Determination of the Inorganic Pollutants in South African Sewage Sludges

By

Fitsum Kidane Tesfai

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University of KwaZulu-Natal

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ABSTRACT

A total of 78 sludge samples originating from 69 sewage works of South Africa were used in this investigation. Seven of the sludge samples were liquid and the rest were solid. Moisture content, pH and mineral ion determination using ICP-OES were carried out. The methods used to digest the samples were EPA 3050B and 3010A for solid sludge and effluent (liquid sludge) respectively. The moisture content determination showed that fresh wet sludge was composed of water between 40 to 90 %. The minimum moisture content was found to be 2.70 % while the maximum was 88.50 % with a mean value of 41 %. The pH results showed that the majority sludges produced had pH values between 4.8 – 6.5. The ICP-OES results which involved analysis and quantification of 22 mineral ions showed that the order of abundance that was most common to the majority of the samples was P, Ca, Fe, Al, Mg, K, Zn, Na, Si, Mn, Cu, Cr, Ba, Pb, Sr, Se, B, Ni, Co, Mo and Cd. Even though phosphorus was the most abundant, 11 of the samples had calcium as the highest element. Looking at the heavy metals, zinc was the highest with cadmium being the least. The order of abundance in majority of the solid samples (64 in total) was Zn > Pb > Ni > Cd with the relative metal concentrations of Cu, Se, B, Cr, Co & Mo varying among the sewage works. The liquid samples also had phosphorus as one of the most abundant elements but was 10^2 times smaller comparing to solid sludges. In addition, most of the transition elements were found to be below the detection limit. Beryllium was exceptionally found to be below detection limit in all sludge samples. The results have pointed out that industrial effluent have 3 times the level of pollutants when compared to the domestic effluents. However, the methods of preparing sludge have no influence on the content or quantity of mineral ions. The results have been compared with 1989 data. The outcome shows that concentrations of the major nutrients namely calcium, magnesium and potassium remained relatively constant whereas phosphorus increased by more than 3 fold. On heavy metals, the data shows that the mean concentration level of Zn, Cu, Cr, Pb, Ni and Cd declined whereas that of Se, B and Mo showed an increase in 2002, all to a varying degree.

The current results were also compared with the current maximum limits as stipulated in the permissible utilization and disposal of sewage sludge government guideline. The amount of Cu, Se, Pb and Zn were found to be above the limit in more than 90 % of the samples. There was no sewage works that met the required limits for all the elements of interest. When these results are compared with the international limits, all the elements fall within the acceptable range. It is therefore clear that the current South African guideline limit is too restrictive.

DECLARATION

I hereby declare that this work was carried out in full at the School of Chemistry, University of KwaZulu-Natal, Pietermaritzburg.

I hereby certify that this investigation, unless otherwise stated, is the result of my own research.

Signed:

F. K. Tesfai, BSc.

I hereby certify that the above statement is correct.

Signed:

Prof. D. Jaganyi, MSc, PhD
Supervisor

Signed:

Dr. C. Southway, PhD
Co- Supervisor

Pietermaritzburg
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ABBREVIATIONS

AES	Atomic Emission Spectroscopy
ANOVA	Analysis of Variance
Av.	Average
AWT	Advanced Wastewater Treatment
BOD	Biochemical Oxygen Demand
COD	Chemical Oxygen Demand
ECP	Eastern Cape Province
Eds.	Editor(s)
EIEs	Easily Ionizable Elements
EPA	Environmental Protection Agency
EU	European Community
FAAS	Flame Atomic Absorption Spectrophotometry
FSP	Free state Province
GFAAS	Graphite Furnace Atomic Absorption Spectrophotometry
GP	Gauteng Province
ICP-OES	Inductively coupled Plasma - Optical Emission Spectroscopy
JHB	Johannesburg
KZNP	KwaZulu -Natal Province
L	Low Risk
LP	Limpopo Province
MP	Mpumalanga Province
na	Not Applicable
NCP	Northern Cape province
NWP	North West Province
P	Possible Risk
PPM	Parts per million
PTEs	Potentially Toxic Elements
RF	Radio Frequency
SA	South Africa
SBR	Signal-to- Background Ratio
SD	Standard deviation

SNR	Signal- to-Noise- Ratio
SS	Suspended solids
UK	United Kingdom
USA	United States of America
WAS	Waste Activated Sludge
WCP	Western Cape Province
WWTPs	Wastewater Treatment Plants

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CHAPTER 1

SEWAGE SLUDGE : GENERAL COMMENTS

CHAPTER 1

1 Sewage Sludge: General Comments

1.1 Generation and Nature of Sewage Sludge

Sewage sludge may contain every conceivable element or compound found in wastes from human, domestic, commercial, and industrial sources; and this includes substantial quantities of organic matter, plant nutrients, trace metals, and some potentially hazardous compounds.[1] By Applying the appropriate methods of treatment, sewage (wastewater) is converted to the final product, sludge.

Sewage (wastewater) treatment is categorized into three:

- Preliminary treatment,
- Primary treatment and
- Secondary treatment.

However, there is also a tertiary treatment, which mainly depends on the final disposal selection. These processes comprise a series of process steps involving the removal of pollutants from the original raw sewage by mechanical, physical, biological and chemical processes.[2] In essence, sewage is separated into two streams: a clarified water containing around 20-30 mg l^{-1} of suspended solids and a sludge stream of 1-3 % solids dry weight. The sludge stream usually contains 80 to 90 % of the contaminants originally present in the raw sewage.[3] The final product that is produced after the treatment process is called sludge; this is a partially aqueous suspension of solids containing microorganisms including pathogens.[2]

Sludge can be applied to improve soil fertility and to act as a soil conditioner due to the major and micro plant nutrients that it contains. The major plant nutrients are phosphorus, potassium and nitrogen. The inorganic nutrients also include such essential micronutrients as zinc, copper, molybdenum, and manganese. Sludge also causes an improvement in the soil physical properties, i.e. improved soil structure, increased water-holding capacity, and improved soil water transmission characteristics.[4] In contrast to its beneficial effects, its toxicity occurs due to the presence of heavy metals, which accumulate in the soil to phytotoxic concentrations for crops due to repeated sludge application as a soil-conditioner.[5] Furthermore, the presence of nitrates, phosphorus and halogenated organic compounds have an environmental pollution effect. In addition, microorganisms such as bacteria and viruses also have an adverse health effect on human beings.

Although sewage treatment is not generally performed with a view to reducing the sludge metal content, some of the treatment options may act to alter the speciation of the indigenous metals and hence affect the potential of their bioavailability within the treated product.[6] Therefore, the nature of the sludge depends, to some extent, on the type of process used to treat the sewage.[7] This means that concentrations of the pollutants from different wastewater treatment plants will vary. Among the main sources of the pollutants are industries. Industrial pretreatment of the pollutants is an important aspect of reducing the pollutants input to the sewage works directly and to food chains indirectly. Thus, considering the above effects of sludge application due to the pollutants on the environment, it is necessary to have an overall guideline for the permissible utilization and disposal of sewage sludge.

1.2 Wastewater Treatment

For an environmental protection from pollutants, wastewater treatment is crucial. The important pollutants of concern are as shown in Table 1.1. The main objective of sewage treatment is to correct characteristics of the sewage in such a fashion that the final disposal of the treated effluent can take place in accordance with the rules set by legislative bodies without causing an adverse impact on the ecosystem of the receiving body.[7]

Table 1.1 Important contaminants of concern in wastewater treatment.[9]

Contaminants	Reason for importance
Suspended solids	Suspended solids can lead to the development of sludge deposits and anaerobic conditions when untreated wastewater is discharged in the aquatic environment.
Biodegradable Organics	Composed principally of proteins, carbohydrates, and fats, biodegradable organics are measured most commonly in terms of biochemical oxygen demand (BOD) and chemical oxygen demand (COD). If discharged untreated to the environment, their biological stabilization can lead to the depletion of natural oxygen resources and to the development of septic conditions.
Pathogens	Communicable diseases can be transmitted by the pathogenic organisms in wastewater.
Nutrients	Both nitrogen and phosphorus, along with carbon, are essential nutrients for growth. When discharged to the aquatic environment, these nutrients can lead to the growth of undesirable aquatic life. When discharged in excessive amounts on land, they can also lead to the pollution of groundwater.
Priority pollutants	Organic and inorganic compounds selected on the basis of their known or suspected carcinogencity, mutagenicity, teratogenenicity, or high acute toxicity. Many of these compounds are found in wastewater.
Refractory organics	These organics tend to resist conventional methods of wastewater treatment. Typical examples include surfactants, phenols, and agricultural pesticides.
Heavy metals	Heavy metals are usually added to wastewater from commercial and industrial activities and may have to be removed if the wastewater is to be reused.
Dissolved inorganics	Inorganic constituents such as calcium, sodium, and sulfate are added to the original domestic water supply as a result of water use and may have to be removed if the wastewater is to be reused.

One of the main concerns for wastewater treatment is the removal of metal and nutrient contaminants during the course of the process. Both primary and secondary treatments have an effect in the removal of metals and phosphorus. The principal factors for removal of metals and phosphorus during primary sedimentation are the efficiency of removal of suspended solids and the chemical species of the element i.e. whether it is soluble or insoluble. Accordingly, minimal removal of dissolved metals occurs during this process and the proportion of dissolved metal to the total in the effluent increases as a result.[10] It has also been found that in primary effluents, a higher concentration of toxic elements is associated with smaller particles (size fractions 0.2 to 8 μm) than with larger (>44 μm) ones.[11] Therefore, by controlling influent composition and operating at an optimum flow rate, minimum particle size of the sediments and an effluent of desired quality may be achieved.[12]

To increase the removal of the pollutants, further treatment of sewage is necessary due to the fact that there are some pollutants, which have not been removed during the primary sedimentation as desired. Metal removal during primary sedimentation is a physical process, dependent on the settling out of precipitated metal or the association of metals with settleable particulates. In the case of biological treatment, several possible mechanisms for the removal of dissolved and fine particulate metal in the activated sludge process have been proposed, and include: [13]

- physical trapping of precipitated metals in the sludge floc matrix,
- binding of soluble metal to bacterial extracellular polymers,
- accumulation of soluble metal by the cell and
- volatilization of metal to the atmosphere.

For this reason, a biological treatment for the removal of the pollutants is considered efficient. It has been proposed that the greater efficiency of the activated sludge process in metal removal is due to the greater efficiency of suspended solids removal, and hence insoluble metal removal, in the secondary sedimentation tanks than in primary sedimentation tanks.[14, 11] Additionally, biological removal can, at best, achieve effluent concentrations of about 0.2 mg l^{-1} total phosphorus but usually reduces phosphorus to about 1 mg l^{-1}.[15]

Wastewater treatment results in sludge, which requires further treatment before disposal. Under optimum conditions of anaerobic (a process occurring in the absence of oxygen) and aerobic (a process requiring oxygen) treatment (i.e. tertiary treatment) in activated sludge plants, up to 90 % removal of phosphorus can be achieved.[15] Activated sludge results when primary effluent is mixed with bacteria-laden sludge and then agitated and aerated to promote biological treatment. A comparison of metal speciation in dried as opposed to liquid forms of the same sludge, made by sequential chemical extraction, indicated that the drying process may have some influence on the subsequent metal status in the treated matrix.[16] It was also shown that chemical conditioning of sewage sludges by the addition of lime would probably result in an increase in the proportion of metal hydroxides and carbonates,[17] and this process has been shown to reduce the bioavailability of sludge metals in practice.[18] The addition of lime during treatment is mainly used for pH control and to some extent as a bulking agent that increases sludge porosity while resisting compression, pathogen reduction and drying due to release of heat.[27]

In general, on average, approximately 1 % of the total flow entering a sewage works is ultimately converted to sludge, and since 50 to 80 % of the metals in the raw sewage are removed during treatment, there is considerable concentration of metals within the sludge.[19] In this respect, the type of process adopted will have an effect on the metallic content of the sludge produced; a survey of more than 180 sludges carried out in the U.K. in 1975 recorded that heavy metals and other inorganic materials comprised 20 to 40 % of the dry solids of untreated sludge, 25 to 55 % of mechanically dewatered sludge solids, 30 to 50 % of heated treated sludge solids, and 40 to 50 % of digested sludge solids.[20]

Conventionally, sewage treatment is a three-stage process: preliminary treatment, primary sedimentation and secondary (biological) treatment, however, there is also a tertiary treatment based on the final disposal selections.

1.2.1 Preliminary Treatment

The first stage in the wastewater treatment is the preliminary treatment. At this stage of the treatment, larger floating, hard solids and suspended materials are removed with the aid of grinders (comminuters), bar screens, and grit channels. This helps to protect other equipment from blockage or damage. However, this process does not make a significant contribution to reducing the polluting load, but makes the sewage more amenable for further treatment in the primary and secondary treatments.

1.2.2 Primary Treatment

Primary treatment is the second process of treatment, where the separation of suspended solids and greases occurs. In the settling tank, the particles are allowed to settle to the bottom and the grease to float to the top. The solids are drawn off the bottom and the grease skimmed off the top. This process results in a significant change in the suspended solids (SS) and the biological oxygen demand (BOD). The suspended solids experience a change from approximately 400 mg l^{-1} to the final concentration of approximately 150 mg l^{-1} and similarly for BOD from approximately 300 mg l^{-1} to a final concentration of 200 mg l^{-1}.[21] In general, this process plays an important role in the reduction of the pollutant load since the sedimentation effects the exclusion of suspended solids and concentrates these solids to a smaller volume, as primary sludge, and produces an effluent appropriate for secondary or biological treatment.

1.2.3 Secondary Treatment

In the biological, which is the secondary treatment, the removal of remaining dissolved or colloidal organic matter takes place. In this case, the sewage microorganisms are cultivated and added to the wastewater so that they absorb organic matter from sewage as their food supply. Generally, the biodegradation of the pollutants is allowed to take place in a location where plenty of air can be supplied to the microorganisms. As a result, less offensive and oxidized products are produced. However, since the amount of microorganisms or biomass increases as a result of this process, some must be removed on a regular basis for further treatment and disposal, adding to the solids produced in primary treatment.[22] Finally, after anaerobic digestion, the sludge will be much more stable containing less heavy metals, the quality of pathogenic bacteria will have been reduced as well as the volume of the sludge. In addition the sludge will be easy to dewater and dry.[23]

1.2.4 Tertiary Treatment

Tertiary treatment is defined as the level of treatment required beyond conventional secondary treatment to remove constituents of concern including nutrients, toxic compounds, and increased amounts of organic material and suspended solids.[9] This treatment employs chlorination, microscreening or filtration, coagulation, precipitation and activated carbon adsorption, which further removes suspended particles, nutrients, eutrophication factors and turbidity, and virtually eliminates residual pathogens.[24] However, high levels of chlorine may be harmful to aquatic life in receiving streams and hence a chlorine-neutralizing chemical is added to the treated wastewater before the stream is discharged.[25] These processes have little effect in the removal of the materials remaining in secondary effluents (non-biodegradable) organic compounds, surfactants/detergents, inorganic dissolved salts and dissolved plant nutrients particularly nitrogen and phosphorus, whose removal generally requires more sophisticated processes, classified as advanced wastewater treatment (AWT).[26] Advanced treatment aims at upgrading the effluent to the level of fresh potable water and employs techniques such as ultrafiltration, ion exchange, reverse osmosis, electrodialysis or distillation, by which any undesirable constituent, including excess salinity, can be removed from the water. [24]

1.3 Disposal of sewage sludge

The threat of environmental pollution due to sludge disposal means that the sludge must be treated by appropriate processes. This gives a way for the final disposal either to land, air (i.e. incineration) or sea (ocean). On the basis of the selected option for final disposal, the sludge is treated. If the final disposal is to sea, little treatment is required whereas if it is land disposal especially agricultural application then the sludge has to be treated. The main treatment processes for sludge are sludge stabilization and sludge conditioning. Sludge stabilization is very important and has a two fold purpose: [27]

- to substantially reduce the number and prevent regrowth of pathogenic organisms and, thereby, minimize the health hazard associated with the sludge; and
- to substantially reduce the number of odour-producing organisms and, thereby, minimize nuisance conditions created during sludge disposal.

The most commonly used stabilization processes are anaerobic, aerobic, composting and chemical stabilization (alkaline stabilization) (Table 1.2).

Table 1.2 A summary of the stabilization processes that produce biosolids.[28]

Stabilization processes
Alkaline stabilization: Use of lime or other alkaline materials, such as cement kiln dust, limekiln, Portland cement and fly ash. Increase of pH to reduce pathogens and achieve vector attraction reduction.
Anaerobic digestion: Involves biologically stabilizing biosolids in a closed vessel to reduce the organic content, mass, odour and pathogens. During this process, methane is generated and can be used as an energy source. Both mesophilic temperatures (35 °C) and thermophilic temperatures (55 °C) are used.
Aerobic digestion: Utilizes oxygen or air to biologically stabilize biosolids in an open or closed vessel or lagoon. The organic matter is converted to carbon dioxide, water, and nitrogen. Pathogens and odours are reduced. High thermophilic temperatures are recently being used.
Composting is the biological decomposition of the organic matter. Generally, biosolids composting is done at thermophilic temperatures (>55 °C) in order to destroy pathogens. During composting, the odorous compounds are reduced.
Heat drying involves using active or passive dryers to remove water from biosolids. It is used to destroy pathogens and remove water, which reduces the volume of material. In some cases, heat-dried products are formed into pellets.

Sludge conditioning is an efficient technique for increasing the efficiency of dewatering or thickening of the sludge solids and it includes both chemical and physical conditioning: [27]

- Chemical conditioning involves organic polymers, inorganic salts, and a combination of both. The conditioning of inorganic and biological sludges with inorganic chemicals is predominantly associated with the charge neutralization mechanism. The neutralization of particles involves the discharging of the layers of electrical charge surrounding the suspended particles by the addition of conditioning agents with an opposite electrical charge, which eventually produces flocs that can closely pack together. The conditioning of biological sludges with organic polymers is predominantly associated with the bridging of the sludge particles. The bridging is the simultaneous attachment of polymer molecules, which disperse as a long chain in a sludge medium, to two or more sludge particles producing flocs that are loosely packed together.

- Physical conditioning involves heat treatment, freezing followed by thawing, and elutriation, which alters the surface structure of suspended solids. In physical conditioning, the gel-like structure of the cellular material of the biological sludge breaks down when sludge is subjected to stress and lysis of the cellular material. Finally, the bound water in the cellular material with a gel structure is released and results in the aggregation of the suspended solids.

Therefore, the sludge conditioning relies upon reducing the mobility of the hazardous constituents by binding them into a solid matrix, which has low permeability and is therefore resistant to leaching.[21]

Since sludge is a complex mixture of organic and inorganic compounds, it must be disposed of properly taking into consideration the main limiting factors such as: [29]

- economic constraints (cost of energy),
- an abundance of legislation because of the large quantities, which must be disposed of, and
- the relatively high levels of some pollutants, which become concentrated in the sludge during wastewater treatment.

The main cause for concern about environmental pollution from sludge disposal is whether the pollutants are removed from the resting place of the sludge effectively in such a manner that the least environmental damage may be incurred.

1.3.1 Disposal to Land

Land filling and application to agricultural land are the main routes for sludge disposal to land. Due to continued application of sludge to land, soil pollution is the main effect. Present research is indicating that while organochlorines at low concentrations in the soil do not transfer to crops and are eventually degraded by soil microorganisms, heavy metals do accumulate and have a significant transfer to the food chain, and hence a cost effective means for removing heavy metals from sludge is required.[7] However, land application of sludge is the only option that promotes beneficial reuse or recycling of sludge and will, under good management, cause the least harm to the environment. [30]

1.3.2 Disposal to Air (Incineration)

This disposal option requires high temperatures and is very capital demanding. It includes incineration and pyrolysis. Incineration converts all the organic matter in the sludge to carbon dioxide and leaves behind most of the inorganic materials as a dry ash. Pyrolysis converts organic matter and produces liquid hydrocarbon, carbon dioxide and ash. However, incineration does not provide complete disposal since about 30 % of the solids remain as ash.[27] Similarly pyrolysis does not give complete disposal of the pollutants; though it can reduce the formation of ash during combustion compared to incineration.

1.3.3 Disposal to sea (oceans)

Oceans and sea have been used as alternatives for sludge disposal, however this has the risk of affecting biological ecosystems. The main threatening materials to the water bodies are:

- Organic matter,
- Oil and grease,
- Bacteria and viruses,
- Heavy metals,
- Organochlorines and
- Nutrients such as nitrate and phosphate.

Organochlorines accumulate up the food chain and can cause severe health problems in higher species, but heavy metals at low concentrations do not appear to accumulate through the oceans food chain.[7] Disposal to sea is therefore capable of diluting acute toxins below their threshold but problems may arise with substances that accumulate due to geochemical or biochemical mechanisms.[21]

1.4 Pollution Due to the Disposal of Sewage Sludge

The risks due to sludge application are mainly related to the constituents it has. Compositionally, sludge is made up of organic matter, inorganic and microorganisms. An application of sludge can cause environmental pollution. There are generally four fundamental classes of pollutants associated with sewage sludge disposal and environmental pollution.

1.4.1 Pollution Associated With Metals

Concern has been expressed over the presence of heavy metals in sludge applied to agricultural land since these may occur in concentrations sufficient to cause contamination of soils, crops, and groundwater, leading to mobilization of toxic elements in food chains.[3] Specifically, there is special concern for cadmium because it has a tendency to enter the food chain where high concentrations can be harmful. For example, a prolonged high level of cadmium in the diet has been shown to cause kidney failure in human beings.[31] However, plant uptake is not the only route of metal accumulation, and a further hazard resulting from sludge disposal to land is the potential for its direct ingestion by grazing animals and subsequent accumulation of metal content in the kidney and liver.[32] Concern over the discharge and disposal of heavy metals encompasses not only their deleterious effects towards man but also to the receiving environment. The environmental risk posed by metals to the aquatic systems can be divided into hazards pertaining to terrestrial organisms utilizing the aquatic systems and those relating to the components of the aquatic ecosystem itself.[7] This will have an effect on man through consumption of food items originating from the marine environment.

In general, numerous research studies, in both the laboratory and field, have shown that there are no short-term risks to agricultural field crops when biosolids are applied at recommended rates based on the nitrogen content of the biosolids. However, in the long term, metals will accumulate in the soil to the point that crop uptake of them will increase,[30] and this will eventually cause soil pollution as well as health risks.

1.4.2 Pollution Associated With Nutrients

The term eutrophication refers to the excessive growth of usually algae but also higher plants, or waterweeds in water bodies due to the supply of nutrients. Nitrogen and phosphorus are the two nutrients most implicated in eutrophication and, because growth is normally limited by phosphorus rather than by nitrogen, it is the increase in phosphorus, which stimulates excessive plant production in freshwaters.[21] The major concerns about eutrophication include: [15]

- problems with the treatment of water for potability, where algae and their chemical products have to be removed;
- deterioration in the quality of freshwater;
- deoxygenating of lakes and rivers, as microbial communities break down the primary products of plant growth;
- obstruction of water flow in rivers by dense stands of plants; and the reduction in the diversity of animal and plant populations (or at least, the loss of the more desirable species).

Therefore, the presence of phosphorus as one of the main nutrients in sewage sludge plays a significant role in eutrophication. Moreover, the loss of nitrogen and phosphorus from soil by various biological processes and physical mechanisms results in significant pollution of the aerial environment by ammonia volatilization and denitrification, and contamination of ground and surface water supplies through leaching of nitrate and surface run-off of both nitrate and phosphate.[33]

1.4.3 Pollution Associated With Pathogenic Organisms

Sewage sludge contains a variety of pathogenic organisms, and land application of sludge will affect human and animal health. Land application of sewage sludge is an indirect determinant in the epidemiology of human salmonellosis, which also leads to increased pollution of the environment in general and possibly to direct infection of animals grazing on treated land.[34] Apart from this, there are potential problems of biological pollution by sewage sludge application such as contamination of surface waters and ground water by runoff and percolation water, adherence of sludge to crops and indirect ingestion of the sludge by grazing animals.[4]

1.4.4 Pollution Associated With Organic Pollutants

As with heavy metals, organochlorines in sewage are largely concentrated in the sludge and subsequent ocean dumping of the sludge will add significantly to the local organochlorine content of the water. Hence, bioaccumulation of such materials in the ocean food chain has been the main centre of concern and, in contrast to the situation with heavy metals, the evidence accumulated to date indicates that there is indeed a problem.[7] Therefore, the role of toxic organic compounds (the most common being pesticides, polychlorinated biphenyls, halogenated aliphatics, ethers and aromatic hydrocarbons) in sewage sludge must not be underestimated.[41] The overall environmental impact of sewage sludge is summarized in the Table 1.3.

Table 1.3 Environmental impact, risk and benefit assessment for sewage sludge recycling to agricultural land.[33]

Environmental Parameter	PTEs	Organic contaminant	Pathogens	Nitrogen	Phosphorus	Organic matter
Human health	L	P (L)	L	B	B	B
Crop yields	L	L	L	B	B	B
Animal health	L	L	L	B	B	B
Ground water	L	L	L	P	L	L
Surface water	L	L	L	P (L)	P (L)	B
Air quality	L	L	L	P (L)	na	na
Soil fertility	P	L	L	B	B	B
Natural ecosystems	P	P	L	P	P	B

(B =beneficial effect L= low risk, P = possible risk, na = not applicable, PTEs = potentially toxic elements)

1.5 Benefits of Sewage Sludge

Agricultural application of sewage sludge is widespread throughout the world due to the fact that it can provide some essential nutrients to plants. It contains appreciable amounts of nitrogen and phosphorus. Phosphorus has important effects on the general vigour and root growth of newly established vegetation, and thus helps the restoration of soil structure by root activity and subsequent incorporation of organic matter.[1] Potassium, magnesium, calcium and other trace elements are also beneficial nutrients.[35] Furthermore, biosolids are like vitamin pills for soils because they contain nearly all the essential trace elements, such as zinc (which is chronically deficient in soils but essential for crop growth), vanadium, chromium, iron, copper, cobalt, and molybdenum.[30] Hence, disposal of sludge to agricultural land plays a significant role in providing partial replacement of chemical fertilizers, which improves the nutritional status of soils and of plants in turn. Another aspect of sludge application is that it improves the physical condition of the soil by increasing the organic content, enhancing the water-holding capacity of the soil (water retention), and improving water stability of the soil structure. Consequently, the improved soil physical status following the amendment by sludge frequently would result in improved water transmission characteristics and reduced amounts of runoff and erosion.[36] In general, sludge acts as a soil conditioner to facilitate nutrient transport, increase water retention and improve soil tilth.[4]

1.6 Overview on Land Application of Sewage Sludge in South Africa

It is obvious that sewage sludge is the end product of sewage (wastewater) treatment. In South Africa, sewage sludges are classified in four categories according to the potential to cause odour nuisances, fly breeding and transmit pathogenic organisms to man and his environment.[37] These are shown in Table 1.4 below:

Table 1.4 Classification of sewage sludge to be disposed of on land.[38]

Type of sludge	Origin (Product of treatment)	Characteristics of sewage sludge
Type -A	Primary / raw sludge	Unstable sludge with an unpleasant odour, it contains a high level of pathogenic organisms
Type -B	Humus, waste activated and anaerobically digested sludge	Stable sludge with a low and less offensive odour, it contains a reduced amount of pathogenic organisms.
Type -C	Anaerobically digested and pasteurized sludge	Stable with an insignificant odour, and it contains an insignificant amount of pathogenic organisms,
Type -D	Anaerobically digested and pasteurized sludge	Stable with an insignificant odour, and it contains an insignificant amount of pathogenic organisms, but has a specified maximum concentration of metals and certain other elements.

Soils in South Africa are generally low in organic matter (due to rapid decomposition by microorganisms and use of mineral fertilizers), and this has led to widespread erosion and deterioration of soil physical status.[4] An estimated 28 % of the sludge generated at wastewater treatment plants (WWTPs) in South Africa is used beneficially as shown in Figure 1.1. When one compares the beneficial usage of sludge in countries such as Japan, United Kingdom (UK) and USA, which use 42, 50, and 35 % of their sludge respectively, it is clear that South Africa needs to improve its usage of sludge.[39] However, the agricultural application of sewage sludge has to comply with the government guidelines known as *Permissible Utilization and Disposal of Sewage Sludge* whose limits are a possible cause for the low usage of sewage sludge as a source of cheap fertilizer.[38]

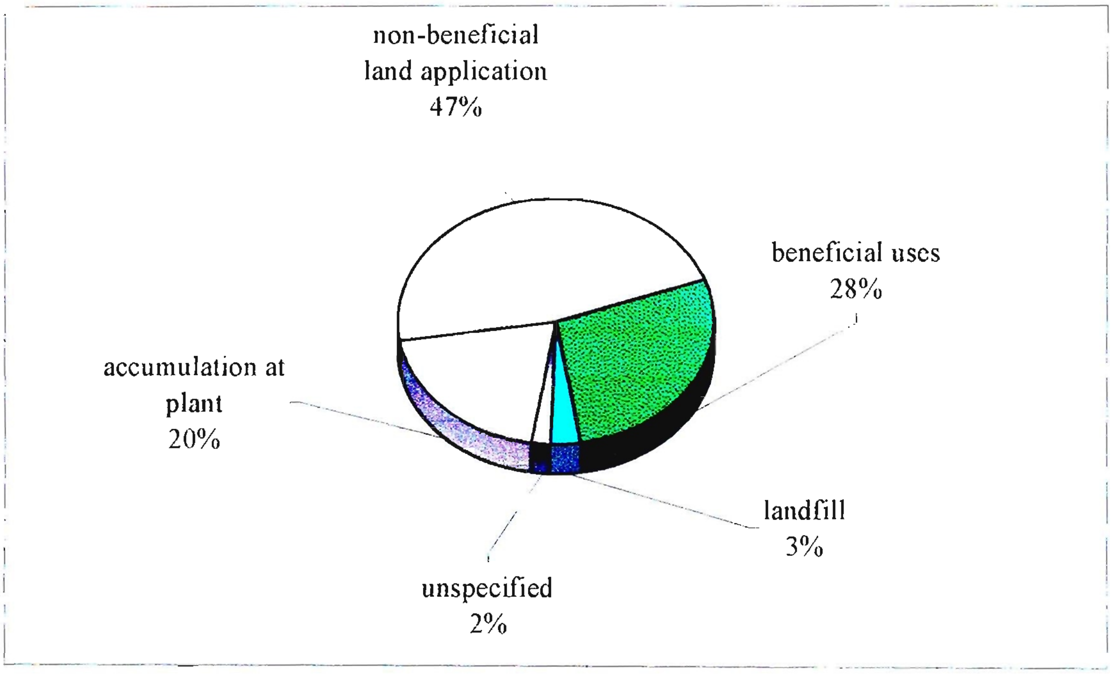

Figure 1.1 Sludge Disposals in South Africa. [40]

CHAPTER 1

SEWAGE SLUDGE : GENERAL COMMENTS

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CHAPTER 2

INORGANIC POLLUTANTS IN SEWAGE SLUDGE

CHAPTER 2

2 Inorganic Pollutants in Sewage Sludge

The term pollutant refers to substances which bring about an undesirable environmental effect be it to plants, animals or human beings. Some of the components of sewage sludge are organic or inorganic substances. Some of these substances can have beneficial effect for plants as a nutrient and others can have a toxic effect. Input of these substances to the sewage sludge is due to industrial, domestic discharge and storm runoff. Upon the application of sewage sludge for agricultural use, input of the pollutants to the soil increases. As a result of the mobility of the pollutants in the soil and their subsequent uptake by plants and animals, this can have a health effect on man.

