An evaluation of predictive environmental test procedures for sewage sludge

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Declaration

These studies have not been submitted in any form to another University and, except where acknowledged in the text, are results of my own work.

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Summary

This research project aimed at evaluating four internationally accepted leachate extraction tests to determine their applicability on sewage sludge samples. Furthermore, the present analytical method to determine the leachable fraction of sludge for compliance to South African sludge legislation was evaluated.

Leaching tests are done on sludge samples to determine element mobility. This is important since land application of sewage sludge is an accepted and regulated sludge management practice.

A literature survey was done to evaluate the mobility over time of metals originating from sludge-amended soils. Mobility is initially due to the organic content of the soil and after organic matter decomposition, it is dependant on the inorganic content. Mobile metals in sludge-amended soil can cause potential environmental risks like groundwater contamination and metal accumulation in soil. Metal accumulation can further lead to increased plant uptake of metals.

To determine the partitioning or fractionation of metals found in sludge-amended soil, selective sequential extractions and single extractions can be used. Since South African sludge legislation specifies a single extraction procedure, four were selected for comparative studies. The selected procedures were the USA Environmental Protection Agency (EPA) Toxicity Characteristic Leaching Procedure (TCLP) the Australian Standard Bottle leaching Test (AS 4439.3) the Nederlands Normalisatie-Insitiuut availability test (NEN 7341) and the Deutches Institut für Normung water leachability test (DIN 38 414-S4). A variation of the TCLP is specified for use in South Africa.

Three sewage sludge sample lots were collected. The first consisted of 24 sub-samples that were collected from 24 different wastewater treatment works on the East Rand. Both leachable (TCLP) and total (*aqua regia*) extraction was done on these samples for Cd, Co, Cr, Cu, Hg, Mo, Ni, Pb, Zn, Se, B and Fe. A relationship between the leachable and total extractions was found for Co and Pb but could not be tested by literature values due to a variation in the sample preparation. The TCLP leachates were also analysed by Atomic Absorption and Inductively Coupled Plasma techniques to compare the applicability of the two. It was found that both techniques are acceptable for leachate analysis.

The second sample lot collected from a single wastewater treatment plant was used to determine the leachable effect of the difference between the South African adapted TCLP and the USA EPA procedure as well as the NEN procedure. The EPA specifies all samples be extracted on an “as is” basis while the South African adaptation specifies dry samples. It was found that no element was comparative between dry and wet sample for both extraction procedures. It was observed that wet extractions yield generally higher values than dry extractions.

A third sample lot was collected two months after the second sample lot at the same wastewater treatment works. It was used to compare the four extraction procedures. From this it was found that the DIN yielded the highest results for the specified elements. This procedure could not be recommended since the experimental difficulties and the duration of the test make it an unsuitable regulatory compliance tests protocol.

Key Words: sewage sludge, leaching, total extraction, TCLP, sludge-amended soil, metal mobility, leachable extraction, extraction, elemental analysis, environmental test procedure

Science is built up of facts, as a house is built of stones; but an accumulation of facts is no more a science than a heap of stones is a house. *Henri Poincaré (1854 – 1912) French mathematician and philosopher of science. Excerpt from "Science and Hypothesis" (1905) ch. 9*

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% RSD	Percent Relative Standard Deviation
°C	Degrees Celsius
µ Ω cm^{-1}	Micro-ohms per centimeter
µm	Micrometre
µS cm^{-1}	Micro-Siemens per centimetre
AA	Atomic Absorption
AFNOR	Association Française de Normalisation
Al	Aluminium
APHA	American Public Health Association
As	Arsenic
AS	Australian Standard
B	Boron
Ba	Barium
BCR	Bureau of Reference
Be	Beryllium
c	*y*-intercept of graph
$C_2H_8N_2O_4$	Ammonium oxalate
$C_5H_{15}NO_3$	Triethanolamine
$C_6H_6Na_2O_7$	Sodium citrate
$C_{10}H_{16}N_2O_8$	Ethylene-di-amine-tetra-acetic acid
$C_{14}H_{23}N_3O_{10}$	Di-ethlyene-tri-amine-penta-acetic acid
Ca	Calcium
$Ca(NO_3)_2$	Calcium nitrate
$CaCl_2$	Calcium chloride
$CaCO_3$	Calcium carbonate
Cd	Cadmium
CEN	European Committee for Standarization
CFU mL^{-1}	Colony forming units per millilitre
CH_2Cl_2	Dichloromethane
CH_3COOH	Acetic acid
CH_3COONa	Sodium acetate
CH_3COONH_4	Ammonium acetate
Cl	Chlorine
cm	Centimetres
Co	Cobalt
CO_2	Carbon dioxide
Cr	Chromium
CRM	Certified Reference Material
Cu	Copper
DIN	Deutsches Institut für Normung
DL	Decanted liquid
DOC	Dissolved Organic Carbon
doi	Digital object identifier
DTPA	Di-ethlyene-tri-amine-penta-acetic acid ($C_{14}H_{23}N_3O_{10}$)
EDTA	Ethylene-di-amine-tetra-acetic acid ($C_{10}H_{16}N_2O_8$)
EEC	European Economic Community

EPA	Environmental Protection Agency
EP-TOX	Extraction Procedure Toxicity Test
FAAS	Flame Atomic Absorption Spectroscopy
Fe	Iron
FLAA	Flame Atomic Absorption
G	Centrifugal force
g	Gram
GFAAS	Graphite Furnace Atomic Absorption Spectroscopy
H_2O	Water
H_2O_2	Hydrogen peroxide
H_3BO_3	Boric acid
HCl	Hydrochloric acid
HClO	Perchloric acid
HF	Hydrofluoric acid
Hg	Mercury
HNO_3	Nitric acid
ICP	Inductively Coupled Plasma
ICP-AES	Inductively Coupled Plasma Atomic Emmission Spectroscopy
ICP-MS	Inductively Coupled Plasma Mass Spectroscopy
K	Potassium
$kg\ L^{-1}$	Kilogram per litre
kg	Kilogram
$kg\ m\ s^{-2}$	kilograms meter per second squared
KNO_3	Potassium nitrate
$L\ kg^{-1}$	Litres per kilogram
L	Litre
L/S	Liquid-to-solid ratio
M Ω cm	Mega-ohms centimeters
m	slope / gradient of graph
m/m	Mass per mass
max	Maximum
Me	Metal
$MeCO_3$	Metal carbonate
$Me(CO_3)_2^-$	Metal carbonate
$MeHCO_3^-$	Metal bicarbonate
$MeNO_3^+$	Metal nitrate
$MeOH^+$	Metal hydroxide
$Me(OH)_2^+$	Metal hydroxide
$MeSO_4$	Metal sulphate
$mg\ ha^{-1}$	Milligrams per hectare
$mg\ kg^{-1}$	Milligrams per kilogram
$mg\ L^{-1}$	Milligrams per litre
Mg	Magnesium
$MgCl_2$	Magnesium chloride
min	Minute
mL	Millilitres
mm H_2O	Millimetres Water (pressure unit)
mm	Millimetre
$mmol\ L^{-1}$	Millimole per litre
Mn	Manganese

Mo	Molybdenum
mol L^{-1}	Moles per litre
mS cm^{-1}	Milli-Siemens per centimetre
MS	Mass Spectrophotometer
N	Nitrogen
N	Normal / Normality
n	Number of samples
Na	Sodium
$Na(C_{13}H_{11}N_4S)$	Di-phenyl-thio-carbazone (sodium dithionite)
$Na_2B_4O_7 \cdot 10H_2O$	Deca-aqua-ammonium borate
$Na_4P_2O_7$	Sodium phyrophosphate
Na_4PO_7	Sodium phosphate
NaClO	Sodium hypochlorite
$NaHCO_3$	Sodium bicarbonate
$NaNO_2$	Sodium nitrate
NaOH	Sodium hydroxide
Nb	Niobium
nd	Not detected
NEN	Nederlands Normalisatie-Instituut
$NH_2OH \cdot HCl$	Hydroxylamine hydrochloride
NH_3	Ammonia
NH_4Cl	Ammonium chloride
$(NH_4)_2CO_3$	Ammonium carbonate
NH_4NO_3	Ammonium nitrate
Ni	Nickel
P	Phosphorus

Pb	Lead
pers. comm.	Personal communication
ppt	Parts per trillion
PTME	Potentially Toxic Metals and Elements
r	Pearson correlation coefficient
r^2	Coefficient of determination (Square of Pearson correlation coefficient)
rpm	Revolutions per minute
S	Sulphur
SA	South Africa
Se	Selenium
Si	Silicon
SiO_2	Silica
Sn	Tin
SO_4^{2-}	Sulphate ion
Sr	Strontium
TCLP	Toxicity Characteristic Leaching Procedure
Ti	Titanium
TÜV	Technische Überwachungsverein
V	Vanadium
W	Tungsten
WAS	Waste activated sludge
Zn	Zinc
Zr	Zirconium
ρ	Density

1 Introduction

Treatment of wastewater results in undesirable sewage sludge. Safe disposal of sewage sludge is internationally a concern. This is primarily due to the large volumes generated and the potential hazardousness of the sewage sludge. However, there are also beneficial uses for sewage sludge. In many European countries sewage sludge is used as a fuel for incinerators. This reduces the volume and generates energy. Sewage sludge is also beneficially used as a soil conditioner, recycling nutrients such as N and P. For this application the potentially toxic metals and elements (PTME) in the sewage sludge are of importance. When applying sewage sludge to land, pollution of the soil, plants and groundwater needs to be prevented.

The beneficial use of sewage sludge as a soil conditioner is restricted by mans' ability to determine the fate of unwanted contaminants in the sludge on the environment. The fate of PTME applied to soil from sewage sludge is twofold. They will either remain in the soil or leach into the water. Leachable elements can become available to plants for uptake or move into surface or groundwater resources and cause pollution. The measurement of the leachability of sludge borne metals is of concern and was researched.

Test procedures to measure the leachability of metals are readily available. These are usually sample and site specific since they aim to reflect what is expected to happen in the environment under defined conditions. Test procedures for the metal leachability from mainly organic, multiphase samples like sewage sludge are rare. They are not used for compliance or regulatory adherence, but rather for investigative purposes to determine constituents or properties of the waste. This research investigated compliance test procedures for leachable metal determination and the applicability of these procedures on sewage sludge.

1.1 Statement of the problem

In South Africa the test procedure specified for risk assessment of sewage sludge to agricultural land or disposal is the Toxicity Characteristic Leaching Procedure. It is incorrectly applied and unsuitable for a multiphase waste. This could be detrimental to the receiving environment.

1.2 Objectives of the study

The research objectives are:

1. To conduct a literature survey on:
    - Present South African Sludge Management with regards to the South African Sludge Guidelines.
    - The influence of time on metal mobility in sludge-amended soil.
    - The application of single and sequential extraction test procedures for use on sewage sludge and sludge-amended soil samples.
    - The parameters of importance when leaching sludge and soil samples.
2. To determine the relationship between total and leachable elemental extractions of anaerobically digested sewage sludge.
3. To determine if Inductively Coupled Plasma Mass Spectroscopy (ICP-MS) and Flame Atomic Absorption Spectroscopy (FAAS) elemental analysis of leachates can be used interchangeably on sewage sludge samples.
4. To determine if drying of sewage sludge samples, prior to leaching will change the amount of element that leaches out.
5. To compare four leachable extraction procedures for their applicability to elemental leaching and make recommendations on selecting a leaching test procedures for the South African Sludge Guidelines.

1.3 Methodology of the study

An extensive literature review was done encompassing various aspects of sludge and leaching. The behaviour of metals in soil and sludge-amended soil was researched to determine the effect of the addition of metal into the soil from the sludge. The literature review also included the different extraction protocols and what they aim to extract, as well as specific properties of the extraction tests and their effect on the amount of element that leaches.

Twenty-four wastewater treatment plants were sampled to compare total and leachable metal extraction procedures. The two extractions obtained were analysed for Cd, Co, Cr, Cu, Hg, Mo, Ni, Pb, Se and Zn using Inductively Coupled Plasma (ICP) techniques. Cd, Cu, Pb and Zn were analysed by Atomic Absorption (AA) techniques as well. This was to determine the interchangeability of these two techniques for sewage sludge samples. Thereafter two grab samples (two months apart) of anaerobic digested sewage sludge were collected from one of the twenty-four wastewater treatment plants. One of these samples was used to compare four different compliance leachate tests. The other sample was used to vary the sample preparation techniques and then apply the differently prepared samples to two leachate tests. Leachate analysis was done for B, Cd, Co, Cr, Cu, Fe, Hg, Mo, Ni, Pb, Se and Zn.

Using the results obtained, specific recommendations to the present South African Sludge Guidelines and related methods could be made. Future research was also identified and recommendations made.

2 South African sludge management and the behaviour of metals in soil: A literature review

2.1 The advantages and disadvantages of using sewage sludge as a soil conditioner

Sewage sludge can be divided into two components; they are nutrients and pollutants. The objective of a wastewater treatment plant is to accumulate the pollutants in the sludge (Dichtl, 2003) leaving the water clean. Due to the large amount of plant nutrients such as N, P and K in sewage sludge it is can be used as a soil conditioner. Organic matter in sewage sludge also assists in improving the soil physical conditions by improving soil structure, soil water capacity, and soil water transmission characteristics (Korentajer, 1991, McGrath *et al.*, 2000 and Ščančar *et al.*, 2000). Application of sewage sludge to soil also supplies essential plant micronutrients like Zn, Cu, Mo and Mn. Despite these advantages, careful consideration must be given to the land-application of potentially toxic metals and elements (PTME) derived from sludge. They have the potential for contamination of the neighbouring environment by transportation through leaching and runoff processes (Burton *et al.*, 2003).

Ekama (1992) identifies three areas of general concern with the land-application of sewage sludge. They are:

- groundwater contamination
- aerosol production (odours), and
- food chain contamination.

The food chain contamination could be due to three groups of pollutants found in sewage sludge. These are (Ekama, 1992):

- toxic organic material
- pathogens, and
- trace elements and metals

This research focuses on trace elements and metals found in sewage sludge.

The decision to apply organic waste such as sewage sludge to agricultural land should be governed by the knowledge of the resource characteristics of the soil on a regional scale i.e. the specific local potential of a soil to buffer heavy metal input (Horn *et al.* 2003). The soil buffer capacity for toxic ions could be reduced due to heavy metal accumulation. This could lead to an imbalance between the input and output of the metals in the soil (McGrath *et al.*, 2000). The beneficial use of sewage sludge has been regulated in South Africa, due to its potential to contaminate. The regulations and current sewage sludge management practices are addressed below.

2.2 South African Sludge Guidelines

Management of sewage sludge in South Africa is controlled by the South African Sludge Guidelines. Two separate publications exist and sludge generators are required to use both of them. The first is the "*Guide, Permissible Utilisation and Disposal of Sewage Sludge Edition 1*" issued in 1997 (Water Research Commission *et al.*, 1997). The second is the "*Addendum No 1 to the Guide, Permissible Utilisation and Disposal of Sewage Sludge*" issued in 2002 (Water Research Commission *et al.*, 2002). The addendum was developed out of a need to clarify aspects of the 1997 Guideline (Snyman *et al.*, 2004).

One of the points of concern in the 1997 Sludge Guideline (Water Research Commission *et al.*, 1997) was the low total extraction limit values for Cd, Co, Pb and Zn allowed in sludge aimed at unrestricted use. The wastewater industry in general was unable to comply with the specified limits (Snyman *et al.*, 2004). Analysis by Snyman, (2001) of data from Smith and Vasiloudis (1989) revealed that of 77 wastewater treatment plants studied throughout South Africa none complied with all the total metal limits. After further investigation it was found that for Cd, Cu, Pb and Zn, leachable values were specified in the 1997 Guideline as total values. The 2002 Addendum corrected this by retaining the Cd, Cu, Pb and Zn leachable values found in the 1997 Guideline except now clearly indicated as leachable limits and adding total limits for Cd, Cu, Pb and Zn.

2.2.1 The lack of specified analytical procedures in the Sludge Guidelines

Another point of concern emanating from the 1997 Guideline (Water Research Commission *et al.*, 1997) was the analytical methods to determine the total extraction and analysis of elements after extraction. No analytical methods were specified by the 1997 Guideline. The compilers of the Addendum did not want to specify methods for analysis, citing that it was too complex a subject and required further research. But "*to reach a degree of interim conformity*," it was recommended that total extraction be done by *aqua regia* and leachable fractions by the Toxicity Characteristic Leaching Procedure (TCLP) (Water Research Commission *et al.*, 2002).

Prior to these amendments to the Sludge Guidelines, the TCLP was already in use in South Africa. It was specified as the procedure to determine if a hazardous waste could be co-disposed with general waste on a landfill site. For this reason, the Department of Water Affairs and Forestry already outlined a condensed form of the TCLP, in their publication "*Minimum Requirements for the Handling, Classification and Storage of Hazardous Waste*" (1998). This procedure was altered from the original Unites States of America Environmental Protection Agency TCLP (USA EPA, 1992).

Scientific debate with respect to the applicability of the TCLP on sewage sludge has not yet arisen. The selection of the total *aqua regia* and leachable TCLP procedures are as a result of generally accepted norm. Quevauviller (1998a) criticizes the use of an analytical procedure because it is the accepted norm without the procedure being strongly supported by practical considerations such as ease, scientific soundness and robustness.

2.2.2 The applicability of the TCLP as a leaching test for sewage sludge

Even though sewage sludge is specifically mentioned as a waste that can be leached with the TCLP (USA EPA, 1992) the applicability of this leaching procedure on such a sample is being questioned. Kimmell *et al.* (2001) refers to criticism that the TCLP is not applicable to waste materials that are difficult to filter or stabilised.

For the South African situation, a contrast needs to be made between the intended co-disposal scenario inherent in the TCLP (USA EPA, 1992) and the beneficial use of sewage sludge as a soil conditioner. The intended co-disposal scenario of a hazardous waste material on a general landfill with general waste would not yield the same environmental conditions as the application of sewage sludge to agricultural lands. Since the TCLP was developed to simulate the co-disposal scenario, the applicability of the procedure to simulate the land application scenario is being questioned.

The conceptual model used to develop the TCLP aimed to estimate the concentration of contaminants in the leachate at the interface between the bottom of a landfill and the underlying strata (Kimmell *et al.*, 2001). The criteria used to specify an acetate buffer solution for the TCLP was due to the type of waste and contaminants expected to leach out in a co-disposal scenario (Kimmell *et al.*, 2001 and USA EPA, 1999). How can the TCLP estimate contaminants in sludge and soil particles for sludge-amended soil?

2.2.3 Regulatory limits of metals in sewage sludge for beneficial use

McBride (2003) lists five important factors than need to be considered when setting limit values. These factors were not considered for sludge in the USA (McBride, 2003). They are:

- the cumulative soil-loading limit for the specifed metals,

- the properties of the soil being amended,
- the natural inherent metal concentrations in the soil prior to amendment,
- the physio-chemical properties of the sludge, and
- the crop uptake coefficients of metals found in amended soil.

The South African Sludge Guidelines (Water Research Commission *et al.*, 1997 and 2002) attempt to address the soil-loading capacity by placing a 25-year restriction for application of sludge to land. The four remaining factors do not appear in the Guidelines.

Development of limit values based on toxicity

The origin of the leachable limits in the South African Sludge Guidelines (Water Research Commission *et al.*, 2002) were explained by Snyman *et al.*, (2004) as being based on aquatic toxicity. The science of toxicology can be used for risk assessment prediction of effects at chronic exposure and sustained low levels, but toxic effects at fluctuating levels are not examined by toxicology (Kimmell *et al.*, 2001). With the beneficial use of sewage sludge aquatic toxicity levels fluctuate since the moisture content in the soil and the mobility of metals added to the soil will vary.

Synergistic effects

The synergistic effect that multiple metals may have when present in the sludge (Wallace and Berry, 1989) should also be considered when developing limit values. McBride (1995) claims that crops grown in soil with multiple metals near phytotoxic levels may indicate yield reductions at lower concentrations than expected due to the synergy between the metals. The extent to which phytotoxic metals are additive is also still contested. Synergy between metals in high concentrations is not addressed by the South African Sludge Guidelines.

Synergistic effects were considered for the limit values used by landfill facilities in Spain for inert waste. They were derived from the 1991 European

Economic Community (EEC) Landfill Directive Draft (Viguri *et al.*, 2000) and are detailed in table 2.4-A.

Table 2.2-A: The limit concentrations of leached metals as specified by the 1991 European Economic Community Landfill Directive Draft and used in Spain (Viguri *et al.*, 2000)

Metal	**Hazardous Waste Range**	**Inert Waste**
	mg L^{-1}	
Pb	0.4 – 2.0	The sum of the metals listed must be below 5 mg L^{-1} and no single metal value above the minimum fixed for hazardous waste
Cd	0.1 – 0.5	
Cr	0.1 – 0.5	
Cu	2 – 10	
Ni	0.4 – 2.0	
Zn	2 – 10	

Synergistic effects were also considered in South Africa for the Regulation regarding the purification of wastewater or effluent for discharge (South African Regulation, 1984).

Table 2.2-B: The limit concentrations of constituents as specified by the South African Regulation 991 for discharge of wastewater. (excerpt)

Metal	**Maximum allowable concentration**	**Synergistic Effect**
	mg L^{-1}	
Cd	0.05	The sum of the metals listed must be below 1 mg L^{-1}.
Cr	0.5	
Cu	1.0	
Hg	0.02	
Pb	0.1	

This General Standard includes compliance to specified constituents. Table 2.2-B details only the metals where synergy is considered and the cumulative limit.

2.3 Sources of metal addition to soil

Metals are added to soil by various processes. Increased metals in soil are due to (Han and Banin, 1999 and McGrath *et al.*, 2000):

- the increased use of reclaimed sewage water for irrigation,
- the disposal of wastewater sludge,
- the disposal of municipal and industrial refuse, and
- atmospheric fallout.

Table 2.3-A: The percentage of annual metal inputs to agricultural land in England and Wales for 2000

Source	Zn	Cu	Ni	Pb	Cd	Cr	As	Hg
Atmospheric Deposition	49	39	60	78	53	25	56	85
Livestock Manure	37	40	18	6	11	11	26	2
Sewage Sludge	8	17	9	14	4	24	5	8
Industrial “waste”	1	1	1	0	2	1	0	1
Inorganic Fertilisers	5	3	12	2	30	39	14	1
Other[#]	1	1	0	0	1	0	0	3

[#] Other consists of Agrochemicals, Irrigation Water and Composts

Table 2.3-A lists the sources of select metals found in agricultural soil in England and Wales for 2000 (Nicholson *et al.*, 2003). The addition of metals from sewage sludge application to agricultural soil is less than that of atmospheric deposition and livestock manure (Nicholson *et al.*, 2003 and Xue *et al.*, 2003).

2.4 Metal partitioning between the solid and liquid phase

Metals are distributed between the solid and liquid phases of the sludge (Angelidis and Gibbs, 1989). They have a high preference for the solid phase over the liquid phase (Han and Banin, 1999; Neufeld and Hermann, 1975). The distribution between the solid and liquid phase is dependant on the chemical properties of the metal and the physio-chemical properties of the sludge. Physio-chemical properties are in turn dependant on the sludge treatment process, pH, temperature, redox potential, and presence of complexing or precipitating agents (Fytianos et al, 1998). Micro-organisms used in sludge treatment processes will both actively and passively concentrate metals in the solid phase of the sludge (Unz and Shuttleworth, 1996). Legret (1993) did a six step sequential extraction on anaerobically digested sewage sludge and measured Pb, Cu, Cd, Cr, Ni and Zn values. Both the free liquid and the solid phase of the sludge was analysed. Ni was the most soluble in the free liquid while Cd and Pb were entirely associated with the solid phase that was sequentially extracted.

2.5 Metal accumulation in sludge and sludge-amended soil

In sludge treatment processes metals are accumulated in the sludge. When the sludge is used as a soil conditioner the concentration of metal in the sludge is higher than the concentration in the soil. The metals added to the soil by the sludge are retained in the soil and not leached out. This is often referred to as the soil being a “sink” for the metals (Álvarez *et al.* 2002; Ashworth and Alloway, 2004; Bhogal *et al.*, 2003; Ekama, 1992; Healey, 1983; McGrath and Cegarra, 1992; and McGrath *et al.*, 2000).

McGrath and Lane, (1989) found an eighty-percent retention of Cd, Zn, Cu, Ni, Cr and Pb in soil twenty-four years after the sludge application ceased. McGrath *et al.,* (2000) found negligible metal removal by agricultural crops (0.6% for Zn and 0.3% for Cd) for the same experimental data. The metal retention ability of soil can be explained by noting that with multiple applications of sewage sludge, metal accumulation occurs due to the low solubility and mobility of the metals (Gove *et. al.,* 2001). While sludge application increases the total metal concentration in soil, it also increases the metal adsorption capacity of the soil and the total metal bioavailability (Hooda and Alloway, 1994). From the conclusions drawn by McGrath *et al.*, (2000) and Hooda and Alloway (1994) in can be assumed that although metals become more bioavailable, they are not necessarily taken up by crops.

McBride (1995) explains the expected release of metals into a more soluble form as follows. The residue from the sludge decomposition can maintain the metal solubility at low levels. If it is assumed that sludge is applied to soil until the entire soil surface is sludge residue the availability of metals would be at best a linear function of the cumulative sludge application. This is because the sludge is also adding metal adsorptive capacity to the soil (McBride, 1995).

2.6 Metal mobilisation from sludge-amended soil

The viewpoint by Hooda and Alloway (1994) claiming metal retention in the soil does not consider the mineralisation of organic matter from the sludge and the subsequent release of metals into more soluble forms making them more available. Bioavailability, and mobility of metals in soil and sludge-amended soil are governed by:

- the kinetic distribution between the solid and liquid phases and between the different components in the solid-phase (Han *et al.*, 2001),
- the application rate of sludge, and
- both the annual and the cumulative metal loading (Mahler *et al.*, 1987).

2.6.1 Groundwater contamination from sludge borne metals

According to Wang and Viraraghavan, (1997) the most important environmental concern for the disposal of sludge is that the leachate from the waste should not contaminate the groundwater. However, once contamination is detected it could be too late to stop or limit the contamination (Vogeler, 2001). Some authors emphasise that percolation of metals into groundwater does occur (Vanni *et al.*, 1994). Packed columns have proven that migration of Cu and Ni into the water phase occurs (Ashworth and Alloway 2004). McBride (1995) cites numerous references where metal mobility perpendicular to the soil surface is very slow, with one specific case where after nineteen years and 205 mg ha^{-1} of dry sludge added, metal mobility was still less than 60 cm into the soil (Dowdy *et al.*, 1993). The risk of metal contamination to groundwater was therefore insignificant. Jørgensen (1976) developed a model that predicted the risk to plants is greater than that to the groundwater.

2.6.2 Bioavailability of metals

Of greater concern appears to be the risk of non-available metals becoming available over a long period of time (McBride, 1995). McBride (2003) cites numerous references that have determined that the bioavailability of the metal is highest in the first three to four years of application. Once long term sludge application has ceased, there is a distinct possibility that if the pH of the soil is not monitored, it will decrease and this will cause more bound metals to solubilise and leach out (McBride, 2003).

In contrast, McGrath and Cegarra (1992) found a difference between the sequential extraction of metals from soil and sewage sludge when sludge application had ceased 30 years ago compared to when application was still occurring. They concluded that once sludge application ceased, the chemical forms of the metals in the soil remained constant for a long period of time. This implies that the bioavailability and the threat of the potentially toxic metals to plants, animals or micro-organisms may also remain unaltered (McGrath and Cegarra, 1992).

2.7 The speciation of metals in soil

The speciation of metals in soil is affected by accelerating and inhibiting factors. Speciation is accelerated by; the lowering of the pH, redox changes, inorganic and organic complexation and microbially mediated species transformations like biomethylation. Speciation is inhibited by; adsorption, sedimentation, filtration, complexation, precipitation, and biological barriers that are often associated with membrane processes that limit the translocation of metals. Complexation is situation dependant and can be both an accelerating or inhibiting factor (Förstner, 1993).

2.8 The different fractions in the solid phase

In particles from a natural or anthropogenic source, metals can be (Angelidis and Gibbs, 1989):

- transported and adsorbed to the surface of the solids by ion-exchange,
- scavenged by Fe / Mn hydrous oxides that form coatings on the surface of the solids,
- enclosed in carbonates,
- enclosed and / or bound into the organic matter that adheres to the particles,
- contained in sulphides that may be present in the particle, or
- constituents of the crystal lattice of the mineral particle themselves.

These six processes are simulated in the laboratory by sequential extraction techniques with the aim of determining the species and amount of metal that is found in each fraction.

2.8.1 Redistribution of metals in the soil

The redistribution and transformation of added metals in soil is affected by many factors. These include (Han and Banin, 1997; Han and Banin, 1999; Xue *et al.*, 2003; Merrington and Smernik, 2004):

- the distribution of the metals in the native soil,
- the metal loading level,
- the duration of time since the metal addition,
- the moisture content of the soil,
- the organic matter in the soil, and
- the inorganic fraction (P and metal oxides) in the soil.

Non-amended soil undergo similar but limited changes to sludge-amended soil. The rate of distribution has mathematically been treated as a ratio between sludge-amended and non-amended soil (Han and Banin, 1997; Han *et al.*, 2003). These changes result in the redistribution of the metals among the various solid phase components, and hence the distribution of non-amended soil is regarded as nearer to equilibrium than newly added metals in sludge-amended soil (Han and Banin, 1999). At low levels of addition (single application), the trend is towards a fractional distribution more similar to that of untreated soil, even though the total metal concentration in the soil is higher. At higher levels (single application), the soil does not fully return to the distribution coefficient characterising the untreated soil. As the fractional distribution pattern in amended soil approaches that of non-amended soil, the rate of metal redistribution and transformation slows. An oversupply may saturate a certain "component sink" and create new partitioning patterns (Han and Banin, 1999).

Gove *et al.*, (2001) suggests that the soil physical properties are more important than the chemical processes in determining the distribution and mobility of metals within a soil profile.

2.8.2 The kinetics of metal redistribution

The redistribution index is a parameter that can be used to quantify metal redistribution processes. Analyses of redistribution kinetics is essential in gaining an understanding of the stability of metals in sludge-amended soil and in estimating the time required to reach a steady-state distribution. These considerations are important in the management of sludge-amended soil (Han *et al.*, 2003) and could assist in predicting leachable fractions.

The repartitioning occurs by an initial fast retention of metal added to the soil, followed by slower reactions that depend on the metal species, soil properties, and level of input and time (Han and Banin, 1997; Han and Banin, 1999).

The second slower reactions are long-term transformations of metals added to water saturated soil as a result of two opposite processes. The first is the mobilisation of the native metals due to mild chemical reduction after saturation of the soil. The second is the immobilisation of the added metals due to their transfer from the more labile fraction into the stable fraction. (Han and Banin, 1999)

The long-term transformations are driven by the tendency of the system to return to chemical equilibrium, but limited by the kinetics of the involved reactions. (Han and Banin, 1999) For Cu, Zn and Ni the moisture of the soil affects the redistribution pathway while for Cd and Cr this moisture effect is less important (Han and Banin, 1997; Han and Banin, 1999).

2.9 Soil organic matter

Organic matter has the ability to form stable, soluble complexes with metals such as Cd, Cu, Ni, Pb and Zn (Ashworth and Alloway, 2004). Soil organic matter plays an important role in the transfer of metals from the solid to the liquid phase in soil. Soil containing more organic matter transfer metals into liquid better than mineral soil that has less organic matter. Soil containing more organic matter also trap the metal ions more efficiently than mineral soil. The trapped metal ions then attach to the dissolved organic ligands forming dissolved metal complexes (Xue *et al.*, 2003).

The dissolved fraction of the organic matter has a net negative charge at typical soil pH values and is therefore mobile in soil (Ashworth and Alloway, 2004). It does not remain in the soil but is decomposed by micro-organisms (McGrath *et al.*, 2000; Merrington and Smernik, 2004). It initially decomposes rapidly but the recalcitrant fraction remains in the soil for a long time and will take hundreds of years to return to the concentration prior to sludge amendment. The recalcitrant fraction of the organic matter is more important for metal adsorption and therefore metal retention in the soil than the biodegradable fraction of the organic matter (McGrath *et al.*, 2000). McBride (1995) maintains that despite the importance that organic matter plays in metal mobility, it is not permanent and the soil will eventually mineralise. For this reason it is important to replenish organic matter in agricultural soil.

2.9.1 The effect of organic matter on sludge-amended soil

Organic matter reduces the metal adsorption onto the soil surface by either; competing more effectively for the free metal ion and then forming soluble organo-metallic complexes, or being preferentially adsorbed onto the soil surface instead of the metal (Giusquiani *et al.*, 1998).

This reduction in metal adsorption has two important considerations. The first is that reduction occurs at the pH generally found in agricultural soil by organic matter that effectively competes with the metal for adsorption onto the soil. This means that the metal retaining ability of the soil is decreased by the addition of organic matter in agricultural soil. It further yields an increased risk for metal accumulation in crops or metal contamination of the groundwater by leaching (Antoniadis and Alloway, 2002).

The second consideration is that once the sludge application has ceased, the effect of the added organic matter can become more pronounced. Linehan (1985) states that dissolved organic carbon (DOC) increases metal solubility. This DOC increase is amplified over time as the total organic matter decreases. (Antoniadis and Alloway, 2002; Antoniadis, V 2004, pers. comm., 4 March). The amount of trace metals adsorbed in the soil is dependant on the soil organic matter while the strength of the adsorption is pH dependant. This means that for soil with a low organic matter content, metal adsorption is lower and leaching is higher than soil with a higher organic matter content (Gerritse *et al.*, 1982; Gove *et al.*, 2001). The mobilisation of metals in sludge-amended soil is dependant on the organic matter content. Low organic matter yields high leaching and high organic matter content yields low leaching.

2.10 Metal mobility over time with respect to the inorganic fraction

The long-term metal mobility is dependant on the inorganic fraction (being P and metal oxides) for sludge-amended soil. Once the organic fraction has been oxidised, some of the metals are found bound to the inorganic fraction (Merrington and Smernik, 2004). Common metal (Me) inorganic pairs found in soil and sludge are metal hydroxides ($MeOH^+$ and $Me(OH)_2^+$), metal carbonates and bi-carbonates ($MeHCO_3^-$, $MeCO_3$ and $Me(CO_3)_2^-$) metal nitrates ($MeNO_3^+$,) metal sulphates ($MeSO_4$) and complexes with remaining organic matter (Sauvé *et al.*, 2000).

2.11 Conclusion

There are distinct advantages of beneficially using sewage sludge as a soil conditioner. But due to the pollutants inherent in the sludge, care must be taken. The use or disposal of sewage sludge in South Africa is dictated by the Sludge Guidelines. There are however, concerns with these guidelines. Some of the concerns are the lack of specified test procedures for analysis, the applicability of the currently recommended procedures on sewage sludge and the methodology used to determine the limit values of metals in sludge.

The beneficial use of sewage sludge for agricultural purposes adds metals in both the solid and liquid phases to the soil. There is a strong preference for the metals in the solid phase but transport from the solid to the liquid phase does occur. The mobilisation occurs with the aid of organic matter found in the soil. This mobilisation of the metals from the solid phase to the liquid phase yields the potential to pollute the groundwater or for the metals to become bio-available. Bioavailability occurs when the organic matter to which the metals are bound decomposes and the metals are now either available as ions or bound to inorganic species.

Metals in the solid phase are partitioned into various fractions depending on the compound that they are bound to. Section 3 reviews the different test procedures applied to sewage sludge, with respect to what fractions of the solid phase are leached out.

3 Extraction tests for elements in environmental samples: A literature review

3.1 Introduction

Extraction tests are used to determine to which fractions PTME are bound. They provide information on both the amount and location of the elements. Fractionation also includes the binding strength between the element and other constituents in the sample. The short, medium and long-term fate of the elements can be experimentally determined by various extraction tests. In South Africa the TCLP extraction is used to determine the available fraction while the *aqua regia* extraction is used to determine total metal content. Sequential extraction techniques can determine the movement and distribution of metals in sludge-amended soil.

3.2 Selection of analytical methods for elemental extraction

The choice of an analytical method depends on the type of information desired. Environmental analysis attempts to assess the effect of a waste material on the environment by analysing the waste material prior to it being exposed to the environment, or by analysing the receiving environment after addition to the environment. A comparison is then drawn between introducing the waste material into the environment and the conditions prior to the introduction.

Evaluation prior to the addition of the waste is used to model the effect that the waste will have on the environment. It is done by characterisation testing of the waste. Waste characterisation needs to identify factors that will classify a waste as usable or not (Fällman and Hartlén, 1994). These factors are the physical properties and the elemental speciation in the waste material (Eighmy and van der Sloot , 1994). The analytical methods chosen should also consider the possible environmental aspects of beneficially using the residue or waste (Fällman and Hartlén, 1994). The usefulness of evaluation prior to the addition will depend on the ability of the method to model the true conditions (van der Sloot, 1996).

When a previously untested sample is being tested for the first time, a full characterisation is necessary. This is to evaluate the properties and potential management options for the waste. This data can then be used to predict results for compliance and verification testing (van der Sloot *et al.*, 1994). A full characterisation should consist of: (van der Sloot, 1996)

- a total concentration analysis of the constituents,
- the potential of leachability of the constituents including the acid neutralisation capacity and reducing potential,
- the pH sensitivity of leaching (a pH static test) and,
- a column test for granular materials with a liquid-to-solid ratio ranging from 0.1 to 10 so that long term leaching is simulated.

