Determination of Inorganic and Polynuclear Aromatic Hydrocarbon Contents in South African Sewage Sludges

By

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ABSTRACT

A total of 34 sewage sludge samples were collected from South African provinces: KwaZulu-Natal, Gauteng, North West and Western Cape province. The samples were analysed for mineral ions and polynuclear aromatic hydrocarbons (PAH). The methods used for sample preparation were US-EPA 3050B and 3540C for mineral ions and PAHs respectively. The moisture content was also analysed. A minimum of 4.5 % and maximum of 99.5 % moisture were detected in the samples. The sludge that had stayed longer in their sampling points had low moisture contents than those that were sampled immediately after production. A total of 22-minaral ions were detected in the samples. When these were quantified an abundance trend that was found to be most common was:

P>Ca>Fe>Al>Mg>K>Zn>Na>Mn>Cu>Ba>Cr>Pb>Si>Se>Sr>B>Ni>Mo>Co>Cd>Be.

Phosphorous was the most abundant mineral ion in most of the samples apart from calcium, which was found to be abundant in a few cases. Comparing these results to the South African guideline limits, it emerges that most of the sewage works are compliant with the guidelines. The mineral ion that was found to be above the set limit in most occasions was selenium. The current South African guidelines were found to compare favourably to those of other countries.

In the study 16 PAHs were also analysed, based on frequency of occurrence these were found to be:

benzo(b)fluorathene ~ benzo(k)fluoranthene> phenanthrene> acenaphthylene> fluorine> naphthalene> benzo(a)anthracene> chrysene> acenaphthene> benzo(a)pyrene> fluoranthene> anthracene ~ pyrene> benzo(g,h,i)perylene> indeno(1,2,3-cd)pyrene> dibenzo(a,h)anthracene

Dibenzo(a,h)pyrene was below the detection limit in all the samples analysed while benzo(b)fluoranthene and benzo(k)fluoranthene were the most abundant compounds. All the samples analysed had concentration of benzo(a)pyrene below the South African limit of 2.53 mg kg^{-1}. Comparing these guidelines with other international countries, South Africa specifies a single compound for monitoring while in other countries more than one compound is monitored. Thus South African guidelines need to be put in line with those of major EU countries such as Germany and Denmark with respect to PAH limits.

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:

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I hereby certify that the above statement is correct.

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ABBREVIATIONS

AES	Atomic Emission Spectroscopy
AOX	Sum of halogenated organic compounds
BOD	Biochemical Oxygen Demand
DDT	1,1,1-Trichloro-2,2-bis(4-chlorophenyl)ethene
DEHP	Di-2-(ethylhexyl)phthalate
DOC	Dissolved Organic Carbon
EDTA	Ethylene diaminetetraacetic acid
EIEs	Easily Ionizable Elements
EPA	Environmental Protection Agency
EU	European Union
FAAS	Flame Atomic Absorption Spectrometry
FID	Flame Ionization Detector
GC	Gas Chromatography
GP	Gauteng Province
HCB	Hexachlorobenzene
ICP-OES	Inductively Coupled Plasma – Optical Emission Spectrometry
JHB	Johannesburg
KZNP	KwaZulu-Natal Province
LAS	Linear Alkylbenzene Sulphonates
LD50	Lethal Dose
NP	4-Nonylphenole
NPE	Nonylphenole(+ethoxylate)
PAH	Polynuclear Aromatic Hydrocarbon
PCB	Polychlorinated Biphenyl
PCDD/F	Polychlorinated dibenzo-p-dioxins and furans
PPM	Parts Per Million
POP	Persistent Organic Pollutant
PTEs	Potentially Toxic Elements
PVC	Polyvinyl chloride
RF	Radio frequency

SA	South Africa
SBR	Signal To Background Ratio
SD	Standard Deviation
SNR	Signal to Noise Ratio
UK	United Kingdom
USA	United States of America
UWW	Urban Waste-Waters
VOC	Volatile Organic Compound
WAS	Waste Activated Sludge
WWTPs	Wastewater Treatment Plants

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Sewage Sludge Production and Treatment

CHAPTER 1

1 SEWAGE SLUDGE PRODUCTION AND TREATMENT

1.1 Introduction

Sewage sludge is defined as thick, malodorous slurry left behind in a sewage treatment plant after its load of human and industrial chemical wastes have been treated and the wastewater discharged.[1] From a chemical viewpoint, municipal wastewater (sewage) contains a large number of different chemical compounds, which are both organic and inorganic.[2] Sewage may also contain some non-biodegradable constituents such as pathogens, plastics, sand, grit and other material of dissolved and particulate form. Thus the resultant sludges would be a concentration of these non-water components of wastewaters.

Over the past decades quantities of sewage sludge have been increasing around the world for reasons such as:

- increasing populations,
- increasing access to sanitation and
- stricter regulations imposed on sewage works by governments requiring cleaner effluents.