2.1 Properties, Uses and Effects of Inorganic Pollutants in Sewage Sludge

The inorganic pollutants that exist in the sewage sludge include cadmium (Cd), cobalt (Co), chromium (Cr), copper (Cu), molybdenum (Mo), nickel (Ni), lead (Pb), zinc (Zn), selenium (Se), boron (B), aluminum (Al), barium (Ba), silicon (Si), manganese (Mn), iron (Fe), sodium (Na), beryllium (Be), strontium (Sr), calcium (Ca), phosphorus (P), magnesium (Mg) and potassium (K). The micronutrients of importance for plant growth out of the named pollutants are Cu, Zn, Fe, Mn, Mo, Co, Na, and B.[1] The major nutrients include P, K, Ca and Mg. Although waste materials often supply an appreciable amount of essential nutrients, toxic levels of certain elements, especially the heavy metals, may be present and result in long term hazard to the environment.[2] Considering their effect in the environment to plants, animals and man, these pollutants are classified into two categories according to their potential effect on the environment:

- Major pollutants: Co, Cd, Cr, Cu, Mo, Ni, Pb, Zn, Se and B.
- Minor pollutants: Al, Ba, Si, Mn, Fe, Na, Be, Sr, Ca, P, Mg, and K.

In the current research, 22 inorganic pollutants were identified. These include metals and non-metals such as phosphorus in particular. Details about each of the elements relating to their importance to man and plant is discussed here while their general physical properties are listed in Table 2.1.

Table 2.1 General physical properties of the inorganic elements.[3]

Elements	Symbol	Atomic number	Atomic mass (g)	Melting Point (°C)	Boiling Point (°C)
Boron	B	5	10.811	2079	2550
Cadmium	Cd	48	112.41	320.9	765
Chromium	Cr	24	51.996	1857	2672
Copper	Cu	29	63.546	1083	2567
Lead	Pb	46	106.42	1552	3140
Molybdenum	Mo	42	95.94	2617	4877
Nickel	Ni	28	58.693	1453	2732
Selenium	Se	34	78.96	217	684.9
Zinc	Zn	30	65.39	419.6	907
Beryllium	Be	4	9.012	1278	2970
Cobalt	Co	27	58.933	1495	2870
Aluminum	Al	13	26.982	660.37	2467
Barium	Ba	56	137.33	725	1640
Silicon	Si	14	28.086	1410	2355
Manganese	Mn	25	54.938	1244	1962
Iron	Fe	26	55.845	1335	2870
Sodium	Na	11	22.990	97.81	882.9
Strontium	Sr	38	87.62	769	1384
Phosphorus	P	15	30.974	44.1	280
Calcium	Ca	20	40.078	839	1484
Magnesium	Mg	12	24.305	648.8	1090
Potassium	K	19	39.098	63.65	774

2.1.1 Boron (B)

Boron is a widely distributed metalloid. It occurs mainly in the form of its sodium salt, borax (sodium tetraborate, $Na_2B_4O_7$). It has both agricultural and industrial applications. Agriculturally, it is an essential nutrient for plant growth. However, boron appears to be readily accumulated by most plants, and its uptake is associated with severe toxicity symptoms.[4] A high intake of the element from pasture on boron-rich soil has been known to cause gastro-intestinal and pulmonary disorders in lambs.[4] It plays a great role in steel production, in the manufacturing of electric wires, in glass, enamel and ceramic making. In addition, boron and borax are used in water softeners, fertilizers and in pharmaceuticals.[4]

2.1.2 Cadmium (Cd)

Cadmium belongs to the second row of the transition metals in the periodic table. Cadmium is one of the heavy metals. It is relatively volatile and readily soluble in nitric acid, but slowly in hydrochloric acid and sulfuric acids. It has several compound forms such as chloride, sulfate and acetate. Its industrial applications include: being used as an antirust coating on iron, as a component of solder alloy, and as an electrode component in alkaline accumulators. There are several possible sources of cadmium in the environment and these include, from industries in the form of dusts and aerosols into the atmosphere, effluents into rivers and lakes, and as solids from point sources (waste, slag, incineration, coal combustion, phosphate fertilizers, sewage sludge).[5] Cadmium is very toxic to plants, animals and human beings. The ingestion of cadmium in food or in drink can cause symptoms of nausea, vomiting, abnormal cramp and headache within minutes of ingestion, and long-term ingestion of cadmium results in serious diseases of the kidneys as well as of the bone.[4]

2.1.3 Chromium (Cr)

Chromium is found in many minerals, which are widely distributed in the earth's crust. It is very hard, shiny, malleable (that is, it can be beaten flat with a hammer and cut with a knife easily), and it is resistant to corrosive agents. It has about nine oxidation states;[7] among which trivalent and hexavalent are the most common ones. It is an essential element to animals and man as chromium(III) for metabolizing glucose. On the other hand, chromium is useful in many industries, for example: paint (for pigments), building, printing (photochemical reproduction processes), oil (as anti corrosive), textiles (chromium mordant for textiles and chrome dyeing processes), matches,[6] electroplating (for modifying metal surfaces), wood (treatment for preservation against insect attack) and leather (for tanning and curing).

Trivalent chromium compounds, ingested as part of food are relatively innoxious, while hexavalent Cr compounds are poisonous.[6] A potential source of increased concentrations of chromium in food, as of many of the other industrially important heavy metals, is sewage sludge; and levels of as high as 8 g kg^{-1} have been reported in dry sludge and thus, the use of such material for agricultural purposes could result in the uptake of chromium by plants as well as by animals.[4]

2.1.4 Copper (Cu)

Copper is one of the most widely distributed elements in the earth's crust. It is ductile and a good conductor of heat and electricity. Industrially, it is used for manufacturing of electrical goods, electric cables, water piping, roofing material and in making alloys such as brass and bronze. Biologically, it is an essential element used in processes of blood formation and iron utilization, with a human daily requirement of 0.03 mg kg^{-1}.[7] Nevertheless, an intake of large amounts of copper causes toxicity to animals as well as man.[13] Furthermore, high concentration of copper in soils interferes with biochemical reactions in soils which leads to a decreased turnover of organic matter and hence causes a decrease in crop yields.[8]

2.1.5 Lead (Pb)

Lead is one of the heavier metals, which occurs widely in trace amounts. Characteristically, it is soft and malleable. Though it has three oxidation states (zero, +2 and +4) most of its salt compounds exist in the +2 oxidation state. It is non-essential to organisms, yet it has some industrial purposes such as making solder, batteries (electrical accumulators for cars and other electrical vehicles), emergency lights, lead salts for glazing of ceramics, in glass manufacture for high-quality crystal and for television tubes and fluorescent lights, and as petroleum additives.[4] Although, it has industrial applications, it has toxic effects on animals and human beings. Lead is likely to cause problems in man's food chain because it normally accumulates in roots, with a little being transported to the leaves of plants.[9]

2.1.6 Molybdenum (Mo)

Molybdenum occurs widely in trace amounts in the earth's crust. It is silvery white, and very hard. It is an essential nutrient for plants, animals and even for human health according to recent investigations.[10] Industrially, it has various uses such as making special steel alloys, screens and grid tubes for radio tubes and x-ray tubes, as a ferromolybdenum alloy, in addition as a dry lubricant and lubricant additive.[11] High molybdenum uptakes from diet results in growth retardation and weight loss in different animals.[11] However, toxic manifestations of molybdenum in humans are rare.[12]

2.1.7 Nickel (Ni)

Nickel is a silvery white metal, which occurs naturally in combined form. It is a good conductor of heat and electricity and highly resistant to corrosion. Therefore, it is industrially used as a protective plating on other metals, and in manufacturing food-processing vessels and other equipment, in the production of heat resisting steels, and as a catalyst in the hydrogenation of oils. In general, nickel is essential for animals and man; and is non-toxic to man.[4] However, one form of nickel sulfide (NiS, i.e. nickel subsulfide) is known to be carcinogenic to higher organisms, including man.[13] Despite its benefits to plants, its toxicity manifests itself in chlorosis and yield reduction.[12]

2.1.8 Selenium (Se)

Selenium is a widely distributed metalloid and is found in trace amounts in the earth's crust. It has biological, and industrial significance. It is an essential element in many species, including humans, in whom it is a component of glutathione peroxidase, which is required for the metabolism, and removal of hydrogen peroxide and lipid peroxides from cells.[14] Selenium and its compounds have a wide range of industrial applications. It is used in the manufacturing of semiconductors, rectifiers, and photoreceptors for the electric and electronic industries, ceramics, glass, pigments, alloy making, catalysts, deodorants, lubricants, pesticides, pharmaceuticals, and in the rubber industry for vulcanization.[15] Nevertheless, an exposure to this element has side effects; in acute selenosis, animals suffer from blindness, abdominal pain, and some degree of paralysis and in extreme cases, death results from respiratory failure, as well as from starvation and thirst; but selenium deficiency in humans has not been clearly established.[11] It is not required by plants but it is toxic when present above 50 mg kg^{-1}.[16]

2.1.9 Zinc (Zn)

Zinc is a bluish white, rather soft, lustrous metal. It is ductile and malleable at 100 °C. It is a reactive metal. It is one of the heavy metals, with both biological and industrial applications. It is a micronutrient for plants, and it plays a great role in man for growth, development, and reproduction. Industrially, it is used in alloy making, paints, plastics, rubber, cosmetics, pharmaceuticals, batteries, fertilizers, lights, televisions, and tyres.[31] Considering its environmental impact, the toxicity of zinc and most zinc containing compounds is generally low and, with certain exceptions, of minor importance compared with the significance of zinc deficiency in plants, animals, and man; disorders of zinc metabolism in human beings are usually due to deficiency rather than a surplus of zinc. [17]

2.1.10 Cobalt (Co)

Cobalt is a grey, lustrous, and hard metal, relatively rare in the earth's crust. It has both biological and industrial applications. Cobalt is needed by man only as a component of vitamin B_{12}. However, toxic effects of excessive amounts of cobalt have only been reported rarely and then only when cobalt compounds had been deliberately added during food processing or were used in high doses therapeutically for the treatment of certain forms of anaemia.[4] Its industrial applications include making high strength alloy and permanent magnets and it is used in some pharmaceuticals. However, its availability has toxic effects, for instance, it is toxic to tomato plants at 0.1 mg l^{-1} in the nutrient solution and its toxicity level in plant foliage is 25-100 mg kg^{-1} dry matter.[16]

2.1.11 Beryllium (Be)

Beryllium is one of the most rare and expensive of the alkaline earth metals. Beryllium and its compounds play a great role in industries, such as making electrical equipment, optical glass, and ceramics, as a catalyst in organic reactions and in nuclear reactors. It has no biological significance. Exposure to it can cause a disease called berylliosis. Some plants have been reported to accumulate beryllium and these could be a potential source of high beryllium intake for stock as well as man.[4]

2.1.12 Aluminium (Al)

Aluminium is the most common metal in the earth's crust. It is silvery white, ductile, and a good conductor of heat and electricity. It is mostly used for industrial applications, such as electrical equipment, alloy making, packaging foil, and heat resistant paints; pharmaceutically, it is used as an antacid in its basic hydroxide solution. When Aluminium ions enter plant cells, they can interfere with different enzymes and cause disturbances to the cell metabolism. Moreover, for Al-intolerant plant species, even the very low Al concentrations in the soil solution in the pH range of 5 to 4.5 are already sufficient to cause severe root damage.[18] However, in the case of humans, it has been reported to be toxic to the nervous system. [11]

2.1.13 Barium (Ba)

Barium is silvery yellow and the heaviest of the alkaline earth metals. It has no biological importance. Industrially, barium and its compounds are of great use for example as a contrast medium in X-ray examinations, in lubricating oil and grease, as a mordant for printing fabrics, as a corrosion inhibitor for low carbon steel, in ceramics, paints and enamels, in the manufacture of marble substitutes, rubber, paper, electrodes and optical glasses, in pigments, and in the manufacture of fireworks. Furthermore, it is involved in electroplating, textiles and leather, glass manufacture, sugar refining, and it is used in photocells, television tubes and explosives. It has a biological toxic effect which is characterized by very intense stimulation of muscles of all types, regardless of innervations, leading to paralysis of respiratory muscles and even death.[11] Though evidence regarding Ba toxicity to plants is conflicting, it was shown that a significant yield reduction occurs when barley and bush beans are grown in soils containing 2000 ppm Ba as $Ba(NO_3)_2$.[19]

2.1.14 Silicon (Si)

Silicon is one of the most abundant elements in the earth's crust. It is one of the micronutrient elements for the body's functions and it participates in the normal metabolism of higher animals.[20] It is also essential for plants because it controls root system development, increases plant resistance to abiotic (low or high temperature, wind, salt, heavy metals, hydrocarbons, Al etc) and to biotic stresses (insect, fungi, disease).[21] It has many industrial applications such as:[22] silica, as sand, which is a principal ingredient of glass, used in computer chips, lubricants, used to make concrete and bricks and used in medicine for silicone implants.

2.1.15 Manganese (Mn)

Manganese is a very brittle, hard heavy metal of white–grey colour. It is an essential element for the maintenance of normal health in animals and man. It has industrial applications such as steel making, in the manufacture of electric accumulators, and as an oxidizing agent in the chemical industry. Manganese compounds are used as feed additives, fertilizers, pigments, dryers, wood preservatives, and for coating welding rods; black manganese oxide is used as a depolarizer in dry-cell batteries. Manganese deficiency in animals is manifested by skeletal abnormalities[4] and in plants, it causes growth disturbances and yellowing of the needles of conifers. Furthermore, although the tolerance of most plants towards excessive manganese is very high, its excessive presence causes chlorosis, [23] which is manifested by the yellowing or blanching of normally green parts such as leaf tops (due to insufficient chlorophyll production). Additionally, an exposure to manganese in the work place causes a disease known as manganism, this is a serious neuro-psychiatric disease, which is caused by inhalation of manganese in quantities of probably more than 100 mg day^{-1} over a period of some months or years. [23] However, there is no evidence that manganese in food is toxic.[4]

2.1.16 Iron (Fe)

Iron is the second most abundant metal in the earth's crust. It is silvery white in its pure state, and also it is malleable and magnetic. It is an essential element for all living organisms, especially as a component of haemoglobin in the blood. Iron and its compounds are involved in various industrial applications: in the making of alloy steel, as mordant in dyeing and printing textiles, photoengraving, pigments, water purification systems, as a polishing agent for glass and precious metals, and in magnets and magnetic tape.[11] Biologically, iron toxicity is low; the problem of iron overload is limited to man and is far less frequent than iron deficiency. Furthermore, acute iron poisoning from ingested iron is unlikely to be encountered from any source other than medicinal iron.[24] Although iron is one of the microelements for plants, its toxicity effect has been reported to occur in plants that have received soluble Fe-salts either as sprays or as soil amendments in excess quantities.[25]

2.1.17 Sodium (Na)

Sodium is a silvery white and very reactive metal and is not found freely in nature. It is an essential element for growth and development of all animals and man. Industrial uses of sodium compounds involve glass manufacture, industrial chemicals, water purification, food, detergent and textiles, pulp and paper, and oil refining. In the context of health, the development of hypertension may be considered by some as a manifestation of chronic sodium chloride toxicity.[26] Moreover, its availability in soil may affect the potassium nutrition of plants, since at high concentrations Na^+ may compete with K^+ uptake: Specific toxicities are usually limited to fruit trees, where leaf injury occurs.[16]

2.1.18 Strontium (Sr)

Strontium is relatively abundant in the lithosphere (average abundance in the earth's crust is 370 ppm). It is a silvery-white, malleable and ductile metal. Industrially, strontium and its compounds are important, they are used as 'getter' to remove traces of gas from vacuum tubes, it gives brilliant colors for fireworks and flares, in ceramics, plastics, purifying zinc, permanent magnets and in iron casings and in pharmaceuticals.[23] As far as its toxicity is concerned, no evidence has been produced indicating toxic effects of ingestion of non-radioactive strontium.[4] However, the strontium-90 (radioactive) is taken up into the food chain through the roots of plants and finds its way into the human diet through dairy products. This is eventually deposited by the body in the bones, where it is thought to cause bone cancer.[27]

2.1.19 Phosphorus (P)

Phosphorus is abundant in the earth's crust and is found in the combined state. It has a wide range of uses both biological as well as industrial. It is one of the major nutrients for plants. It has also a major role in the biological functioning in the human body. For instance, it is the major structural material in vertebrate bone. In its phosphate form it provides energy storage and transfer mechanisms in all living systems.[28] Apart from its biological importance, it has incredible industrial value in many fields such as animal foodstuffs, dental materials, detergents, electrical materials, fertilizers, flame retardants, food additives, glass technology, luminescent phosphorus, matches, medicines, metal treatment, nerve gases, oil additives, pesticides, pigments, plastics, refractories, smoke generators, surfactants and water treatment.[29] However, the presence of phosphorus in the environment can promote excessive plant growth in the water systems and as a result eutrophication occurs and as eutrophication progresses, a decline in the species diversity of the phytoplankton and a change in species dominance as overall populations and biomass increases.[30]

2.1.20 Calcium (Ca)

Calcium is one of the macronutrient metals required by our body, and it is also an essential nutrient for plants. The free calcium ion is now recognized as a major intracellular regulator of numerous biochemical and physiological processes in plants.[31] Industrially, calcium compounds are involved in many fields such as manufacturing of toothpaste, chalk, as filler in plastics, paints, paper, board, cement, in fertilizer, soil conditioner, and as a neutralizer of natural waters and industrial acids and as a flux in the metallurgical industry.[32] Deficiency of calcium is manifested by bone defects.

2.1.21 Magnesium (Mg)

Magnesium is widely distributed in the earth's crust. It is one of the essential nutrients for man and plants. Industrially magnesium oxide is used in alloy making, production of fire-resistant materials, as ceramic heat accumulators and as an additive in fertilizers.[32] However, its deficiency is a much greater risk than is its toxicity for all living organisms.[33]

2.1.22 Potassium (K)

Potassium, the principal cation in humans, is physiologically important in many of the functions of the human body such as the functional integrity of cardiovascular, respiratory, digestive, endocrine, renal and neurological systems.[34] It is also one of the macronutrients for plants. It is involved industrially in the manufacture of fertilizers. Potassium deficiency can have pronounced effects on cardiac, skeletal and muscle.[35]

2.2 Sources of Pollutants in Sewage Sludge

The input of all pollutants into sewage sludge is associated with domestic discharge, runoff and industrial discharges; the process shown pictorially in Figure 2.1

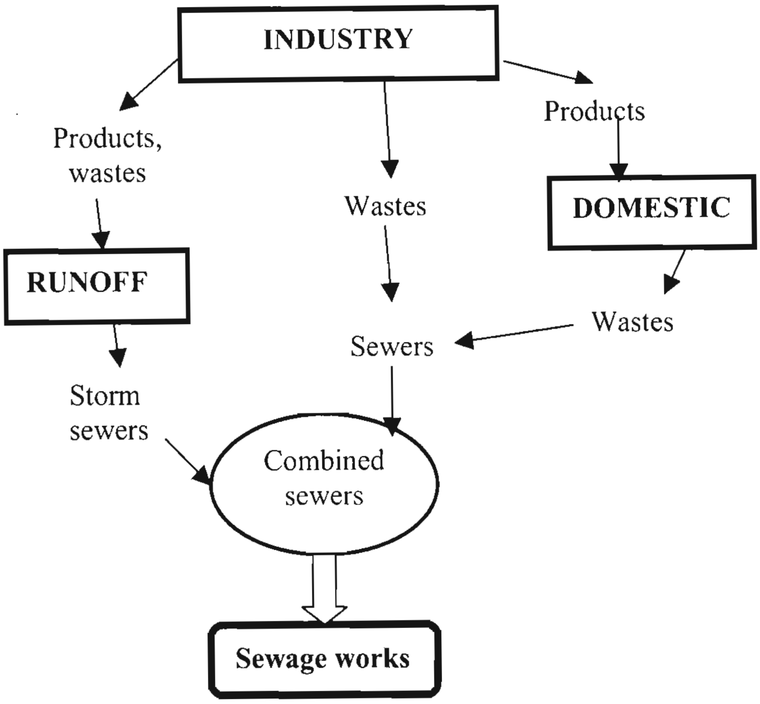

Figure 2.1 The sources and pathways of pollutants to the sewage works.[15]

2.2.1 Domestic Discharge

This includes all discharges from residential areas and automobile repair shops, restaurants, hotels, hospitals, laboratories, car washes, warehouses and shopping centres. Community residents discharge significant amounts of potentially toxic elements probably originating from cosmetics, hobby materials, and medicines and particularly from metal plumbing pipes.[36] As a whole the main sources of pollutants especially heavy metals in the domestic areas are shown in Table 2.2.

Table 2.2 Sources of pollutants in domestic wastewater.[15]

Product type	Al	Be	Cd	Cr	Co	Cu	Fe	Pb	Mn	Mo	Ni	Se	Zn
Automotive products	*	*		*	*		*	*		*			*
Caulking compounds	*	*		*	*		*	*					*
Cleaners	*			*		*	*						*
Cosmetics	*	*	*		*	*	*	*	*		*	*	*
Driers	*												
Fillers	*												*
Fire extinguishers	*			*			*						*
Fuels		*				*		*					
Pesticides	*		*	*		*	*	*	*	*			*
Inks	*					*							*
Lubricants		*		*				*		*			*
Medicine	*				*	*	*						*
Oils		*				*		*					*
Ointments	*				*	*							*
Paints	*	*		*	*		*	*	*				*
Photography	*			*			*	*					
Pigments	*	*	*	*	*	*	*	*	*		*	*	*
Polish	*	*				*							*
Powders	*						*						*
Preservatives							*	*					*
Suppositories													*
Water treatment	*					*	*		*				*

2.2.2 Runoff

This is related to water originating from the surfaces of roads and highways. According to Pope *et al.*,[37] the seven sources of road surface pollutants are:

- Vehicle lubricant loss,
- Load loss,
- Tyre degradation,
- Exhaust emission,
- Road-surface degradation,
- Road cleaning and deicing
- Atmospheric precipitation.

The numerous investigations of heavy metals in the vicinity of busy streets and highways have identified elevated concentrations of heavy metals in soils, plants, soil animals, and air that are related to traffic density, mode of vehicle operation, and distance from the highway.[38] These are also inputs to the sewers in urban areas and thereby to sewage sludge and finally to the final disposal areas of agricultural lands after final treatment of the sludge. Hence, runoff will have a substantial contribution as a source of pollutants to sewage sludge.

2.2.3 Industrial Discharge

The main source of most inorganic pollutants is found to be industries. Industries reported to cause significant heavy metal pollution of soils include chemical manufacturing, oil refining, metal processing and plating, tanneries, and fertilizer manufactures.[38] The types of pollutants and their associated industries are summarized in Table 2.3.

Table 2.3 Sources of pollutants to wastewater from different industries.[15, 39]

Industries	Al	Cr	Co	Cu	Fe	Pb	Mn	Mo	Ni	Se	Zn	Cd
Metal industries												
Power plants (steam)		*									*	
Foundries (ferrous)		*	*	*	*	*	*	*	*	*	*	*
Foundries (nonferrous)	*	*		*		*	*			*	*	*
Metal vehicles, aircraft, plating	*	*		*					*			*
Chemical industries												
Glass, cement, asbestos		*								*		
Organic and petrochemicals	*	*										*
Inorganic chemicals	*	*			*	*					*	*
Fertilizers	*	*		*	*	*	*		*		*	*
Petroleum (oil) refining	*	*		*	*	*			*		*	*
Other industries												
Pulp and paper		*		*		*			*		*	
Leather tanning		*										
Textiles		*										
Electronics				*						*		

2.3 Mobility and Fate of Inorganic pollutants

Land application of sewage sludge as a source of fertilizer results in the introduction of pollutants hazardous to the environment. These pollutants include a variety of organic and inorganic substances. The chemical forms of heavy metals in soils can greatly influence their fate in terms of plant uptake or soil profile migration.[40] Generally, heavy metals (Co, Se, Mo, Ni, Cr, Cd, Pb, Zn, Hg, B, As and Cu) contamination has received much attention with regard to accumulation in soils, uptake by plants, and contamination of waters.[41, 42]

With the increased interest in land disposal of sewage effluents and sludge, some of which have high concentrations of trace metals, the movement and availability of these elements becomes important from both a water quality and crop production points of view.[43] Heavy metal movement will most likely occur with large application to a sandy, acid, low organic matter soil, which receives high rainfall or irrigation and also through open soil channels or cracks where the soil has no opportunity to attenuate them.[37] In areas with high organic matter accumulation, organo-metal-ion complexes are formed which may exist in soluble or colloidal form and, therefore, differ in degree of mobility.[44] Besides, as the soil solution becomes increasingly acidic, the influence of organic ligands on heavy metal uptake diminishes due to a decreasing ability of the ligands to bind the metal. Hence, metal binding organic substances in wastewater or sludge destined for land application may influence the fate of toxic metals also contained therein.[45] In general, environmental hazards derived from heavy metals are linked closely to movement of the metals in soil profiles because even slow transport through soil and subsoil materials may eventually increase the content of heavy metals in the ground water.[40]

Transfer of trace elements in agricultural and environmental food-chains is important because crops absorb trace elements from soils, since soils may become enriched in trace elements due to disposal of sewage and other wastes on cropland.[13] Heavy metal pollution is derived from various sources as solids, liquids, and frequently, as fine particles directly into the atmosphere, but is ultimately deposited on the surface of water bodies and land.[37]

Generally, one of the sources of the heavy metals in agricultural land is sewage sludge. After its application for agricultural purposes, the fate of the heavy metals has been found to either accumulate in the soil or be taken up by plants. This eventually results in phytotoxicity, zootoxicity and human health effects.

2.3.1 Accumulation of Pollutants in Soil

Soil texture, surface area, the hydrous oxide content, and the free lime content provide the most useful information for predicting a soil's effectiveness for trace element retention.[46] Chang *et al* [47] showed that plant absorption of metals was insignificant compared with the total metal inputs. He also reported that there appeared to be no deep leaching which as a result all applied heavy metals due to the sludge addition should have remained in the soil. In support, Williams *et al* found that after six years of sludge addition, the concentrations of Cd, Cu, Pb, and Zn were found to have increased in the surface soil to an extent consistent with the rate and number of years of sludge addition.[48] Moreover, it was also shown that concentrations of Zn, Cd, Mn, Ca, Mg, Na, K, Cl, P as PO_4^{-2} and S as SO_4^{-2} in the soil solution increased with sludge application, particularly in plots receiving multiple sludge applications whereas soil solution concentrations of Cu, Ni, Pb, and Fe were generally low ($<10^{-6}$ M) at all sludge application rates. However, soluble Cu and Ni concentrations in soil treated with sludge at 800 t ha^{-1} were markedly higher than those in soil receiving lesser amounts of sludge. Soluble Al levels in soils were not increased by sludge addition and were reduced at high loading rates, probably because of the liming effect of sludge additions.[49] In general, apart from the properties of the soils, the reason for accumulation is the great stability of the chemical complexes formed between heavy metal ions and negatively charged organic groups.[50] The behaviour of heavy metals is usually seen in the context of precipitation and organometallic complexing reactions; however, chlorides, under certain circumstances, may also be of great significance in determining heavy metal distributions in the environment.[43]

2.3.2 Accumulation of Pollutants in Crops

Once heavy metals are introduced into croplands, they can be taken up by plants and subsequently become incorporated into the food chain.[51] However, the uptake of heavy metals from sludge-amended soils depends on metal concentration and on plant genotype, temperature, dose rate, and equilibration period, and is mediated by soil physicochemical properties, especially pH.[37] Specifically, injury to crops is associated with accumulation of metals in the soil and generally occurs under predisposing conditions, i.e. low pH, sandy soils, and/or with crops that have low tolerance to heavy metals, notably some vegetables.[52] In contrast to this, it has been shown that there is no decrease in yields of red beet, leeks, carrots, or potatoes when grown on a sandy soil that had received 1426 tonnes of sludge per hectar over a 19-year period.[53] Furthermore, it is documented that accumulation of certain heavy metals such as Cd, Cr, Ni, and Zn exist in the leaves and grains of maize where the land was treated with sludge for three years. The finding is shown in Table 2.4. However, there was no significant accumulation of Pb and Hg.[53]

Table 2.4 Concentrations of heavy metals in maize ($\mu g\ g^{-1}$) grown on untreated soil (-) and on soil irrigated with sewage sludge as a slurry (+); total addition of 168 t ha^{-1} of dry sludge made over 3 years.[54]

Metal	Metal content of sludge ($\mu g\ g^{-1}$)	Amount of metal applied (kg ha^{-1})	Metal content of leaves ($\mu g\ g^{-1}$)		Metal content of grain ($\mu g\ g^{-1}$)	
			—	+	—	+
Cd	474	80	3.3	11.6	0.3	1.0
Cr	4217	708	4.1	4.5	0.3	0.4
Cu	1760	295	8.9	8.7	5.2	5.6
Hg	0.51	0.09	0.03	0.04	0.005	0.004
Ni	425	71	2.8	4.3	2.3	3.1
Pb	1503	252	7.1	6.3	0.03	0.03
Zn	6782	1139	58	212	89	152

Generally, determining the soil factors that affect heavy metals availability is necessary, so toxicities in crops, animals, and humans can be avoided.[55] Application of sludge should be made to well-drained soils of high cation exchange capacity and, perhaps more importantly, the pH of the treated soil should be monitored and adjusted to at least 6.5 and finally, as plants differ in their ability to take up Cd, and other heavy metals, the selection of a particular crop offers an additional means of reducing the extent of movement from soil through plant to animals and man.[51]

2.3.3 Phytotoxicity Effects of Metals

Elements like Ni, Cu, Zn and Cd have a toxic effect on plants. However, no toxic effect of Pb has been shown. This is because Pb uptake by plants is so small and when lead is equilibrated with soil, it tends to become very insoluble and is not readily translocated by plants.[56] The-determining factor on whether the element is taken up by plants is its presence in its aqueous form in the soil. However, most trace elements are quite insoluble in soil water, or adsorbed strongly by the soil except Se, Mo, B and other elements that are anionic in soils. This shows that the uptake of Se, Mo, B and other elements in anionic form is probable. Though copper, zinc, boron, selenium and molybdenum are essential for plant growth, they are found to be toxic when they are present in excess.[65]

2.3.4 Zootoxicity Effects of Metals

After repeated application of sewage sludge to land, the most highly toxic elements are found to accumulate by adsorption on the surface of soil, or to be accumulated on the growing crops. As a result of this accumulation of these toxic elements, grazing animals feed on them and get poisoned. Generally, any effects that heavy metals in sewage sludges applied to agricultural land might have on the health of animals could arise in either of two ways, namely: [57]

- By direct ingestion of sludge on herbage, or of metal-contaminated soil
- By consumption of crops containing high concentrations of metals absorbed from the soil

2.3.5 Human Health Effects of Metals

Any potentially adverse effect that heavy metals in sewage sludge applied to agricultural land might have on human health could arise in a number of ways including: [57]

- Direct ingestion of sludge or sludge-soil mixtures
- Consumption of water contaminated with heavy metals through leaching from amended soils.
- Ingestion of foods (of both plant and animal origin) containing high concentrations of metals.