Three broad categories of metal analysis of sludge and soil exist. They are:

- total extraction methods,
- selective sequential extraction methods, and
- leachable extraction methods

3.3 Total extraction methods

Total extraction methods have two major classifications dependant on the reagents used for the extraction. The first uses a combination of HNO_3 and HCl and is known as *aqua regia* extraction. The second, a USA EPA method uses HNO_3 and H_2O_2. Within each class there are three different protocols. They depend on the physical method used to do the digestion. The first is a heated digestion, the second a microwave digestion and the third a microwave digestion with the addition of HF. The addition of HF to the reagents allows the silicate bound metals to digest as well (Chen and Ma, 2001). Table 3.3-A highlights the differences and similarities between the total methods. The three *aqua regia* types have been numbered 1,2, and 3 for clarity only.

Table 3.3-A: The similarities and differences between various types of total extraction methods

Extraction Name		Type of Digestion	Reagents
Aqua regia[#]	1	Heated Acid Digestion	$HNO_3 + HCl$
	2	Microwave Digestion	
	3		$HNO_3 + HCl + HF$
EPA	3050 B*	Heated Acid Digestion	$HNO_3 + H_2O_2 + HCl$°
	3051[¶]	Microwave Digestion	HNO_3
	3052[§]		$HNO_3 + HF + HCl$[«] + H_2O_2[¤]

[#] Chen and Ma (2001);

* USA EPA (1996b); [¶] USA EPA (1994); [§] USA EPA (1996a)

° Optional when analysis is being done with FLAA or ICP-AES.

[«] Optional for stabilisation of Ag, Ba Sb Fe and Al.

[¤] Optional to aid complete oxidation of organic matter

Snyman *et al.*, (2004) compared the *aqua regia* and EPA 3050 test methods on sewage sludge and found that the *aqua regia* yielded higher values and was more reliable on repeat analysis than the EPA 3050.

Chen and Ma (2001) compared *aqua regia* extraction methods for three certified reference materials (CRM) and 20 different soils. They found that of the 20 elements analysed only As, Se and Cd did not give precise results irrespective if the digestion was done by hotplate or microwave for the certified reference materials. Silicate-binding metals including Al, Ba and K yielded higher microwave + HF extraction. For the 20 soil samples, microwave assisted *aqua regia* yielded higher digestion efficiencies for some elements and lower than hotplate digestion for others.

3.4 Selective sequential extraction

Metals in sludge-amended soil exist in various solid-phase fractions. This fractionation can be measured by selective sequential dissolution (Tessier *et al.*, 1979). The approach is based on the solubility of individual solid-phase components by selective reagents. Each reagent in a selective sequential procedure dominantly targets one major solid-phase component. In no case can an extraction solution remove the entire targeted solid-phase component without attacking other components. (Belzile *et al.*, 1989). Sequential extraction procedures also assume that each sequential reagent will extract the sum of the contaminants extracted by the previous reagents. This is not necessarily true (Campanella *et al.*, 1987). Sequential tests aim to determine the state or chemical form of the contaminant in the waste (Environment Canada, 1990).

Selective sequential extraction procedures are not without limitations.

- At each step these procedures have problems in selectivity, dependant on the chosen reagents (Han and Banin, 1999).
- During these sequential extraction procedures trace metals are changed from the metal hydroxide into solution, and then re-fix themselves onto other solid sites. This means that the measurements made at equilibrium, underestimate the amount of metal cations in the reducible fraction of the soil (Bermond *et al.*, 1998 and Belzile *et al.*, 1989).

Despite these shortcomings that are common to any chemical extraction procedure, sequential extraction procedures furnish more useful information on metal binding, mobility and availability than obtained from a single extraction solution (Han *et al.*, 2000).

3.4.1 Sequential extraction solutions commonly used

Table 3.4-A represents some of the soil extraction solutions (reagents) and the fractions that they extract. The soil solution fraction contains the most mobile and therefore available metals, usually at very low concentrations.

Table 3.4-A: Soil partitioning fractions and possible extraction solutions for each fraction

Fraction	Possible extraction solutions	Chemical Formula
Soil Solution	calcium chloride[¶]	$CaCl_2$
	sodium nitrate[¶]	$NaNO_3$
	magnesium chloride[†]	$MgCl_2$
	deionised water[‡]	H_2O
Exchangeable Species	ammonium acetate at pH=7[¶]	CH_3COONH_4
	ammonium nitrate[¶,§]	NH_4NO_3
	ammonium chloride[¶]	NH_4Cl
	acetic acid[¶,*]	CH_3COOH
	calcium chloride[‡]	$CaCl_2$
	potassium nitrate[#]	KNO_3
Organically Complexed Metals	sodium phyrophosphate[¶]	$Na_4P_2O_7$
	sodium phosphate[‡]	Na_4PO_7
	EDTA[¶]	$C_{10}H_{16}N_2O_8$
	sodium hypochlorite[¶]	$NaClO$
	hydrogen peroxide acidified + ammonium acetate[¶,§]	$H_2O_2 + CH_3COONH_4$
	hydrogen peroxide + nitric acid[†,*]	$H_2O_2 + HNO_3$
	DTPA buffered with triethanolamine [¶]	$C_{14}H_{23}N_3O_{10}$ and $C_5H_{15}NO_3$
	dichloromethane[#]	CH_2Cl_2
Carbonate Fractions	sodium acetete acidified by acetic acid[¶,§,‡]	CH_3COONa and CH_3COOH
	EDTA[¶]	$C_{10}H_{16}N_2O_8$
	acetic acid[¶]	CH_3COOH
Hydrous Oxides of Fe and Mn	hydroxylamine hydrochloride[¶,§,†,*]	$NH_2OH \cdot HCl$
	sodium citrate + sodium dithionite (diphenylthiocarbazone)+ sodium bicarbonate[¶]	$C_6H_6Na_2O_7$ + $Na(C_{13}H_{11}N_4S)$ + $NaHCO_3$
	acid ammonium oxalate[¶]	$C_2H_8N_2O_4$
	EDTA[‡,#]	$C_{10}H_{16}N_2O_8$
Residual	nitric acid[§,#]	HNO_3
	hydrogen fluoride + hydrochloric acid + perchloric acid [‡]	$HF + HCl + HClO_4$
	Microwave digestion *	

[¶] Ure, (1996); [§] Han *et al.*, (2003); [†] Angelidis and Gibbs, (1989); [‡] Qi-tang *et al.*, (1998)
[*] Álvarez *et al.*, (2002); [#] Vanni *et al.*, (1994)

The exchangeable species are mainly ions that are electrostatically bound and move from being soluble to insoluble by ion exchange. The soluble metals are then complexed in the liquid. Soluble concentrations are still low. The organically complexed metals, is that fraction that aims to leach all the metals attached to organic matter without forming metal hydroxides.

The carbonate fraction aims to leach metals bound to inorganic carbon but also leaches metals found strongly bound to clay particles and Fe and Mn oxide surfaces. The hydroxides of Fe and Mn fraction, leaches both crystalline and amorphous Fe and Mn oxides (Ure 1996). The residual fraction, aims to leach all the remaining metal. If silicate bound metal is also required, the HF is added as a leaching reagent (Chen and Ma, 2001).

3.4.2 Sequential extraction solutions aimed specifically at landfilling sludge

There are sequential extraction procedures that are more focused on sludge to be landfilled. Vanni *et al.*, (1994) did a sequential extraction on aerobic sludge. The choice of reagents was specifically to simulate certain conditions found in a landfill site. KNO_3 was used since it is known to desorb trace metals sorbed onto sludge. CO_2-H_2O was used to simulate acid rain, while EDTA was used to simulate the mobilisation effect between soil humic substances and water-softening reagents used in surfactants. CH_2Cl_2 was intended to simulate co-disposal conditions for sludge. From their research it was found that the metals are mostly bound in the organically bound faction and are easily mobile under mineral acid conditions (Vanni *et al.*, 1994).

3.5 Leachable extraction methods

A leaching test is one where a liquid makes contact with a waste body. Certain components from the waste body are then dissolved into the liquid. Before this occurs the liquid is known as a leachant and once the transportation process has occurred the liquid is called the leachate. (Environment Canada, 1990 and Lewin, 1996).

Leaching includes the chemical and physical actions that transport a contaminant from the waste to the leachate. In sludge and slurries the waste is a porous multiphase sample. It has both solid and liquid phases in a single waste. Multiphase waste is usually at equilibrium between the phases and the contaminants can be found unequally distributed in both phases. As soon as a leachant is introduced, this equilibrium is disrupted and contaminant transfer occurs. If there is sufficient time available a new equilibrium can be reached. For single-phase solid samples contaminants that were immobile now mobilise on contact with the leachant. This leaching process only becomes a concern to the environment when the leachate is transported away from the waste source (Environment Canada, 1990).

3.5.1 Classification according to the type of information desired from the test

The European Commission adopted a classification according to the type of information desired from the test (Fytianos *et al.*, 1998). The three classifications are: (van der Sloot, 1996)

- characterisation tests – with an aim of understanding the leaching behaviour of materials,
- compliance tests – that yield direct comparisons with regulatory limits and,
- on-site verification tests.

A specific experimental procedure could yield results for more than one of the above classifications. An example would be a column test that will provide characterisation data as well as compliance to a specified limit (van der Sloot, 1996). van der Sloot (1998) compared characterisation tests, compliance tests and on-site verification tests on a coal fly-ash sample. The results indicated that for leached concentrations at different pH values, the test procedures yielded comparable data. Regulatory compliance tests are researched further in this project.

Leaching tests have also been classified as follows: (Kosson *et al.*, 1996)

- tests designed to simulate constituent release under specific environmental conditions,
- sequential chemical extraction tests ,and
- tests which assess fundamental leaching parameters.

The first classification, tests designed to simulate constituent release under specific conditions, is researched further in this project. This type of test is very limited since it does not provide information of release over a time interval or under a different environmental condition to that specified in the test outline (Kosson *et al.*, 1996).

3.5.2 What a leachate test aims to achieve

The initial motivation for the development of leaching tests was to assess the short-term environmental impacts of solid waste disposed at landfills. Once a waste has been disposed of, the chance of it coming into contact with a leachant of some kind is inevitable. This leachant may be in the form of rainwater, surface water, groundwater or another liquid waste source disposed of on the same disposal site (Environment Canada, 1990).

The inherent assumption behind most leaching tests is that an infinite amount of waste with an infinite amount of contaminant will leach indefinitely at essentially the same concentration. This is termed the “infinite source assumption” (Kimmell *et al.*, 2001).

The objective of doing a leaching test on waste can include (Environment Canada, 1990):

- an identification of the leachable constituents in the waste,
- a classification of the hazardousness of the waste,

- an evaluation of any waste treatment process modifications (or general process modifications),
- a comparison of various treatment methods employed on a specific waste and,
- a quality control measure for waste treatment.

Fällman and Aurell (1996) pose five questions that need to be answered for waste characterisation. The questions are:

1. How much of the total content of a pollutant can be released in leaching processes?
2. What is the time dependant release from the material by equilibrium or diffusion controlled leaching?
3. What changes will the material undergo with time by atmospheric impact, changes in geochemistry, or by leaching?
4. What influence does pH and redox potential have on the leaching process and what changes in these parameters are likely to occur in the leachate from the waste?
5. What is the time dependant release from the waste with the proposed technique for utilisation / disposal?

Often the data required to answer the above five questions will not come from one test but rather a combination of leachate tests (Fällman and Aurell, 1996) as well as a total extraction test.

3.6 Classification of leaching tests

Leaching tests are classified into two categories with the distinction being that of leachant renewal or no renewal. Extraction tests are those without leachant renewal that aim to reach equilibrium while dynamic tests are those with leachant renewal that do not necessarily reach equilibrium (Environment Canada, 1990; van der Sloot,. 1996; Fytianos *et al.*, 1998). Table 3.6-A comments on three important properties of equilibrium and dynamic tests.

Table 3.6-A: Properties of equilibrium and dynamic leaching tests (Environment Canada, 1990)

Parameter	Equilibrium Tests	Dynamic Tests
Leachant	No renewal	Intermittent or continuous renewal
State	Steady State	Dynamic State
Equilibrium	Equilibrium reached	Equilibrium not necessarily reached

Equilibrium tests can further be subdivided into four. Their subdivisions are; agitation extraction tests, non-agitation extraction tests, sequential extraction tests and concentration build-up tests (Environment Canada, 1990). Table 3.6-B lists the aims of these four subdivisions.

Table 3.6-B: Aims of various equilibrium extraction tests. (Environment Canada, 1990)

Test	Comment	Aims
Agitation	Reaches equilibrium as quickly as possible	Used to determine the chemical properties of the waste
Non-Agitation	Takes longer than agitation to reach equilibrium	Used to determine the physical mechanisms that are rate limiting in the extraction
Sequential	Same sample exposed to increasingly stronger leachates	Used to determine the metal fractionation in the sample
Concentration Build-up	Same leachate is repeatedly exposed to fresh sample	Used to simulate leachate passing over a large volume of waste where the contaminants will approach saturation in the leachate

Dynamic tests are divided into four subclasses according to the definition of the interface between the leachant and the waste. Serial batch tests are where the individual particles of the waste define the interface. Flow-around, flow-through and soxhlet tests are examples of tests where the dimensions of the waste define the interface (Environment Canada, 1990).

3.6.1 Single Extraction Tests

Single extraction procedures are generally used when studying the eco-toxicity and the mobility of metals in soil. This includes the bioavailable metal fraction and environmentally accessible metals upon disposal of a waste (Quevauviller *et al.*, 1996a).

Single extraction procedures are used in soil and sludge-amended soil samples to determine the chemistry of metals and their interaction with other soil components. The components include clay minerals, organic matter, soil solution and the interactions are mobility, retention and availability to plants of the metals in the soil (Ure, 1996).

3.7 Leachable versus total extractions

3.7.1 Reasons for selecting total and leachable extraction procedures

A consideration of the reason for doing leaching analysis in addition to total analysis needs to be made clear. Total methods are the most used and recommended by environmental protection agencies (Sauvé *et al.*, 2000). When characterising sewage sludge, the total metal content is important, yet it is insufficient in predicting the effect sludge will have on plant growth (Fytianos *et al.*, 1998). McBride (1995) makes the following statement: *"The most critical soil parameter that indicates whether that soil has exceeded the threshold of metal phytotoxicity for any particular crop is not the total metal content, but the activity of the free metal cation in soil solution."* A leaching test provides useful information on bioavailability and toxicity of the metals, as they are present in the soil (Álvarez *et al.*, 2002 and Sauvé *et al.*, 2000).

The effects of long-term (more than thirty years) land application of sewage sludge have not been researched. The lack of fresh organic matter and the decomposition of organic matter previously added to the soil may result in changes in the binding of metals due to the changes in their chemical forms in the soil. Associated changes in bioavailability may then produce large increases or decreases in the risks of PTME to crops, animals or man (McGrath and Cegerra, 1992). McBride (2003) cites an extensive list of research that makes it clear that the physio-chemical forms of metals in different sludge products exert strong control over immediate or short-term solubility and extractability, and that total metals in sludge have limited predictive value for short-term crop uptake or leachability of toxic metals. Short-term behaviour of the metals in sludge-amended soil is unlikely to be closely correlated to sludge quality as defined by total metal concentrations. (McBride, 2003)

3.7.2 The relationship between total and leachable fractions

The leachable value for a specific contaminant can be significantly less than the total value or it may be equal to the total value (Kosson *et al.*, 1996). Viguri *et al.*, (2000) compared the metal hydroxide solubility factors with the leachable amounts from metal finishing sludge. They concluded that the mobility of metals from industrial waste could not be related to pH or solubility of their related metal hydroxides. Yet small amounts of soluble metal species in the waste could be responsible for dramatic changes in the concentrations of the metals in the leachate.

An often-misleading estimate of inorganic leaching from wastes and soil is to assume that release continues until the total constituent content has been depleted. The cumulative leaching over an extended period of time will not equal the total fraction (van der Sloot *et al.*, 1994).

3.8 Materials being leached

3.8.1 Inorganic and organic materials

Waste materials that have the ability to leach contaminants include; ashes, sludge, contaminated soil, mine tailings and slurries (Environment Canada, 1990). Leachate tests are usually done on inorganic materials like municipal solid waste incinerator bottom ash, blast furnace slag, steel slag, wood ash, fly ash; air pollution control residues and slags from ferrochrome industries (Fällman and Hartlén, 1994; Kosson *et al*., 1996; Fällman, 1997; Hattingh and Friend, 2003). Since these types of waste materials are all dry samples that are wetted during the leaching, solubility is of vital importance (Kosson *et al*., 1996).

Many leachate tests are used to leach both organic and inorganic constituents. The TCLP is one of these that has a special condition, applicable to organic fraction only (Kimmell *et al*., 2001; USA EPA 1992, and USA EPA 1999).

3.8.2 Multiphase materials

Leaching of multiphase wastes includes metal finishing sludge and digested sewage sludge (Fytianos *et al*., 1998; Viguri *et al*., 2000; Snyman, 2001). For multiphase waste, solubility is not a crucial factor since the contaminants from the sample are already soluble. Wang and Viraraghavan (1997) leached mixtures of organic and inorganic waste (fly ash from an electricity generation station and primary digested sludge), finding that the mixtures leached out less metal than the organic material (digested sludge) and claimed it to be due to precipitation followed by sorption of the metals onto the solid particles.

3.8.3 Leaching of sewage sludge

The reason that leaching tests on sludge needs to be done is to gain sufficient characterisation knowledge to (Fytianos *et al.*, 1998):

- assess the elemental leaching behaviour of sludge-amended soil to devise environmentally and agronomically sound management practices,
- determine what proportion of the elements present in the residue can be removed by leaching,
- determine what will be the behaviour of a pile of this material when exposed to external influences and how this will affect the environment.

Sludge is being co-disposed with municipal waste in Kuwait. It is a major contributor to the formation of toxic or potentially toxic leachate in such a co-disposal situation. The formation of potentially toxic leachate is of vital importance in arid conditions with low rainfall since the chemical composition of the leachate is dependant on the water content of the waste material (Al Yaqout, 2003).

3.9 Conclusion

Analysis of waste materials is important to determine the usability of the waste and the effect it will have on the surrounding environment whether it is disposed of or beneficially used.

Total extraction, although not discussed in depth is most used for elemental determinations. Sequential extractions yield information about the chemical form of the contaminants in the waste as well as to what they are bound.

Leaching tests consider the available fraction of the contaminants. This data can be further used to determine the short-term impacts of the contaminant.

Leaching tests are broadly categorised into equilibrium tests and dynamic tests. The two categories are used to determine different effects that contaminants will have on the environment where they are used, or disposed.

The three types of extraction tests are all equally important and one cannot be used as a replacement for any of the others. They all determine the effect a contaminant from a waste will have on the receiving environment, but different effects are considered depending on the selected test.

The test types discussed here can be applied to a variety of waste. Sewage sludge is a difficult material test due to both solid and liquid phases in the same sample. Four single step equilibrium leaching tests were chosen for further evaluation of sewage sludge and they are reviewed in Section 4.

4 A literature review of the selected leaching procedures

4.1 Test types

There are various tests available for leaching of soil and sludge. They focus on metal bioavailability and mobility in soil and sludge. No commonly accepted method is in use. This has led to studies being incomparable.

Some of the leaching tests considered for this study were:

- The Netherlands availability test (Nederlands Norm, 1995; Fällman and Aurell, 1996; Fytianos *et al.*, 1998) that is a pH static test. A pH static test can be used when one expects a dramatic pH change. This is usually for waste materials from thermal processes (Fällman and Aurell, 1996).
- The USA Toxicity Characteristic Leachate Procedure (TCLP) that was designed to determine the mobility of organic and inorganic constituents in liquid, solid and multiphase wastes under specific conditions (USA EPA, 1992, and Fytianos *et al.*, 1998).
- The DIN test that was developed to assess the leaching of sludge and sediments from water and wastewater. It is applicable to solids, pastes and sludge. This test makes a distinction between readily soluble constituents and sparingly soluble constituents by repeat extractions (German Standard, 1984; Fytianos *et al.*, 1998 and, van der Sloot, 1996).
- The AFNOR test is a leachate test that is specifically restricted to solids (Fytianos *et al.*, 1998 and van der Sloot, 1996).
- The Swiss TÜV test simulates leaching under saturated carbon dioxide conditions (Fytianos *et al.*, 1998 and van der Sloot, 1996)

4.1.1 Selection of a leaching test

Selection of a leaching test needs to consider the nature of the sample being leached as well as the waste disposal practice for the specific sample (Shieh, 2001). When there is a lack of an appropriate test for specific needs authorities tend to choose an inappropriate test. Fytianos *et al.*, (1998) cites an example where an inappropriate test was chosen for Greece. This might also be the case in South Africa concerning the applicability of the TCLP on sewage sludge.

The four test procedures chosen for this study were the:

- United States of America (USA) Environment Protection Agency (EPA) Toxicity Characteristic Leaching Procedure (TCLP), since it is currently begin done on sludge in South Africa,
- Australian Standard 4439.3 that is meant to leach wastes, sediments and contaminated soil,
- DIN 38 414 S4 that is also meant to determine the leachability of sludge and sediment, and
- NEN 7341 that is meant to leach soil, building rubble and other waste materials.

4.2 The USA EPA TCLP

4.2.1 The history of the TCLP

The original intention when developing the TCLP was to replace the EP-TOX test. Both the TCLP and the EP-TOX were developed with the intention of simulating leaching in a municipal landfill environment where hazardous waste is assumed to be co-disposed with municipal waste (Kimmell *et al.* 2001). It is commonly referred to as a mismanagement scenario, but the test developers at the time found to be the most appropriate reasonable worst-case scenario (USA EPA, 1999).

Operational difficulties required replacement of the EP-TOX test. These difficulties included problems with generating a reproducible leachate, questionable applicability of the generated leachate, and the test being inappropriate for analysis of volatile organic carbons (USA EPA, 1999). The TCLP was then developed to address these issues.

In the research done as part of the TCLP development the following was found: (USA EPA, 1999)

- a batch extraction format as the basic mode of test was preferred over a column test since it yielded more accurate results,
- an acetate buffer extraction solution should be used to simulate the effect of leaching decomposition,
- the TCLP was more accurate than other presently available leaching tests, and
- the TCLP was suitable for leaching organic compounds while the EP-TOX was not.

From this we can note that the mandate given to the TCLP developers was met.

4.2.2 Choice of leachate solution and liquid-to-solid ratio for the TCLP

The choice of leachate solution and liquid-to-solid ratio for the TCLP was explained at an EPA Public Meeting (USA EPA, 1999). The leachate solution ratio was determined by first assuming that the potentially hazardous waste on a landfill site would be 5% of the total volume of material on the site. The next assumption was that the waste on the landfill would decompose to produce acidic liquid. These two assumptions led to the choice of CH_3COOH as leachate solution.

The liquid-to-solid ratio (L/S) was chosen from laboratory experimentation done prior to the TCLP development that linked the volume of leaching fluid to the amount of waste. A concentration plateau of liquid-to-solid between 10:1 and 20:1 was found. From the assumption that the waste source will provide an infinite source of contaminants over time, the higher value was chosen. Many of the assumptions made in the TCLP development and mentioned above increase the reasons for a re-evaluation of the TLCP (USA EPA, 1999).

4.2.3 Current uses of the TCLP

Kimmell *et al.* (2001) specified two of the major intended uses of the TCLP in the USA. It is used to predict leachate concentrations of organic and inorganic contaminants in the specific land disposal scenario of co-disposal of an industrial waste on a municipal waste site. This application is also used in South Africa (Department of Water Affairs and Forestry, 1998). The second intended use is as a method to assess the degree to which treatment technologies are able to reduce the mobility of certain contaminants, mainly metals in the many Superfund sites found in the USA (Kimmell *et al.*, 2001).

4.2.4 Concerns with the TCLP

Since the development of the TCLP it has been applied extensively on various types of waste. This use has resulted in new concerns and problems. The concerns were expressed at the EPA Public Meeting, and included (USA EPA, 1999):

- questioning if the municipal co-disposal mismanagement scenario is the correct scenario to model,
- questioning of the accuracy and precision inherent in the TCLP,
- the difficulties encountered with certain wastes types and,
- questioning the appropriateness of the end-point (concentration on leachate compared to regulatory level) of the TCLP.

There is a programme to re-examine the TCLP in the USA. This re-evaluation is due to the relative inability of the method to adequately reflect the variety of conditions under which specific types of waste are disposed (Kimmell *et al.*

2001). The TCLP needs to be reviewed for three specific reasons (USA EPA, 1999). These are that:

- the TCLP is too broadly applied,
- a leach test can be improved by accounting for additional parameters, and
- the reliance of the EPA on a single mismanagement scenario has caused difficulties. The difficulties specified include legal proceedings against the EPA that they lost.

The EPA leachability tests have only been scientifically validated for limited applications. The most important of these is hazardous waste characterisation. Even for the applications where the EPA tests have been validated the procedures have known weaknesses (USA EPA, 1999). This is a situation where a test procedure was developed for a specific case and then the questions the test answers were adapted to the results obtained from the test. The question should first be asked and then a test procedure developed to answer that question (Quevauviller, *et al.*, 1996b).

The following suggestions were made:

- Additional extraction solutions for different test characteristics and disposal options (USA EPA, 1999). This is already the case in Australia where the Australian Standard a variant on the TCLP has allocated extraction solutions according to the disposal practice under consideration (Australian Standard, 1997 and Halim *et al.*, 2003).
- The TCLP could remain unchanged, and additional tests developed based on the material being leached and the disposal option (USA EPA, 1999).

The Australian Standard has not been discussed because of the similarities with the TCLP. The variation between the two procedures does not warrant any additional comments presently.

4.3 The NEN availability leaching test

4.3.1 Purpose of the NEN

According to the NEN availability test procedure, “availability” is defined as the maximum quantity or soluble fraction of a residue constituent that can be released into solution under aggressive leaching conditions. The values obtained from the test results should estimate maximum release over 1 000 to 10 000 years (Kosson *et al.*, 1996).

The purpose of the availability test is to indicate the quantity that may be leached out from a material under environmentally extreme conditions, for example, in the very long term, after disintegration of the material, fully oxidised, and complete loss of acid neutralising capacity (de Groot and Hoede, 1994).

The test aims to create a leaching optimum by decreasing the retarding effect of (Fällman and Aurell, 1996):

- diffusion length by using finely ground material,
- the concentration build-up by using a high liquid-to-solid ratio, and
- the pH influence on the solubility by using fixed pH values that promote dissolution.

The results are regarded as the maximum leachable specific amounts available over geological time (Fällman and Aurell, 1996). The test does not measure the silicate matrix and very poorly soluble mineral phases (van der Sloot ,1996).

The following aspects were considered during the development of the availability test (Garrabrants and Kosson, 2000):

- the fractional solubilisation needed to be maximised over the range of environmentally significant pH values.

- the extraction must be completed in a short time frame, usually one day (Fällman, 1997), and
- sample preparation, manipulations and specialised equipment are all minimised.

4.3.2 Validation of the NEN

To validate the NEN, extraction was done using six different materials (de Groot and Hoede, 1994) including incinerator fly ash, pulverised coal bottom ash, bottom ash, pulverised coal fly ash / cement stabilisation, calcium silicate brick with coal fly ash and bricks. A standard deviation of 5.2 % was obtained and it was found that the influence of different elements on the precision was low when the concentration was above 20 times the detection limit.

Lewin (1996) used the NEN pre-standard and did repeat analysis of Na, Cl, Ca, Ba, Zn, Pb and Cd on cement based solid waste. The percent relative standard deviation for the different metals ranged from 4.5 % for Ca to 95 % for Pb.

4.3.3 Areas of concern in the NEN

Fällman (1997) states that the definition of the availability test is not sufficiently clear and requires improvement. She explained that the basic principle of the test is to maximise the water solubility of the constituents and the diffusion from the particles to the bulk solution. This is done by three means:

- increasing in the solubility of the substance in relation to the pH,
- maintaining a steep concentration gradient between the pores and the bulk solution and,
- creating a large specific surface area by the small maximum particle size. This facilitates higher leaching values.

4.3.4 Suggested modifications to the NEN

Fällman (1997) found the three most important parameters in the NEN availability test are particle size, time of the second leaching and the liquid-to-solid ratio. She recommended a particle size where 95 % of the sample is below 125 µm, a leaching time of 18 hours in the second step and at liquid-to-solid ratio of 100:1 in both steps.

Since the initiation of this test, three modifications have been suggested. Table 4.3-A lists the parameters of concern, the current specified value and the recommended value.

Table 4.3-A: The recommended changes to the NEN availability test

Parameter	NEN 7341	Recommended Change
Liquid-to-solid Ratio[#]	50:1	100:1
Particle size[§]	> 100 µm	> 300 µm
Change to ensure fully oxidisible conditions[#]		

[#] Fällman, 1997; [§] van der Sloot *et al*., 1994

Garrabrants and Kosson (2000) used EDTA as a chelating agent and a single step, single pH extraction to achieve the procedure objectives more efficiently. The choice of EDTA was due to the fact that for many metals the chelated metals have larger solubility constants than metal hydroxides. Therefore EDTA will increase the metal solubility and many low solubility metals will become soluble as the EDTA complexes (Garrabrants and Kosson, 2000). They found values for EDTA extraction to be higher than that of the NEN availability test for both soil and municipal solid waste incinerator ash.

4.4 The DIN

The German procedure for determining the leachability of water-soluble compounds, determines the short-term release of harmful species only (Paschke *et al*., 1999). It is not only used in Germany but also in Spain as a compliance test done by landfill facilities. The chemical composition of the leachate is then compared to the limit values specified by the 1991 European Economic Community (EEC) Landfill of Wastes Draft (Viguri *et al.*, 2000).

4.4.1 Validation of the DIN

Extraction and analysis of Na, Cl, Ca, Ba, Zn, Pb and Cd was done by Lewin (1996) using the DIN. The percent relative standard deviation on a cement based solid waste varied from 0 % for Cd to 18 % for Zn.

In a comparison between the results obtained from the TCLP and DIN on a municipal solid waste incinerator bottom ash sample, in-homogeneity on the sample had a lesser effect on the DIN leachate concentrations than on the TLCP concentrations. This is because the DIN works in a pH range where solubility is controlled (van der Sloot, 1996). The addition of acid to the waste forces the leachate solution into a pH range where solubility of metals is changed due to the pH change.

4.4.2 Accelerated leaching test procedures

Maurer *et al.*, (1998) assessed accelerated on-site leaching methods and compared them with the DIN for soil and industrial sludge. The accelerated methods and some parameters are listed in table 4.4-B.

These methods were compared using a contaminated soil and an industrial sludge sample. For the soil sample, sonication yielded results the closest to the DIN while for the industrial sludge, it was one of the least suitable methods. Percolation and vortexing were the preferred methods for the sludge (Maurer *et al.*, 1998).

Table 4.4-A: Accelerated leaching methods and their associated parameters compared to the DIN (Maurer *et al.*, 1998)

Method	**Time** (min)	**Speed** (rpm)	**Temperature** (℃)	**Pressure** (mm H_2O)
DIN	1 440	35	21	
Stirring	5	max	21	
Shaking	5	max	21	
Sonication	5		21	
Vortexing	5	15 000	21 to 34	
Percolation	> 5		21	90
Heating	5		21 to 34	
Microwave irradiation	5		600 Watts	

A further case study was done on various test materials in an ultrasonic bath. For metal leaching an accelerated test speed of 20 min was found to be sufficient. The results were not equivalent to the DIN values, but revealed a constant ratio of between 20 and 80 % for the accelerated test against the DIN test values for metals. The correlation coefficient between the two tests was 0.95 for metals. Maurer *et al.* (1998) found the accelerated test methods to be sufficiently precise and reliable for accelerated on-site verification.

4.5 Leaching tests of the future

The present generation of leaching tests that are mainly used on building materials and municipal solid waste incinerator ash do not simulate oxidation and carbonation (Hage and Mulder, 2004). This needs to be addressed to better simulate the conditions found in the environment.

Hage and Mulder (2004) studied three next generation leaching tests that are used for building material leaching analysis. They are two characterisation tests, the Dutch Column Leaching Test and the new European pH-static test as well as one compliance test being the new European Shake test. All three tests are being standardised by the European Committee for Standardization (CEN) Technical Committee for Characterisation of waste (CEN TT 292). Hage and Mulder (2004) suggest that once characteristic leaching has been done (by the percolation test, or another column test) then shorter tests like the Shake test can be useful in ensuring legislative compliance.

4.6 Conclusions

Four test procedures were selected. The USA EPA TCLP, the Australian Standard bottle leaching procedure, the NEN water soluble leaching test and the DIN availability test.

The TCLP was developed for a co-disposal scenario where hazardous waste is co-disposed with municipal waste. It is currently being used for a wide variety of applications including to determine the effectiveness of specific treatment technologies. There is currently unhappiness about the wide use of the TCLP in the USA and therefore it is under review.

The NEN was developed to determined leaching under environmentally extreme conditions. Current concerns surrounding this procedure are with respect to specified physical parameters like particle size, extraction time and liquid-to-solid ratios.

The DIN was developed to leach water-soluble contaminants. It is focused on short-term release of harmful species.

Once leaching has been done, accelerated test methods can be used to ensure that leaching changes do not occur. New leaching tests consider two new factors during leaching. These are oxidation and carbonation reactions that occur during the test due to the properties of the waste being leached.

Many physical and chemical parameters are shared between these the chosen procedures. Section 5 investigates some of the important parameters and their effect on the amount of contaminant leached.

5 Parameters of importance when leaching

5.1 Introduction

There are many parameters that can be varied when doing leachable extractions. Some of these make a vital difference to the results while others yield little to no change in the results. The parameters can be divided physical and chemical parameters.

5.2 Physical Parameters

Physical parameters include sample mass, age, drying, particle size, liquid-to-solid ratios, method of contact; temperature during extraction and leachate separation. Table 5.2-A lists and comments on these parameters. Some of the more influential parameters are discussed individually in the sections below the table.

Table 5.2-A: Physical parameters of importance when leaching

Parameter	Comment
Sample Mass	Sequential extraction with varied sample mass had no improvement in precision[#].
	Aqua regia extraction with smaller mass than prescribed had no effect on final result[§].
Sample Age	Increases and decreases in leachable amounts of municipal solid waste incinerator bottom ash when dry samples stored. Change due to crystallisation and hydration of sample and increased surface area due to grinding[¶].
	No change in EDTA extractions of air-dried soil samples stored in glass bottles for Cd, Ni, Pb and Zn. But change for Cu and Cr[¦].
Sample Preparation	See Section 5.2.1

Particle Size	No change with for dried sewage sludge for Cd, Mn and Pb[*]. Decrease in leachability with increase in particle size for Fe, Zn and Cu[*].
	Decrease in leachability of Pb with increase in particle size for cementitious material. Trend reversed when leachate solution was changed from 0.1 mol L^{-1} to 0.6 mol L^{-1} TCLP solution[+].
	125 µm reduction leached more than 250 µm (with NEN) for Si, Fe, Ca, Al, Na, K, Mg, S, Ti, P, Cu, Zn, Mn, Sr, Cr, Zr, Sn, V, W, Co, As, Mo, Nb, Cd, Be, and Hg in municipal solid waste incinerator bottom ash[¶]. For Pb and Ni particle size made little difference[¶]. For Ni larger particle size leached more[¶].
	Leaching is sub-surface controlled process for particle sizes between 63 and 2000 µm. Therefore minimum particle size is also recommended [Π]. Below 63 µm leachability decreases due to co-precipitation. This can under-estimate hazardous potential of waste [Π].
Liquid-to-solid Ratio	See Section 5.2.2
Method of Contact	Use glass, stainless steel or plastic depending on contaminant under investigation to prevent unwanted exchange between leaching vessel and leachant[¤].
	Using reciprocating shaken instead of an end-over-end shaker caused lower values for Cd, Cr, Cu, Ni and Zn for both EDTA and CH$_3$COOH extraction solutions[°]. For Pb EDTA was more with end-over-end shaker. Pb was also more with CH$_3$COOH and reciprocating shaker than end-over-end shaker[°].

	Speed tolerance of 30% (21 to 39 rpm, when 30 rpm stipulated) yielded comparable results. Rotation speed of 14 rpm was also comparable[¬]
	DIN specifies no rotation speed[»].
Contact Time	See Section 5.2.3
Temperature	Leaching test are usually done at room temperature[¤]
Leachate Separation	Three main types of filter paper are recommended: • Cellulose nitrate[×]. • Membrane[*]. • Borosilicate glass microfibre[Ŧ].
	Centrifugation prior to filtration is recommended to prevent clogging of filter paper[×]. This has no effect on final leachate concentrations. [°]

[#] Davidson *et al.*, (1999); [§] Ščančar *et al.*, (2000); [¶] Fällman (1997); Ure *et al.*, (1993);
[*] Fytianos *et al.*, (1998); [+] Halim *et al.*, (2003); [Π] Karius and Hamer (2001);
[¤] Environment Canada (1990); [°] Quevauviller (1998a); [¬] Quevauviller (1998b);
[»] German Standard (1984); [×] Fällman and Aurell (1996); [Ŧ] USA EPA (1992)

5.2.1 Sample preparation

Sample preparation usually includes a partitioning between different phases in a waste. Phase separation is done on waste that contains free liquid. The leaching test is done on the solid portion of the waste. The free liquid is the initial leachate and is analysed for contaminants. It can be analysed separately or in conjunction with the waste leachate. Liquid / solid separation can be done by settling, decanting, centrifuging and pressure filtration (Environment Canada, 1990).