Sewage sludge has been around for a very long time, and different disposal methods have been tried.[3,4] Some have even become obsolete due to the potential dangers they impose upon the environment. The aim of this review is to give an insight into the past and future possibilities with regard to the disposal and potential dangers associated with sewage sludge.

1.2 History

The practice of community-wide systematic collection, treatment and disposal of waste is fairly new, having evolved in the late 19th century.[3] During the initial stages of the practice, municipal wastewaters were directly discharged into rivers and on land at a safe distance from town;[4] hence all the wastewater collected got dispersed. Improvements in the wastewater treatment technologies led to the removal of most of the substances that were regarded as pollutants. The treatment processes for wastewater lead to solid residues that are basically an agglomeration of pollutants that were originally present in wastewaters. This in turn leaves water that is suitable and harmless for dispersal to the environment.

The first method to be adopted was that of allowing sewage to percolate through soil to which it was applied by various forms of irrigation.[4] Advancement led to soil being replaced by beds of stone. These beds were first operated on a batch mode. Percolating biological filters in which sewage trickled down the bed as it was being sprinkled continuously soon superseded this mode of operation.[4]

During early developmental stages of filters, it was found that by decanting off the liquid and replacing it with fresh liquid at intervals, the sludge retained in the vessel was gradually becoming a culture capable of oxidising the organic material in a matter of hours.[4] This was a big discovery as treatment times were to be reduced significantly. The sludge resulting from this treatment process is called activated sludge and has the property of being flocculent and thus can be settled with ease. The principal difference between filters and activated sludge plants is that the latter is cheaper in capital costs and occupies much less space.

As an alternative to filters and activated sludge treatments algal ponds were also developed.[4] In this process algae use solar energy to provide oxygen through photosynthesis. The aerobic bacteria that oxidize sludge organic matter as a source of food and cell materials utilize the oxygen that is generated in this process. However this process takes place mainly at the bottom levels of the pond, the surface of the pond is mainly aerated by atmospheric oxygen[4]. The main objective of a wastewater treatment process is to reduce the chances of waste-borne diseases such as typhoid and cholera. This is achieved by treating wastewater to acceptable levels of biochemical oxygen demand (BOD).

Biochemical oxygen demand is defined as the amount of oxygen required by bacteria while stabilising decomposable organic matter under aerobic conditions.[5] The BOD test acts as a measure of total organic (biodegradable) pollution of a water sample, by measuring the amount of oxygen they will require if they were to be discharged into a natural watercourse where aerobic conditions exists.[5] The above-mentioned wastewater treatment technologies form part of a secondary stage in the wastewater treatment process. Included as part of the process are stages such as preliminary treatment, primary treatment, secondary treatment, sludge treatment and sometimes tertiary treatment.

1.3 The Sewage Treatment Process

A typical sewage treatment process is a three-stage process with the first step being preliminary treatment, followed by primary sedimentation and the last being a secondary treatment stage. A flow diagram indicating these three stages is shown in Figure 1.1. The three stages will be discussed in detail and their significance in the sewage treatment process highlighted.

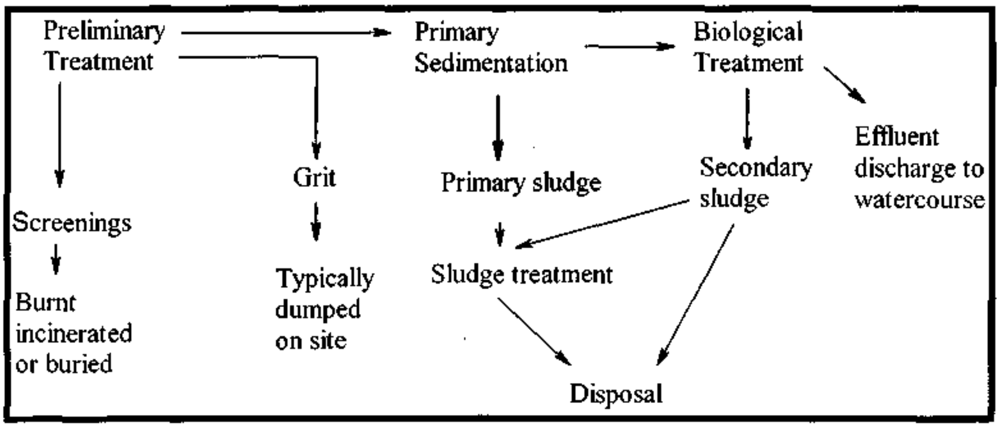

Figure 1.1 Flow diagram of a conventional sewage treatment works[6]

1.3.1 Preliminary treatment

Preliminary treatment is probably the first treatment procedure on entry of the sewage in a wastewater treatment process. This process is intended to remove all the floating and suspended materials from the entering sewage. The treatment at this stage has no significant impact on the removal of pollution in the sewage but rather to make the sewage more manageable in downstream processing. This is achieved through the removal of the large objects that might block or damage the equipment. Preliminary treatment is a two-stage process consisting of screening and grit removal stages.