These metals are present in different levels in our daily food we take and can have toxic effect depending on the permissible limit of them in our body. The levels of them in human body are as shown in Table 2.5.

Table 2.5 Daily dietary intake of inorganic elements & their Toxic levels. [3]

Elements	Daily dietary intake (mg)	Toxic intake (mg)	Lethal intake (mg)
Boron	1-3	4×10^3	n.a
Cadmium	0.007-3	3-330	1.5×10^3-9×10^3
Chromium	0.01-1.2	200	$>3.0\times10^3$
Copper	0.5-6	>250	n.a
Lead	0.06-0.5	1	1×10^4
Molybdenum	0.05-0.35	5	50 (rats)
Nickel	0.3-0.5	50 (rats)	n.a
Selenium	0.006-0.2	5	n.a
Zinc	5-40	150-600	6×10^3
Beryllium	0.01	n.a	n.a
Cobalt	0.005-1.8	500	n.a
Aluminum	2.45	5×10^3	n.a
Barium	0.6-1.7	200	3.7
Silicon	18-1200	Non-toxic	n.a
Manganese	0.4-10	10-20 (rats)	n.a
Iron	6-40	200mg	7×10^3-35×10^3
Sodium	2-15×10^3	Non-toxic	n.a
Strontium	0.8-5	Non-toxic	n.a
Phosphorus*	900-1900	Phosphates non toxic	60 as P_4
Calcium	600-1400	Non-toxic	n.a
Magnesium	250-380	Non-toxic	n.a
Potassium	1400-7400	6×10^3	14×10^3

* Phosphorus is exceptionally a non-metal in this case. n.a – not available

In summary, there are different pathways whereby contaminants from sludge applied to agricultural land enter the food chain in the environment. These are tabulated in Table 2.6.

Table 2.6 Pollutant exposure pathways for land-applied sludge. [58]

Pathway	Description of highly exposed individual
Sludge →soil → plant → human	Consumers in regions heavily affected by land spreading of sludge.
Sludge → soil → plant → human	Farmland converted to residential home garden five years after reaching maximum sludge application.
Sludge → soil → human	Farmland converted to residential use five years after reaching maximum sludge application with children ingesting sludge-amended soil.
Sludge → soil → plant → animal → human	Households producing a major portion of their animals used for dietary consumption on sludge-amended soil.
Sludge → soil → plant → animal → human	Households consuming livestock that ingest sludge-amended soil while grazing.
Sludge → soil → plant → animal	Livestock ingesting food or feed crop grown in sludge-amended soil.
Sludge → soil → animal	Grazing livestock ingesting sludge/soil.
Sludge → soil→ plant	Crops grown on sludge-amended soil.
Sludge→ soil → soil Biota	Soil Biota living in sludge-amended soil.
Sludge → soil → soil Biota → Biota predator	Animals eating soil biota living in sludge – amended soil.
Sludge → soil→ airborne dust → human	Tractor operator exposed to dust from sludge-amended soil.
Sludge soil →surface water/fish → human	Humans eating fish and drinking water from watersheds draining sludge-amended soils.
Sludge → soil→ air → human	Humans breathing fumes from any volatile pollutants in sludge.
Sludge → soil → groundwater → human	Humans' drinking water from wells surrounded by sludge-amended soils.

2.4 General Approaches on the Reduction of Pollutants

The above-mentioned effects of pollutants in sewage sludge arise from the source of input of the contaminants. Although various methods have been examined, the economics of extraction of pollutants from sewage sludge are always unfavourable and the conclusion is that the best way of reducing the problem of contamination is to control the source, i.e. trade waste control.[59] As a result, regulations on the discharge to sewer is mainly concerned with industries. For controlling the discharge of the pollutants, industrial effluent pretreatment is found to be the best option for reduction of the pollutants in the environment. Recent technological advances in industrial pre-treatment systems have drastically reduced the likelihood of introducing pollutants into biosolids; consequently, there has been reduction in the concentration of heavy metals and other pollutants in the resulting municipal wastewater biosolids.[57]

2.4.1 Reduction of Heavy Metals

There are different approaches to the pretreatment of effluents containing metals especially the most important heavy metals at the industrial centres. Basically, there are three approaches available for reducing the concentration level of heavy metals in sewage sludge: [60]

- Firstly, strict controls can be put on industrial sources and other point sources of wastewater discharge to the sewer system. With this approach, considerable improvements have been achieved in the past.
- Secondly, an attempt can be made to control diffuse sources. While this is generally more difficult to achieve, some progress can be made by using lead-free petrol, zinc-free roof gutters and copper-free tap water transport systems.
- The third approach is the extractive removal of heavy metals from sewage sludge, for which technology has been developed but which is yet to be proven cost effective.

2.4.2 Reduction of Phosphorus

There are several technologies, which have been applied successfully at full scale to remove phosphorus from wastewaters, usually to form a solid amenable to conventional solid-liquid separation technology: [61] These are:

- Biological techniques, which employ microorganisms to remove phosphorus through synthesis, metabolic processes and adsorption, incorporating the phosphorus into biological solids.
- Chemical techniques which utilize precipitation, coagulation and flocculation to incorporate the phosphorus in a chemical sludge by the use of lime, aluminium or iron salts.
- Physical techniques, which removes phosphorus through the processes of adsorption, sedimentation and filtration.
- Combined processes which involve the use of the above-mentioned techniques either simultaneously or in sequence.

2.4.3 Reduction of Organochlorines

There are two approaches, which could be used to remove organochlorines from sludge: [60]

- The physiochemical approaches: these involve either high temperature oxidation (incineration) or reductive dechlorination (pyrolysis) in an atmosphere of hydrogen
- The microbiological approach: this does not require sophisticated capital equipment, but would utilize sophisticated know how about the behaviour of anaerobic bacteria.

2.5 Aim of The Project

Sewage sludge contains a variety of species such as organic, inorganic and pathogenic organisms. Sludge as a product of the treatment of the sewage, has to be disposed off in accordance with the rules set by legislative bodies without causing an adverse impact on the environment. Some of the main final disposal options are disposal to land, to sea and incineration. A well-treated sludge can be used as a nutrient source for vegetation. It also improves the soil physical properties such as soil structure, water retention and transmission characteristics. However, its use is restricted because of the presence of hazardous materials such as organic compounds, inorganic chemicals and the presence of certain harmful microorganisms. Some of the toxic inorganic chemicals mainly heavy metals have an adverse effect in the environment due to their characteristic effect of accumulation in the soil and in crops which finally results in phytotoxic, zootoxicity and human health effects. The potential for toxic effects on humans resulting from sludge disposal to land varies with a multiplicity of factors, such as the nature and metal content of the soil and the sludge, the rate and frequency of sludge application, the species of metals in the sludge and subsequently in the sludge-amended soil, the type of crop grown, and the part of the plant consumed.[7] The agricultural application of sludge is practised in many countries of the world by imposing certain regulations. South Africa uses 28 % of the treated sludge of type D.

Application of sewage sludge to agricultural land is of economic importance to the sewage works as a source of income. To the farmers it is a source of cheap fertilizer. Because of the dangers associated with sewage sludge, there is a need to conduct a study on the inorganic composition of South African sewage sludges. The findings are important in making decisions with regard to the disposal options. In addition, these are likely to have an impact on the existing guideline, which was last reviewed in 1997.

It was therefore the aim of this project to quantify the amounts of inorganic pollutants and nutrients in sludge from 69 sewage works covering the entire 9 provinces of South Africa. This was to provide the much needed information on the quality of the South African sewage sludge.

In summary, the aims of the project were to:

- Carry out literature review on inorganic pollutants i.e. their negative and positive effects in the environment.
- Sample sludges (both solid and liquid) from the main sewage works of South Africa.
- Extract and analyse for inorganic pollutants in the sludge.

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CHAPTER 3

EXPERIMENTAL

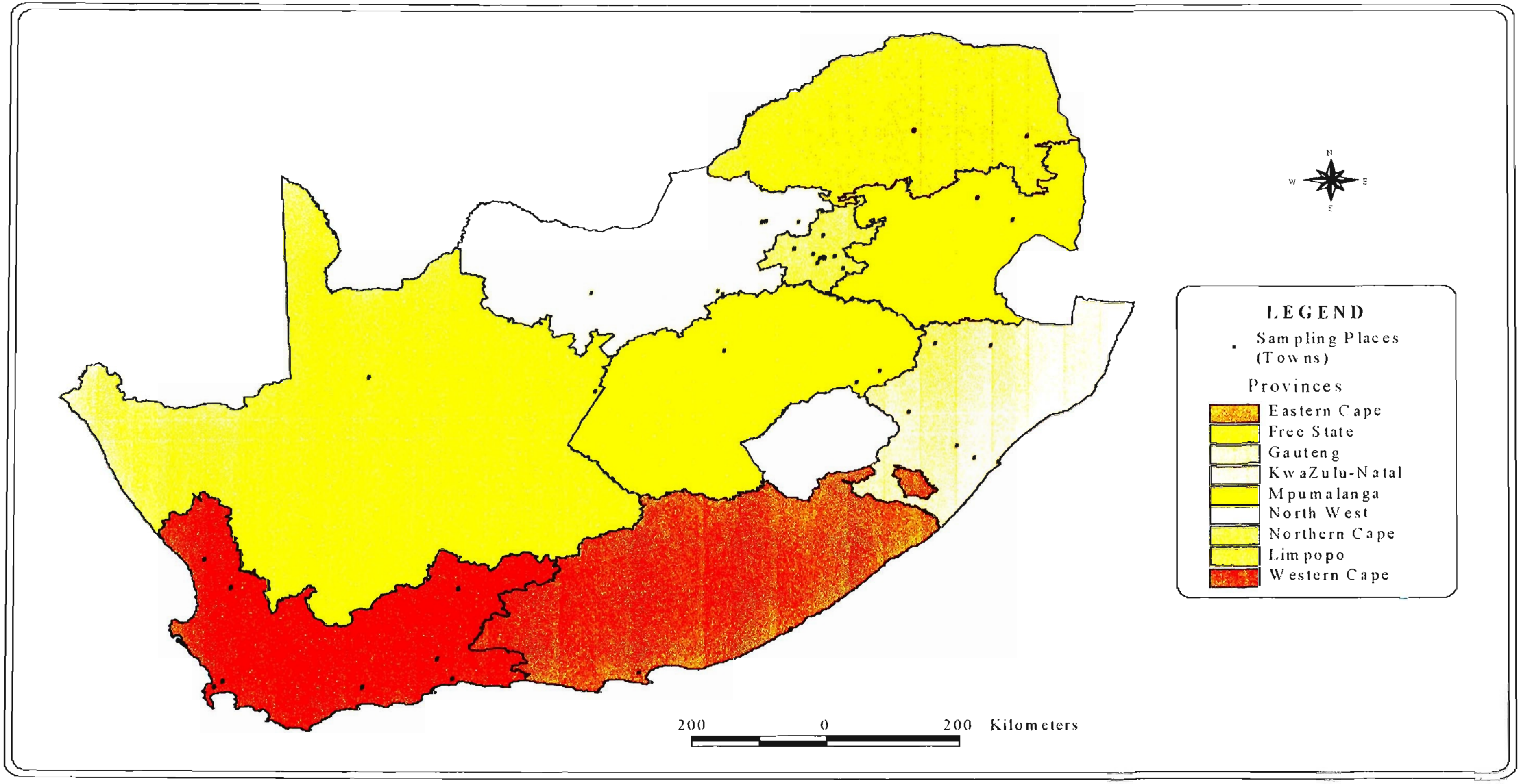
CHAPTER 3

3 EXPERIMENTAL

3.1 Sampling of Sewage Sludge

3.1.1 Introduction

There are nine provinces in South Africa and these are Gauteng (GP), Mpumalanga (MP), Free State (FSP), Western Cape (WCP), KwaZulu Natal (KZNP), Limpopo (LP), North West (NWP), Eastern Cape (ECP) and Northern Cape province (NCP). The geographical location of each of the provinces and towns, where sampling was carried out, is shown in Figure 3.1 and the distribution of sampled sewage works from different towns of the provinces is depicted in Figure 3.2. As far as the type of sludges produced from the sewage works of South Africa is concerned, they are categorized into nine in this research. These include aerobic digested, anaerobic digested, compost, digested sludge, heated sludge, pellets, petro sludge, waste activated sludge (WAS) and a mixture of waste activated sludge and digested (WAS/digested). The overall distribution of sludge types produced in South African sewage works is shown in Figure 3.3. The research consists of analyzing for 22 inorganic elements in sewage sludges, which were obtained from the nation-wide mapping of the main 69-wastewater treatment centres in South Africa. The details of the sewage works that were sampled, the names and sample number allocated to each one, the sludge type, the sampling points, the towns where they were sampled with their respective provinces are shown in Appendix A. The majority of sludges (71) were wet solids and seven of them were liquids sludges mostly from Gauteng province. Over 90 % of sewage works in Gauteng province receive over 10 % industrial effluents. This is believed to contribute significantly to the pollution of the sewage sludges from the area. However, according to the survey about the sources of sludges already obtained, almost above 50 % of the sewage works receive ≥ 10 % industrial effluent, the rest receive effluents > 90 % domestic effluents (Appendix B).



NB: This Map was taken from SA expolorer Municipality Demarcation Board (MDB). Spot locations with the aid of a software, ARCVIEW GIS 3.2.
The total number of towns in each province. ECP=2, FSP=3, GP=10, KZNP=6, MP=2, NWP=6, NCP=3, LP=3, & WCP=9.[Total=44]
The locations of some towns in GP are clustered in one spot because of proximity.

Figure 3.1 The different sampling places in the 9 provinces of South Africa.

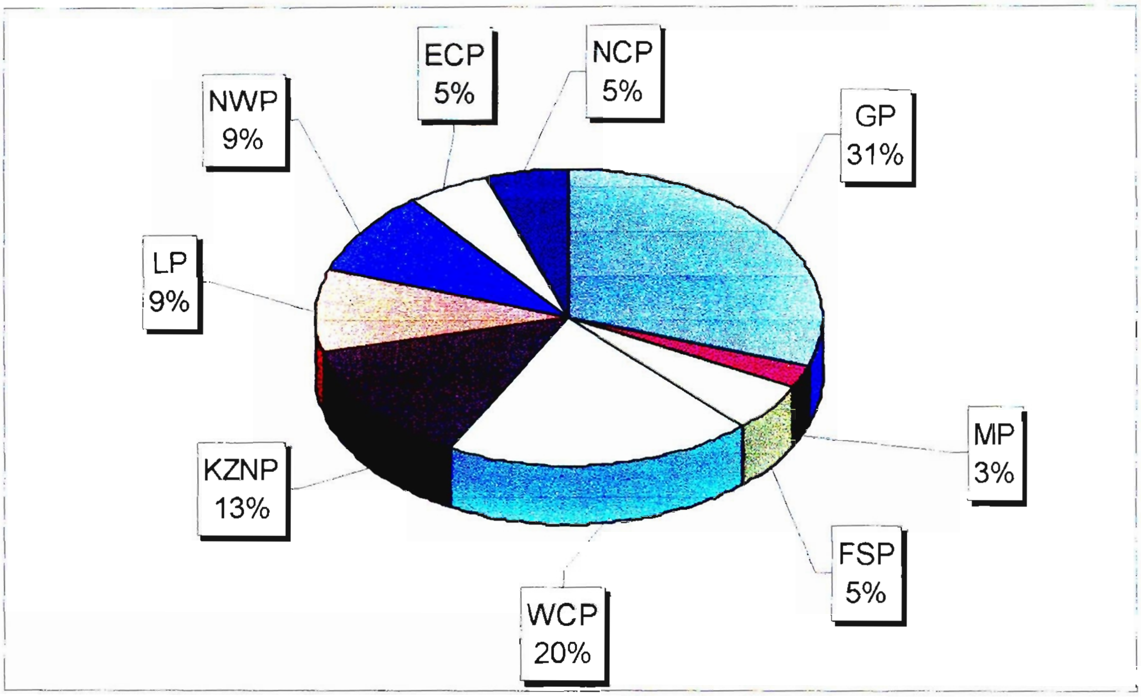


Figure 3.2 Provinces with respect to the number of sewage works.

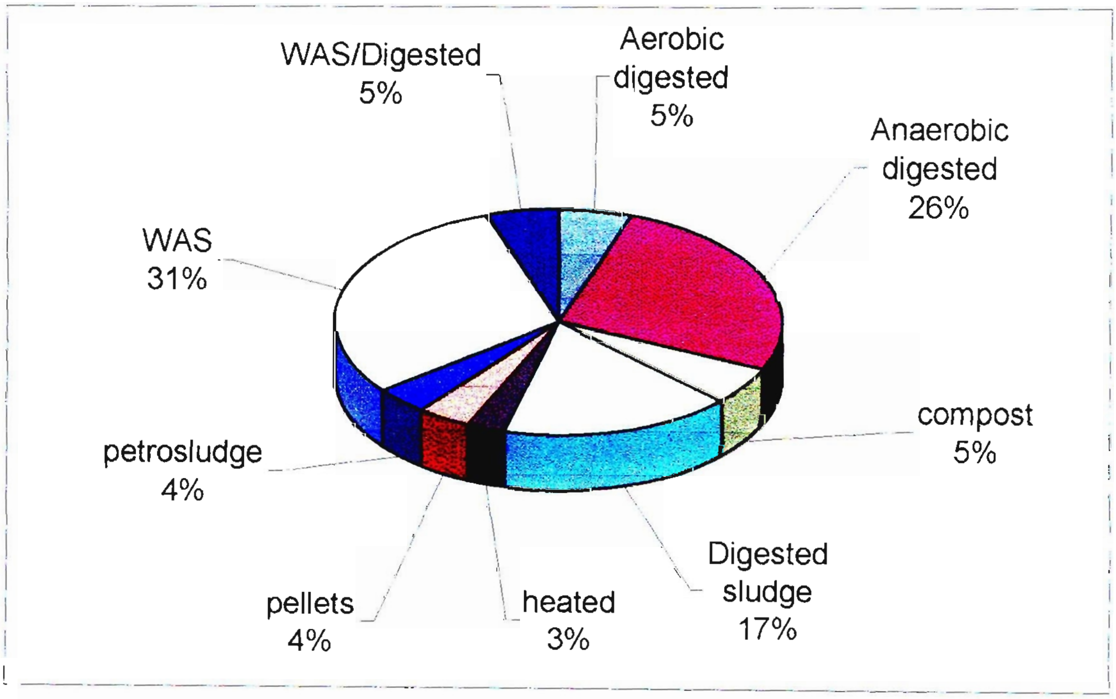


Figure 3.3 The types of sludges produced in the sewage works of South Africa.

3.1.2 Collection and Sampling of Sludges

The sludge samples were collected at different sampling points and the sludges were of different types from all provinces of South Africa. The sampling of the sludge was carried out over a period of three months from July to early November 2002 (Appendix B). However, most of them were sampled in August 2002 (Table 3.1).

Table 3.1 The sampling period of the sewage sludges.

Sampling Date	Number of Samples
July 2002	17
August 2002	38
October 2002	22
November 2002	1

Hence, the important objective in sampling is to extract a small portion from the source, which is representative of that source.[1] In each of the sewage works, a series of smaller samples were taken randomly in a single container from the respective sampling points of the sewage works and mixed to make the sample composition uniform. The samples were put in a glass container having a lid lined with Teflon (clearly marked and dated with labels). These were transported to the laboratory by keeping in an icebox at a temperature of approximately 4 °C and finally refrigerated until analysis. However, it should be noted that the same sample bottles were used for the same type of sample to prevent cross-contamination, besides the sample scoop and bottles were cleaned thoroughly before sampling commenced.

The chosen sampling points were 17 and these were belt press, bins, centrifuge, compost, digesters, drying beds, drying lagoons, fenced area, heaps, old stock bags, peddies, pit, plough fields, return flow, stockpile, waste activated sludge (WAS) and wet sludge. The sources of the sludges were of domestic and industrial origin.

3.2 Experimental Procedures

3.2.1 Sample Preparation and Determination of Moisture Content

The solid sludge was dried for two days in an oven set at 105 °C. The samples were then cooled in a dessicator having silica gel as a drying agent before re-weighing. The moisture content of the sample was then determined as a percentage of the dry mass. To have homogeneity, the sample was then crushed into a semi-fine powder and sieved using a set of stainless steel and brass coated Endecott sieves. The fraction range selected for the determination of metals and phosphorus (mineral ions) was less than 0.60 mm. After drying, four 1 g aliquots of each sludge were accurately weighed to four decimal places using the digital weighing balance, Mettler AJ100. So, each samples had 4 sub samples. In the case of liquid samples, four 100 ml samples were measured using a 100 ml pipette for analysis. However, the moisture content determination was carried out only for solid sludges.

3.2.2 pH Determination

The pH for solid sludge was determined as follows:[2] 5 g of sludge dried at 105 °C was transferred to 150 ml stoppered conical flask (alternatively graduated cylinder) and ultra pure deionized MilliQ water was added to make the total volume of 100 ml. The solution was shaken on a magnetic stirrer for approximately 15 minutes until the sample was thoroughly dispersed. Finally, the pH meter (Crison micropH 2000 microprocessor controlled pH meter) was set up and pH was measured according to the manufacturer's instructions. However, the pH of the liquid sludge was measured directly.

3.2.3 Determination of the Density of liquid sludge

The 10 ml volume of the liquid sample was measured in three replicates with 10 ml pipette. The temperature of the samples was measured with a thermometer and immediately the mass of 10 ml replicates of the samples were each determined. Finally, by taking the average mass of the replicates and the volume, the density of each sample was determined (Appendix C).

3.2.4 Digestion of Sewage Sludge

Although there is a possibility of analysis of solid samples without digestion using in some instrumental analytical methods, (e.g. X-ray Fluorescence), the results are of poor precision. Potential problems with solid sampling include incomplete atomization, the microgram masses frequently used may be unrepresentative of the bulk properties of the sample, high background continuum on a weak metal signal, standardization is difficult to achieve resulting in reduced accuracy, and reduced or poor precision.[3] So, digestion of solid samples like sewage sludge is the best alternative so that the sample will be taken up into solution, which is a convenient form for most sample introduction systems, like an ICP-nebulizer. Acid digestion of sewage or effluent samples involves the destruction of organic matter, and dissolution of all inorganic forms of the mineral ions (metals and phosphorus) upon the use of acid. Different types of acids can be used depending upon the properties of the mineral ions. In this project, nitric acid, hydrochloric acid and hydrogen peroxide were used for the digestion of both solid sludge and effluent (liquid sludge) samples. Sewage and effluent samples require careful attention in the selection of appropriate pretreatments, which involves the destruction of organic compounds and extraction of analytes of interest into aqueous medium. This process is of great importance in terms of minimizing the interferences during analysis. So, drying of the solid sludge followed by digestion of both solid and liquid samples is necessary. In general, liquid sludge samples by virtue of their lower solids contents are expected to require smaller volumes of acids and less rigorous pretreatments than solid sludge samples.[4] In this study, two EPA methods were used, namely EPA METHOD 3050B & EPA METHOD 3010A for solid sludge and effluent (liquid sludge) digestion respectively.[5] The digestion converts metals and their salts present in the sample into their nitrates. This is because all nitrate salts are readily soluble in water.[6] All the glassware and plastic ware used in the experiment were washed with a detergent and tap water followed by dilute nitric acid (0.1 M HNO_3) and finally rinsed with MilliQ (Modulab water purification systems, U.S filter corporation) water.

3.2.5 Acid Digestion of Solid Sludge

A 1 g sample of the previously dried and sieved solid sludge was used for acid digestion. The samples were transferred into four 100 ml digestion vessels after which 10 cm^3

1:1 HNO_3 (Fluka, 65% purity, 1:1 HNO_3 was prepared by taking equal volumes of both conc HNO_3 (65 %) and ultrapure water) was added and the slurry mixed. The sample was covered with a watch glass, and allowed to reflux at approximately 98 °C for 15 minutes without boiling in a steam bath. The four were then allowed to cool down to room temperature (~23 °C) before 5 ml of concentrated HNO_3 was added and the mixture allowed to reflux for another 30 minutes. Brown fumes were generated, an indication that oxidation of the sample was taking place. Addition of 5 ml of conc. HNO_3 was repeated every 30 minutes until no brown fumes were observed. This was an indication that the destruction of the organic matter was complete. Using a watch glass as already mentioned, the solution was allowed to reflux at 98 °C without boiling for two hours. The samples were then let to cool to room temperature (~23 °C) after which 2 ml of ultra pure deionized MilliQ water and 3 ml of H_2O_2 (Merck, 30 % purity) were added. After covering with the watch glass, these were allowed to warm to 98 °C or until the effervescence had subsided. At this stage, the reaction was carefully observed to ensure that losses of solution did not occur due to excessively vigorous effervescence. The samples were cooled to room temperature (~23 °C) before 1 ml aliquots of H_2O_2 (Merck, 30 % purity) were added continually with warming until the effervescence was minimal or until the general sample appearance was unchanged. In general, a maximum of 10 ml was added depending on the sample, as the amount of the effervescence produced differed from one sludge to another. This mixture was continuously heated until the final volume had reduced to approximately 5 ml, after which 10 ml of conc. HCl was added and the solution allowed to reflux for a further 15 minutes. Finally, the sample was cooled to room temperature (~23 °C) before filtering it through Whatman No.41 filter paper into a 100 ml volumetric flask. Using ultra pure deionized MilliQ water, the flask was filled to the mark and mixed thoroughly, and the sample was finally ready for analysis by ICP-OES. A flow chart describing the process is shown in Figure 3.4.

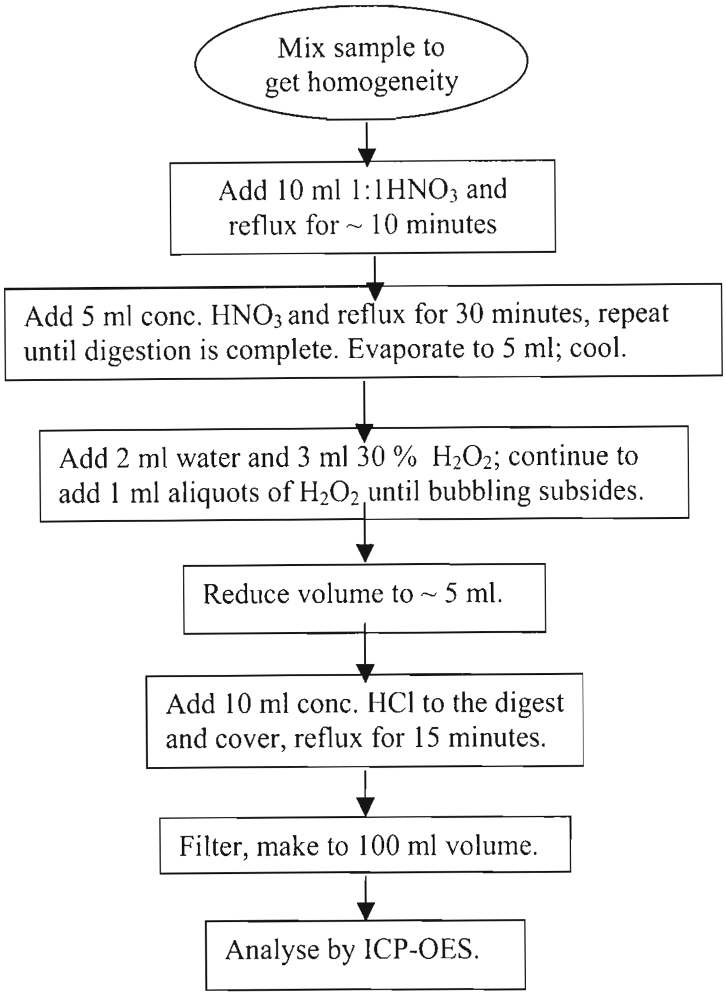


Figure 3.4 Digestion process for solid sludge (EPA Method 3050B).

