**
Si	0.0001	0.0001	NS
K	0.0001	0.004	0.0001
Na	NS	0.003	0.0001
Ca	0.0001	0.0001	0.0001
Mg	0.0001	0.0001	0.0001
Ni	NS	0.001	0.0001
Zn	0.0001	NS	0.0001
Cu	0.01	0.0001	0.002
Cd	NS	0.0001	NS
Pb	0.0001	0.0001	NS
Al	0.0001	NS	0.0001
Fe	0.0001	NS	0.0001
Co	NS	0.0001	0.0001
Mn	0.0001	0.0001	0.0001
Ti	0.0001	0.0001	0.0001
Sc	0.0001	0.0001	0.007
Cr	0.02	NS	NS
Li	0.0001	0.0001	0.0001
V	NS	0.0001	0.0001
Cl	0.0001	0.0001	0.0001
NO_3	0.0001	0.001	NA
SO_4	0.0001	0.0001	0.001

Table 4.8: Statistical differences (in green) found between component leachate concentration and increasing L/S ratio for CLO, sewage sludge and the agricultural soil control. NS - Not significant. NA - Not applicable.

The statistical differences found for sewage sludge component releases and L/S indicate that increasing water-washing volumes up to L/S 5 significantly increased component extraction amounts (post-hoc test results can be seen in Table 4.9). These significant differences were, however, of little overall interest with respect to pre-washing as a potential remediation process. The relatively low extraction efficiencies comparative to field releases for all components highlighted above (Table 4.2) have been shown to be minor.

Component	L/S 2 - L/S 3	L/S 2 - L/S 5
Si	0.0003	0.0002
K	0.0113	0.011
Na	0.0079	0.0069
Ca	0.0002	0.0001
Mg	0.0008	0.0002
Cl	0.0003	0.00001
NO_3	0.0411	0.0007
SO_4	0.00001	0.00001

Component	L/S 2 - L/S 3	L/S 2 - L/S 5	L/S 3 - L/S 5
Ni	0.0014	0.0028	NS
Zn	NS	NS	NS
Cu	NS	0.00001	0.00001
Cd	0.0112	0.00001	0.00001
Pb	NS	0.0086	0.00001
Al	0.0458	NS	NS
Fe	NS	NS	NS
Co	0.0049	NS	0.0001
Mn	0.0392	0.00001	NS
Ti	0.0003	NS	0.0229
Sc	NS	0.00001	0.00001
Cr	NS	NS	NS
Li	0.0011	0.0005	0.00001
V	0.0004	0.00001	0.0002

Table 4.9: Statistical differences between L/S ratios for sewage sludge a) base cation salt component and b) trace metal releases. NS – Not significant. NA – Not applicable.

The CLO material displayed significant differences between the individual steps of the multi-stage washing procedure, in particular between initial washing step component releases and successive steps (2 and 3). Post-hoc test results have been tabulated in Table 4.10. Nearly all component releases display significantly higher extracted amounts on their first washing step, Cd, Pb and Sc being the only exceptions. The findings are of more importance to those described above for sewage sludge with L/S ratio. Firstly, CLO was shown to be more responsive to the pre-washing experiments in that significant quantities of trace metals were capable of being extracted by this simple 5 minute agitation with tap water at L/S 2. Secondly, these significant differences occur during the first washing step and so the major beneficial flushing of potentially toxic metals (PTM) has been readily achieved under the most economical conditions. Statistical findings for CLO component releases therefore further certify that the pre-washing procedure described here could be economically used as a potential means of trace metal amelioration before the CLO is used on land.

Component	Step 1 - Step 2	Step 1 - Step 3
Si	0.00001	0.00001
K	0.00001	0.00001
Na	0.00001	0.00001
Ca	0.00001	0.00001
Mg	0.00001	0.00001
Cl	0.00001	0.00001
NO_3	NA	NA
SO_4	0.0325	0.0428
Component	**Step 1 - Step 2**	**Step 1 - Step 3**
Ni	0.00001	0.00001
Zn	0.0003	0.0023
Cu	0.00001	0.0001
Cd	NS	0.0099
Pb	NS	NS
Al	0.00001	0.00001
Fe	0.00001	0.00001
Co	0.00001	0.00001
Mn	0.0002	0.0005
Ti	0.00001	0.0002
Sc	NS	0.0023
Cr	0.00001	0.00001
Li	0.00001	0.00001
V	0.00001	0.00001

Table 4.10: Statistical differences between step releases for the CLO treatment for a) base cation salt component and b) trace metal releases. NS – Not significant. NA – Not applicable.

4.4.3 Rainwater/Tap water comparisons

In order to help explain the lower than expected base cation salt component extraction efficiencies relative to field lysimeter releases for CLO, significance tests were performed between rainwater and tap water samples. Any potential discrepancy that may exist between 'background' component concentrations in field rainwaters and laboratory tap waters needed to be assessed as this could affect the pre-washing results. Statistical analyses revealed that the only components displaying a significant difference between rainwater and tap water samples were Ca and Mg (both $P<0.0001$); rainwater sample concentrations were significantly higher than those found in tap water. This, when considering extraction efficiencies of pre-washing for these 2 elements relative to field lysimeter leachates, would incur an underestimation of extraction efficiencies (the extent of which is, however, limited). The proportion of elemental releases found in rain/tap waters relative to levels in field leachates from CLO showed that 0.65% and 1.84% of Ca and 1.27% and 9.09% of Mg held in solution could be accounted for by tap and rainwaters, respectively. The contributions of rainwater dissolved Ca and Mg levels were therefore considered to be of minor importance when taking into account the overall amounts recorded capable of being leached from CLO. In any case, it must be remembered that these minor underestimations, making no significant difference to the overall component extraction efficiency and thus practicality and validity of the pre-washing method, will be included in leachates exuded from CLO if it were to be used outdoors.

The effect of these tap/rainwater background concentrations on sewage sludge extraction efficiencies was again negligible relative to rainwater field leachate levels. Sample heterogeneity and the overall display of low extraction efficiency of the pre-washing method remain the main governing factors over component releases into solution. The effect seen on agricultural component extraction efficiencies is unimportant as this treatment was included for comparison of fluxes only.

4.5 Discussion

The 3 materials differed significantly in both their release patterns and total amounts of metal salts released during the tap water pre-washing procedure described. Treatment extraction efficiencies relative to levels attained in field lysimeter leachates have also been shown to be significantly different. The main component differences seen for sewage sludge were with changing L/S, and for CLO with the initial component flushes during a multi-stage washing procedure. Agricultural soil component behaviour was less important, exhibiting an inverse correlation with reaction/contact time. This treatment did, however, reveal that conductivities and component releases were significantly ($P < 0.006$) lower than those seen in sewage sludge and CLO extracts. The agricultural soil was considered to be a well stabilised material and so was included as a comparative treatment against which contaminant levels leached from CLO and sewage sludge could be evaluated. More 'stable' releases were observed for the majority of metal salt components (Al and Fe to lesser extents) with almost constant release patterns seen, irrespective of reaction time and number of washing steps. This steady discharge indicates that an equilibrium has been attained between the solid and liquid phases, which was unaffected by contact time or washing step. Increasing the volume of wash water (L/S 2 – L/S 3 – L/S 5), showed an almost perfect positive correlation with amounts of base cation salt component released further supporting a state of equilibrium, particularly for these conductivity controlling species.

This behaviour was not seen in either sewage sludge or CLO treatment leachates. The major components released from CLO were the base cations (K, Na and Ca) and trace metals, Al and Fe. Cl was found to be the dominant counter ion, and no detectable levels of NO_3 were recorded throughout. This suggests the most readily removed metal salts were those of the alkali chlorides (NaCl, KCl) and the alkaline-earth chloride ($CaCl_2$). These salt releases are in agreement with X-ray diffraction (XRD) examination results performed by Wang et al (2001). The high levels of Al and Fe also released into solution indicate that these two elements were also easily de-adsorbed from the solid phase by water. Thus, as with the aforementioned base cation salts, a significant proportion of the water-extractable Al and Fe were likely to be complexed to surface particles and not exist as nucleation elements, as has been described for MSWI fly ashes. This was also true, to lesser extents, for Co, Mn and Zn.

As mentioned above, the primary finding concerning the leaching behaviour during the pre-washing of CLO was characterised by greater initial step releases relative to steps 2 and 3. Considerable release of leachate constituents during the first phase of washing was both economical and the most environmentally favourable. It was evident that some sort of stabilisation relative to consecutive water washings had occurred, thus the need for additional washing steps was reduced since over 90% of the potential removal of contaminants over a cumulative 3 step washing procedure has occurred during the initial phase. This is particularly apparent for trace metal releases (initial step releases being: Fe – 76.3%, Al – 59%, Co – 48.7%, Zn – 45.5% and Mn – 28.7%), suggesting that aerobic digestion of MSW is capable of making available large proportions of field-based leachable contaminants for extraction by means of a water-based medium. These results could also indicate that washing CLO may incur physical changes, both within and between the individual particles, which decreases the potential reactive surface area upon which leaching can occur (Abbas *et al.*, 2002). In addition, the fact that CLO component releases into solution were not strongly related to L/S ratio, unlike sewage sludge and agricultural soil, favours the monetary potential of this process. On the down-side, the inherent heterogeneity of CLO does raise the question of repeatability of efficacy of the pre-washings. This was exemplified in the considerable variation seen in released amounts of all leachate constituents at L/S 2 and 3 with those seen at L/S 5. For example, releases at L/S 3 for Co, Al and Ca were over 350% greater and levels of Fe, Mn and Zn were around 10 times those recorded at L/S 5.

Conductivity levels have also been shown to be significantly higher in initial step extracts relative to successive step ionic strengths. This conductivity change, in conjunction with the observed lack of dependability upon L/S, further supports the utilisation of pre-washing as a successful means for reducing conductivity levels. However, the extent to which conductivity levels can be reduced is limited, as demonstrated by the low (<12%) extraction efficiencies for CLO wash extracts relative to levels recorded in the field over a 2 year period. This suggests that the release of conductivity controlling components from CLO is not as reliant upon neutral conditions as was first thought. Higher flushes were expected, based on levels attained in leachates emanating from the field lysimeter trials together with numerous batch test and pre-washing studies carried out on MSWI ashes (Wang *et al.,* 2001, Abbas *et al.,* 2002, Kim *et al.,* 2002, 2003 and 2005 and Ludwig *et al.,* 2005). For example the Abbas group demonstrated that up to 80% of the total water-extractable contents of chlorides could be removed by pre-washing at L/S 2 with de-ionised water. Wang et al (2001) increased this removal capacity to over 95% at L/S ratios equal to or greater than 2, as well as more than 50% of the major elements Ca, K and Na. Finally, Kim et al (2003 and 2005) showed a significant reduction of 56-57% of Ca soluble species in leachate exuded from a MSWI washed ash relative to an ash treated with a carbonation/phosphate stabilisation process. All these studies were performed on MSW incinerator ashes which significantly differ, both physically and chemically, from aerobically digested MSW. These temperature incorporated changes in conjunction with the use of tap water (with its higher levels of base cation salt components and so reduced loading capacity), as opposed to de-ionised water, were possible reasons for the lower observed extraction efficiencies.

In addition, component releases in the field were shown (Chapter 5) to correlate strongly with oxidative conditions, and this may help explain the lower than predicted levels of extraction efficiency seen under neutral tap water washes displayed here. PCA results of a joint Tessier and leachate dataset showed a strong Ca, and to a lesser extent Mg, release during acid-reducible conditions. Although this does not directly explain the lower extraction efficiencies relative to field leachates (as acidic conditions were not evidenced during the field lysimeter trials), it does afford some explanation why these elements are not solely affiliated with salt-displaceable conditions (neutral). In contrast, K was shown to be strongly associated with this salt-displaceable phase and PCA results revealed that this behaviour was also observed in field leachates for undiluted CLO 2004. It must be noted however, that this behaviour was not seen for CLO 2006 digestate and so may partially explain the low (4.3%) cumulative 3 step extraction efficiency relative to 2 year field flushes for K. The low extraction efficiencies seen for the anions (Cl, NO_3 and SO_4) cannot, however, be explained in this manner since all detectable releases during Tessier extractions (Chapter 3) were shown to be associated exclusively with the salt-displaceable fraction.

Although the high levels of salts exuded from CLO pose a significant threat to the environment, it must be noted that if similar high levels of salt removals to those described by the said authors were seen in pre-washed leachates, then the buffering capacity of CLO may be seriously affected. The 3 year field lysimeter trials (Chapter 2) showed that all leachates emanating from diluted and undiluted forms of CLO were alkaline throughout (pH 7 – 9.2) which was most likely due to the presence of high levels of base cation salts in solution. Removal of substantial quantities of these components may enhance the effects of acid rain waters considerably and present a whole new order of acid-based contaminants and PTM releases, reducing the materials' resonance time in the field or potential as a soil amendment. Sequential extraction data under acidic conditions (Chapter 3) revealed the cohort of impurities potentially being released into the environment if acidic conditions, and more importantly, reducing conditions, prevail. Consequently, this significantly increases the risk of potential groundwater and surrounding surface water contamination from CLO leachates.

It is hypothesised that, from the results presented here, the 2 problem trace metals were likely to be Mn and Ni. These metals have shown persistently high levels of release, relative to drinking water MACs, even after 2 years of field leaching. In addition, the lower maximum extraction efficiencies (Mn – 36.7% and Ni – 15.6%) after a 3 stage cumulative washing process (relative to field leached levels) do not offer much remediation value. With these findings, it may prove beneficial to investigate the possibility of recirculating the once-used wash waters back through the CLO material. A point of saturation does not appear to have been achieved in leachates exuded from the pre-washed CLO, and so further extraction using the same waters may present a potentially more effective remediation and economic process. Levasseur et al (2006) recently demonstrated this approach to metal removal and reuse of treated leachates on MWI fly ashes, achieving high levels of extraction for toxic metals Cd (72%) and Pb (30%). In principle, the recirculation of leachate waters would be the same but Levasseur accomplished these figures after acid washing steps, which have been shown from Tessier extracts (Chapter 3) to considerably increase the mobility (concentrations in solution) of base and trace metals.

The results attained for sewage sludge have shown all 3 factors (contact time, L/S ratio and multi-stage washings) control, to some degree, the release of conductivity-governing components. Significant differences between L/S 2 and the higher L/S's (L/S 3 and L/S 5) represent the major finding characteristic of sewage sludge releases. Exuded amounts of base metal salt components increased with number of washings at L/S 2. The opposite was seen at L/S 5 with significantly greater initial flushes being recorded. This was likely to result from material heterogeneity. The use of pre-washing for the effective removal of trace metal salts was also greatly affected by the heterogeneous release behaviour of sewage sludge. Al and Fe displayed overall heterogeneous releases; Mn, Zn and Ni all vary with change in L/S ratio; Al, Fe and Zn were subject to variations with number of washings.

Extraction efficiencies relative to 2 year field fluxes were shown to be effective for the anions, in particular NO_3 (~50% on the first 2 washing steps and a further 92% on the third washing). Cl and SO_4 cumulative removal percentages after 3 washings were 28.5% and 38.5%, respectively. However, with these reasonably high levels of extraction comes the problem of increasing extraction efficiencies, especially for NO_3, on 2nd and 3rd washing phases, demonstrating a lack of stabilisation relative to extractable water contents. The reason for this, and other observed increases with increased number of washing steps, maybe due to the exposure of new mineral surfaces within the material after initial contact with water, so that certain water-soluble species were made more accessible (Abbas *et al.,* 2002). Equivalent base cation and trace metal extraction efficiencies were below 5% and 10%, respectively.

All things considered, the pre-treatment pre-washing method under any of the conditions described was regarded as an unsuitable means of effectively removing substantial amounts of contaminants from sewage sludge with the attempt of making it more stable to leaching.

The agricultural soil component releases have been shown to be significantly lower for both base cation salts (<50mg/kg, and for NO_3 ~ 100mg/kg) and the trace metals (<1mg/kg) relative to CLO and sewage sludge releases. These levels were an order of magnitude lower than equivalent releases observed for CLO and, relative to sewage sludge the base cation salt releases, were 2-3 times lower. Trace metal releases were similar in concentration for sewage sludge although Al and Fe releases are actually greater in the soil. The agricultural soil has therefore been shown to release significantly lower overall concentrations of contaminants into solution and to achieve this via a more stable and relatively consistent manner. It is worth noting that agricultural soil field leachate component levels (Chapter 2) were mainly in compliance with drinking water legislation for the entirety of the study, as opposed to after 2 years as with CLO and sewage sludge releases. In view of this, extraction efficiencies relative to recorded levels in field leachates were less important.

The results show that component releases from both sewage sludge and CLO treatments are significantly higher than levels achieved in leachates from an agricultural soil. CLO extraction efficiencies were higher than those from sewage sludge for all base cations, as well as for all trace metals analysed. However, the removal of anions from CLO was lesser in extent than for sewage sludge, particularly for NO_3 and Cl. This signifies that, although the extraction of anions from sewage sludge was significantly more favourable than from CLO, the remaining elements were more readily available to water leaching in CLO material.

4.6 Conclusions

The materials studied in this chapter were an aerobically digested MSW, a certified sewage sludge from a waste water treatment plant, and an agricultural soil typical of the Durham region. A factorial design was employed for the pre-washing methods used in an attempt to ascertain potential remediation criteria and subsequently attribute this to each recycled waste product. The following conclusions can be drawn:

- CLO wash solutions contained considerable amounts of soluble salts of trace metals including: Al, Fe, Co, Zn and Mn. These trace metal flushes, both in concentration and behavioural releases, demonstrate beneficial extraction efficiencies when compared to field flux data (<83.8%). Furthermore, >90% of the releases occurred for the best economic-environmental case scenario (a single, 5 minute washing at L/S 2).

- The importance of these major trace metal releases during the initial washing stage were signified in both the large proportions removed but also the significantly lower levels exuded in subsequent washes, indicating that a certain degree of leaching stability had been achieved.

- Significant releases of alkali and alkaline earth metal salts from the CLO were also recorded and as conductivity results indicated, these releases were most prolific during the initial washing step. Extraction efficiencies (<12%) relative to levels attained both in the field and laboratory were however, not of a suitable level for this method to be of significant importance for these species.

- The potential for using this simple pre-washing method to effectively reduce trace metal contamination from CLO before application to land was shown to be potentially viable under the correct conditions.

- The washing of sewage sludge had given high releases of NO_3 and, to lesser extent, SO_4 and Cl. Both washing step and contact time showed significant differences in conductivity levels. Despite these elevated levels and subsequent high component extraction efficiencies relative to field lysimeter releases, substantial liberation of NO_3 was still evident after a third stage of washing. This indicated that little leaching stability had been achieved for these anions.

- This, in conjunction with limited extraction efficiencies, a greater dependency on L/S found for all other leachate components, as well as inhomogeneous release patterns showed that the pre-treatment pre-washing method was an unsuitable means of effectively removing substantial amounts of contaminants from sewage sludge typical of that tested here.

- Concerns were also raised regarding the repeatability and reproducibility of the washing results, especially for sewage sludge. Further experimentation would be necessary to confirm this.

- Component releases from agricultural soil were shown to be significantly lower than both sewage sludge and CLO component releases. Further experimentation concerning post-pre-washing stability tests may provide a comprehensive account of the level of contamination possible after the pre-washing method, relative to that seen from an agricultural soil. Tessier extraction data, together with PCA analysis performed on field leachates, pre-washing releases and sequential extract data would further understanding of the underlying processes controlling component releases under the various conditions described.

Chapter 5

Multivariate statistical analyses of treatment leachates and sequential extractions

5.1 Introduction

It has been shown, thus far, that not only do CLO and its associated 'soils' contain, and leach, a large number of potential contaminants, but the distribution of these species was controlled by a complex array of interacting processes, which typically gave rise to a large range of chemical compositions. Moreover, trace element and anion composition, as well as a number of physical and chemical parameters of the various leachates and extracts, were assessed temporally over a 3 year period. The leachates were constantly monitored over this time, and samples were collected from 27 field lysimeters, which were intermittently introduced on an annual basis. The chemical sequential extractions were attained from sub-samples of the lysimeter core materials themselves, sampling events being on a yearly time-scale. Within this factorial design, 'control' treatments consisting of a typical acid-loamy agricultural soil of the Durham region and pasteurised sewage sludge were also included, further increasing the solute concentration range. Therefore, the structure of the datasets involved were not only complicated by having a large number of highly variable treatments (including within and between treatment variations), but also the release patterns of over 25 different species have to be considered. Finally, it was interesting to transpose these component datasets, both directly from the field lysimeter leachates and from laboratory Tessier sequential extractions, in an attempt to identify any existing similarities or underlying trends. A sophisticated data analysis technique was required to effectively interpret the component behaviour described in this thesis – principal component analysis (PCA).

5.2 Principal Component Analysis (PCA)

The central initiative governing the use of PCA is to reduce the dimensionality of a data set consisting of a large number of interrelated variables and to extract a small number of latent components capable of evaluating and explaining the relationships among these variables. At the same time, as much of the original variation present in the dataset is retained as possible. Essentially, this is achieved by transforming a set of variables, several or all of which may correlate in some way, to a new set of variables – the principal components (PCs) – which are uncorrelated or orthogonal to each other (Jolliffe 1986). These components, consisting of linear combinations of the original variables, are ordered so that the first few projections encapsulate the maximum variation contained within the entire original dataset. The rationale behind using this exploratory analysis technique on environmental datasets such as this is concentrated around two main functions of PCA:

Firstly, it can provide a significant insight into the structure of the dataset matrix and facilitate in the identification of any underlying linear structure, trends or dimensions (or factors) which otherwise may not have been possible using simple two dimensional analysis techniques (as used in previous chapters). This is primarily achieved by the grouping of variables into components, under the assumption that these variables that can be identified as being related to a common cause will also be found to be strongly related to a common component. The very nature of PCA, in that each principal component is uncorrelated from the next, helps ensure that different trends or dimensions within the data are being measured, thus minimising cross correlation (Manly, 1986).

Secondly, the reduction in the data's dimensionality can prove extremely effective in determining overall controlling factors on contaminant releases under specific environmental conditions. Typically, the raw data matrix can be reduced to a small number of principal components (in this case usually 5-7 accounting for ~80% of the total variation). This is because each PC signifies the variance responsible of several variables and because these components are mutually orthogonal such that the first PC loading explains the most variance and each subsequent component accounts for progressively less. The resulting fewer number of factors can, therefore, usually describe a similar proportion of the variance that all of the original variables could in the untransformed dataset (Chen *et al.,* 2007).

The calculation of PCA results generally involves the computation of PCs using either a symmetric covariance or correlation matrix which, when large standard deviation of variables exists, can differ considerably (Davis, 2002). In this case, PCA represents a normalisation technique where the data are standardised. A correlation matrix was employed in this study since the concentrations of the 26 species studied in leachates and sequential extracts were on separate scales – (mg/l) and (μg/kg), respectively, and the range of values on each of these scales varied over at least two orders of magnitude. The raw data sets (lysimeter leachates and sequential extracts) were each 'z transformed' which required the data matrices to be centered about zero by subtracting the means from each column (species) data point and then dividing this value by the column standard deviation. The transformed datasets were then analysed, individually and as a merged matrix, using the multivariate PCA application tool in Minitab 15. This statistical package computes the data as eigenvalues, PC scores and PC loadings. Eigenvalues represent the variance of the PCs and are a product of eigenvectors, which are equivalent to the coefficients of the PCs in terms of the standardised variables. The elements or species of these eigenvectors signify the PC loadings and the PC scores represent individual points of the PC coefficients. They were calculated from each original observation by projecting them onto the principal axes. This process is explained in detail by Chatfield and Collins (1980).

In order to select an appropriate number of principal component axes to further examine PC scores and loadings, it was decided that Kaiser's rule (Kaiser and Rice, 1974 in Skrbic *et al.,* 2007) and the principal according to Morrison (1967) would be used. Morrison (1967) suggested that PCs should account for approximately 75% of the total variance. Kaiser's rule states that eigenvalues > 1 should be retained for further analysis (eigenvalues > 1 explain more variance than any one of the original variables could). The first eigenvalue < 1 was also included as this value was usually very close to 1. These criteria, in conjunction with the application of scree test plots (graphical representation of eigenvalue vs. principal component number) allowed visual selection of PC numbers and ensured that ≥ 80% of the total variation of each data matrix was accounted for. It is worth noting, however, that a considerable proportion (> 60%) of the total variance could usually be accounted for by the first 3 PCs. The PC loadings were then examined to provide information concerned with the factors or processes responsible for the similarities observed in component behaviour for both leachates and sequential extractions. The PC scores were plotted against one another to highlight similarities or trends that may exist between samples as a function of time, fractionation behaviour (in the sequential extracts only) and treatment.