Drying of samples

The TCLP as specified in the USA requires that samples should not be dried if they are multiphase and above a percent solids content of 0.5 % (USA EPA, 1992). The South African adapted procedure specifies that all sampled should be entirely dry (Department of Water Affairs and Forestry, 1998). The effects of drying on the results obtained will be further investigated in this research.

Drying is said to be the best compromise for achieving stability and homogeneity of samples (Davidson *et al.*, 1999 and Ure, 1996). Sludge samples have been dried at 40℃ (Snyman *et al.*, 2004), and 105℃ (Campanella *et al.*, 1987; Fällman and Hartlén, 1994; Fytianos *et al.*, 1998; Snyman, 2001; Welgemoed, 2002). Air drying with continuous movement to prevent fungal development was used by Álvarez *et al.*, (2002). Ure (1996) suggests soil drying at temperatures below 40℃.

Rudd *et al.*, (1988) did sequential extractions on both dry and liquid sludge samples. They found that there was generally a smaller variation between repeat samples of dry sludge than liquid sludge. They also found that metals are more readily soluble in dry sludge than liquid sludge. Rudd *et al.*, (1988) suggests that since liquid sludge is applied to land and not dry sludge, liquid sludge should be analysed. Even if the liquid is concentrated up, the hydration state remains. Field-moist soil samples were compared to air-dried samples with *aqua regia* extraction and found that air-dried values were lower (Davidson *et al.*, 1999). This suggests that the changes due to drying affect the extraction of trace elements.

The drying of soil is still considered advantageous (Quevauviller, 2002) and is encouraged (Ure, 1996) as being a practical solution to prevent storage difficulties under conditions where oxidation and reduction processes as well as microbiological transformations and loss of volatile components can occur. Despite these recommendations Ure (1996) acknowledges that vital information on speciation may be lost due to sample drying.

5.2.2 Liquid-to-solid ratios

Liquid-to-solid ratio (L/S) is the ratio of the amount of leachate to the amount of waste during leaching. It can be expressed in many ways; these include (Environment Canada, 1990):

- volume of leachant to mass of waste (Eighmy and van der Sloot *et al.*, 1994);

- mass of leachate to mass of waste, or (Environment Canada, 1990)
- volume of leachate to surface area of waste (Environment Canada, 1990). This is for monolithic waste only.

An additional complication arises since the mass of the waste can be expressed on a dry or wet basis. This becomes a concern when multiphase waste samples are being considered. For some leachate tests the liquid phase of the waste is included as part of the leachant (Environment Canada, 1990).

The effect of the change in the liquid-to-solid ratio gives an indication of whether solubility of diffusion-controlled leaching conditions prevail. Solubility-controlled conditions result in concentrations in the leachate independent of the liquid-to-solid ratio, and unconstrained diffusion-controlled conditions result in leached amounts from the material independent of the liquid-to-solid ratio (Fällman, 1997).

For highly soluble contaminants the leachate concentration is inversely proportional to the liquid-to-solid ratio. This means that for highly soluble contaminants a high liquid-to-solid ratio yields a low concentration of that species in the final leachate. For contaminants with a low solubility the final leachate concentration of that contaminant is independent of the liquid-to-solid ratio. The final leachate concentration of contaminants will depend upon (Environment Canada, 1990):

- the amount of contaminant in the waste,
- the solubility of that contaminant and,
- the transport of the contaminant from the waste to the leachate.

The effect of liquid-to-solid ratio on amount leached out is element specific. Fällman (1997) reported no change for K, Ni, Co, Mo and Cl when the liquid-to-solid ratio was changed, and an increase for many other elements with almost a doubling for Pb, Ba, Cd, Al and As when the leaching solution was increased from 50:1 to 100:1 in the NEN availability test. A further change in leached amounts was observed when the liquid-to-solid ratio was again increased to 200:1. Cu, Cr and Pb increased by between 30 and 40 % respectively after 3 hours. Yet Fe and Cd experienced a decrease in leached amounts under the same conditions. The effect of increasing the liquid-to-solid ratio up to 100:1 in the second step of the NEN availability test is that there is a greater chance of interference from air in the form of carbon dioxide adsorption into the solution (Fällman, 1997).

Townsend *et al.*, (2001) did TCLP on contaminated soil samples with liquid-to-solid ratios of 5:1, 10:1, 20:1, 50:1, 100:1 and 150:1. When considering the leachability of As and Cr they found that as the liquid-to-solid ratio increased so the metal concentration decreased with two exceptions. For As the ratio of 5:1 and 10:1 yielded the same concentration and for Cr the liquid-to-solid ratio of 100:1 and 150:1 yielded the same concentration.

Halim *et al.*, (2003) used various liquid-to-solid ratios ranging from 10:1 to 60:1. With a 0.1 mol L^{-1} CH_3COOH solution the cementitious material leached Pb higher at ratios between 10:1 and 20:1 and dropped down to the detection limit at 50:1. Cd was not measurable. Changing the solution from 0.1 mol L^{-1} to 0.6 mol L^{-1} CH_3COOH the leachability of Pb and Cd was dependant on the change in pH rather than the increase in liquid-to-solid ratio.

Selecting optimal liquid-to-solid ratios

An optimal liquid-to-solid ratio for the van der Sloot test for Zn, Fe, Pb, Mn and Cd was found to be between 60 and 100 to one. No increase for Fe, and Zn was found with an increase in the liquid-to-solid ratio while a slight increase for Cd, Pb and Mn was found (Fytianos *et al.*, 1998).

Kimmell *et al.*, (2001) suggested that site-specific precipitation and evaporation data should be investigated to determine the liquid-to-solid ratio required for a leachate test to replace the TCLP. When relating liquid-to-solid ratios with field conditions, liquid-to-solid ratios lower than 2:1 represent a restricted throughput of water through a waste material in the environment.

This is usually for sealed waste materials. Liquid-to-solid ratios of 10:1 and larger are usually representative of waste materials that will be exposed to a larger throughput of water. It is usually used for waste materials that are unsealed or to be reused (Wahlström, 1996).

Liquid-to-solid ratio selection should be chosen so that final contaminant concentrations are above detection limits and that the solubility of the contaminants is not jeopardised (Fällman, 1997 and Environment Canada, 1990).

5.2.3 Contact time

Contact time needs to be long enough for equilibrium to occur in extraction tests (Environment Canada, 1990; Fällman and Aurell, 1996). Equilibrium is reached when there is no concentration gradient between the waste particles and the leachant (Fällman and Aurell, 1996). Townsend *et al.*, (2001) claims that the TCLP, with its specified leaching time of 18 hours might not be sufficient for equilibrium to occur. This would lead to a mis-estimation of the amount of contaminant that will be leached. Fällman (1997) determined that for the NEN availability test the time dependence of the second step is more important than that of the first step and therefore suggested an amendment to the NEN availability test by increasing the leaching time of the second leach to 18 hours (presently 3 hours).

Extended leaching tests

Townsend *et al.*, (2001) did TCLP extraction with leaching times between 0.1 and 1000 hours on a contaminated soil sample to determine As, and Cr. The mass of metal leached increased throughout the extended test and did not reach an equilibrium value for As and Cr. Halim *et al.*, (2003) also did TCLP extraction with extended leaching times on cementitious material with times from 18 hours to 168 hours. Pb increased rapidly for the first 50 hours and thereafter gradually increased to a plateau at 150 hours.

Fällman (1997) did extended leaching using the NEN availability test on Cu, Cd, Cr, Pb and Fe. The test ran for 100 hours. The maximum leached amounts were generally obtained around 24 hours. These amounts were not all stable after 24 hours.

The effect of particle size on contact time

Fällman (1997) also reported the effect of particle size on contact time. The smaller the particle size, the longer the contact time required to reach the same amount of leaching. A particle size of 125 µm with contact time of 10 to 20 hours corresponded to a particle size of 250 µm and contact time of 25 to 60 hours.

5.3 Chemical Parameters

Chemical parameters include reagent water, extraction solutions and pH and buffer capacity. Table 5.3-A lists and comments on these parameters.

Table 5.3-A: Chemical parameters of importance when leaching

Parameter	Comment
Reagent Water	DIN requires single distilled water[#].
	TCLP requires Type II reagent grade water*. (Bacteria < 1000 CFU mL^{-1}; Resistivity > 1 MΩ cm at 25℃; Conductivity < 1 µΩ cm^{-1} at 25℃; SiO_2 < 0.1 mg L^{-1})[¤].
	NEN uses water with electrical conductivity below 1.0 µS cm^{-1}[§].
	Water with final electrical conductivity less than 0.2 mS cm^{-1} was made by reverse osmosis followed by ion exchange for NEN[¶].
Extraction Solution	See Section 5.3.1
pH and Buffer Capacity	See Section 5.3.2

[#] German Standard, (1984); * USA EPA 1992; ¤ USA Standard Methods, (USA APHA *et al.*, 1995); [§] Nederlands Norm, (1995); [¶] Fällman and Aurell (1996)

5.3.1 Extraction solutions

Leachant composition (or extraction solution) is a vital consideration in leaching tests. The type and quantity of contaminants that will be released is dependant on the leachant composition. Chemical properties of the leachant that will influence the mobilisation of contaminants are pH, redox potential, ionic strength, chelating and complexing ability and buffering capacity. Commonly used leachants can be grouped into water, site-specific liquids (either real or synthetic) and chemical solutions (Environment Canada, 1990).

Table 5.3-B represents some common soil leachates and what they aim to extract (adapted from Quevauviller *et al.*, 1996a).

Table 5.3-B: Some common soil extraction solutions and why they are used

Extraction solution	Extracts
Aqua regia HF	Risk assessment prior to spreading sludge on agricultural soil
EDTA DTPA CH_3COOH	Trace metal mobility Soil-plant transfers Study of physio-chemical processes
$CaCl_2$ $Ca(NO_3)_2$ HCl DTPA NH_4NO_3[#]	Plant uptake studies Soil deficiency assessment and remediation Fertility studies Risk assessment Also applied to sludge samples
$Ca(NO_3)_2$ CH_3COONH_3	Risk Assessment Evaluation of soil multi-functionality
NH_4Cl Acid oxalates	Differentiation of lithogenic and anthropogenic origin of some critical elements in soils

[#] Bhogal *et al.*, 2003

Bioavailability of metals is determined by $CaCl_2$ (Antoniadis and Alloway, 2002) or NH_4NO_3 (Bhogal *et al.*, 2003). McGrath *et al.*, (2000) used $CaCl_2$ to extract the exchangeable and soluble metal fractions in soil. McGrath and Cegarra (1992) sequentially extracted sludge samples and found that the $CaCl_2$ (first extraction) extracted similar amounts of metal except for Cd from sewage sludge-amended soil and inorganic fertilised soil.

Halim *et al.*, (2003) did TCLP extractions using CH_3COOH and HNO_3 on cementitious material and analysed for Cd and Pb. For Cd the two solutions were in comparable but not for Pb.

Garrabrants and Kosson (2000) used single extraction with an EDTA solution to determine the potential mobile content of inorganic constituents on wastes. Bermond *et al.* (1998) used EDTA as a non-specific reagent that extracted trace elements from several soil fractions. Quevauviller (1998b) reports that from an inter-laboratory study, EDTA extracted both carbonate bound and organically bound metals from calcareous soil. EDTA was chosen by the European Bureau of Reference (BCR) as the extraction solution of choice for leaching metals from soil in place of CH_3COOH since CH_3COOH is less suitable for calcareous soil (Ure, 1996). Snyman (2001) compared EDTA and CH_3COOH extraction data for Cd, Cu, Pb and Zn with soil, sludge and sludge-amended soil. She found that higher results for EDTA than CH_3COOH extractions.

The EPA has reviewed the applicability of the TCLP and found that in some specific cases the acidity of the TCLP leachate solution meant that metals were precipitating out of the final leachate. To overcome this problem the EPA suggested that a replacement of the acetate buffer solution with deionised water. No further developments have to date been noted on this point (Kimmell *et al.*, 2001). Kimmell *et al.*, (2001) further suggests that the leachate solution be deionised water or a synthetic site-specific rainwater.

Water is also used as an extraction solution. It was used to determine the water-soluble phase of air dried sewage sludge before the sludge was added to a soil and packed in a column (Ashworth and Alloway, 2004). The Australian Standard (1997) uses water as a site-specific leachate. If the waste material is to be disposed of on an on-site undisturbed landfill or without any additional treatment, then water is used as leachant. If the waste is non-putrescible then a basic tetraborate buffer leachant ($Na_2B_4O_7 \cdot 10H_2O$) is used (Australian Standard, 1997 and Halim *et al.*, 2003).

Varing the type of acid for the NEN availability test affects the amounts leached. Using HNO_3 only silicas and fully-oxidisable conditions are not obtained. Changing to HCl increases the Cl content and affects the ICP analysis of As and Cr (Fällman, 1997).

Care should be taken that the chosen leachate solution does not interfere with the matrix of the sample. Shieh (2001) cites an example where a HCl + HNO_3 leachant is used on municipal solid waste incinerator ash and the SO_4^{2-} in the leachant interferes with the metal concentrations being leached out, since minerals in contact with SO_4^{2-} don't leach under these conditions.

5.3.2 pH and buffer capacity

pH

pH influences both the speciation and the solubility of the metals in the leaching procedure (Halim *et al.*, 2003 and Glasser, 1997). As the pH decreases so the percentage of metals leached increases (Fytianos *et al.*, 1998). Halim *et al.* (2003) found that pH has an influence on amount of Pb and Cd that leached out of cementitious waste since it affects the solubility of the metals. At high pH values the metals form insoluble hydroxides that precipitate out of the leachate (Halim *et al.*, 2003).

Most leachate tests have uncontrolled final pH values. This means that the solubility of the metals in the waste is dependant on the buffer capacity of the waste or the leachant. The pH of the leachant will also affect the solubility of the metals. Therefore both the leachant and the waste properties will influence the amount of metal leached. The DIN, AS and TCLP all are categorised as fixed pH tests (German Standard, 1984; Australian Standard, 1997 and USA EPA, 1992). A pH static test maintains a constant pH throughout the test by adjustment with acid or base. (Fällman and Aurell, 1996). The DIN, AS and TCLP have a fixed pH for the leachant but once it comes into contact with the waste the pH changes and is not adjusted during the course of the leaching. The NEN is a pH static test where the pH is adjusted throughout the leaching process (German Standard, 1984; Australian Standard, 1997; USA EPA, 1992 and Nederlands Norm, 1995).

In a comparison where waste was leached with a pH static test, sewage sludge and sludge-amended *terra rossa* soil displayed high leachate concentrations at small and large pH values and low concentrations at pH values near 6 for Cd and 8 for Zn (van der Sloot, 1996). Karius and Hamer (2001) found that leachability of Mg, Ca, V, Cr, Mn, Ni, Cu, Zn, As, Sr, Cd and Ba was high at pH 4 and decreased as pH increased for bricks made from harbour sediment. They also found that Al and Si leached least in the neutral pH range and more in the higher and lower pH ranges. Townsend *et al.*, (2001) did pH static leachate tests on contaminated soil and determined the leachate concentrations at various pH values ranging from 2 through until 13 for As, Cr and Cu. The highest values were at pH 2 and the lowest at pH 6 for all the metals. Halim *et al.* (2003) leached cementitious waste with varying CH_3COOH concentrations ranging from 0.1 mol L^{-1} to 5.7 mol L^{-1}. At concentrations between 0.1 mol L^{-1} and 1.0 mol L^{-1}, an increase in the acid concentration resulted in a decrease in the leachate pH from 12 to 4. A further increase in the acid contribution did not change the pH. This indicates that the acid neutralisation capacity of the waste material was met at pH values above 1.0 mol L^{-1}.

Buffer capacity

Due to the buffer caacity of the sample, the pH of the final product is mainly dependant on the waste sample and not the extraction solution. For waste samples with a high alkalinity, the buffer capacity is large and it affects the final pH by buffering the acid added as leachant (Wahlström, 1996).

Halim *et al.* (2003) claim that the ability of the waste to modify the pH of the leachant can have major implications on regulatory decisions that are based on leaching results. Using the USA TCLP or Australian Standard on basic wastes, would underestimate the amount of metal that leaches out of the waste (Halim *et al.*, 2003).

Fällman (1997) determined the factors that play an important role in acid consumption are particle size, liquid-to-solid ratio, and time dependence of leaching.

Paschke *et al.*, (1999) did a pH static test on four different sediment samples continuing the test until the acid neutralisation capacity of the sediment did not change for more than 12 hours. They found that the samples all consumed between 1500 and 2000 mmol L^{-1} of HNO_3 per kg sediment and it took roughly 186 hours before the neutralisation capacity was exhausted. The acid neutralisation capacity was also compared with a mathematically determined acid requirement. This requirement was calculated based on the assumption that all the Ca in the sample was in the form of $CaCO_3$. These values compared very well with each other (r^2=0.9816).

The neutralising capacity of the waste is of concern when cementitious waste materials are leached with acid (Garrabrants *et al.*, 2004). Since cementitious wastes have a high acid neutralising capacity, they neutralise the leaching fluid and this leads to high pH leachates and precipitation of the metals to form metal hydroxides (Halim *et al.*, 2003).

5.4 Additional parameters

5.4.1 Units of leaching data

Leaching data can be expressed in two different ways. The first is as the leachate concentration expressed as mass of contaminant leached out per volume of leachant (mg L^{-1}). The second way is as mass of element leached out per mass of dry sample (mg kg^{-1}) (Eighmy and van der Sloot, 1994; and Kossen et al, 1996). To compare data where different liquid-to-solid ratios are used, the dry solid basis is required (van der Sloot, 1996).

5.4.2 Statistical analysis

Leachate tests need to be repeatable, especially if they are used for regulatory compliance. Repeatability is the precision under conditions where independent test results are obtained with the same method on identical test materials in the same laboratory by the same operator using the same equipment within short intervals of time (de Groot and Hoede, 1994). Repeatability depends on the combination of sampling error, variation in the test performance, the final pH of the test and the analytical error in assessing the leachate composition. The final pH will affect the size of the standard deviation (van der Sloot, 1996) for metals since the solubility is pH dependant. A large standard deviation can also be attributed to sample in-homogeneity (van der Sloot, 1996).

The experimental accuracy and trueness to the real environmental situation is an important aspect of a leaching test. Kimmell *et al.*, (2001) claim that the level of accuracy required for a leachate test needs to be of such a nature that critical decisions based on the test results are easily made.

5.4.3 Analysis of leachate

Leachate analysis is usually done by atomic absorption (AA) or inductively coupled plasma (ICP) techniques. McGrath *et al.*, (2000) found a very good agreement between inductively coupled plasma atomic emission spectrometry (ICP-AES) and graphite furnace atomic absorption spectrometry (GFAAS) with a linear regression equation of GFAAS = 0.92 ICP-AES (r^2= 0.96, n=124). Quevauviller (1998b) found that when analysing metals extracted with EDTA, flame atomic absorption spectrometry (FAAS) with an air / acetylene flame was unacceptable but for CH_3COOH extractions worked well, except for Pb that was too near the detection limit. The use of standard addition is a possible option to obtain accurate data for value near or below the detection limit (Quevauviller *et al.*, 1996a).

5.5 Important parameters for the TCLP, AS, DIN and NEN

Table 5.5-A indicates the important parameters considered above for the TCLP, AS, DIN and NEN as they were done in this research.

Table 5.5-A: Important parameters for the TCLP, AS, DIN and NEN

Parameter	**TCLP**[#]	**AS**[*]	**DIN**[§]	**NEN**[¶]
Sample Mass	100 g			16 g
Extraction Solution	CH_3COOH	Demineralised water		HNO_3
Liquid-to-solid ratio	20:1		10:1	50:1
Method of Contact	End-over-end rotator at 30 rpm			Magnetic stirrer
Contact Time	18 hours	20 hours	24 hours	3 hours
Number of sequential extractions	None		Optional. Two used	Two. pH =7 then pH = 4

[#] USA EPA (1992); [*] Australian Standard (1997); [§] German Standard (1984); [¶] Nederlands Norm, 1995

6 Materials and methods

All apparatus used was initially soaked in a HNO_3 (1 *N*) for a minimum of 24 hours. Thereafter the apparatus was rinsed three times with distilled water. All reagent water used in this research was demineralised water irrespective of the procedure. The DIN (German Standard, 1984) suggests distilled water but to make the procedures comparable it was not used.

6.1 Sampling

Sludge samples were collected from twenty-four different wastewater treatment plants (Samples A1 to A24). These samples were used to determine the relationship between the total (*aqua regia*) and leachable (TCLP - as practised in South Africa) extraction procedures.

Two additional anaerobically digested samples were collected at one wastewater treatment plant on the East Rand (Sample B and C). The samples were taken two months apart. Sample B (100 L) was used to determine the relationship between dried and wet sample preparation. This is the major difference between the TCLP as practiced in South Africa and the USA EPA regulated TCLP. Sample C (250 L) was used to extract elements according to the USA EPA TCLP, AS, NEN and DIN. It was further used to compare dried and wet samples with the NEN. The samples were stored at 4℃.

6.2 Total and leachable fractions

Samples A1 to A24 were oven dried at 50℃. They were then each split into two sub-samples. One was used to determine total extraction with *aqua regia* (Section 6.2.1) according to the procedure outlined by the Soil Science Society of America (1996). The second sub-sample was used to determine the leachable TCLP fraction (Section 6.2.2) according to the procedure by the

South African Department of Water Affairs and Forestry (1998) and the USA EPA (1992) TCLP where the condensed South African version was not clear. Figure 6.2-A is a schematic diagramme of the experimental procedure followed for Sample A1-A24.

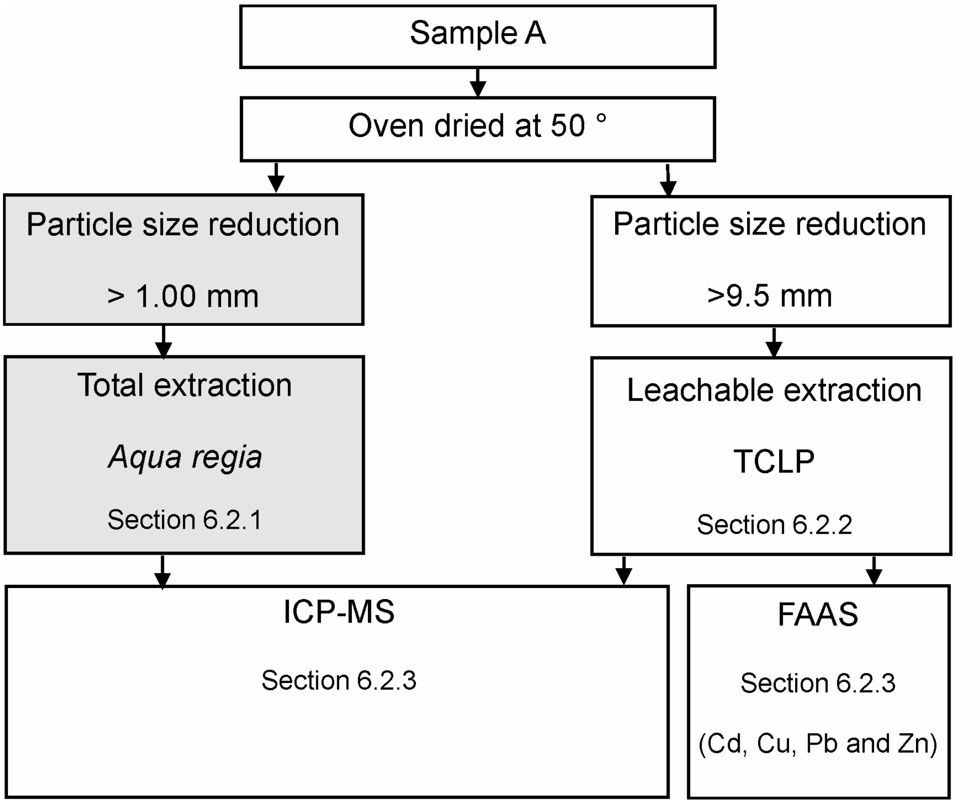


Figure 6.2-A: Schematic diagramme for procedures followed for Sample A

6.2.1 Total *aqua regia* extraction

The samples were crushed to pass through a 1.0 mm sieve. An *aqua regia* reagent was prepared by mixing 3.0 mL of 12.0 mol L^{-1} 36 % (m/m) HCl with 1.0 mL of 15 mol L^{-1} 70 % HNO_3. A half a gram (0.5 g) of the crushed sample was placed in a polypropylene bottle and 1.0 mL *aqua regia* reagent was added. Ten (10) mL of 29 mol L^{-1} 48 % (m/m) HF was also added to the polypropylene bottle. The bottle thread was double wrapped with Teflon tape and closed to a tight fit. It was shaken for a maximum of 8 hours to dissolve the entire sample. After two hours of shaking the bottle was heated between 75° and 100 °C for 30 min to assist in dissolving the still undissolved portion of the sample. Once the entire sample was dissolved, the bottle was allowed to cool to room temperature. One hundred (100) mL saturated H_3BO_3 was added to the sample and the bottle was immediately capped. The bottle was then cooled to 25 ℃ since the addition of the H_3BO_3 produces an exothermic reaction. The bottle was placed on an analytical balance and distilled water was added to the sample until the total mass of the sample and the water was 200 g. The samples were then stored at 4℃ until further analysis (Section 6.2.3).

6.2.2 Leachable TCLP extraction

The sample was crushed to pass through a 9.5 mm sieve. A 5 g subsample was initially used to determine the correct extraction solution. Demineralised water (96.5 mL) was added to the 5 g and it was stirred for 5 min using a magnetic stirrer. The pH was measured. If the pH was below 5.0 pH units, extraction solution one was to be used. If the pH was above 5.0 pH units 3.5 mL HCl (1 *N*) was added to the sample. It was placed in a hot water bath at 50℃, allowed to reach 50℃ and left at that constant temperature for 10 min. The sample was then allowed to cool to ambient temperature and the pH measured. If the pH was below 5.0 pH units then extraction solution one was to be used. If the pH was above 5.0 pH units, extraction solution two was to be used.

The extraction solutions were prepared as follows:

Extraction solution one: 5.708 mL glacial CH_3COOH was added to 500 mL demineralised water. 64.3 mL standardised NaOH (1 *N*) was added and then diluted to 1 L. The pH was measured and any solution with pH range outside of 4.93±0.05 pH units was discarded.

Extraction solution two: 5.708 mL glacial CH_3COOH was added to demineralised water and then made up to a volume of 1 L. The pH was measured and any solution with a pH range outside of 2.88±0.05 pH units was discarded.

One hundred (100) grams of dry sewage sludge (Samples A1 to A24) was weighed off to an accuracy of 0.01 g in a 2 L glass bottle with a screw cap. Two (2) L of relevant TCLP extraction solution was added to the bottle and it was fastened into an end-over-end rotator that rotated the bottles at 40 rpm for 20 hours. Once the samples were removed from the rotator, 250 mL of the mixture was centrifuged at 12 000 rpm (G = 21 000 kg m s^{-2}) for 20 min. The liquid portion was filtered through 0.7 µm Gelman glass filter paper. The pH was recorded and the leachates acidified with 25 % (m/m) HNO_3 to a pH below 2.00 and stored at 4℃ until the metal analysis was done (Section 6.2.3). Leachate (250 mL) was collected, acidified and stored.

6.2.3 Metal determination

The *aqua regia* digested and TCLP leached samples were analysed on a VG Plasmaquad PQ2 Turbo Plus Inductively Coupled Plasma Mass Spectrometer (ICP-MS) for Cd, Co, Cr, Cu, Hg, Mo, Ni, Pb, Se and Zn. The TCLP leached samples were also analysed on a flame atomic adsorption spectrometer (FAAS) for Cd, Cu, Pb and Zn. The FAAS analysis was done in triplicate and the mean value of the three determinations was used.

6.3 Variation in sample preparation

Samples B and C were used in this section. Forty (40) L of sample B (Sample B1) was air dried for 4 weeks in drying pans indoors. An empty drying pan was used as a blank to determine atmospheric metal deposition. The empty pan was washed out with 2 L of the relevant TCLP extraction solution and the pH of the solution recorded. The leachable extraction procedure followed the procedure exactly as outlined in Section 6.2.2. Four repeat analyses were simultaneously done with two at half the specified mass (50 g of sample) and half the extraction solution (1 L of extraction solution). These four analyses are further referred to as the South African TCLP extracts (SA TCLP).

Figure 6.3-A is a schematic diagramme for the experimental procedure followed for Sample B.

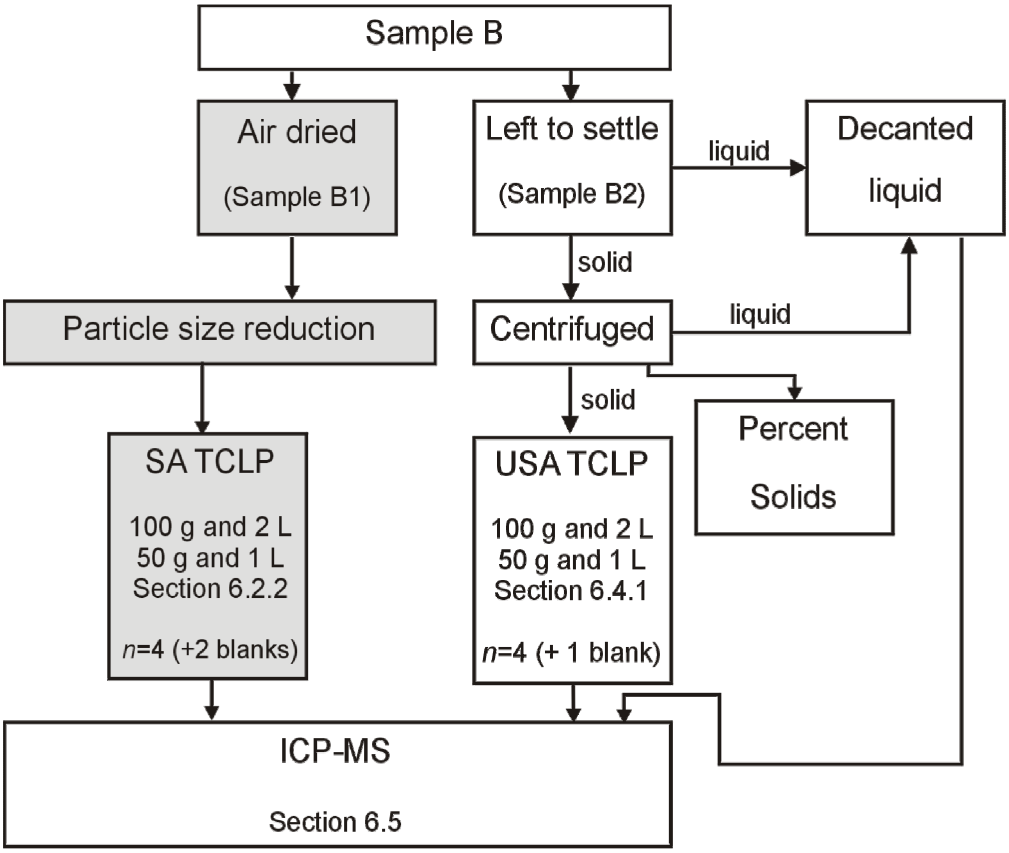


Figure 6.3-A: Schematic diagramme for procedures followed for Sample B

A 25 L portion of sample C (Sample C1) was also placed into drying pans, and dried in an oven at 30℃ to 60℃ under a pressure slightly below atmospheric until dry.

The remainder of sample B (Sample B2) and sample C (Sample C2) were allowed to settle. The liquid phase was decanted off and retained. The solid phase was further dewatered by centrifugation at 4000 rpm (G=8000 kg m s^{-2}) for 20 min. The liquid phase from the centrifugation was added to that of the decanted liquid and the solid phase stored at 4℃. A percent solids analysis was done on the solid phase according to Standard Methods (USA APHA *et al.*, 1995). The solid phase was homogenised before extraction was done. Sample B2 followed the USA EPA (1992) TCLP procedure (Section 6.4.1).

Sample C1 followed the NEN (Nederlands Norm, 1995) availability procedure (Section 6.4.4) and Sample C2 followed the USA EPA (1992) TCLP (Section 6.4.1), AS (Australian Standard. 1997) (Section 6.4.2), DIN (German Standard, 1984) (Section 6.4.3) and NEN (Nederlands Norm, 1995) (Section 6.4.4) procedures.

Figure 6.3-B is a schematic diagramme for the experimental procedure followed for Sample C.

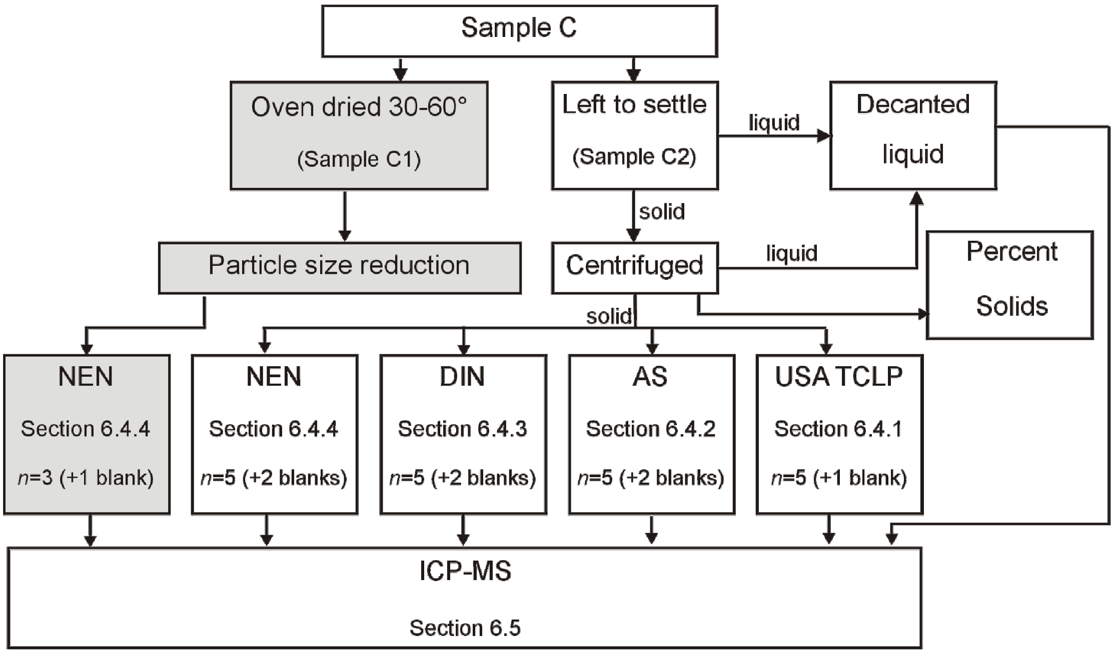


Figure 6.3-B: Schematic diagramme for procedures followed for Sample C

The decanted liquid was filtered through a Gelman 0.7 µm glass fibre filter paper, the pH recorded and then acidified with 25 % (m/m) HNO_3 to a pH below 2.0 pH units and stored at 4℃.

6.4 Leaching test protocols

6.4.1 The USA EPA TCLP

The variation between the USA EPA TCLP and the procedure specified in Section 6.2.2 relates to the time of rotation (18 hours not 20 hours) and the percent moisture of the sample. Sample B2 and C2 were used in this procedure.

The leachable extraction procedure followed from this point was in accordance with the United States of America Environmental Protection Agency, procedure (1992).

A sub-sample equivalent of 5.0 g dry mass was taken and was used to determine the correct TCLP extraction solution as specified in Section 6.2.2. The equivalent of 100 g dry mass (± 815 mL) was weighed out and added to a 2 L glass bottle, TCLP extraction solution was added to make up a total liquid content of 2 L including the free liquid originating from the centrifuged sample. The bottles were loaded into an end-over-end rotator and rotated at 40 rpm for 18 hours. The liquid portion was filtered through 0.7 µm Gelman glass filter paper. The pH was recorded and the leachates acidified with 25 % (m/m) HNO_3 to a pH below 2.00 and stored at 4℃ until the elemental analysis was done. Leachate (250 mL) was collected, acidified and stored. Five (5) repeat analyses of Sample C2 and four repeat analyses of Sample B2 were done. Two blanks were done, one for each extraction solution used.

6.4.2 The Australian Standard

This procedure was used according to the Australian Standard (AS 4439.3) (1997). Sample C2 was used and two blanks were done.

A percent solids analysis was done according to Standard Methods (USA APHA *et al.*, 1995). This procedure is the same as the USA TCLP (as in

Section 6.4.1) with the exception of the leaching solution being demineralised water. Five repeat analyses were done.

6.4.3 The German DIN

This procedure was used according to the Deutsche Norm (DIN 38414 -4) (German Standard, 1984). Sample C2 was used.

The solids content was determined according to Standard Methods (USA APHA *et al.*, 1995). A sample of 100 g (dry mass equivalent) (± 815 mL) was placed in a 2 L glass bottle. Demineralised water (1 L) was added to the bottle. The bottle was loaded into an end-over-end rotator and left to rotate at 40 rpm for 24 hours. The entire content of the bottle was separated by centrifugation at 4000 rpm ($G = 8\ 000\ kg\ m\ s^{-2}$) for 20 min. The solid was collected and returned to the unwashed glass bottle. The liquid was filtered through a 0.7 µm Gelman glass fibre filter. Two-hundred and fifty (250) mL was acidified with 25 % (m/m) HNO_3 and stored at 4 °C.