3.2.6 Acid Digestion of Effluent (Liquid Sludge)

A well-mixed 100 ml of the sample measured using a 100 ml pipette was transferred into a 150 ml beaker followed by addition of 3 ml of conc. HNO_3. The beaker was placed on a hot plate and allowed to evaporate to a low volume of 5 ml. Care was taken to make sure that the sample did not boil and that no portion of the bottom of the beaker was allowed to go dry. The sample was allowed to cool to room temperature (~23 ^{o}C) before adding another 3 ml of conc. HNO_3. The sample was covered with a watch glass and for gentle refluxing the sample was heated by increasing the temperature of the hot plate. Heating and addition of acid continued as necessary until the digestion was complete which was generally indicated when the digestate was light in color or did not change in appearance with continued refluxing. After complete digestion, the sample was allowed to evaporate to a low volume of 3 ml making sure that any portion of the bottom of the beaker did not go to dryness. After cooling the sample, 10 ml of 1:1 HCl (1:1 HCl was prepared by taking equal volumes of HCl and ultrapure water) was added and covered with a watch glass to reflux for additional 15 minutes to dissolve any precipitate or residue resulting from evaporation. The sample was then filtered using a Whatman No. 41 filter paper and the final volume made up to 100 ml with ultra pure deionized MilliQ water in a volumetric flask. This process removed the silicates and other insoluble material that could clog the nebulizer during analysis. The sample was therefore ready for analysis by ICP-OES. The above procedure is illustrated in a chart form in Figure 3.5.

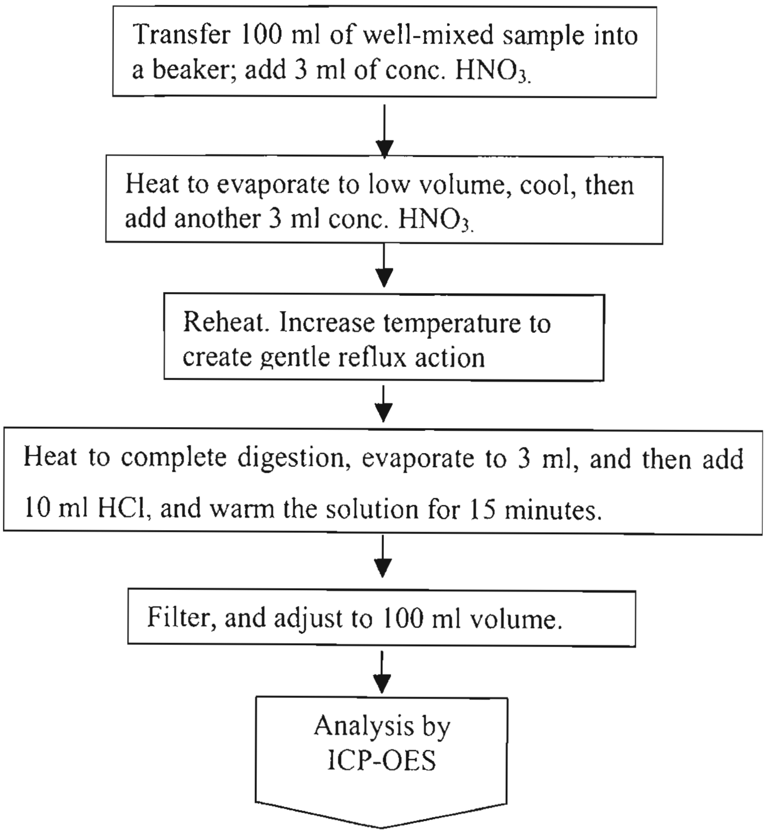


Figure 3.5 Digestion process for Liquid Sludge (EPA Method 3010A).

3.3 Analysis of Mineral Ions

3.3.1 Introduction

Atomic emission spectroscopy (AES) was the first to re-enter the field of analytical chemistry, initially in arc and spark spectrography and then through the work of Lunegardh, who in 1928 demonstrated AES in an air – acetylene flame using a pneumatic nebulizer.[7] Historically, the extent of the application of atomic emission spectroscopy has depended very largely on the properties of the excitation sources available. Attempts to improve the performance of the traditional arc and spark sources led to the development of various plasmas.[8] (A plasma is an electrical conducting gaseous mixture containing a significant concentration of cations and electrons.[9]) This effort laid a foundation to the discovery of ICP-OES, which took place in the early 1960s. Its application to analysis was pioneered independently by Greenfield, and his colleagues working at Albright and Wilson, Oldbury, England in 1964 and by Fassel and co-workers at Ames laboratory, Iowa State University in the United States of America in 1965.[8] This instrument became commercially available in the mid 1970's and offers several advantages over flame sources for emission spectroscopy.[10]

The ICP-OES was chosen for the analysis of cations and phosphorus in this particular research due to the efficiency with which it is able to analyse a range of species.[11] This is a significant advantage over other spectroscopic techniques such as Flame Atomic Absorption Spectrophotometry (FAAS) and Graphite Furnace Atomic Absorption Spectrophotometry (GFAAS). The disadvantages of using the latter two instruments include the time needed for multi-element analysis owing to their single element capabilities.[12] Furthermore, ICP-OES enjoys excellent freedom from interferences, with an apparent absence of chemical interferences. There is controversy about the extent of ionization interferences, and equivalent problems with spectral interferences to those encountered with those emission techniques (i.e. good resolution is required).[7] This is due to the high temperature, which is higher than the maximum temperature of flames or furnaces (3300K).[13] Another advantage over absorption spectroscopic methods is that the more energetic plasma sources permit the determination of low concentrations of elements that tend to form refractory compounds (that is, compounds, such as the oxides of boron, phosphorus, tungsten, uranium, zirconium, and niobium that are highly resistant to thermal decomposition).[10] Boron and phosphorus were among the elements of our interest in this research. The other advantage is that ICP-OES can cope with a much larger range of concentrations than can absorption techniques. This is important when one considers that the concentrations of the species in sewage sludge vary quite significantly requiring a large calibration range. An additional drawback associated with FAAS is its poor precision. As for GFAAS, another disadvantage is its small dynamic concentration range. In general, the use of ICP-OES is an attractive alternative to traditional atomic absorption and is considered a good technique for wastewater analysis.[4]

3.3.2 The Principles of the ICP-OES

The ICP-OES comprises of many components such as peristaltic pump, nebulizer, torch, RF generator, monochromator, photomultiplier, detector and computer. The analysis of samples involves nebulization, vaporization, atomization or ionization, detection and data processing. The components are shown in the schematic diagram in Figure 3.6. These instruments are used for the determination of mineral species that will emit characteristic radiation on excitation. This includes all metals and some non-metals such as phosphorus.

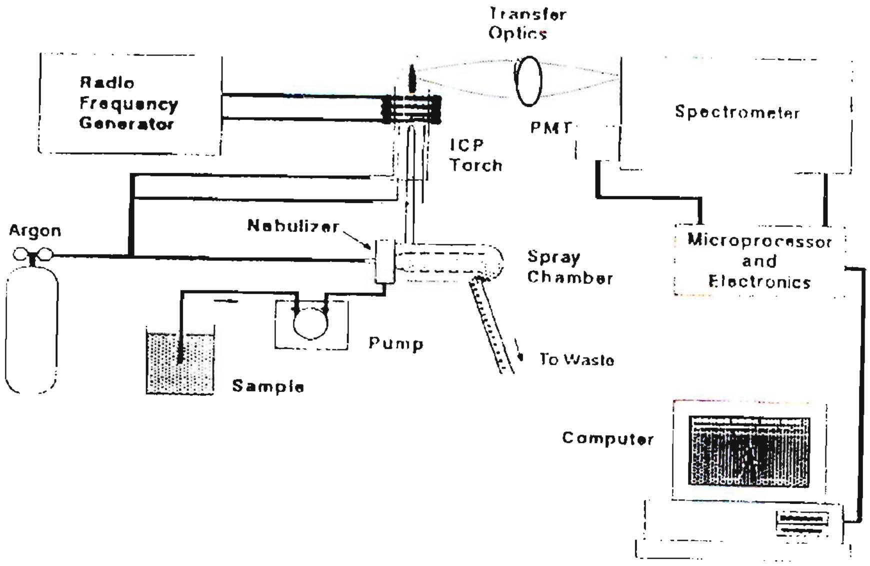


Figure 3.6 Schematic Diagram of ICP-OES.[14]

The sample solution is initially pumped by a peristaltic pump to a nebulizer, which converts it into an aerosol.[15] There are many different types of nebulizers, the cross-flow, concentric (pneumatic) and ultra-sonic nebulizers.[16] In this research, the latter two were used. The difference lies in the analyte transport efficiency of the nebuliser, with the ultrasonic being far more efficient than the concentric (pneumatic) nebuliser, resulting in much greater intensities for respective concentrations on the ultrasonic nebuliser.[9] Once the sample is converted into a mist (fine droplets), the spray chamber filters out the larger droplets to waste and allows the finest fraction to be transported to the central channel of the plasma by an inert carrier gas, usually argon. The plasma, which is a conducting gaseous mixture of electrons and cations, is sparked by a Tesla coil. The plasma is sustained by means of ohmic resistance resulting from the interaction of cations and electrons with the fluctuating magnetic field supplied to the coil from the radio frequency (RF) generator. Harbouring the plasma is a quartz torch, which is cooled also by argon, as it yields temperatures between 6000 K and 10000 K.[17] At this high temperature of plasma, the aerosol is quickly vaporized which means analyte elements are liberated as free atoms or ions in the gaseous state. Further collisional excitation within the plasma leads atoms and ions to emit photons; the amount of the photons emitted is directly proportional to the concentration of the originating element in the sample. The emitted photons are monitored by spectrometer. The high temperature leads to a multiplicity of intense emission lines in the spectrum.[14] Generally, atomic or ionic spectra emitted by the analyte have two dimensions.[17] Firstly, the wavelength at which the emission is made is used to determine the elemental composition, and secondly, the intensity of the emitted radiation is proportional to concentration. The wavelength selection device, the monochromator, monitors the wavelength. Subsequently, the radiation exiting the monochromator is converted and enhanced to an electrical signal by a photomultiplier tube detector (PMT). The final signal is then stored in the computer upon amplifying and processing by the detector electronics. In the current research, ICP-OES (Varian liberty AX150) has been used and can be seen in Figure 3.7 below.

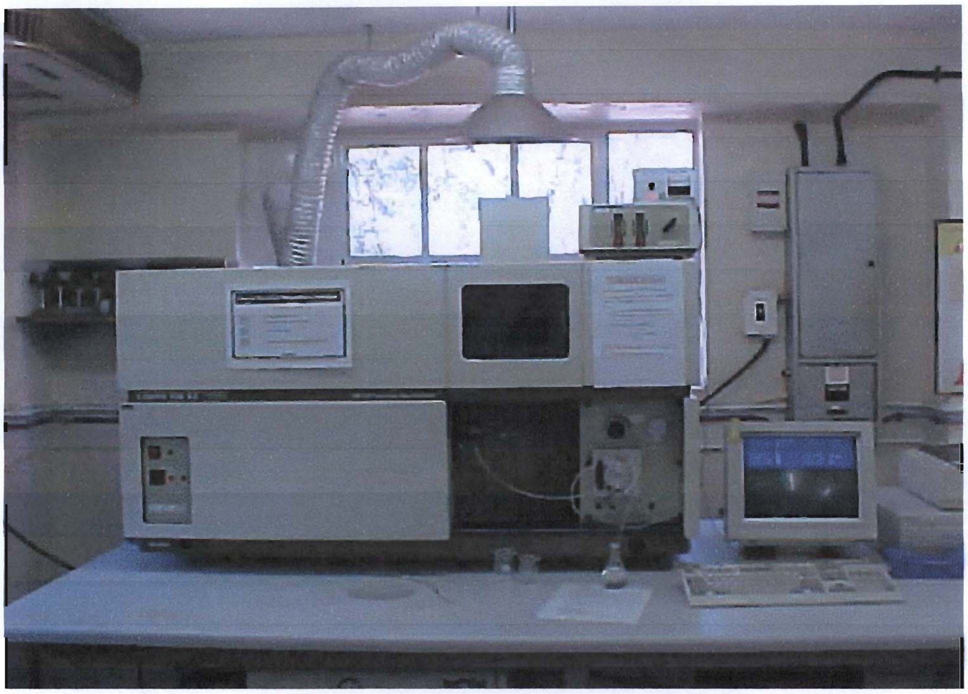


Figure 3.7 ICP-OES (Varian Liberty AX150) used in the current research.

The overall process from the sample treatment to the final data processing is shown in the schematic diagram in Figure 3.8.

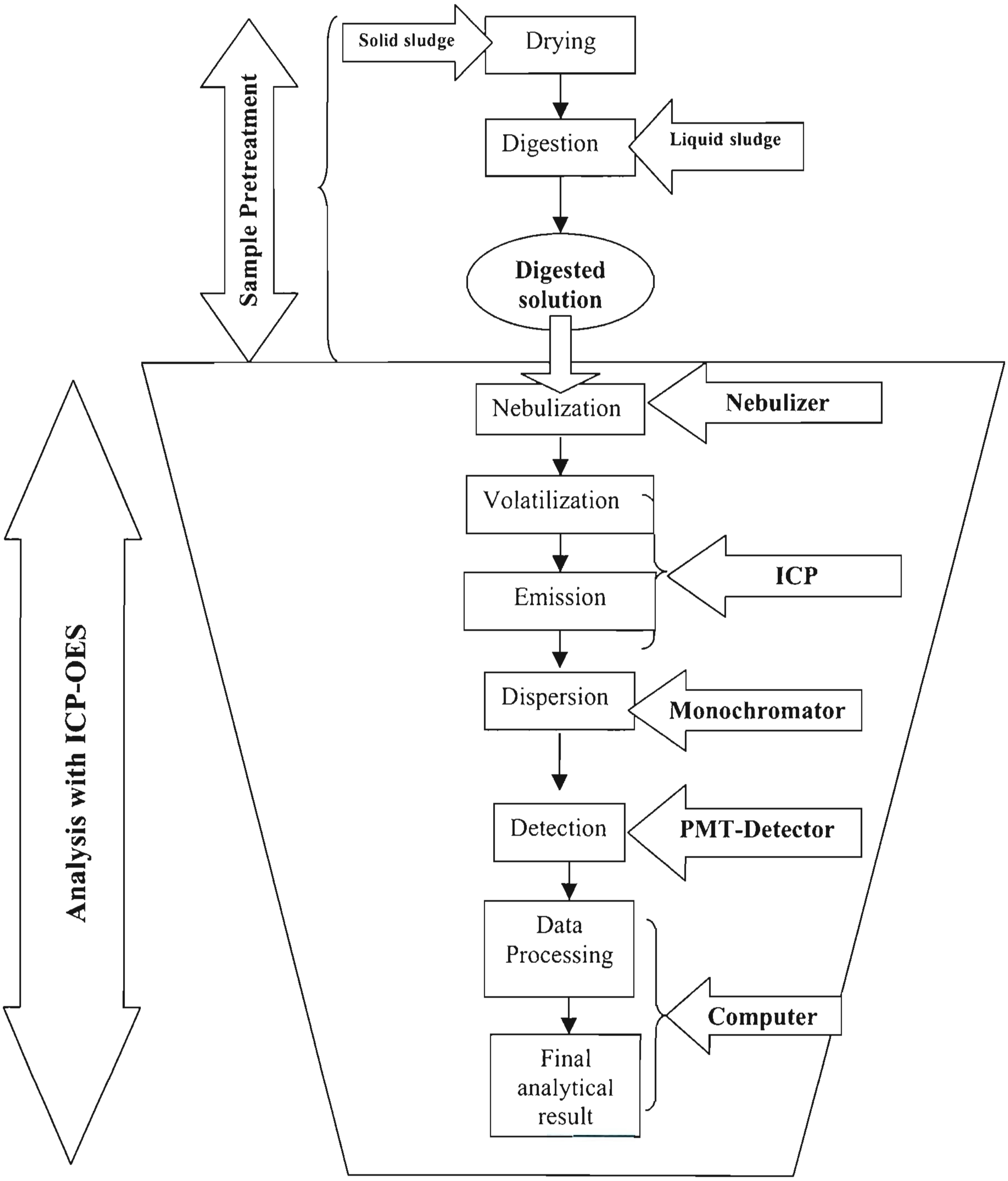


Figure 3.8 Schematic layout of the overall analysis of sewage sludge.

3.3.3 Optimization of ICP-OES and Conditions in the Current Work

One of the crucial aspects of effective analysis of samples is the prior optimization of the instrument, in this case ICP-OES. The optimization of ICP-OES involves the adjustment of the operating conditions, which results in the desired results of the signal-to- background ratio (SBR) and the signal- to-noise- ratio (SNR) determining the final analysis.

The operating parameters to be considered include RF power, nebulizer pressure, photomultiplier voltage, plasma argon flow, auxiliary argon flow, and pump speed and nebulizer pressure. Optimization of these parameters gives rise to highest net signal-to-background ratio (SBR), highest signal-to-noise ratio (SNR) which means lower interferants and minimum matrix effects due to easily ionizable elements (EIEs) like sodium because high concentration of EIEs can suppress or enhance emission signals, depending on the analyte species. One way to reduce the EIEs effect is to dilute the sample solution to the point that the EIE effect is not measurable or sometimes, higher RF power or mathematical correction may be used to compensate for EIE interference.[13] In this project, the EIE effect was solved by diluting of the samples especially the liquid sludges. Therefore, operation under conditions that give the least interference is preferable, provided that other desirable criteria are met, such as high signal to background ratios, low background levels, and low background fluctuations.[8]

The optimum operational conditions of ICP-OES along with the specifications of the instrument as used in the current work are reflected in Table 3.2. In accordance with the settings for optimization, the instrument shows the peaks of each analytes under the Rapid Scan in form of plot of intensity versus wavelength. These analytes are phosphorus, aluminium, calcium, iron, sodium, zinc, potassium, magnesium, barium, silicon, manganese, cobalt, beryllium, lead, boron, strontium, copper, chromium, selenium, molybdenum, cadmium and nickel. They are shown in Table 3.3 with their respective lines (i.e. wavelengths) that were chosen according to their freedom from spectral interference and range of calibration curve linearity. To have the correct peak intensity of the analytes, the peak search window was made narrow. The window is the wavelength range scanned for a peak of a particular analyte. The peak depicts the presence of an analyte or any interferants. However, the presence of the suspected interferant can be monitored at different wavelengths or spiking with the appropriate standards.

Table 3.2 Operating Conditions and Specifications of ICP-OES.

Instrument	Liberty 150 AX Turbo (Varian)
Torch mounting	Axial, Low flow
Nebulizer	
1.	Ultrasonic (Cetac U-5000AT$^+$)
2.	Pneumatic (Concentric)
RF power supply	40.68 MHz
Operating power	1.00 kW
Nebulizer pressure	
1.Ultrasonic (Cetac U-5000AT$^+$)	200 kPA
2. Pneumatic (concentric)	240 kPA
Photo multiplier voltage	800 V
Plasma argon flow	15.0 L/min
Auxiliary argon flow	1.50 L/min
Pump speed	
1.Ultrasonic (Cetac U-5000AT$^+$)	12 rpm
2. Pneumatic (concentric)	15 rpm

Table 3.3 Mineral ions and phosphorus detected in sewage sludge using ICP-OES rapid scan including their respective wavelengths and peak search windows.

Element	Wavelength (nm)	Peak search window (nm)
Aluminium(Al)	396.152	0.08
Barium(Ba)	455.403	0.08
Beryllium(Be)	313.042	0.04
Boron(B)	208.959	0.027
Cadmium(Co)	214.438	0.027
Calcium(Ca)	396.366	0.08
Chromium(Cr)	267.716	0.04
Cobalt(Co)	228.616	0.027
Copper(Cu)	324.754	0.04
Iron(Fe)	259.940	0.04
Lead(Pb)	220.353	0.027
Magnesium(Mg)	279.553	0.04
Manganese(Mn)	257.610	0.04
Molybdenum(Mo)	202.030	0.08
Nickel (Ni)	231.604	0.04
Phosphorus (P)	213.618	0.027
Potassium (K)	766.49	0.08
Selenium (Se)	196.026	0.08
Silicon (Si)	251.611	0.04
Sodium (Na)	589.592	0.08
Strontium (Sr)	407.771	0.08
Zinc (Zn)	213.856	0.027

Compositionally, all samples are different and hence there must be the probability of contamination from other samples as long as the same instrument is used. So, the safety measures for ICP-OES are important as they play a great role in minimizing the contamination. As it is recommended in the instruction manual of ICP-OES, [18] the torch was cleaned at least once a week depending on the number of samples analysed and their composition. The torch was submerged in aqua-regia overnight, and then rinsed with ultra pure deionized MilliQ water and oven dried at 105 °C. When it was extremely soiled, 2 % HF was used to soak only the soiled section for a few minutes and then rinsed as before. The optical window was also cleaned at the same time using lint free tissue moistened with ethanol. The base plate was removed and polished with Brasso (a metal polish) and rinsed thoroughly with ultra pure deionized MilliQ water before being placed back into its position. The peristaltic pump tubing was replaced when necessary so as to ensure that the performance of the sample introduction system was not affected due to the aging of the tube.

3.3.4 Calibration Curves for Cations and Phosphorus

The ICP-OES solutions for all analytes were obtained from Fluka except for phosphorus. The concentration of each analyte was 1000 ppm with guaranteed minimum levels of impurity. The micropipette used in the preparation of stock solutions was calibrated by weighing ten 1 ml aliquots of water whose temperature had been measured using a thermometer. The density of water at the specific temperature was determined by interpolation of data provided by Robinson and Stokes.[19]

The stock solution of phosphorus was prepared by dissolving 4.264 g of dibasic ammonium phosphate (BDH) in ultra pure deionised MilliQ water and diluting to exactly one litre to give a stock solution of 1000 ppm as P. The phosphate compound was dried in the oven at 105 °C before use. Using the 1000 ppm stock solutions, weaker stock solutions of each analyte was prepared with the exception of phosphorus (P) and aluminum (Al). A 100 ppm solution for calcium, iron, sodium, zinc and potassium was prepared by diluting 10 ml of the 1000 ppm stock solution to exactly 100 ml in a volumetric flask, and 10 ppm of magnesium, barium, silicon, manganese, cobalt, beryllium, lead, boron, strontium, copper, chromium, selenium, molybdenum, cadmium and nickel was prepared by diluting 1 ml of the 1000 ppm stock solution to exactly 100 ml, in both cases using a 0.1 M HNO_3 (Fluka, 65%) solution. The reason for using acid solution was to preserve the solution and to minimize the absorption of the analytes onto the surface of the container at trace level. Plastic containers were used in all of the standard preparations.

To avoid the possibility of precipitation and for convenience, the analytes were divided into two groups. Group-1 included Ca, Al, Ba, Si, Mn, Fe, Mg, Na, Be, P and Co while group-2 was made up of Se, Mo, Sr, Ni, Cr, B, Zn, Co, Cu, Pb and K. A mixed stock solution for each group was prepared by taking known volumes of each analyte into a 500 ml volumetric flask and filling it to the mark with a blank solution (0.1 M HNO_3). For group-1 analytes, 50 ml of P, Ca, Fe, Ba, Si, Mn, Co, and Be, plus 25 ml of Al, Na, and Mg were mixed and made to the volume of 500 ml by adding 25 ml of the blank. In case of group-2, 50 ml of Pb, B, Sr, Cu, Cr, Se, Mo, Co, and Ni, including 25 ml of Zn and K were mixed in a 500 ml volumetric flask.

Using the mixed stock solution, standard concentrations (ppm) were prepared by dilution . Taking known volumes (12.5, 25, 50, 75 and 100 ml) into a 100 ml volumetric flask and diluting with 0.1 ml HNO_3, five standards were made for each group. The analytes and their respective standard concentrations used to calibrate the ICP-OES for both groups 1 and 2 are shown in Table 3.4 and Table 3.5 respectively.

Table 3.4 Group-1 analytes and standard solutions (in ppm) used to calibrate The ICP–OES.

Analyte	Standard 1	Standard 2	Standard 3	Standard 4	Standard 5
Al	6.25	12.5	25	37.5	50
Ba	0.125	0.25	0.5	0.75	1
Be	0.125	0.25	0.5	0.75	1
Ca	1.25	2.5	5	7.5	10
Co	0.125	0.25	0.5	0.75	1
Fe	1.25	2.5	5	7.5	10
Mg	0.0625	0.125	0.25	0.375	1
Mn	0.125	0.25	0.5	0.75	1
P	12.5	25	50	75	100
Si	0.125	0.25	0.5	0.75	1
Na	0.625	1.25	2.5	3.75	5

Table 3.5 Group-2 analytes and standard solutions (in ppm) used to calibrate the ICP–OES.

Analyte	Standard 1	Standard 2	Standard 3	Standard 4	Standard 5
B	0.125	0.25	0.5	0.75	1
Co	0.125	0.25	0.5	0.75	1
Cr	0.125	0.25	0.5	0.75	1
Cu	0.125	0.25	0.5	0.75	1
Pb	0.125	0.25	0.5	0.75	1
Mo	0.125	0.25	0.5	0.75	1
Ni	0.125	0.25	0.5	0.75	1
K	0.625	1.25	2.5	3.75	5
Se	0.125	0.25	0.5	0.75	1
Sr	0.125	0.25	0.5	0.75	1
Zn	0.625	1.25	2.5	3.75	5

Referring to the conditions in Table 3.2, the standard solutions were run on the ICP-OES. The procedure included a blank correction using 0.1 M HNO_3 solution as the blank. The instrument was programmed to do a " dynamic" background correction and construct its own calibration curves rejecting any calibration with a correlation coefficient (R) of less than 0.995. The instrument was calibrated each time before use since extended use of the instrument changed slightly the working conditions in terms of the cleanliness of the sample introduction system, torch, and optical window. The calibration equations in the form of $y = mx + c$ using both nebulizers are shown in Table 3.6, where y = peak intensity, x = concentration (ppm), m = slope and c = intercept. The correlation coefficient for each line is given by the R term. Calibration graphs for all the elements analysed are shown in Figures 3.9 – 3.12, as constructed with the help of Origin 5.0 a data analysis and technical graphics software.

To make sure that all the data points were within the calibration curve, it was found necessary to dilute some of the samples especially those that had high concentrations of sodium. These were diluted using the 0.1 M HNO_3 solution.

Table 3.6 Calibration equations and their respective correlation coefficient **(R)** for pneumatic and ultrasonic nebulizers in the form of linear equation: **$Y = mX + c$.**

	Nebulizers					
	Pneumatic nebulizer			Ultrasonic nebulizer		
Elements	Coefficients			Coefficients		
	m	c	R	m	c	R
Al	1.67×10^3	-3.75×10^2	0.9999	-	-	-
B	-	-	-	8.96×10^4	-3.20×10^2	0.99992
Ba	7.96×10^6	5.15×10^3	0.99999	-	-	-
Be	3.38×10^5	-5.51×10^2	0.99998	-	-	-
Ca	1.88×10^7	4.99×10^6	0.99855	-	-	-
Cd	-	-	-	6.11×10^6	4.05×10^3	0.99999
Co	1.41×10^5	-4.10×10^2	0.99996	-	-	-
Cr	-	-	-	3.51×10^5	-1.63×10^3	0.9999
Cu	-	-	-	1.82×10^5	-2.71×10^2	0.99997
Fe	4.41×10^4	2.80×10^3	0.99989	-	-	-
K	-	-	-	5.31×10^5	4.17×10^4	0.99873
Mg	7.44×10^5	2.13×10^3	0.99994	-	-	-
Mn	2.21×10^5	7.66×10^1	0.99999	-	-	-
Mo	-	-	-	1.92×10^6	-5.84×10^3	0.99993
Na	6.28×10^5	-2.85×10^4	0.99955	-	-	-
Ni	-	-	-	1.13×10^5	-1.67×10^2	0.99998
P	5.64×10^1	3.67×10^1	0.99995	-	-	-
Pb	-	-	-	4.94×10^5	-1.55×10^3	0.99996
Se	-	-	-	1.32×10^5	-1.11×10^3	0.99985
Si	1.36×10^4	1.39×10^2	0.99943	-	-	-
Sr	-	-	-	1.51×10^8	4.47×10^6	0.99832
Zn	-	-	-	6.74×10^6	1.19×10^6	0.99647

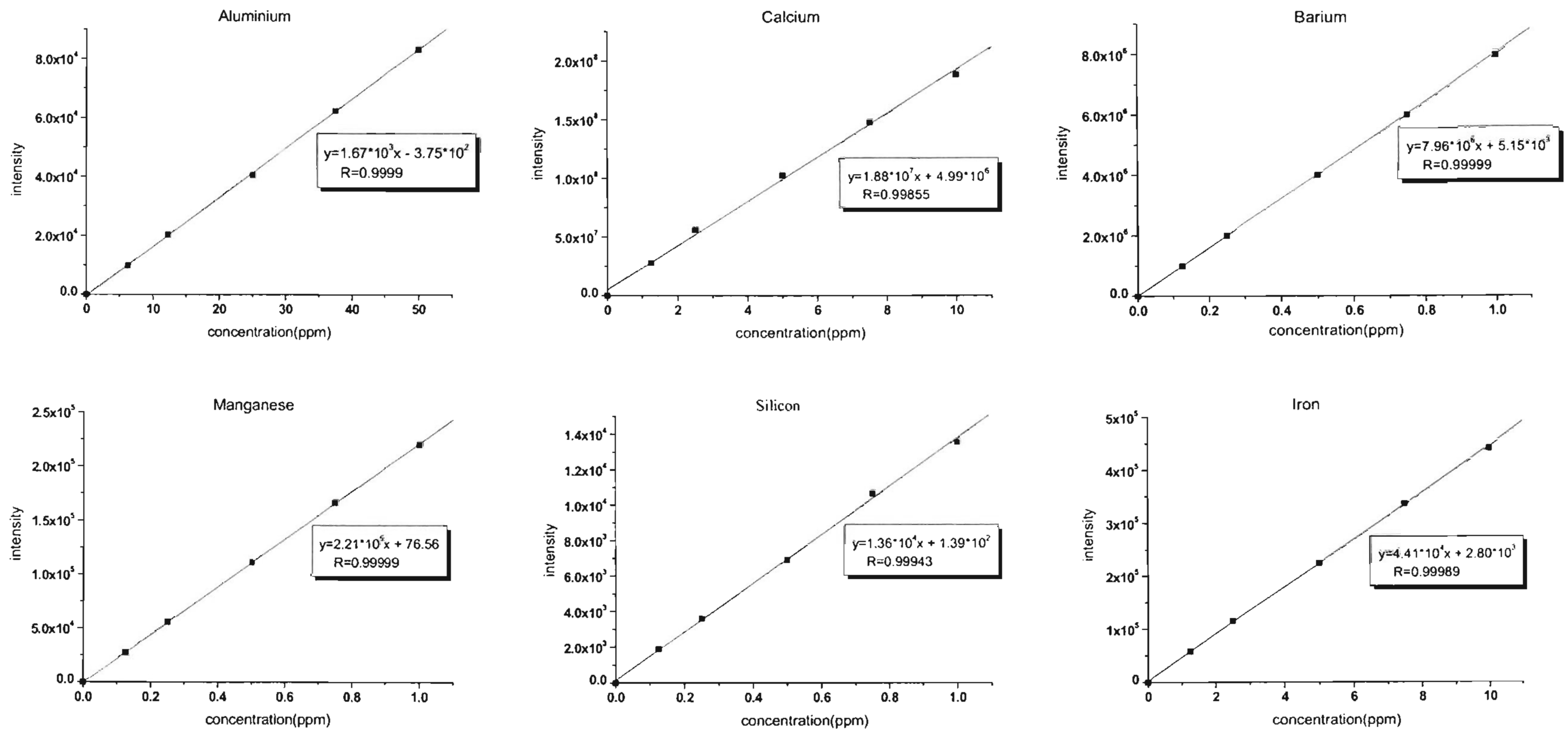


Figure 3.9 Calibration graphs for aluminum, calcium, barium, manganese, silicon, and iron.