5.3 Analyses

PCA was performed separately on field lysimeter leachates and Tessier extraction data, as well as on a combined data set. Each chemical component (Si, K, Na, Ca, Mg, Ni, Zn, Cu, Cd, Pb, P, Al, Fe, Co, Mn, Ti, Sc, Cr, Li, V, Cl, NO_3, SO_4, pH, conductivity and DOC) were assessed as a function of treatment and time (weekly intervals) for the leachate analyses, and the sequential extraction data was assessed by treatment but on an annual basis and did not include Cl, NO_3, SO_4 pH, conductivity and DOC measurements. For the sequential extraction data, chemical component fractionation or 'step' releases were also considered. In addition to findings described in Chapter 2, it was evident from preliminary PC score plots that field lysimeter leachates exuded from New CLO 2005 and New CLO 2006 treatments dominated most component behaviour and so additional leachate analyses, excluding these 2 treatments, were conducted. These treatments were also excluded in the overall leachate/extract dataset. This ensured that no potential correlations were left uncovered because of the extreme nature displayed by undiluted CLO digestates. The PCA runs are described in turn; firstly for the leachate samples (with and without CLO 2005/6 treatments), secondly for the Tessier extractions and finally as a combination of lysimeter leachates and sequential extracts (again, with and without CLO 2005/6 treatments in the leachate data). All PCA score plots have been included at the end of each PCA section.

5.3.1 Leachate samples (all treatments)

5.3.1.1 Analysis output and component loadings

The scree plot of eigenvalues computed for the leachate sample PCA run is given in Figure 5.1 and also in Table 5.1 along with component loadings for each retained PC. As mentioned earlier, the first 6 PCs usually accounted for $\geq$ 80% of the original variance. The first PC is often found to represent an overall concentration or size, with similar loadings on most variables (e.g. Worrall *et al.,* 2003b and Manly, 1986). Indeed, this appeared to be the case here, with nearly all components displaying similar medium loadings of negative sign, except for NO_3 and pH which showed very little or no correlation with PC1. Zn, although of negative sign, shows a limited correlation with overall concentration. It is worth noting here that the designation of sign (as a consequence of the presence of square root terms in the correlation matrix manipulation) is arbitrary; the signs of an entire component can be reversed without having any bearing on the underlying relationship (Gibson, 2006). It is the relative sign and magnitude of the loadings between PC variables that are important. It is likely that, because the 3 exceptions named above (NO_3, pH and Zn) all showed high loadings on other PCs, this could mask their overall loadings in this general concentration component. PC2 has strong (> ±3) loadings of identical sign (positive) for Si, Cd, Co and Ti and to lesser extents for Pb, Mn and Sc. PC3 showed strong positive loadings in decreasing order for Conductivity > pH > SO_4 > Cl > Na and the equivalent for negative loadings for Fe > Mn > Ca. PC4 demonstrated strong negative affiliations for SO_4 > NO_3 > Ca > Zn. Component 5 showed strong negative loadings for Zn and Sc and medium loadings for Cu, NO_3 and DOC but also a strong positive loading for pH. The loadings on PC5 suggested that these leachate components (Zn, Sc, Cu, NO_3 and DOC) were released into solution independently of pH. Conversely, PC6 showed strong negative loadings for pH and DOC and, as with PC5, Sc was strongly loaded of opposite sign, as was Cl.

	PC1	PC2	PC3	PC4	PC5	PC6
Eigenvalue	**9.9925**	**5.1332**	**1.6278**	**1.3987**	**1.3465**	**0.9681**
Proportion	**0.384**	**0.197**	**0.063**	**0.054**	**0.052**	**0.037**
Cumulative	**0.384**	**0.582**	**0.644**	**0.698**	**0.75**	**0.787**
Si	-0.1519	0.3091	0.0933	-0.0438	-0.0468	0.1283
K	-0.1994	-0.1811	0.1731	0.0559	0.1723	0.1367
Na	-0.2231	-0.1877	0.2262	0.0303	0.1992	0.1542
Ca	-0.1987	0.0003	-0.2485	-0.4116	0.0520	-0.0551
Mg	-0.2671	0.1427	0.0022	-0.1023	0.1768	0.0012
Ni	-0.2769	-0.1791	-0.0794	0.1021	-0.0701	-0.0651
Zn	-0.0549	-0.0203	0.1036	-0.3439	-0.5710	-0.0864
Cu	-0.2158	0.0837	0.1612	0.1600	-0.2825	-0.2180
Cd	-0.1431	0.3868	0.0068	0.0308	0.0704	-0.0362
Pb	-0.2156	0.2844	0.0775	0.1033	-0.0103	-0.0574
P	-0.2490	-0.1922	-0.1176	0.0127	-0.1066	0.0488
Al	-0.2836	-0.0929	-0.1352	0.1318	-0.0879	-0.1201
Fe	-0.2096	-0.1090	-0.3807	-0.1124	0.1164	0.0272
Co	-0.1471	0.3748	-0.0284	0.0083	0.1012	-0.0688
Mn	-0.2047	0.2287	-0.2782	-0.1743	0.1278	-0.0009
Ti	-0.1617	0.3596	-0.0220	0.0265	0.0905	-0.0786
Sc	-0.0702	0.2172	0.1014	0.1989	-0.3056	0.3707
Cr	-0.2738	-0.1926	-0.0797	0.1143	-0.0535	-0.0327
Li	-0.2534	-0.1863	-0.1921	-0.0103	0.0498	0.0044
V	-0.2541	-0.1814	0.0198	0.1936	-0.1422	-0.0715
Cl	-0.1882	-0.0715	0.2442	-0.0345	0.1220	0.3202
NO3	0.0274	0.0030	-0.0489	-0.4498	-0.2766	-0.0516
SO4	-0.1123	-0.0516	0.2744	-0.5059	0.0430	0.2200
DOC	-0.1420	0.0130	0.1878	0.0939	-0.2800	-0.3510
pH	0.0069	-0.0738	0.3075	-0.1451	0.3399	-0.6463
Conductivity	-0.1722	-0.0371	0.4717	-0.0860	0.0717	0.0869

Table 5.2: PCA results showing eigenvalues, proportional and cumulative variances, and component loadings for all field leachates.

The information presented in Figure 5.1 and Table 5.1 was not enough to adequately explain these findings and so component scores and trends as a function of treatment, displayed below, were plotted.

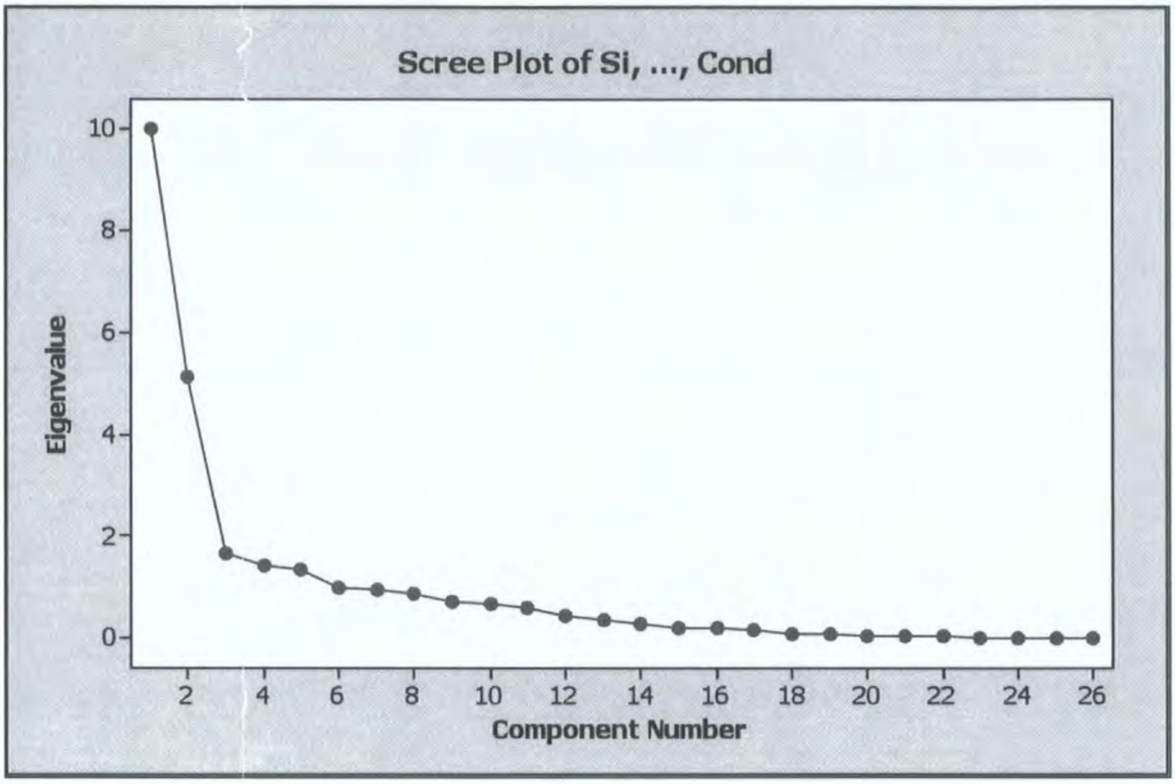


Figure 5.1: PCA scree plot showing the eigenvalues of each principal component for all leachates.

5.3.1.2 Component scores and trends

A matrix plot, not shown here, displayed the overall distribution of treatment trends over the first 6 PC plots, from which the most clearly well defined trends were then re-plotted individually on scatter plots for easier interpretation. From these individual scatter plots, 5 main treatment trends were identified.

Firstly, from the plot of PC1 vs. PC2 (Figure 5.2), 2 trends can be clearly defined, both of which were strongly exemplified by CLO 2005; decreasing PC1 against increasing PC2 (trend *a*) and decreasing PC1 against decreasing PC2 (trend *b*). Trend *b*, which was signified by negative PC's, wass also characterised, to lesser extents, by all treatments. It was trend *b*, therefore, which lies close to the negative PC1 axis that can be confirmed to be associated with overall leachate concentration. The larger values in decreasing order observed for CLO 05 > CLO 06 > CLO 04 > Comp > (BDA, ML) > SS > Soil, support the findings depicted in measured leachate concentrations in Chapter 2. The components that gave heavy positive loadings for

PC2 (i.e., trend *a* - Si, Cd, Co and Ti, and to a lesser extent Pb, Mn and Sc) appeared strongly correlated with an additional component trend introduced by CLO 2005. Thus, the CLO 2005 digestate seemed to have introduced into the MSW stream a source common to all of these elements. This was not to say that this was the *only* source of the said elements in field leachates, since other trends have been identified that distinguish these components.

Secondly, as can be seen from the plot of PC2 vs. PC3 in Figure 5.3, a trend existed that almost parallels the positive PC3; the larger scores of which were seen for CLO 2004, CLO 2006 and Comp trials. As mentioned above, this component showed high positive loadings for Na, Cl, SO_4, conductivity and pH. In addition, the high negative loadings of this PC were associated with that of CLO 2005 treatment leachates – mainly Fe but also Ca and Mn. The high negative loading of Fe associated with PC3 signified the extremely high concentrations (~450mg/l) in leachates exuded during the main flush event for CLO 2005 poon after the treatment was established in the field lysimeters. It was likely that the high positive loadings were a result of the highly labile base metal salts, which have been shown (Chapter 2) to be dominated by NaCl, with SO_4 also an important contributing anion. It would be expected that Ca would also show a positive loading (as does K which is another base cation that was shown to be important in controlling leachate conductivity), but the observed negative value was probably due to the presence of this element occurring strongly negative in PC4 (as shown in Table 5.1) which was likely to mask any other behaviour displayed by this component. The initial flush events over which undiluted CLO leachate samples were shown to accumulate extremely large levels of Na (~1.8g/l) and Cl (~8g/l), and consequently gave conductivity readings nearing 20 $mScm^{-1}$, coincide with the high positive PC3 scores. Component 3, therefore, although not considered to be an overall measure of concentration like PC1, did appear to reflect the extreme concentration highs measured in undiluted CLO 2004, CLO 2006 and Comp trials for the readily flushed metal salts and that of Fe (possible as Fe hydroxides) in the CLO 2005 treatment.

Thirdly, the strong negative loadings described above for PC4 have been revealed in the score plot (best exemplified by PC2 vs. PC4 in Figure 5.4) to be associated with the sewage sludge treatment. All other treatment leachate scores also fell close to this

PC4 trend, but the only components that coul be identified to be strongly loaded were those mentioned (Ca, Zn, SO_4, and NO_3). All of these components were shown, along with Mn (which displays a medium negative loading), to be strongly affiliated with sewage sludge leachates typical of those analysed in this study. PC4, therefore, was taken to represent a component trend for sewage sludge.

A fifth trend can be seen by plotting PC scores 2 and 5 against one another (Figure 5.5). What this trend represented was difficult to interpret, but it is certain that the components it highlights, which were strongly negatively loaded (Zn, Cu, Sc, NO_3 and DOC), were treatment related. The treatments in question were sewage sludge and CLO 2006. The timing at which these end member flushes occurred in the field for both treatment leachates was the October to January period. Although this occurs on separate years (2005/6 for sewage sludge and 2006/7 for CLO 2006) for each treatment, the actual exposure time, from establishment in the field to when these sampling events occurred, was the same (i.e., after ~3 months). At the other end of the PC5 scale, a high positive loading existed for pH which could either be interpreted as being a controlling factor for the releases from CLO 2004, CLO 2005 and Comp, the scores for which fell at this end of the axis, or may suggest that the above releases for sewage sludge and CLO 2006 were independent of pH concentration. However, as will be described later, once the CLO 2005 and CLO 2006 treatments were removed, neither of these suggestions proved conclusive.

Finally, the scatter plot of PC2 vs. PC6 (Figure 5.6) showed that, as with the score plot of PC2 vs. PC4, nearly all treatment scores fell upon the PC6 axis, again with the exception of CLO 2005 treatment leachates. However, the only discernable components associated with high negative loadings were pH and DOC, and those associated with high positive loadings were Sc and Cl. The positive scores were associated with that of CLO 2006, the reason for this was unknown. The very strong negative pH loading observed here could be associated with CLO 2005. This was based on additional score distributions of PC6 plots with PC3 and PC5 (both of which showed high positive loadings together with large negative loadings on PC6), as well as a large drop in recorded leachate pH at the time the CLO 2005 leachate sample was collected. However, by this stage of the PCA analysis it must be remembered that any correlations or trends only account for 3.7% of the total variance of the data set and, with an eigenvalue of 0.9681, the likelihood of accurately identifying a treatment or period as well as defining an overall causation factor was limited. The same can be said for the negative DOC loading on PC6.

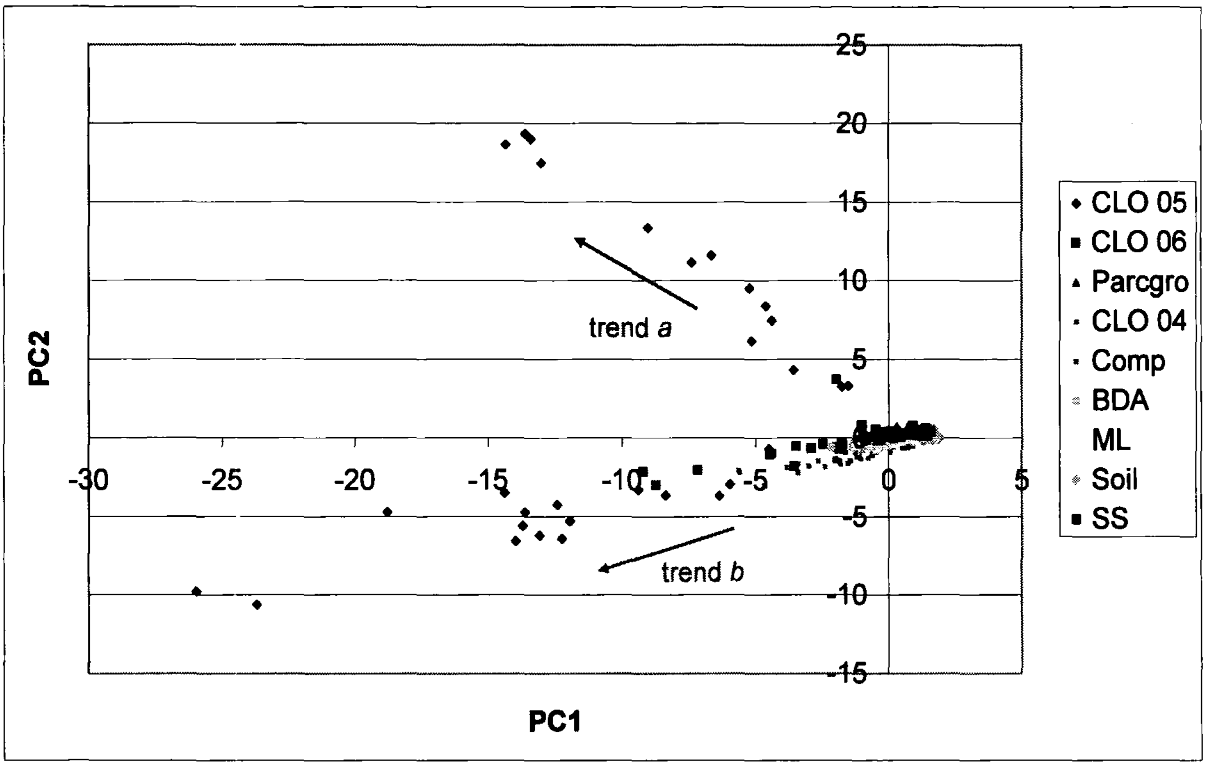


Figure 5.2: Score plot of PC1/PC2 for the analysis of all field leachates, grouped by treatment.

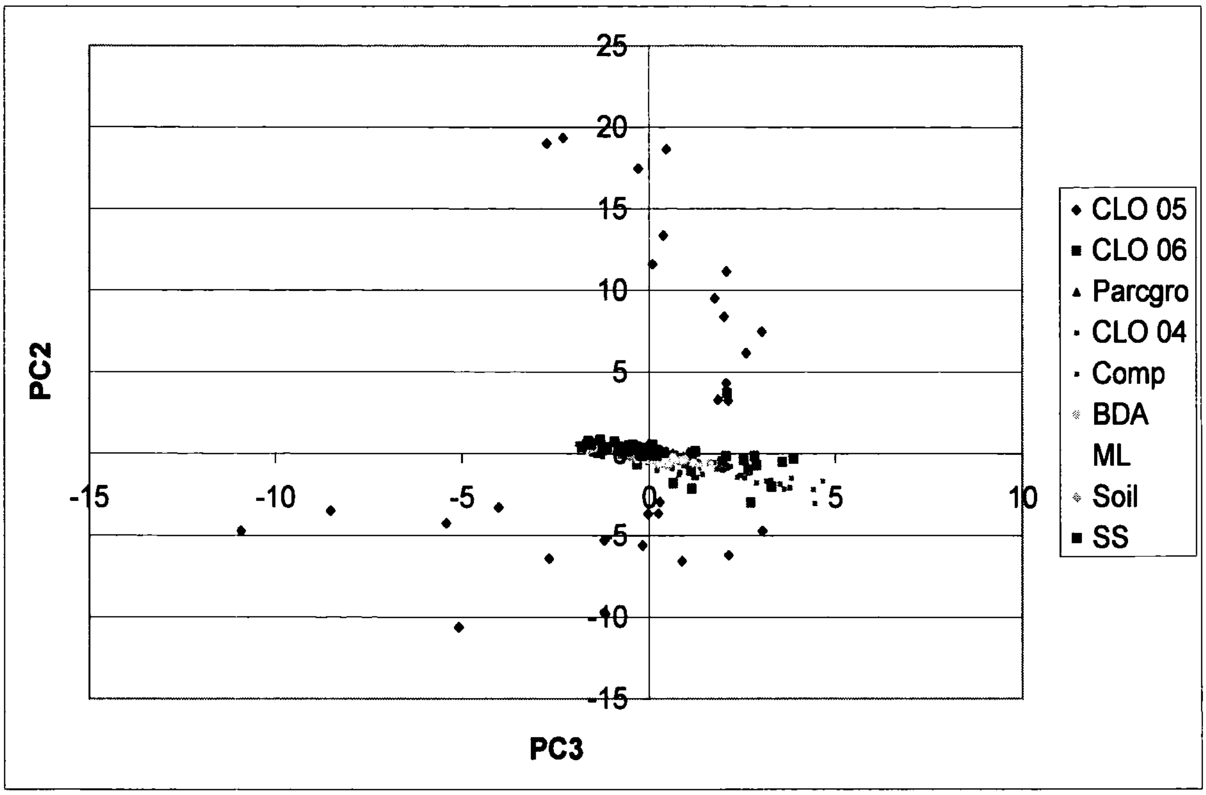


Figure 5.3: Score plot of PC2/PC3 for the analysis of all field leachates, grouped by treatment.

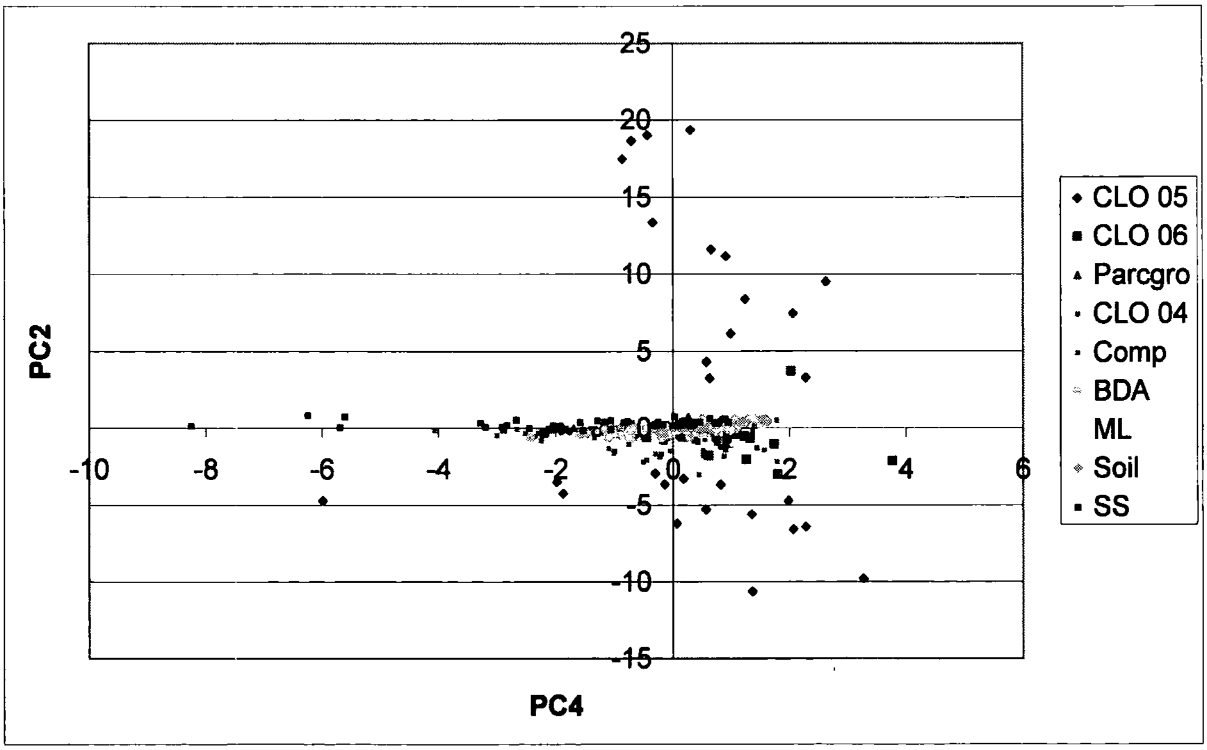


Figure 5.4: Score plot of PC2/PC4 for the analysis of all field leachates, grouped by treatment.