Demineralised water (1 L) was again added to the solid portion and the bottle loaded into the rotator and set to rotate at 40 rpm for another 24 hours. Extraction after 24 hours was the same as described above. The two leachates were not added together. Five repeat analyses were done with two demineralised water blanks.

6.4.4 The NEN Availability Test

This procedure was used according to the Netherlandse Normalisatie-Instituut (NEN) (1995). Samples C1 and C2 were used.

The solids content of the sample as determined according Standard Methods (USA APHA *et al.*, 1995). The dry samples were crushed to 300 µm despite the requirement to reduce the particle size to 125 µm (see Figure 6.3-B). This is not possible for dried sewage sludge samples since the paper content of the sample is high and the fibrous material from the paper does not allow milling to that particle size (Loock, A 2003, pers. comm., 17 November).

A sample mass of 16.00 g was weighed off into a 1 L Erlenmeyer flask. Eight hundred (800) g of demineralised water (ρ = 1.00 kg L^{-1}) was added. The flask was placed on a magnetic stirrer and magnetic rod inserted. The rotation speed was set so that all the material remained in suspension (approximately 300 rpm). The instantaneous pH was recorded after 1 min of stirring. The stabilised pH was recorded after 10 min of stirring. If the pH was below 7.00 pH units, no addition to the sample was made and it was left to stir for 3 hours. If the pH was above 7.00 pH units, standardised HNO_3 (1 *N*) was added to maintain the pH at 7.00±0.05 pH units. The addition was checked every 5 min for the first hour thereafter every 10 min. The total volume of HNO_3 added was recorded after 3 hours of stirring.

The entire sample was filtered through a 0.7 µm Gelman glass fibre filter paper. The pH of the liquid was recorded. Two hundred and fifty (250) mL was acidified with 25 % (m/m) HNO_3 and 200 mL stored. The solid phase with the filter paper was again inserted into the original unwashed Erlenmeyer flask. Eight hundred (800) g of demineralised water (ρ = 1.00 kg L^{-1}) was added. (The demineralised water was used to wash as much of the solid material back into the flask). The solution was again placed on a magnetic stirrer and stirred as previously. The instantaneous pH was recorded after 1 min and the stabilised pH was recorded after 10 min. The pH was adjusted with standardised HNO_3 (1 *N*) to a pH of 4.00±0.05 every 5 min for one hour and every 10 min for a further two hours. The total acid added was recorded.

The sample was again filtered through a 0.7µm Gelman glass fibre filter paper and the liquid portion collected. Two hundred and fifty (250) mL was acidified with 25 % (m/m) HNO_3 and 200 mL stored.

The two 200 mL leachates were added together and acidified with 25 % (m/m) HNO_3.

An additional extraction was done under the same procedure except that instead of a sequentially extraction at pH 7.00 and then at pH 4.00, this sample was only extracted at pH 4.00 without any prior pH 7.00 extraction for 3 hours. The leachate was collected, acidified and stored in the same manner as indicated above.

Five repeat analyses of sample C2 were done and three repeat analyses of sample C1 were done. Three blanks were done. For each sample there was one leachate that represented the exact procedure and two variations. The first variation was the extractions at the two separate pH values that yielded two leachates and then an additional single extraction at pH 4 for the final variation.

6.5 Methods for the analysis of metals in leachate

Extracts of samples B and C were analysed for B, Cd, Cr, Co, Cu, Fe, Pb, Hg, Mo, Ni, Se and Zn with an ICP-MS.

6.6 The acid neutralisation capacity of the sample

An attempt was made to determine the acid neutralisation capacity of the sample based on the NEN procedure. Sixteen (16) grams of dry sample was placed in an Erlenmeyer flask and 800 g (ρ=1.00 kg L^{-1}) demineralised water added. The solution was placed on a magnetic stirrer and allowed to equilibrate for 30 min while stirring (approximately 300 rpm) so as to keep the entire sample in suspension. The pH was recorded. Standardised HNO_3 (1 *N*) was added drop-wise. After each drop addition the solution was given 5 to 10 minutes to equilibrate, the pH was noted and recorded with the volume of acid added. The addition was done for 8 hours.

7 Results and discussion

The three samples (A, B and C) were used as follows.

Sample A was used to:

- compare the total and leachable extractions (Section 7.2), and
- to compare ICP-MS and FAAS analysis of leachates generated from TCLP extractions (Section 7.3).

Sample B was used to:

- determine the effect that sample drying has on the TCLP extractions of sewage sludge (Section 7.4),
- determine the elements found in the liquid portion associated with the entire sludge sample when wet TCLP extractions were done (Section 7.5), and
- determine the acid neutralisation capacity of the sludge using the TCLP extractions (Section 7.8).

Sample C was used to:

- determine the elements found in the liquid portion associated with the entire sludge sample when wet NEN extractions were done (Section 7.5),
- compare wet NEN, DIN, AS and TCLP extraction procedures (Section 7.6),
- determine the effect that sample drying has on the NEN extractions of sewage sludge (Section 7.4.2),
- compare the elements found in free liquid of the centrifuged sludge samples as opposed to that which was leached out of the solid portion of the sample (Section 7.7), and
- determine the effect of pH change and the related acid neutralisation capacity of sewage sludge samples (Section 7.8).

7.1 Demineralised water

Demineralised water with conductivity near to 1.0 µS cm^{-1} was made and used. As this water came into contact with the atmosphere, it adsorbed CO_2 until saturated.

7.2 Total and leachable fractions

7.2.1 Correlation between total and leachable fractions

The Pearsons correlation coefficient (*r*) can be used to determine the relationship between total and leachable extractions. Table 7.2-A lists the correlation coefficient between the total and leachable fractions for the 24 sites sampled (Samples A1 to A24) for the specified elements. The *aqua regia* extractions were done as outlined in Section 6.2.1 and the raw data can be found in Appendix 10.1.1.

Table 7.2-A: The correlation coefficients between the total (*aqua regia*) and leachable (TCLP) fractions for the specified elements

Element	**Correlation coefficient (*r*)**
Cd	0.5264
Co	0.9754
Cr	0.5478
Cu	0.7167
Hg	-0.0053
Mo	0.0031
Ni	0.8675
Pb	0.9042
Se	0.2568
Zn	0.7850
	n=24

The TCLP extractions were done as outlined in Section 6.2.2 and the raw data can be found in Appendix 10.1.2.

For Cd, Cr, Cu, Hg, Mo and Se no clear correlation was found. For Co, Ni, Pb and Zn a correlation of above 75 % between the total *aqua regia* and leachable TCLP fractions was found.

For each of the four elements that correlated more than 75 %, logarithmic radar graphs have been plotted (Co: figure 7.2-A; Ni: figure 7.2-B; Pb: figure 7.2-C and Zn: figure 7.2-D). The white inner area represents the leachable fraction in units of mg kg^{-1} while the grey outer area represents the total fraction in mg kg^{-1}. Adjacent to the logarithmic radar graphs are *x-y* scatter graphs for each of the elements were a correlation greater than 75 % was found (Co: figure 7.2-A; Ni: figure 7.2-B; Pb: figure 7.2-C and Zn: figure 7.2-D). For the elements where correlation was below 75 %, the graphs appear in Appendix 10.1.4.

For each of the four elements where the correlation was above 75 %, a third-order polynomial regression line was plotted as a dashed line on the graphs (Co: figure 7.2-A; Ni: figure 7.2-B; Pb: figure 7.2-C and Zn: figure 7.2-D) and calculated (Table 7.2–B). The *x* represents the total extraction and the *y* the leachable fraction both in mg kg^{-1}. The *y*-intercept was set to zero. When the total extraction concentration is zero, the leachable is expected to be zero as well.

Table 7.2-B: The equations relating the total *aqua regia* and leachable TCLP extractions for 24 samples for the specified elements

Element	Equation	r^2
Co	$y=\left(-3.00\times10^{-5}\right)x^3+0.0082x^2-0.0212x$	0.9838
Pb	$y=\left(3.00\times10^{-9}\right)x^3-\left(6.00\times10^{-6}\right)x^2+0.0033x$	0.9632
Zn	$y=\left(-5.00\times10^{-8}\right)x^3+0.0004x^2-0.111x$	0.6333
Ni	$y=\left(-4.00\times10^{-6}\right)x^3+0.0029x^2-0.1379x$	0.7549

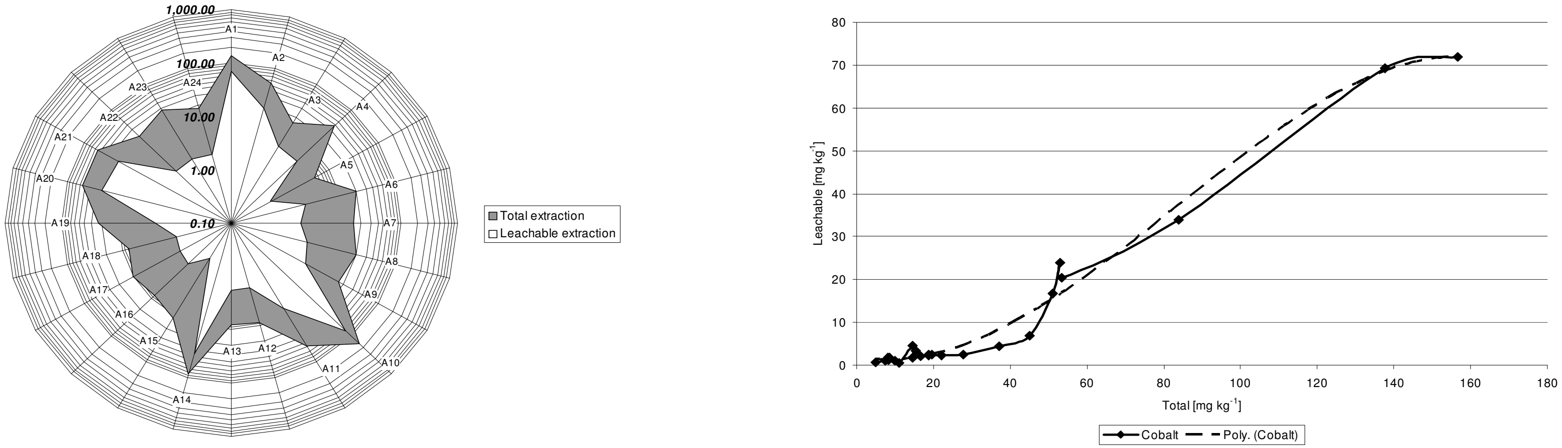


Figure 7.2-A: Total and leachable fractions for Co for the 24 sewage sludge samples analysed in mg kg^{-1}

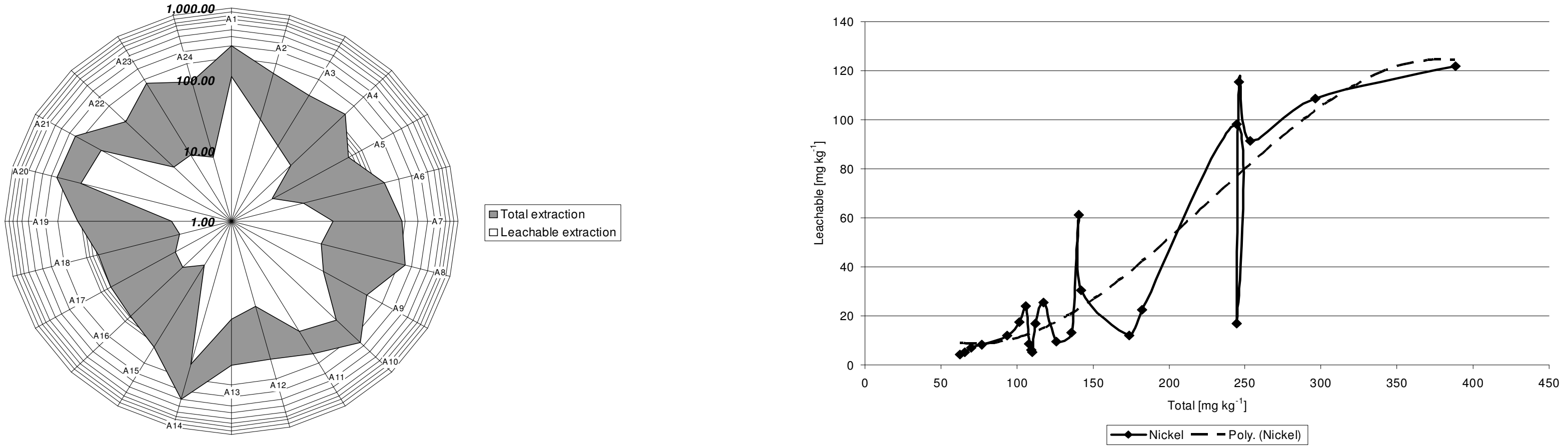


Figure 7.2-B: Total and leachable fractions for Ni for the 24 sewage sludge samples analysed in mg kg^{-1}

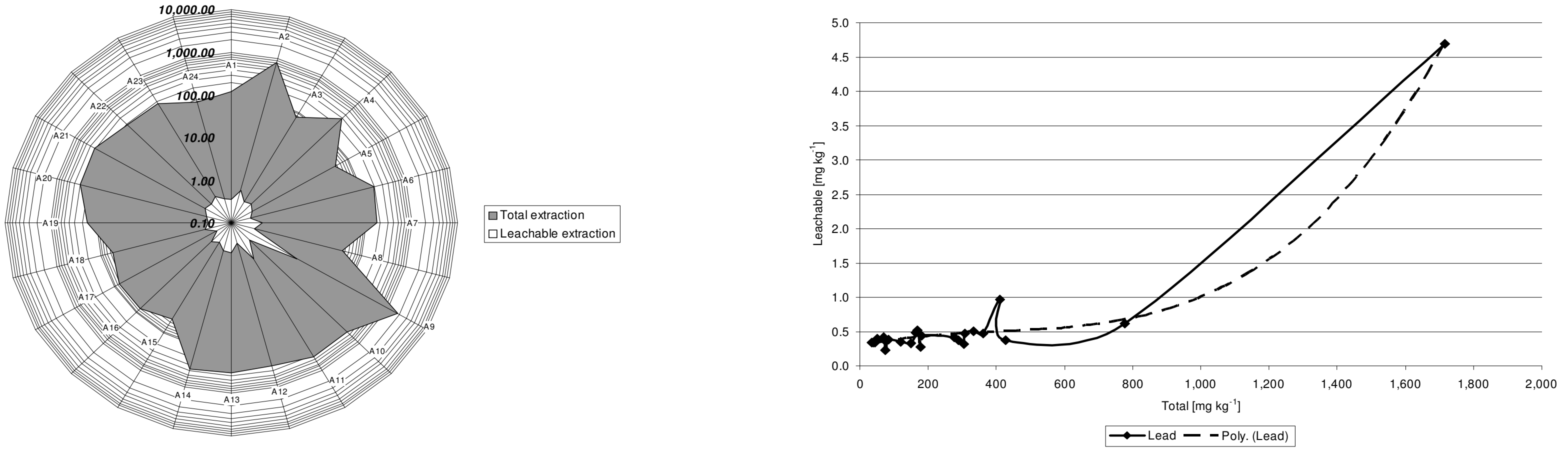


Figure 7.2-C: Total and leachable fractions for Pb for the 24 sewage sludge samples analysed in mg kg^{-1}

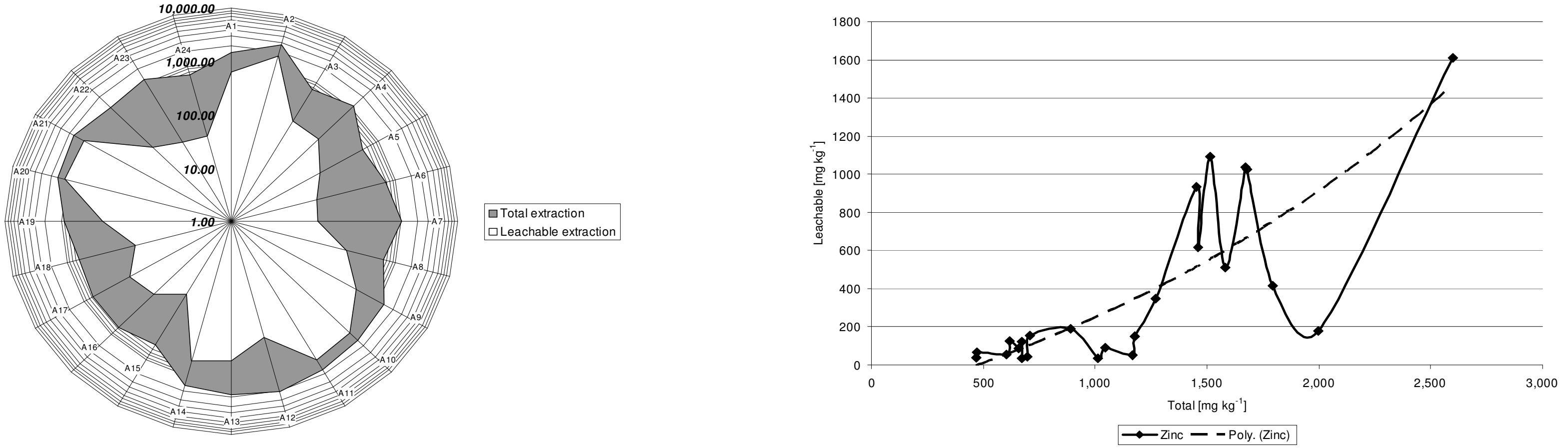


Figure 7.2-D: Total and leachable fractions for Zn for the 24 sewage sludge samples analysed in mg kg^{-1}

The coefficient of determination (r^2) was also calculated. These four equations and their coefficients of determination are found in table 7.2-B. The correlation coefficients (r) in table 7.2-A and the coefficients of determination (r^2) in table 7.2-B are not the same. The coefficient of determination is the square of the correlation coefficient. Both correlate, but the r^2 value is more stringent than the r value (r = 0.75 is the same as r^2 = 0.5625). The coefficient of determination in table 7.2-B correlates the plotted values with the regression line. The Pearson correlation coefficient in table 7.2-A correlates the total and leachable extraction values.

7.2.2 Predicting leachable values from total values

Using the equations in table 7.2-B for Co and Pb, it is possible to predict leachability of the element from the total extraction results with an 80 % certainty (r^2 = 0.64). For Zn and Ni, the coefficient of determination between the data plotted and the regression line is too low (r^2<0.64 therefore less than 80 %) to use the regression line equation to accurately predict leachable fraction from total extraction data.

The equations for Co and Pb were used to predict the leachable amount from the total *aqua regia* amount with data of 77 South African wastewater treatment plants from a study by Snyman *et al.*, (2004). This proved unsuccessful since the correlation between the calculated values (using the above derived equations) and the experimentally determined values (Snyman *et al.*, 2004) were 0.588 for Co and 0.264 for Pb. The mean percent difference between the calculated values and experimentally determined values was –1521 % for Co and –158 % for Pb.

A possible explanation for the incomparability of the two studies (and therefore why the derived equations do not work), is that all the samples collected by Snyman *et al.*, (2004) were from heaps or piles of sludge. This means that all the elements of concern in the liquid phase of the sample were irrecoverably lost prior to sampling. The samples collected for this study were all wet samples that were air-dried. Therefore all the elements of concern in the liquid portion of the sludge were allowed to dry and therefore retained during drying.

Richards *et al.*, (1997) proved that leachability varies with sludge processing techniques. The variety of processing techniques for the sludge in both this study (Sample A only) and Snyman *et al.*, (2004) could also explain why no relationship between total and leachable extractions could be found.

7.3 Methods for the analysis of elements in leachate

The elemental analysis of the above extraction (Section 7.2) and that of Snyman *et al.*, (2004) was done using an ICP-MS. An alternative and cheaper method for similar elemental analysis is by using AA techniques. The importance of comparing the two techniques is due to the availability of apparatus and the cost implications of ICP analysis when compared to that of AA analysis. This comparison between the two techniques for elemental determination in leachates was done using the TCLP extractions for Sample A according to the method outlines in section 6.3.2. The raw data for the ICP-MS analysis can be found in Appendix 10.1.2 and for the FAAS in Appendix 10.1.3.

Table 7.3-A: The leachable limits for Cd, Cu, Pb and Zn as specified in the Addendum No 1 to the Guide: Permissible Utilisation and Disposal of Sewage Sludge (Water Research Commission *et al.*, 2002)

Element	**Leachable Limit** *mg kg^{-1}*
Cd	15.7
Cu	50.5
Pb	50.5
Zn	353.5

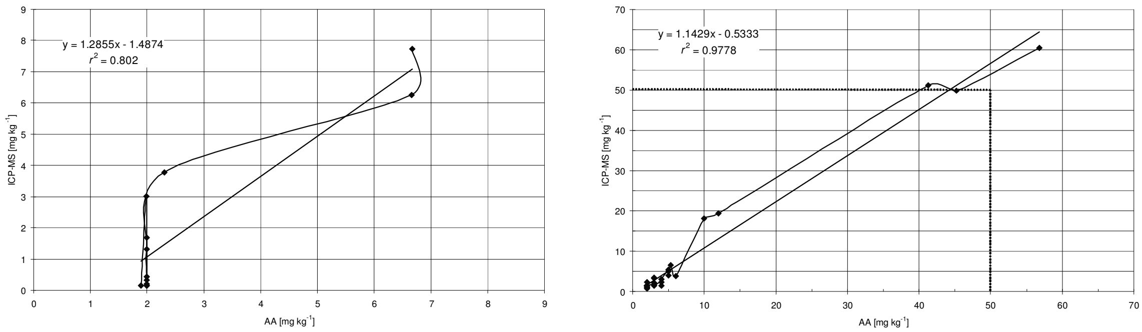
The TCLP is a compliance test that is used to determine the type of sewage sludge according to the Guide: Permissible Utilisation and Disposal of Sewage Sludge (Water Research Commission *et al.*, 1997) and related addendum (Water Research Commission *et al.*, 2002), in South Africa. The introduction of leachable fractions for Cd, Cu, Pb and Zn into the limit values is found in the Addendum No 1 to the Guide (Water Research Commission *et al.*, 2002). The leachable limits for the four specified elements as extracted from the Addendum to the Guide are in table 7.3-A.

The desired result when doing a TCLP extraction test is simply to obtain a "yes" or "no" answer. "Yes", the sample does comply with the leachable limits specified in the Addendum to the Sludge Guidelines or, "no" it does not comply. The deviation of the sample from the limit is insignificant when considering sludge classification according to the guidelines.

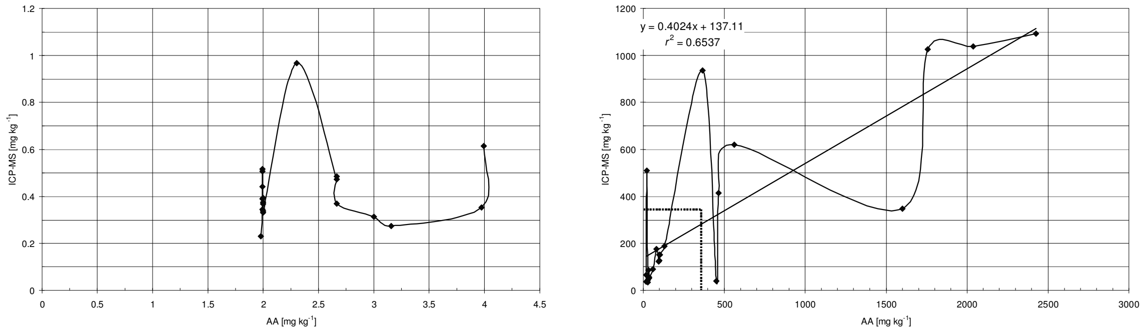
Figure 7.3-A represents the data for Cd, Cu, Pb and Zn on an *xy*-scatter graph with the *x*-axis representing the FAAS data and the *y*-axis representing the ICP-MS data. A linear regression line with equation and a coefficient of determination (r^2) between the plotted value and the regression line, is also displayed on each graph.

From the equation of the linear regression line (y=1.2855x-1.4874) for Cd, (Figure 7.3-A (i)), it can be seen that the ICP-MS data generally yields values lower (c = - 1.4874 mg kg^{-1}) than the FAAS data. This means that the bias is in favour of the FAAS data. It is important to note that the smallest interval of measurement for FAAS analysis was specified at 1.00 mg kg^{-1}.

The slope of the linear regression line is just above 1.0 (m = + 1.1492), which means that the relationship between the FAAS and ICP-MS data is almost 1:1. The data does not extend to the limit value of 15.7 mg kg^{-1} since all the samples analysed complied with the limit value. For this reason the limit value is not indicated on the figure. McGrath *et al.*, (2000) found a very good agreement between inductively coupled plasma atomic emission spectrometry (ICP-AES) and graphite furnace atomic absorption spectrometry (GFAAS) with a linear regression equation of ICP-AES = 1.09 GFAAS (r^2 = 0.96, n=124). The linear regression line is a fairly good indication of the measured values. This can be noted by the coefficient of determination (r^2) that is +0.802.



(i) Cd (ii) Cu



(iii) Pb (iv) Zn

Figure 7.3-A: The relationship between the FAAS and ICP-MS results for Cd, Cu, Pb and Zn

For Cu (figure 7.3-A (ii)), the linear regression line (y=1.1429x-0.5333) indicates that the ICP-MS data is generally lower (c = - 0.5333 mg kg^{-1}), than the FAAS data. The bias is towards the FAAS data. This difference is less than the smallest interval the FAAS analysis was set to determine. The slope of the linear regression line is above one (m = + 1.1429) and slightly higher than that of Cd. The relationship between the linear regression line and the measured values is good (r^2 = + 0.9778). This makes prediction from the linear regression line accurate.

For Pb, (figure 7.3-A (iii)), no clear trend is observed. This is due to the difficulty associated in analysis of Pb using FAAS at such low levels. It is important to note that the maximum ICP-MS value obtained was 0.967 mg kg^{-1} and the smallest measurable values for FAAS was 2.0 mg kg^{-1}. The use of standard addition is a possible option to obtain accurate data for values near or below the detection limit (Quevauviller *et al.*, 1996).

For Zn, (figure 7.3-A (iv)), there are large deviations from the linear regression line. This is numerically indicated by the coefficient of determination (r^2) that is + 0.6537. Eight samples are above the Zn metal limit of 353.5 mg kg^{-1} that is indicated on the graph with a dashed line (on both axes). From the equation of the linear regression line (y=0.4024x+137.11) we can note that ICP-MS values are generally higher than FAAS values (c = + 137.11 mg kg^{-1}) and that the bias is towards the ICP-MS analysis method. The slope of the linear regression line (m = + 0.4024) is much less than the expected value of 1.00. Since the coefficient of determination (r^2) between the measured values and the linear regression line is 0.6537 the regression line is not a good indication of the measured values and should not be used to compare the two elemental analysis methods.

7.3.1 Correlation between ICP-MS and FAAS data

The correlation coefficient (r) between the FAAS and the ICP-MS data for the four elements of concern were also calculated. They appear in table 7.3-B.

Cd, Cu and Zn correlate well with each other while Pb does not. This can be explained by noting that the values of the leachates are near to the detection limit for FAAS. If the AA had a graphite furnace attached, detection at such low levels would be more precise. It is important to realise that since none of the Pb samples exceeded the Sludge Guideline limit values, using FAAS instead of ICP-MS will still yield the same classification with respect to Pb.

Table 7.3-B: The correlation coefficients between the ICP-MS and FAAS data for 24 different samples for Cd, Cu, Pb and Zn

Element	Correlation Coefficient
Cd	0.90
Cu	0.99
Pb	0.08
Zn	0.80

7.3.2 Units of Limit Values

The limit values specified in the Addendum to the Sludge Guideline (Water Research Commission *et al.*, 2002) are in units of mg kg^{-1}. This refers to milligrams of element leached out of one kilogram of sludge. ICP and AA analysis data is in units of mg L^{-1} and refers to milligrams of element leached into one litre of extraction solution. The TCLP (USA EPA, 1992) specifies in its procedure values that can be used for a generic conversion between the two units. The conversion factor from mg L^{-1} to mg kg^{-1} is 20 L kg^{-1}, since the TCLP requires 2 L of extraction solution and 100 g (0.1 kg) of sample.

7.3.3 Lowest detected values

The lowest detected value for all the elements was 0.1 mg L^{-1} (2.0 mg kg^{-1}) for the FAAS. The lowest values obtained for the ICP-MS analysis was 0.0011 mg L^{-1} (0.022 mg kg^{-1}) for Cd, 0.0336 mg L^{-1} (0.671 mg kg^{-1}) for Cu, 0.0117 mg L^{-1} (0.234 mg kg^{-1}) for Pb and 1.695 mg L^{-1} (33.989 mg kg^{-1}) for Zn. These values are not the detection limits, but rather lowest measured concentrations in the Sample A dataset for a specific element. These values are not below the ICP-MS instrument detection limits used for the analysis (Kirsten, W 2004 pers. comm., 23 April).

7.3.4 Smallest detected interval for FAAS

The FAAS samples only indicate differences of 1.0 mg kg^{-1} (0.05 mg L^{-1}). This was set during the operation of the FAAS. The choice of 0.05 mg L^{-1} was to gain successful comparable results with repetition of a sample. The analysis was initially done with a choice of 0.01 mg L^{-1} and it was found that background noise interference was too high.

7.3.5 Compliance to the Limit Values

The most important aspect is to determine if the compliance of the sample to the limit values changes when another method of elemental analysis is used. For Cd and Pb all the samples complied irrespective of the analysis method (Figure 7.3-A). Snyman *et al.*, (2004) also found no Cd or Pb samples that exceeded leachable limit values for a study encompassing 77 wastewater treatment plants throughout South Africa.

For both Cu and Zn, one sample per element changed compliance depending on the method of elemental analysis. For Cu, the sample value that changed compliance was near the Sludge Guideline limit value. For Zn, an extreme value was found with the ICP-MS data and this caused the change in compliance.

Samples with elemental concentration values below the detection limits for the FAAS are of no concern. Samples that were undetectable, or yielded inaccurate results due to background noise at low levels, were not going to exceed the limit value.

From the above results it can be concluded that FAAS analysis of leachate is precise and successful as a method of element analysis for TCLP compliance testing to classify sewage sludge. Further comparison between the ICP-MS and FAAS analysis can be found in Appendix 10.2.

7.4 Variation in sample preparation

Sample preparation techniques can affect the amount of element that leaches out of the solid phase. Two of these parameters are further researched. They are a variation in the sample mass (see Table 5.2-B) and a variation in the moisture content of the sample (see Section 5.2.1).

Moisture content of the sample is important since it directly affects the ease of extraction. The anaerobically digested sludge (Sample B and C) used in this research had a wet sludge density of 1.00 kg L^{-1}. This means that for a TCLP extraction that requires 100 g of dry sludge, 10 L of wet sludge is required. Rudd *et al.* (1988) did sequential extractions on sewage sludge and found the dry sample to be more homogeneous and yield higher extractions than the wet samples. Despite this, they recommended that samples should be analysed on an “as applied” basis.

Two sets of comparisons were done to determine the effect of different sample preparation methods. The first (Section 7.4.1) was to compare TCLP extractions on air-dried and un-dried (wet) samples (Sample B). A sample mass variation was also included to determine if the results are affected by sample mass. The second (Section 7.4.2) was to compare NEN extractions on oven dried and un-dried (wet) samples. No sample mass variation was done, but three variations to the NEN procedure were done (Sample C).

Figures 7.4-A to 7.4-C represent the data of the dried and wet TCLP samples. Four repeat analyses were done according to the method outlined in Section 6.3, two at 100 g sample with 2 L of extraction solution and two at 50 g sample and 1 L of extraction solution.

Figures 7.4-D to 7.4-F represent the data of the dried and wet NEN samples with three variations in the procedure. The three variations to the NEN are outlined in table 7.4-A.

Table 7.4-A: The three variations done on the NEN in this study

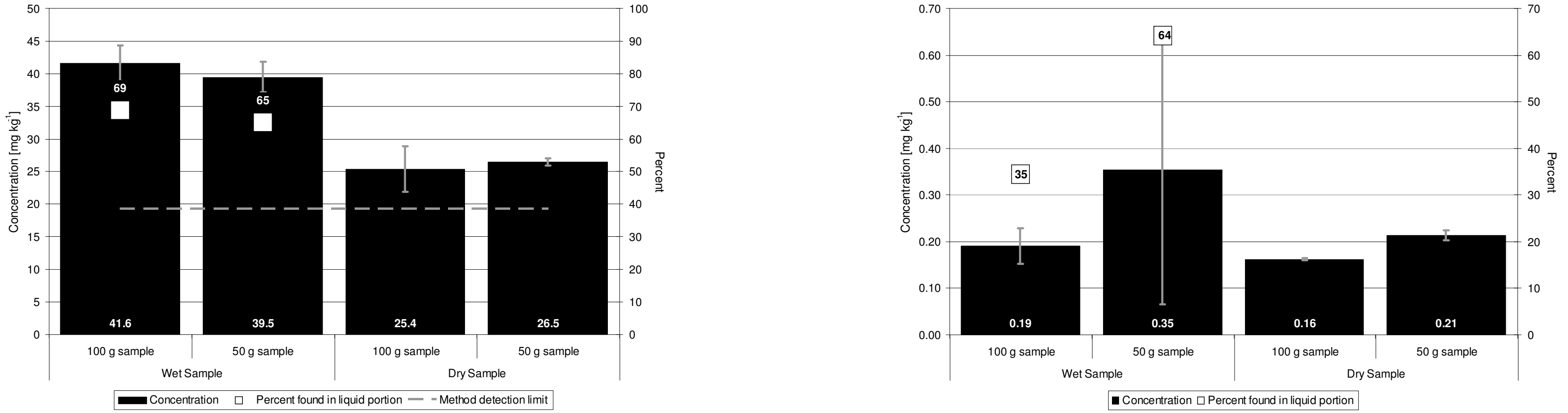
Methods	pH	Contact Time	Leachates
NEN original	4 and 7	3 + 3 hours	added together
Variation 1	4 and 7	3 + 3 hours	analysed separately
Variation 2	only 4	3 hours	only one leachate

The method entitled "NEN original" was exactly as outlined by the NEN procedure and specified in Section 6.4.4. "Variation 1" was where the two leachates from pH 7 and pH 4 were not added together prior to analysis, but rather analysed separately and mathematically added together. "Variation 2" was where only leaching at pH 4 was done for 3 hours.

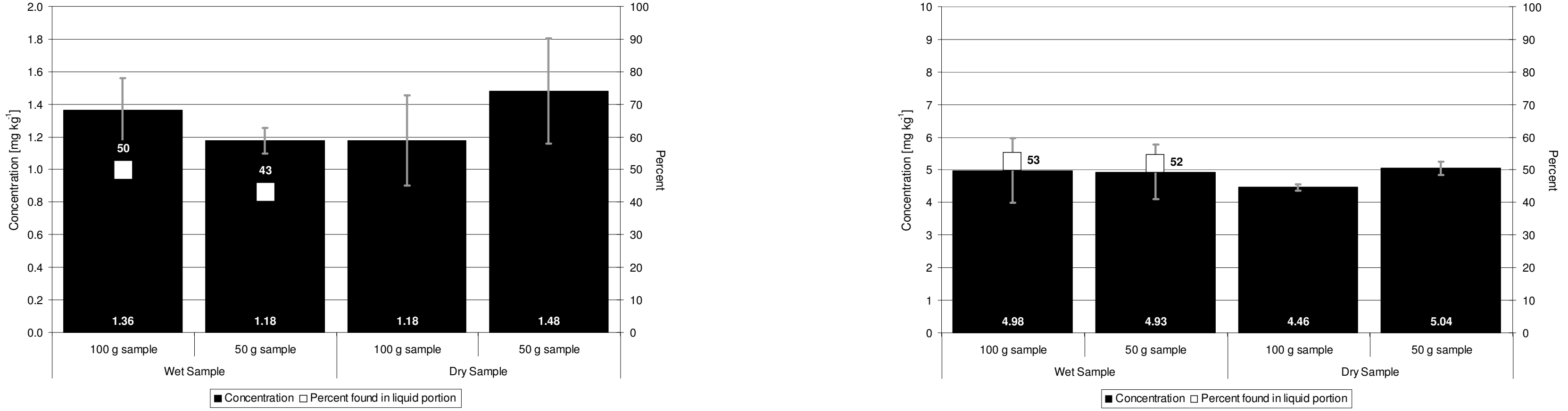
For both the TCLP and NEN extractions, the wet samples were calculated to include the amount of element in the decanted liquid that was not included in the actual extraction but discarded. This was done by calculating the volume of liquid removed by decanting and centrifuging then analysing the liquid with an ICP-MS to determine the element content. It was then mathematically added to the wet sample. The dry sample inherently included this since the entire sample was taken and air-dried and no dewatering was done.

7.4.1 TCLP extractions

Sample B1 (see figure 6.3-A) was air-dried over four weeks under ambient conditions. Drying samples in ambient conditions will result in atmospheric element deposition. The effect of the atmospheric element deposition on the samples was measured by allowing a single empty drying pan to stand with the sludge-loaded drying pans for the duration of the drying. This empty pan was then washed out with TCLP solution once all the sludge-loaded pans were fully dry. The TCLP solution was analysed for all the relevant elements with an ICP-MS and from that data, the effect of atmospheric element contamination was subtracted for the air-dried sludge samples.