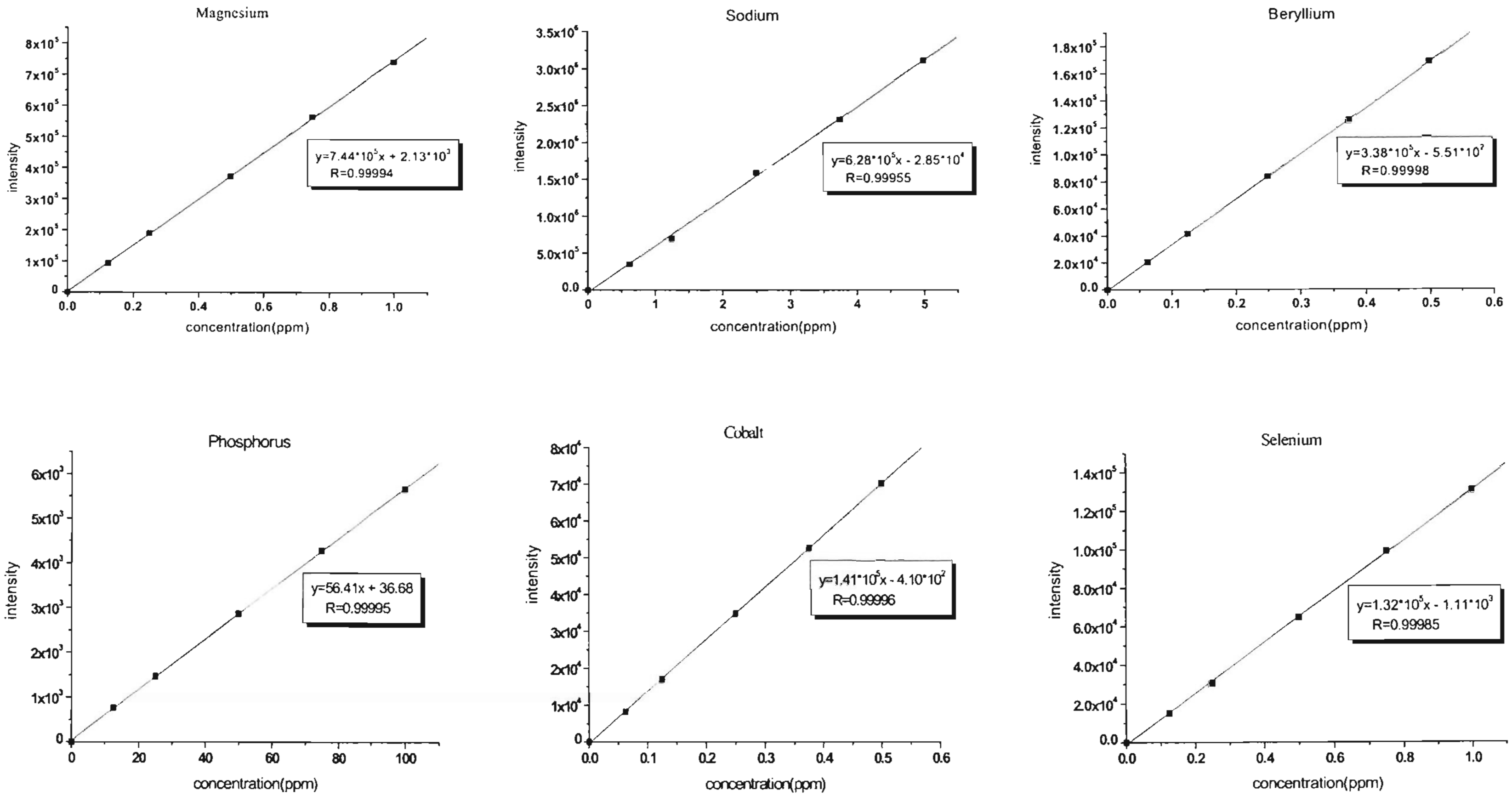


Figure 3.10 Calibration graphs for magnesium, sodium, beryllium, phosphorus, cobalt and selenium.

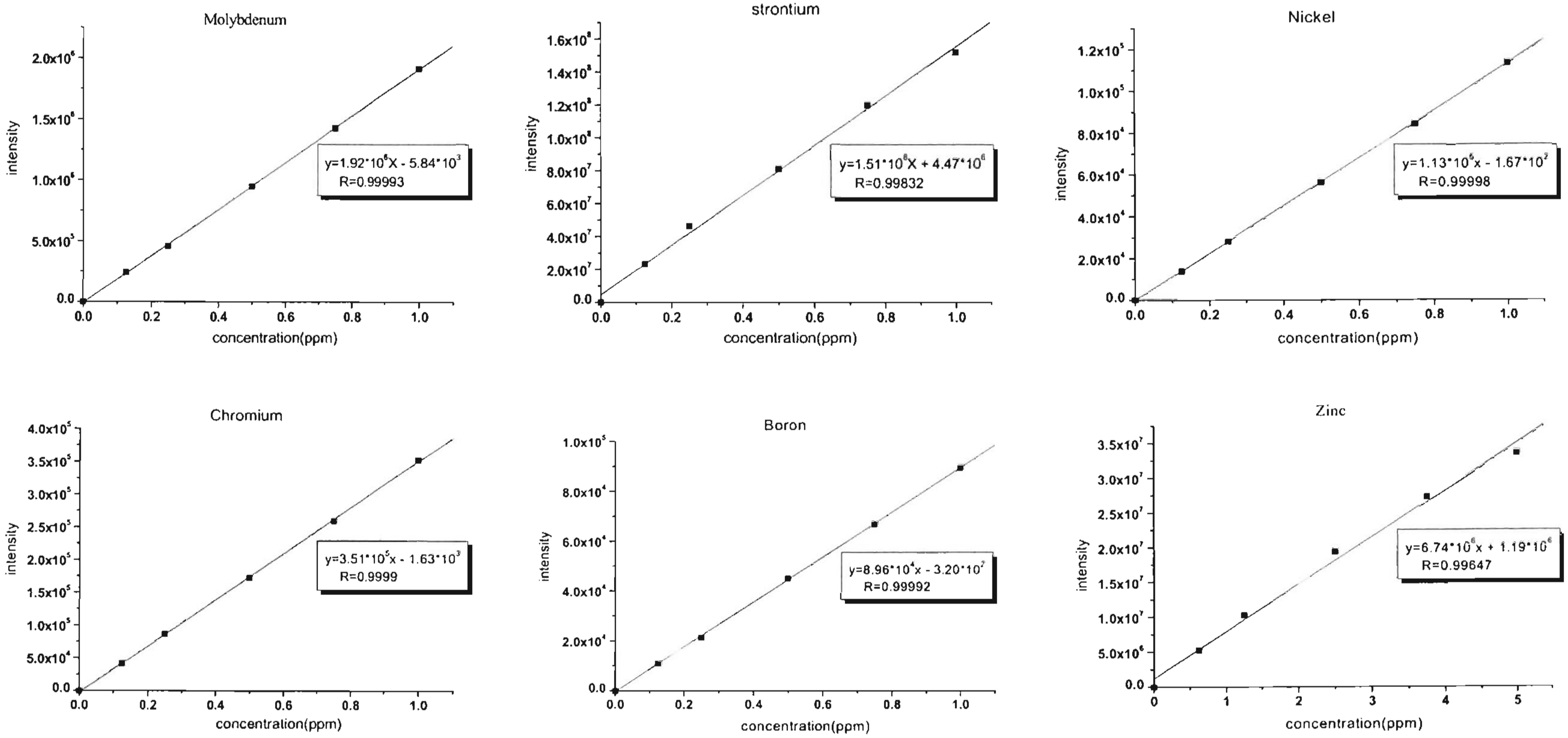


Figure 3.11 Calibration graphs for molybdenum, strontium, nickel, chromium, boron and zinc.

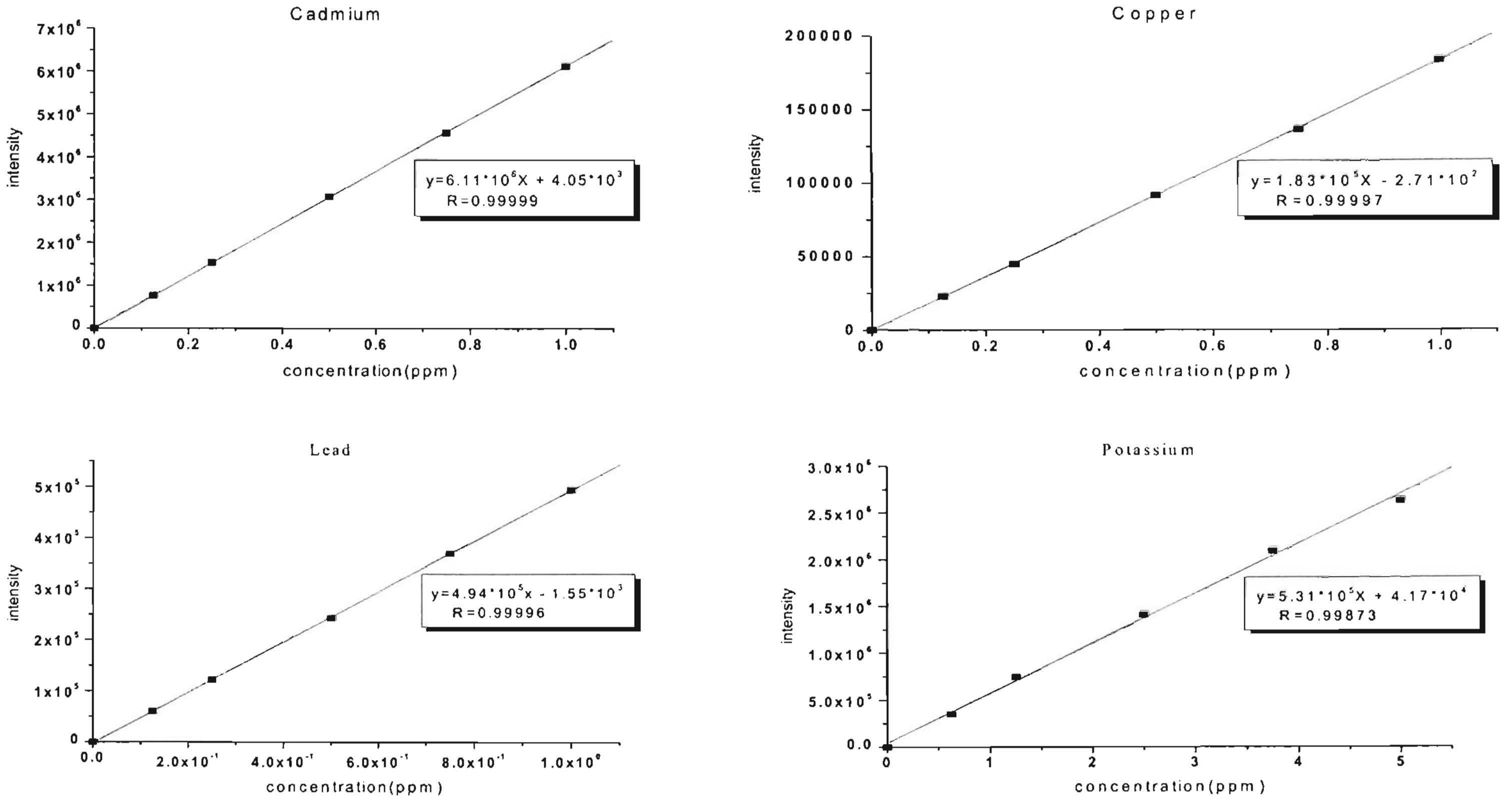


Figure 3.12 Calibration graphs for cadmium, copper, lead and potassium

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CHAPTER 4

RESULTS AND DISCUSSION

CHAPTER 4

4. RESULTS AND DISCUSSION

4.1 Moisture Content and pH of Sewage Sludge

4.1.1 Moisture Content

The moisture content of the solid sludge was determined following the procedure in section 3.2.1. The moisture content of the sludge from each of the individual sewage works was calculated (Appendix D) and the results are shown in Appendix E. The results summarized in terms of the sampling points are tabulated in Table 4.1. The standard deviation included with the data represents the variation of the mean.

Table 4.1 Moisture content (%) with respect to the sampling points.

	Mean (±SD)	No of sewage works
Belt press	82.9±3.7	6
Bins	7.8±0.1	2
Centrifuge	73.3±17.7	3
Compost	32.3±11.4	6
Digesters	16.5±8.0	2
Drying beds	39.8±27.2	33
Peddies	33.7±20.7	3
Pit	45.3±59.4	2
Return flow	43.2±39.0	3
Stockpile	16.4±12.9	3
Wet sludge	44.3±34.3	3
*Others**		
Drying lagoons	69.8	1
Fenced area	48.7	1
Heaps	9.7	1
Old stock bags	6.3	1
Plough fields	19.9	1

As shown in Table 4.1, there exists a significant variation in the moisture contents. This can be explained in terms of the sampling points and time. The sludge from belt press, centrifuge, pit, return flow and wet sludge were samples collected from the production line. The other samples were not fresh samples i.e. their time of production can not be estimated, most of these had been exposed to the sun where evaporation and possibly leaching to the ground had taken place. The fresh samples give an indication as to how much water is impeded in the sludge just after its production with the results showing that water makes up 40 - 90 % of the fresh wet sludge. An overall look at the moisture content of the solid sewage sludges sampled reveals that the minimum moisture content was 2.70 % while the maximum was 88.50 % with a mean of 41.29 % as detailed in Table 4.2.

Table 4.2 Overall moisture content values of the sewage sludges.

Statistical values	Moisture content (%)
Mean	41.29
Min	2.70
Median	34.10
Max	88.50

Although there are no specific regulations on the amount of moisture content for sludges, the evidence is that some of the sludge samples had high moisture content. In addition, if the sludge is to be marketed as cheap fertilizer, moisture content will have to be regulated to safeguard the farmers who may end up paying for moisture content up to 40 %.

4.1.2 pH of Sludge Solution

The pH of sewage sludges was determined as outlined in section 3.2.2. The results of the individual sewage plants are given in Appendix D. A summary of the pH values grouped in terms of sludge type is shown in Table 4.3 with their corresponding standard deviations.

Table 4.3 Mean pH value of sewage sludges with respect to the sludge types.

Sludge type	Mean	No of sewage works
Aerobic Digested	6.1±0.3	3
Anaerobic Digested	6.7±2.2	21
Compost	6.2±0.6	4
Digested Sludge	6.0±0.6	13
Heated	7.0±0.7	2
Pellets	6.1±0.2	3
Petro Sludge	5.9±1.6	3
WAS	6.4±0.4	23
WAS &Digested	6.0±0.3	4

The pH values with respect to the sludge type were subjected to statistical analysis (ANOVA, Completely randomized design, F-test/ two samples taken from each randomly). This showed that there was no significant difference in pH values since the p-factor obtained was 0.366 which is greater than 0.05. For the difference to be significant p-factor must be less than 0.05.

Looking at the individual sludge works (Appendix E), the pH was found to vary between 4.75 and 13.09 as shown in Table 4.4 with a mean value of 6.35. Two liquid samples were exceptionally basic, having pH values of 12.87 and 13.09. The two samples having a high pH value are probably due to overliming of the sludge.[1] The uniformity in pH value of most of the sludges is most likely due to the use of lime in the stabilization of sewage sludge. However, most of the sludges had the pH value between 4.75 and 6.5.

Table 4.4 Overall pH values of the sewage sludges of South Africa.

Statistical values	pH
Mean	6.35
Min	4.75
Median	6.22
Max	13.09

The determination of pH of sewage sludge is very important. This is because it determines the fate of the mineral ions present in the sludge when the material is disposed off in the environment as a source of cheap fertilizer. Some of the sludges of the sewage plants namely Waterval (plant no.5), Phuthaditjhaba (plant no.39), Mankweng (plant no.52) and Newcastle (plant no.76) had pH values below 5 (Appendix E). These groups of sludge are not ideal for land application or disposal because the optimum pH for adsorption of all metals, except gold, has been determined to be between 4 and 5.[2] This means that these groups of sludge are likely to be hazardous to the environment. This is because the mineral ions in them can readily be leached into ground water or any water stream. It also means that they can readily be taken up by plants which end up being consumed by both man and animals.

Moreover, the result shows that the majority of the sewage works produce sludge having pH between 4.75-6.5. This sludge, as it is, is not suitable as a source of fertilizer since most crops grow best when the soil pH is between 6.5-7.0.[3] This means the pH of sludge needs to be monitored before it can be added to land. It is also important to note that despite the fact that liming is crucial in increasing the pH of sewage sludge, overliming can reduce the availability of major nutrients by tying them to the soil such that they become unavailable to the plant when the sludge is disposed of to land for agricultural purposes.[4] It will also be important to regulate the pH of sludge if it has to be used as fertilizer.

4.2 Total Mineral Ion Content in the Individual Sewage Works

Mineral ions in sewage sludges were identified and their concentration determined as explained in the experimental procedure in section 3.2.4 and 3.2.5 for liquid and solid sludges respectively. The different mineral ions that were determined were Ca, P, Fe, Al, Mg, K, Na, Zn, Mn, Ba, Cu, Si, Cr, Pb, Sr, Se, B, Ni, Cd, Mo, Co and Be for each sewage work. The results obtained are expressed in mg kg^{-1} on dry basis (Appendix F) and tabulated in Appendix G. Looking at the results in general, it is clear that phosphorus is the most abundant element in the sludge with cadmium being the least abundant. Beryllium was below the detection limit of the instrument for all the samples analysed. The order of abundance that is most common to majority of the samples is P, Ca, Fe, Al, Mg, K, Zn, Na, Si, Mn, Cu, Cr, Ba, Pb, Sr, Se, B, Ni, Co, Mo and Cd. A detailed look at the individual samples reveals that even though phosphorus was generally the most abundant, 11 of the samples had calcium as the highest element.

On the other hand, looking at the major pollutants, zinc was the highest with cadmium being the least abundant. The order of abundance in majority of the solid samples (64 in total) was Zn > Pb > Ni > Cd with the relative metals concentrations of Cu, Se, B, Cr, Co and Mo varying among the sewage works.

The liquid sample numbers 9, 21 and 22 (Appendix H) also show phosphorus as the most abundant element whereas the rest show sodium as the most abundant element. But the values of phosphorus for the liquid samples in general when compared with the solid samples are 10^2 times smaller. The other observation is that most of the transition elements were below the detection limit. To be able to get a good picture of the distribution of pollutants, the results have been compared at provincial level and provided in section 4.2.1.

4.2.1 A Summary of Mineral Ion Content of Sludge from Different Provinces of South Africa

To compare the level of pollution in different provinces, the mean value of the results for the solid samples of the sewage works in a province was used to represent pollution level per province. The standard deviation of the mean was also determined. The results obtained are tabulated in Table 4.5. These values have been arranged from the most abundant to the least. The results show that the content and variability of pollutants in each province is approximately the same. If one was to be very critical, on the results, it can be said that Gauteng's sludge contains in some cases up to 100 % higher concentration of the mineral ions investigated.

What is obvious from the table of results is the huge standard deviation associated with some elements. This points out the variability of pollutants in different sewage works within the same province. It also indicates that the type of sludge received by individual sewage works is very different.

Since the major concern of South African legislation is on the major pollutants, they are indicated in italics in Table 4.5. The most common order of abundance being:

$$Zn > Cu > Cr \approx Pb > Ni > Se > B > Co > Mo > Cd$$

where zinc is the highest in concentration while cadmium is the least. The concentration ranges from 1.7×10^3 mg kg^{-1} to 1.7 mg kg^{-1}, a difference of 10^3 times in magnitude.

Table 4.5 Mean Concentrations (mg kg $^{-1}$) of mineral ions with respect to the provinces.

Elements	GP	MP*	FSP	WCP	KZNP	LP	NWP	ECP	NCP
[P] /10^4	10.4±5.2	5.0	4.2±1.2	5.5±3.1	3.9±1.8	4.0±2.0	4.8±2.3	3.4±1.8	3.5±1.3
[Ca] /10^4	2.94±2.0	6.4	1.9±1.2	2.5±1.8	2.4±1.4	2.1±1.4	2.4±1.7	3.6±4.7	2.6±0.9
[Fe] /10^4	5.1±6.2	1.8	1.3±0.5	1.2±0.9	2.2±1.5	1.2±0.4	1.5±1.1	1.5±0.8	1.1±0.3
[Al] /10^4	1.43±1.3	1.1	1.2±0.6	0.7±0.3	1.8±1.7	1.2±0.6	0.9±0.4	1.3±0.6	0.6±0.2
[Mg] /10^3	6.7±6.9	3.1	2.4±0.6	4.1±2.1	3.3±1.1	3.5±1.9	45.0±2.6	3.8±2.7	4.7±1.2
[K] /10^3	5.7±7.4	1.2	2.6±1.9	2.9±2.4	2.7±1.7	2.7±2.5	2.9±1.4	2.0±0.5	2.1±2.2
[Zn] /10^3	**2.3±2.9**	**1.1**	**1.0±0.1**	**1.0±0.5**	**1.2±1.5**	**0.9±0.3**	**1.4±0.8**	**1.0±0.4**	**0.8±0.6**
[Na] /10^3	1.4±0.8	1.4	0.9±0.3	1.2±0.6	1.1±1.2	1.5±1.1	1.7±0.9	<0.10	1.2±0.8
[Si] /10^3	2.1±5.5	0.3	0.3±0.1	0.3±0.1	0.3±0.1	0.4±0.1	0.3±0.1	0.3±0.1	9.5±18.8
[Mn] /10^2	12.6±22.7	8.5	3.7±3.3	1.5±0.9	6.5±7.8	2.2±0.8	3.2±2.6	4.9±5.8	4.9.±5.4
[Cu] /10^2	**4.7±3.5**	**4.3**	**2.2±0.7**	**3.0±1.7**	**2.6±1.1**	**3.2±1.6**	**5.7±8.4**	**4.4±1.3**	**2.7±0.9**
[Cr] /10^2	**3.4±2.6**	**1.9**	**0.6±0.1**	**1.6±1.2**	**1.0±0.5**	**1.2±0.7**	**24.9±64.2**	**2.0±3.6**	**0.4±0.1**
[Ba] /10^2	0.9±0.7	1.9	2.0±0.1	2.4±0.2	3.0±0.1	3.3±0.1	3.6±0.1	4.1±4.5	5.4±1.0
[Pb] /10^2	**2.2±2.5**	**1.7**	**1.7±1.2**	**0.8±0.5**	**1.1±0.4**	**1.3±0.9**	**1.4±0.7**	**1.7±0.8**	**1.1±0.4**
[Sr] /10^2	10.0±0.5	0.9	0.8±0.2	1.6±0.9	0.6±0.3	0.7±0.3	1.0±0.4	1.4±0.7	1.2±0.8
[Se] /10^2	**2.2±3.6**	**0.3**	**0.3±0.2**	**0.9±1.5**	**1.7±1.1**	**0.9±1.60**	**0.8±0.70**	**2.5±1.6**	**1.1±0.7**
[B] /10^2	**0.3±0.2**	**<4.74**	**0.5±0.6**	**1.4±1.0**	**1.6±1.0**	**1.1±1.5**	**1.4±1.3**	**2.2±1.2**	**1.5±1.2**
[Ni] /10^2	**1.1±1.3**	**0.4**	**0.3±0.03**	**0.4±0.3**	**0.5±0.4**	**0.4±0.2**	**0.5±0.3**	**0.7±0.2**	**0.3±0.1**
[Co]	**30.5±53.7**	**12.78**	**13.5±4.6**	**5.1±4.4**	**11.3±9.6**	**9.4±3.2**	**12.9±7.1**	**7.8±2.2**	**5.1±3.0**
[Mo]	**11.7±6.5**	**7.4**	**7.9±1.7**	**6.1±4.5**	**9.8±5.0**	**7.7±2.6**	**8.7±3.1**	**11.2±4.3**	**6.4±2.4**
[Cd]	**10.8±13.1**	**2.8**	**2.5±1.2**	**2.6±1.9**	**6.7±10.4**	**2.6±1.2**	**3.9±4.2**	**3.2±0.6**	**1.7±0.8**
Be	<0.16	<0.16	<0.16	<0.16	<0.16	<0.16	<0.16	<0.16	<0.16
No of samples	18	2	4	15	10	7	7	4	4

All bolds are mineral ions considered in the current South African guidelines [10]

*The Mean value for MP but SD was not included for it had only two samples

4.2.2 Comparing the Amount of Mineral Ions in the Liquid and Solid Sludges

The leaching of mineral ions into underground water and the uptake of elements by plants depends on the solubility of these compounds in the aqueous medium. In order to compare liquid sludge to solid sludge ideally it would be best to have one sludge sample and produce a liquid and solid sludge from it. Since this could not be achieved in the investigation, liquid sludge and solid sludge from Gauteng province were compared. The data compiled in Table 4.6 represent the mean values of 5 liquid samples and 18 solid samples.

Table 4.6 Mean concentration of mineral ions in liquid and solid sludges of the Gauteng province (GP).

	Concentration (mg kg^{-1}, dry basis)	
Elements	Solid	Liquid
P	$(10.4\pm5.2)\times 10^4$	$(3.7\pm1.7)\times10^2$
Ca	$(2.94\pm2.0)\times10^4$	41.6 ± 26.0
Fe	$(5.1\pm6.2)\times10^4$	1.5 ± 1.3
Al	$(1.43\pm1.3)\times10^4$	1.1 ± 1.3
Mg	$(6.7\pm6.9)\times10^3$	28.8 ± 25.2
K	$(5.7\pm7.4)\times10^3$	$(1.2\pm0.8)\times10^2$
Zn	$(2.3\pm2.9)\times10^3$	0.3 ± 0.33
Na	$(1.4\pm0.8)\times10^3$	$(4.0\pm8.2)\times10^3$
Si	$(2.1\pm5.5)\times10^3$	3.8 ± 5.7
Mn	$(12.6\pm22.7)\times10^2$	2.1 ± 4.1
Cu	$(4.7\pm3.5)\times10^2$	*
Cr	$(3.4\pm2.6)\times10^2$	0.1 ± 0.2
Ba	$(0.9\pm0.7)\times10^2$	0.2 ± 0.5
Pb	$(2.2\pm2.5)\times10^2$	*
Sr	100.0 ± 5.0	0.2 ± 0.15
Se	220.0 ± 360.0	*
B	30.0 ± 20.0	0.02 ± 0.04
Ni	111.2 ± 134.3	0.10 ± 0.14
Co	30.5 ± 53.7	*
Mo	16.5 ± 20.2	*
Cd	10.8 ± 13.1	*
Be	<0.16	<0.16
No of samples	18	5

*Elements not detected

The results in Table 4.6 show that mineral ions are predominantly concentrated in the solid sludges rather than in the liquid sludge. Reasons for this could be associated with the organic matrix and pH of the system since it is one of the factors which affect the availability of metals.[5] In the current investigation, the pH range for most samples from Gauteng province was found to be between 5.7-7.1 (Appendix E). This means that the possibility of variation due to pH is not significant according to the results obtained. However, the variation in the availability of the mineral ions especially heavy metals can be associated with organic matrix. This is because the formation of insoluble colloidal products due to organic matrix and further aggregation to larger flocs, leads to the sorption of the metals and removal of the complex from the aqueous phase.[6] Furthermore, the degradation of metal complexing agents may result in the precipitation of the released ion as water-insoluble hydroxides, oxides or salts thereby retarding metal solubility and eventual migration.[7] These processes result in the reduction of the total mineral ion concentrations from the liquid sludge and eventual accumulation in the solid sludge. For this reason mineral ion content (on dry basis) is much higher for dry than wet sludge. The current data in Table 4.6 is possibly due to this process. However, the quantity and form of organic matter for both solid and liquid sludges was not determined in the current investigation.

Hence, supporting the explanation given in terms of mineral ion quantities, the application of the liquid sludges on agricultural land when compared to the solid sludge will be environmentally less harmful since the majority of the heavy metals were found to be below the detection limit. Nevertheless, since the need is for sludge to be used as a source of fertilizer, the liquid sludge is not suitable. One reason is that it has a low level of the major and minor nutrients necessary for plants, secondly it can not provide the organic matter for conditioning the soil, in addition, it is cumbersome to transport.

4.2.3 Influence of Effluent Source and Treatment of Sewage Sludge on the Amount of Mineral Ions

In order to control the level of pollution, it is important to try to determine its source. It is for this reason that the sewage works investigated were grouped into two different categories. These were sewage works that received more than or equal to 10 % industrial effluent and the ones that had more than 90 % domestic effluent. Only sewage works that had these details i.e. 61 in total were considered in this comparison. The data representing the mean values including standard deviation of the mean is shown in Table 4.7. From the table, it is clear that on average, the sludge, which had more than or equal to 10 % industrial effluent, had higher values when compared to those that were from more than 90 % domestic effluents. The biggest difference between the two is that for some elements (Ca, Fe, K, Mn, Ni & Cd) the concentration in the industrial sludge was almost double that of domestic. Statistically, it can be concluded that the industrial and domestic sludge have mineral ions that are of similar magnitude in concentration terms. Therefore, it can be concluded that industrial influence on the level of mineral ions in sewage sludge is not significantly greater than that from the domestic effluents. Therefore, it is likely to be counter- productive to impose stringent regulation on the industrial sector to meet level of pollution that is below that of the domestic level. It can also be speculated that most of the industries probably have pretreatment programs, which reduce the amounts of mineral ions being released into the sewage. This is why the industrial influence is of the same magnitude as that of domestic.