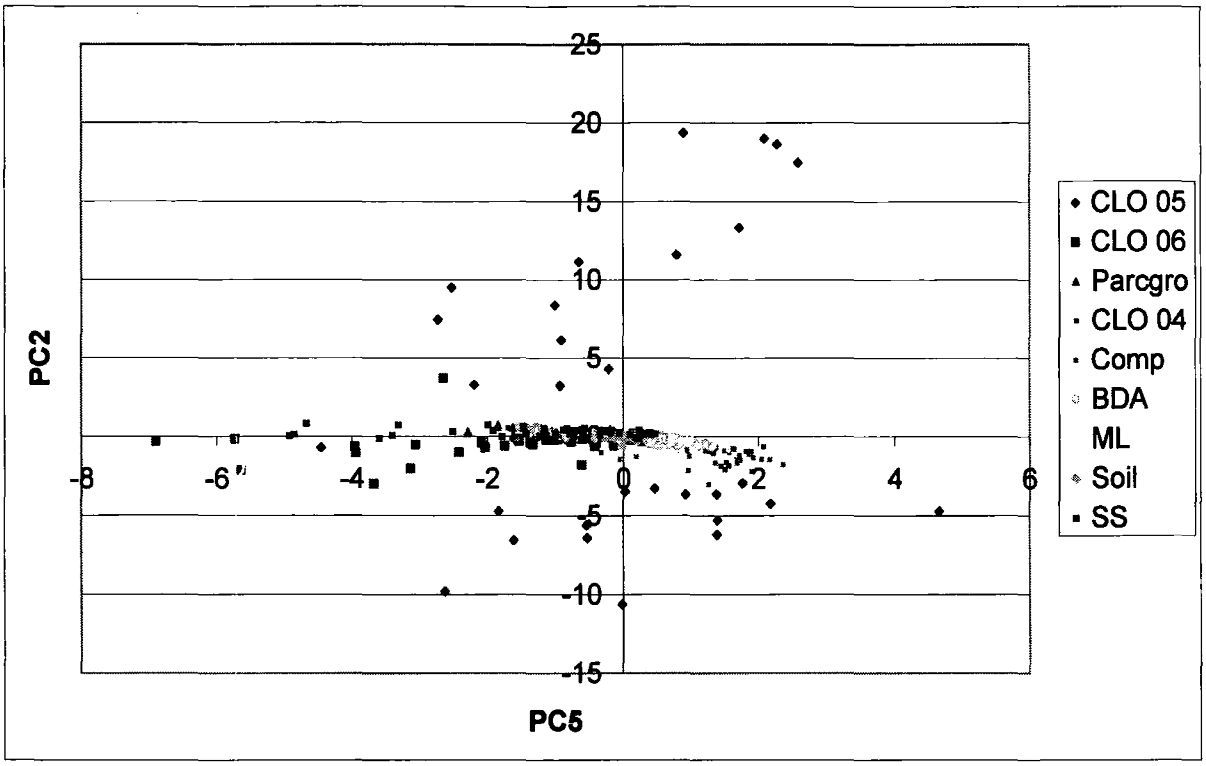


Figure 5.5: Score plot of PC2/PC5 for the analysis of all field leachates, grouped by treatment.

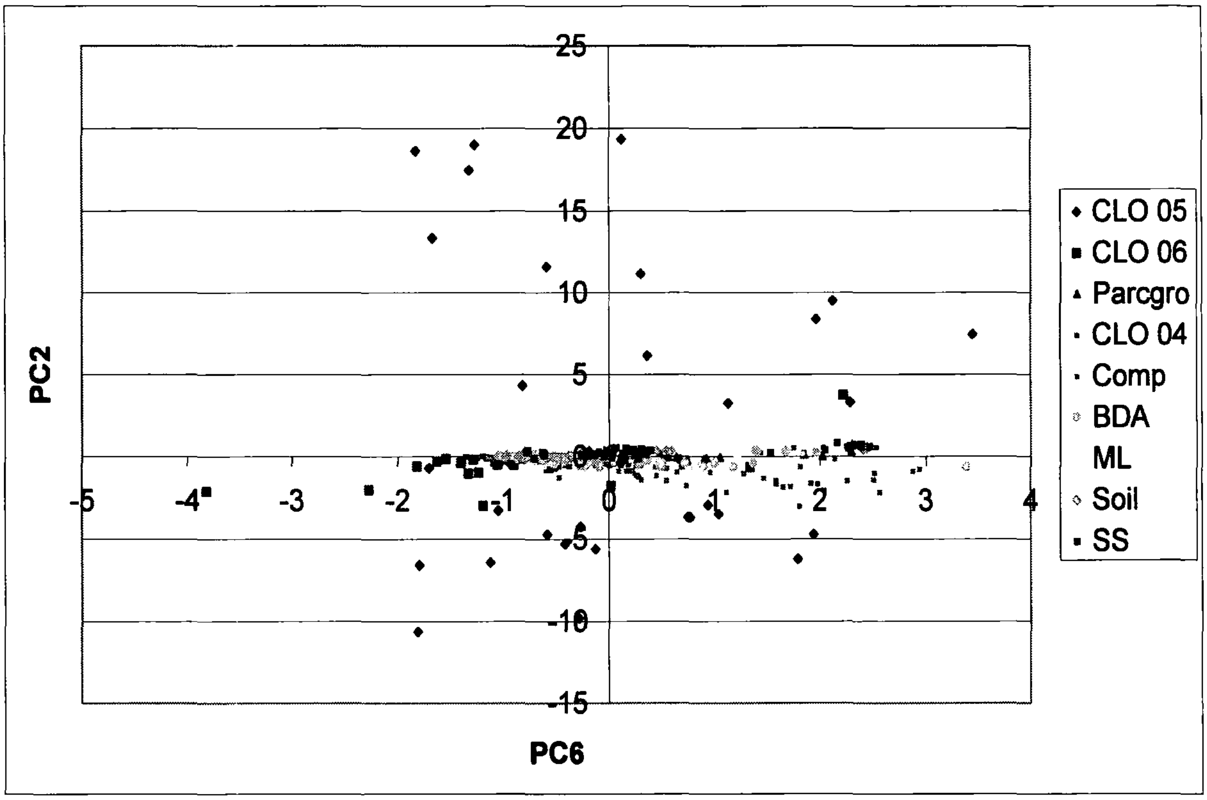


Figure 5.6: Score plot of PC2/PC6 for the analysis of all field leachates, grouped by treatment.

5.3.2 Leachate samples (CLO 05 and 06 excluded)

5.3.2.1 Analysis output and component loadings

In this instance, the first 6 PCs only accounted for 72.1% of the total data variance and so a seventh component was included which increased the figure to 75.9%. The eigenvalues, loadings and proportions of variance accounted for in this PCA analysis are shown in Table 5.2. The scree plot in Figure 5.7 represents the eigenvalues. It can be seen, as with PCA results inclusive of all treatment leachates, that PC1 is likely to represent an overall concentration gradient, giving medium negative loadings for most components but again not for NO_3, and this time Sc displayed very little change in concentration. However, as can be seen below in the score plots, CLO 2004 appeared to dominate this trend. PC2 gives high positive loadings for Si, Ca, Zn and Mn, and PC3 distinguished between very high positive loadings for Cd and Sc, and a high negative loading for pH. There appeared to be a similar distinction between loadings for Cu and Li (negative) and that of P (positive) in component 4. PC5 appeared to represent the base cation salt component giving high positive values for K, Cl and conductivity and medium positive loadings for Na, Mg, NO_3 and SO_4. Na loadings would be expected to be higher if this component was indicative of labile salt releases, but a higher than normal value seen in the overall concentration component (PC1) may help explain this. PC6 revealed positive loadings for Ca, Cl, NO_3, SO_4 and DOC which contrasted with a negative loading seen for Si. Finally, PC7 was primarily defined by a very high positive loading for DOC.

	PC1	PC2	PC3	PC4	PC5	PC6	PC7
Eigenvalue	**8.4276**	**3.3156**	**2.5431**	**2.1432**	**1.2248**	**1.09**	**0.9998**
Proportion	**0.324**	**0.128**	**0.098**	**0.082**	**0.047**	**0.042**	**0.038**
Cumulative	**0.324**	**0.452**	**0.549**	**0.632**	**0.679**	**0.721**	**0.759**
Si	-0.1546	0.3572	0.0127	0.1600	-0.0456	-0.3399	-0.0293
K	-0.2110	-0.0597	-0.0617	-0.1874	0.3990	-0.2374	0.2369
Na	-0.3103	-0.0809	-0.0794	-0.1380	0.1456	-0.1559	0.0654
Ca	-0.0765	0.3781	-0.0156	-0.0979	-0.2004	0.3498	0.0647
Mg	-0.2240	0.2386	-0.1477	-0.2619	0.1618	-0.1094	0.0472

Ni	-0.3279	-0.0187	-0.0237	-0.0552	-0.0160	-0.1362	0.0010
Zn	-0.0394	0.3573	0.0747	0.2732	0.0551	-0.0991	-0.0123
Cu	-0.1539	0.0287	0.0798	-0.3940	-0.3585	0.0962	-0.0310
Cd	-0.0053	0.0013	0.5780	-0.1190	0.2067	0.1154	0.0457
Pb	-0.2130	-0.1905	0.0554	0.2726	-0.1542	0.2044	-0.1494
P	-0.1987	0.0945	0.1129	0.3641	-0.0102	-0.2093	0.0693
Al	-0.2640	-0.1949	-0.0030	0.1861	-0.0483	0.0506	0.0200
Fe	-0.2211	-0.1213	0.0410	0.2372	-0.1859	0.1402	-0.1190
Co	-0.2382	0.2274	0.1633	-0.1104	-0.2986	-0.1354	-0.0393
Mn	-0.0803	0.4215	0.0170	0.2263	0.0381	0.0249	0.0702
Ti	-0.2458	-0.0896	0.1607	-0.1311	-0.2549	0.0195	0.0792
Sc	0.0145	-0.0027	0.5759	-0.1222	0.1994	0.1173	0.0411
Cr	-0.3151	-0.1515	-0.0174	-0.0209	-0.0251	-0.1108	-0.0068
Li	-0.1462	0.1560	-0.0220	-0.3620	-0.0483	0.1303	-0.1910
V	-0.2715	-0.2295	0.0797	0.1786	-0.0457	0.0412	-0.0126
Cl	-0.1955	-0.0698	-0.0056	0.0855	0.2638	0.3455	-0.2272
NO3	0.0206	0.1695	0.0669	0.1407	0.1978	0.2393	0.0609
SO4	-0.1508	0.2496	-0.1333	0.0261	0.1763	0.3641	-0.2302
DOC	-0.0479	-0.0004	-0.1192	0.0629	-0.1490	0.3133	0.8377
pH	-0.0330	-0.0202	-0.4055	-0.0737	0.0228	0.1570	-0.1249
Conductivity	-0.2452	-0.0441	-0.1049	-0.0338	0.3912	0.1215	0.1030

Table 5.3: PCA results showing eigenvalues, proportional and cumulative variances, and component loadings for field leachates after the removal of CLO 05 and CLO 06 treatments.

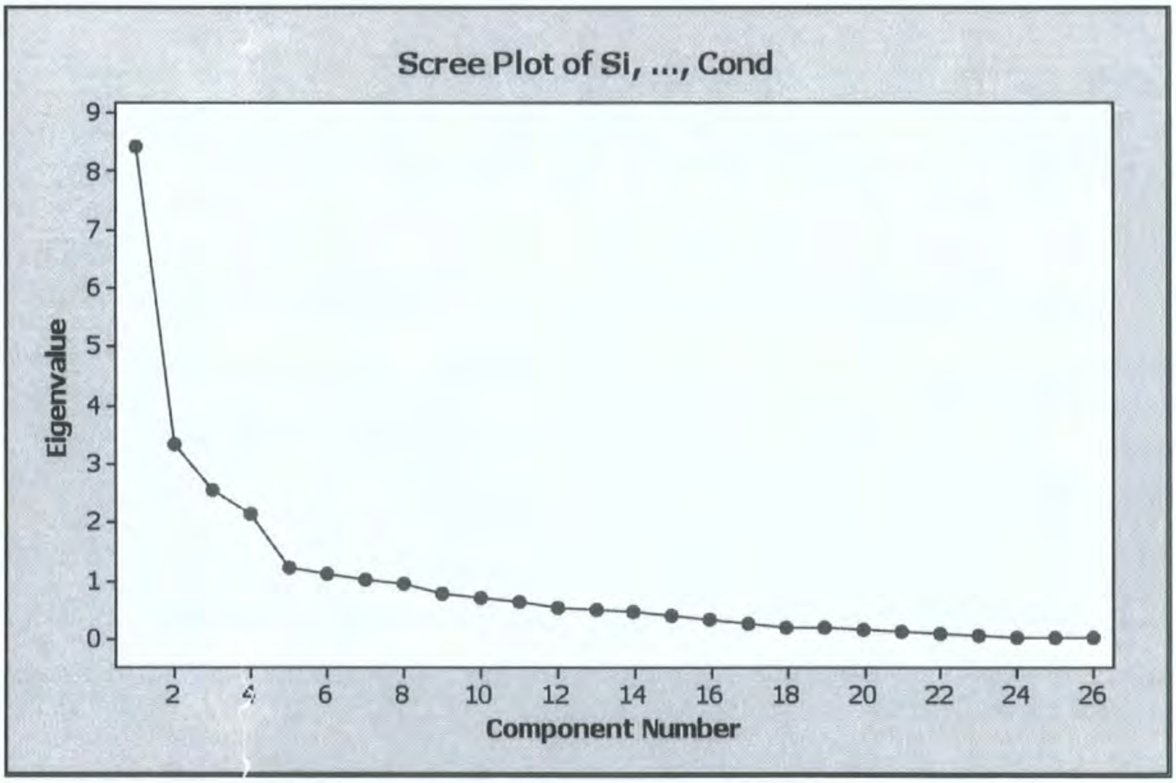


Figure 5.7: PCA scree plot showing the eigenvalues of each principal component for leachates not including the CLO 05 and CLO 06 treatments.

5.3.2.2 Component scores and trends

The first PC, which accounted for 32.4% of the total variance, was a general representation of concentration with the relative positioning of agricultural soil as a low-end member and all other samples, being associated with CLO or sewage sludge materials, scoring higher. This was exemplified in the PC1 vs. PC2 plot - Figure 5.8 which shows a clear distinction between undiluted CLO, mixed CLO, sewage sludge and the soil control. This component therefore displayed major elemental flushes at the extreme which occurred soon after lysimeter establishment in the field.

PC2 seemed to be associated with the sewage sludge trial (Figure 5.8); displaying high loadings for Si, Ca, Zn and Mn which would be expected from the leachate analyses presented in Chapter 2. This treatment trend was exemplified by PC4 in the previous run (the percentage of total variance between runs increased from 5.4% to 12.8%) and so the significance of sewage sludge releases relative to other treatments had increased, which in itself is an important observation but also indicates the highly contaminated nature of the CLO 200 and 2006 materials.

PC3 seemed to be a function of time with the formation of clusters being apparent along its axis, each of which contained samples from all or most treatments. The plot of PC1 against PC3 (Figure 5.9) exemplified this pattern. The timing of the top 2 cluster flushes correlated with the largest period of rainfall experienced throughout the 3 year study, and the subsequent production of the largest volumes of leachate. This event occurred during the autumn period of 2006, by which time the ML treatment had been terminated, explaining its absence from the top 2 clusters. The lower scoring cluster did, however, contain ML treatment leachates and coincided with the next largest rainfall event (in late July 2005), which also explains the lower scorings. The main elements with high loadings for these events were Cd and Sc; the large negative pH loading calculated was unexplainable. It is assumed, therefore, that PC3 was a reflection of rainfall pattern which, at its highest, can be considered related to, and thus help explain, the release into solution of elements such as Cd and Sc. The strong opposing loadings for Sc (positive) and pH (negative) in PC3 may be related to the trend findings described earlier for PC5 in the PCA run that included CLO 2005 and CLO 2006.

PC4 was not specifically related to any single treatment and looked as if it was responsible for component releases in sewage sludge, CLO 2004 and BDA. Figure 5.10 depicted these trends by plotting scores of PC2 against PC4. Similar elemental loadings were seen for sewage sludge as described above for PC2 but, in addition, P also showed a high positive loading. This component therefore identified a separate source/factor responsible for the release of P, in addition to the other characteristic sewage sludge releases including Si, Zn and Mn. The underlying factor causing these releases also appeared to be liable for the release of Mg, Cu and Li from the BDA treatment, linked with high negative PC4 and positive PC2 scores. Finally, this component (PC4) scored highly (positive) for Al, Fe and Pb, which correlated with negative scores on both PC1 and PC2 axes for CLO 2004.

PC5 indicated a relationship with the Comp and KCl releases (and thus conductivity) being positively loaded and Ti and Co forming the negative end members for the BDA treatment. Strong negative Cu loading, as with PC4, was again correlated with BDA. These opposing trends were illustrated in Figure 5.11 of PC3 against PC5. Further PC score plots proved insignificant at identifying and resolving any other trends in the dataset which, when considering that PC6 and PC7 only accounted for around 4% of the total leachate variance for this data set, was acceptable.

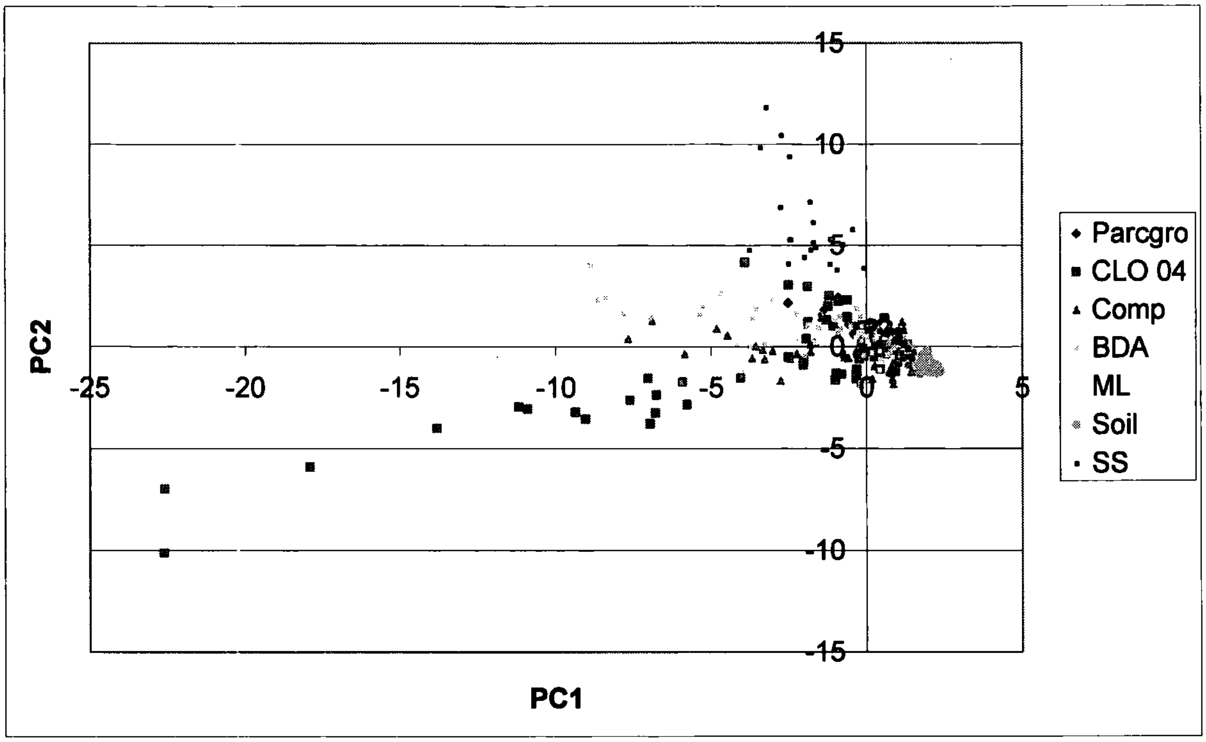


Figure 5.8: Score plot of PC1/PC2 for the analysis of field leachates (excluding CLO 05 and 06), grouped by treatment.

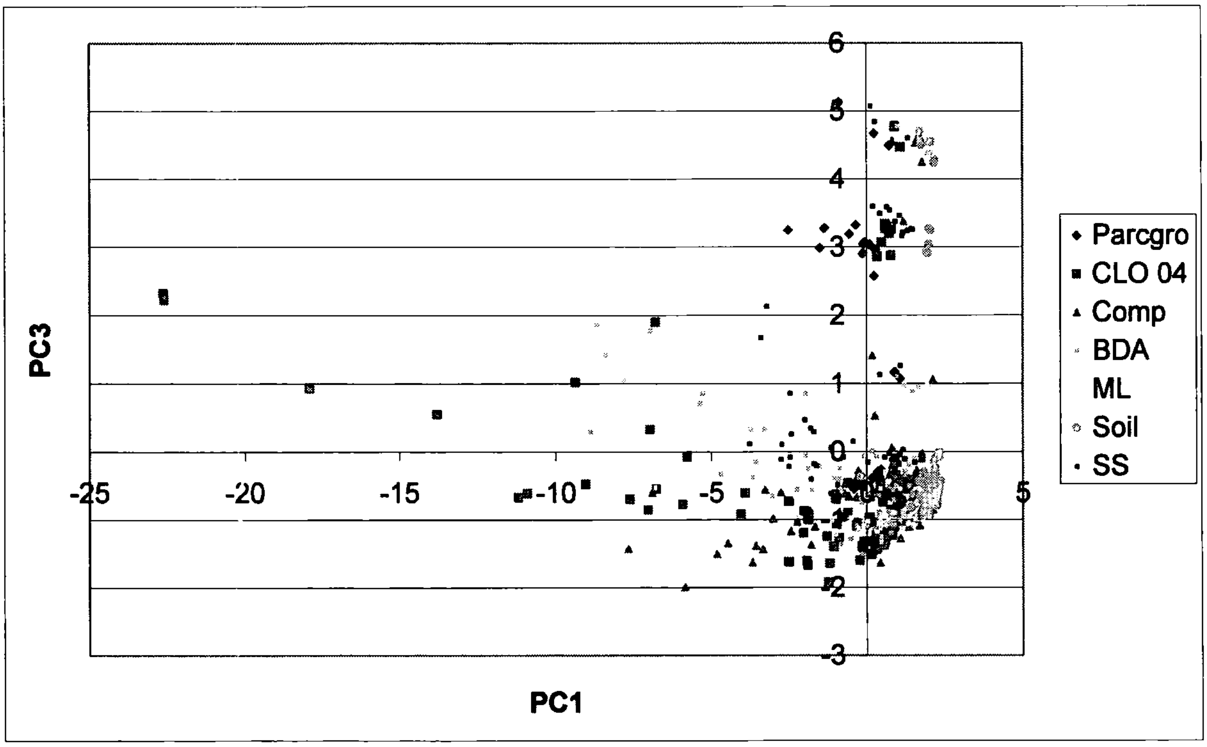


Figure 5.9: Score plot of PC1/PC3 for the analysis of field leachates (excluding CLO 05 and 06), grouped by treatment.

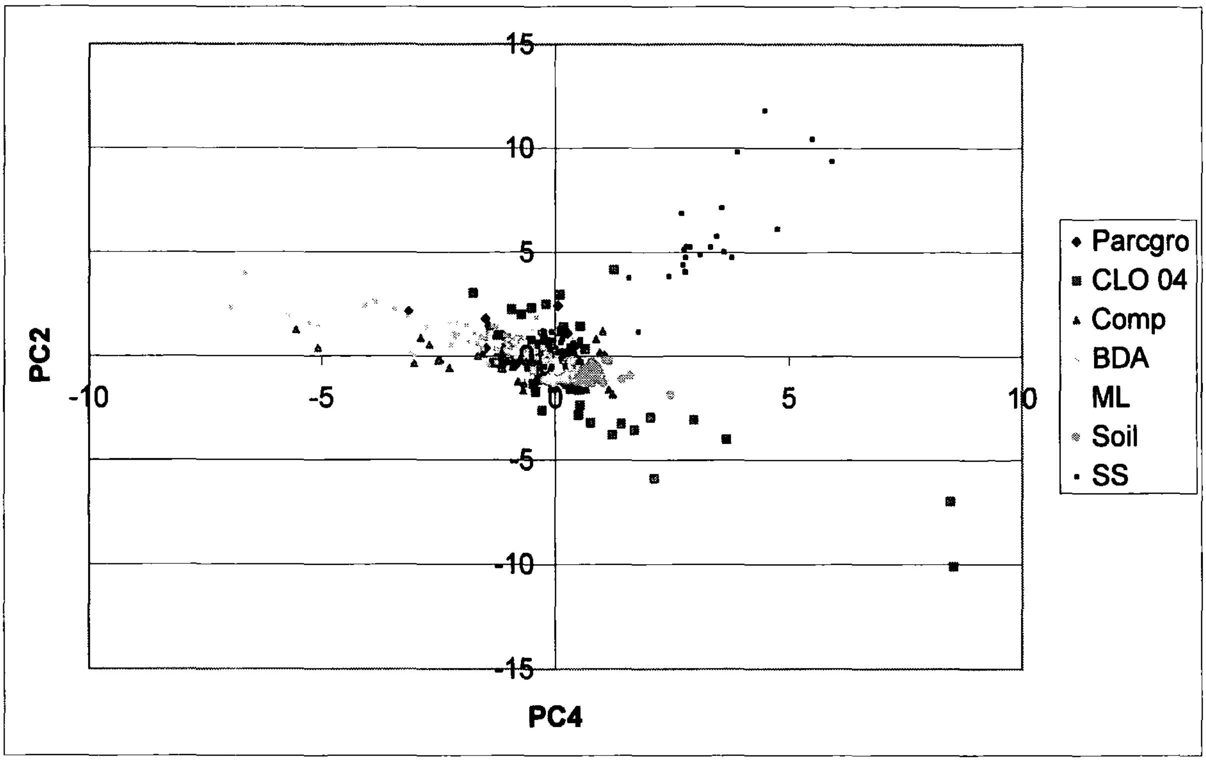


Figure 5.10: Score plot of PC2/PC4 for the analysis of all field leachates (excluding CLO 05 and 06), grouped by treatment.