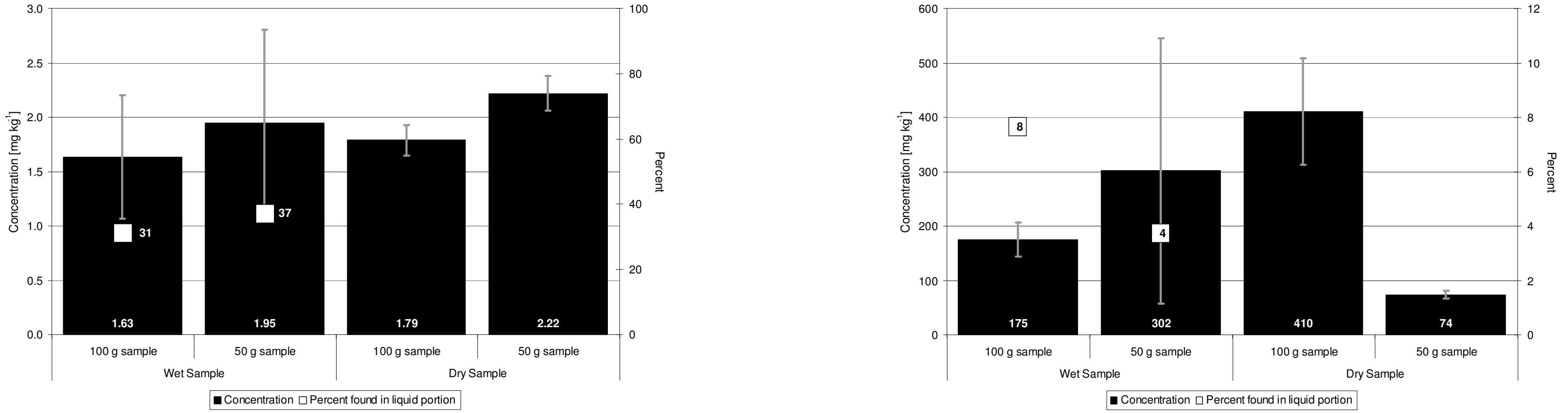


(i) B (ii) Cd



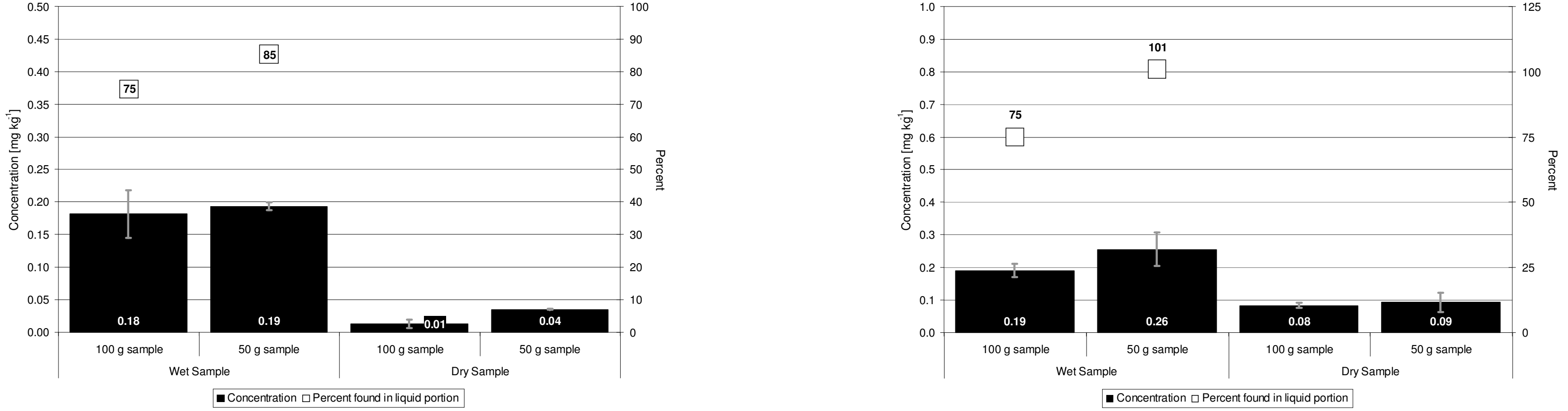
(iii)Cr (iv) Co

Figure 7.4-A: The mean leachable fractions for B, Cd, Cr and Co depending on sample preparation extracted with the TCLP



(i) Cu

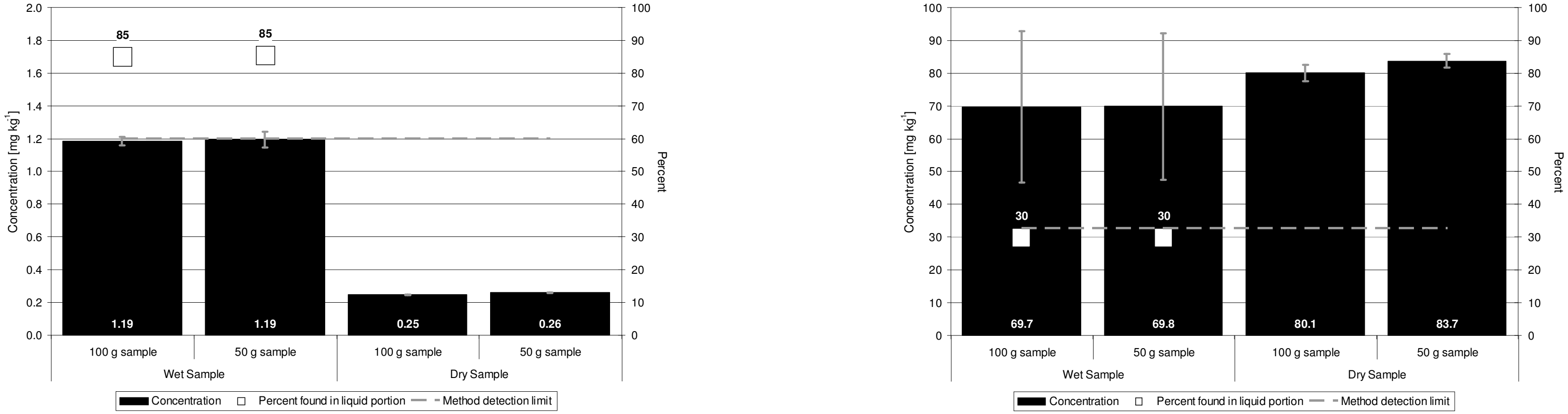
(ii) Fe



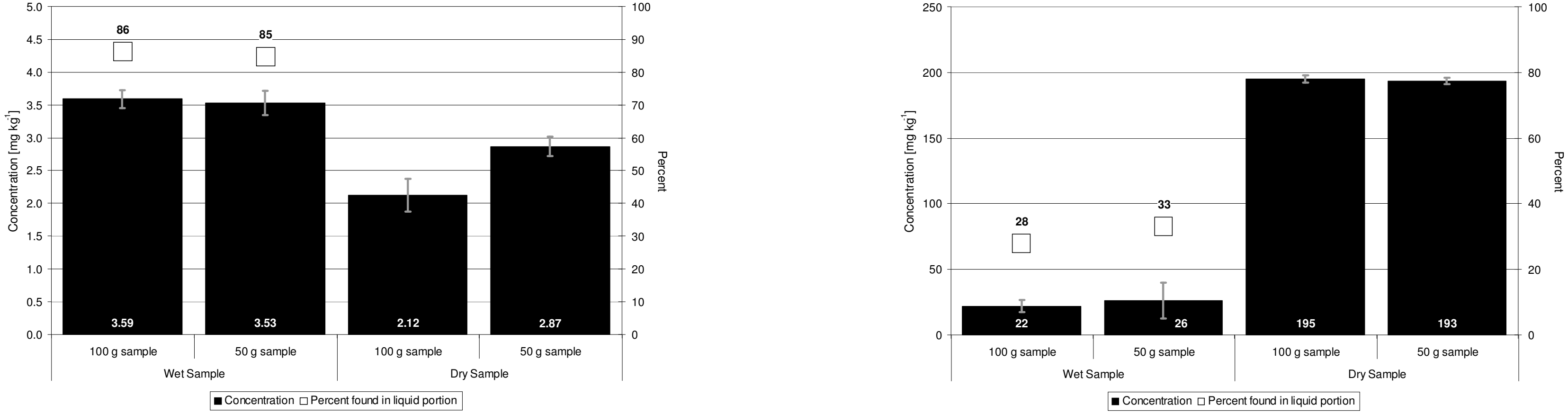
(iii) Pb

(iv) Hg

Figure 7.4-B: The mean leachable fractions for Cu, Fe, Pb and Hg depending on sample preparation extracted with the TCLP



(i) Mo (ii) Ni



(iii) Se (iv) Zn

Figure 7.4-C: The mean leachable fractions for Mo, Ni, Se and Zn depending on sample preparation extracted with the TCLP

Four wet (two at 100 g and two at 50 g) and four dry (two at 100 g and two at 50 g) extractions were done. The variations with respect to sample size and moisture content cannot be definitively established by these results. The intention is simply to emphasise that sample size and moisture content may have an influence on the leachability of specific elements and for this reason when doing a standardised extraction test, deviations from the prescribed procedure could yield incorrect results.

From figures 7.4-A to 7.4-C the difference in the leachable fractions between dried and wet samples can be determined. It was assumed that a difference only occurred when the percentage of the largest value minus the smallest value divided by the largest values yielded a number greater than 10 %.

The large black bars represent the element concentrations and are read off along the left-hand-side *y*-axis. The actual value is printed in white at the base of the graph. The shaded vertical lines on each bar represent the standard deviation of the samples. The large white squares represent the percentage of the element that originated from the liquid portion of the sample. It is read off the right-hand-side *y*-axis as a percentage of the total element in both the solid and liquid portions of the graph.

Many of the concentrations measured are very low. To ensure the reliability of the data, detection limits from Standard Methods (USA APHA *et al.*, 1995) for ICP-MS as well as unit conversions to mg kg^{-1} are found in table 7.4-B. This was also done for the ICP-MS used in the determination. The large difference between the Standard Methods values and those of the used ICP-MS is due to the fact that of the various ICP methods of analysis, the Mass Spectrophotometer (MS) has the lowest detection limits. From table 7.4-B we can note that all the determined values are above the ICP-MS detection limits.

The dry and wet samples (Figure 7.4-A to 7.4-C) yielded comparable results for B, Ni and Mo irrespective of the sample mass. The dry and wet samples of sample mass 100 g were comparable for Cu and for sample mass 50 g they were comparable for Co.

Table 7.4-B: Detection limit values for ICP-MS from Standard Methods (USA APHA *et al.*, 1995) and for the ICP-MS used in this research

Element	Standard Methods		ICP-MS used	
	µg L^{-1}	mg kg^{-1}	ppt	mg kg^{-1}
B	5	0.1	10 – 100	1×10^{-5} to 1×10^{-4}
Cd	4	0.08	1 – 10	1×10^{-6} to 1×10^{-5}
Cr	7	0.14	1 – 10	1×10^{-6} to 1×10^{-5}
Co	7	0.14	< 1	$< 1 \times 10^{-6}$
Cu	6	0.12	1 – 10	1×10^{-6} to 1×10^{-5}
Fe	7	0.14	1 – 10	1×10^{-6} to 1×10^{-5}
Pb	40	0.8	< 1	$< 1 \times 10^{-6}$
Hg	-	-	< 1	$< 1 \times 10^{-6}$
Mo	8	0.16	1 – 10	1×10^{-6} to 1×10^{-5}
Ni	15	0.3	1 – 10	1×10^{-6} to 1×10^{-5}
Se	75	1.5	10 – 110	1×10^{-5} to 1×10^{-4}
Zn	2	0.04	1 – 10	1×10^{-6} to 1×10^{-5}

The wet samples in figures 7.4-A to 7.4–C cannot be compared with the results in Section 7.5 since in these calculations the elements from the decanted liquid were added to the wet sample so that the wet and dry methods were done on samples with comparable total element content. The raw data for the wet and dry samples is found in Appendix 10.2.

To determine method detection limits the assumption has to be made that the dry and wet samples are comparable irrespective of the sample mass used. Since this was not the case for all the elements analysed, method detection limits were only calculated for the elements where the samples were comparable (B, Mo and Ni) irrespective of sample mass. Method standard deviation was calculated using the following formulae; $\Delta x_{\min} = \bar{x}_1 - \bar{x}_b > ts_b\sqrt{\frac{N_1 + N_2}{N_1 N_2}}$ (Skoog *et. al.,* 1996), with α set at 95 %. The method standard deviation is indicated as a dashed horizontal line on figures 7.4-A (i) and 7.4-C (i) and (ii) and in table 7.4-C.

Table 7.4-C: Method detection limits for B, Mo and Ni

Element	Method Detection Limit (mg kg^{-1})
B	19.23
Mo	1.20
Ni	32.71

7.4.2 NEN extractions

The NEN extractions of the three method variations (as outlined in table 7.4-A) were used to determine the effect of element concentration in the leachate. The prescribed method requires that the leachates from extraction at pH = 7 and pH = 4 be added together and analysed as one leachate. This was done and is indicated as "NEN original" in table 7.4–A and figures 7.4–D to 7.4–F. The leachates from the two extraction procedures were also analysed separately (one at pH 7 and the other at pH 4) and mathematically added together. This is indicated as "Variation 1" in table 7.4–A and figures 7.4–D to 7.4–F. An additional non-sequential extraction at pH 4 only was also done. This is indicated as "Variation 2" in table 7.4–A and figures 7.4–D to 7.4–F. All three these analysis methods were done on one sample (B1) with three dry and five wet repeat analysis.

Repeatability is measured by the percent relative standard deviation (% RSD). The % RSD is a calculation of the accuracy of repeat determinations with respect to the mean value. It is calculated by determining the percentage difference between the standard deviation and the mean (McCormick and Roach, 1987). The % RSD is plotted on figures 7.4-D to 7.4-F as a square marker. Values for % RSD can exceed 100 % where the standard deviation of the repeat determinations is larger than the mean of the repeat determinations.

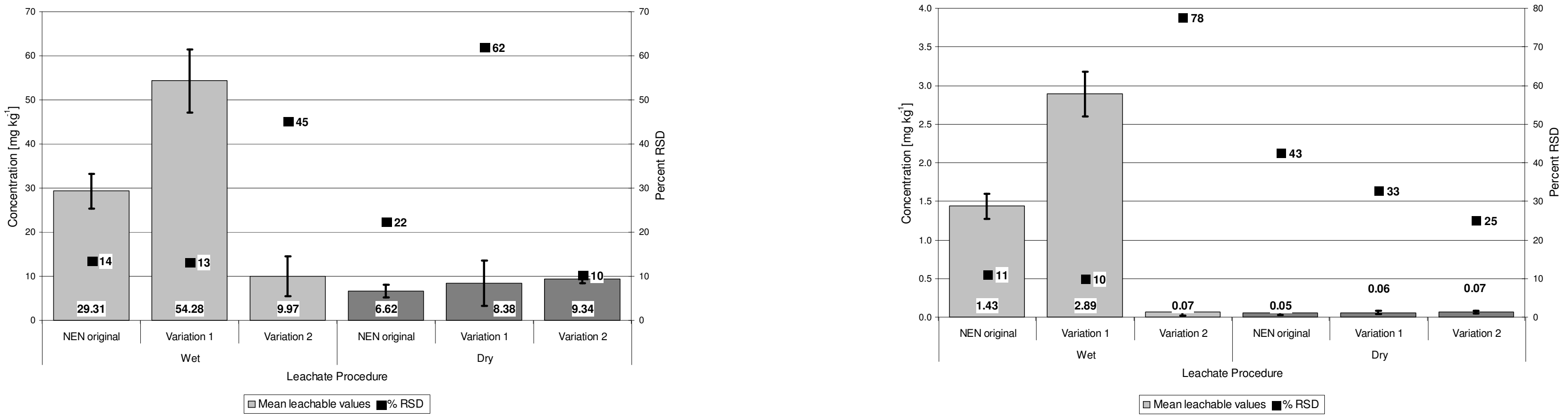
Atmospheric elemental deposition was not considered for the second drying method (Sample C2 and figure 6.3-B) since the drying occurred in an oven under reduced pressure.

For “Variation 1”, the wet samples all had a higher concentration than the “NEN original” concentration. This can be explained by the fact when the two leachates were physically added together, the pH changed from 4 and 7 respectively to pH 5.5. This meant that elements from the pH 4 leachates were precipitated out when the pH was increased to 5.5 by the addition. There would also have been capacity for more elements to solubilise in the leachate from pH 7 with a decrease in pH to 5.5 as well, but it is assumed to be insufficient.

When considering the effect of sample drying on the NEN procedure, (Figure 5.4-D to 5.4-F) it is found that wet samples have higher leachate concentrations for B, Cd, Cr, Co, Pb, Hg and Zn than dry samples. Dry samples yield higher leachates than wet samples for Mo, Ni and Se. Cu appears to be similar.

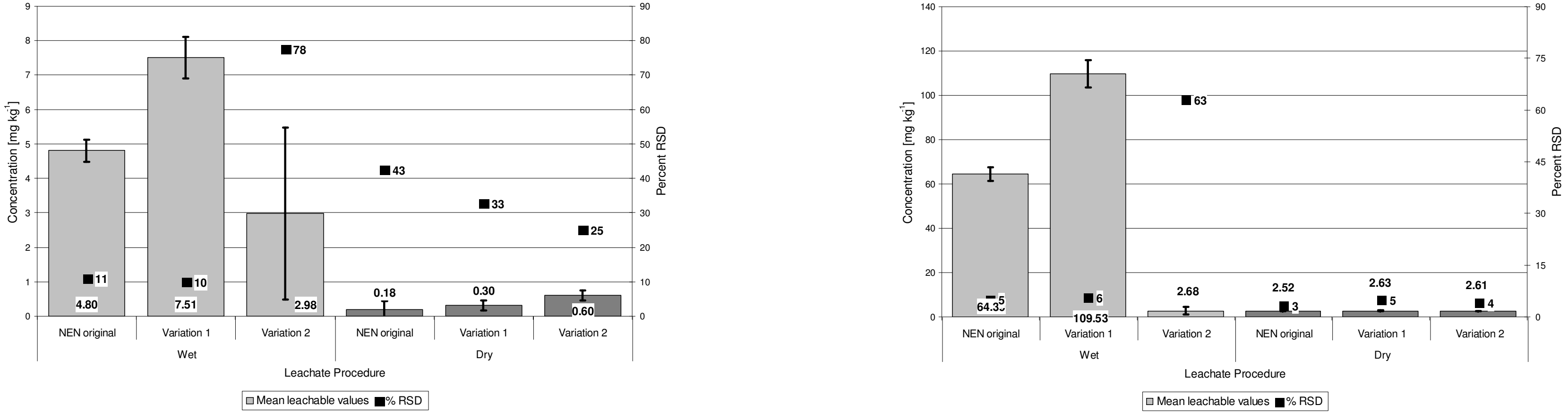
Comparing the three method variations (Table 7.4–A), for the wet versus the dry samples, only “Variation 2” yielded comparable results for B, Cd and Co.

Considering the wet samples, only Cu and Se were comparable between methods “NEN original” and “Variation 2”. Considering the dry samples only, Co, Ni, and Zn were comparable across all three methods while B and Cu were comparable between methods “Variation 1” and “Variation 2” and Mo was comparable between “NEN original” and “Variation 1”. All the elements analysed for (wet samples) had a difference greater than 50 % between the three methods. For the dry samples Cr, Fe, Pb, Hg and Mo had differences greater than 50 % between the three methods



(i) B

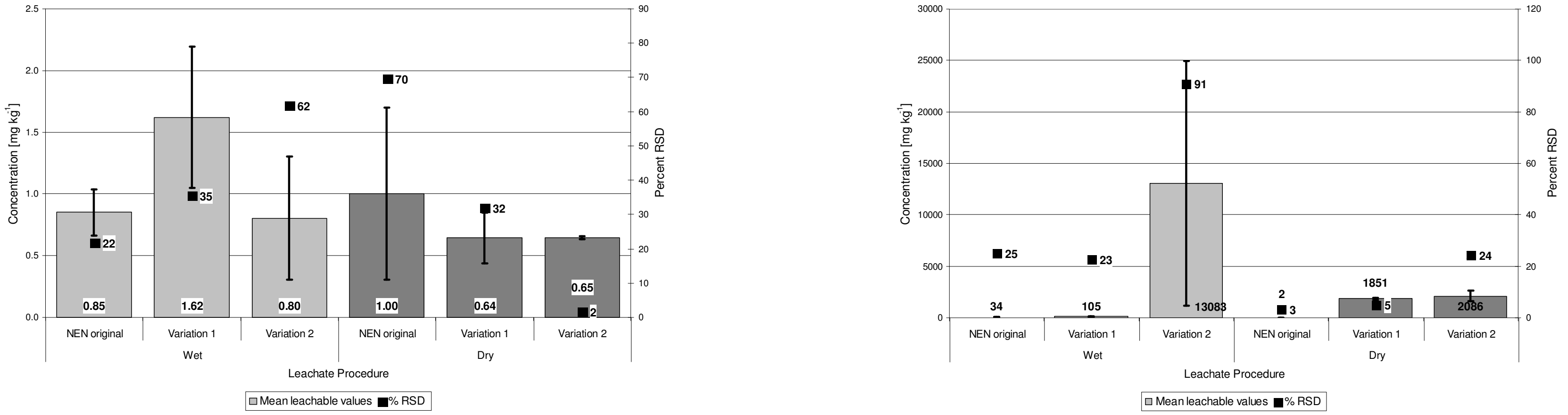
(ii) Cd



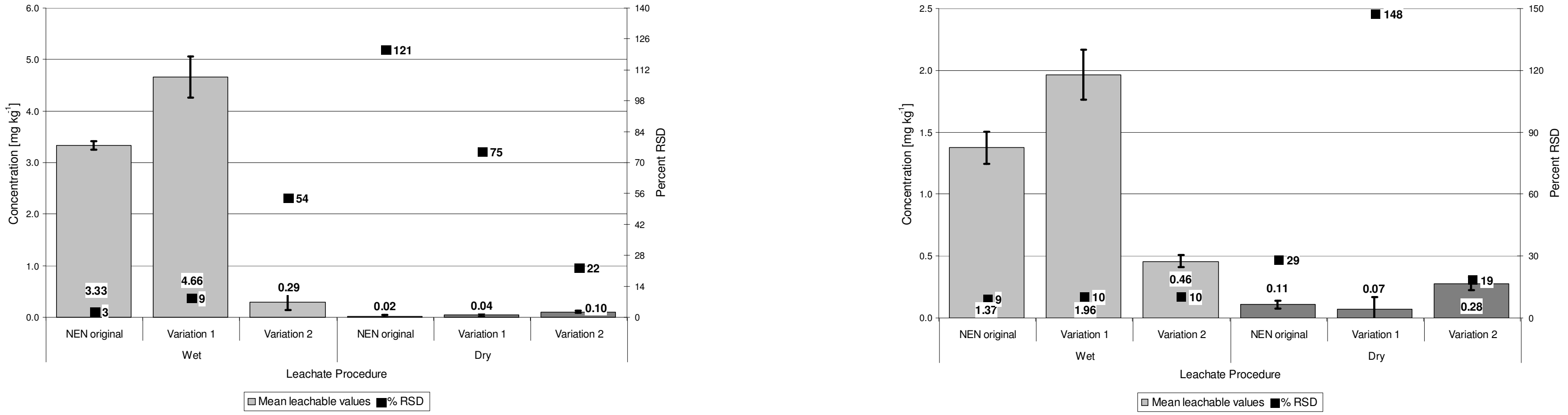
(iii) Cr

(iv) Co

Figure 7.4-D: The mean leachable fractions for B, Cd, Cr, and Co depending on sample preparation extracted by the NEN

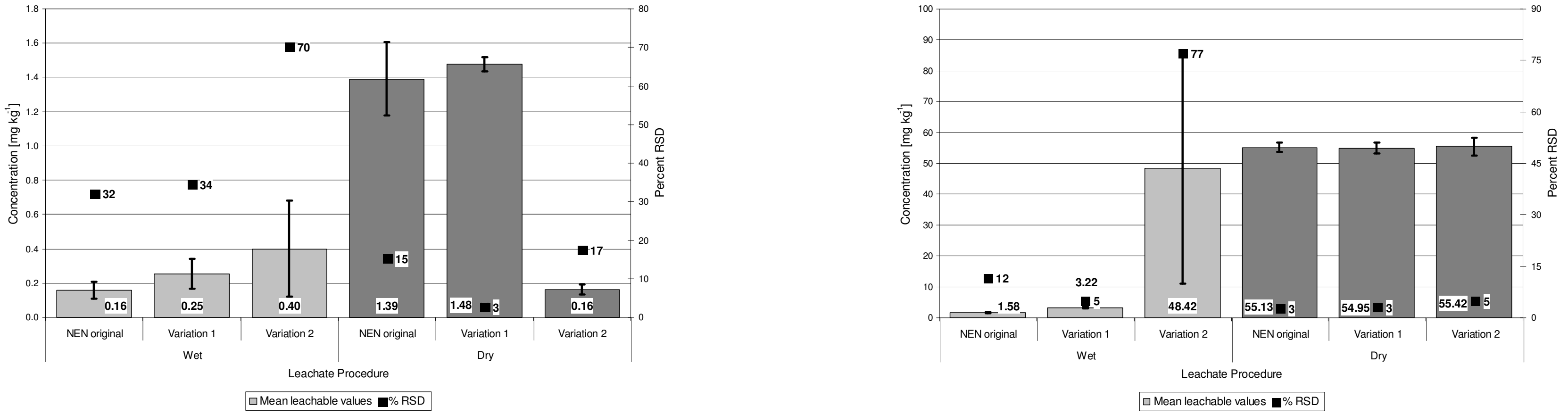


(i) Cu (ii) Fe

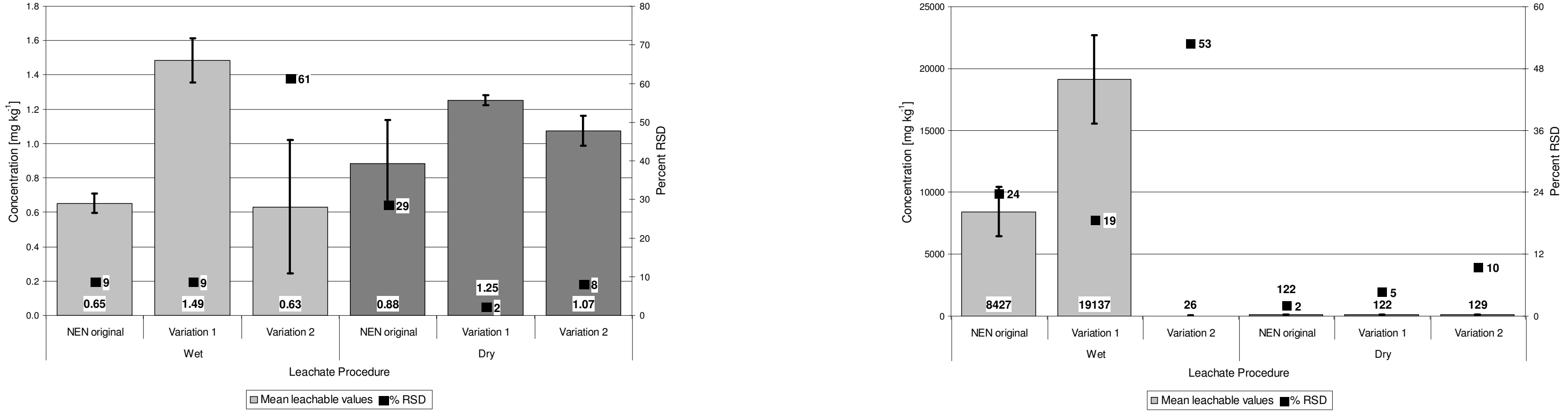


(iii) Pb (iv) Hg

Figure 7.4-E: The mean leachable fractions for Cu, Fe, Pb and Hg depending on sample preparation extracted by the NEN



(i) Mo (ii) Ni



(iii) Se (iv) Zn

Figure 7.4-F: The mean leachable fractions for Mo, Ni, Se and Zn depending on sample preparation extracted by the NEN

For the NEN extractions overall, Cr, Pb and Hg always yielded higher wet extraction values irrespective of the method. No element yielded higher dry values for all the method options.

When comparing the % RSD for the wet samples, B, Cd, and Se all had comparable values for “NEN original” and “Variation 1” and higher values for “Variation 2”. Hg revealed comparable % RSD’s for all three methods. All the elements except for Hg had the highest % RSD for variation 2.

When considering the % RSD for the wet and dry procedures it was found that “NEN original” and “Variation 1” was repeatable while “Variation 2” was less repeatable for wet samples and more repeatable for dry samples. It therefore concludes that “Variation 1” (mathematically adding the sample leachates together) yielded the highest and most repeatable values for the wet samples. The raw data for the NEN extractions can be found in Appendix 10.3.4.

7.4.3 Comparison between TCLP and NEN extractions for wet and dry samples

When comparing the effect that drying samples has on the TCLP (Section 7.4.1) and NEN (Section 7.4.2), B, Cd, Pb, and Hg yield higher values for wet samples than dry samples irrespective of the extraction procedure. Ni yielded higher values for dry samples than wet samples irrespective of the extraction procedure.

From this the conclusion can be made that wet extractions generally yield higher values than dry extractions. A sequential extraction procedure will be able to determine the difference in leachable element content between dry and wet samples. Since drying at temperatures below 100℃ will not volatilise any of the elements under investigation it is assumed that the fraction to which they are bound changes during the drying process. Drying will initially saturate the liquid phase with ions and thereafter force precipitation of these ions once super-saturation of the solution occurs. This precipitation could take many forms that include ion sorption onto solid particles and precipitation with other ions in solution. This would in turn change the fractions to which the elements of concern are bound. The TCLP and NEN leaching procedures only extract a certain fraction. Drying will change the constituents of concern within that fraction and therefore yield different results. This is one possible reason for the difference between the wet and dry samples.

When reviewing the three method variations done on the NEN (Table 7.4-A) “Variation 2” yielded unrepeatable results. This is probably due to the duration of the extraction. It is assumed that in three hours equilibrium did not occur. Fällman (1997) recommended extensions to the current NEN procedure to allow for equilibrium to occur.

7.5 Elements extracted from the free liquid in the sample

The elements associated with the free liquid in the sludge samples were determined in addition to the constituent concentrations in the leachate. This has significant application in land disposal practices of sewage sludge, as the free liquid associated with the sludge could also contain elements that are potentially mobile. When considering land application for sludge disposal, the free liquid that was decanted in the experiment should be referred to as the first leachate (Environment Canada, 1990). Figures 7.5-A and 7.5-B represent the mass percentage of each element found in the decanted liquid and that extracted from the solid into the liquid during the extraction when applying the TCLP and the NEN respectively.

Waste activated sludge (WAS) is the excess activated sludge that is removed on a daily basis from the aeration basin in a biological nutrient removal plant. Typically, WAS contains between 0.4 % (m/m) and 3 % (m/m) solids depending on the operational configuration. The water associated with the WAS, is the same quality as the effluent of the plant. Most of the metals are therefore associated with the solid fraction of the sludge (Snyman, HG 2004 pers. comm., 16 March).

Anaerobically digested sludge is normally the product of anaerobic primary sludge digestion (although other sludge is often also blended before digestion). The components in the sludge are hydrolysed and solubilise many of the lignocellulose materials that includes the bacterial cell walls. These processes could be responsible for increasing the metal concentration and metal speciation of the metals associated with the free liquid (supernatant). It is therefore speculated that if the supernatant and the sludge were applied to soil in dedicated land disposal practices such as canon spraying, the metals would be more mobile compared to the situation where the sludge is applied after a dewatering process. Preliminary research results confirm this observation (Snyman, HG 2004 pers. comm., 16 March).

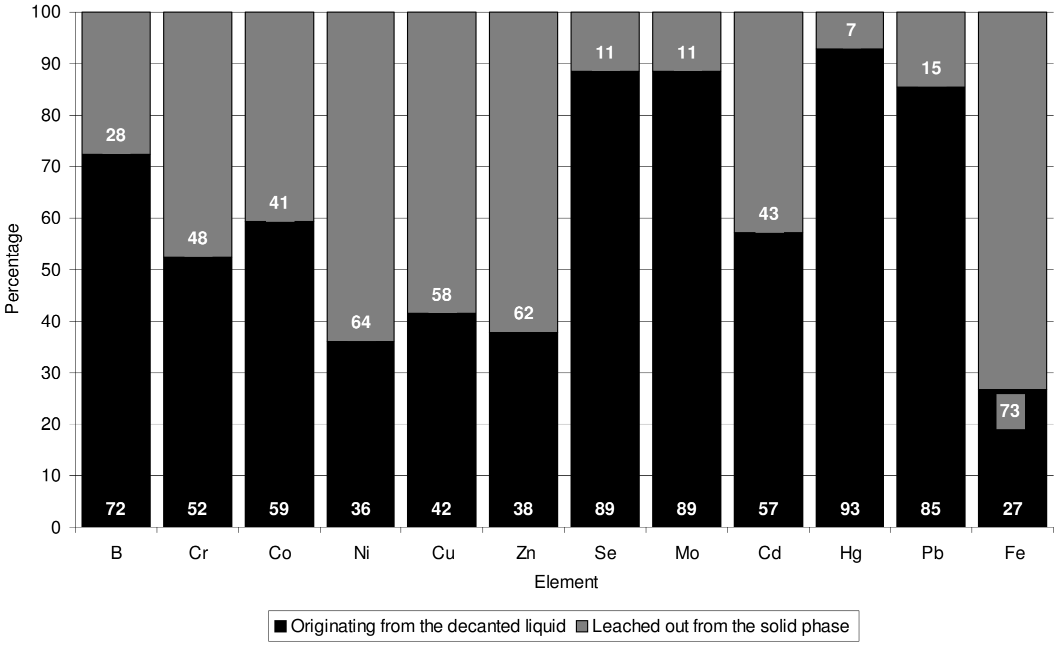


Figure 7.5-A: The mass percentage of element originating from the decanted liquid and leached from the solid phase using the TCLP for anaerobically digested sludge

When considering the TCLP extraction (Figure 7.5-A), more than half of the B, Cr, Co, Se, Mo, Cd and Pb originated from the decanted liquid. More than half of the Ni, Cu, Zn, Hg and Fe originated from the solid phase. Except for Fe all the other elements had more than 35 % of the total amount originating from the decanted liquid.

When considering the NEN extraction (figure 7.5-B), more than half of the B, Co, Cu, Se, Mo, Cd, Hg and Pb originated from the decanted liquid. More than half of the Cr, Ni, Zn and Fe leached from the solid phase.

Reviewing the results from figures 7.5-A and 7.5-B, the inclusion of the decanted liquid in the analysis is important. The method of sample preparation with respect to the moisture content of the sample will have an effect on the concentrations that will leach during the leaching test for all the elements considered except for Fe. For this reason the sample of sludge used to do the analysis must be exactly the same as the sludge to be disposed of or beneficially used. If the moisture content is decreased in sample preparation there will be an underestimation of the leachable fraction.

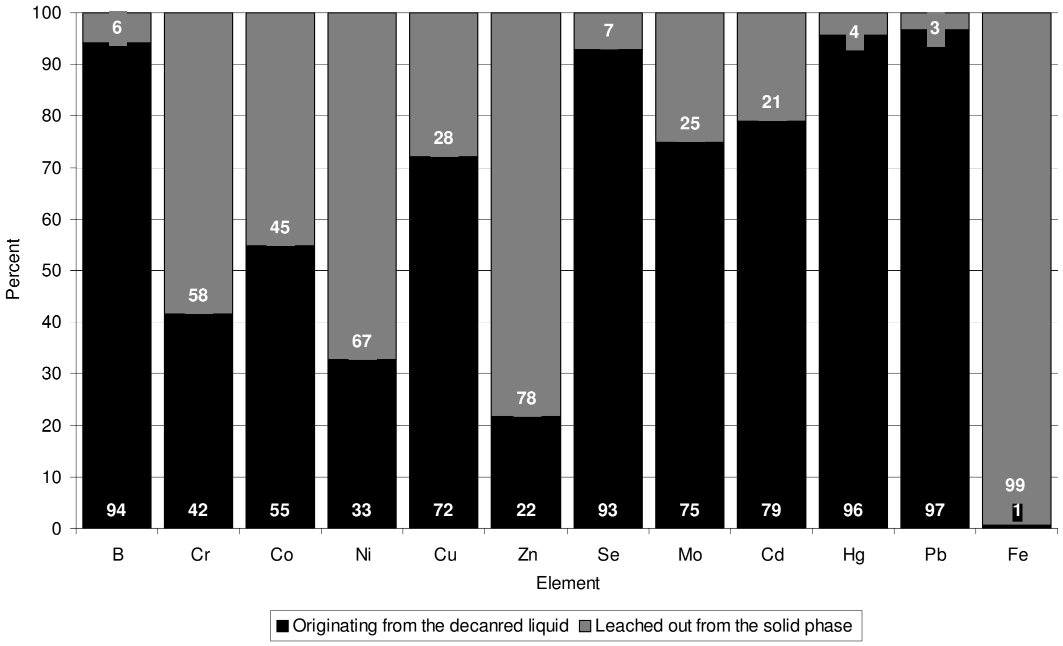


Figure 7.5-B: The mass percentage of element originating from the decanted liquid and leached from the solid phase using the NEN for anaerobically digested sludge

The USA TCLP test procedure specifies that samples with a moisture content above 0.5 % should not be dewatered or dried. The South African adaptation of the TCLP specifies that the sample must be dry. This drying will lead to an incorrect TCLP element concentration. This is substantiated when a similar leaching procedure (the NEN) is evaluated in the same way and yields the same conclusion.