Table 4.7 Mean Concentrations (mg kg $^{-1}$) of mineral ions comparing industrial and domestic influence.

Elements	≥10 % Industrial effluent	>90 % Domestic
[P] /10^4	7.3±5.1	4.6±2.2
[Ca] /10^4	4.4±8.1	2.9±3.3
[Fe] /10^4	2.9±4.8	1.6±0.9
[Al] /10^4	1.1±1.0	1.1±0.5
[Mg] /10^3	4.3±2.7	3.8±1.8
[K] /10^3	4.1±2.6	2.7±1.8
[Zn] /10^3	1.5±2.1	1.3±1.3
[Na] /10^3	1.4±1.0	1.1±0.8
[Si] /10^2	9.1±34.9	22.4±77.5
[Mn] /10^2	6.9±16.5	3.0±3.2
[Cu] /10^2	3.7±2.7	3.8±4.5
[Cr] /10^2	2.0±2.0	7.9±33.9
[Ba] /10^2	2.0±1.5	2.9±0.9
[Pb] /10^2	1.5±1.4	1.0±0.6
[Sr] /10^2	0.9±0.4	1.2±0.9
[Se] /10^2	1.4±2.5	1.3±1.5
[B] /10^2	0.8±1.0	1.2±1.0
[Ni] /10^2	0.7±1.0	0.4±0.3
Co	18.1±10.9	7.8±5.0
Mo	9.7±5.6	7.5±2.7
Cd	7.5±11.2	3.1±2.7
Be	<0.16	<0.16
No of samples	36	25

Since the sludges sampled and analysed were prepared in different ways, it is important to analyse the data based on the method of preparation. This is likely to throw some light on the efficiency and possible differences between the methods. Therefore, samples were grouped into 9 sludge types based on the method of preparation. Using the data in Appendix G, the average values were calculated and are compiled in Table 4.8, where the standard deviation is that of the mean. The order of abundance of the mineral ions is the same for all method types. In terms of concentration, these are relatively the same in magnitude with the biggest variation being approximately 3 fold. Therefore, it can be stated that the different methods of preparation produce sludge that are of the same composition. The slight variation is most likely due to the source and variation in the effluent received at the plant

Table 4.8 Mean Concentrations (mg kg $^{-1}$) of mineral ions with respect to the sludge types.

Element	Aerobic Digested	Anaerobic Digested	Compost	Digested Sludge	Heated* Sludge	Pellets	Petro Sludge	WAS	WAS &Digested
|P|/10^4	8.9±6.0	8.2±5.4	8.0±7.4	4.2±1.7	2.2	7.0±1.7	3.8±2.7	5.61±2.9	3.0±1.4
|Ca|/10^4	2.4 ± 1.1	4.7±8.5	3.1±2.0	3.4±2.5	5.4	2.6±0.5	6.6±9.1	3.7±7.4	2.2±0.8
|Fe|/10^4	2.0± 0.7	4.1±5.9	5.0±6.7	1.9±1.7	4.2	1.7±0.7	2.3±1.0	1.1±0.7	1.4±0.4
|Al|/10^4	1.0± 0.5	1.5±1.4	1.0±0.2	1.2±0.5	4.2	1.2±0.3	1.2±0.3	0.8±0.4	0.8±0.2
|Mg|/10^3	6.0± 3.5	6.0±7.2	5.3±2.2	2.5±0.7	5.6	5.4±0.7	3.0±1.1	4.4±2.1	3.7±2.2
|K|/10^3	4.7± 3.4	4.9±7.7	4.8±2.6	1.8±1.2	2.2	2.7± 1.2	1.6±0.2	3.3±2.2	2.7±2.4
|Zn|/10^3	4.9±6.7	1.7±1.1	0.5±0.4	1.2±1.1	0.8	2.7± 2.3	1.2±0.5	0.9±0.5	1.0±0.3
|Na|/10^3	1.8±0.1	1.6±1.1	1.2±0.2	0.91±0.4	<0.1	1.4±0.4	0.5±0.7	1.5±0.8	0.7±0.5
|Si|/10^3	0.3±0.07	1.6±5.1	0.4±0.2	3.2±1.0	0.3	0.3±0.1	0.3±0.8	0.8±2.5	0.3±0.1
|Mn|/10^2	2.5±0.8	10.7±23.5	6.4±3.1	6.2±6.3	20.3	2.7±1.3	2.5±2.9	1.7±1.0	3.4±1.2
|Cr|/10^2	3.5±2.9	12.8±40.8	1.0±0.6	0.9±0.8	37.9	1.8±0.5	1.1±0.2	1.5±1.2	0.8±0.3
|Cu|/10^2	4.2±2.5	5.7±6.0	2.6±1.2	3.0±1.6	1.7	4.0±0.6	3.9±0.8	3.0±1.6	2.9±0.5
|Ba|/10^2	1.8±1.2	1.7±1.5	2.4±1.0	2.6±0.9	3.6	2.8±0.5	3.2±0.8	2.6±1.0	4.2±1.6
|Pb|/10^2	1.3±0.4	2.0±1.9	1.1±0.7	1.9±2.2	1.6	1.3±0.1	1.7±0.4	0.8±0.4	1.0±0.2
|Sr|/10^2	0.8±0.4	0.9±0.4	1.3±0.6	1.0±0.6	1.2	1.0±0.3	0.8±0.1	1.1±0.6	0.8±0.1
|Se|/10^2	0.4±0.01	1.2±2.1	3.8±5.9	1.6±2.1	2.5	1.4±1.9	2.8±2.4	0.9±1.2	1.2±0.9
|B|/10^2	0.4±0.1	8.4±11.1	0.8±0.7	1.0±0.8	2.4	1.0±1.2	1.7±0.2	1.3±1.3	0.9±1.0
|Ni|/10^2	0.8±0.6	1.0±1.4	0.6±0.5	0.4±0.2	0.8	1.0±0.3	0.5±0.1	0.4±0.3	0.5±0.1
Co	7.3±1.7	29.3±55.0	16.7±21.6	11.4±9.1	22.4	7.9±2.7	10.9±8.1	6.4±4.3	12.51±6.4
Mo	10.7±4.0	11.0±6.5	8.1±4.3	8.2±3.3	15.7	11.8±1.9	12.9±4.8	6.0±2.3	9.8±3.3
Cd	18.9±25.4	7.9±9.9	4.9±4.4	2.8±1.3	4.9	3.5±0.4	4.1±1.1	4.1±7.3	2.5±1.0
Be	<0.16	<0.16	<0.16	<0.16	<0.16	<0.16	<0.16	<0.16	<0.16
No of samples	3	17	4	13	2	3	3	22	4

*The Mean value for heated sludge but SD was not included for it had only two samples

Based on the information so far generated, it can be generalized that the sewage sludge within the country is very similar in terms of its mineral ion type and abundance. Therefore, the data given in Appendix G can be combined and a summary table generated to give a picture of the pollution status of the South African sewage sludge. This was done and the values based on dry mass are shown in Table 4.9.

Table 4.9 Overall statistical results of the concentrations (dry basis, mg kg^{-1}) of the mineral ions in South African sewage sludges.

Mineral Ions	Mean	Median	Range	No of samples that were below Detection limits
[P] /10^4	6.0	5.1	0.8 - 16.7	0
[Ca] /10^4	3.8	2.5	0.2 - 36.7	0
[Fe] /10^4	2.4	1.4	0.2 - 25.2	0
[Al] /10^4	1.2	1.0	0.2 - 6.7	0
[Mg] /10^3	4.5	3.7	0.6 - 31.4	0
[K] /10^3	3.4	1.9	0.5 - 33.3	0
[Zn] /10^3	1.4	9.0	0.001 - 12.6	0
[Si] /10^3	1.3	3.0	0.09 - 37.7	0
[Na] /10^3	1.2	1.1	<0.1 - 4.2	4
[Mn] /10^2	6.0	2.5	0.3 - 99.7	0
[Cr] /10^2	5.1	1.1	0.1 - 170.6	0
[Cu] /10^2	3.7	2.9	0.6 - 24.6	0
[Ba] /10^2	2.5	2.5	<0.013 - 6.6	1
[Pb] /10^2	1.5	1.0	0.2 - 8.7	0
[Se] /10^2	1.4	0.004	<1.9 - 12.6	1
[Sr] /10^2	1.1	0.009	0.003 - 4.1	0
[B] /10^2	0.9	0.005	<4.47 - 4.2	11
[Ni] /10^2	0.6	0.4	0.0002 – 5.9	0
Co	14.5	8.3	0.9 - 232.1	0
Mo	8.9	8.0	0.1 – 24.7	0
Cd	5.4	2.8	0.5 - 48.2	0
Be	<0.16	<0.16	<0.16	71

What is noted is that the order of the mean abundance does not change from what has been shown in the other Tables 4.5, 4.7 and 4.8. The range is wide and an indication of the variability from one sewage works to another. This variation is due to the different sources of pollutants that are received by individual sewage works. This depends on the type of industries and in case of domestic, the population dynamics that feed particular sewage works.

The abundance of mineral ions such as Ca, Fe and Al can possibly be due to the fact that the sewage works use lime, alum and iron compounds (e.g. ferric chloride, ferric sulfate or ferrous sulfate copperas) to stabilize the sludge.[8] Consequently, the additions of these chemicals do contribute to the mineral ions abundance other than from industrial or domestic sources. Looking at the top six mineral ions, four of these namely P, Ca, Mg and K are major plant nutrients. This means that sewage sludge is a potential source of these nutrients; hence it can be used as a fertilizer for agricultural applications. The limitation facing its wider application for agricultural purposes is the presence of the heavy metals.

Among the pollutants of major concern in the South African guidelines that were found to be present in the sludge are: Zn, Cu, Cr, Co, Pb, Se, B, Ni, Cd and Mo. The occurrence of these in the sludge is of concern to the government because of their possible adverse effects in the environment. The order of abundance of them was found to be:

$$Zn > Cr > Cu > Pb \approx Se > B > Ni > Co > Mo > Co$$

This order of abundance involving Zn, Pb, Ni and Cd was also found to be true in the survey conducted by the Association of Municipal Sewerage Agencies under the U.S.EPA in 1987.[9] Similarly, this order was also true in the survey conducted by Smith for the inorganic chemical characterization of South African municipal sewage sludges in 1989.[4] The only difference being between Cu and Cr. Looking at the overall picture of the relative abundance in Table 4.9, the greatest mean concentrations of the heavy metals from the 71-sewage works surveyed were zinc and chromium (1.4×10^3 mg kg^{-1}, 5.1×10^2 mg kg^{-1} respectively) followed by copper, lead and nickel (3.7×10^2 mg kg^{-1}, 1.5×10^2 mg kg^{-1} and 62.5 mg kg^{-1}) respectively.

If this sludge is land disposed or used as a fertilizer, the presence of these metals especially the heavy metals could have an adverse effect on the soils. As most soils, especially in the higher rainfall areas, are acidic or can easily be acidified because of poor buffer capacity.[10] According to the current research data on pH, the majority of the sewage works (57 of them) were found to have pH values of between 4.75 and 6.5. This means that the mobility and availability of these metals in the environment is possible since these are greatly increased at soil pH values of 6.5 and below, with the exception of As, Mo, Se, V and some valence states of Cr.[10] The net effect of heavy metals poisoning to plants is to prevent its normal growth. Zinc, in particular, is a very common element in contaminated areas, although it is one of the essential elements for plants.[11] Therefore, apart from the other heavy metals, zinc mobility needs to be controlled. Anderson and Christensen have showed that controlling soil pH is more important than any other single property in curbing Zn mobility.[12] Moreover, Chaney has proposed that to prevent the excessive cadmium uptake by plants, the ratio of cadmium : zinc should not exceed 1:100. The rationale being that zinc would become phytotoxic before cadmium is accumulated to excessive levels.[13] The South African sludge has a ratio of 1 : 259, which means the plants are likely to die before accumulating high levels of cadmium. This means the levels of cadmium is likely to increase with each disposal of sludge on a particular land site or agricultural land.

4.3 Comparing the Total Mineral Ions between 1989 and 2002

The comparison of the concentrations of mineral ions within a period of 5 to 10 years is significant since it assesses the changes in the level of the pollutants. This information equips the necessary government departments with scientific data that they can use to devise ways of controlling the levels by imposing certain regulations where necessary. Because of these reasons, the data obtained in 1989 were compared with the current values. The total mean concentration of the mineral ions Ca, P, Mg, K, Zn, Cu, Cr, Pb, Se, B, Ni, Cd and Mo for the whole country as a whole were selected and are shown in Table 4.10.

Table 4.10 Concentrations of mineral ions in sewage sludges from sewage treatment works throughout the South Africa in 1989 and 2002.

	Mineral Ions	1989[a] survey [4]			2002[b] survey		
		Range	Mean	Median	Range	Mean	Median
Conc (g kg^{-1})	**P**	4-41	16	14	8 - 167	60	51
	Ca	11-79	32	29	2 - 367	38	25
	Mg	2-13	6	5	0.6 - 31	5	4
	K	1-11	3	2	0.5 - 33	3	2
Conc (mg kg^{-1})	**Zn**	237-17680	2054	1432	1 - 12569	1377	900
	Cu	80-17217	654	355	61 - 2458	373	289
	Cr	25-10015	551	220	13 - 17057	511	108
	Pb	67-10137	452	214	18 - 871	146	104
	Se	<1-107	4	2	<2 - 1263	142	41
	B	6-78	31	28	<5 - 417	95	48
	Ni	6-2660	154	55	0.02 - 591	62	42
	Mo	1-24	6	5	0.07 - 25	9	8
	Cd	<1-122	12	3	0.5 - 48	5	2.8

a – represents an average of 77 sewage sludge samples while b 71 sewage sludge samples.
Upper part refers to nutrient concentrations in g mg^{-1} and the lower part to heavy metal concentrations in mg kg^{-1}.

Making reference to Table 4.10, the observation is that the concentrations of the major nutrients namely calcium, magnesium and potassium did not change very much, the values remained relatively constant. The dramatic increase was in the amount of phosphorus, which increased by more than 3 fold from 16 g kg^{-1} in 1989 to 60 g kg^{-1} in 2002. The concentration range between these mineral ions is much wider in 2002 compared to 1989 with the upper limit being bigger. However, on considering the heavy metals, the data shows that the mean concentration level of Zn, Cu, Cr, Pb, Ni and Cd declined "from a value of 2054 mg kg^{-1} for Zn and 12 mg kg^{-1} for Cd in 1989 to 1337 and 5 mg kg^{-1} respectively for year 2002." All the middle mineral ions showed a similar decline. The remaining mineral ions i.e. Se, B and Mo showed an increase from 4, 31 and 6 mg kg^{-1} in 1989 to 142, 95 and 9 mg kg^{-1} in 2002 respectively. The concentration range fluctuated with elements such as Cr, Se and Mo showing an increase in the range with higher maximum values in 2002 compared to 1989. The remaining species had smaller maximum values for the range in 2002 compared to 1989. The trend discussed was also true for the median values. The above information reveals that in 13 years the quality of sewage sludge has not changed much. What is of major concern is the increasing concentration of phosphorus, whose major origin in the sludge is probably from washing detergents and dental materials. Therefore, there is a possible need to control the amount of phosphates and all phosphorus based compounds that are added in washing detergents and dental materials.

4.4 Comparison of the Current Results with the Existing South African Guideline Limits

The 1997 sludge guideline (Table 4.11) on permissible utilization and disposal of sewage sludge lists 13 elements and the maximum limits allowed. Since the survey has looked at the concentration of different mineral ions in the sludge, it is appropriate to compare these results with the maximum limits. Therefore, the guideline values were compared with the data from Table 4.9 that represents the national average concentrations. These are shown in Table 4.11. In order to have a broad view that links the individual sewage works and the maximum limits, Table 4.12 was generated. This information is also represented in a pictorial format in Figure 4.1. In general, half of the average values are below the suggested limits. The elements that exceeded the limit were copper, lead, zinc, selenium and boron. These exceeded the limit by 1-10 times the recommended values.

Table 4.11 Comparison of maximum inorganic limit in sludge (dry mass, mg kg^{-1}) permitted for land applications in the current South African legislation (1997) [14] and the current total average concentrations in the sewage sludge.

	Cd	**Co**	**Cr**	**Cu**	**Hg**	**Mo**	**Ni**	**Pb**	**Zn**	**As**	**Se**	**B**	**F**
Maximum Limits	15.7	100	1750	50.5	10	25	200	50.5	353.5	15	15	80	400
*Mean	5.4	14.5	510	370	-	9	61.5	150	1400	-	140	90	-

*The total mean concentrations mineral ions taken from Table 4.9 (at the national level).

Table 4.12 A list showing the sewage works in numbers and the respective metals that were found to exceed the current South African legislation guide i.e 1997 sludge guidelines.

Plant no	Elements									
	B	Cr	Cu	Se	Ni	Cd	Pb	Co	Zn	Mo
2			*	*		*	*		*	
3			*	*	*		*		*	
4			*	*			*		*	
5			*	*						
6			*	*	*	*	*	*	*	
7			*	*			*		*	
8			*	*			*		*	
10			*						*	
11			*						*	
13			*	*			*		*	
14			*	*			*		*	
15			*	*		*	*		*	
16			*	*			*		*	
17			*	*			*		*	
18			*	*			*			
19			*	*			*		*	
20			*	*			*		*	
23			*	*			*		*	
24			*	*			*		*	
26			*	*			*		*	
27	*		*	*			*		*	
28			*	*			*		*	
29			*	*			*		*	
30	*		*	*			*		*	
31			*	*			*		*	
32	*		*							
33	*		*						*	
34	*		*						*	
35	*		*	*			*		*	
36	*		*	*			*		*	
37			*	*						
38			*	*			*		*	
39			*	*			*		*	
40	*		*	*			*		*	
41			*	*		*	*			
44	*		*	*			*		*	
45	*		*	*			*		*	
46	*		*	*			*		*	
47			*	*			*		*	
48			*	*			*		*	
49			*				*		*	
50			*	*			*		*	
51	*		*	*			*		*	
52			*	*			*		*	
53	*		*	*			*		*	
54	*		*	*			*		*	
55	*	*	*	*			*		*	
56			*	*			*		*	
57			*	*			*		*	
58	*		*	*			*		*	
59	*		*	*			*		*	
60			*				*		*	
61	*		*	*			*		*	
62	*		*	*			*		*	
63	*		*	*			*		*	
64			*	*			*		*	
65	*		*	*			*		*	
67	*		*	*			*		*	
68			*	*			*		*	
69			*	*			*		*	
70			*	*			*		*	
71	*		*	*			*		*	
72	*		*	*			*		*	
73			*	*			*		*	
74	*		*	*			*		*	
75	*		*	*						
76	*		*	*			*		*	
77			*	*			*		*	
78	*		*				*		*	
79	*	*	*	*			*		*	
80	*		*	*			*		*	

NB: Plants no. 1,9,12,21,22,25, 42 (liquid samples) have been omitted. Plant no 43 & 66 were not sampled.

A detailed information linking individual sewage works can be seen in Table 4.12 and Figure 4.1. The result shows that the amount of copper in the sludge was above the permissible limits in all of the sewage works whereas selenium, zinc and lead were above the limit in over 90 % of the sewage works. In the case of boron, almost half of the sewage works produced sludge that had high content of this element. There was not even one sewage work that met the requirement of the current guideline.

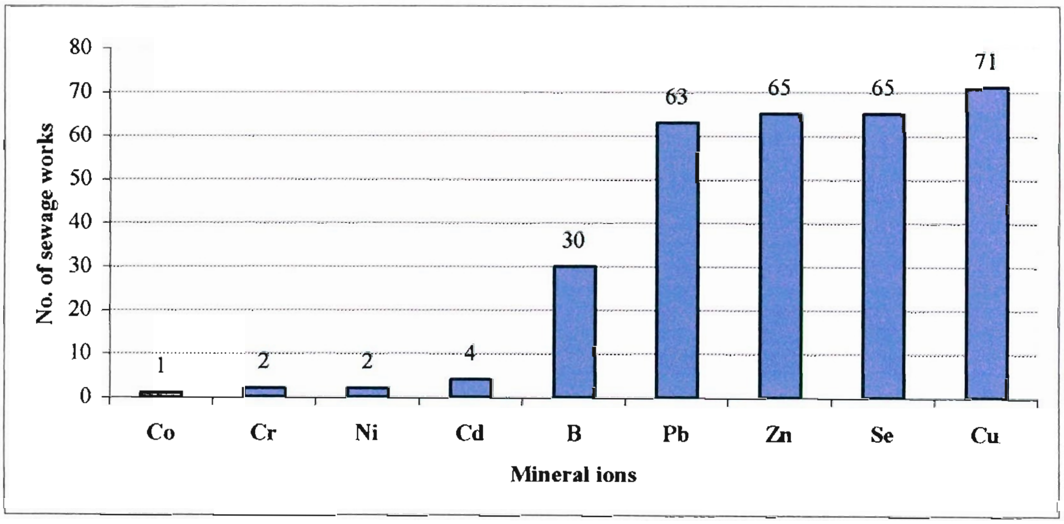

Figure 4.1 Number of sewage works exceeding the maximum concentration limit of mineral ions as stipulated in the 1997 guideline.

Looking at the possible sources of copper, selenium zinc and lead pollution, it is hard to pinpoint one major contributor of each. This is because as mentioned in sections 2.1.1, 2.1.4, 2.1.5, 2.1.8 and 2.19, these elements or compounds that contain them are used in a wide range of industries as summarized in Table 4.13.

Table 4.13 Possible industrial sources of Cu, Se, Zn, Pb and B.

Element	Industries
Copper	Manufacturers of Electrical goods, water piping, roofing material, alloys
Selenium	Semiconductors, rectifiers, and photoreceptors for the electric and electronic industries, ceramics, glass, pigments, alloy making, catalysts, deodorants, lubricants, pesticides, pharmaceuticals
Zinc	Alloy making, paints, plastics, rubber, cosmetics, pharmaceuticals, batteries, fertilizers, lights, televisions, and tyre.
Lead	Making solder, batteries, emergency lights, lead salts for glazing of ceramics, in glass manufacture for high-quality crystal and for television tubes and fluorescent lights, and as petroleum additives
Boron	Steel production, electric wires, glass, enamel and ceramic making, water softeners, fertilizers and pharmaceuticals.

NB: For domestic sources of the above metals see Table 2.2.

However, even though boron and selenium are used in a range of industries, one can speculate about their major contributor. This is likely to be the use of water softeners that normally contains boron and borax and the use of shampoo containing selenium. Therefore, domestic effluents are likely to be the major source of boron and selenium compounds that end up in the sludge. Moreover, the domestic effluent may also be a source of Cu, Zn and Pb as indicated in Table 2.2 since all the sewage works receive a large proportion of domestic effluent.

On the other hand, when the 1991 guidelines of South African permissible utilization and handling of sewage sludge is compared with the current findings, most of the average values are below the suggested limits. The exception is with selenium and boron that exceeds the limit, selenium being approximately 10 times the recommended value (Table 4.14).

Table 4.14 Comparison of maximum limit (1991 guideline) and the total average concentrations of the current findings.[15]

	Cd	Co	Cr	Cu	Hg	Mo	Ni	Pb	Zn	As	Se	B	F
Maximum Limits	20	100	1750	750	10	25	200	400	2750	15	15	80	400
*Mean	5.4	14.5	510	370	-	9	61.5	150	1400	-	140	90	-

*The total mean concentrations mineral ions taken from Table 4.9 (at the national level).

Furthermore, on considering the individual sewage works with the 1991 guideline Table 4.15 and Figure 4.2 are obtained. The result shows that the amount of selenium in the sludge was above the permissible limits in almost all of the sewage works. In case of boron, almost half of the sewage works produced sludge that had high content of this element. The third element, which appeared to be above the limit at individual level to a small extent, was zinc. As a result, only 4 sewage works would have had all the elements fall below the recommended limit. These were plant number 10, 11, 49 and 60 that represents Heidelberg (both with plant no. 10 & 11), Phalaborwa and Beaufort West respectively.

Table 4.15 A list showing the sewage works in numbers and the respective metals that were found to exceed the previous South African legislation guide i.e 1991 sludge guidelines.

Plant No.	Elements									
	B	**Cr**	**Cu**	**Se**	**Ni**	**Cd**	**Pb**	**Co**	**Zn**	**Mo**
2				*			*		*	
3				*	*		*		*	
4				*					*	
5				*						
6				*	*	*		*	*	
7				*						
8				*						
10										
11										
13				*						
14				*						
15				*		*			*	
16			*	*						
17			*	*					*	
18				*						
19				*						
20				*						
23				*						
24				*						
26				*						
27	*			*						
28				*						
29				*						
30	*			*						
31				*						
32	*									
33	*									
34	*									
35	*			*						
36	*			*						
37				*						
38				*						
39				*						
40	*			*						
41				*		*				
44	*			*						
45	*			*						
46	*			*						
47				*						
48				*						
49										
50				*						
51	*			*						
52				*						
53	*			*						
54	*			*						
55	*	*	*	*					*	
56				*					*	
57				*						
58	*			*						
59	*			*						
60										
61	*			*						
62	*			*						
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64			*	*						
65	*			*						
67	*			*						
68				*						
69				*						
70				*						
71	*			*						
72	*			*						
73				*						
74	*			*						
75	*			*						
76	*			*						
77				*			*		*	
78	*									
79	*	*		*						
80	*			*						

Plants no. 1,9,12,21,22,25, 42 (liquid samples) have been omitted. Plant no 43 & 66 were not sampled.

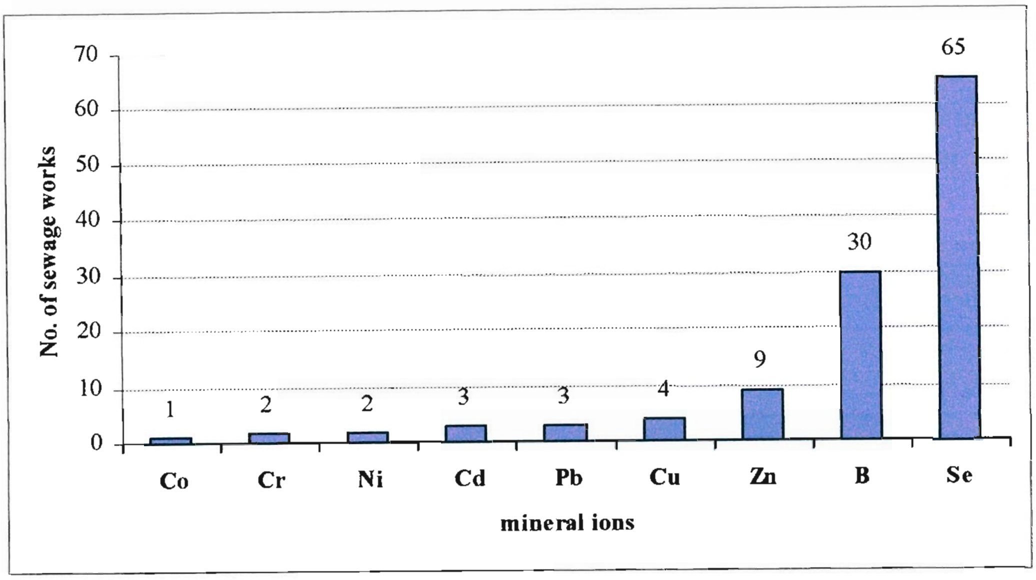

Figure 4.2 Number of Sewage works exceeding the maximum concentration limit of mineral ions as stipulated in the 1991 guideline.

From the above informations, it can be inferred that the current legislation is more restrictive compared to the previous legislation of 1991. This is due to the reduction in the maximum permissible values of copper, zinc, lead and cadmium contents from 750, 2750, 400 and 20 to 50.5, 353.5, 50.5 and 15.7 mg kg^{-1} respectively. The effect of this is that not even one sewage works can meet the requirements of disposing the sludge as a source of cheap fertilizer.

Based on the assessment made above, it motivates to compare the current results with the limits of other countries. Therefore, the current South African limits and the results obtained in this study were compared with USA and EU limits as shown in Table 4.16. With reference to the tabulated information, it is clear that South African limits are much lower compared to USA and EU limits. The exception was with Mo and Cr. This means that all the elements that do not meet the current South African legislation requirement do certainly meet the USA and EU limits. In general, it can be said that South African sludge is good for agricultural use in USA and EU but not in South Africa. This points to the fact that South African legislation is too restrictive. It is also worth mentioning that South African limits include elements such as Co, B and F which have no restriction internationally.

Table 4.16 Comparison of maximum inorganic limit in sludge (dry mass, mg kg^{-1}) permitted for land applications in the current South African legislation (1997) and the international limits.

Elements	**SA**[14]	**USA**[16]	**EU**[1]	Current total Means•
Cd	15.7	39	20-40	5.4
Co	100	-	-	14.5
Cr	1750	1200	200-1200*	510
Cu	50.5	1500	1000-1750	370
Hg	10	17	16-25	-
Mo	25	18	20*	9
Ni	200	420	300-400	61.5
Pb	50.5	300	750-1200	150
Zn	353.5	2800	2500-4000	1400
As	15	41	10-75*	-
Se	15	36	14-100	140
B	80	-	-	90
F	400	-	-	-

•The total mean concentrations of mineral ions taken from Table 4.9 (at the national level).

*Recommended values for European Community.[17]

Therefore, it is a recommendation of this study that the government reviews its limit if it is to encourage the use of sewage sludge for agricultural purposes.

4.5 Conclusion

It can therefore be concluded that the current South African legislation on permissible utilization and disposal of sewage sludge is too restrictive. The government needs to revise the current limits to be in line with the international limits. This will in turn encourage the use of sludge being produced in the country to be used for agricultural purposes.

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APPENDICES

APPENDIX A

Details about Sewage Works of South Africa

Appendix A Details about Sewage Works of South Africa.