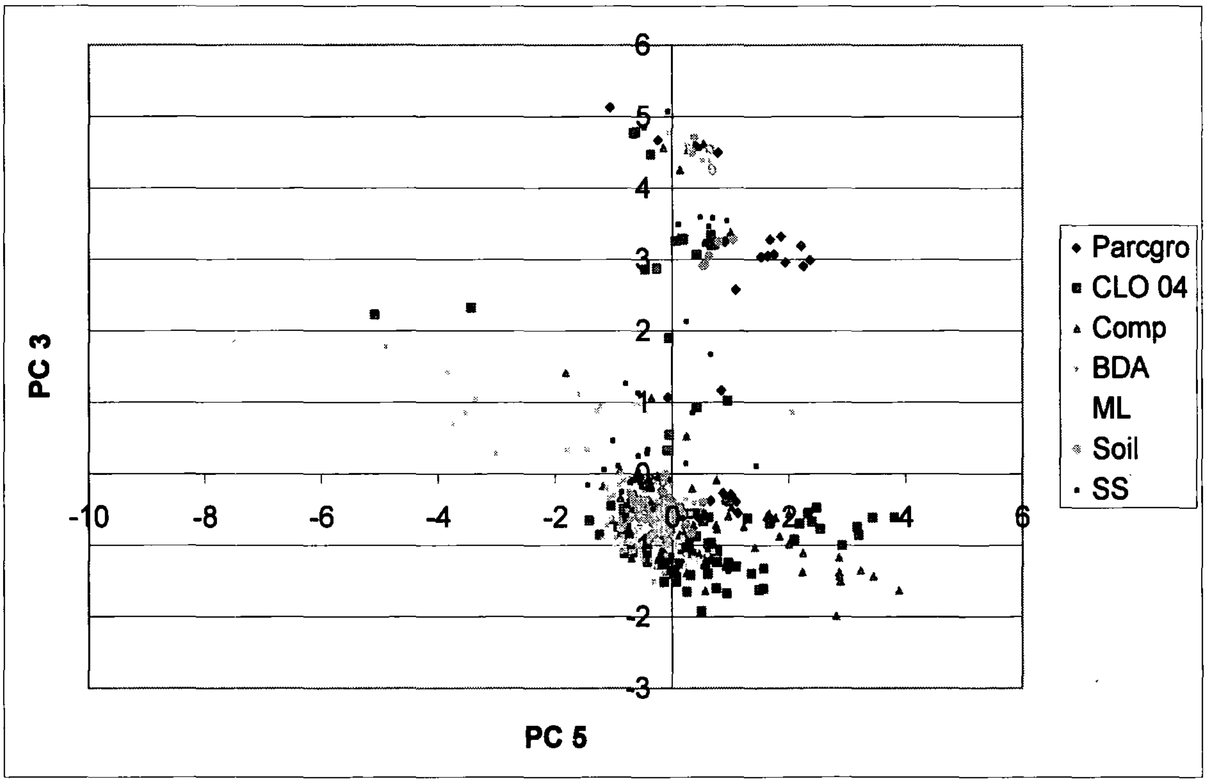


Figure 5.11: Score plot of PC3/PC5 for the analysis of all field leachates (excluding CLO 05 and 06), grouped by treatment.

5.3.3 Tessier sequential extractions

Unlike with PCA analysis of leachate samples, the Tessier extracts could also be assessed on the basis of fractionation step (Chapter 4 – step 1 (salt displaceable), step 2 (acid-soluble), step 3 (reducible) and step 4 (oxidisable)), in addition to treatment and time variations. More specifically, it was hoped that the PCA technique would help constrain specific elemental/component fractionation assemblages related to the redox-dependant phases (reducible/oxidisable). In addition, some degree of clarification to treatment grouping with regard to fractionation step and what this may reveal about the major controlling conditions and the effect that these theorised scenarios might have on metal behaviour in each treatment was sought.

As with the leachate data separate PCA runs were carried out on data sets that excluded CLO 2005 and CLO 2006 treatments, as well as data sets that excluded the CLO 04 and Comp trial original year Tessier extracts. These additional PCA runs were performed based on findings in Chapter 4, which showed that these treatments and annual sampling events demonstrated considerable variation between fractionation steps and so these data was removed in an attempt to better constrain PC score trends. Unfortunately, these efforts were to no or little avail, and so the following results were based upon the entire sequential extraction dataset only.

A few general points, which aid in the interpretation of the PCA results, include observations that, firstly, there was very little or no discernable evidence of any relationships in variation between extraction results and annual sampling events, i.e., there appeared to be no relationship with time (as seen in Chapter 3). The only familiar trend to be revealed from the various principal score plots was that for the end members (i.e., those components that scored highest at either the negative or positive ends of the axes) for CLO 2004 and sewage sludge sequential extracts. These high loadings were shown to correlate with original and second year sampling events. This was expected for the original year materials, as they had not yet been exposed to any external weathering and so had not undergone any external leaching, but the 2 year-old samples would be expected to exude smaller quantities under experimental conditions. The elevated elemental releases may therefore suggest that after 2 years under conditions typical of those experienced for the lysimeter trials, the action of rainwater leaching and the physical restructuring of the materials exposed new mineral surfaces to which substantial elements may be adsorbed. Any other findings related to material contact time in the field proved unsubstantial; subsequently, PCA results as a function of time have been assessed no further.

Secondly, the spread of the extraction data was quite diverse depending on fractionation step, and the following decreasing order of variation could be applied in nearly all cases: oxidisable > reducible > acid soluble > salt displaceable. This observation was testament to the increasingly harsh conditions used during the sequential extraction procedure, and the associated decrease in extraction efficiency and accuracy.

5.3.3.1 Analysis output and component loadings

The first 6 PCs, shown in Table 5.3 and Figure 5.12, accounted for 82.3% of the total variance seen in the dataset. As was the case with leachate PCA results, the first PC displayed medium loadings of identical sign for most elements except K, Mg and Ca. These minor loadings may result from these elements having very high loadings for later PCs; this was thought to mask their 'true' value for this component. PC2 displayed large negative loadings for Sc, Cr and V, but other elements (Si, Ni) of lesser negative loading also existed. A common source of these elements was shown (Chapter 3) to be a result of oxidation, so these trace metals were considered affiliated with organic matter or sulphides. It would be expected, based on observed fractionation patterns, that if this component was representative of an 'oxidisable trend,' then Cu and P would also show a high negative loading. This was not the case, which could be explained (only for Cu) by a high negative loading seen for Cu on PC5. P did not show any high loading for any PC, and so this element's only substantial loading was a medium loading for the overall concentration component (PC1).

It was thought that PC3 had some bearing on fractionation step 3 (reducible phase). Initially, from loadings seen for PC3 (Table 5.3), there was little evidence to support this statement; to the contrary, in fact, high negative loadings could be seen for elements, such as Si, Ca and Mg, which have been shown not to be overly affiliated with this phase. However, as discussed later, the assignment of PCs to individual fractionation steps was more complicated as it had become apparent that, unlike leachate analyses, the sequential extracts demonstrated a greater level of clustering. Component loadings alone, therefore, were not of particular definitive use with regard to constraining component pattern labelling, and so the remaining PC loadings are referred to throughout the following section which evaluates PC scores and trends. It is however worth mentioning that PC6 clearly underlay the release of the easily displaceable metal salt, K, in the first step of the sequential extraction procedure, which was in agreement with Chapter 3 findings. This was signified here by a very large loading (-0.829) for K.

	PC1	PC2	PC3	PC4	PC5	PC6
Eigenvalue	**7.8153**	**3.1746**	**1.7802**	**1.432**	**1.2312**	**1.017**
Proportion	**0.391**	**0.159**	**0.089**	**0.072**	**0.062**	**0.051**
Cumulative	**0.391**	**0.549**	**0.639**	**0.71**	**0.772**	**0.823**
Si	-0.215	-0.229	-0.363	0.201	-0.115	0.058
K	0.077	-0.048	0.134	0.046	-0.342	-0.829
Na	-0.179	0.140	0.365	0.225	0.199	0.068
Ca	0.072	0.144	-0.348	-0.500	0.241	-0.245
Mg	-0.034	-0.188	-0.345	0.126	0.513	-0.224
Ni	-0.265	-0.241	0.180	-0.278	-0.075	-0.074
Zn	-0.268	0.193	-0.161	-0.187	-0.241	-0.010
Cu	-0.271	0.048	-0.070	0.100	-0.302	0.139
Cd	-0.252	0.283	-0.210	-0.110	-0.023	-0.137
Pb	-0.199	0.070	0.389	-0.190	0.186	0.087
P	-0.281	0.227	-0.175	0.172	-0.187	-0.052
Al	-0.336	-0.093	-0.020	-0.043	-0.100	0.000
Fe	-0.281	0.237	0.172	0.077	0.138	-0.105
Co	-0.316	0.198	0.042	0.058	0.021	-0.057
Mn	-0.120	0.273	-0.158	-0.352	0.199	0.144
Ti	-0.182	0.152	0.016	0.399	0.347	-0.217
Sc	-0.179	-0.325	-0.262	0.250	0.111	0.075
Cr	-0.238	-0.355	-0.055	-0.151	-0.154	0.079
Li	-0.208	-0.284	0.161	-0.152	0.209	-0.217
V	-0.201	-0.349	0.179	-0.195	0.122	0.001

Table 5.4: PCA results showing eigenvalues, proportional and cumulative variances, and component loadings of Tessier extracts for all treatments.

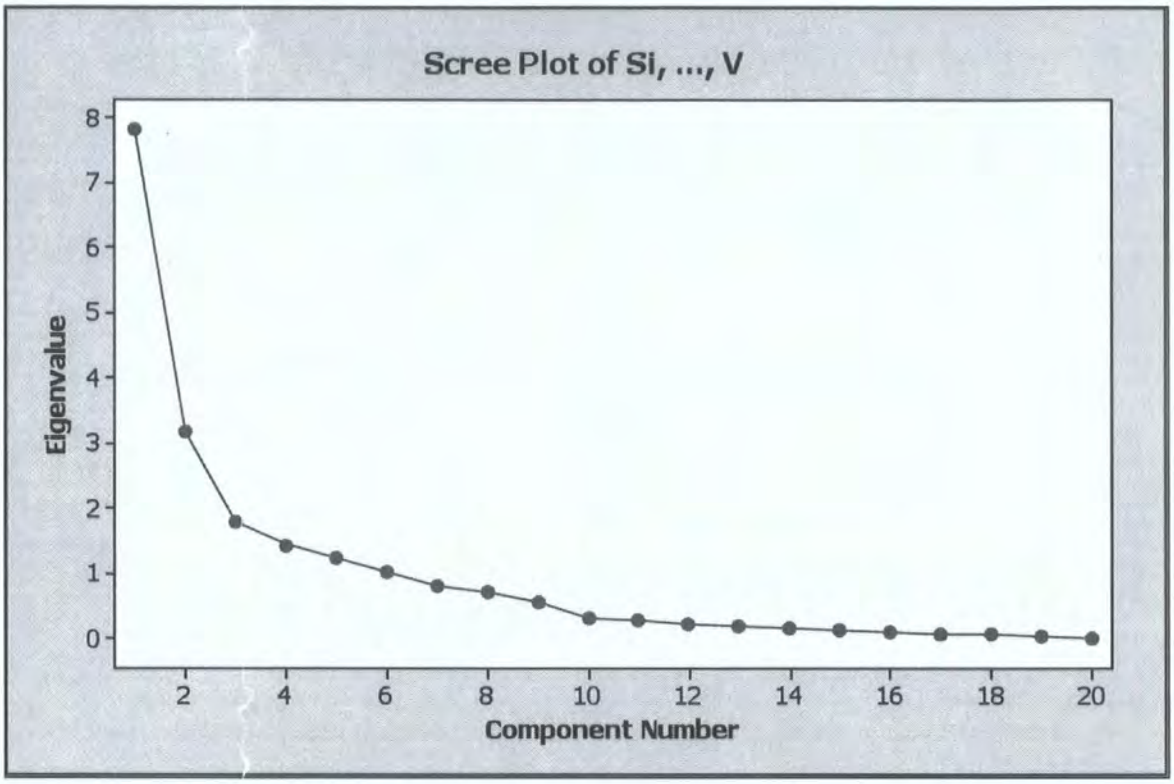


Figure 5.12: PCA scree plot showing the eigenvalues of each principal component for all Tessier extracts.

5.3.3.2 Component scores and trends

The first 6 PCs accounted for: 39.1%, 15.9%, 8.9%, 7.2%, 6.2% and 5.1% of the total variance, giving an overall variance accountability of 82.3%. PC1 was likely to be a representation of the overall concentration differences seen during the sequential extraction procedure. Again, this was typified by a greater clustering of small positive PC scores for agricultural soil and progressively larger negative PC1 scores for the mixed and sewage sludge treatments and, finally, the largest negative scores were achieved by the undiluted CLO treatments (see Figure 5.13b, which depicts PC1 against PC2 with respect to treatment). The 2 distinct trends (trend *a* - negative PC1 and positive PC2, and trend *b* negative PC1 and negative PC2) were due to fractionation step variation, with trend *a* representing step 3 and trend *b* representing step 4. This can be seen in Figure 5.13a which presents the data as a function of fractionation step. The grouping of component scores in Figure 5.13a clearly indicates that the main control on sequential extract releases was derived experimentally (i.e., fractionation step) as opposed to treatment type or time (annual sampling event). This score plot was also a good example of the general statement defined earlier concerning the order of data spreading with regard to progressively harsher reagents used in each fractionation step; steps 1 and 2 were well constrained in decreasing amount to the right hand side of the plot, and steps 3 and 4 increasingly spread to the left hand side (Figure 5.13a – trends *a* and *b*).

Component 2 gave the first indication of elemental assemblages with regard to fractionation step, best illustrated in Figures 5.13a and 5.14a, which showed score plots of PC1 vs. PC2 and PC2 vs. PC3, respectively. It can immediately be seen that both plots reveal a clear step 4 grouping which correlated with negative PC2 scores. In addition, due to the ideal distribution of the data in this way with no other fractionation steps scoring negatively with respect to PC2, any element that gave a negative loading can be said to represent the oxidisable fraction. The elemental assemblage included Si, Mg, Ni, Al, Sc, Cr, Li and V. These findings were all in agreement with those described in Chapter 3, but this technique offered greater clarification and thus certainty of this elemental/oxidisable relationship as all other 'background noise' were removed by the PCA technique. Furthermore, due to the orthogonal nature that existed between the principal components, the ambiguity brought to the analysis of fractionation pattern, undertaken in Chapter 4 by differences with time and treatment, was reduced.

With respect to treatment, the isolation of elements was less informative, as can be seen from the score plots of PC1 against PC2 and PC2 against PC3 (Figures 5.13b and 5.14b). Only a few elemental releases could be further distinguished into treatment groups (CLO 2004, sewage sludge and ML treatments for both steps 3 and 4). However, this did serve as a means of identifying which treatments were the most prolific for these component releases. The highest component loadings for CLO 2004 extracts, which were distinguishable from the PC score plot PC1 vs. PC2 (Figure5.13b), giving negative loadings for both axes, were Si, Ni, Sc, Cr, Li and V. This suggested that CLO 2004 digestate, under oxidising conditions (step 4), released the largest concentration of these elements into solution relative to all other treatments, including CLO 2005 and CLO 2006. This will be further assessed later when transposing leachate and sequential extraction data together. For sewage sludge, the major loadings were seen for a negative PC1 and a positive PC2 and represent Cd, P and Fe, and to a lesser extent Co and Zn. This assemblage of elements was at the other end of the PC2 scale (positive scores) and can also be seen in the plot of PC2 vs. PC3 (Figure 5.14b). The final trend mentioned concerning the ML treatment can also be seen in this plot, defined by negative loadings on both axes. The components of interest shown to be released under oxidisable conditions were Si, Mg and Sc, and to lesser extents Al and Cr. These elements have all been shown to be strongly affiliated with the oxidisable fraction for this treatment (Chapter 3).

As mentioned above, the PC score plots revealed trends in the data which would otherwise not be identifiable simply from evaluating component loading patterns. Moreover, different end member scores (when in clusters such as with the sewage sludge) at opposing ends of a particular PC axis (i.e, positive and negative ends) can represent component releases associated with different fractionation steps. This was exemplified here with sewage sludge releases (Cd, Fe, P and to lesser extents Co and Zn), representing the reducible phase (step 3), forming the positive PC2 end members and the aforementioned CLO 2004 releases (Si, Ni, Sc, Cr, LI and V) and ML releases (Si, Mg, Sc and to lesser extents Al and Cr), representing the oxidisable phase (step 4), forming the negative end members. In simplified terms, as with increasing/decreasing overall concentration signified by PC1 in most score plots, a change from positive to negative PC scores can relate to a change in fractionation step.

PC3, the positive end of which was thought to predominantly signify the reducible phase (step 3) of the sequential extraction procedure, was exemplified in the score plot as a function of fractionation step for PC2 vs. PC3 (Figure 5.14a). The black cluster towards the top of the plot, described above, represented releases from sewage sludge only. The positioning of the reducible phase scores almost always placed them with positive loadings for PC2 and PC3 (except for the sewage sludge cluster which displays opposing negative PC3 loadings). This, therefore, showed Na, Pb, Fe, Co and Ti as being independently associated with the reducible phase which, again, agreed with Chapter 3 findings. Elemental releases similar to both clusters (positive PC2 and PC3, and negative PC3 loadings) were therefore Fe and Co. Further designation of components to individual treatments proved unhelpful owing to the non-linear cluster formation of this trend, and so no treatment labelling of elements, other to that seen for sewage sludge, could be defined. The PC3 results therefore suggested that, if reducing conditions prevail for sewage sludge, then considerable amounts of Cd, P and Zn would be exuded, in addition to the other elemental releases (Na, Pb, Fe, Co and Ti) seen for all CLO-containing treatments.

Figure 5.15 depicts the trends seen for PC4 scores when plotted against PC1. This plot is the clearest example showing the separation of the second fractionation step (acid-soluble) from the remaining 3 steps. PC4 was considered to be associated with step 2, as this component displayed high negative loadings for Ca and Mn and medium loadings for Ni, Zn and Pb; these elements were all shown to have increased acid-soluble releases relative to other elements (Chapter 3). A high positive loading was also seen for Sc, which could be explained by its positioning on Figure 5.15 – a high PC4 positive loading would place PC scores in the oxidisable range with which Sc has been shown to be strongly affiliated. There is evidence of some overlap with the salt-displaceable fraction at lower PC4 scorings but, for the main part, the acid-soluble fraction could be said to be well separated into a positive PC1, negative PC4 allocation. Additional assessment of this fractionation step also proved informative from the score plot of PC2 vs. PC3 (Figure 5.14a). The repositioning of the acid-soluble fraction by rotation in this way also suggested that the release of Cd was related to this trend. This agreed with the fraction pattern described in Chapter 3. Grouping the data by treatment, while providing discernable assemblages, did not clearly assign individual component loadings, since the scores were too closely grouped.

The underlying factor controlling PC5 scores and loadings was unclear. The major loadings concerned with this component were those of Mg and Ti (positive) and Cu and K (negative). The only discernable sources of these elements were the ML treatment for Mg and the BDA treatment for Ti. These correlations were shown from the score plots of negative PC2 vs. positive PC5 and negative PC3 vs. positive PC5 trends for Mg and for Ti by a positive PC4 vs. positive PC5 trend (Figures 5.16, 5.17 and 5.18). Both of these elements were shown to be released during phase 4 (oxidisable) of the sequential extraction procedure. These findings concur with recorded flux levels exuded from these treatments under oxidisable conditions (Chapter 3). It was also shown that Cu was strongly affiliated with this fraction, particularly for these 2 treatments. Potassium was anomalous to the rest of the findings, being majorly partitioned to the salt-displaceable phase, exemplified by the very large loading seen for PC6 (see below). It is this extremely high loading that could be responsible for this 'anomalous' K loading for PC5, and it is therefore proposed that this component was, to a degree, accountable for BDA and ML treatment releases specifically associated with the oxidisable phase. The observed elemental releases for Mg and Ti from these treatments may be indicative of their high carbonate contents, a reason why they have performed similarly throughout this study. Oxidation of these metal species may encourage their dissolution further to that expected under acidic conditions.

Finally, it can be seen from Figure 5.19a of PC3 vs. PC6, that negative PC6 and weakly positive PC3 scorings show a clear trend related to salt-displaceable releases (step 1). As can be observed from component loadings (Table 5.3), that the major element this axis defined was K, the releases of which were shown to be primarily confined to the initial step of the sequential extraction procedure. Together with the treatment plot of PC3 vs. PC6 (Figure 5.19b), an order of concentration gradient for K was defined as follows:

CLO 06 > CLO 05 > Parcgro > Comp > CLO 04 > remaining treatments.

The remainder of the treatment K extracts cannot be defined from the PC score plots.

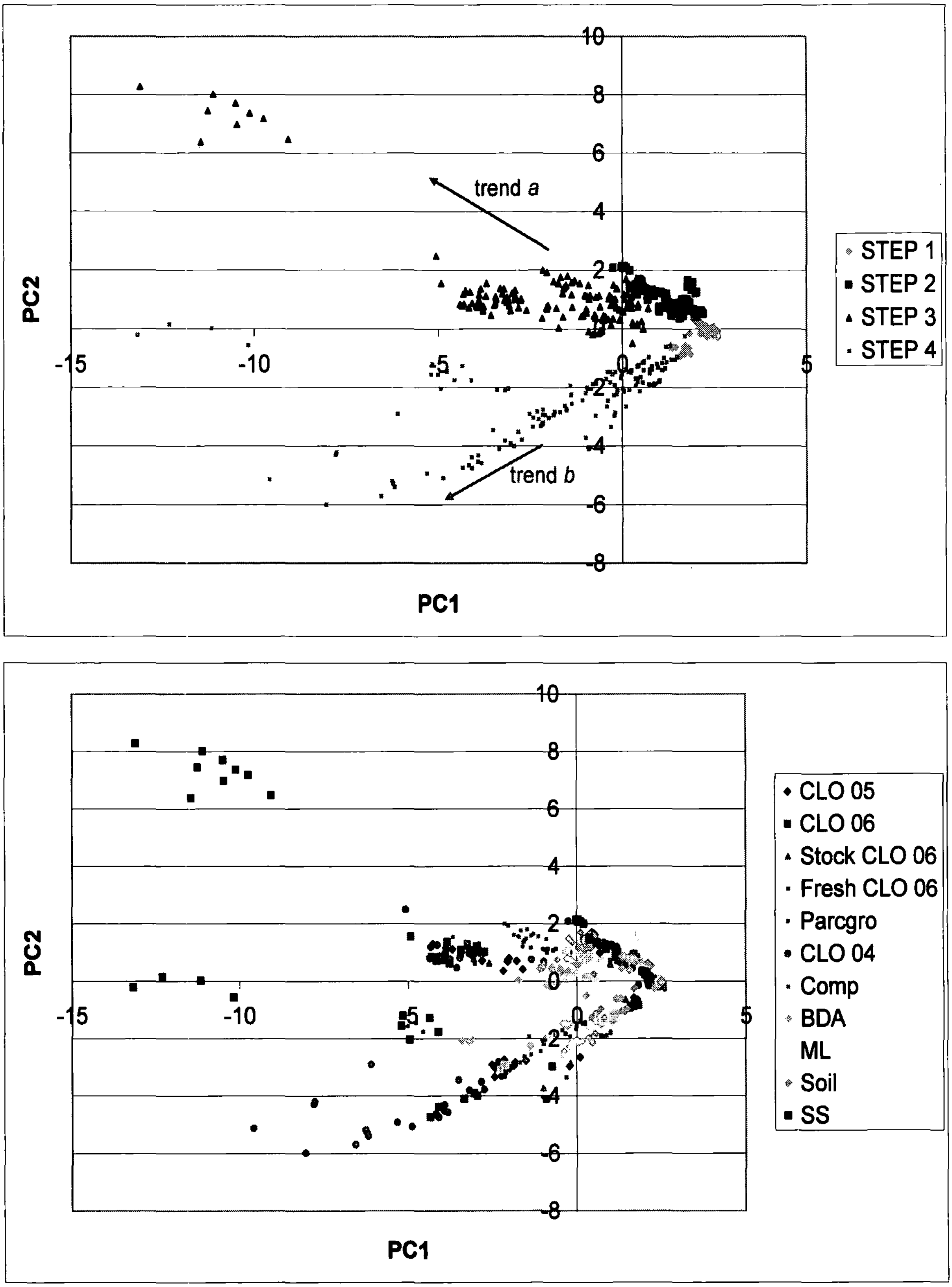


Figure 5.13: Score plots of PC1/PC2 for the analysis of all Tessier extracts, grouped by a) step and b) treatment.