7.6 Leaching test protocols

Sample C (Figure 6.3-B) was used to compare four different leaching protocols. They were the USA TCLP (1992), the AS (1997), the DIN (German Standard, 1984) and the NEN (1995). Table 5.5-A lists some of the important parameters for these four procedures. They are all outlined in Section 6.4. The choice of these four procedures (Section 4.1) considered the type of sample that was to be leached and the waste disposal practice.

There are two main criteria used to determine the applicability of the four selected tests. The first is the Precautionary Principle and the second practicality and ease of use of the analytical protocol. Ellis (2003) refers to two similar understandings of the Precautionary Principle. The first is that *"if information about the environmental impacts of a development is sparse, then appropriate action should be taken"*. The second understanding is applicable to the situation of sludge disposal. It states that *"if a development cannot be proved environmentally safe, then it should not proceed"*. For both of these understandings, replacement of the word "development" with "activity" is more suitable to a sludge disposal situation.

From the two understandings of the Precautionary Principle, it can concluded that when a decision has to be made that may adversely affect the environment, obeying the Precautionary Principle means to err on the safe side. Erring on the safe side in terms of elements possibly leaching out of waste means that all the test procedures being compared should extract the same fraction and the procedure that leaches the most is the best to use.

Practicality and ease of use of an analytical test procedure is important to prevent unnecessary delays and therefore not delay important decision making results. Ease of use and good repeatability of a selected procedure also means that various results can be compared to each other. An important consideration for the South African situation is to critically evaluate the current test procedure with respect to similar procedures used internationally.

7.6.1 Element concentration in the leachate and repeatability

Figures 7.6-A to 7.6-C represent the four selected test procedures (TCLP, AS, DIN and NEN) leachate extraction values obtained for B, Cd, Cr, Co, Cu, Fe, Pb, Hg, Mo, Ni, Se and Zn. Table 7.6-A indicates which procedure yielded the largest concentration of element in the leachate and which yielded the smallest concentration in the leachate.

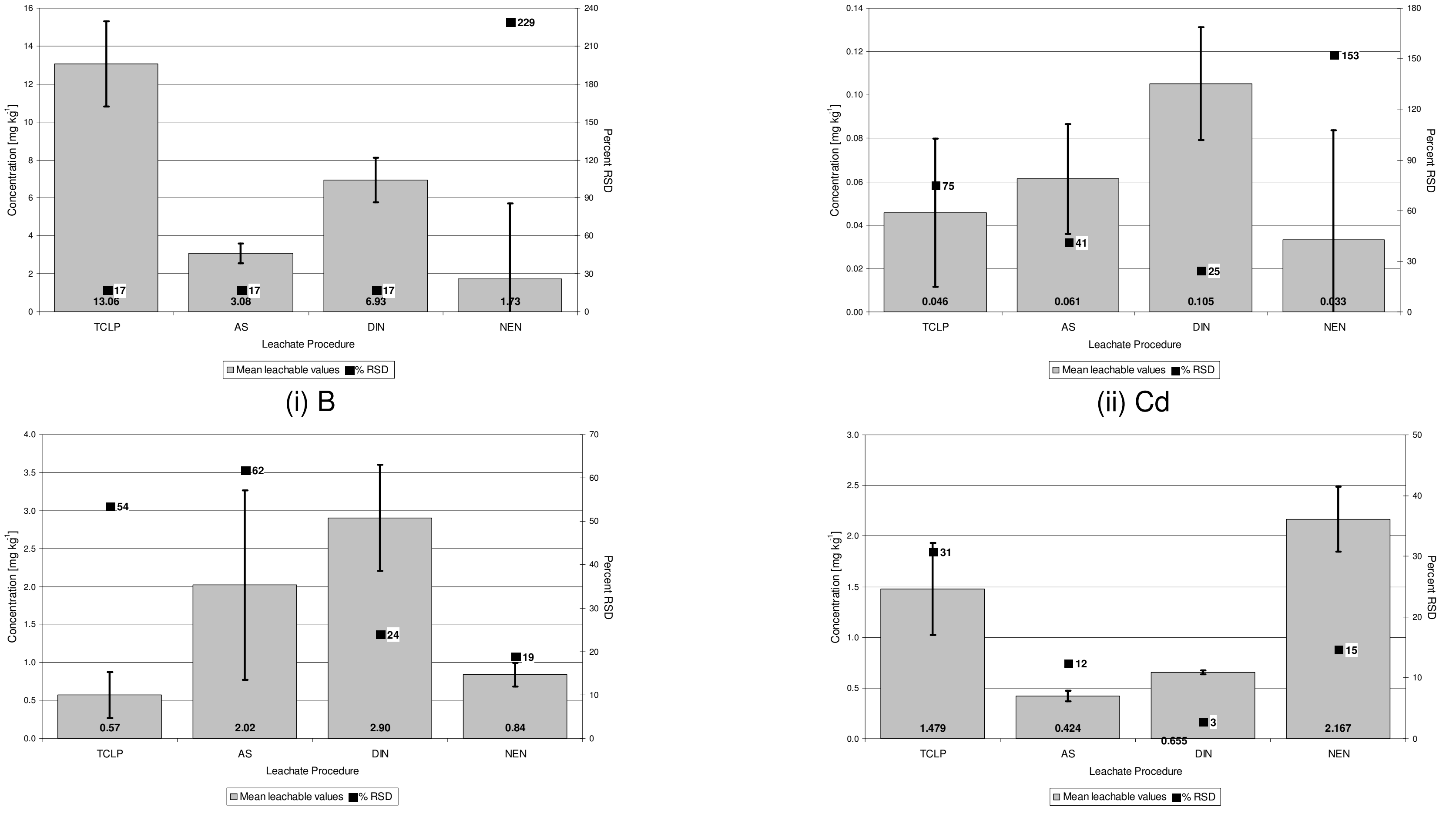
Table 7.6-A: Largest and smallest concentrations extracted by the four selected methods for the specified elements

Procedure	**B**	**Cd**	**Cr**	**Co**	**Cu**	**Fe**	**Pb**	**Hg**	**Mo**	**Ni**	**Se**	**Zn**
TCLP	L		S						S		L	
DIN		L	L		L		L	L	L			
NEN	S	S		L	S	L	S			L		L
AS				S		S		S		S	S	S

L = largest concentration leached
S = smallest concentration leached

The DIN yielded the highest element concentration in the leachate for all the elements analysed followed by the NEN, TCLP and the AS.

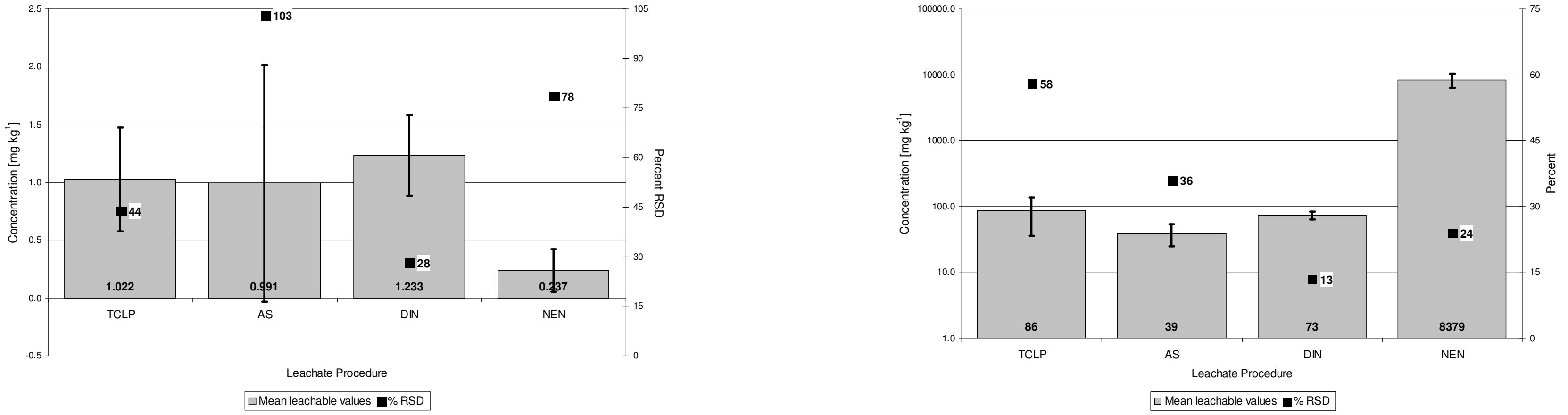
The repeatability of the methods was compared by their percentage relative standard deviations (% RSD). The % RSD is indicated (▪) on figures 7.6-A to 7.6-C and read off the right-hand-side *y*-axis.



(i) B (ii) Cd

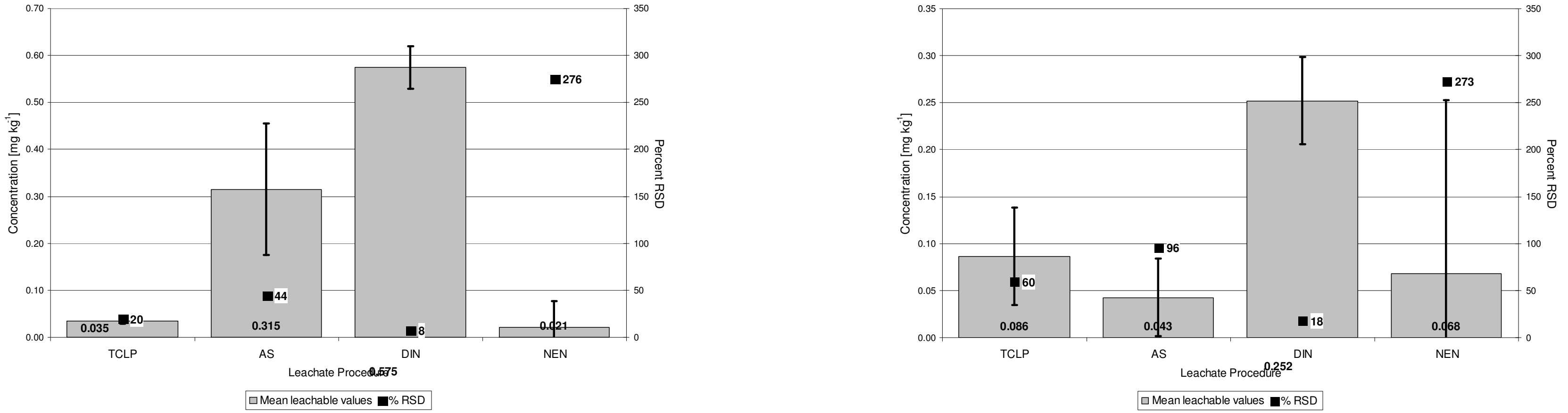
(iii) Cr (iv) Co

Figure 7.6-A: The mean leachable fractions for B, Cd, Cr and Co depending on the extraction procedure



(i) Cu

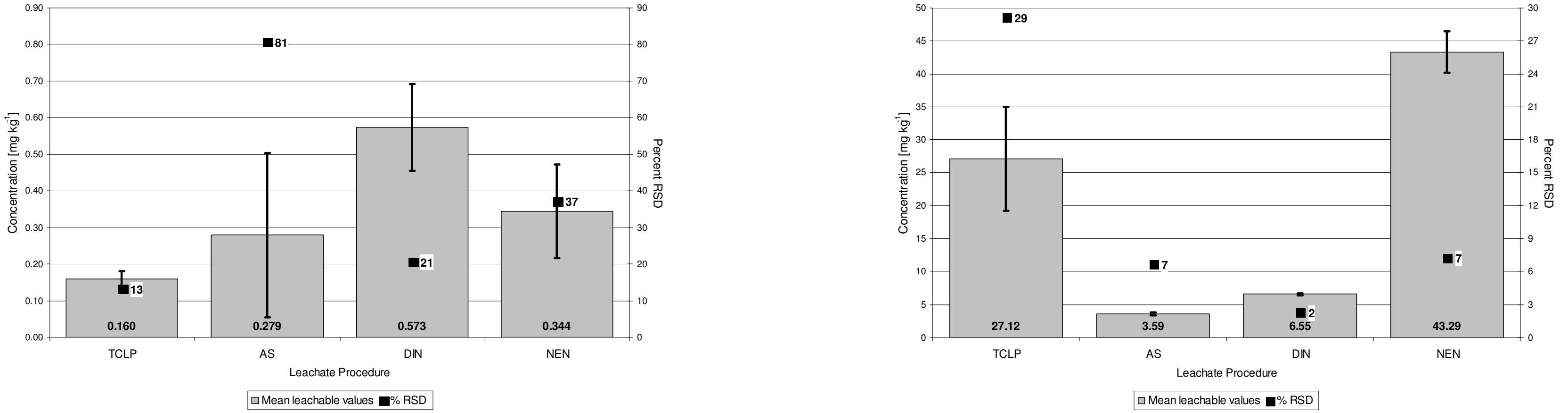
(ii) Fe



(iii) Pb

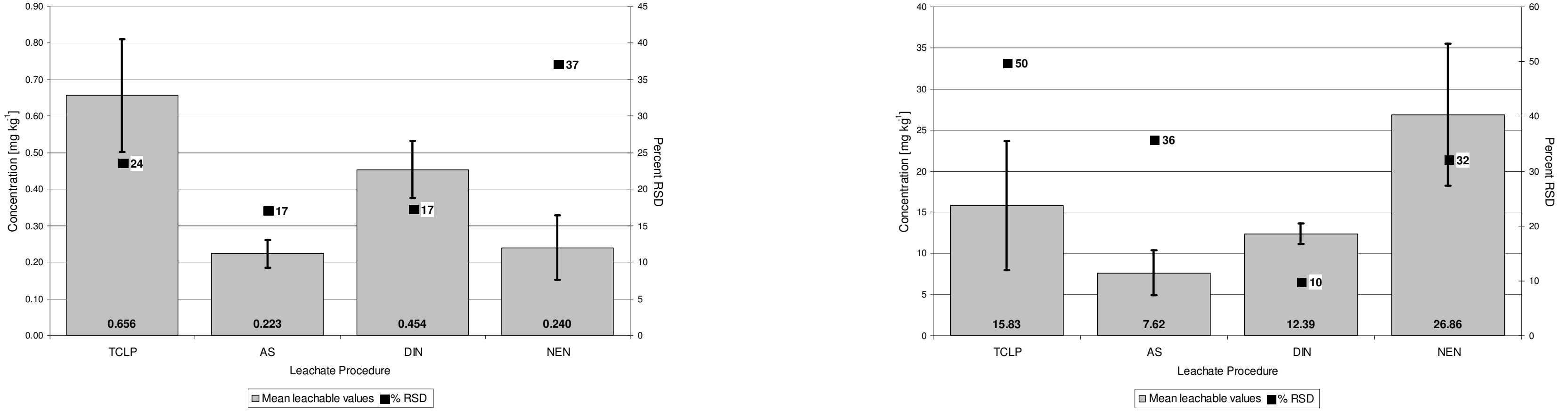
(iv) Hg

Figure 7.6-B: The mean leachable fractions for Cu, Fe, Pb and Hg depending on the extraction procedure



(i) Mo

(ii) Ni



(iii) Se

(iv) Zn

Figure 7.6-C: The mean leachable fractions for Mo, Ni, Se and Zn depending on the extraction procedure

A low % RSD value is an indication of good repeatability. Table 7.6-B indicates which procedure yielded the highest % RSD and lowest % RSD.

Table 7.6-B: Highest and lowest % RSD for the four selected methods and the specified elements

Procedure	B	Cd	Cr	Co	Cu	Fe	Pb	Hg	Mo	Ni	Se	Zn
TCLP	L			H		H			L	H		H
AS		H	H		H				H		L	
DIN		L		L	L	L	L	L		L		L
NEN	H		L				H	H			H	

H = highest % RSD; L = lowest % RSD

From this we can conclude that the DIN was the most repeatable test procedure when comparing the % RSD for the 12 elements analysed.

It was followed by the TCLP, NEN then AS. The raw data for the four test procedures can be found in Appendix 10.3.

7.6.2 Applicability of leaching methods for sludge samples

Many experimental difficulties were encountered when applying the four different leachable extraction procedures to sewage sludge samples. These problems can increase the time required to do a specific step or cause incorrect final results due to loss of sample material. Some of the difficulties encountered as well as additional comments with respect to the procedures are outline below.

TCLP

The TCLP requires an initial step to select the appropriate extraction solution. For all the TCLP extractions done in this research (Samples A, B and C), the addition of acid followed by further heating was required. The initial step to select the appropriate extraction solution did not change between dry and wet samples.

DIN

The sequential leachate procedures caused practical problems with extracting the liquid from the first extraction step and retaining the entire sample for the second extraction step. Sample loss could therefore have occurred. An attempt was made to determine the possible sample loss. This was done after the second extraction step. The sample was separated by centrifuge, it was weighted and a percent solids analysis was done. Using this data and the mass of sample added into extraction step two, the percent dry mass in the second extraction step was determined. After the calculation it was found that there was 16 % more dry mass in the second extraction step than in the first. Since no additional sample was added, this is not possible. An assumption was made that the loss of sample between the two extraction steps was minimal and had no effect on the results.

General comments

- Loading of the wet extraction bottles is difficult due to the consistency of the sample and the required mass.
- The sludge samples have a bad odour.
- During particle size reduction a face-mask needs to be worn to prevent possible infection of the analyst by the pathogens in the sample.
- Filtration of the leachate always caused clogging of the filter paper. Both centrifugation of the leachate as well as multiple filtration steps with decreasing pore sizes were used. This increased the time required for separate the leachate. For sequential extraction (NEN and DIN) the entire sample required separation prior to the second extraction.
- Laboratory centrifuges have limited working volume and they are usually insufficient for the large volumes that needed to be centrifuged.
- Sample preparation per extraction (TCLP, AS and NEN) required that 10 L of sludge be decanted and centrifuged. Decantation resulted in a

50 % decrease of the volume required for centrifugation. This meant that 5 L of sludge needed to be centrifuged for each analysis.

Despite these practical considerations there is also a specific concern about the applicability of these extraction procedures on sewage sludge and other multiphase samples. The % RSD values obtained are unacceptably high for general environmental examples. The high % RSD values for then NEN are attributed to incomplete equilibrium during the second extraction. This is confirmed by the variation in the amount of acid added to the repeat extractions. Percent relative standard deviations are both method and elemental specific. For some procedures, certain elements have sufficiently low (< 10 %) % RSD values but this is not the case for all the elements and procedures.

7.7 The distribution of elements for the various extraction procedures

In sections 7.4 and 7.5 the free liquid associated with the entire sludge sample was discussed. Figure 7.7-A outlines the steps for the extraction procedures. The black squares are the second extractions and were only done for the NEN and DIN procedures. This section focuses on the water in the “concentrated up” or centrifuged sludge samples only (indicated by (a) and (c) on figure 7.7-A). Using these samples one is able to determine how much element found in the leachate was transferred from the solid in the sample to the liquid during leaching and how much was already present in the sample in the liquid form.

Figures 7.7-B to 7.7-D represent the distribution of the elements for the various procedures with respect to the partitioning between the solid and liquid phases of the sample as well as between the steps of the sequential extractions. For each element, the mass found in the liquid fraction of the sample was calculated (see figure 7.7-E). It was subtracted from the amount that was extracted in the test procedure (Section 7.6 and figure 7.7-F). The result represents the amount that was leached out of the solid phase of the sample by the extraction solution. The whole calculation was repeated a second time for the sequential procedures (NEN and DIN). Figures 7.7-B to 7.7-D indicate the percentage of element found in the free liquid added with the sample in black (see also figure 7.7-E). Stacked above this is the percentage of element that was extracted by the extraction solution from the solid phase of the sample, indicated with a white bar filled with small black dots (see figure 7.7—F).

For the two sequential extraction procedures, the percentage of an element found in the free liquid for the second extraction was assumed to have a concentration exactly that of the first leachate. This is indicated on the graphs by the third (figure 7.7-G) and fourth (figure 7.7-H) stacks for the DIN and NEN only. Figures 7.7-E to 7.7-H associate each stack in Figures 7.7-B to 7.7-D with the outline of the extraction procedure in figure 7.7-A.

From figures 7.7-B to 7.7-D, the partitioning of elements between the solid and liquid phase is visible.

The elements that preferentially remain in the solid phase are Cd, Cr, Cu, Fe, Pb, and Zn while B, Co, Hg, Mo, Ni, and Se are largely partitioned to the liquid phase.

The only parameters that differ between the TCLP and AS is the extraction solution and the contact time (see Table 5.17-A). The TCLP has CH_3COOH as an extraction solution and the AS uses demineralised water. The TCLP has an extraction time of 18 hours against the AS extraction time of 20 hours. Since the acceptable standard deviation on the extraction time for the TCLP is 2 hours (USA, 1992) the two methods contact times are accepted to yield no effect on the leachable amount.

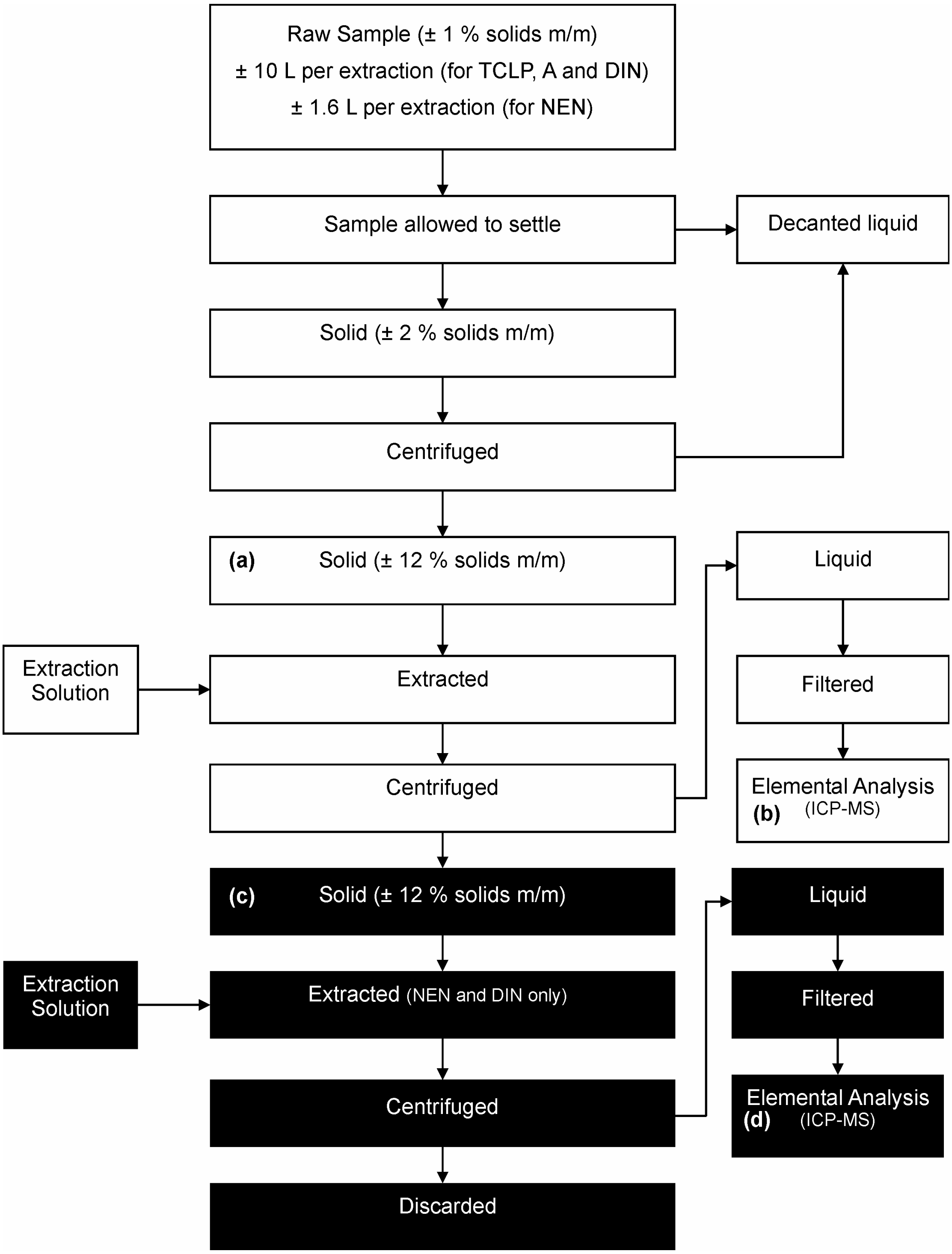
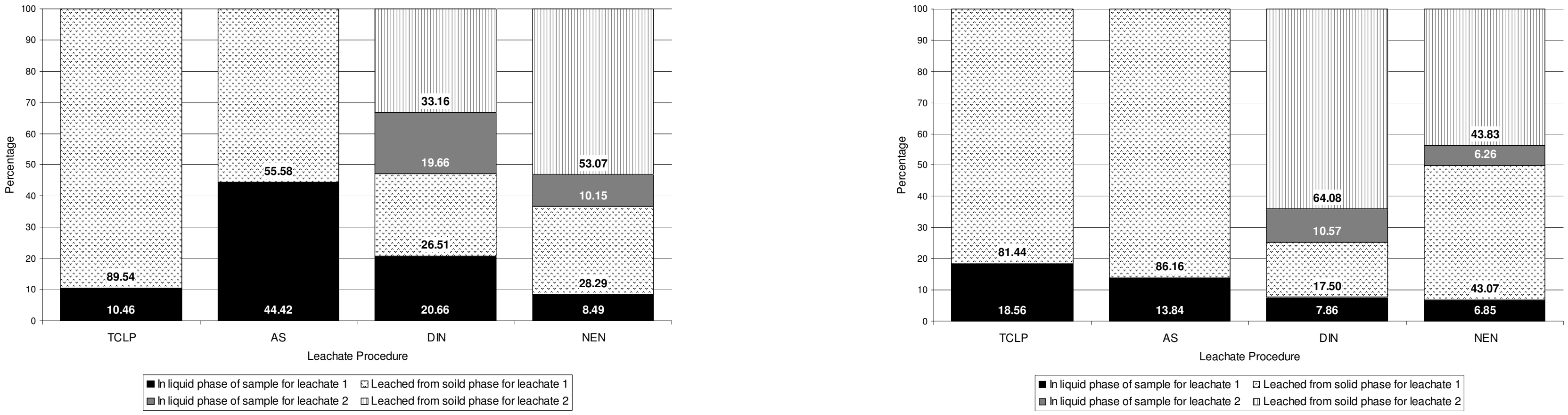


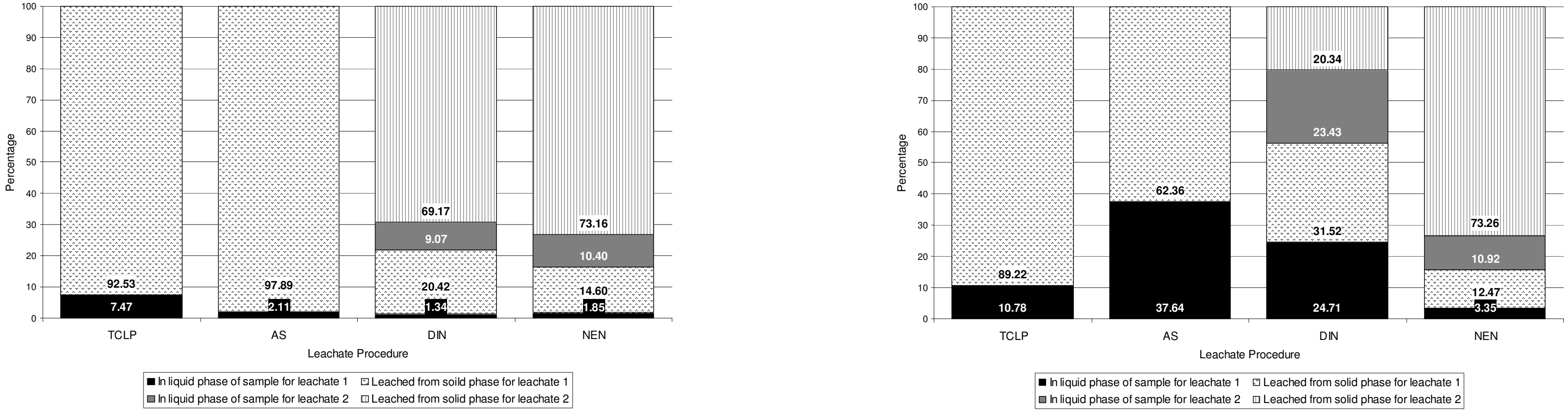
Figure 7.7-A: Outline of the steps in the extraction procedures

Using these two procedures and figures 7.7-B to 7.7-D it can be determined if more element is extracted out of the solid phase (Figure 7.7-F) of the sample than that which is already present in the liquid phase of the sample (Figure 7.7-E). Table 7.7-A indicates this for the specified elements.



(i) B

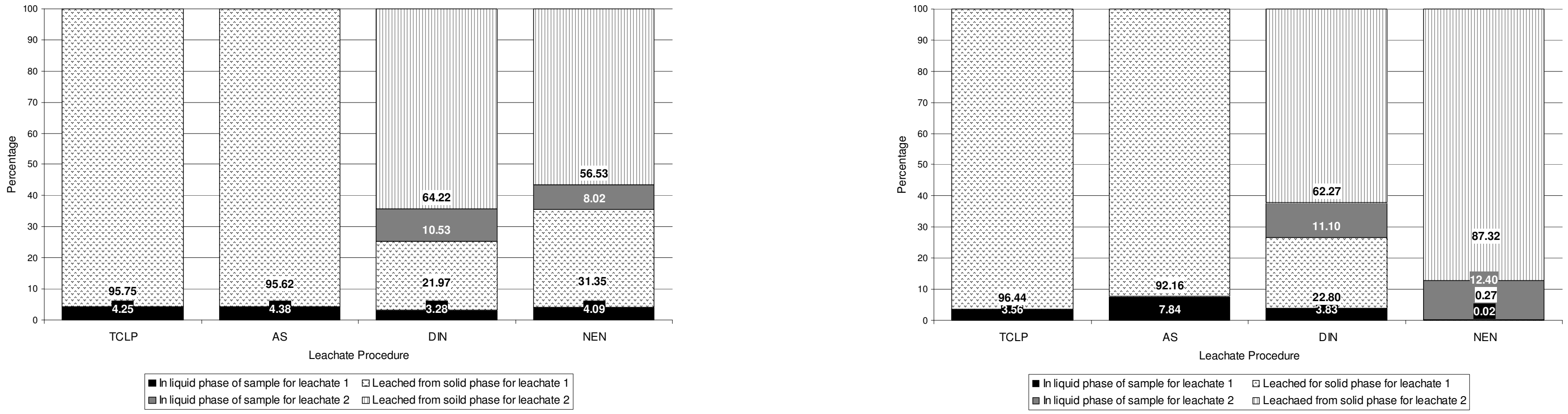
(ii) Cd



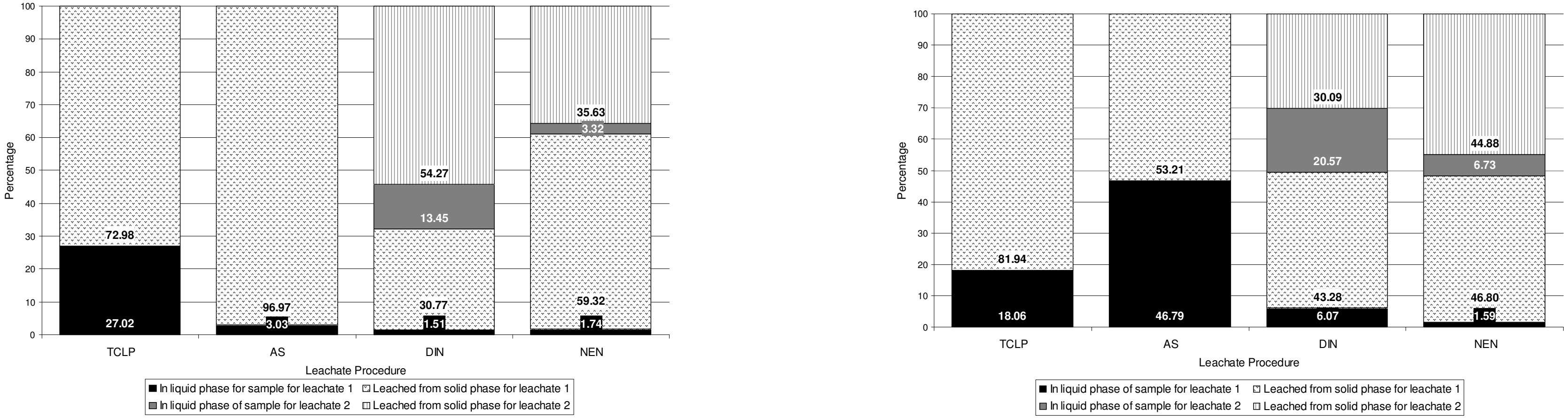
(iii) Cr

(iv) Co

Figure 7.7-B: The extraction efficiency for B, Cd, Cr and Co depending on the extraction procedure

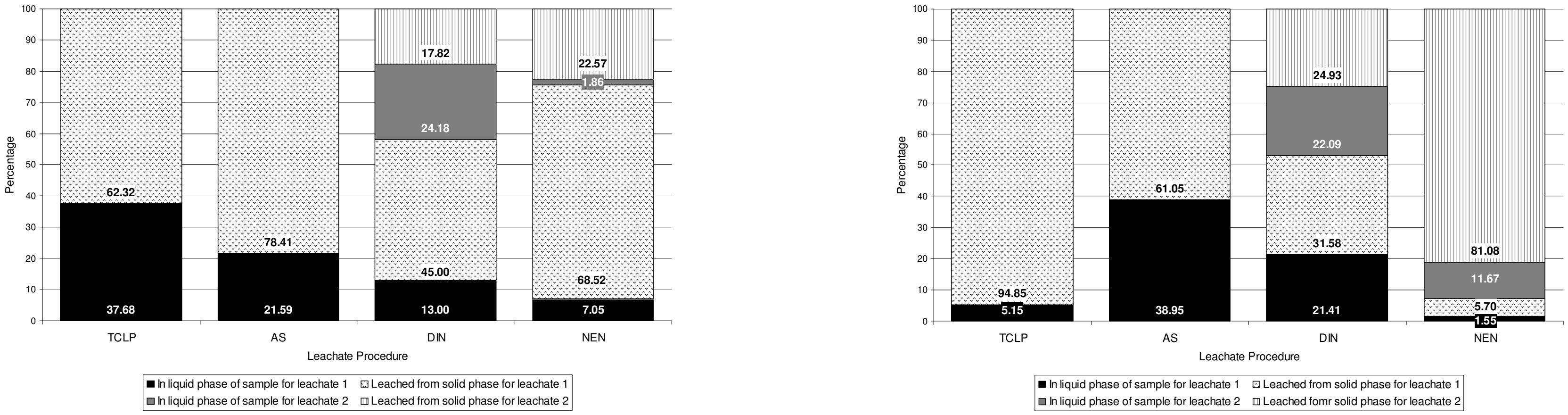


(i) Cu (ii) Fe

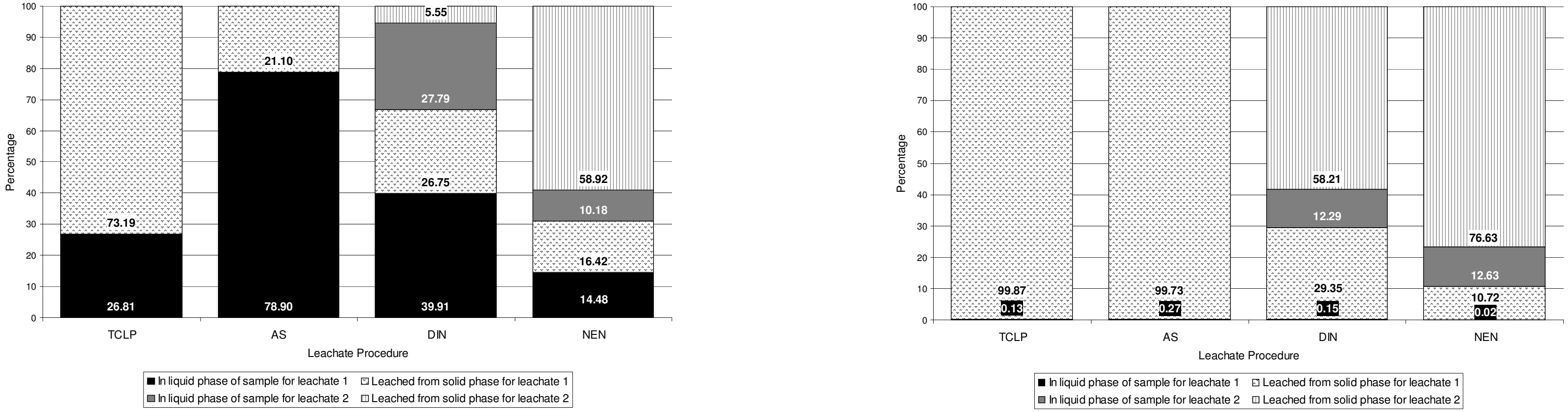


(iii) Pb (iv) Hg

Figure 7.7-C: The extraction efficiency for Cu, Fe, Pb and Hg depending on the extraction procedure