Plant No	Wastewater plant name	Sample description	Town	Sampling point	Province
01	Vlakplaats	Anaerobic Digested	Alberton	Wet sludge	Gauteng
02	Vlakplaats	Anaerobic Digested	Alberton	Compost	Gauteng
03	Vlakplaats	Anaerobic Digested	Alberton	Paper, pulp compost	Gauteng
04	Dekema	Anaerobic Digested	Germiston	Peddies	Gauteng
05	Waterval	Anaerobic Digested	Germiston	Peddies	Gauteng
06	Rondebult	Anaerobic Digested	Alberton	Peddies	Gauteng
07	Cf Grundlingh	WAS	Nigel	Return flow	Gauteng
08	Herbert Bickley	Anaerobic Digested	Nigel	Digesters	Gauteng
09	Tsakane	WAS	Brakpan	WAS	Gauteng
10	Heidelberg	WAS	Heidelberg	Pit	Gauteng
11	Heidelberg	Anaerobic Digested	Heidelberg	Digesters	Gauteng
12	Baviaanspoort	Anaerobic Digested	Pretoria	Wet sludge	Gauteng
13	Rooiwal Northern	Anaerobic Digested	Pretoria	Wet sludge	Gauteng
14	Rooiwal West/East	Anaerobic Digested	Pretoria	Wet sludge	Gauteng
15	Zeekoegat	Anaerobic Digested	Pretoria	Wet sludge	Gauteng
16	Centurion	Anaerobic Digested	Verwoedburg	Belt press	Gauteng
17	Daspoort	Anaerobic Digested	Pretoria	Drying beds	Gauteng
18	Olifantsvlei	Compost	JHB	Compost heap	Gauteng
19	JHB Northern Works	WAS	JHB	Belt press	Gauteng
20	JHB Northern Works	Compost	JHB	Compost heap	Gauteng
21	Percy Steward	Anaerobic Digested	Krugersdorp	Wet sludge	Gauteng
22	Flip Human	Anaerobic Digested	Krugersdorp	Wet sludge	Gauteng
77	Rietspruit	Digested	Rietspruit	Drying beds	Gauteng
23	Kingstonvale	Digested Sludge	Nelspruit	Drying beds	Mpumalanga
24	Lydenberg	Digested Sludge	Lydenburg	Drying beds	Mpumalanga
25	Thabong	WAS	Welkom	Return flow	Free state

Appendix A Continued.

Plant No.	Wastewater plant name	Sample description	Town	Sampling point	Province
26	Witpan	Digested Sludge	Welkom	Drying beds	Free state
27	Theronia	Digested Sludge	Welkom	Drying beds	Free state
38	Harrismith	Digested	Harrismith	Drying beds	Free state
39	Phuthaditjhaba	Digested Sludge	Qwaqwa	Drying beds	Free state
28	Borcherds Quarry	WAS	Cape Town	Return flow	Western cape
29	Bellville	WAS	Cape Town	Belt press	Western cape
30	Athlone	WAS	Cape Town	Drying lagoons	Western cape
31	Cape Flats	Pellets	Cape Town	Old stock bags	Western cape
32	Mitchell's Plain	Digested Sludge	Cape Town	Centrifuge cake	Western cape
33	Wesfleur	WAS	Cape Town	Industrial drying beds	Western cape
34	Wesfleur	WAS	Cape Town	Domestic drying beds	Western cape
35	Gwain	Petro Sludge	George	Drying beds	Western cape
36	Mossel Bay	WAS	Mossel Bay	Drying beds	Western cape
37	Oudshoorn	Compost	Oudtshoorn	Compost heap	Western cape
60	Beaufort West	WAS	Beaufort West	Drying beds	Western cape
62	Vredenburg	WAS	Vredenburg	Fenced area	Western cape
63	Saldanha	WAS	Saldanah bay	Drying beds	Western cape
64	Clanwilliam	WAS	Clanwilliam	Drying beds	Western cape
65	Vredendal	WAS	Vredendal	Stock pile	Western cape
40	Estcourt	Digested Sludge	Estcourt	Drying beds	Kwazulu natal
41	Hammarsdale	WAS	Hammarsdale	Centrifuge	Kwazulu natal
42	Darvill	WAS+ Digested	Pietermaritzburg	Return flow	Kwazulu natal
44	Isipingo	Digested Sludge	Durban	Drying beds	Kwazulu natal
45	Kwa-Mashu	Digested Sludge	Durban	Belt press	Kwazulu natal
56	Kwa-Mashu	Pellets	Durban	Bins	Kwazulu natal
57	Phoenix	WAS	Pietermaritzburg	Belt press	Kwazulu natal
58	Durban Northern	WAS/Digested	Durban	Belt press	Kwazulu natal

Appendix A. Continued.

Plant No	Wastewater plant name	Sample description	Town	Sampling point	Province
59	Durban Northern	Pellets	Durban	Bins	Kwazulu natal
75	Klipfontein	Heated, Digested	VryHeid	Heaps	Kwazulu natal
76	Newcastle	Petro	New castle	Drying beds	Kwazulu natal
46	Pietersburg	Anaerobic Digested	Pietersburg	Stockpile	Limpopo
47	Pietersburg	Anaerobic Digested	Pietersburg	Plough fields	Limpopo
48	Seshego	Anaerobic Digested	Pietersburg	Drying beds	Limpopo
49	Phalaborwa	WAS	Phalaborwa	Drying beds	Limpopo
50	Tzaneen	Anaerobic Digested	Tzaneen	Drying beds	Limpopo
51	Mankweng	Anaerobic Digested	Pietersburg	Drying beds	Limpopo
52	Mankweng	Anaerobic Digested	Pietersburg	Compost	Limpopo
53	Rustenburg	Anaerobic Digested	Rustenburg	Drying beds	North west
54	Boitekong	WAS	Rustenburg	Return flow	North west
55	Brits	Anaerobic Digested	Brits	Drying beds	North west
69	Orkney	WAS &Digested	Orkney	Stock pile	North west
70	Klerksdorp	WAS &Digested	Klerksdorp	Drying beds	North west
71	Wolmaranstad	Compost	Wolmaranstad	Pit	North west
73	Vryburg	WAS	Vryburg	Drying beds	North west
61	East London	Petro Process	East London	Drying beds	Eastern cape
78	Potsdam	Digested	East London	Drying beds	Eastern cape
79	Fishwater Flats	Heated, Centrifuged	Port Elizabeth	Centrifuge	Eastern cape
80	Cape Recife	WAS	Port Elizabeth	Drying beds	Eastern cape
67	Kameelmond	WAS	Upington	Drying beds	Northern cape
68	Kameelmond	Digested Sludge	Upington	Drying beds	Northern cape
72	Homevale	WAS &Digested	Kimberley	Drying beds	Northern cape
74	Kuruman	WAS	Kuruman	Drying beds	Northern cape

APPENDIX B

Sludge Sampling Date and Relevant Informations.

Appendix B Sludge Sampling date and other relevant informations.

Sample number	Date of sampling	Form of sludge (Solid or Liquid)	Sources
01	10/10/2002	Liquid	>10 % (I)
02	10/10/2002	Wet solid	>10 % (I)
03	03/10/2002	Wet solid	>10 % (I)
04	10/10/2002	Wet solid	>10 % (I)
05	10/10/2002	Wet solid	>10 % (I)
06	10/10/2002	Wet solid	>10 % (I)
07	10/10/2002	Wet solid	>90 % (D)
08	10/10/2002	Wet solid	>10 % (I)
09	10/10/2002	Liquid	>90 % (D)
10	10/10/2002	Wet solid	>10 % (I)
11	10/10/2002	Wet solid	>10 % (I)
12	10/10/2002	Liquid	>10 % (I)
13	02/10/2002	Wet solid	>10 % (I)
14	02/10/2002	Wet solid	>10 % (I)
15	02/10/2002	Wet solid	>10 % (I)
16	02/10/2002	Wet solid	>10 % (I)
17	02/10/2002	Wet solid	>10 % (I)
18	03/10/2002	Wet solid	>10 % (I)
19	03/10/2002	Wet solid	10 % (I)
20	03/10/2002	Wet solid	>10 % (I)
21	04/10/2002	Liquid	>10 % (I)
22	04/10/2002	Liquid	>10 % (I)
23	23/07/2002	Wet solid	-
24	23/07/2002	Wet solid	-
25	18/07/2002	Liquid	-
26	18/07/2002	Wet solid	>10 % (I)
27	18/07/2002	Wet solid	>90 % (D)
28	05/08/2002	Wet solid	>10 % (I)
29	05/08/2002	Wet solid	>10 % (I)
30	12/08/2002	Wet solid	>90 % (D)
31	05/08/2002	Wet solid	>10 % (I)
32	08/08/2002	Wet solid	>90 % (D)
33	05/08/2002	Wet solid	>10 % (I)
34	08/08/2002	Wet solid	>90 % (D)
35	21/08/2002	Wet solid	>90 % (D)
36	21/08/2002	Wet solid	>10 % (I)
37	08/08/2002	Wet solid	>10 % (I)
38	14/08/2002	Wet solid	>90 % (D)
39	14/08/2002	Wet solid	>90 % (D)
40	13/08/2002	Wet solid	>10 % (I)
41	12/08/2002	Wet solid	>10 % (I)
42	29/11/2002	Liquid	>10 % (I)

Appendix B. Continued

Plant Number	Date of sampling	Form of sludge (Solid or Liquid)	Sources
44	12/08/2002	Wet solid	>90 % (D)
45	12/08/2002	Wet solid	>90 % (D)
46	25/07/2002	Wet solid	>10 % (I)
47	25/07/2002	Wet solid	>10 % (I)
48	25/07/2002	Wet solid	>90 % (D)
49	24/07/2002	Wet solid	-
50	24/07/2002	Wet solid	10 % (I)
51	25/07/2002	Wet solid	>90 % (D)
52	25/07/2002	Wet solid	>90 % (D)
53	16/07/2002	Wet solid	>10 % (I)
54	16/07/2002	Wet solid	>90 % (D)
55	16/07/2002	Wet solid	>90 % (D)
56	12/08/2002	Wet solid	>90 % (D)
57	12/08/2002	Wet solid	>90 % (D)
58	12/08/2002	Wet solid	>90 % (D)
59	12/08/2002	Wet solid	>90 % (D)
60	05/08/2002	Wet solid	>90 % (D)
61	20/08/2002	Wet solid	>10 % (I)
62	05/08/2002	Wet solid	>90 % (D)
63	05/08/2002	Wet solid	>10 % (I)
64	05/08/2002	Wet solid	-
65	05/08/2002	Wet solid	>90 % (D)
67	05/08/2002	Wet solid	>90 % (D)
68	05/08/2002	Wet solid	>90 % (D)
69	05/08/2002	Wet solid	>10 % (I)
70	05/08/2002	Wet solid	-
71	08/08/2002	Wet solid	-
72	12/08/2002	Wet solid	>10 % (I)
73	05/07/2002	Wet solid	-
74	05/08/2002	Wet solid	-
75	12/08/2002	Wet solid	10 % (I)
76	05/08/2002	Wet solid	>10 % (I)
77	18/07/2002	Wet solid	-
78	20/08/2002	Wet solid	>10 % (I)
79	20/08/2002	Wet solid	-
80	21/08/2002	Wet solid	-

I= industry D = Domestic.

APPENDIX C

Determination of Density for Liquid Sludge Samples

Appendix C Determination of density for liquid sludge samples.

Plant	Temp	V	Mass replicates			M	Density (ρ)(g/ml)
No.	(°C)	Volume (ml)	m1	m2	m3	Av.mass (g)	= M/V
01	21	10.00	10.04	10.03	10.03	10.03	1.003
09	21	10.00	9.78	9.80	9.79	9.79	0.979
12	16	10.00	9.83	9.87	9.85	9.85	0.985
21	19	10.00	9.82	9.89	9.84	9.85	0.985
22	19	10.00	9.77	9.78	9.79	9.78	0.978
25	15	10.00	9.91	9.93	9.90	9.91	0.991
42	19	10.00	10.25	10.26	10.26	10.26	1.026

NB: This data has been used to convert mg l^{-1} to mg kg^{-1}, on dry basis i.e.

$$\text{C (in mg kg}^{-1}) = \frac{\underline{\mathbf{C}}}{\boldsymbol{\rho}}$$

Where:

- **ρ** is density in kg l^{-1}
- **C** is Concentration in mg l^{-1}.

APPENDIX D

Calculation 1 : Moisture Content

Appendix D Calculation: 1 Moisture Content.

Moisture content of the solid sludge can be calculated: [2]

$$\text{Moisture (\%)} = \frac{\text{Loss in weight on drying (g)} * 100}{\text{Initial sample weight (g)}}$$

Where:

Loss in weight on drying (g) = Initial sample weight (g) – dried sample weight (g)

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1. Allen, S.E., *Chemical Analysis of Ecological Materials*, Blackwell Scientific Publications, England, 1989, p. 15.

APPENDIX E

Moisture Content and pH of different Sludges based on Sampling point and Sludge type.

Appendix E Moisture content and pH of different sludges based on sampling point and sludge type.

Plant No.	Moisture Content (%)	pH	Sampling point	Sample description
16	*87.7*	*5.72*	Belt press	*Anaerobic Digested*
58	82.2	6.13	Belt press	WAS &Digested
45	82.9	6.19	Belt press	Digested Sludge
19	*84*	*6.21*	*Belt press*	*WAS*
29	84	6.22	Belt press	WAS
57	76.3	6.23	Belt press	WAS
56	7.9	5.98	Bins	Pellets
59	7.7	5.93	Bins	Pellets
41	88.5	6.17	Centrifuge	WAS
32	53.9	7.05	Centrifuge cake	Digested Sludge
79	77.5	7.55	Centrifuge	Heated
52	31.6	4.87	Compost	Anaerobic Digested
2	*11.8*	*5.68*	*Compost*	*Anaerobic Digested*
20	*42.2*	*5.68*	*Compost heap*	*Compost*
18	*40.7*	*5.96*	*Compost heap*	*Compost*
3	*38.8*	*6.78*	*Compost*	*Anaerobic Digested*
37	28.56	6.98	Compost heap	Compost
8	*22.14*	*6.37*	*Digesters*	*Anaerobic Digested*
11	*10.77*	*7.07*	*Digesters*	*Anaerobic Digested*
39	13.35	4.83	Drying beds	Digested Sludge
76	9.2	4.83	Drying beds	Petro Sludge
61	62.8	5.12	Drying beds	Petro Sludge
78	58.4	5.18	Drying beds	Digested Sludge
27	6.3	5.61	Drying beds	Digested Sludge
26	8.37	5.62	Drying beds	Digested Sludge
50	62.8	5.7	Drying beds	Anaerobic Digested
53	16.9	5.8	Drying beds	Anaerobic Digested
44	16.8	5.86	Drying beds	Digested Sludge
77	*37.4*	*5.91*	*Drying beds*	*Digested Sludge*
49	4.2	5.92	Drying beds	WAS
80	71.5	5.93	Drying beds	WAS
72	87.3	6.03	Drying beds	WAS&Digested
38	73.5	6.05	Drying beds	Digested sludge
17	*22.2*	*6.15*	*Drying beds*	*Anaerobic Digested*
24	65.5	6.16	Drying beds	Digested sludge
51	75.5	6.16	Drying beds	Anaerobic digested
68	67.7	6.16	Drying beds	Digested sludge
70	6.7	6.16	Drying beds	WAS &Digested
48	2.7	6.24	Drying beds	Anaerobic Digested
36	67.9	6.32	Drying beds	WAS
40	74.6	6.34	Drying beds	Digested sludge
33	45.1	6.36	Drying beds	WAS
74	7.5	6.36	Drying beds	WAS
34	51.3	6.42	Drying beds	WAS

Appendix E. Continued.

Plant No	Moisture Content (%)	pH	Sampling point	Sample description
67	26.4	6.43	Drying beds	WAS
23	17.2	6.46	Drying beds	Digested Sludge
55	65.1	6.48	Drying beds	Anaerobic digested
60	53.6	6.56	Drying beds	WAS
73	9.8	6.68	Drying beds	WAS
63	28.59	6.85	Drying beds	WAS
64	34.1	6.92	Drying beds	WAS
35	64.1	7.70	Drying beds	Petro sludge
5	*19.8*	*4.75*	*Peddies*	*Anaerobic digested*
6	*57.5*	*5.52*	*Peddies*	*Anaerobic digested*
4	*23.9*	*6.60*	*Peddies*	*Anaerobic digested*
71	87.3	6.31	Pit	Compost
10	*3.29*	*7.03*	*Pit*	*WAS*
28	88.2	5.67	Return flow	WAS
42	*	6.35	Return flow	WAS&Digested
7	20.8	6.42	Return flow	WAS
54	20.6	6.83	Return flow	WAS
25	*	6.35	Return flow	WAS
69	9.3	5.50	Stockpile	WAS&Digested
65	31.3	5.88	Stockpile	WAS
46	8.7	6.42	Stockpile	Anaerobic digested
14	21.8	5.81	Wet sludge	Aerobic digested
1	*	*6.09*	*Wet sludge*	*Anaerobic digested*
15	27.3	6.33	Wet sludge	Aerobic digested
12	*	*6.36*	*Wet sludge*	*Anaerobic digested*
13	83.8	6.71	Wet sludge	Anaerobic digested
22	*	*12.87*	*Wet sludge*	*Anaerobic digested*
21	*	*13.09*	*Wet sludge*	*Anaerobic digested*
47	19.9	6.16	Plough fields	Aerobic digested
9	*	*6.25*	*WAS*	*WAS*
31	6.3	6.27	Old stock bags	pellets
75	9.7	6.50	Heaps	Heated
30	69.8	6.61	Drying lagoons	WAS
62	48.7	6.80	Fenced area	WAS

*liquid sludge. *Italics* refer to Gauteng samples i.e. both liquid and solid sludges, where pH of most sludges lies between 5.7-7.1. Plant Numbers are not consecutive for the data is sorted with respect to sampling points.

APPENDIX F

Calculation 2 : Concentration

Appendix F Calculation: 2 Concentration.

The sample contains [2]

$$\frac{V\,(W - B)}{M} \qquad \text{mg kg}^{-1}$$

Where

V is volume of sample solution in ml
W is the concentration as mg l^{-1} (ppm) of metal in the digest
B is the concentration as mg l^{-1} (ppm) of metal in the method blank
M is the weight of dry sample used in grams

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APPENDIX G

Concentration (mg kg $^{-1}$, dry basis) of Mineral Ions in the Provinces of South Africa.

Appendix G Concentration (mg kg^{-1}, dry basis) of Mineral ions in South African Sewage Sludges.

G1. Gauteng Province

Plant No.	02	03	04	05	06	07	08	10	11	13
Sewage work	Vlakplaats	Vlakplaats	Dekema	Waterval	Rondebult	Cf Grundlingh	Herbert Bickley	Heidelberg	Heidelberg	Rooiwal Northern
Elements	Mean	Mean	Mean	Mean	Mean	Mean	Mean	Mean	Mean	Mean
[P] /10^4	8.8±0.3	2.8±0.1	15.4±0.01	1.4±0.1	16.7±0.7	7.0±0.02	7.8±0.1	1.5±0.02	1.7±0.01	11.0±0.1
[Ca] /10^4	2.7±0.1	8.4±0.3	3.3±0.1	0.2±0.02	2.8±0.02	0.7±0.01	1.8±0.03	36.1±0.05	36.7±0.2	1.9±0.03
[Fe] /10^4	7.4±0.04	8.5±0.07	4.7±0.04	2.2±0.01	25.2±0.9	3.0±0.1	5.4±0.02	0.4±0.03	0.4±0.003	1.0±0.01
[Al] /10^4	2.0±0.001	1.0±0.01	6.4±0.02	1.8±0.2	1.1±0.03	1.1±0.0003	1.7±0.07	0.7±0.01	0.6±0.0001	0.6±0.01
[Mg] /10^3	23.3±0.01	31.4±0.1	2.8±0.02	0.7±0.06	3.1±0.06	3.0±0.01	2.4±0.05	3.8±0.3	4.0±0.002	7.7±0.12
[K] /10^3	4.8±0.03	33.3±0.5	17.4±0.01	1.4±0.06	1.3±0.04	4.1±0.03	1.9±0.02	1.2±0.03	0.9±0.004	9.5±0.04
[Zn] /10^3	2.8±0.01	2.8±0.02	3.0±0.05	0.2±0.02	3.8±0.2	0.6±0.02	1.6±0.02	0.6±0.01	0.54±0.004	1.2±0.01
[Na] /10^3	0.8±0.04	0.9±0.01	1.1±0.03	0.6±0.02	1.2±0.05	2.4±0.1	1.2±0.02	0.8±0.01	0.7±0.02	4.0±0.01
[Si] /10^3	21.3±0.5	0.4±0.03	0.4±0.004	0.4±0.02	0.3±0.01	12.1±0.02	0.3±0.01	0.3±0.01	0.4±0.02	0.3±0.01
[Mn] /10^2	10.8±0.1	19.6±0.5	12.5±0.1	1.4±0.1	99.7±0.5	8.5±0.1	8.4±0.04	3.3±0.3	87.84±0.64	0.122±0.001
[Cu] /10^2	3.9±0.2	6.7±0.4	5.4±0.1	0.9±0.06	5.4±0.2	1.3±0.1	2.4±0.04	1.6±0.03	1.6±0.04	4.0±0.05
[Cr] /10^2	6.1±0.2	6.3±0.1	6.8±0.1	1.3±0.06	6.7±0.3	4.7±0.1	7.7±0.5	1.2±0.05	0.8±0.004	3.2±0.03
[Ba] /10^2	3.3±0.06	3.3±0.1	3.7±0.04	0.8±0.04	3.0±0.1	1.9±0.1	2.8±0.03	1.5±0.01	1.4±0.02	2.8±0.01
[Pb] /10^2	6.9±0.04	5.6±0.04	2.6±0.02	0.4±0.02	3.9±0.2	0.8±0.02	1.0±0.02	0.3±0.01	0.3±0.002	1.1±0.02
[Sr] /10^2	1.1±0.03	1.1±0.01	1.3±0.01	0.1±0.01	1.2±0.03	0.5±0.01	0.7±0.01	1.1±0.02	1.1±0.003	0.6±0.05
[Se] /10^2	0.9±0.01	0.7±0.06	1.3±0.04	0.4±0.02	1.0±0.05	4.8±0.1	8.4±0.2	0.1±0.01	0.1±0.005	0.2±0.01
[B] /10^2	0.2±0.02	0.07±0.005	0.2±0.01	0.1±0.01	0.3±0.02	0.5±0.01	0.2±0.01	0.08±0.003	<4.74	0.5±0.02
[Ni] /10^2	1.3±0.02	2.8±0.04	0.9±0.02	0.3±0.02	5.9±0.2	0.7±0.02	0.7±0.04	0.2±0.01	0.1±0.004	0.9±0.008
Co	39.7±1.8	69.5±1.2	35.6±0.05	9.2±0.2	232.1±7.7	12.2±0.1	14.6±0.1	2.4±0.1	6.6±0.3	4.3±0.1
Mo	18.1±0.6	18.6±0.3	23.5±0.2	5.0±0.4	24.7±1.2	6.5±0.6	9.4±0.04	4.8±0.1	3.7±0.2	7.5±0.1
Cd	16.4±0.4	14.9±0.1	7.9±0.1	2.5±0.1	41.6±2.0	6.0±0.1	7.4±0.04	2.0±0.2	0.8±0.03	6.4±0.1
Be	<0.16	<0.16	<0.16	<0.16	<0.16	<0.16	<0.16	<0.16	<0.16	<0.16

G1. Continued.

Plant No.	14	15	16	17	18	19	20	77
Sewage work Elements	Rooiwal West/East Mean	Zeekoegat Mean	Centurion Mean	Daspoort Mean	Olifantsvlei Mean	JHB Northern Mean	JHB Northern Mean	Rietspruit Mean
[P] /10^4	8.2±0.1	15.2±0.2	15.1±0.3	15.9±0.8	16.4±0.1	12.4±0.1	12.1±0.08	7.8±0.1
[Ca] /10^4	1.3±0.3	2.3±0.02	4.0±0.06	3.7±0.1	4.9±0.07	1.2±0.004	4.4±0.1	3.6±0.1
[Fe] /10^4	1.9±0.02	2.7±0.02	1.5±0.02	2.0±0.06	14.9±0.02	1.8±0.01	2.7±0.1	7.0±0.02
[Al] /10^4	1.5±0.08	0.5±0.003	1.6±0.03	1.0±0.05	1.1±0.02	0.6 ±0.001	1.1±0.04	1.4±0.02
[Mg] /10^3	5.9±0.09	9.6±0.4	6.9±0.1	12.9±1.2	7.0±0.02	5.6±0.01	7.4±0.1	2.4±0.02
[K] /10^3	5.0±0.10	80.0±0.05	4.6±0.1	5.2±0.2	5.5±0.08	4.2±0.04	8.1±0.1	1.3±0.01
[Zn] /10^3	0.9±0.02	12.6±0.1	1.2±0.02	2.8±0.1	0.01± 0.0001	0.7±0.01	0.8±0.01	4.9±0.1
[Na] /10^3	1.7±0.03	1.7±0.03	1.5±0.05	1.4±0.05	1.4±0.03	0.9±0.01	1.3±0.02	0.8±0.01
[Si] /10^3	0.4±0.02	0.3±0.01	0.4±0.03	0.4±0.01	0.4±0.02	0.4±0.02	0.4±0.02	0.3±0.01
[Mn] /10^2	1.9±0.01	2.4±0.01	4.5±0.1	2.1±0.1	15.6±9.5	4.6±0.03	693.8±5.0	23.0±0.8
[Cu] /10^2	2.8±0.05	7.1±0.06	12.7±0.3	13.0±0.5	3.5±0.05	4.2±0.07	3.8±0.1	4.7±0.1
[Cr] /10^2	2.5±0.07	6.8±0.06	1.2±0.05	0.7±0.02	1.9±0.03	0.9±0.02	0.9±0.03	1.1±0.02
[Ba] /10^2	2.2±0.06	4.8±0.05	3.7±0.03	4.0±0.3	3.6±0.05	3.6±0.02	3.1±0.06	6.6±0.2
[Pb] /10^2	0.9±0.01	1.5±1.9	0.9±0.07	1.5±0.07	1.2±0.07	0.8±0.01	0.8±0.02	8.7±0.2
[Sr] /10^2	0.5±0.01	1.2±0.01	1.1±0.01	0.8±0.03	0.2±0.02	0.9±0.004	1.3±0.01	1.4±0.02
[Se] /10^2	0.4±0.03	0.3±0.03	0.4±0.02	0.3±0.01	12.6±0.1	0.3±0.01	0.4±0.01	7.0±0.1
[B] /10^2	0.4±0.02	0.5±0.01	0.2±0.01	0.3±0.02	0.4±0.01	0.04±0.001	0.3±0.02	0.1±0.01
[Ni] /10^2	0.6±0.02	1.4±0.05	0.6±0.02	0.5±0.04	1.3±0.06	0.6±0.02	0.6±0.02	0.7±0.01
Co	0.06±0.0004	7.1±0.5	6.1±0.1	7.7±0.2	49.0±0.9	6.5±0.5	7.1±0.3	34.6±1.7
Mo	0.08±0.002	15.3±0.1	8.6±0.4	12.6±0.3	13.7±1.2	6.5±0.2	8.2±0.7	16.4±0.3
Cd	0.05±0.002	48.2±0.5	3.6±0.1	5.0±0.2	11.1±0.4	4.5±0.1	4.9±0.1	5.8±0.04
Be	<0.16	<0.16	<0.16	<0.16	<0.16	<0.16	<0.16	<0.16

G2. Mpumalanga Province

Plant No	23	24
Sewage work Elements	Kingstonvale Mean	Lydenburg Mean
[P] /10^4	5.6±0.05	4.5±0.2
[Ca] /10^4	9.9±0.2	2.8±0.1
[Fe] /10^4	1.0±0.05	2.6±0.1
[Al] /10^4	0.8±0.02	1.4±0.02
[Mg] /10^3	2.6±0.03	3.6±0.1
[K] /10^3	1.0±0.005	1.4±0.02
[Zn] /10^3	1.2±0.02	1.1±0.01
[Na] /10^3	1.3±0.03	1.4±0.03
[Si] /10^3	0.3±0.02	3.1±0.1
[Mn] /10^2	13.0±0.2	4.1±0.2
[Cu] /10^2	5.8±0.1	2.7±0.1
[Cr] /10^2	0.5±0.02	3.2±0.1
[Ba] /10^2	3.1±0.1	2.2±0.04
[Pb] /10^2	2.5±0.1	1.0±0.03
[Sr] /10^2	1.1±0.004	0.6±0.02
[Se] /10^2	0.2±0.01	0.5±0.004
[B] /10^2	<4.74	<4.74
[Ni] /10^2	0.3±0.02	0.4±0.02
Co	5.1±0.4	20.3±0.2
Mo	7.2±0.2	7.7±0.1
Cd	2.4±0.1	3.2±0.1
Be	<0.16	<0.16

G3. Free State Province

Plant No	26	27	38	39
Sewage work Elements	Witpan Mean	Theronia Mean	Harrismith Mean	Phuthadithjaba Mean
[P] /10^4	4.3±0.1	2.5±0.1	5.3±0.1	4.8±0.02
[Ca] /10^4	3.5±0.02	0.5±0.01	1.7±0.04	1.8±0.01
[Fe] /10^4	1.1±0.01	1.4±0.05	0.7±0.02	1.9±0.02
[Al] /10^4	0.8±0.02	1.3±0.05	0.7±0.01	2.1±0.04
[Mg] /10^3	2.0±0.1	2.0±0.1	3.2±0.1	2.5±0.03
[K] /10^3	1.2±0.04	1.1±0.03	5.3±0.1	2.7±0.1
[Zn] /10^3	0.9±0.02	1.0±0.01	1.1±0.01	1.0±0.02
[Na] /10^3	0.94±0.05	0.4±0.05	1.2±0.04	0.9±0.03
[Si] /10^3	0.3±0.03	0.3±0.03	0.3±0.2	0.2±0.01
[Mn] /10^2	3.4±0.2	1.5±0.05	1.6±0.02	8.5±0.1
[Cu] /10^2	2.3±0.05	2.9±0.2	1.3±0.03	2.3±0.02
[Cr] /10^2	0.8±0.02	0.5±0.03	0.5±0.02	0.5±0.01
[Ba] /10^2	2.5±0.1	2.9±0.1	2.5±0.02	3.1±0.05
[Pb] /10^2	1.9±0.04	3.3±0.08	0.7±0.04	0.9±0.009
[Sr] /10^2	1.1±0.004	0.6±0.03	0.8±0.01	0.6±0.007
[Se] /10^2	0.2±0.02	0.3±0.02	0.2±0.01	0.6±0.01
[B] /10^2	<4.74	0.9±0.02	<4.74	0.1±0.01
[Ni] /10^2	0.3±0.02	0.3±0.01	0.3±0.02	0.3±0.007
Co	19.5±0.7	14.7±0.5	9.4±0.5	10.5±0.2
Mo	9.9±0.4	8.1±0.3	5.7±0.2	7.9±0.3
Cd	2.4±0.2	2.1±0.03	1.3±0.1	4.2±0.03
Be	<0.16	<0.16	<0.16	<0.16