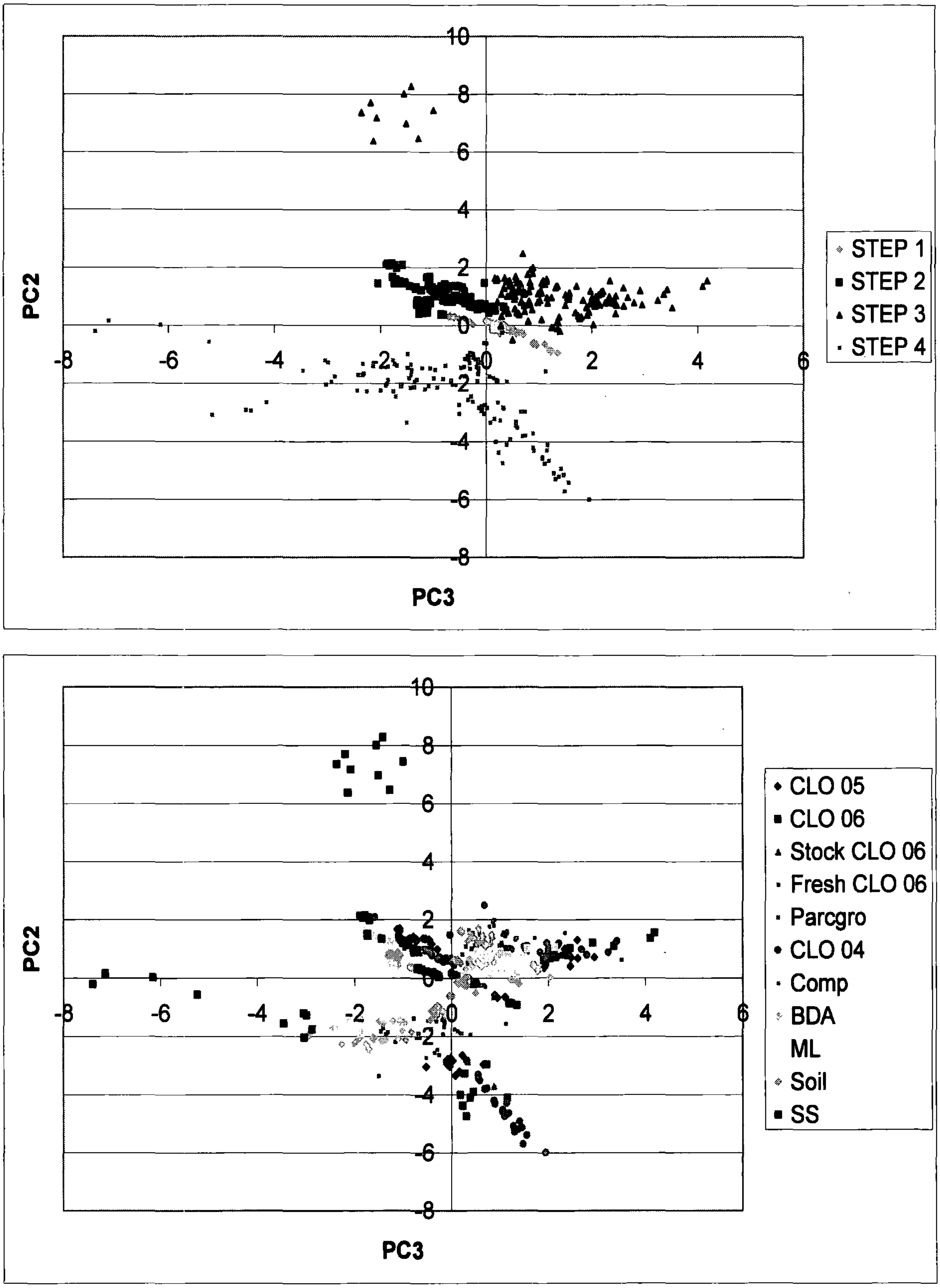


Figure 5.14: Score plot of PC2/PC3 for the analysis of all Tessier extracts, grouped by a) step and b) treatment.

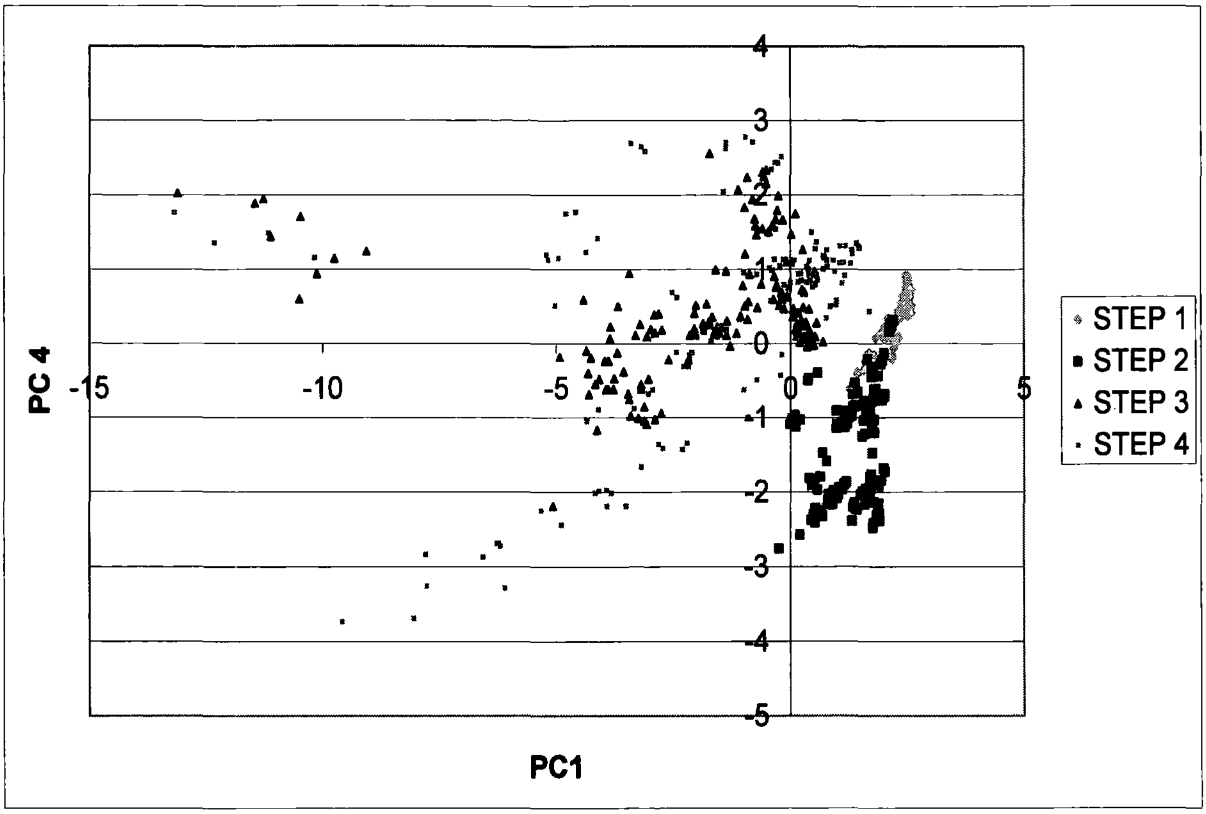


Figure 5.15: Score plot of PC1/PC4 for the analysis of all Tessier extracts, grouped by step.

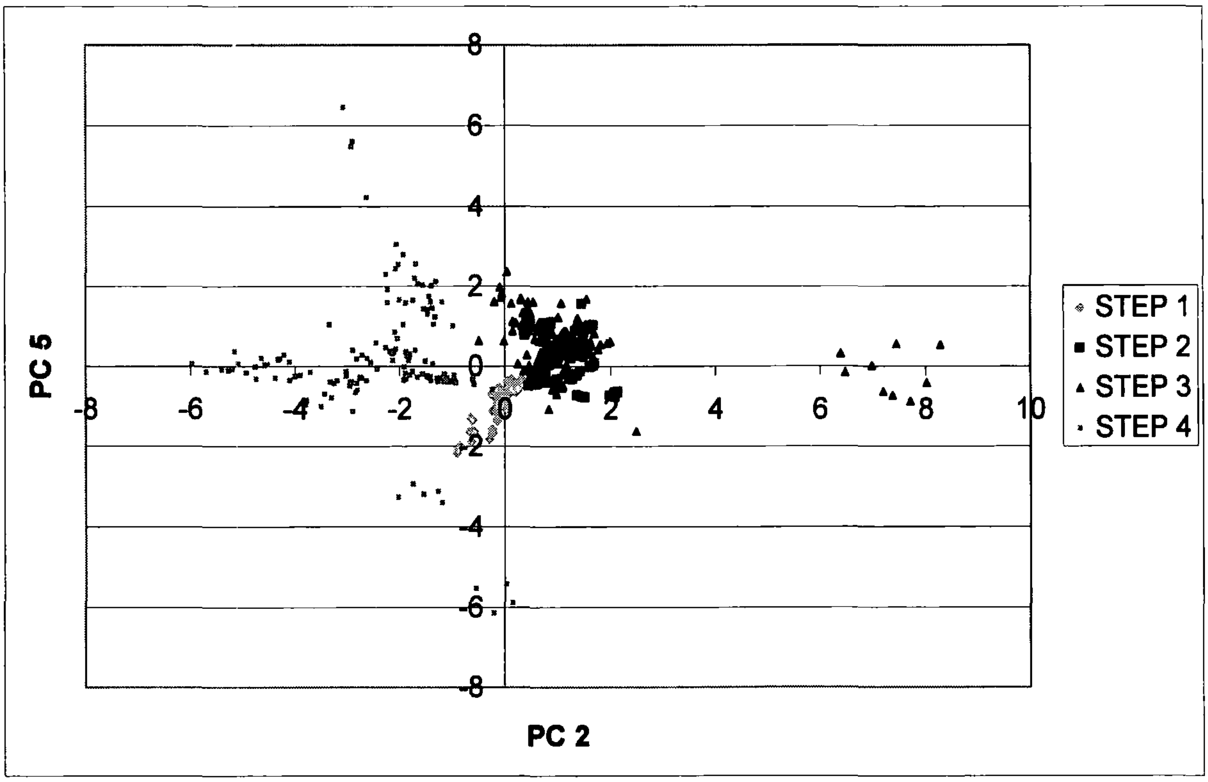


Figure 5.16: Score plot of PC2/PC5 for the analysis of all Tessier extracts, grouped by step.

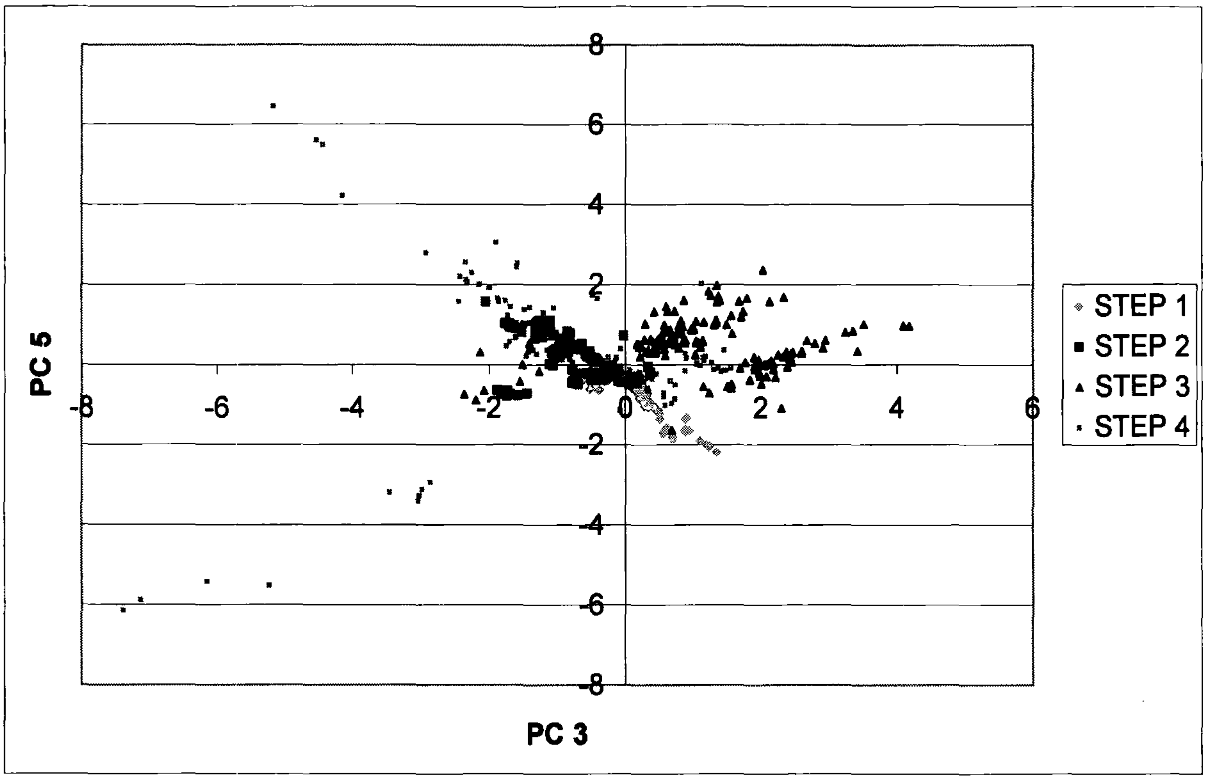


Figure 5.17: Score plot of PC3/PC5 for the analysis of all Tessier extracts, grouped by step.

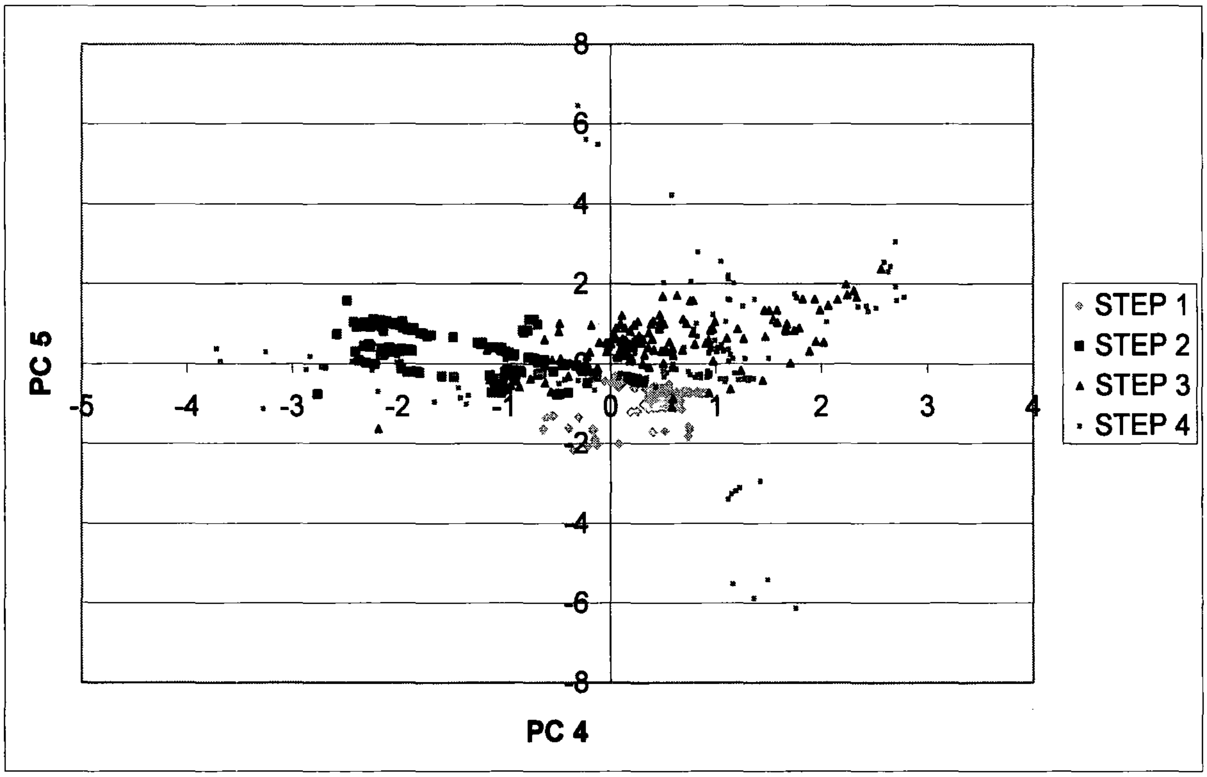


Figure 5.18: Score plot of PC4/PC5 for the analysis of all Tessier extracts, grouped by step.

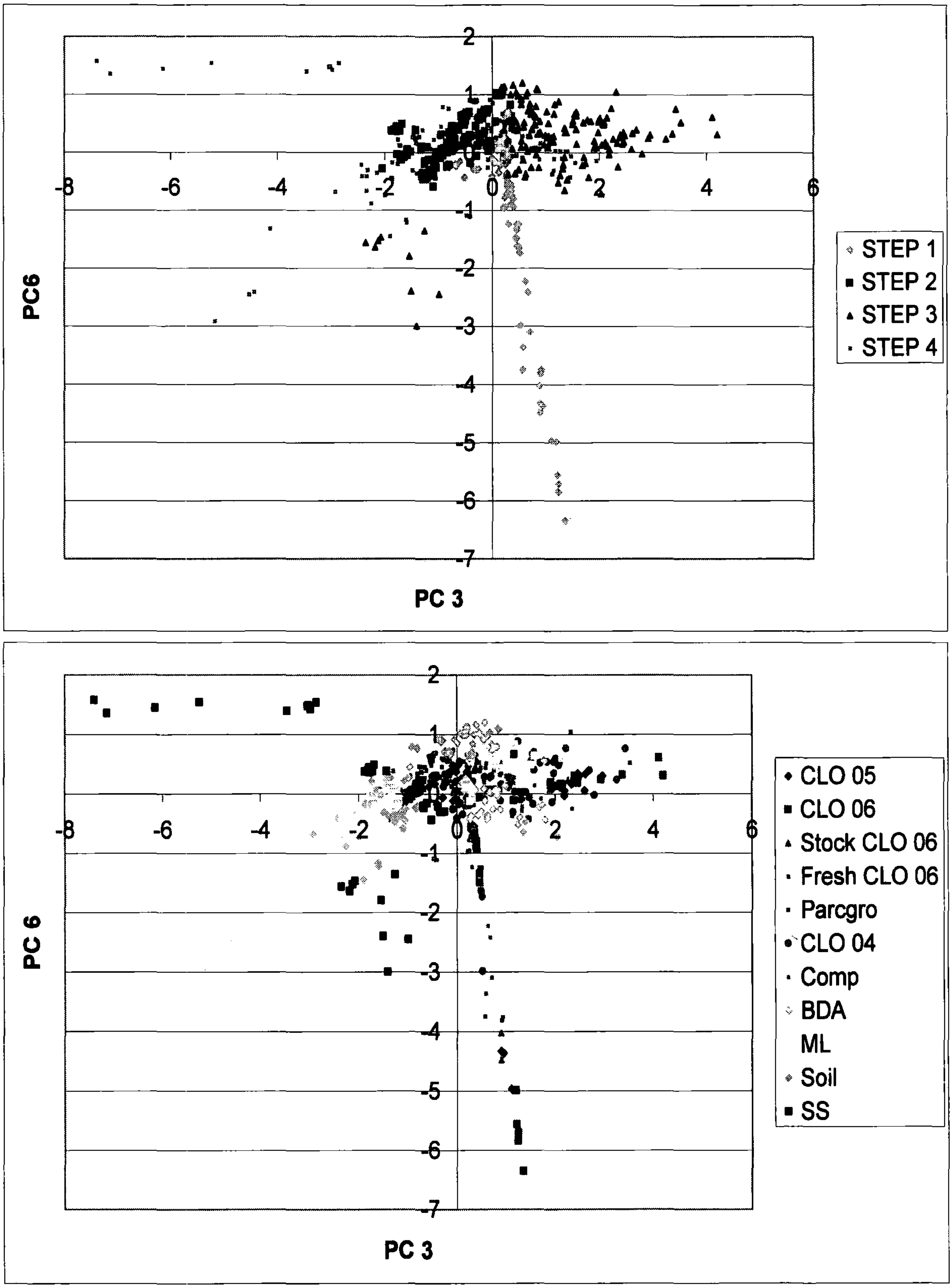


Figure 5.19: Score plot of PC3/PC6 for the analysis of all Tessier extracts, grouped by a) step and b) treatment.

5.3.4 Tessier sequential extracts and Leachate samples

The sequential extraction data were transposed on to the treatment separated leachate sample data, both as a function of fractionation step and treatment. PCA results were again computed for data sets including and excluding CLO 2005 and CLO 2006 treatments in an attempt to further decipher any similar patterns or trends that may have existed within the overlain data. These data sets were assessed individually but, rather than assessing the PCA results by step and treatment separately, it was decided that an overall evaluation would be more informative since interlinking behaviour relating these criteria with that seen in field leachates was the primary objective of this section.

5.3.4.1 Analysis output and component loadings

The component loadings and eigenvalues (Table 5.4 and Figure 5.20) showed that the first PC remained the most likely to represent the overall concentration variation seen within the emerged data set and accounted for 39.1% of the total variance. Values were all of negative sign and were all within the range indicative of medium strength loadings (± 2 – 2.5). PC2 was more difficult to define as it also showed a number of elemental loadings of medium value with no obvious chemical union between them. The elements for which the largest negative loadings were seen were: Ni, Cr, Li and V; those elements showing the highest positive loadings are: Si, Cd, Co, Mn and Ti. A possible explanation for these findings may be as a result of the combined effect of CLO 2005 leachate samples (representing the positive loadings) and the oxidisable fractionation step (representing the negative loadings). This explanation was by no means solid, as Fe did not show a high positive loading as would be expected from CLO 2005 leachates, but all positive loadings diminished when the CLO 2005 and CLO 2006 leachates were removed from the data set. PC2 accounted for 15.6% of the total variation, and so would explain a similar proportion of variance to that found during the separate PCA runs on leachate and extract data. The major loadings highlighted for PC3 were for Si and Sc (negative) and Fe (positive). The high value for Fe may help to explain the limited loading seen in PC2. PC4 gave large negative loadings for Ca and Mg (and to a lesser extent for K) and could represent the labile base cation flushes seen in field leachates for all CLO-containing treatments. It was more difficult to confirm this finding, found in leachate PCA results above, because anion data and conductivity readings were not available for this dataset. Furthermore, Na loadings will be skewed as a result of the Tessier extractions, which showed extremely large affiliations with step 3 due to the presence of Na in one of the reagents used in this extraction phase. High Zn loadings appear to form the end member at the positive end of the PC4 scale. PC5 gave large positive loadings for Ca and Zn. Ti displayed a negative loading but not as intense as that seen for Ca and Zn. Finally, PC6 showed the largest loading of any component (albeit for K). This was thought to represent the finding described for the salt-displaceable phase of the sequential extraction procedure and accounted for 4.5% of the total dataset variance.

	PC1	PC2	PC3	PC4	PC5	PC6
Eigenvalue	**7.8112**	**3.1182**	**1.7317**	**1.4515**	**1.1463**	**0.8934**
Proportion	**0.391**	**0.156**	**0.087**	**0.073**	**0.057**	**0.045**
Cumulative	**0.391**	**0.546**	**0.633**	**0.706**	**0.763**	**0.808**
Si	-0.206	0.205	-0.413	-0.076	0.149	-0.199
K	-0.066	-0.254	0.131	-0.265	-0.267	-0.640
Na	-0.197	-0.158	0.212	0.047	-0.443	-0.158
Ca	-0.086	0.025	0.320	-0.520	0.453	-0.024
Mg	-0.184	0.056	-0.161	-0.541	-0.023	-0.167
Ni	-0.288	-0.281	-0.038	0.029	0.039	0.139
Zn	-0.162	0.079	0.163	0.384	0.454	-0.282
Cu	-0.258	0.054	-0.050	0.250	0.041	-0.300
Cd	-0.220	0.389	0.067	0.010	0.021	-0.054
Pb	-0.235	0.176	0.013	0.017	-0.293	0.180
P	-0.268	-0.082	0.211	0.189	0.109	-0.240
Al	-0.327	-0.134	-0.025	0.111	0.066	0.067
Fe	-0.251	-0.023	0.336	0.077	-0.065	0.202
Co	-0.252	0.343	0.039	0.092	-0.166	0.073
Mn	-0.188	0.253	0.285	-0.214	0.164	0.227
Ti	-0.197	0.336	-0.029	-0.097	-0.317	0.020
Sc	-0.141	0.115	-0.552	-0.017	0.101	-0.061
Cr	-0.270	-0.297	-0.164	0.007	0.153	0.092
Li	-0.248	-0.282	-0.042	-0.173	-0.003	0.227
V	-0.245	-0.304	-0.170	0.002	-0.031	0.221

Table 5.5: PCA results showing eigenvalues, proportional and cumulative variances, and component loadings of leachate and Tessier extracts for all treatments.