(i) Mo (ii) Ni



(iii) Se (iv) Zn

Figure 7.7-D: The extraction efficiency for Mo, Ni, Se and Zn depending on the extraction procedure

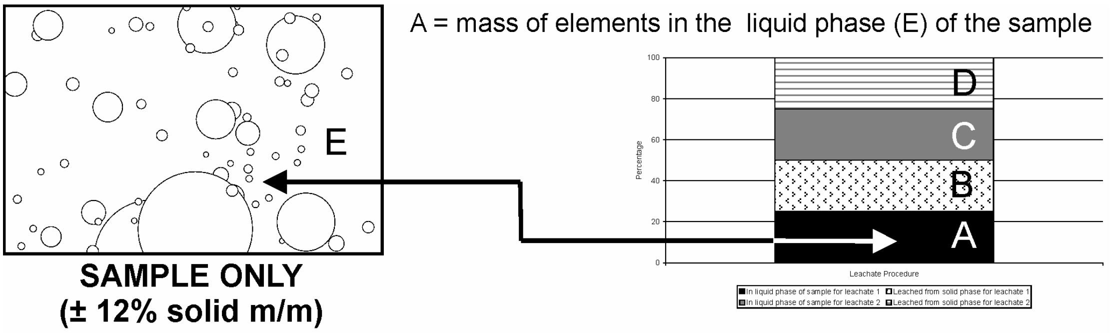


Figure 7.7-E: A graphical representation of the first stack in figures 7.7-B to 7.7-D. Also indicated by (a) in figure 7.7-A

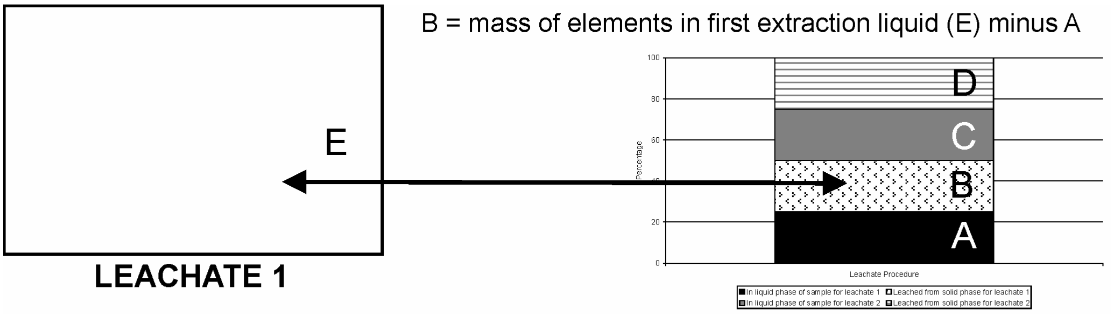


Figure 7.7-F: A graphical representation of the second stack in figures 7.7-B to 7.7-D. Also indicated by (b) in figure 7.7-A

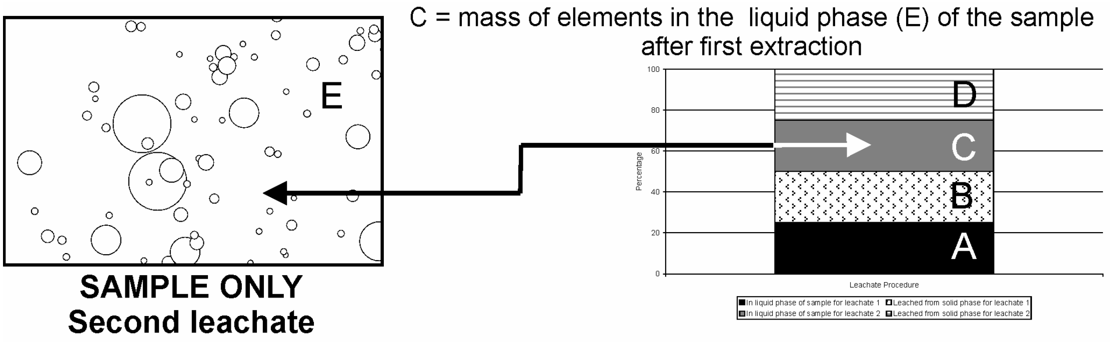


Figure 7.7-G: A graphical representation of the third stack in figures 7.7-B to 7.7-D. Also indicated by (c) in figure 7.7-A

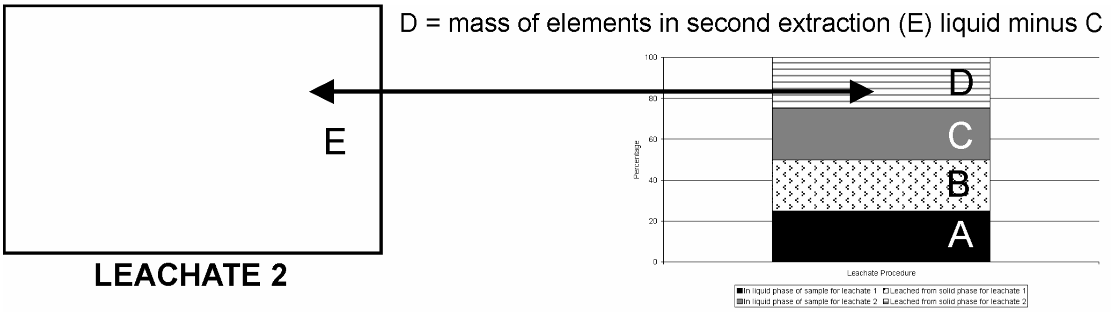


Figure 7.7-H: A graphical representation of the fourth stack in figures 7.7-B to 7.7-D. Also indicated by (d) in figure 7.7-A

The NEN and DIN procedures are not as similar with respect to experimental parameters. From figures 7.7-B to 7.7-D the percentage of the total extracted with respect to the two sequential extractions can be determined. Table 7.7-A also indicates if the first or the second extraction yielded more than 50 % of the total extraction for the specified elements.

Table 7.7-A: The comparisons between the AS and TCLP as well as between the DIN and NEN as found in figures 7.7-B to 7.7-D

Procedure	B	Cd	Cr	Co	Cu	Fe	Pb	Hg	Mo	Ni	Se	Zn
AS		S	S		C		S		S			C
TCLP	S			S		S		S		S	S	
DIN	1	1	1		1	1	1	1				1
NEN	1	1	1		1	1		1		1	1	1

S = more was extracted out of the solid phase (see Figure 7.7-F)
C = comparable extractions between the solid phase and that already present in the liquid phase
1 = the first extraction leached less than 50 % of the total extracted amount

Two important conclusions can be drawn from this section. The first is that when leaching wet anaerobically digested sludge, a portion of the elements leached can be found in the liquid associated with the sample and is not necessarily leached from the solid phase to the liquid phase. The second conclusion is that sequential extractions (irrespective if the two extraction solutions are of the same concentration or not) yield varying portions of the total mass of the element leached out. For some elements it is greater than the first extraction while for others it is less than the first extraction. This means that the leachable fraction was not all leached out in the first step for the DIN.

7.8 The buffer capacity of sewage sludge and its affect on pH and metal mobility

The buffer capacity of sewage sludge is dependant on the raw water entering the wastewater treatment plant and the treatment methods used to generate the sludge. For this reason sewage sludge buffer capacity differs between plants and also differs within a plant over time. Buffer capacity can be measured by the amount of acid required to neutralise a sample. The NEN procedure requires the addition of acid to maintain the pH of the sample at the specified value. The amount of acid required to maintain the pH is dependant on the buffer capacity of the sample.

The TCLP, AS and DIN do not specify final or initial pH constraints on the sample. Metal solubility in water and pH are directly related. The lower the pH the greater the solubility of the metal. In sludge samples the relationship is not as clearly defined since there are many other influencing factors in the sludge matrix that affect the solubility. For the TCLP, AS or DIN, different samples are not being compared on an equal level since final pH values are different. Sludge with a higher buffer capacity would appear to leach less metal than sludge with a lower buffer capacity if the total metal content is the same. With respect to sludge disposal, it means that over time, as the buffer capacity of the sludge is decreased, more metals will become available. A pH-static test will account for this in the test method.

The experimental procedures used, all required the recording the final leachate pH. Figure 7.7-A represents the pH data for the four extraction procedures that were compared.

The two procedures that leach with water (AS and DIN) yielded the highest leachate pH values. This was expected since the buffering capacity of the sludge is large and the extraction solution is not strong. From figure 7.8-A, the TCLP (CH_3COOH) and NEN (HNO_3) yielded comparable final leachate pH values. The NEN done on dry and wet samples have, as expected comparable values since it is a pH-static test.

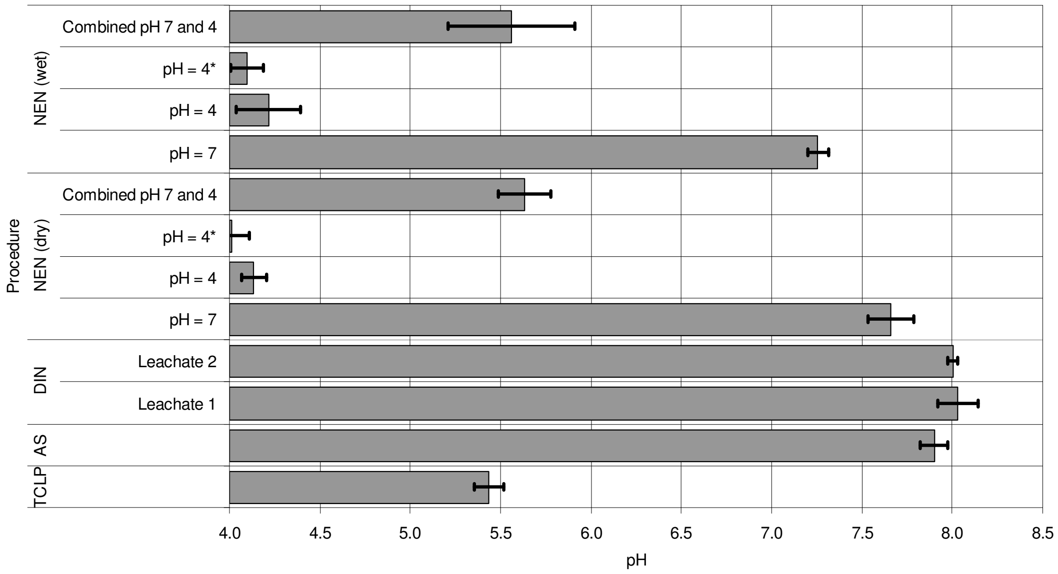


Figure 7.8-A: The mean pH values for the four different extraction procedures

* pH = 4: NEN with single non-sequential extraction. (“Variation 2”)

The pH-static test (NEN) always yielded final leachate pH values higher than the pH of the extracted sludge mixture. This is probably due to the solid / liquid phase separation after extraction.

A further explanation on the acid neutralisation capacity of the sludge can be found in Appendix 10.5.

8 Conclusions and recommendations

8.1 Conclusions

The research objectives were:

1. To conduct a literature survey on:
   - Present South African Sludge Management with regards to the South African Sludge Guidelines.
   - The influence of time on metal mobility in sludge-amended soil.
   - The application of single and sequential extraction test procedures for use on sewage sludge and sludge-amended soil samples.
   - The parameters of importance when leaching sludge and soil samples.
2. To determine the relationship between total and leachable elemental extractions of anaerobically digested sewage sludge.
3. To determine if Inductively Coupled Plasma Mass Spectroscopy (ICP-MS) and Flame Atomic Absorption Spectroscopy (FAAS) elemental analysis of leachates can be used interchangeably on sewage sludge samples.
4. To determine if drying of sewage sludge samples, prior to leaching will change the amount of element that leaches out.
5. To compare four leachable extraction procedures for their applicability to elemental leaching and make recommendations on selecting a leaching test procedures for the South African Sludge Guidelines.

A review of how successfully these aims were achieved is outlined in the following sections.

8.1.1 The influence of time on metal mobility in sludge-amended soil

During the literature investigation on the behaviour of metals in sludge-amended soil, it was found that organic matter has an important role in the short-term availability and release of metals. The long-term contribution of organic matter is not yet widely accepted although the role of inorganic soil constituents is understood. It was found in literature that metals in various sludge types prefer the liquid phase to the solid phase. When leachate tests were done on anaerobically digested sludge, the amount of metal originally found in the liquid phase was often more than that which was leached out (on a dry mass basis). Literature indicates that metals applied to soil originating from sludge accumulate in the soil. Metal uptake by plants as well as metal leachability is limited. The potential risk of groundwater contamination could be much lower than presently anticipated. Metals further redistribute within the solid soil particles. This was alluded to by the experiments that compared the dry and wet sludge samples. Sequential extraction can be used to determine the fraction in which the metals are found and to predict the availability of potential for release from the solid phase.

8.1.2 The applicability of single and sequential extraction tests on sewage sludge and sludge-amended soil and important properties for these tests

Leaching tests are classified according to chemical / experimental conditions (two classification methods) or according to the intended use of the results obtained from the test.

The protocols that were considered, were the USA Toxicity Characteristic Leaching Procedure (TCLP), Australian Standard (AS), Nederlands-Normalisatie-Instituut Availability test (NEN 7341) and the Deutches Institut für Normung water leachability test (DIN 38 414-S4). The experimental procedure between the TCLP and AS is similar. The applicability of the TCLP for any scenario other than the original intention of co-disposal of hazardous waste with municipal solid waste has generated extensive debate and research. International research has generally been critical of varied uses of the TCLP. The TCLP and its applicability is presently being reviewed. The NEN is mainly applied to inorganic samples. Extensive research into the test development occurred and there are reserved concerns about specific aspects of the test. The DIN is the only test protocol aimed at organic soil and sludge samples. Its use internationally is limited.

Sample Mass

The mass of the sample analysed was generally found not to affect the results obtained. Literature established this and experimentally it was proven correct for B, Cr, Co, Cu, Mo, Ni and Zn. There was a difference for Cd, Fe, Pb, Hg and Se. The number of samples was too small to confirm this.

pH

The final pH of the neutral extraction solution (demineralised water) was comparable despite the experimental procedure being different between the AS and the DIN. The acid neutralisation capacity of the dry and wet samples was different. The dry sample had a lower acid requirement than the wet sample. Sludge acid neutralisation capacity is difficult to determine. As expected, acidic extraction solutions leached more metals than neutral solutions. The final pH of the fixed pH tests procedures was comparable to the final pH of the variable pH tests for acidic extraction solutions.

8.1.3 The relationship between total and leachable extractions of sewage sludge

Literature cites relationships between leachable NH_4NO_3 extractions, and total *aqua regia* extractions as well as between DTPA and *aqua regia*. Experimental evidence for a relationship between TCLP leachable extractions and *aqua regia* extractions done on dry samples was only found for Co, Ni, Pb and Zn. The relationship was calculated for Co and Pb. This relationship could not be proven since the sampling procedure of the literature data and this research was incomparable.

8.1.4 The interchangeability of ICP-MS and FAAS elemental analysis data for leachates

When choosing an analytical technique to determine the element leached, this research clearly indicates that despite the lower detection limits of ICP-MS, FAAS is totally suitable and comparable to ICP-MS data for regulatory compliance. For research and detailed investigation ICP-MS can yield more useful data.

8.1.5 Drying sludge samples

Experimental results between dried and wet samples differed. It was found that the effect of drying on leachability is both dependant on the element and the extraction procedure used. For B, Pb, Hg and Se wet samples yielded higher element concentrations than dry samples irrespective of the extraction procedure followed. For Ni and Zn dry samples yielded higher element concentrations than wet samples irrespective of the extraction procedure followed. The dry samples have a small variation among repeat extractions when compared to the wet samples both in literature and experimentally. This can be explained by the sample homogeneity being better in the dry samples.

When doing leachate extraction procedures, it is important to adhere to the specified procedure, especially for regulatory compliance. South Africa currently dries sludge samples and this research indicates that there will be a variation in results depending on the samples being dried on not.

8.1.6 A comparison of the various test procedures

The test procedures were evaluated on two parameters. The first parameter that was used was to determine which procedure leached the largest amount of element (in accordance with the Precautionary Principle). The second parameter was the ease of use of the experimental procedure. Considering the two single extraction procedures used, the TCLP was found to be better than the AS. This meant that a preference for a CH_3COOH solution over a demineralised water extraction solution exists.

The variations considered in the NEN procedure with respect to addition of leachates determined that the present experimental procedure, despite the objective to yield a maximum availability, does not do so. It was found that the separate analysis of leachate one and two followed by mathematical combination yielded higher results.

The comparison of the four different leachate extraction procedures indicates that the DIN was not only the most repeatable, but also yielded the highest values. There is an experimental concern about the DIN procedure. The method specifies that the analyst chooses the number of sequential extractions and this research indicated that one extraction is insufficient for anaerobically digested sludge samples. For the two sequential extraction procedures it was found that the second extraction step extracted more than the first for most of the elements irrespective of the procedure. This emphasises the importance of sequential extraction procedures for regulatory compliance and not solely for research purposes. The time required to extract according to the DIN procedure also raises a concern. It took four days for extractions of one sample to be completed. This is very long for a regulatory compliance test procedure.

8.2 Recommendations

In reviewing the present South African Sludge Guidelines for shortcomings it was found that as an extraction method for sewage sludge the TCLP needs to be replaced. Furthermore, future changes to the Sludge Guidelines need to clearly specify both total and leachable extraction procedures and provide detailed methods for the analysis thereof. This research considered three other options to replace the TCLP as a leachable extraction procedure and concluded that presently the German DIN appears to give the best results despite the length of the procedure. There are other practical considerations that also deter from using the DIN. For this reason the DIN is not recommended as an alternative to the TCLP.

To make sewage sludge samples comparable nationally it is recommended that a pH static test be adopted. The NEN is a good basis to begin with, but chemical and physical parameters like particle size, contact time, acid neutralisation capability of the extraction solution and choice of final leachate analysis (added together prior to analysis or not) are vitally important and require further study.

Sample preparation prior to leaching also needs to be clearly specified and defined in the Sludge Guidelines. It is recommended that the moisture content of the sludge samples by analyses on an “as used” (for beneficially using sludge) or “as disposed of” (for sacrificial land disposal or delisting) basis. If the sludge sample contains a large portion of free liquid is it further recommended that the liquid is decanted and analysed then mathematically added to the leached amount.

Elemental analysis of the leachate can successfully be done by FAAS or any similar or more precise technique.

The present leachable limits for South Africa are based on protection of the groundwater. Literature has clearly stated metal availability in the soil poses a higher risk than groundwater contamination does. Limit values need to protect all areas of the environment that could be in danger not just select areas. It is also important to note that limit values need to be adjusted to the chosen extraction procedure. This research has indicated that different elements are leached differently by the various procedures. A limit value is therefore unrealistic if it does not also consider the method used to do the extraction.

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10 Appendices

10.1 Total and leachable fractions

10.1.1 Total *aqua regia* extraction data (ICP-MS)

Table 10.1-A: Total *aqua regia* extraction of sewage sludge samples for 24 sites for the specified elements

Site	Cd	Co	Cr	Cu	Hg	Mo	Ni	Pb	Se	Zn
	mg kg^{-1}									
1	58.02	137.62	132.16	311.45	2.27	3.96	296.10	119.19	9.13	1,459.62
2	10.39	51.09	237.73	504.10	2.27	8.61	142.35	775.83	25.91	2,598.34
3	2.34	14.66	270.80	218.27	1.53	3.59	112.11	71.84	5.76	709.21
4	13.79	37.16	172.38	284.65	2.67	8.86	135.93	277.11	7.40	1,177.94
5	2.10	4.90	78.55	185.08	2.79	14.41	62.61	43.79	3.02	474.20
6	7.94	18.70	221.16	206.23	2.12	1.18	125.75	178.19	7.46	672.98
7	14.16	14.68	175.66	239.13	2.84	5.51	182.29	163.24	6.75	1,012.67
8	2.38	18.75	165.23	165.77	4.21	57.39	244.33	34.50	3.29	618.72
9	5.20	15.38	214.23	305.51	2.88	21.15	117.70	1,715.29	11.28	1,272.60
10	7.56	156.64	156.09	667.93	3.41	12.12	253.53	426.94	8.27	1,453.28
11	11.05	45.08	61.47	384.86	4.74	11.27	140.68	410.91	14.58	1,679.41
12	2.38	8.60	52.41	160.91	2.48	4.43	101.75	304.61	11.97	1,997.84
13	3.13	8.16	59.20	153.71	2.59	9.26	106.12	332.27	7.81	1,793.17
14	38.43	83.78	243.09	340.91	2.15	9.42	388.46	361.86	6.89	1,583.01
15	2.33	11.09	128.35	157.62	2.08	7.35	110.04	41.00	7.09	469.55
16	2.81	8.30	80.72	262.62	3.55	10.61	76.93	70.08	4.00	656.96
17	3.01	10.11	67.23	236.53	3.81	10.22	70.23	74.13	3.53	672.74
18	2.22	7.60	36.36	139.30	1.90	3.91	66.13	50.63	4.32	606.79
19	13.53	22.21	77.24	200.68	9.99	11.70	109.44	149.94	3.49	890.46
20	27.10	52.98	195.31	496.21	3.21	17.40	246.32	288.83	9.74	1,514.56
21	26.42	53.45	220.56	567.42	2.88	11.61	244.29	307.32	6.98	1,670.78
22	6.97	19.54	83.96	265.86	4.93	6.28	93.68	181.28	3.92	1,045.43
23	15.31	27.69	165.82	267.89	1.83	7.89	174.03	168.24	9.08	1,168.54
24	2.48	16.65	103.92	156.41	1.96	1.05	107.84	84.49	7.39	697.84

10.1.2 Leachable TCLP data (ICP-MS)

Table 10.1-B: The TCLP solutions, sample mass and final leachate pH for the 24 sewage sludge samples

Site	**TCLP solution**	**Mass of sample**	**Final Leachate pH**
		g	
1	1	100.61	5.11
2	2	100.13	3.94
3	1	100.03	5.27
4	1	100.22	5.53
5	1	100.04	5.49
6	1	105.66	5.58
7	1	100.01	5.63
8	2	100.01	6.34
9	2	100.29	3.91
10	2	100.01	4.19
11	2	86.81	4.43
12	1	100.06	5.22
13	1	100.19	4.24
14	1	100.00	5.14
15	1	100.29	5.3
16	1	100.38	5.22
17	1	100.94	5.33
18	1	100.04	5.11
19	1	100.00	5.07
20	2	100.00	4.44
21	2	100.05	4.56
22	1	100.22	5.41
23	1	100.19	5.55
24	1	100.17	5.18

Table 10.1-C: The leachable TCLP extraction data for 24 sewage sludge samples for the specified elements using an ICP-MS

Site	Cd	Co	Cr	Cu	Hg	Mo	Ni	Pb	Se	Zn
	mg kg^{-1}									
1	3.01	69.27	0.38	6.61	0.84	0.56	108.59	0.35	2.66	618.82
2	1.69	16.71	0.79	51.17	0.53	0.48	30.38	0.61	8.89	1611.75
3	0.23	4.60	1.92	3.79	0.81	0.75	16.88	0.37	1.43	152.44
4	0.44	4.33	0.46	2.33	0.49	0.62	13.08	0.41	1.49	152.20
5	0.24	0.63	0.23	3.30	0.65	0.60	4.17	0.34	1.66	65.47
6	0.14	2.27	1.64	1.45	0.47	0.40	9.65	0.27	1.69	37.19
7	0.45	1.71	0.85	1.42	0.59	0.83	22.34	0.48	1.56	33.69
8	0.33	2.41	0.39	4.94	0.33	0.62	16.98	0.34	2.76	126.48
9	0.20	3.28	5.81	1.37	0.24	0.50	25.67	4.69	1.67	347.73
10	1.32	71.84	0.97	49.83	0.57	0.57	91.44	0.38	3.92	935.03
11	3.79	6.77	0.82	60.42	0.69	0.73	61.29	0.97	3.86	1025.76
12	0.33	1.83	0.41	1.16	0.56	0.56	17.53	0.31	1.98	177.19
13	0.15	1.81	0.33	1.46	0.22	0.32	23.91	0.51	2.44	414.72
14	0.61	34.01	1.35	4.00	0.500	1.07	121.87	0.47	2.46	509.92
15	0.33	0.57	0.46	3.36	0.34	0.54	5.09	0.34	1.99	38.52
16	0.47	1.20	0.87	5.43	0.69	0.57	8.22	0.42	2.29	85.65
17	0.14	1.11	0.74	2.08	1.02	0.67	7.16	0.23	1.88	121.38
18	0.16	0.99	0.42	1.06	0.45	0.55	5.14	0.39	1.57	57.22
19	0.63	2.22	0.38	1.76	0.40	0.56	6.25	0.33	1.96	189.08
20	7.73	23.88	3.03	18.09	0.37	0.60	115.44	0.37	3.26	1091.45
21	6.26	20.35	3.12	19.47	0.39	0.48	98.18	0.47	2.70	1037.24
22	0.09	2.39	0.58	2.33	0.57	0.58	12.02	0.44	2.13	90.84
23	0.21	2.40	1.13	3.02	0.17	0.80	12.14	0.52	0.34	52.00
24	0.02	2.12	0.44	0.67	0.77	0.60	8.62	0.39	2.47	44.66

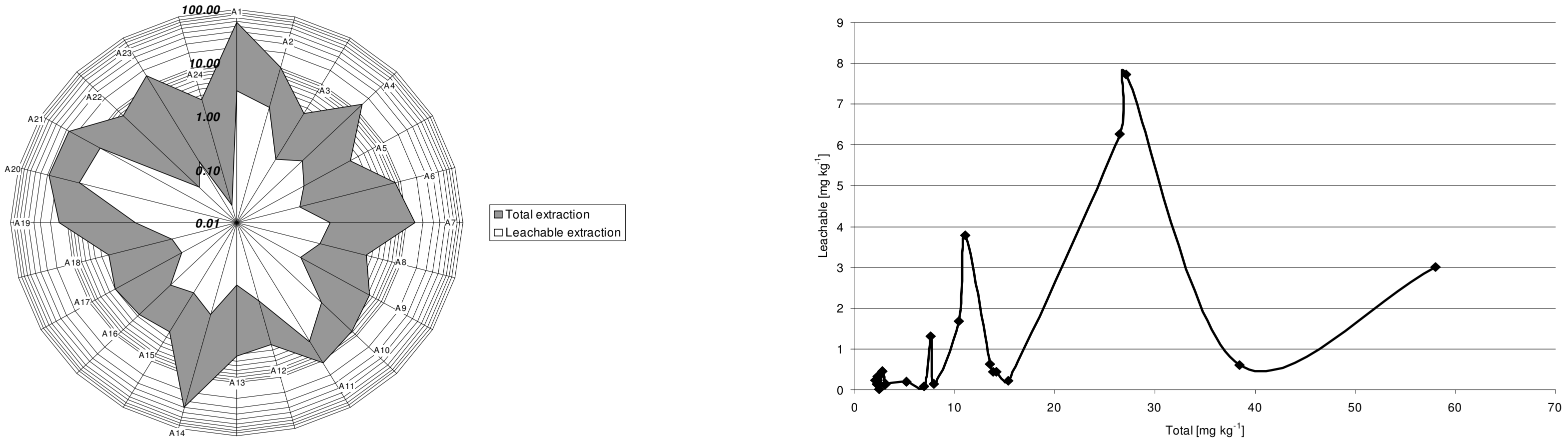
10.1.3 Leachable TCLP data (FAAS)

Table 10.1-D: The FAAS data of the concentration of 24 sewage sludge samples for Cd, Cu, Pb and Zn

Site	**Cd**	**Cu**	**Pb**	**Zn**
Units	mg kg^{-1}			
1	2.0	5.3	3.98	563.2
2	2.0	41.3	3.99	8722.0
3	nd	6.0	2.00	104.0
4	nd	4.0	nd	100.4
5	nd	3.0	nd	19.3
6	1.9	1.9	3.15	18.3
7	2.0	2.0	2.67	28.7
8	nd	5.0	2.00	101.3
9	2.0	45.2	nd	1602.0
10	2.0	3.0	2.00	366.6
11	2.3	56.8	2.30	1758.6
12	nd	2.0	3.00	80.6
13	2.0	4.0	2.00	465.8
14	nd	5.0	nd	22.7
15	2.0	3.0	1.99	452.0
16	nd	5.0	nd	30.6
17	nd	3.0	1.98	95.1
18	2.0	2.0	2.00	35.3
19	nd	3.0	2.00	130.7
20	6.7	10.0	2.67	2426.7
21	6.7	12.0	2.67	2039.0
22	nd	2.0	2.00	59.9
23	nd	4.0	2.00	36.6
24	nd	2.0	2.00	28.6

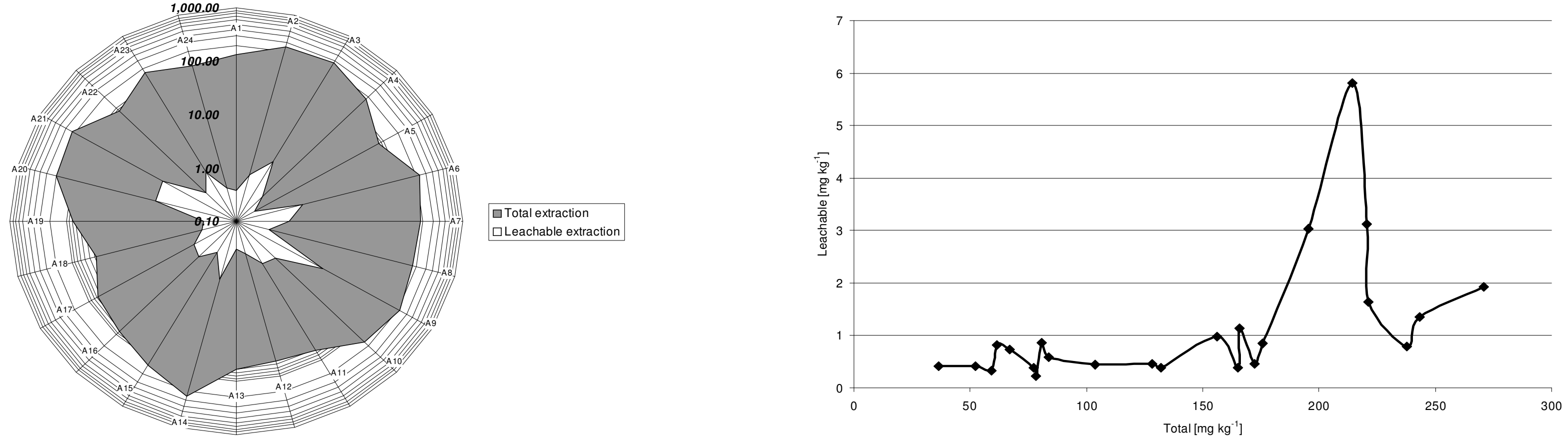
nd = not detected

10.1.4 Total and leachable comparison graphs for metals below 75 % correlation



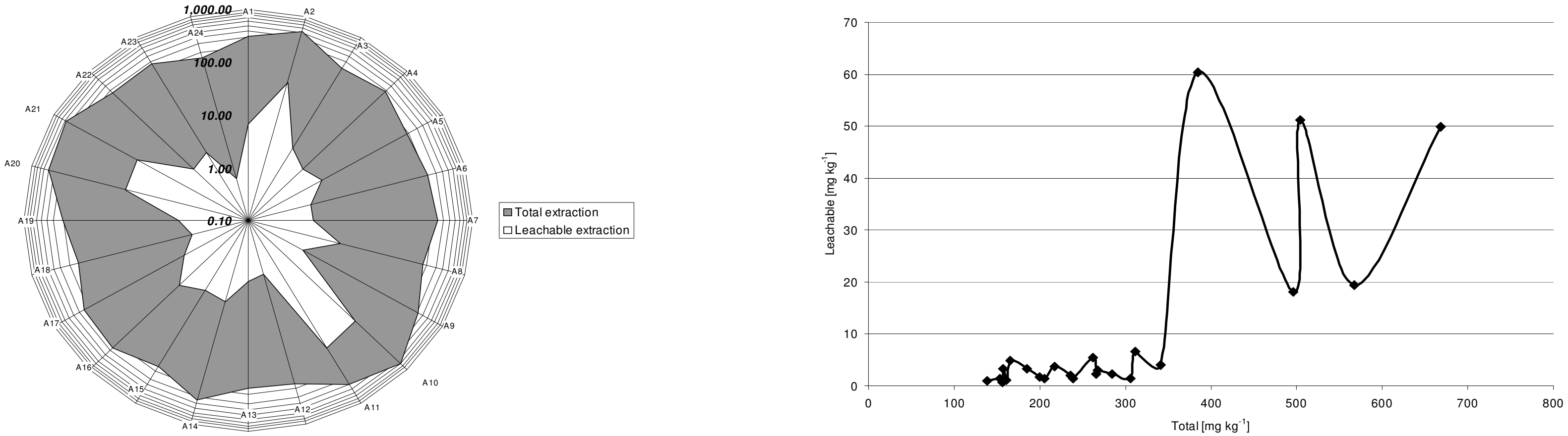
(i) (ii)

Figure 10.1-A: The total and leachable fractions for Cd for the 24 sewage sludge samples analysed for in mg kg^{-1}



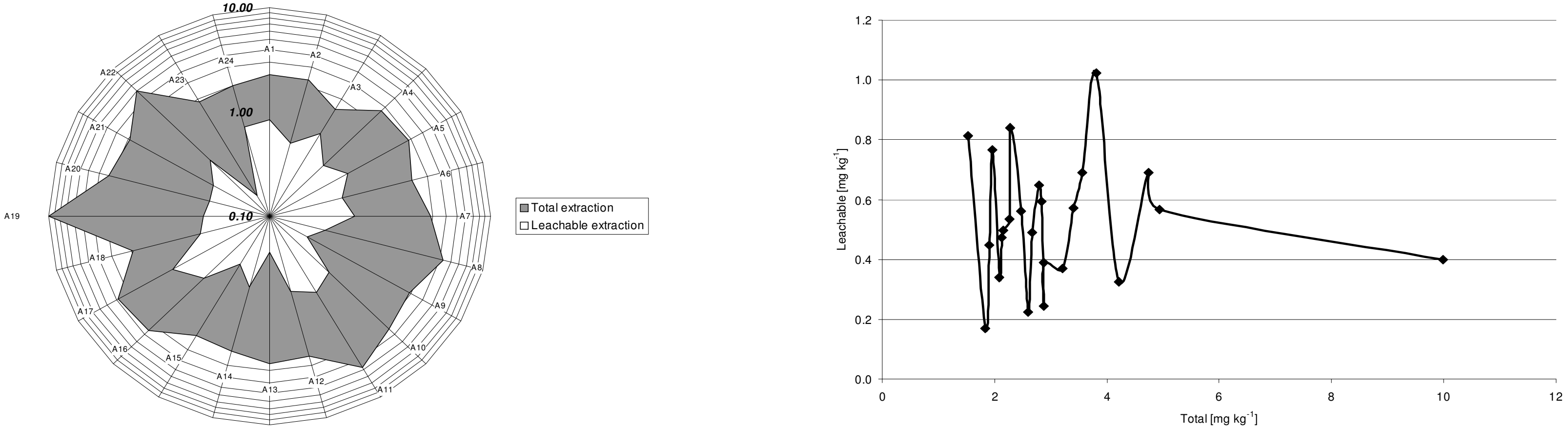
(i) (ii)

Figure 10.1-B: Graph of the total and leachable fractions for Cr for the 24 sewage sludge samples analysed in mg kg^{-1}



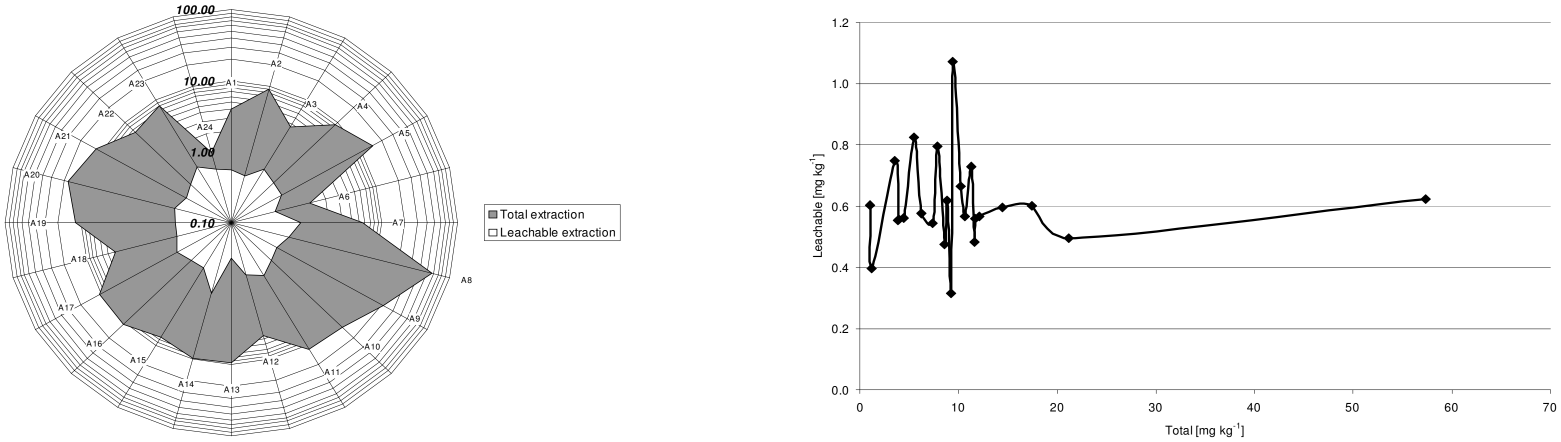
(i) (ii)

Figure 10.1-C: Graph of the total and leachable fractions for Cu for the 24 sewage sludge samples analysed in mg kg^{-1}



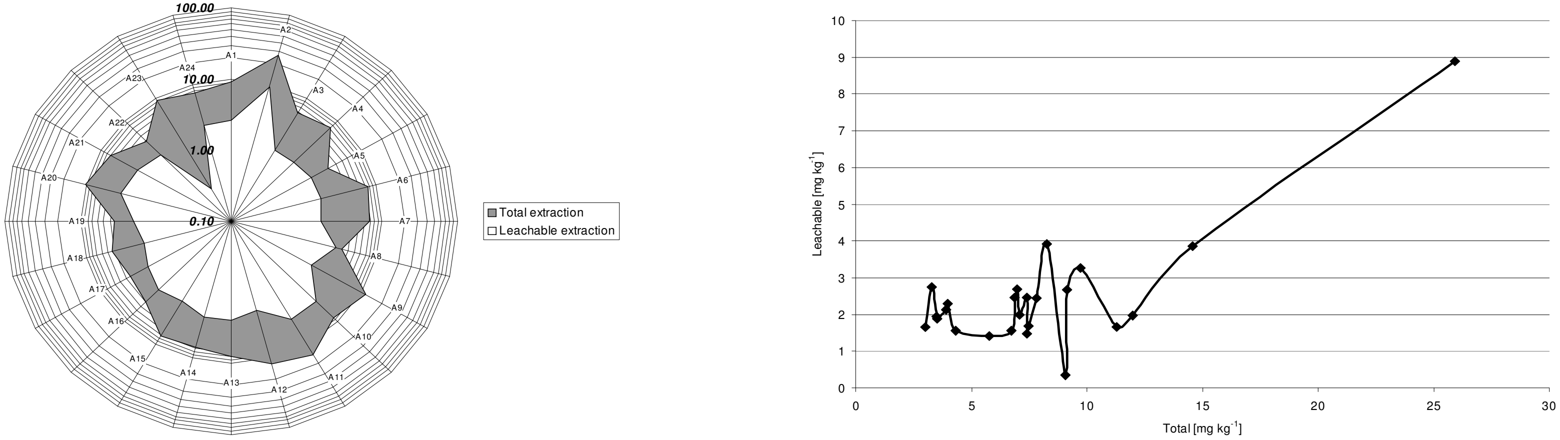
(i) (ii)

Figure 10.1-D: Graph of the total and leachable fractions for Hg for the 24 sewage sludge samples analysed in mg kg^{-1}



(i) (ii)

Figure 10.1-E: Graph of the total and leachable fractions for Mo for the 24 sewage sludge samples analysed in mg kg^{-1}



(i) (ii)

Figure 10.1-F: Graph of the total and leachable fractions for Se for the 24 sewage sludge samples analysed in mg kg^{-1}

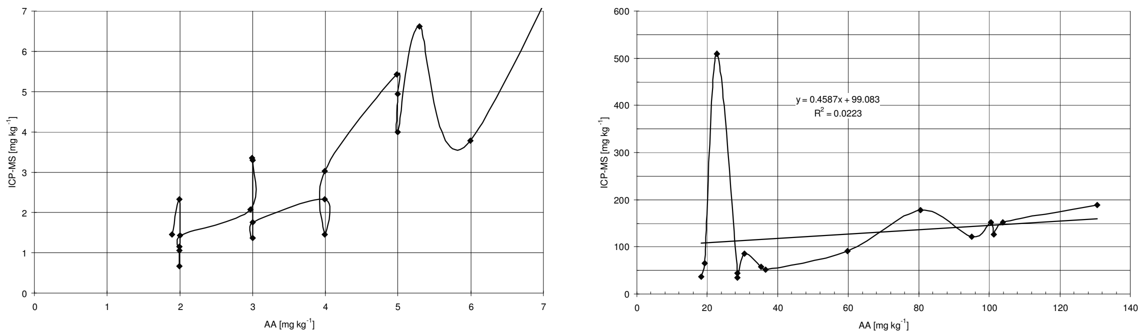
10.2 Correlation between the ICP-MS and FAAS data

The correlation coefficients (*r*) for the four metals between the FAAS and the ICP-MS data was calculated. They appear in table 10.2-A. For Cd, Cu and Zn the FAAS and ICP-MS data correlates more than or equal to 80%. It appears that lead does not correlate. This can be explained by noting that the values obtained for the leachates are so near to the detection limit for FAAS that analysis is hindered. The ICP-MS analysis of Pb, yielded values all below the detection limit for the FAAS.