G4. Western Cape Province

Plant No.	28	29	30	31	32	33	34	35	36	37
Sewage work	Borcherds quarry	Bellville	Athlone	Cape Flats	Mitchell's Plain	Wesfleur	Wesfleur	Gwain	MosselBay	Oudtshoorn
Elements	Mean	Mean	Mean	Mean	Mean	Mean	Mean	Mean	Mean	Mean
[P] /10^4	10.4±0.6	5.3±0.1	8.4±0.3	9.0±0.1	1.6±0.2	2.1±0.02	2.2±0.1	6.9±0.1	6.4±0.1	1.4±0.03
[Ca] /10^4	1.6±0.1	3.7±0.02	1.4±0.002	3.2±0.03	5.4±0.2	0.4±0.01	1.1±0.1	17.1±0.2	1.3±0.02	0.4±0.01
[Fe] /10^4	0.5±0.03	0.7±0.02	0.8±0.02	1.0±0.01	0.2±0.01	0.3±0.01	0.3±0.01	3.3±0.05	1.4±0.01	1.2±0.01
[Al] /10^4	0.4±0.03	0.5±0.003	0.6±0.02	1.1±0.006	0.2±0.01	0.3±0.02	0.2±0.01	0.9±0.03	0.6±0.04	0.8±0.01
[Mg] /10^3	6.2±0.4	3.0±0.03	5.1±0.5	6.1±0.6	1.7±0.02	1.2±0.02	1.2±0.1	3.8±0.02	4.9±0.02	4.1±0.1
[K] /10^3	9.0±0.6	3.4±0.02	6.4±0.1	1.6±0.01	0.8±0.05	1.0±0.02	1.2±0.04	1.6±0.03	5.3±0.03	3.65±0.02
[Zn] /10^3	1.6±0.02	1.3±0.02	2.1±0.1	1.2±0.03	0.3±0.003	0.6±0.02	0.7±0.03	1.4±0.03	0.8±0.05	0.2±0.001
[Na] /10^3	1.5±0.1	1.6±0.03	2.6±0.2	1.7±0.06	0.4±0.1	1.6±0.06	1.0±0.05	0.07±0.005	1.5±0.1	1.0±0.03
[Si] /10^3	0.3±0.003	0.2±0.005	0.4±0.02	0.4±0.04	0.3±0.006	0.3±0.01	0.2±0.01	0.2±0.02	0.4±0.02	0.7±0.06
[Mn] /10^2	0.7±0.05	2.2±0.05	0.9±0.01	1.3±0.01	0.3±0.02	1.0±0.03	1.2±0.1	3.6±0.06	1.3±0.05	1.5±0.03
[Cu] /10^2	1.6±0.03	2.6±0.05	3.3±0.03	4.5±0.05	0.7±0.05	2.1±0.09	1.9±0.1	3.2±0.1	2.2±0.1	1.3±0.1
[Cr] /10^2	1.5±0.03	3.4±0.05	2.8±0.04	1.9±0.04	0.1±0.005	2.91±0.1	3.5±0.2	1.2±0.06	1.6±0.1	0.6±0.05
[Ba] /10^2	2.2±0.02	1.6±0.01	2.8±0.03	2.7±0.02	0.5±0.04	0.8±0.03	1.1±0.05	4.8±0.04	1.7±0.02	1.0±0.04
[Pb] /10^2	0.8±0.01	0.8±0.02	1.0±0.02	1.3±0.03	0.4±0.03	0.2±0.06	0.2±0.01	1.9±0.05	0.8±0.06	0.4±0.03
[Sr] /10^2	1.4±0.01	1.1±0.01	1.4±0.01	1.3±0.01	2.8±0.2	0.6±0.01	0.7±0.02	4.1±0.2	1.1±0.03	0.9±0.01
[Se] /10^2	0.2±0.001	0.2±0.07	0.2±0.01	0.2±0.002	<1.87	0.09±0.001	0.06±0.005	5.3±0.1	1.9±0.05	0.2±0.01
[B] /10^2	0.5±0.02	<4.74	1.9±0.03	0.1±0.003	0.9±0.09	1.5±0.09	1.4±0.09	1.6±0.05	4.2±0.4	0.6±0.05
[Ni] /10^2	0.5±0.03	0.7±0.04	1.0±0.01	0.8±0.03	0.06±0.006	0.3±0.01	0.3±0.007	0.4±0.01	0.3±0.004	0.2±0.005
Co	1.1±0.09	15.2±0.2	3.9±0.04	4.9±0.4	0.7±0.02	13.7±0.7	2.4±0.1	4.5±0.1	3.9±0.3	3.5±0.1
Mo	8.1±0.2	7.0±0.2	8.5±0.2	9.8±0.3	1.3±0.1	3.4±0.3	2.3±0.1	8.0±0.3	7.4±0.6	3.2±0.3
Cd	3.7±0.2	3.2±0.1	7.8±0.4	3.7±0.1	0.6±0.02	0.7±0.01	0.5±0.04	4.6±0.1	1.9±0.03	1.6±0.04
Be	<0.16	<0.16	<0.16	<0.16	<0.16	<0.16	<0.16	<0.16	<0.16	<0.16

G4. Continued.

Plant No	60	62	63	64	65
Sewage work	Beaufort West	Vredenburg	Saldanha	Clanwilliam	Vredendal
Elements	Mean	Mean	Mean	Mean	Mean
[P] /10^4	3.2±0.2	8.2±0.3	5.1±0.04	9.1±0.2	3.0±0.1
[Ca] /10^4	3.3±0.1	3.2±0.1	4.5±0.04	5.1±0.01	0.4±0.002
[Fe] /10^4	1.9±0.03	0.9±0.02	2.7±0.03	1.4±0.1	0.8±0.03
[Al] /10^4	0.8±0.05	0.8±0.02	1.0±0.01	1.3±0.01	0.8±0.04
[Mg] /10^3	3.0±0.1	8.2±0.4	3.8±0.03	6.8±0.3	2.5±0.1
[K] /10^3	2.2±0.1	1.8±0.03	1.1±0.01	3.4±0.03	0.5±0.01
[Zn] /10^3	6.0±0.1	1.1±0.01	131±10.5	0.8±0.01	0.7±0.02
[Na] /10^3	0.8±0.01	1.3±0.01	1.2±0.2	1.2±0.02	0.7±0.01
[Si] /10^3	0.2±0.005	0.2±0.008	0.3±0.005	0.3±0.01	0.2±0.01
[Mn] /10^2	1.6±0.1	1.3±0.03	3.0±0.02	166.46±0.81	0.7±0.02
[Cu] /10^2	2.8±0.1	3.8±0.1	3.8±0.05	8.0±0.2	3.5±0.1
[Cr] /10^2	0.4±0.02	0.9±0.02	1.9±0.02	0.2±0.02	0.5±0.02
[Ba] /10^2	1.6±0.1	2.0±0.03	3.6±0.09	1.9±0.04	1.2±0.01
[Pb] /10^2	0.6±0.04	1.1±0.03	1.6±0.02	0.6±0.02	0.8±0.01
[Sr] /10^2	2.3±0.02	1.6±0.03	1.2±0.005	2.3±0.01	0.8±0.02
[Se] /10^2	2.6±0.07	1.2±0.004	0.4±0.001	0.3±0.01	0.2±0.01
[B] /10^2	0.7±0.04	2.4±0.06	1.4±0.05	0.5±0.02	1.4±0.06
[Ni] /10^2	0.3±0.04	0.3±0.004	0.9±0.005	0.2±0.01	0.2±0.008
Co	5.7±0.1	2.9±0.04	9.5±0.2	2.2±0.1	2.4±0.07
Mo	7.6±0.3	6.4±0.06	10.1±0.2	4.9±0.2	4.6±0.2
Cd	1.6±0.04	2.3±0.05	2.7±0.1	1.9±0.1	1.6±0.05
Be	<0.16	<0.16	<0.16	<0.16	<0.16

G5. KwaZulu - Natal Province

Plant No	40	41	44	45	56	57	58	59	75	76
Sewage work	Estcort	Hammarsdale	Isipingo	Kwamashu	Kwamashu	Phoenix	Durban Northern	Durban Northern	Klipfontein	New castle
Elements	Mean	Mean	Mean	Mean	Mean	Mean	Mean	Mean	Mean	Mean
[P] /10^4	6.1±0.2	5.1±0.1	3.4±0.1	2.6±0.02	6.2±0.02	3.0±0.03	3.6±0.2	5.8±0.2	0.8±0.02	2.5±0.1
[Ca] /10^4	4.7±0.2	0.4±0.002	2.3±0.02	4.4±0.1	2.5±0.03	2.7±0.01	2.2±0.02	2.2±0.04	0.4±0.002	1.9±1.1
[Fe] /10^4	1.3±0.01	0.3±0.01	2.8±0.03	1.6±0.02	1.7±0.01	1.4±0.01	1.8±0.02	2.5±0.1	5.9±0.04	2.3±0.1
[Al] /10^4	1.8±0.05	1.3±0.006	1.3±0.02	0.8±0.08	1.0±0.02	1.2±0.01	1.0±0.09	1.6±0.04	6.7±0.08	1.4±0.04
[Mg] /10^3	1.84±0.07	1.9±0.01	2.7±0.03	3.2±0.03	5.2±0.1	2.6±0.01	4.0±0.1	4.8±0.1	3.8±0.04	3.3±0.2
[K] /10^3	1.3±0.008	5.0±0.1	1.8±0.02	1.8±0.1	2.4±0.03	1.4±0.01	6.1±0.03	4.0±0.1	1.8±0.02	1.4±0.04
[Zn] /10^3	0.9±0.02	0.001±0.00001	0.9±0.02	0.5±0.02	5.4±0.1	0.5±0.01	0.8±0.06	1.6±0.01	0.3±0.03	1.6±0.1
[Na] /10^3	0.8±0.01	4.2±0.1	<0.10	0.2±0.003	1.5±0.01	1.1±0.1	0.3±0.03	1.0±0.02	0.4±0.02	1.03±0.03
[Si] /10^3	0.2±0.01	0.2±0.01	0.4±0.01	0.3±0.03	27.8±1.2	0.3±0.02	0.3±0.001	0.2±0.02	0.3±0.02	0.4±0.01
[Mn] /10^2	10.9±0.1	0.7±0.01	7.3±0.03	2.7±0.03	3.1±0.02	1.7±0.01	3.6±0.2	3.8±8.0	27.1±0.2	3.7±0.2
[Cu] /10^2	2.3±0.1	1.3±0.2	2.8±0.1	2.5±0.1	429.22±4.32	2.5±0.02	3.0±0.2	3.3±0.04	0.6±0.01	3.7±0.04
[Cr] /10^2	0.5±0.01	0.9±0.08	0.8±0.03	0.7±0.07	117.28±4.84	0.3±0.002	1.3±0.01	2.2±0.02	1.4±0.01	0.9±0.01
[Ba] /10^2	2.5±0.02	0.5±0.01	4.0±0.1	2.5±0.03	404.83±4.85	2.5±0.02	3.4±0.2	3.8±0.04	2.7±0.02	4.1±0.1
[Pb] /10^2	0.8±0.01	0.8±0.01	0.9±0.01	1.4±0.1	142.60±8.25	1.0±0.02	1.1±0.1	1.3±0.01	0.5±0.01	1.9±2.4
[Sr] /10^2	0.7±0.002	0.003±0.00001	0.7±0.01	0.7±0.01	81.40±1.43	0.5±0.003	0.7±0.06	0.9±0.02	0.4±0.003	0.8±3.5
[Se] /10^2	1.8±0.004	2.2±0.1	3.3±0.1	0.3±0.004	39.65±2.45	1.8±0.03	2.3±0.01	3.5±0.04	1.4±0.02	0.4±0.2
[B] /10^2	1.6±0.03	0.002±0.00002	1.4±0.1	2.5±0.2	<4.74	0.07±0.01	2.2±0.2	1.9±0.07	2.8±0.08	1.9±0.7
[Ni] /10^2	0.3±0.008	0.0001±0.00001	0.4±0.03	0.3±0.008	0.9±0.04	0.1±0.0003	0.5±0.05	1.3±0.02	0.7±0.02	0.5±0.008
Co	5.8±0.3	2.9±0.1	8.9±0.3	6.6±0.6	10.1±0.5	8.4±0.1	6.4±0.5	8.8±0.1	35.5±0.4	20.0±1.4
Mo	8.5±0.2	0.07±0.005	7.3±0.1	8.2±0.4	13.5±0.7	6.4±0.45	8.7±0.04	12.0±0.2	15.9±0.5	17.6±0.1
Cd	2.6±0.2	36.0±0.4	2.7±0.1	3.5±0.2	3.8±0.2	2.3±0.1	2.1±0.2	3.0±0.1	5.8±0.1	4.8±0.1
Be	<0.16	<0.16	<0.16	<0.16	<0.16	<0.16	<0.16	<0.16	<0.16	<0.16

G6. Limpopo Province

Plant No	46	47	48	49	50	51	52
Sewage work	Pietersburg	Pietersburg	Seshogo	Phalaborwa	Tzaneen	Mangweng	Mangweng
Elements	Mean	Mean	Mean	Mean	Mean	Mean	Mean
[P] /10^4	6.9±0.05	3.3±0.06	4.2±0.1	6.6±0.2	2.6±0.04	2.3±0.08	2.2±0.08
[Ca] /10^4	0.4±0.01	3.4±0.03	4.6±0.02	1.6±0.05	1.0±0.01	1.5±0.05	1.8±0.1
[Fe] /10^4	0.7±0.01	1.4±0.02	1.6±0.01	0.7±0.02	1.3±0.02	1.5±0.05	1.5±0.04
[Al] /10^4	0.5±0.01	0.9±0.03	2.0±0.01	0.3±0.01	1.4±0.02	1.5±0.03	1.5±0.03
[Mg] /10^3	5.6±0.1	2.6±0.02	3.5±0.02	6.5±0.2	1.9±0.02	2.2±0.03	2.0±0.1
[K] /10^3	7.0±0.08	1.2±0.08	1.9±0.02	5.4±0.1	1.2±0.01	1.0±0.01	0.001±0.02
[Zn] /10^3	0.7±0.01	1.1±0.1	1.4±0.03	0.8±0.03	0.8±0.02	0.9±0.02	0.7±0.001
[Na] /10^3	3.8±0.04	1.8±0.05	1.4±0.02	1.0±0.1	1.2±0.03	0.5±0.01	0.8±0.03
[Si] /10^3	0.4±0.008	0.4±0.03	0.4±0.007	0.7±0.06	0.3±0.006	0.3±0.01	0.3±0.1
[Mn] /10^2	2.2±0.04	3.4±0.04	2.8±0.02	0.9±0.04	1.8±0.02	2.5±0.04	1.8±0.02
[Cu] /10^2	1.8±0.02	2.6±0.2	4.6±0.1	6.2±0.1	3.1±0.3	1.6±0.04	2.8±0.09
[Cr] /10^2	0.7±0.02	1.3±0.08	2.5±0.2	1.6±0.05	0.5±0.01	0.6±0.01	0.9±0.02
[Ba] /10^2	2.0±0.07	3.3±0.09	3.0±0.02	2.3±0.1	2.4±0.1	2.7±0.03	1.9±0.02
[Pb] /10^2	1.5±0.09	1.6±0.1	0.9±0.02	0.7±0.05	3.3±0.01	0.7±0.05	0.5±0.05
[Sr] /10^2	0.6±0.01	0.9±0.04	1.3±0.01	0.7±0.03	0.3±0.002	0.5±1.04	0.4±0.02
[Se] /10^2	0.2±0.01	0.3±0.001	0.5±0.02	0.09±0.01	4.6±0.4	0.4±0.01	0.3±0.002
[B] /10^2	3.1±0.2	<4.74	<4.74	0.09±0.01	<4.74	1.2±0.04	<4.74
[Ni] /10^2	0.3±0.01	0.4±0.03	1.0±0.09	0.3±0.03	0.3±0.003	0.3±0.003	0.4±0.02
Co	4.4±0.1	9.1±0.3	13.7±0.1	9.7±0.5	12.1±0.3	6.4±0.2	10.1±0.4
Mo	6.1±0.2	8.8±0.6	11.2±0.5	4.5±0.1	10.7±0.2	6.7±0.08	5.7±0.3
Cd	5.0±0.1	3.2±0.1	2.7±0.2	2.0±0.1	2.2±0.02	1.7±0.03	1.5±0.02
Be	<0.16	<0.16	<0.16	<0.16	<0.16	<0.16	<0.16

G7. Northwest Province

Plant No	53	54	55	69	70	71	73
Sewage work Elements	Rustenburg Mean	Boitekong Mean	Brits Mean	Orkney Mean	Klerksdorp Mean	Wolmranstad Mean	Vryburg Mean
[P] $/10^4$	6.7±0.3	4.9±0.06	7.7±0.2	1.5±0.01	4.7±0.01	2.2±0.02	5.9±0.1
[Ca] $/10^4$	4.5±0.03	0.5±0.003	0.4±0.01	1.6±0.02	3.3±0.02	2.5±0.2	4.3±0.03
[Fe] $/10^4$	1.0±0.04	1.1±0.001	3.9±0.1	0.9±0.01	1.4±0.01	1.0±0.08	1.3±0.01
[Al] $/10^4$	0.4±0.01	1.6±0.03	1.1±0.009	0.6±0.01	0.9±0.03	0.8±0.01	1.1± 0.01
[Mg] $/10^3$	5.6±0.3	6.4±0.3	6.7±0.3	1.0±0.004	3.7±0.03	2.8±0.2	8.5±0.1
[K] $/10^3$	1.8±0.02	3.7±0.03	5.4±0.04	1.4±0.02	2.2±0.03	1.9±0.01	3.6±0.03
[Zn] $/10^3$	0.7±0.01	0.9±0.01	2.9±0.03	1.2±0.04	1.3±0.03	0.9±0.06	1.6±0.01
[Na] $/10^3$	2.8±0.2	1.2±0.04	3.2±0.04	1.1±0.04	1.2±0.03	1.0±0.003	1.6±0.02
[Si] $/10^3$	0.3±0.01	0.2±0.01	0.3±0.007	0.3±0.02	0.4±0.02	0.3±0.01	0.3±0.002
[Mn] $/10^2$	0.9±0.03	2.0±0.03	8.2±0.2	4.1±0.3	4.3±0.05	1.5±0.1	1.4±0.01
[Cu] $/10^2$	2.2±0.04	2.3±0.03	24.6±0.1	3.2±0.1	3.3±0.1	2.0±0.03	2.1±0.02
[Cr] $/10^2$	0.4±0.01	1.0±0.01	171.0±0.9	0.7±0.05	0.5±0.01	0.6±0.01	0.5±0.01
[Ba] $/10^2$	0.9±0.04	2.4±0.01	1.8±1.00	3.4±0.1	2.3±0.03	1.7±0.01	1.6±0.02
[Pb] $/10^2$	2.4±0.03	0.6±0.02	0.8±0.001	1.1±0.05	1.1±0.02	2.0±0.03	1.7±0.1
[Sr] $/10^2$	1.8±0.1	0.9±0.01	1.0±0.01	0.8±0.01	1.0±0.002	0.9±0.01	0.6±0.01
[Se] $/10^2$	0.2±0.01	1.8±0.03	0.4±0.002	0.4±0.03	0.3±0.02	1.9±0.01	0.4±0.02
[B] $/10^2$	3.2±0.1	2.7±0.2	1.4±0.04	0.1±0.01	0.2±0.01	1.8±0.1	0.2±0.01
[Ni] $/10^2$	0.3±0.003	0.9±0.01	0.9±0.01	0.4±0.02	0.4±0.03	0.3±0.02	0.4±0.02
Co	2.8±0.05	9.9±0.1	23.1±1.3	19.3±0.6	16.7±0.4	7.2±0.3	11.6±0.2
Mo	4.5±0.1	8.8±0.6	10.1±0.1	13.8±1.2	10.7±0.9	7.1±0.1	6.2±0.5
Cd	1.6±0.05	1.8±0.04	13.3±0.2	2.8±0.1	3.8±0.1	2.0±0.1	1.7±0.04
Be	<0.16	<0.16	<0.16	<0.16	<0.16	<0.16	<0.16

G8. Eastern Cape Province

Plant No	61	78	79	80
Sewage work	East London	Potsdam	Fishwater flats	Cape Recife
Elements	Mean	Mean	Mean	Mean
[P] /10^4	1.9±0.01	2.2±0.1	3.5±0.05	5.8±0.6
[Ca] /10^4	0.90.09	0.4±0.01	10.4± 0.3	2.5±0.05
[Fe] /10^4	1.3±0.1	1.8±0.02	2.5±0.07	0.6±0.05
[Al] /10^4	1.3± 0.004	1.5± 0.03	1.7± 0.01	0.5±0.002
[Mg] /10^3	1.7±0.1	1.6±0.02	7.4±0.1	4.6±0.4
[K] /10^3	1.7±0.05	2.0±0.04	2.7±0.02	1.6±0.01
[Zn] /10^3	0.7±0.05	1.4±0.02	1.3±0.02	0.7±0.07
[Na] /10^3	<0.10	<0.10	0.9±0.01	<0.10
[Si] /10^3	0.4±0.01	0.3±0.01	0.3±0.03	0.4±0.1
[Mn] /10^2	1.7±0.02	3.2±0.1	13.5± 0.5	1.2±0.01
[Cu] /10^2	4.8±0.4	5.8±0.1	2.7±0.1	4.3±0.06
[Cr] /10^2	1.3±0.03	1.6±0.05	74.3±1.1	1.1±0.08
[Ba] /10^2	3.4±0.3	3.3±0.02	3.1±0.05	2.4±0.03
[Pb] /10^2	1.3±0.03	1.3±0.07	2.8±0.05	1.3±0.1
[Sr] /10^2	0.8±0.04	0.9±0.07	2.1±0.02	1.8±0.02
[Se] /10^2	2.7±0.1	3.7±0.04	3.6±0.04	0.2±0.01
[B] /10^2	1.6±0.1	1.4±0.02	2.0±0.03	3.9±0.1
[Ni] /10^2	0.6±0.008	0.7±0.009	0.9±0.02	0.5±0.006
Co	8.3±0.1	9.1±0.4	9.2±0.1	4.5±0.01
Mo	13.2±0.2	9.4±0.2	16.1±0.8	6.2±0.1
Cd	2.8±0.03	3.4±0.1	4.0±0.2	2.6±0.1
Be	<0.16	<0.16	<0.16	<0.16

G9. Northern Cape Province

Plant No	67	68	72	74
Sewage work Elements	Kameelmond Mean	Kameelmond Mean	Kimberley Mean	Kuruman Mean
[P] /10^4	3.2±0.03	3.5±0.03	2.1±0.1	5.3±0.1
[Ca] /10^4	2.6±0.03	3.8±0.03	1.6±0.04	2.3±0.04
[Fe] /10^4	1.0±0.01	1.0±0.01	1.5±0.1	0.7±0.03
[Al] /10^4	0.6±0.01	0.8±0.01	0.8±0.04	0.4±0.02
[Mg] /10^3	5.1±0.03	3.6±0.03	6.2±0.3	3.9±0.1
[K] /10^3	5.3±0.03	1.5±0.02	0.9±0.0	0.7±0.02
[Zn] /10^3	0.9±0.02	0.8±0.01	0.8±0.03	0.8±0.01
[Na] /10^3	2.0±0.1	1.6±0.05	0.2±0.01	0.9±0.02
[Si] /10^3	0.3±0.02	37.7± 0.3	0.1±0.003	0.1±0.001
[Mn] /10^2	13.0± 0.2	2.3±0.01	1.6±0.1	2.7±0.1
[Cu] /10^2	3.5±0.03	3.3±0.1	2.3±0.1	1.5±0.01
[Cr] /10^2	0.4±0.01	0.2±0.02	0.6±0.02	0.3±0.004
[Ba] /10^2	3.0±0.03	1.9±0.1	3.1±0.1	0.8±0.01
[Pb] /10^2	1.5±0.01	1.4±0.1	0.8±0.04	0.8±0.01
[Sr] /10^2	2.2±0.02	1.5±0.01	0.8±0.04	0.3±0.01
[Se] /10^2	0.3±0.01	1.5±0.02	1.8±0.1	0.8±0.03
[B] /10^2	3.1±0.1	0.2±0.01	1.2±0.02	1.5±0.1
[Ni] /10^2	0.3±0.001	0.2±0.009	0.5±0.02	0.2±0.004
Co	7.8±0.2	2.8±0.1	7.6±0.4	2.2±0.04
Mo	7.3±0.1	9.1±0.7	5.9±0.2	3.5±0.05
Cd	1.6±0.04	2.8±0.1	1.4±0.1	0.9±0.04
Be	<0.16	<0.16	<0.16	<0.16

APPENDIX H

Concentration (mg l^{-1}) of Mineral Ions of Liquid Sludges from Gauteng, Freestate and KwaZulu-Natal Provinces

Appendix H Concentration (mg l^{-1}) of Mineral Ions of Liquid Sludges from Gauteng, Freestate and KwaZulu Natal Provinces.

Provinces	**Gauteng**					**Free state**	**Kwa Zulu-Natal**
Plant No	01	09	12	21	22	25	42
Sewage work	Vlakplaats	Thakane	Baviaanspoort	Percy Steward	Flip Human	Thabong	Darvill
Element	Mean	Mean	Mean	Mean	Mean	Mean	Mean
[P]/ 10^2	1.6±0.03	2.2±0.1	5.2±0.1	4.0±0.02	5.1±0.5	3.3 ±0.01	0.1 ±0.003
[Ca]/10	0.6±0.01	2.9±0.1	4.0±0.2	6.2±0.03	6.8±0.02	5.1 ±0.2	13.9 ±0.3
Fe	*	0.6±0.04	1.3±0.1	2.9±0.2	2.4±0.2	*	*
Al	0.1±0.01	0.1±0.002	0.2±0.001	3.0±0.01	1.8±0.01	0.6 ±0.004	0.8 ±0.007
Mg	0.8±0.01	19.2±0.4	44.9±3.0	62.3±2.1	14.3±1.1	58.7 ±2.7	0.1 ±0.007
[K]/10	18.8±0.3	3.1±0.07	20.9±0.2	5.7±0.3	9.6±0.9	11.0 ±0.4	0.08 ±0.002
Zn	0.04±0.0002	0.04±0.003	0.2±0.01	0.4±0.01	0.8±0.07	11.8 ±0.2	0.09 ±0.005
[Na]/10^2	186.6±0.7	0.3±0.01	10.3±0.7	1.7±0.1	0.8±0.07	87.4 ±2.0	15.4 ±1.3
Si	14.0±0.5	1.1±0.01	1.6±0.02	1.0±0.02	1.3±0.01	1.2 ±0.01	0.6 ±0.01
Mn	*	0.58±0.03	0.6±0.04	9.2±0.3	0.06±0.001	0.6 ±0.02	*
Cu	*	*	*	0.07±0.003	*	*	*
Cr	*	*	*	0.2±0.01	0.4±0.03	*	*
Ba	0.02±0.002	*	0.02±0.0009	0.07±0.002	1.1±0.08	0.01 ±0.001	0.04 ±0.003
Pb	*	*	*	*	*	*	*
Sr	0.02±0.001	0.11±0.001	0.1±0.01	0.4±0.01	0.2±0.01	0.1 ±0.002	0.1 ±0.006
Se	*	*	*	*	*	*	*
B	*	*	*	0.1±0.01	0.02±0.001	0.05 ±0.002	0.2 ±0.01
Ni	*	*	0.01±0.001	0.2±0.007	0.3±0.02	0.02 ±0.001	*
Co	*	*	*	*	*	*	*
Mo	*	*	*	*	*	*	*
Cd	*	0.0008±0.00	*	*	*	*	*
Be	*	*	*	*	*	*	*

***Below detection limit (mg l^{-1}) (Appendix I): [Mn]** $<4.0\times10^{-4}$, **[Fe]** $<5.5\times10^{-3}$, **[Cu]** $<3.0\times10^{-3}$, **[Ba]** $<1.3\times10^{-4}$, **[Cr]** <0.004, **[Pb]** $<6.6\times10^{-3}$, , **[Se]** <0.019, **[B]** <0.047, **[Ni]** <0.012, **[Co]** $<8.0\times10^{-4}$, **[Mo]** $<2.7\times10^{-3}$, **[Cd]** $<4.5\times10^{-4}$, **[Be]** $<1.6\times10^{-3}$

APPENDIX I

Calculated Detection Limits of Elements

Appendix I Calculated Detection Limits of Elements.

	Detection limit	
Elements	mg kg^{-1}	mg l^{-1} (ppm)
P	420	4.2
Ca	0.26	0.0026
Fe	0.55	5.5×10^{-3}
Al	2.80	0.028
Mg	0.08	8.0×10^{-4}
K	0.90	9.0×10^{-3}
Zn	0.019	1.9×10^{-4}
Na	0.10	1.0×10^{-3}
Si	0.60	6.0×10^{-3}
Mn	0.04	4.0×10^{-4}
Cu	0.30	3.0×10^{-3}
Cr	0.40	0.004
Ba	0.013	1.3×10^{-4}
Pb	0.66	6.6×10^{-3}
Sr	0.005	5.0×10^{-5}
Se	1.90	0.019
B	4.74	0.047
Ni	1.20	0.012
Co	0.08	8.0×10^{-4}
Mo	0.27	2.7×10^{-3}
Cd	0.045	4.5×10^{-4}
Be	0.16	1.6×10^{-3}