5.3.4.2 Component scores and trends

Component score plots revealed a number of trends in the data which helped identify and further define treatment and fractionation constraints for each PC. The first component was taken to represent the overall variation in concentration, but what also became apparent were parallel trends which seemed to exist between the sequential extracts and the leachate samples for this component. This was shown in Figure 5.21, which illustrates the score plot of PC1 vs. PC2 and signifies the principal finding, both in terms of variance accountability and component relations. The main concentration trend, depicted by PC1, coincides with step 4 of the fractionation scheme. These findings, in conjunction with PC1 vs. PC4 trends (Figure 5.23), reveal that the oxidisable fraction (step 4) was strongly correlated with undiluted CLO leachate samples (2004,2005 and 2006), suggesting that a large proportion (39.1%) of the component behaviour seen in field leachates from undiluted CLOs were a result of oxidative-dependant releases. The additional trend introduced by CLO 2005 leachates (depicted by positive PC1 and negative PC2 scores), however, does not correlate with the equivalent CLO 2005 treatment fraction, or indeed any fraction, and so these supplementary component releases seen in the field (Si, Cd, Co, Mn and Ti) for this treatment cannot be solely explained by the Tessier fractionation pattern used here.

Another trend or component cluster depicted by these 2 score plots was that associated with sewage sludge sequential extractions for both steps 3 and 4 (redox-related fractions), as highlighted in Figure 5.21 by the red circle. Sewage sludge, as shown previously in the PCA results for the Tessier extracts and flux releases in Chapter 3, was taken to be the treatment of most environmental concern (particularly under anoxic/reducing conditions). This cluster (as can be seen from plot positive PC1 vs. negative PC2 – Figure 5.21) appeared to represent the end member (Zn) of an overall fractionation trend (steps 3 and 4) that included all CLO-containing treatments and was not typified by leachate behaviour. This was clarified below, when assessing PC4 (Figure 2.3).

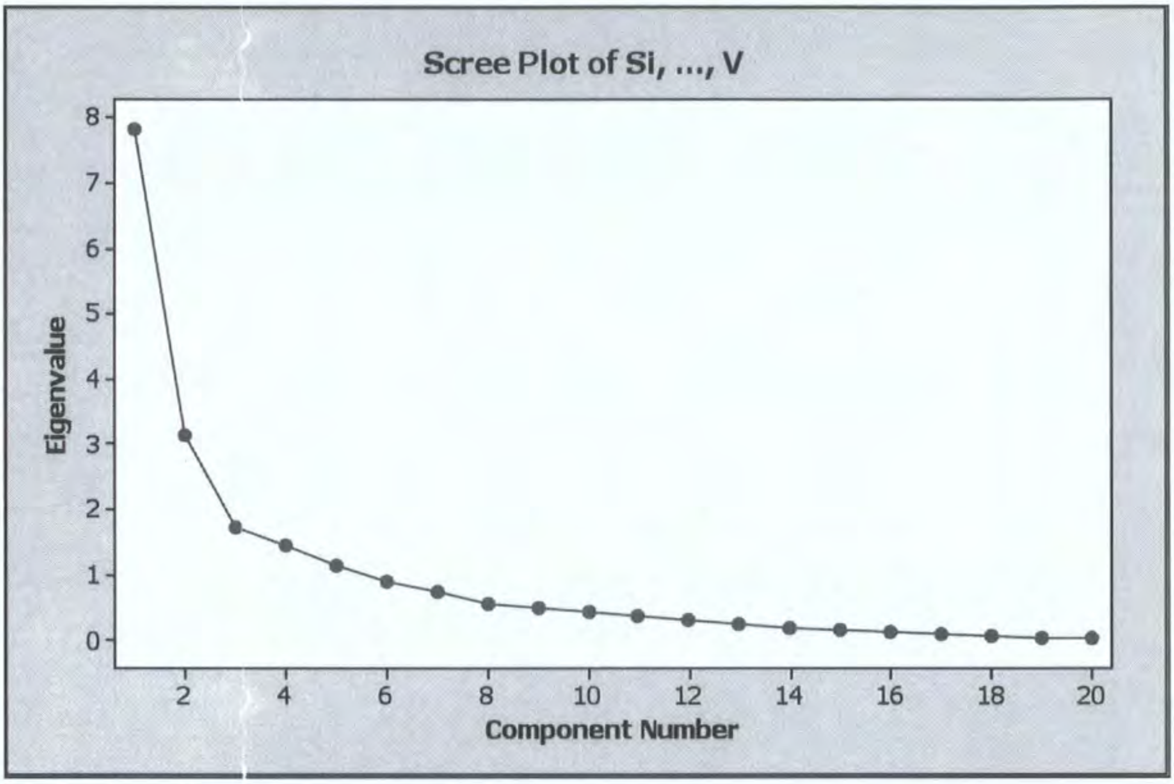


Figure 5.20: PCA scree plot showing the eigenvalues of each principal component for all leachate and Tessier extracts.

The score plots for the second component did not prove any more informative than the component loadings described earlier, and so the only reasonable explanation that could be proposed was that mentioned earlier. PC2 was thought to represent, to some extent, both CLO 2005 supplementary element releases (Si, Cd, Co, Mn and Ti - positive end) and the oxidisable fraction (negative end). Again, the score plots for PC3, although clearly separating the oxidisable fraction to the negative end, which correlated strongly with Si and Sc loadings, did not prove that informative in further identifying overlying trends. The small cluster of positively loaded scores (Figure 5.22 of negative PC1 vs. positive PC3) were a result of sewage sludge Tessier step 3 releases and typify the release of Mn. These isolated component distributions therefore suggest that a large proportion of the total variance (8.7%) can be associated oxidising conditions with the Si and Sc releases at the extreme and Mn release from sewage sludge if anoxic conditions prevail. These releases were not similar to those exuded under field conditions, implying that Sc and Si do not necessarily conform to the oxidisable-dependant releases described above for undiluted CLO digestates.

PC4 score plots (exemplified by PC1 vs. PC4 – Figure 5.23) reveal that much of the data was plotted close to this axis. This in turn makes treatment and step relationships more difficult to decipher, but the main points were as follows: at the positive end of the scale, this component gave high loadings for Ca and Mg, which may in itself explain a strong treatment dependency as these two base cations were found in large concentrations for all treatments analysed (particularly leachate samples in Chapter 2). These 2 elements have their strongest affiliations with steps 2 (acid-soluble) and 4 (oxidisable) of the sequential extraction procedure, respectively. Unfortunately, the only treatment leachates that could be clearly seen to correlate with these fractions were those exuded from CLO 2005. At the opposing end of the scale, represented by a large positive loading for Zn, were, again, CLO 2005 leachates but also leachates from CLO 2006 and sewage sludge. These leachates coincide with step 3 (reducible) of the fractionation pattern. It was suggested therefore that PC4 was yet another component characterised at the extreme by undiluted CLO materials and sewage sludge.

Unfortunately, component 5, as exemplified by Figure 5.24 which plots PC2 against PC5, failed to produce any definitive placement of the highly positively loaded Ca and Zn releases and negatively loaded Ti and Pb releases in addition to those already described.

Finally, the last component score plots for PC6 (exemplified by PC5 vs. PC6 – Figure 5.25) identified this component as strongly associated with the release of K during the salt-displaceable phase. This behaviour was clearly depicted in the Tessier extract PCA results described earlier but, in addition, was characterised here by leachate releases, particularly from the Comp trial but also from CLO 2004.

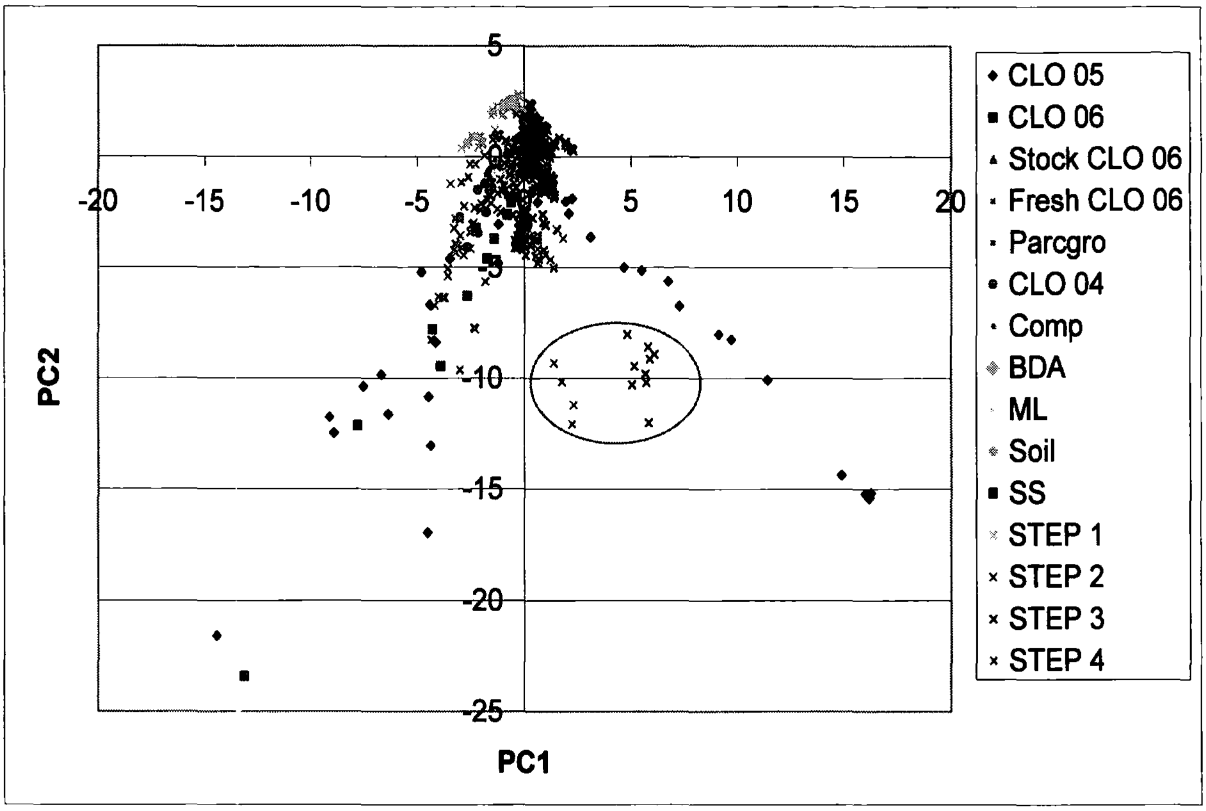


Figure 5.21: core plot of PC1/PC2 for the analysis of all leachates, field leachates grouped by treatment and Tessier extracts grouped by step.

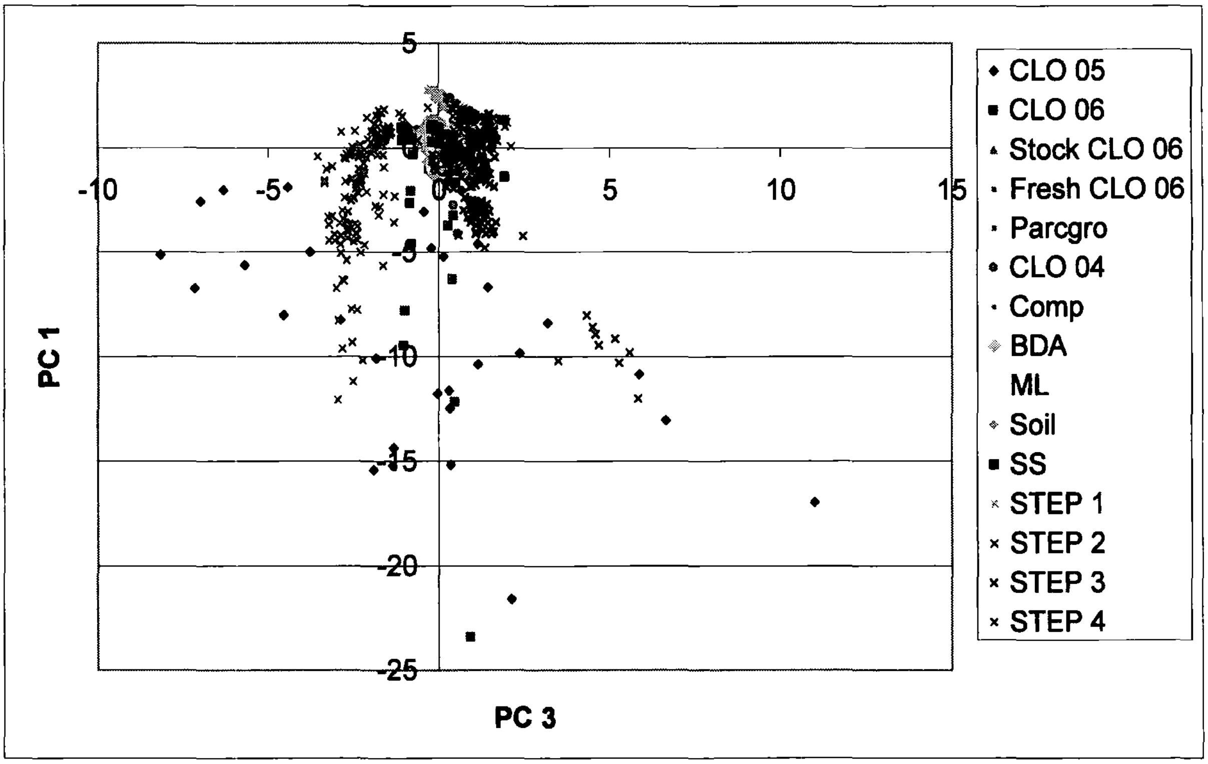


Figure 5.22: Score plot of PC1/PC3 for the analysis of all leachates, field leachates grouped by treatment and Tessier extracts grouped by step.

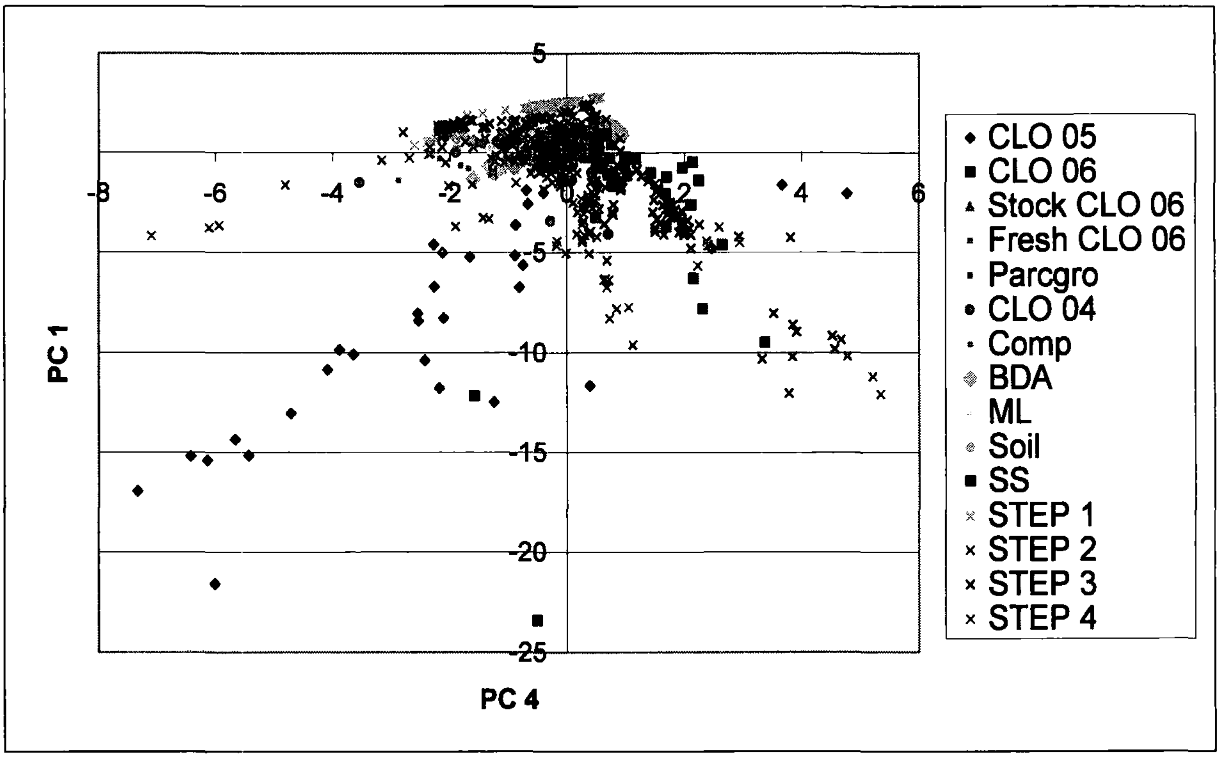


Figure 5.23: Score plot of PC1/PC4 for the analysis of all leachates, field leachates grouped by treatment and Tessier extracts grouped by step.

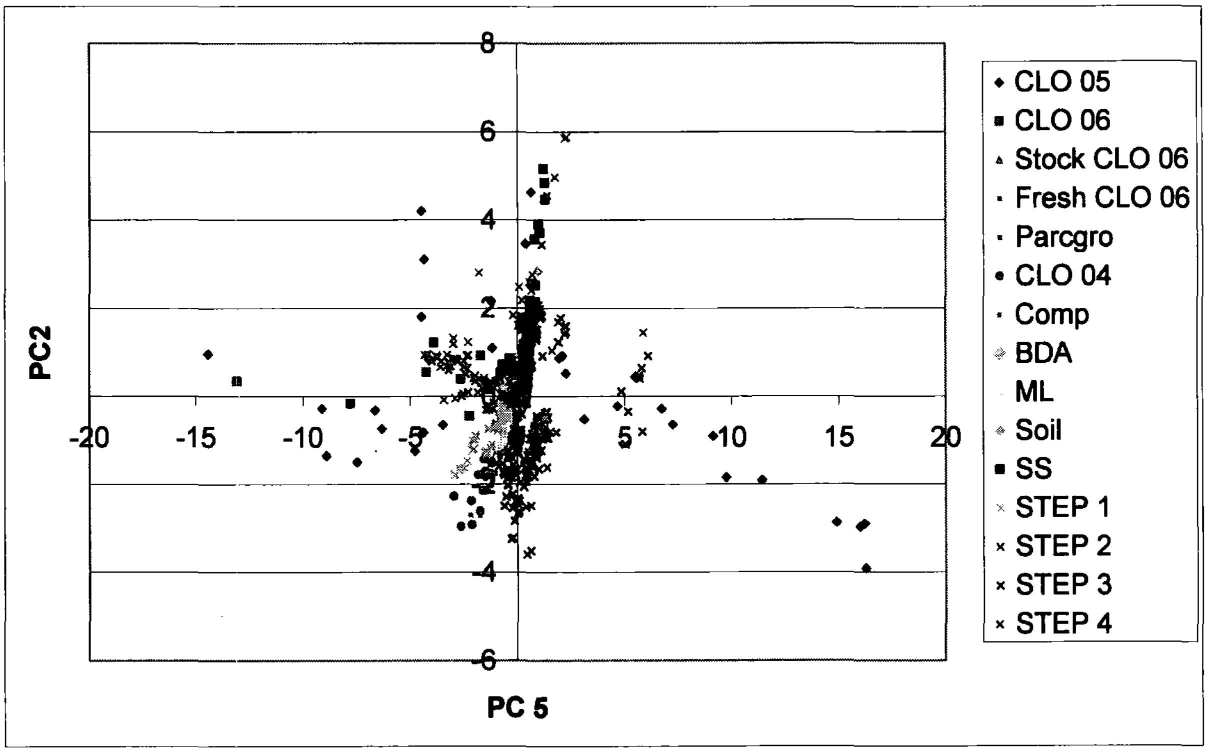


Figure 5.24: Score plot of PC2/PC5 for the analysis of all leachates, field leachates grouped by treatment and Tessier extracts grouped by step.

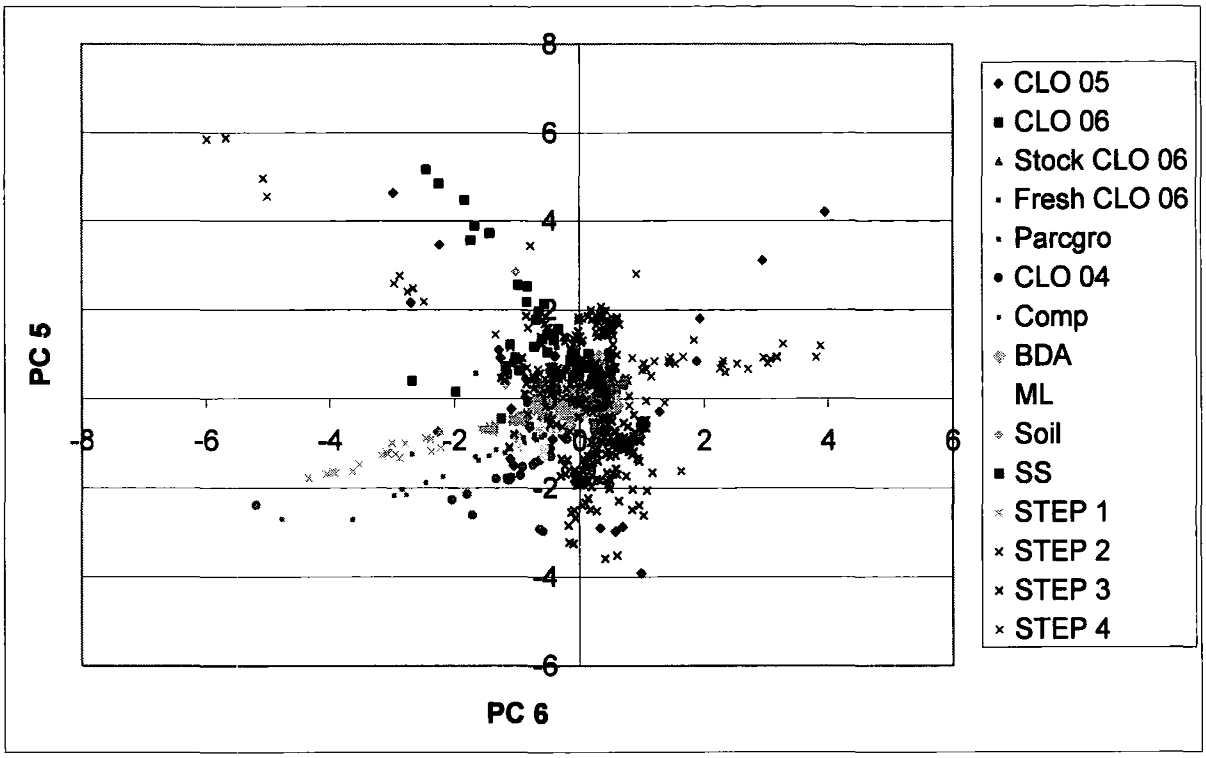


Figure 5.25: Score plot of PC5/PC6 for the analysis of all leachates, field leachates grouped by treatment and Tessier extracts grouped by step.

5.3.5 Tessier sequential extracts and Leachate samples (excluding CLO 05 and 06)

This section was included in the hope that, by removing the dominant CLO 2005 and CLO 2006 treatments, additional overlying trends between leachates and extracts for the less component-prolific mixed treatments may become apparent.

5.3.5.1 Analysis output and component loadings

Eigenvalues, cumulative variance and component loadings can all be seen in Table 5.5 and Figure 5.26. After review of the loading patterns, it appears that the major loadings seen for the first 2 PCs were quite similar. Fe and Sc were the exceptions but, generally speaking, the 'oxidisable' component loadings (Ni, Cr, Li and V) increase and the CLO 2005 associated loadings (Cd, Co and Mn) decrease with removal of the two undiluted CLO treatments. PC3 loadings still displayed high negative loadings for

Si and Sc, but Na and Pb did become positively more prolific. The high Na loadings may be a result of the problems encountered during step 3 of the sequential extraction. CLO 2005 showed a very low association for this element in the fractionation pattern, described in Chapter 3, which would cause a relative increase in Na loading once this treatment was removed from the PCA run. Na loadings were therefore not considered further. The main change to PC4 was the replacement of a high Ca loading with K, and also the appearance of an elevated loading for Ti (Mg remains high). The main change in loading pattern could be said to occur at PC5 level, where a very large negative loading was observed for Ca and a large loading for Mg of equal sign. Previously high positive loadings were seen for Ca and Zn and high negative loadings for Ti and Pb. In addition to the high positive loading seen for PC6 in the previous run, Cu has also increased its positive loading and high negative loadings were also observed for Ti and Mg. Possible explanations for these observations are presented below in the trends revealed by component score plots.