Table 10.2-A: The correlation coefficients between the ICP-MS and FAAS data for 24 sewage sludge samples and four specified elements

Element	Correlation Coefficient
Cd	0.90
Cu	0.99
Pb	0.08
Zn	0.80

10.2.1 The relationship between ICP-MS and FAAS



(i) Cu

(ii) Zn

Figure 10.2-A: The relationship between the AA and ICP-MS results for Cu and Zn up to a maximum of 7 mg kg^{-1} and 200 mg kg^{-1} respectively

From figure 10.2-A (i) it can clearly been noted that the smallest interval of analysis from the FAAS was set to 1.00 mg kg^{-1} for Cu. For this reason, multiple ICP-MS values only yield one FAAS value. This makes a linear relationship difficult to determine and was therefore not done.

From figure 10.2-B (ii), a trend is more clearly visible (y=0.4587x+99.083). It can again be noted that the ICP-MS data is usually higher than the FAAS data (c = + 99.083). The slope of the linear regression line is comparable to the linear regression line in figure 10.2-A (iv) but still far from the expected value of 1.00.

10.3 Variation in sample preparation

Table 10.3-A: The percent moisture calculations for the wet sewage sludge samples

Description	**1**	**2**	**3**
Mass of empty dish (g)	49.5186	47.4504	47.7569
Mass of dish and sample (g)	84.3089	91.0310	110.5524
Calculated mass of sample (g)	34.7903	43.5806	62.7655
Mass of dish and sample after drying at 105℃ (g)	52.1478	53.4136	53.8776
Calculated mass of total solid after drying at 105℃ (g)	2.6392	5.9632	6.1207
Percent Total Solids (m/m)	7.5573	13.6832	9.7470
Average Percent Total Solids (m/m)	10.3292		
Standard Deviation	3.1041		
Average percent moisture	89.671		
Mass of wet sample required for 50 dry sludge (g)	484.067		
Mass of wet sample required for 100 dry sludge (g)	968.133		

Table 10.3-B: The comparison between the wet and dry sewage sludge samples

	USA TCLP				**SA TCLP**			
	1	**2**	**3**	**4**	**1**	**2**	**3**	**4**
Mass of sludge added (g)	484.92	484.36	967.80	971.53	100.28	100.02	50.23	50.02
Calculated mass of liquid in sludge (mL)	434.83	434.33	867.83	871.18	0.00	0.00	0.00	0.00
Calculated mass of solid in sludge (g)	50.09	50.03	99.97	100.35	100.28	100.02	50.23	50.02
Volume of TCLP extraction solution added (mL)	567	566	1131	1136	2000		1000	
Final leachate pH	5.73	5.79	5.55	5.69	4.51	4.47	4.55	4.53
Average final leachate pH	5.69				4.52			
Standard Deviation of average final leachate pH	0.102				0.0342			

Table 10.3-C: The raw ICP-MS data for the wet and dry sewage sludge samples

Sample	B	Cr	Co	Ni	Cu	Zn	Se	Mo	Cd	Hg	Pb	Fe
Units	µg L^{-1}											mg L^{-1}
Elemental Deposition	132.40	0.00	5.17	20.28	2.39	335.85	16.58	4.10	0.00	12.18	36.27	48.00
SA 01	1170.02	68.85	231.07	4116.89	95.47	9775.44	121.48	13.83	8.21	17.54	7.04	24040.00
SA 02	1412.00	49.17	223.34	3932.20	85.24	9942.53	103.31	14.06	8.05	18.11	6.59	17070.00
SA 03	1369.31	63.00	249.75	4143.44	106.44	9731.50	144.88	14.52	11.12	19.37	7.91	3455.00
SA 04	1322.68	85.51	263.95	4277.16	117.39	9864.03	154.60	14.65	10.33	17.25	7.92	3960.00
Decanted liquid	275.59	5.96	26.33	210.85	6.14	74.14	30.90	10.30	1.24	15.13	6.31	0.47
USA 01	502.04	18.59	105.91	2274.39	67.94	1083.96	26.97	6.51	15.21	14.14	7.20	2898.00
USA 02	386.53	22.54	64.55	1173.98	25.72	409.72	17.79	8.87	0.97	16.63	5.93	14920.00
USA 03	583.96	31.86	111.25	2286.45	49.84	712.46	21.09	8.08	3.32	13.61	6.56	3702.00
USA 04	453.27	22.31	62.58	1150.82	21.91	493.17	27.92	6.81	1.43	12.61	4.78	5278.00
Blank 01	26.77	0.00	3.91	11.93	0.00	138.06	2.57	0.57	0.00	11.20	4.56	3.00
Blank 02	0.90	0.00	3.75	11.82	0.00	42.52	8.22	2.29	0.00	15.15	4.92	12.00

10.4 Leaching test protocols

Table 10.4-A: The percent moisture for TCLP, AS and DIN procedures as applied to anaerobically digested sludge

Description	1	2	3
Mass of empty dish (g)	49.5184	47.4499	47.7563
Mass of dish and sample (g)	84.1152	85.2554	104.7587
Calculated mass of sample (g)	34.5968	37.8055	57.0024
Mass of dish and sample after drying at 105℃ (g)	52.2385	53.6902	54.8561
Calculated mass of total solid after drying at 105℃ (g)	2.7201	6.2403	7.0998
Percent Total Solids (m/m)	7.8623	16.5063	12.4553
Average Percent Total Solids (m/m)	12.2746		
Standard Deviation	4.3249		
Average percent moisture	87.725		
Mass of wet sample required for 100 dry sludge (g)	814.689		

10.4.1 TCLP

Table 10.4-B: The repeat TCLP determinations on anaerobically digested sewage sludge

	1	**2**	**3**	**4**	**5**	**B1***	**B2#**	**DL¶**
Mass of sludge added (g)	814.65	814.65	814.65	814.71	814.68	0.0	0.0	
Calculated mass of liquid in sludge (mL)	714.65	714.65	714.65	714.71	714.68	0.0	0.0	
Calculated mass of solid in sludge (g)	100.00	100.00	100.00	100.00	100.00	0.0	0.0	
Volume of TCLP extraction solution added (mL)	1285							
Final leachate pH	5.42	5.50	5.36	5.36	5.54	3.07	3.04	7.83
Average final leachate pH	5.44					3.06		
Standard Deviation of average final leachate pH	0.0817					0.0212		

* B1 Blank 1

[#] B2 Blank 2

[¶] DL Decanted liquid

Table 10.4-C: The raw ICP-MS data for the TCLP determinations on anaerobically digest sewage sludge

Sample	B	Cr	Co	Ni	Cu	Zn	Se	Mo	Cd	Hg	Pb	Fe
Units	μg L^{-1}											
1	655.78	0.00	4.80	41.32	27.24	1696.00	6.14	14.89	9.43	725.36	26.47	912.78
2	848.00	4.83	46.56	104.12	87.51	2662.00	7.02	19.80	10.95	1802.51	46.37	1522.58
3	657.57	2.14	25.83	79.61	50.98	3358.00	6.63	19.91	9.10	1488.37	36.80	829.63
4	633.64	2.12	32.38	83.86	49.72	7562.00	6.22	14.61	8.00	1463.86	44.02	649.58
5	540.14	2.33	32.90	79.86	40.08	6253.00	6.52	18.22	9.64	1359.21	37.41	493.63
Blank 1	26.77	0.00	0.00	3.91	0.00	0.30	4.56	11.20	0.57	11.93	2.57	138.06
Blank 2	0.90	0.00	0.00	3.75	0.00	1.20	4.92	15.15	2.29	11.82	8.22	42.52
Decanted Liquid	264.03	5.54	29.77	276.39	7.45	98.54	28.72	10.27	1.48	12.56	5.71	451.00

10.4.2 AS

Table 10.4-D: The repeat AS determinations on anaerobically digested sewage sludge

	1	**2**	**3**	**4**	**5**	**DL**
Mass of sludge added (g)	814.73	814.65	814.67	814.62	814.69	
Calculated mass of liquid in sludge (mL)	714.72	714.65	714.67	714.63	714.69	
Calculated mass of solid in sludge (g)	100.01	100.00	100.00	99.99	100.00	
Volume of TCLP extraction solution added (mL)	1285					
Final leachate pH	8.01	7.90	7.81	7.92	7.86	7.83
Average final leachate pH	7.90					
Standard Deviation of average final leachate pH	0.0745					

Note: Blank analyses were done with demineralised water, but the pH was not recorded as it depends on the amount of CO_2 the demineralised water has adsorbed from the atmosphere.

Table 10.4-E: The raw ICP-MS data for the AS procedure on anaerobically digested sewage sludge

Sample	B	Cr	Co	Ni	Cu	Zn	Se	Mo	Cd	Hg	Pb	Fe
Units	µg L^{-1}											
1	156.16	2.62	98.15	24.52	32.79	2024.00	21.51	15.60	14.00	193.33	18.90	418.27
2	191.01	5.05	206.20	28.81	139.99	3109.00	31.36	17.34	34.65	207.79	16.32	600.46
3	195.17	2.96	91.36	25.46	23.88	1976.00	20.92	10.73	12.85	193.41	18.18	399.27
4	228.57	1.57	60.40	24.30	16.28	1514.00	16.83	16.69	4.86	187.78	21.62	335.13
5	184.47	3.11	48.48	21.52	34.82	1286.00	12.55	12.90	11.30	174.57	19.03	228.08
Blank 1	24.89	0.00	0.00	3.78	0.00	2.00	4.82	12.69	2.24	11.48	10.30	15.55
Blank 2	49.72	0.00	0.00	3.70	0.00	62.00	4.99	13.28	0.93	12.62	5.02	15.42
Decanted Liquid	264.03	5.54	29.77	276.39	7.45	98.54	28.72	10.27	1.48	12.56	5.71	451.00

10.4.3 DIN

Table 10.4-F: The repeat DIN determinations on anaerobically digested sewage sludge

Description	**1**	**2**	**3**	**4**	**5**	**DL**[¶]
EXTRACTION 1						
Mass of sludge added (g)	814.66	814.71	814.72	814.70	814.71	
Calculated mass of liquid in sludge (mL)	714.66	714.71	714.72	714.70	714.71	
Calculated mass of solid in sludge (g)	100.00	100.00	100.00	100.00	100.00	
Volume of TCLP extraction solution added (mL)	1000					
Final leachate pH	8.22	8.02	7.98	8.00	7.93	
Average final leachate pH	8.03					
Standard Deviation of average final leachate pH	0.111					
EXTRACTION 2*						
Mass of sludge added (g)	731.52	720.87	659.78	701.59	683.10	
Calculated mass of liquid in sludge (mL)	610.55	601.66	550.67	585.57	570.13	
Calculated mass of solid in sludge (g)	120.68	119.21	109.11	116.03	112.97	
Volume of TCLP extraction solution added (mL)	1000					
Final leachate pH	8.04	8.00	8.00	8.01	7.96	8.49
Average final leachate pH	8.00					
Standard Deviation of average final leachate pH	0.0286					

[¶] Decanted liquid

* The calculation of the percent solids for the second extraction was done after the second extraction. It was unsuccessful since the dry mass of sludge added to extraction step two was more than that added in extraction step one.

Table 10.4-G: The percent moisture for DIN after extraction of anaerobically digested sewage sludge

Description	Sample 1	Sample 2	Sample 3
Mass of empty dish (g)	49.5282	47.4567	47.4627
Mass of dish and sample (g)	96.0759	96.4703	117.228
Calculated mass of sample (g)	46.5477	49.1036	69.7653
Mass of dish and sample after drying at 105℃ (g)	57.3478	55.8245	58.4443
Calculated mass of total solid after drying at 105℃ (g)	7.8196	8.3678	10.9816
Percent Total Solids (m/m)	16.799	17.072	15.740
Average Percent Total Solids (m/m)	16.537		
Standard Deviation	0.70333		
Average percent moisture	83.463		
Mass of wet sample required for 100 dry sludge (g)	604.689		

Table 10.4-H: The raw ICP-MS data for the DIN determinations on anaerobically digested sewage sludge

Sample-Leachate	B	Cd	Cr	Co	Cu	Fe	Pb	Hg	Mo	Ni	Se	Zn
Units	µg L^{-1}											
1-1	164.59	2.28	48.90	22.43	24.28	1289.30	17.31	14.70	16.75	217.94	17.13	291.48
1-2	246.37	3.16	80.72	18.69	28.58	2292.00	20.77	12.17	11.66	178.86	8.63	396.31
2-1	167.78	0.79	40.77	22.90	24.40	1778.00	13.07	14.44	18.95	207.26	22.07	240.68
2-2	197.92	5.60	163.35	19.52	71.60	3313.00	26.58	17.22	22.26	192.54	13.48	557.83
3-1	325.80	2.28	40.69	24.37	18.58	1082.00	12.87	11.12	20.81	217.21	22.31	218.13
3-2	182.94	4.76	146.39	17.29	49.06	3596.00	27.65	13.16	9.42	184.53	5.10	567.86
4-1	200.82	2.34	42.29	23.20	17.38	1164.00	13.92	14.73	10.47	200.46	22.07	263.79
4-2	247.78	5.55	181.95	17.56	83.79	4692.00	35.98	14.29	6.55	196.02	10.29	704.97
5-1	145.48	0.29	29.16	24.04	12.93	1008.00	9.98	13.64	15.06	209.28	17.44	171.13
5-2	249.73	4.41	153.16	17.98	55.79	3524.00	29.90	13.62	9.50	181.51	13.01	605.94
Blank 1	74.45	0.00	0.00	4.12	0.00	92.00	4.99	12.29	0.85	19.65	0.69	21.43
Blank 2	6.07	0.00	0.00	3.81	0.00	96.00	4.55	13.40	1.68	13.46	8.50	7.13
Decanted Liquid	312.19	8.44	30.73	209.63	10.97	79.10	39.76	11.36	1.27	15.05	7.50	359.00

10.4.4 NEN

Table 10.4-I: The percent moisture for NEN applied to anaerobically digested sewage sludge

Description	1	2	3
Mass of empty dish (g)	49.5184	47.4499	47.7563
Mass of dish and sample (g)	84.1152	85.2554	104.7587
Calculated mass of sample (g)	34.5968	37.8055	57.0024
Mass of dish and sample after drying at 105℃ (g)	52.2385	53.6902	54.8561
Calculated mass of total solid after drying at 105℃ (g)	2.7201	6.2403	7.0998
Percent Total Solids (m/m)	7.8623	16.5063	12.4553
Average Percent Total Solids (m/m)	12.2746		
Standard Deviation	4.3249		
Average percent moisture	87.725		
Mass of wet sample required for 16 dry sludge (g)	130.3502		

Table 10.4-J: The repeat wet NEN determinations on anaerobically digested sewage sludge

Sample	pH	Mass of flask (g)	Mass of flask & sample (g)	Mass of sludge added (g)	Mass of liquid in sludge (g)	Mass of solid in sludge (g)	Ideal Mass leachate (g)	Total mass of flask, sample & leachate (g)	Mass leachate added (g)	pH_A	pH_B	Vol HNO_3 Added (mL)	Final Leachate pH
1	7	309.18	439.48	130.30	114.31	15.99	799.69	1239.44	799.96	8.19	8.18	5.00	7.78
	4	309.18	439.48	130.30	114.31	15.99	799.69	1257.04	817.56	8.04	7.96	27.53	4.14
	4*	307.86	438.10	130.24	114.25	15.99	799.32	1237.25	799.15	9.19	8.18	34.45	3.95
	7 and 4												5.61
2	7	303.25	433.69	130.44	114.43	16.01	800.55	1235.25	801.56	8.46	8.45	5.08	7.71
	4	303.25	433.69	130.44	114.43	16.01	800.55	1237.59	803.90	8.09	8.09	20.80	4.18
	4*	309.15	439.54	130.39	114.39	16.00	800.24	1240.04	800.50	8.43	8.43	32.20	3.97
	7 and 4	NOT DONE											
3	7	309.36	439.80	130.44	114.43	16.01	800.55	1253.59	813.79	8.42	8.48	5.40	7.73
	4	309.36	439.80	130.44	114.43	16.01	800.55	1239.80	800.00	7.63	7.74	19.50	4.22
	4*	303.24	433.51	130.27	114.28	15.99	799.51	1233.53	800.02	8.40	8.48	33.90	4.18
	7 and 4												5.82
4	7	303.23	433.34	130.11	114.14	15.97	798.53	1233.95	800.61	8.50	8.50	4.40	7.45
	4	303.23	433.34	130.11	114.14	15.97	798.53	1233.41	800.07	7.69	7.70	22.00	4.06
	4*	307.85	438.24	130.39	114.39	16.00	800.24	1238.31	800.07	8.33	8.37	32.90	4.01
	7 and 4												5.47
5	7	309.13	439.44	130.31	114.31	16.00	799.75	1239.49	800.05	8.55	8.62	4.05	7.63
	4	309.13	439.44	130.31	114.31	16.00	799.75	1239.49	800.05	7.89	7.84	12.00	4.07
	4*	303.25	433.58	130.33	114.33	16.00	799.88	1233.61	800.03	8.39	8.42	33.78	3.95
	7 and 4												5.63
Decanted Liquid													7.83
Blank 1	7	309.17	0.00	0.00	0.00	0.00	800.00	1109.40	800.23	6.47	4.50	0.00	below 7
Blank 2	4	307.84	0.00	0.00	0.00	0.00	800.00	1108.07	800.23	6.06	6.20	0.65	4.00
Blank 3	low	307.88	0.00	0.00	0.00	0.00	800.00	1107.86	799.98			34.45	1.30

Table 10.4-K: The raw ICP-MS data for the wet anaerobically digested sludge NEN determinations in units of µg L^{-1}

Sample-Leachate	B	Cr	Co	Ni	Cu	Zn	Se	Mo	Cd	Hg	Pb	Fe
1-1	105.84	7.88	14.24	120.69	2.54	146.08	10.30	11.31	1.00	14.17	7.31	0.26
1-2	254.10	35.33	86.50	1563.23	28.76	1901.85	24.80	4.59	0.16	13.94	5.84	432.10
1-3	367.27	57.82	72.58	1329.92	27.89	891.80	22.07	2.86	1.58	13.29	4.50	397.86
1-4	316.43	14.67	50.17	842.83	4.36	891.94	12.99	7.01	0.00	9.38	5.38	185.67
2-1	150.27	10.01	14.56	130.65	7.21	225.86	3.38	8.95	0.61	13.38	8.67	1.51
2-2	207.86	27.10	79.95	1578.25	13.24	1845.50	15.54	3.35	0.32	14.58	7.14	287.79
2-3	213.82	61.46	69.90	1365.37	9.51	813.82	20.56	3.81	0.14	14.21	4.94	361.48
2-4	307.33	12.78	14.35	121.83	16.77	259.92	11.88	16.13	2.54	15.27	12.73	1.05
3-1	339.83	20.45	63.81	1399.63	4.48	1871.45	22.01	3.73	1.46	17.59	5.29	286.21
3-2	297.11	117.20	71.61	1312.26	8.22	716.30	11.59	7.98	1.35	13.66	6.48	382.56
3-3	191.09	10.64	39.62	755.35	4.93	688.38	9.46	7.92	0.47	16.21	5.61	103.78
3-4	168.81	2.23	13.51	102.92	6.40	185.15	13.59	13.49	1.53	15.01	9.05	0.53
4-1	275.70	38.37	69.74	1474.39	9.33	1471.55	16.18	6.07	2.39	18.07	5.88	329.80
4-2	389.98	54.60	70.05	1340.99	11.00	936.17	15.00	9.71	1.26	14.94	5.76	392.30
4-3	226.41	16.88	39.90	774.58	7.86	741.10	10.61	12.05	2.03	16.12	7.04	157.90
4-4	135.61	0.00	12.43	102.02	0.00	157.22	4.48	16.80	0.10	14.45	7.67	1.36
5-1	414.25	45.96	67.56	1381.33	4.16	1004.85	19.03	3.82	1.47	12.92	4.82	328.13
5-2	208.21	95.44	67.28	1209.06	4.91	488.22	10.96	6.44	0.54	14.18	5.29	392.85
5-3	155.74	16.17	38.71	719.03	0.00	532.12	11.93	8.04	0.48	14.39	4.67	136.42
5-4	318.37	0.00	23.48	344.27	5.11	215.89	25.88	57.35	2.15	16.40	7.75	0.23
Blank 1	237.43	0.00	4.51	21.51	0.00	12.72	3.12	1.12	0.00	12.86	4.54	80.00
Blank 2	209.28	0.00	3.91	12.73	0.00	407.85	12.12	3.45	0.49	14.30	5.19	19.00
Blank 3	130.45	0.00	4.71	23.28	0.50	317.61	5.98	3.72	0.00	11.36	6.22	42.00
Decanted Liquid	250.54	3.89	18.49	146.54	0.00	44.76	24.23	9.27	0.97	17.78	5.73	610.00

Leachate 1pH= 7; Leachate 2 pH=4 sequential; Leachate 3 pH=4 non-sequential; Leachate 5 is combined pH=7 and pH=4

Table 10.4-L: The repeat dry anaerobically digested sewage sludge NEN determinations

Sample	pH	Mass of flask (g)	Mass of flask & sample (g)	Mass of sludge added (g)	Mass of liquid in sludge (g)	Mass of solid in sludge (g)	Ideal mass of leachate (g)	Total mass of flask, sample & leachate (g)	Mass leachate added (g)	pH_A	pH_B	Vol HNO_3 added (mL)	Final leachate pH
6	7	309.17	325.17	16.00	1.19	14.81	740.54	1125.29	800.12	8.09	8.53	3.25	7.23
	4	309.17	325.17	16.00	1.19	14.81	740.54	1125.63	800.46	7.20	7.77	16.05	4.34
	4*	307.87	323.89	16.02	1.19	14.83	741.47	1124.42	800.53	8.01	8.48	20.55	3.99
	7 and 4												5.81
7	7	307.84	323.85	16.01	1.19	14.82	741.01	1123.83	799.98	8.46	8.52	2.37	7.32
	4	307.84	323.85	16.01	1.19	14.82	741.01	1123.94	800.09	7.60	7.78	16.33	4.09
	4*	307.85	323.85	16.00	1.19	14.81	740.54	1123.86	800.01	8.50	8.55	19.65	4.16
	7 and 4												5.16
8	7	309.15	325.22	16.07	1.19	14.88	743.78	1125.24	800.02	8.30	8.58	2.34	7.22
	4	309.15	325.22	16.07	1.19	14.88	743.78	1125.40	800.18	6.70	7.44	16.45	Unrecorded
	4*	303.33	319.35	16.02	1.19	14.83	741.47	1119.39	800.04	7.33	8.33	20.44	4.14
	7 and 4												5.71

* Non-sequential pH=4 extraction

Note: All blanks and decanted liquor is the same for all the NEN determinations

Table 10.4-M: The raw ICP-MS data for the dry anaerobically digested sewage sludge NEN determinations in µg L^{-1}

Sample-Leachate	B	Cr	Co	Ni	Cu	Zn	Se	Mo	Cd	Hg	Pb	Fe
6-1	589.82	8.58	78.44	1672.41	14.35	4801.55	33.90	4.28	0.55	14.11	5.49	71.71
6-2	508.77	25.49	103.98	2185.26	24.51	5530.07	44.53	5.94	3.06	15.52	7.19	98.99
6-3	307.89	8.53	50.48	1025.42	11.61	2484.05	22.08	26.98	1.33	14.23	6.07	31.62
6-4	232.82	6.02	24.03	345.11	18.47	275.20	29.45	53.44	1.76	12.73	6.47	0.48
7-1	406.02	11.51	87.36	1798.64	14.45	4944.04	32.22	5.18	1.35	11.21	5.18	67.86
7-2	440.82	24.81	100.36	2022.83	23.77	4780.12	40.59	5.46	2.83	16.79	5.73	65.98
7-3	345.12	1.67	52.82	1070.29	33.59	2561.01	28.58	25.50	0.69	14.95	5.23	30.32
7-4	235.10	0.08	23.06	336.96	7.05	183.54	27.63	55.36	0.90	15.41	6.46	0.43
8-1	302.73	7.63	81.54	1721.01	13.10	4621.02	32.37	4.99	0.82	14.62	4.77	65.11
8-2	457.31	16.37	96.01	1992.05	23.83	4704.64	47.11	7.47	1.89	19.32	5.76	66.70
8-3	291.77	0.00	49.93	1023.46	10.87	2482.92	19.56	33.07	1.52	15.37	5.68	32.46
8-4	589.82	8.58	78.44	1672.41	14.35	4801.55	33.90	4.28	0.55	14.11	5.49	71.71

Leachate 1 pH= 7; Leachate 2 pH=4 sequential; Leachate 3 pH=4 non-sequential; Leachate 4 is combined pH=7 and pH=4

10.5 Acid neutralisation capacity

10.5.1 Recorded acid addition to determine acid neutralisation capacity

An experiment was done to determine the acid neutralisation capacity based on the NEN availability procedure. The experiment should have taken a few days to complete since the time required for the sample to equilibrate between acid additions was a few minutes. After running the procedure for 6 hours beginning with an initial pH of 8.13, 6.738 mL of standardised HNO_3 (1.0 *N*) was added and the pH had dropped to 5.79. The solution was left to rotate overnight, so that the experiment could continue the following day. Upon initiating the experiment again it was found that that pH had increased overnight from 5.79 to 7.14. No further addition of acid was done and the solution was left stirring for a further 24 hours where upon the pH was again measure to be 7.54.

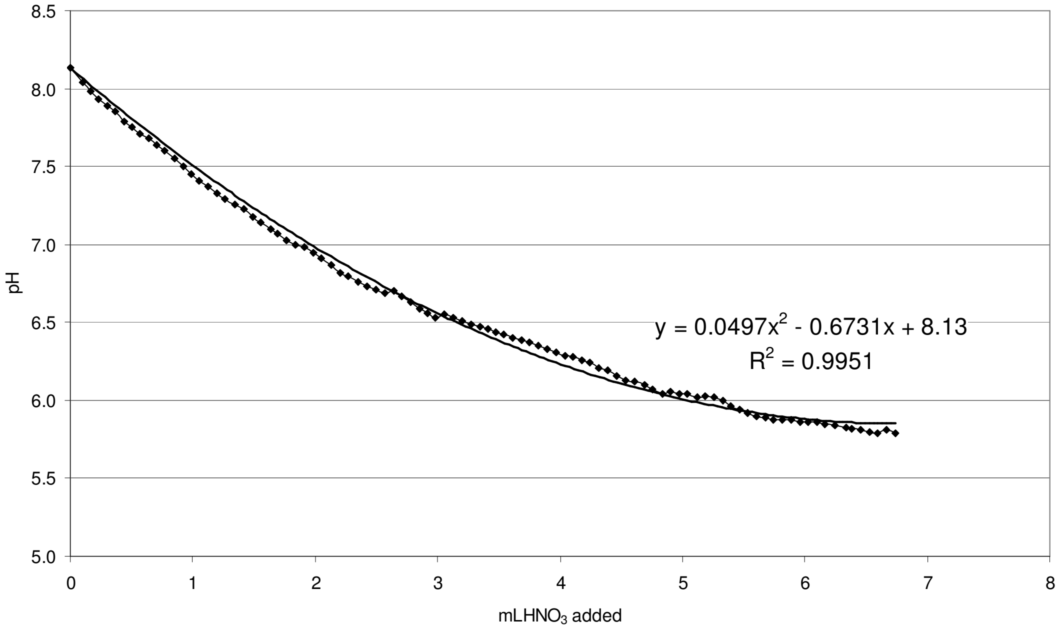


Figure 10.5-A: The acid neutralisation capacity of a dry sample of sewage sludge based on the NEN procedure

The 5 to 10 minute intervals of equilibrium between acid additions was therefore not sufficient to allow for equilibrium to occur. It was also assumed that the length of the stirring of the sample would increase the acid neutralisation capacity. Due to these practical constraints no more acid was added. Figure 10.5-A indicates the acid consumption data against pH for the first day.

This could explain the large % RSD values obtained for the NEN. Even though a homogenised sample was used, stirring for two sets of three hours was insufficient time for equilibrium at a set pH to occur since the sample was so well buffered.

10.5.2 The difference in acid neutralisation capacity between dry and wet samples

Acid neutralisation capacity can also be evaluated by considering the final leachate pH values of the anaerobically digested samples taken two months apart (Sample B). The mean final leachate pH values for the dry samples was 4.52 ± 0.0342 and for the wet sample was 5.69 ± 0.102. Since an equal amount of acid was added to each sample, the acid neutralisation capacity of the wet sample was less than the dry sample.

10.5.3 Determining the acid neutralisation capacity using the volume of acid added during the NEN extractions

Another way to determine acid neutralisation capacity is to use the amount of acid added in the NEN procedure with respect to the final leachate pH for the samples. In figure 10.5-B the final leachate pH and mmol L^{-1} HNO_3 added is plotted for the NEN prcedure for both dry and wet samples. A linear trend line with equation and correlation coefficient is also included in the graph.

Figure 10.5-B indicates that the amount of acid required to obtain a specified pH value is less for a dry sample than for a wet sample. This can be attributed to two factors. The first is that the available $CaCO_3$ in the free liquid of the wet sample is more than the available $CaCO_3$ in the dry sample. It can be

assumed that the $CaCO_3$ was forced to precipitate out and became bound in such a way that when the sample was wetted again, it did not all become available again. The second factor is due to the high levels of ammonium and ammonium salts in the sludge. During drying it is possible that NH_3 and CO_2 gas was released. In the liquid phase the ammonia is in the form of $(NH_4)_2CO_3$ but there are equilibrium reactions between the $(NH_4)_2CO_3$ and water that are pH dependant. The ideal pH is near neutral. This could result in NH_3 and CO_2 gas being released during drying.

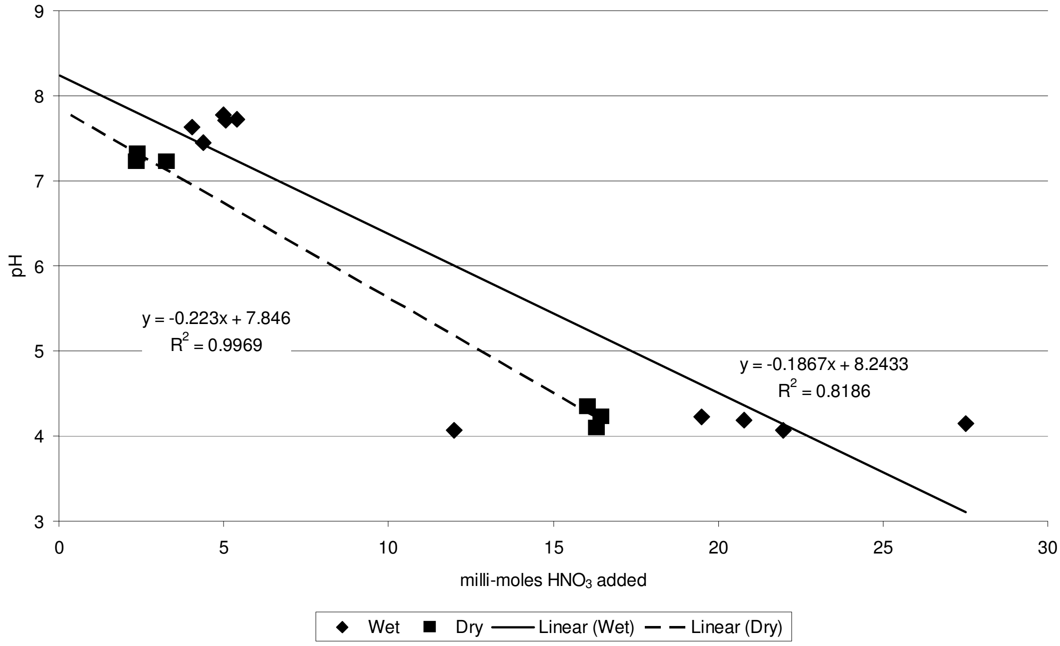


Figure 10.5-B: The acid neutralisation capacity of sludge as extracted from the NEN procedure for both dry and wet samples by considering the final leachate pH and the amount of acid added

This means that the acid neutralisation capacity was affected by sample drying.