	PC1	PC2	PC3	PC4	PC5	PC6
Eigenvalue	**7.6242**	**2.8484**	**1.7127**	**1.396**	**1.3532**	**1.1304**
Proportion	**0.381**	**0.142**	**0.086**	**0.07**	**0.068**	**0.057**
Cumulative	**0.381**	**0.524**	**0.609**	**0.679**	**0.747**	**0.803**
Si	-0.219	-0.142	-0.450	0.128	0.063	0.021
K	0.008	-0.107	0.170	0.573	-0.187	0.400
Na	-0.167	0.023	0.345	0.443	-0.151	0.097
Ca	0.024	0.096	-0.237	-0.165	-0.710	-0.012
Mg	-0.063	-0.185	-0.259	0.332	-0.439	-0.308
Ni	-0.280	-0.265	0.159	-0.185	-0.047	0.119
Zn	-0.229	0.195	-0.211	-0.138	-0.054	0.247
Cu	-0.266	0.034	-0.147	0.085	0.059	0.355
Cd	-0.260	0.311	-0.105	-0.041	-0.024	-0.025
Pb	-0.217	-0.035	0.412	-0.137	-0.142	-0.041
P	-0.272	0.243	-0.187	0.167	0.070	0.186
Al	-0.339	-0.087	-0.040	-0.082	0.093	0.074
Fe	-0.277	0.262	0.214	0.038	0.069	-0.195
Co	-0.308	0.244	0.078	-0.008	0.106	-0.095
Mn	-0.153	0.282	0.068	-0.265	-0.332	-0.006
Ti	-0.175	0.191	0.015	0.310	0.113	-0.535
Sc	-0.160	-0.266	-0.326	0.065	0.190	-0.249
Cr	-0.259	-0.343	-0.059	-0.111	0.034	0.180
Li	-0.225	-0.282	0.151	-0.064	-0.144	-0.237
V	-0.211	-0.372	0.170	-0.134	-0.050	-0.088

Table 5.6: PCA results showing eigenvalues, proportional and cumulative variances, and component loadings of leachate and Tessier extracts after the removal of CLO 05 and CLO 06 treatments.

5.3.5.2 Component scores and trends

The component score plots have, as hoped, revealed further trends in the data which specifically relate to mixed CLO treatments as well as the sewage sludge comparison. The score plot of PC1 vs. PC2 (Figure 5.27) showed that the oxidisable trend associated with CLO 2005 and CLO 2006 treatments was also characteristic of the remaining undiluted CLO 2004, as well as the mixed treatments (Comp, BDA, ML and Parcgro). The presence of Si, Mg, Ni, Sc, Cr, Li and V can therefore be associated with all undiluted CLO samples experiencing oxidising conditions, and the weaker mixed treatment scores were thought to be a result of mixing each amending material with CLO. Another confirmed trend was that for the sewage sludge leachate samples and step 3 of the sequential extraction process. This trend was mentioned above, but particular field lysimeter leachate treatments could not be visually confirmed. The reducible-dependant releases associated with the sewage sludge were for: Cd, P, Fe, Co, Mn, Zn and Ti. This confirmed the environmental concern associated with sewage sludge of this type if prevailing conditions were anoxic.

It can be seen from the plot of PC1 vs. PC3 (Figure 5.28) that sewage sludge field releases, in addition to CLO 2005 as described earlier, exhibit a relationship with the oxidisable fraction (negative PC1 and negative PC3). The components mainly associated with this phase were Si and Sc, both of which give negative loadings and PC scores. This finding was not as critical, environmentally, as the anoxic releases but still worthy of note. A positive PC3 end member was also revealed which was shown to correlate with the anoxic release of Pb from CLO 2004. The release of Pb into water-ways was of major concern as this element is known to be highly toxic and persistent in the environment.

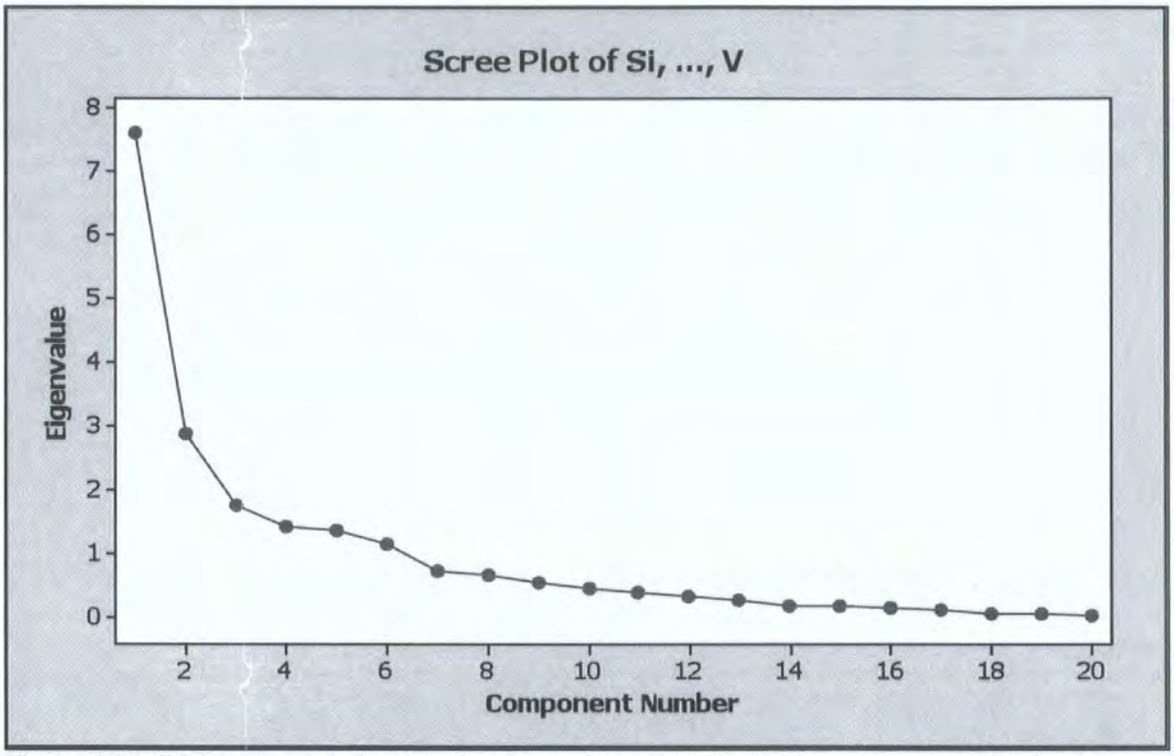


Figure 5.26: PCA scree plot showing the eigenvalues of each principal component for leachate and Tessier extracts not including CLO 05 and CLO 06 treatments.

A final point concerning the trends highlighted by this plot was the dual nature in which the oxidisable fraction appeared to exist. At their extreme, the upper trend (negative PC1 vs. positive PC3) represented Fe releases from CLO 2004 Tessier extracts and the lower trend (negative for both PC1 and PC3) Si and Sc releases from the sewage sludge extracts. This most probably indicated separate sources for the components associated with the oxidisable phase (i.e., 2 separate organic/sulphide sources).

Further to the findings above, it appears that sewage sludge leachates displayed a strong affiliation with the acid-soluble fraction, as depicted by the plot of PC2 vs. PC4 (Figure 5.29). The elements that have the largest negative loadings were those of Ca, Ni and Mn, all of which were shown to be released in the field and under acid controlled conditions in the laboratory.

PC5, in this PCA run without CLO 2005 and CLO 2006, gave high negative loadings for Ca, Mg and Mn. On plotting PC3 against PC5 (Figure 5.30) it was revealed that these component releases were very similar for the acid-soluble fraction and the field leachates exuded from the BDA, ML and CLO 2004 treatments. It was therefore proposed that the releases in the field for Ca, Mg (and Mn to a lesser extent) from these treatments were likely to be acid-dependant dissolutions – possibly a result of acidic microsites. It must be noted, however, that all recorded leachates were weakly alkaline throughout and the solid materials were also shown to remain alkaline in nature, thus displaying a high buffering capacity regarding acidity.

Finally, as with the original PCA results, PC6 was still closely associated with CLO 2004 and Comp treatment leachates, and the salt-displaceable fraction. K was the PC revealed to be released under these conditions but, after removal of the 2 dominating CLO treatments, the affiliation also included Cu. The reason why Cu was released under neutral conditions, and only from the compost/CLO trials, was not certain but may be linked to DOC leaching. Furthermore, a high negative loading was seen for Ti, but this elemental flushing would not be accurately assigned to a particular treatment or fractionation step due to the tightly distributed scores on all plots of this sixth component.

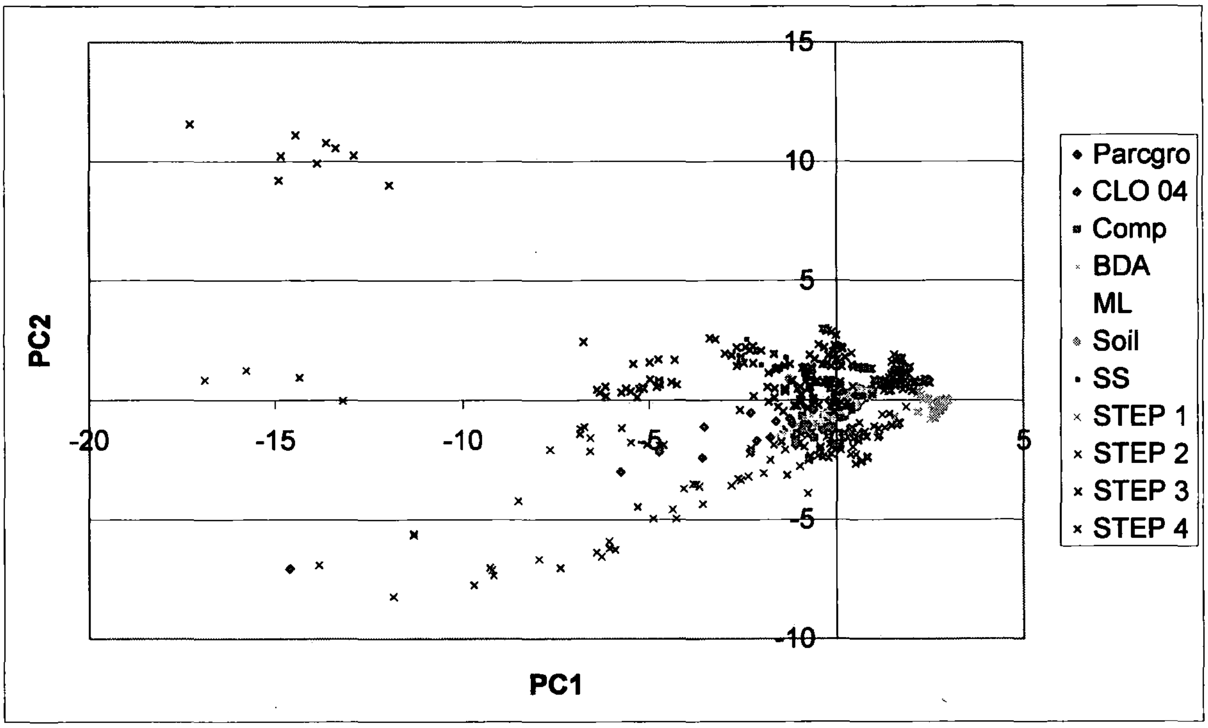


Figure 5.27: Score plot of PC1/PC2 for the analysis of all leachates (excluding CLO 05 and 06), field leachates grouped by treatment and Tessier extracts grouped by step.

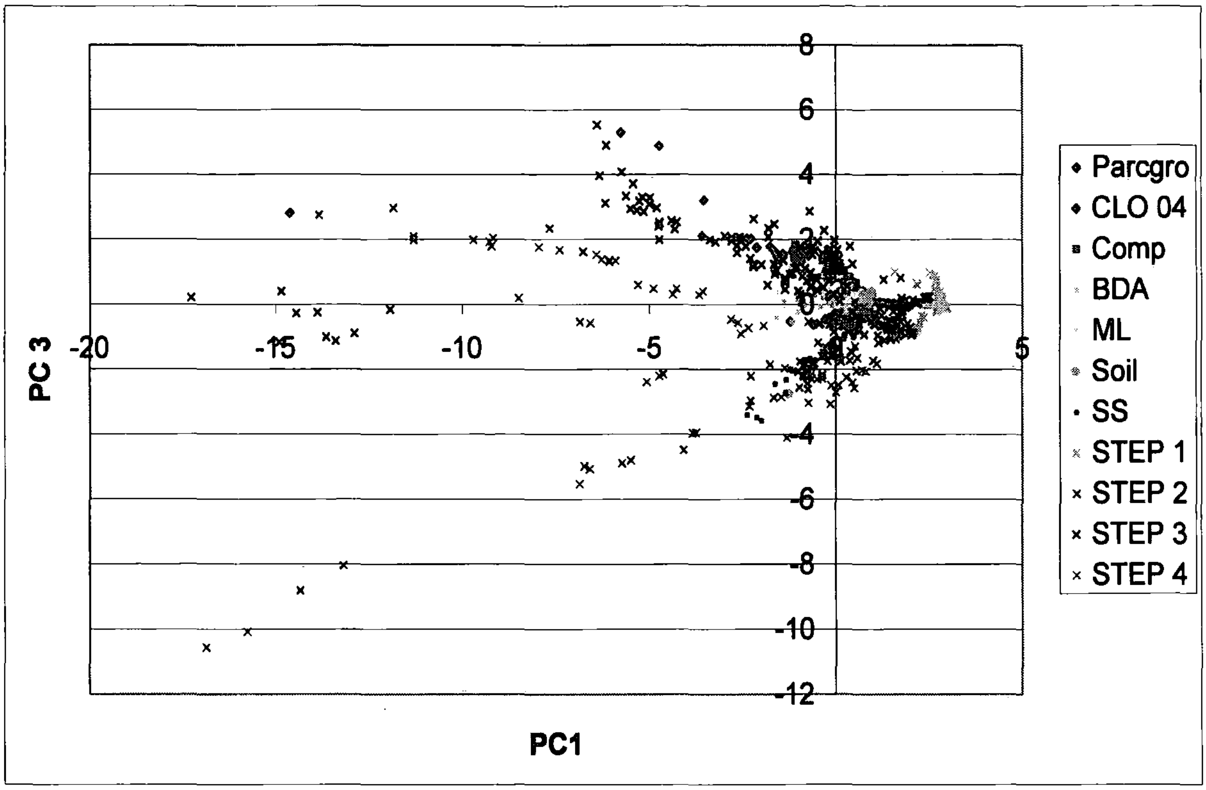


Figure 5.28: Score plot of PC1/PC3 for the analysis of all leachates (excluding CLO 05 and 06), field leachates grouped by treatment and Tessier extracts grouped by step.

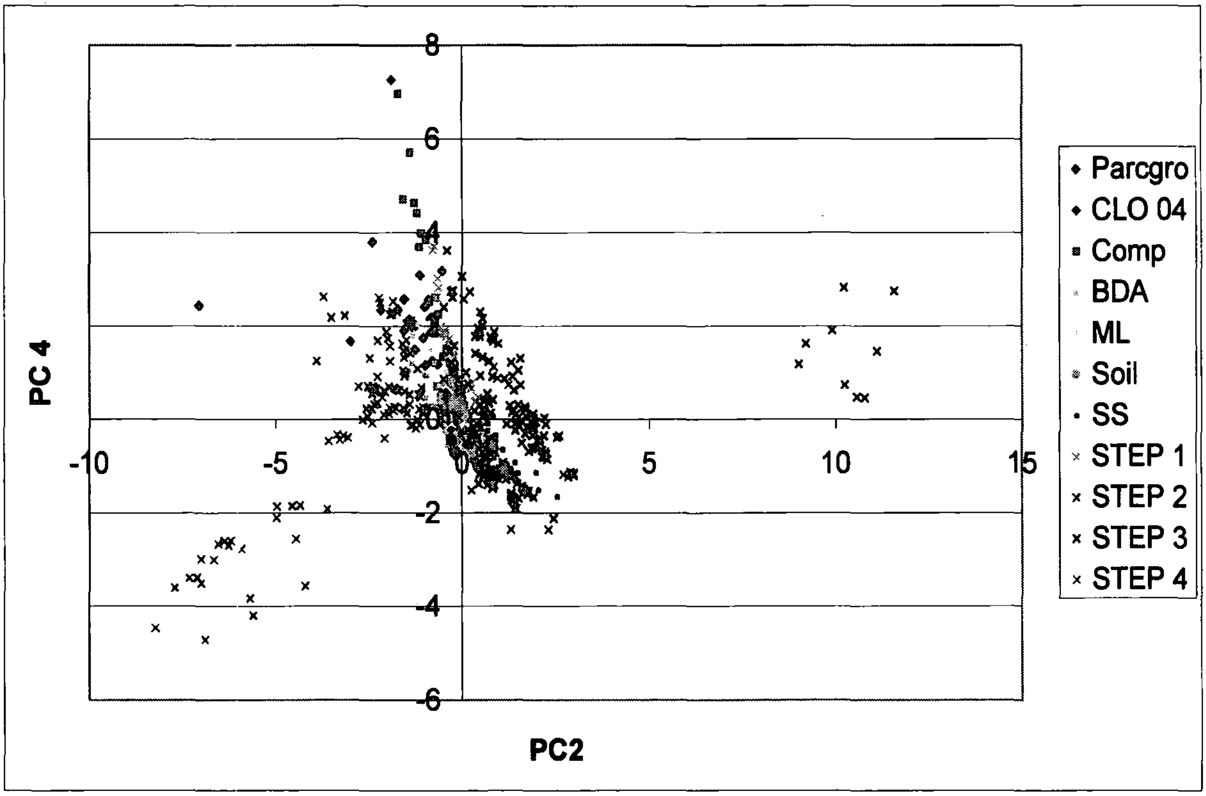


Figure 5.29: Score plot of PC2/PC4 for the analysis of all leachates (excluding CLO 05 and 06), field leachates grouped by treatment and Tessier extracts grouped by step.

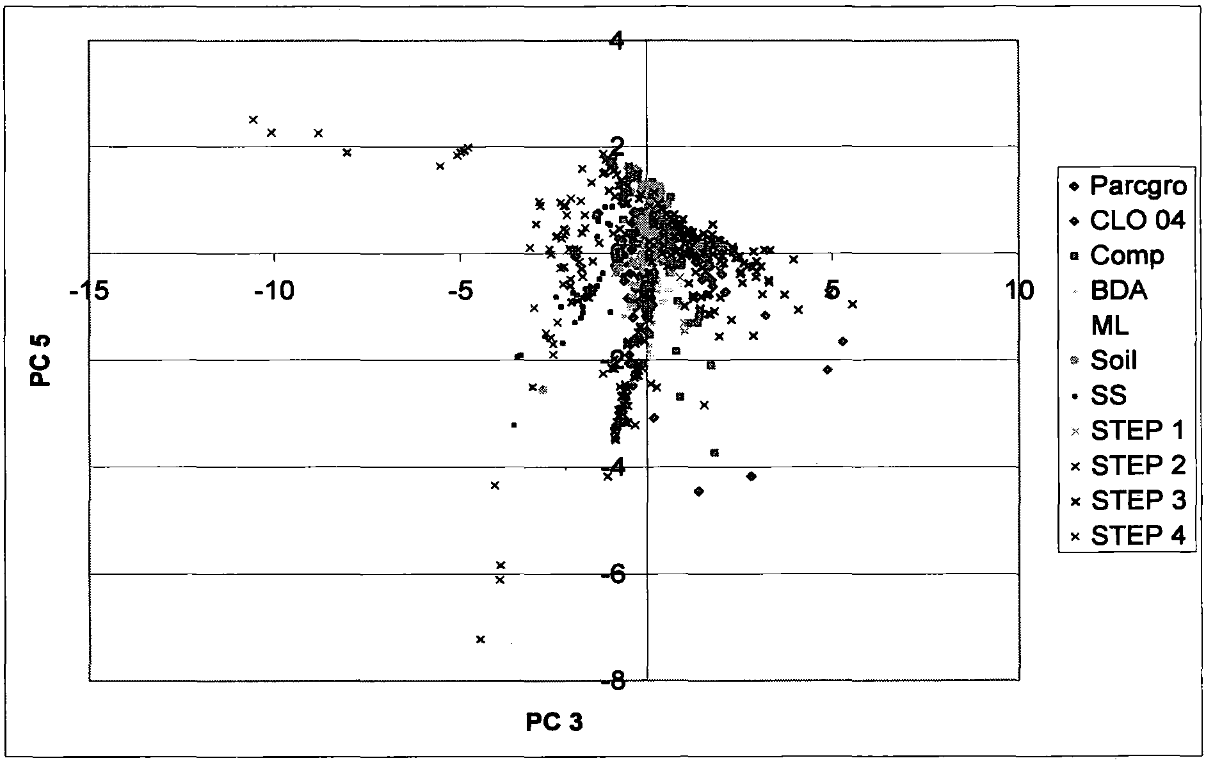


Figure 5.30: Score plot of PC3/PC5 for the analysis of all leachates (excluding CLO 05 and 06), field leachates grouped by treatment and Tessier extracts grouped by step.

5.3.6 Analysis Summary

There was some uncertainty in determining what each PC represents when comparing PCA results of the 2 leachate data sets, particularly at higher PCs, but a grouped summary of the more well defined findings were as follows:

5.3.6.1 Leachate PCA

Firstly, the CLO 2005 treatment exhibited a strong correlation with an assemblage of elements that gave heavy positive loadings for PC2 (Si, Cd, Co and Ti, and, to a lesser extent, Pb, Mn and Sc) and so appeared to not only account for a significant proportion of the total variance (19.7%) but also introduce a unique source of contamination.

Secondly, extreme concentration highs were measured in undiluted CLO 2004 and CLO 2006 treatments, as well as in the Comp trial for the readily flushed metal salts (Na, Cl, SO_4 and subsequent conductivity), but a concentration gradient was also defined for all treatments: undiluted CLOs > mixed CLO treatments > sewage sludge > agricultural soil. Substantial Fe releases (possibly as Fe hydroxides) were also detected in CLO 2005 leachates. Removal of CLO treatments for the second PCA run caused the main conductivity controlling components to be reduced to K and Cl, represented at the extreme by the Comp trial and accounting for only 4.7% of the total variation. Initial salt flushes were therefore considered largely associated with undiluted CLO treatments.

Thirdly, Ca, Zn, SO_4, and NO_3, as well as Mn to a lesser extent, were shown to be strongly affiliated with sewage sludge leachates (as defined by PC2 of the first PCA run). In addition, P was also depicted as an important component of sewage sludge leachates, but this finding was from PC4 of the second run, implying a separate source. Also associated with this variable, were Cu, Li and Mg, which were shown to be released primarily from BDA. However, these elemental releases (P, and Cu, Li and Mg) form opposing end members and so were not, themselves, necessarily linked.

A final point relating Cd and Sc releases with periods of heavy rainfall was highlighted. This relationship was uncertain since accurate constraint of component loadings to individual PC clusters (distributed along the PC3 axis in the first PCA run) was not possible and so only end member flushes could be determined. This was also the case in PC5 in the initial run, which also highlighted Zn as a an important element flushed out during periods of increased rainfall, but this time only from CLO 2006 and sewage sludge treatments. In addition, Cu, NO_3 and DOC components were shown to be important in these field-leachates. NO_3 and DOC could be expected to be prevalent during these times, and Cu was known to complex with DOC.

5.3.6.2 Tessier sequential extraction PCA

The PCA results performed on the Tessier sequential extraction described above have further confirmed findings presented in Chapter 3 concerning treatment releases as a function of both time and fractionation step. There was relatively little variation between annual sampling events, some between treatment and major variation (39.1%) with fractionation step. This again highlighted the key significance of varying environmental conditions governing multiple contaminant releases. For example, all treatments were shown to release sizeable quantities of Na, Pb, Fe, Co and Ti under reducing conditions but, in addition, sewage sludge exuded substantial amounts of Cd, P and Zn. If oxidising conditions prevail in the environmental setting in which these materials were used, then CLO-containing treatments would cause major concern, releasing significant amounts of Si, Ni, Sc, Cr, Li and V. This was particularly true for undiluted CLO material typical of that discharged in the summer of 2004. The ML trial was also shown to introduce considerable amounts of Mg and Sc under the oxidising conditions, and the same was true for Ti releases from BDA. Treatment constraints upon acid-soluble component releases proved inconclusive, but the following elements were shown to be strongly affiliated with this fraction: Ca, Ni, Mn, Pb and Zn. Finally, a concentration gradient was defined between treatments for the major salt-displaceable element, K: CLO 06 > CLO 05 > Parcgro > Comp > CLO 04 > remaining treatments.

5.3.6.3 Leachate and extract PCA

The oxidisable fraction (step 4) was shown to correlate strongly with all CLO-containing treatment leachates, suggesting that a large proportion of the total variance seen in field leachates for these treatments was controlled by oxidative-dependant releases. The components primarily affected by this process were: Ni, Cr, Li and V. In addition, significant Si and Sc releases, also associated with this fraction, were seen in leachates exuded from sewage sludge, as well as from ML and CLO 2005 (accounting for 8.7% of total variance).

An elemental trend (Si, Cd, Co, Mn and Ti) introduced solely by CLO 2005 leachates did not appear to correlate with any Tessier fraction. The same trend was also found to be affiliated with PC2 (in conjunction with the oxidative releases for CLO treatments described above – Ni, Cr, Li and V) and so, together, they accounted for 14.3 – 15.6% of the total variance.

Sewage sludge field releases show strong dependencies upon 3 of the extraction phases examined: the acid-soluble, reducible and oxidisable fractions, the last of which was mentioned above. The main releases were associated with reducing conditions under which Cd, P, Fe, Co, Mn, Zn and Ti have been shown to be important. If acidic conditions were favoured, then release patterns were shown to be dominated by Ca and Mn.

Releases specific to CLO 2004 digestate include that of Pb under reducible conditions and Fe (most probably Fe^{3+}) if an oxidising environment prevailed. Dissolved forms of Ca, Mg (and Mn to a lesser extent) were seen in leachates exuded from this treatment, but also from the BDA and ML mixed trials. These releases were likely to be acid-dependant dissolutions associated with acid microsites.

Finally, K, and to a lesser extent Cu, were highlighted as the PCs released under neutral conditions and it was thought that certain K and Cu species displayed strong tendencies toward salt-displaceable complexes and DOC. This behaviour was mainly affiliated with the Comp trial, but also with CLO 2004 and, to a limited extent (due to limited data), with the Parcgro trial.

5.4 Conclusion

In this chapter, the PCA technique was successfully applied to the main body of component data concerning releases both in field leachates and those under controlled conditions in the laboratory. The method proved extremely informative in constraining component assemblages to individual fractionation step, treatment, periods of elevated rainfall and individual flush events over time. The overriding factor governing contaminant release was shown to be fractionation step. The results presented here theorize that, for specific environmental scenarios, certain treatments will exude large quantities of known contaminants which, under the correct conditions, could easily be transported into water-ways.

The most compelling treatment findings were those relating to the CLO 2005 and sewage sludge treatments. As shown in Chapter 2, the CLO 2005 digestate leachates were significantly more contaminated than the remaining treatment leachates. This was shown to be a result of separately sourced elemental assemblages unique to this treatment, the origin of which could not be firmly associated with any of the 4 Tessier fractionation steps. Potential sources of these elements within the waste stream must therefore be identified and subsequently removed if any effective trace element remediation was to be achieved. The elements of concern were: Si, Cd, Co, Mn and Ti.

The sewage sludge, typical of that tested here, was also of considerable environmental concern releasing substantial amounts of Cd, P, Fe, Co, Mn, Zn and Ti under anaerobic conditions. It was highlighted in Chapter 3 that this material exuded significantly greater amounts of reducible-dependent components relative to all other treatment extractions. The results presented here further illustrate that sewage sludge was the only treatment to exude significant reducible-dependent releases during the field lysimeter leachate study as a result of self-enhanced anoxic conditions (all 3 lysimeters were waterlogged for some period of time). In addition, Si and Sc releases, associated with oxidising conditions as well as substantial Ca and Mn releases under acidic conditions, were evidenced in field leachates. Sewage sludge, therefore, displays a diverse, interchangeable chemical behaviour, capable of exuding large quantities of variable contaminants under a range of self supported environmental conditions, particularly for anoxic scenarios.

It can generally be stated that the CLO-containing treatment field leachates have been dominated by oxidative-dependant component releases. The elements of concern (including Ni, Cr, Li and V, and Fe in CLO 2004) were most likely to be adsorbed to various organic matter (OM) constituents of CLO, as this had been shown to be composed of ~50% OM, and undiluted CLO treatments exhibited the strongest elemental loadings. One thing that must be noted, however, was that the lack of anoxic releases seen in the field were most likely a result of the avoidance of these conditions (partially due to the lysimeter set-up that encourages aeration, but also to the heterogeneous physical nature of CLO material), rather than because reducible-dependant releases are non-existent for CLO material. In fact, Chapter 3 showed that, if anoxic conditions prevail, chemical component releases would proportionally be the most prolific.

With regard to the mixed treatments, the often related BDA and ML trials have both indicated that their field-leachates were, at some point, in close affiliation with acid-controlled releases for Ca, Mg and to a lesser extent Mn, despite leachates consistently being recorded as weakly alkaline. The Comp trial leachates (and, to a lesser extent, due to limited data, the Parcgro trial) were shown to be heavily loaded with K and to a lesser extent Cu, both of which have been identified as principal components released under neutral conditions (i.e., present in salt-displaceable complexes and possibly DOC). This behaviour was also evidenced for CLO 2004 treatment leachates.

A final concluding point was that the agricultural soil demonstrated component releases that were consistently low relative to all other treatments, irrespective of time or prevailing conditions and so constraining component releases using PCA was unsuccessful.

Chapter 6

Chapter Summaries and Conclusions

6.1 Introduction

This thesis sought to provide an insight into the long-term behaviour of artificial soil products (CLO) from the aerobic digestion of MSW, and has quantified the results relative to that of sewage sludge, an agricultural soil, legislative limits, and landfill discharge constraints.

6.2 Objectives and Conclusions

6.2.1 Objective 1

Field lysimeter trials detailed in Chapter 2 were intended to assess long-term leachate production from undiluted CLO treatments and their associated artificial soils compared with leachates exuded from an agricultural soil and sewage sludge. In addition, the relative quality of leachates was investigated by means of comparison against Drinking and Surface Water Directive Maximum Admissible Concentrations, as well as Coxhoe landfill discharge consents. The determination of significant passive or active remediation as a result of amending the CLO material was then assessed.

6.2.2 Summary - Relative leachate performance

The findings within Chapter 2 were central to the rest of the thesis, in providing the materials for characterisation but also in identifying the high levels of metal salts that have been shown to be associated with leachates emanating from treatments containing CLO.

Although leachates from all treatments were found to be consistently weakly alkaline, significant amounts of inorganic contaminants were detected in leachates emanating from all CLO containing treatments and from the sewage sludge. The levels of contamination measured in leachates from all treatments were significantly higher than those recorded for a typical agricultural soil of the Durham region. In particular, extremely high conductivities ($> 20 mS\ m^{-1}$) were recorded in undiluted CLO leachates, as well as those exuded from the mixed Comp trial. These high levels of salinity were shown to be as a result of the presence of large quantities of water-soluble base metal salts inherent in the CLO material, and in the case of the Comp trial, more specifically K concentrations. The metals causing major concern, found in CLO treatment leachates were Al, Ca, Cd, Mn and Mg. The levels of contamination recorded for these metals significantly breached both landfill discharge consents and drinking and surface water directives maximum admissible concentrations.

Active remediation was found to be insignificant for all of the mixed treatments but a degree of passive remediation, relative to landfill discharge consents or the above mentioned legislative limits, was achieved. The metals for which this was true were: Al, Cr, Fe and Ni. Any remediation value achieved was therefore attributed to the dilution of the CLO material with the amending materials used. There were three components that were compliant, with both the aforementioned regulatory levels, for all CLO containing treatment leachates; Cu, P and Zn. Furthermore, sewage sludge field releases were shown to be lower to both undiluted and diluted CLO treatments for a number of concerning elements, particularly Mn, P and Zn.

An additional discovery of the lysimeter trials highlighted the concerns associated with the poor quality of the leachates, for every element and property analysed, relative to all other treatments, produced by the later 2005 and 2006 CLO digestates. Whatever mechanical and structural alterations or physiobiochemical processes that were undertaken in an attempt to manufacture a more environmentally durable and versatile artificial CLO product should be reconsidered. The case may have been that substantial economic benefits were reaped but, environmentally, the changes made have been of detriment to the performance of both leachate quantity and quality.

6.2.3 Conclusion 1

- All CLO treatments produced leachates that breached Drinking and Surface water legislation as well as landfill discharge consents.
- Sewage sludge leachates were however more contaminated than all CLO treatments for Mn, P and Zn.
- No active remediation was observed but significant passive dilution was achieved by all mixed treatments.
- Cu, P and Zn releases from all CLO-containing treatments did not breach legislation limits.
- The undiluted CLO 2005 and CLO 2006 digestates were detrimental for all components measured.

6.2.4 Objective 2

In Chapter 3 it was intended that individual waste component releases for each treatment material could be assigned to specific environmental scenarios.

6.2.5 Summary – Characterisation

The moisture content although initially higher relative to the agricultural soil did display significant dependability upon CLO output and retained less moisture than sewage sludge. In fact once the initial moisture had been lost evidence to support formation of preferential pathways through substantial cracking of the CLO products was observed but further experimentation would be necessary to quantify this.

The CLO and its associated soils were considered to display favourable pH levels relative to both the sewage sludge and agricultural soil, producing weakly alkaline solutions for the entirety of the study. This demonstrated the high buffering capacity of the CLO material, as well as the amending materials chosen. This behaviour, in conjunction with sequential extract data, showed that the effects of acid rain protonation were minimised causing many potentially toxic metals (PTM's) to be immobilised, thus greatly reducing further contamination. Sequential extraction data however, also revealed that the BDA treatment elevated trace metal releases associated with the acid-soluble fraction, relative to levels seen in the undiluted CLO's.

High (>50%) organic matter contents recorded in undiluted CLO digestates were of significant importance, both from a nutrient supply and potential metal adsorption point of view but were not significantly different from levels seen in sewage sludge. Mixing of the CLO with the chosen amendments significantly reduced the overall OM content (<33%) which further suggested that the amending materials offered little more amelioration than that achieved by dilution.

The sequential extraction data were informative in a number of ways. Firstly, trace metal and anion fractionations revealed that the majority of immediately mobile (salt-displaceable and acid-soluble) contamination from all treatments, including the agricultural soil would originate as base metal salts, in particular, those containing K, Ca, Cl and SO_4 components. The mixed Comp trial, sewage sludge and the agricultural soil also showed elevated levels of nitrate release. Ni was also identified as associated with the mobile fraction for the CLO containing treatments, particularly the BDA and ML treatments. Oxidisable releases were also shown to be significant for these two mixed treatments.

Secondly, the major environmental concerns should focus upon the likelihood of major trace metals being released from undiluted CLO's, as well as from Comp and Parcgro treatments, if reducing conditions were to prevail in the field. Even more so for sewage sludge where significantly higher levels of redox-dominated trace metals (Si, Cu, Zn, Cd, Co, P, Al, Fe, Mn and Ti) were seen relative to all other treatment releases. The agricultural soil component releases were almost always, except for Mn, of a low, but not always significantly low level relative to CLO containing treatments and sewage sludge.

It is strongly recommended therefore that if CLO containing materials were applied to land it is imperative that the soil medium upon which it is utilised is kept well aerated and water-logging is prevented. A constant supply of fresh OM, and extensive vegetation cover should also be encouraged, not only to facilitate the growth of a microbial biomass but also in an attempt to limit the inorganic contamination of surrounding water bodies. It must be remembered though that in a more compacted environmental setting, for example, how the Parcgro is currently being utilised as a land cover material, fresh OM could facilitate low redox conditions as oxygen is rapidly consumed on its breakdown.

6.2.6 Conclusion 2

- The initial high moisture retention properties of the CLO-containing treatments were shown to be little overall benefit during prolonged dry periods relative to both sewage sludge and an agricultural soil.
- All CLO treatments displayed beneficial alkaline pH's for the entirety of the 3 year study.
- Raw CLO contains high levels (>50%) of OM, analogous to sewage sludge but this was significantly decreased on mixing with the amending materials.
- Reducible-related releases were of most environmental concern for undiluted CLO, Comp and Parcgro treatments. Well aerated field conditions were recommended to minimise contamination.
- Sewage sludge contamination was significantly greater than all other treatments.

6.2.7 Objective 3

Chapter 4 hypothesised a potentially suitable pre-washing strategy for the pre-treatment of the freshly discharged CLO material. This factorial experiment was devised in an attempt to identify whether simple tap-water washings could effectively (economically and environmentally) ameliorate against the high levels of water-soluble metal salts shown to be released during field lysimeter studies.

6.2.8 Summary - Pre-washing

Chapter 4 successfully showed that a simple pre-washing procedure, using tap-water as the extraction medium, could be employed as an additional remediation pre-treatment technique for the CLO material. Wash solutions extracted from undiluted CLO 2006 under neutral conditions contained considerable amounts of soluble trace metal salt components including: Al, Fe, Co, Zn and Mn. These trace metal flushes, both in concentration and behavioural releases demonstrated beneficial extraction efficiencies relative to field fluxes over a two year period (i.e., <83.8% removal was achieved by pre-washing). Furthermore, >90% of component release occurred during the most economically and environmentally favourable scenario tested (a single, 5 minute washing at L/S 2).

The importance of these major trace metal releases during the initial washing stage were signified in both the relatively large proportions removed but also the significantly lower levels exuded in subsequent washes, indicating a certain degree of leaching stability had been achieved. Thus, the potential for utilising this simple pre-washing method as a means of effectively reducing trace metal contamination from CLO before its application to land was shown to be potentially viable under the correct conditions.

Significant releases of alkali and alkaline earth metal salts from the CLO were also recorded and as conductivity results indicated, these releases were most prolific during the initial washing step. Extraction efficiencies (<12%) relative to levels attained both in the field and laboratory were however, not of a suitable level for this method to be of significant importance for these species.

In contrast, the washing of sewage sludge liberated a significant release of NO_3, and to lesser extents SO_4 and Cl but substantial leaching for these components was still observed after a third stage of washing. Both washing step and contact time showed significant differences in conductivity levels. This indicates that a distinct lack of leaching stability was achieved for these anions. These findings, in conjunction with limited extraction efficiencies found for all other leachate components, a greater dependency on L/S, as well as inhomogeneous release patterns showed that the pre-treatment pre-washing method was an unsuitable means of effectively removing substantial amounts of contaminants from sewage sludge, typical of that tested here. Component releases from the agricultural soil were shown to be significantly lower than both sewage sludge and CLO component releases.

6.2.9 Conclusion 3

- A pre-washing pre-treatment washing procedure proved successful in flushing out significant amounts of trace metals from CLO.
- Major releases occurred under the most economic conditions (a single, 5 minute washing with tap water).
- The pre-washing of sewage sludge is not recommended.

6.2.10 Objective 4

Finally, in Chapter 5 principal component analyses were employed in an attempt to highlight underlying principals responsible for component release behaviours observed in field leachates and characterisation extracts, as well as potential overall governing controls.

6.2.11 Summary – Principal Component Analysis

In this chapter the PCA technique was applied to the main body of component data concerning releases both in field leachates and those under controlled conditions in the laboratory (sequential extracts). The method proved to be very informative for constraining component assemblages to individual fractionation step, treatment and individual flush events during periods of elevated rainfall. The overriding factor governing contamination releases was highlighted to be that of the fractionation step. The results theorized that under specific environmental conditions, certain treatments will exude large quantities of known contaminants, which subsequently could easily be transported into water-ways and thus be of environmental concern. The circumstances under which treatment conditions were most strongly correlated were for CLO containing treatments and oxidising conditions and sewage sludge releases during reducing conditions. The sewage sludge was shown to be of considerable environmental concern releasing substantial amounts of Cd, P, Fe, Co, Mn, Zn and Ti under anaerobic conditions. As highlighted in Chapter 3, it was this material that exuded significantly greater quantities of reducible-dependant components relative to all other treatment extractions. The results presented here further illustrate that sewage sludge was the only treatment to exhibit significant reducing condition-dependant releases in field leachates as a result of self enhanced anoxic conditions (all 3 lysimeters were waterlogged for some period of time). In addition, Si and Sc releases, associated with oxidising conditions, as well as substantial Ca and Mn releases under acidic conditions, were also evidenced in field leachates. Sewage sludge therefore displays a diverse, interchangeable chemical behaviour, capable of exuding large quantities of variable contaminants under a range of self supported environmental conditions but particularly for anoxic scenarios.

Principal component plots revealed that CLO containing treatment leachates from the field were dominated by oxidative-dependant component releases. The elements of concern included Ni, Cr, Li and V (and Fe in the CLO 04 material). These metals were most likely to be adsorbed to OM constituents of the CLO material, as it was the undiluted CLO treatments that exhibited the strongest elemental loadings and it was the undiluted CLO that was shown to be composed of >50% OM. It must be noted however, that the lack of anoxic releases seen in the field was most likely to be as a result of these conditions having been avoided (partially to do with the lysimeter set-up but also due to the heterogeneous physical nature of the CLO material; both of which encourage aeration) rather than because reducible-dependant releases were non-existent for the CLO material (in fact much to the contrary – Chapter 3 showed proportionally this fraction was the most prolific).

With regard to the mixed treatments, the BDA and ML treatments both indicated that their leachates at some point were in close affiliation with acid controlled releases for Ca, Mg and to a lesser extent Mn despite leachates consistently being recorded as weakly alkaline. The Comp trial leachates (and to a lesser extent, due to limited data, the Parcgro trial) were shown to be heavily loaded with K and to a lesser extent Cu, both of which have been identified to be released as principal components under neutral conditions (i.e., present in salt-displaceable complexes) This behaviour was also shown by the CLO 04 treatment leachates.

A final key point highlighted by PCA, supplementary to the findings in Chapter 2, was that the CLO 05 digestate exuded leachates which were significantly more contaminated with certain components (Si, Cd, Co, Mn and Ti) compared with other treatment leachates. This elemental assemblage was unique to this treatment; the origin of which could not be firmly associated with any individual step of the four Tessier fractionation steps tested. Potential sources of these elements within the waste stream must therefore be identified and subsequently removed if any effective trace element remediation was to be induced. This also underlines the complex heterogeneous nature of the CLO materials tested as well as the inherent problems this entails. As has been shown throughout this study, the agricultural soil component releases were consistently of a low level relative to other treatments, irrespective of time or prevailing conditions.

6.2.12 Conclusion 4

- The overriding factor governing contaminant releases was the fractionation step.
- Oxidisable-related releases, as theorised by Tessier, were evident from all CLO-containing field leachates and so major reducible-related releases were avoided.
- Sewage sludge field releases were predominantly reducible-related but acid-soluble and oxidisable releases were also of concern.
- BDA and ML releases in addition to oxidisable fluxes were susceptible to acid-soluble releases under the field conditions described.
- CLO 2004, Comp and Parcgro treatments comprised significant amounts of exchangeable K and Cu species.

- CLO 2005 introduced a separate source of contamination not associated with any other treatment or the specific environmental conditions tested.

6.2.13 Overall conclusions

This thesis has been crucial in identifying the benefits and problems associated with CLO and its amended artificial soils. Quantification of these findings relative to government constraints, sewage sludge and an agricultural soil also proved vital considering the intended utilisation of this material. Soil instabilities, phytotoxicity in plants, groundwater contamination and their related issues concerning human health could all potentially be as a direct consequence of using this aerobically digested soil conditioner on farm land. Leachates emanating from an undiluted aerobically digested CLO were in breach of both water regulation and landfill discharge constraints. Mixing the material with the amending materials has afforded significant passive remediation, particularly with respect to sewage sludge leachates, but at the same time introduced detrimental characteristics comparative to undiluted forms. Significant remediation value would be gained by economically pre-washing the freshly discharged CLO before subsequent mixing and utilisation. The environmental conditions to which the CLO amended soils were likely to be exposed were of central consequence to the incurred level of contamination; as was the case for sewage sludge. Aerobic conditions favour the use of all CLO products and sewage sludge but if anaerobic conditions were to prevail then significantly more contamination of the environment would occur.

From the perspective of Premierwaste this research has highlighted a number of key areas about the potential future of MSW composting both in the UK but also in a global context. If the aerobic digestion technique can be optimised and a more effective homogenisation of MSW can be achieved then, based on comparisons with sewage sludge, this form of waste management could provide viable options for providing energy and recycling and recovering waste materials, all of which help combat the larger problem of global warming.

The main company conclusions were:

- Source separation of MSW is vital both in reducing landfill costs but also from an environmental perspective. The aesthetic quality must be improved if CLO is to be utilised on land, mainly via the removal of plastics and glasses. This is also true from an ecological point of view.
- The stabilisation of the CLO is of major concern. If the organic material from which the CLO is largely composed is decomposed more effectively and so is discharged from the aerobic digester in a more stabilised state then substantial contamination may well be avoided, both of organic and inorganic nature.
- Energy From Waste (EFW), possibly via pyrolysis or incineration would be a recommended subsidiary route, especially if the quality of CLO was not high enough for land application.

6.3 Data Limitations

There were three main data limitations identified within this study which were either as a result of time constraints or directly caused by the experimental set-up. The first of these limitations concerned the establishment of numerous plants on the top of many of the field lysimeters and the subsequent effects this had on leachate production. The situation was further complicated, not only by the variation of the vegetation covers in question but also the temporal establishment of the vegetation, which caused substantial difficulties in accurately assigning any kind of quantitative analyses relating to either the vegetation covers or leachate production. In some cases leaf biomass became so large that it was thought unlikely, judging from the relative lack of leachate data over significant periods that little or no precipitation was reaching the collection vessels. Premierwaste quite clearly stated that these plant species were to stay as they had naturally occurred and these conditions represented, to a certain degree, the field-based/agricultural scenario which the lysimeter trials signified.

Secondly, time constraints meant that the pre-washing experiment replicates, carried out in Chapter 4, were done in duplicate. This may have caused certain differences to be statistically underestimated. The necessary requirement concerning replicate samples certainly became apparent when dealing with such heterogeneous materials as the CLO material; this includes both within and between batch variations. It must be remembered however, that this thesis was designed to be an accurate representation of the CLO and its associated soils and so it must not be attempted to eliminate the inherent heterogeneous nature of the materials in question. Equally, the assessment of a statistically scientific experimental design was essential. The issues arising from the heterogeneous nature of the CLO should be of major concern to Premierwaste both because of its negative aesthetic quality, but also due to the problems encountered during any kind of chemical experimentation. The recent introduction of Durham City's plastic recycling initiative should greatly facilitate this mandatory requirement.

Thirdly, the residual phase of the modified Tessier sequential extraction procedure was not carried out; in part due to time constraints but also due to the extremely hazardous nature of the experimentation involved in these final extractions, especially on material of this nature. The absence of these data have made total flux comparisons with 'similar' studies difficult. However, it must be stressed that the four sequential extraction steps chosen were not only well recognised representations of the environmental conditions they intend to signify but also, together, they symbolize an accurate representation of the total potential contamination that could occur under extreme environmental scenarios. This, indeed, was the main objective of this thesis.

Finally, one of the objectives concerned with PCA was to identify problem components in the waste stream itself and potentially offer a means for their removal. The complex nature of the leachates analysed deemed the latter part of this process unfeasible. Additional statistical analyses would be required to attribute the problem components to individual source materials.

6.4 Recommended future work

As mentioned above, the lysimeter trials were central to assessment of the long term behaviour of the CLO and its associated soils. Now that an initial characterisation of the materials has been carried out, it may prove more informative to observe the extent of contamination that arises after application of CLO and the Parcgro material to field plot scale experiments. This approach may indeed have been a more representative and effective method of theorizing the real environment than the field lysimeter trials. In addition to this structural change, a number of experimental findings have been highlighted in this study, which if investigated further, may reveal potentially key discoveries to the success of aerobic digestion and the subsequent utilisation of the CLO materials. These are as follows:

1. The role played by DOC in the adsorption and potential immobilisation (from plant uptake) of trace metal contamination, which would be an adjustment to the pre-washing experiment. The extremely high levels of DOC exuded from CLO offers a potential adsorption surface for complexation or chelation between the organic and inorganic active groups. If trace metal adsorption can be directly linked to DOC contents and some sort of quantification, possible via regression analysis, can be carried out on CLO leachates, then a potential remediation source as well as the extent to which this may be of use can be determined.

2. The same can be said for the role of black carbon (BC), particularly if the amending materials (BDA and ML) were to be utilised in the future as these treatments displayed elevated BC contents relative to sewage sludge and the agricultural soil. Addition of a BC/CLO mixed treatment may therefore prove beneficial with respect to trace metal retention.

3. Further experimentation concerning post-pre-washing stability tests may also provide a more comprehensive account as to the level of contamination still available after the pre-washing method with tap-water has been carried out. These washed samples could then be further analysed using the modified Tessier extraction method described which additionally could include residual phase extraction steps. PCA could then be performed on these pre-washing and sequential extract releases, as well as on field leachate data.

4. Additionally the potentially toxic wash waters from the pre-treatment method could potentially be chemically treated (raise in pH) to precipitate dissolved trace metals. The remaining leachates could then be re-circulated and used as

further wash, either within the digester itself or as a pre-treatment extraction medium as before.

This work would not only further our understanding of the underlying processes controlling component releases under the various simulated conditions, but would also provide a more detailed environmental impact assessment relative to that of the control materials used, and that presented in existing literature.

Appendix 1

It was decided that the Appendices would be included on a data compact disc in the interests of the environment as well as because of their length. Both excel data files and comma separated value files have been included for the reader's ease. The compact disc can be found in the pocket envelope attached to the back cover of the thesis.

Appendix 1 tabulates the raw physical and chemical data that was collected in the leachates exuded from each field-lysimeter as presented in Chapter 2. Each treatment comprises 3 lysimeters. The CLO 2005 and 2006 lysimeters have been grouped together as these 1 year treatments were temporal variations of each other. This Appendix also includes post-hoc significance results performed on 'trace metal' leachates as seen in Table 2.6.

Appendix 2

Appendix 2 tabulates the blank corrected component (anions and elements) data from the characterisation experiments for each of the materials used in each field-lysimeter as presented in Chapter 3. The results have been grouped by treatment, year of exposure and fractionation step.

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