Floating and/or very large suspended materials are usually removed by screens, which are usually made of parallel rods about 40-80 mm apart.[4] Materials bigger than the screen range are removed from the influent and they accumulate on the screen. These materials are then removed from the screens either manually or automatically. The materials collected from the screens are dispersed through either burial, incineration, digestion or composting [4,7]

On the screens only the largest suspended and floating materials are removed, but other potentially harmful materials such as grit and small stones can still remain in the influent. Materials such as grit and stones have the potential to damage the pumps and sometimes valves, thus for complete preliminary treatment they need to be removed from the influent.[9] The removal of these materials is usually achieved through passing of the influent in a constant velocity channel or in a detritus-settling tank. A constant velocity of about 0.3 m/s is maintained in the channel, which enables the heavier grit particles to settle from the sewage leaving only the lighter organic materials in suspension.[7] The principle is similar to that of a grit settling tank. The settled grit will then be removed from the bottom of the channel.

In other sewage works comminuters can be used as an alternative to screens. Comminuters consist of slotted drums through which sewage must pass; they act like sieves removing all floating and suspended materials bigger than the slots in the drums. Unlike the screens, which precede grit removal, comminuters are normally placed down stream of grit removal process. The removal of floating and suspended materials as well as the suspended stones and grit ensures a completion of the preliminary treatment.

1.3.2 Primary Sedimentation

The raw sewage, which has become more homogenous due to preliminary treatment, enters the primary sedimentation stage, which is the first step of pollution reduction. Rectangular or circular tanks with some sludge scraping mechanism/device are used. In small works hopper bottom tanks are usually used, these do not need any scraping device.

Sewage is clarified by flotation and sedimentation in these tanks. The materials which are less dense than the fluid from preliminary treatment (such as oily, greasy and fatty materials), will rise to the surface of the fluid to form a scum, while the heavier materials sink to the bottom.[4] The scum will be moved along the surface by skimming blades to a decanting device for discharge to the sludge well. Sedimentation in this tank again is a result of decrease in velocity of sewage.

The primary sedimentation stage removes about 55% of the suspended solids (S.S) and since some of the solids are biodegradable, about a 35% reduction in biochemical oxygen demand (BOD) is experienced.[6] The resultant effluent will have about 150 mg/L S.S and about 200 mg/L of BOD. These levels might be acceptable for dispersal on the ocean, however if the effluents are to be dispersed on rivers the levels are not acceptable, thus more treatment is necessary.

1.3.3 Secondary Treatment

There are generally two types of biological treatment process; these are either activated sludge or the percolating filter. Both these treatments use two vessels. In the first vessel there will be some reduction of BOD by microorganisms, while in the second the microorganisms are separated from the final effluent.

1.3.3.1 Percolating filter [6]

Percolating filters consist of beds of stones, slag or similar materials. Sewage is sprinkled on the surface of the bed and flows as a thin film over the stones so that ample air voids are left. The stones become coated with a gelatinous film containing microorganisms, which oxidise organic materials in the sewage. Thus, filtration in this context means passing of the sewage through a device that causes the removal of some characteristics of the liquor.

Percolating filters can either be circular or rectangular beds of broken rocks, gravel, clinker, or slag with sizes in the range 50-100 mm. The beds can be between 1.5-2.0 m deep and their diameters vary according to the population they serve. In between the filling materials are voids (empty spaces) with a proportion of about 45-55% to the filling materials. The settled sewage from the primary sedimentation unit trickles through the medium, which constitutes a very large surface area on which a microbial film can develop. The reduction of BOD takes place in this film made of bacteria, fungi, protozoa and algae on the upper surface.

Near the surface, micoorganisms in the gelatinous layer seem to be organised into three layers. The top layer is a thin layer (~0.3 mm) then the main algal layer of approximately 1.2 mm and they both sit on top of the basal layer of about 0.5 mm containing algae, fungi, and bacteria. However, algae seem to be in all three layers to some extent. Beneath the surface the film is modified into two layers due to the absence of algae as a result of the sunlight being excluded. Photosynthesis supplies about 5% or less of the oxygen requirements of the microorganisms in the filter. Oxygen supply is an intermittent supply since it can only occur under sunlight. Fungi are efficient in decreasing of BOD but are the least desirable since they produces more biomass than bacteria per unit mass of BOD oxidised. Moreover, the accumulation of fungal film may result to impeding of aeration and drainage since it can cause blockage in the interstices of the filter.

1.3.3.2 Activated Sludge Process

The activated sludge process is a two-vessel process, with the first vessel (reactor) containing microorganisms, which oxidise organic matter and hence reduce BOD, while the second is a sedimentation tank designed to separate the affluent from microorganisms. Development of this process dates back as early as 1913 when it was first used in Manchester.[6] In this process microorganisms removed in the sedimentation tank are recycled. The feedback of the cells from the sedimentation tank promotes rapid adsorption of pollutants in the incoming sewage and also stabilise the operation over a wide range of dilution factors and substrate concentrations.

The reactor in the activated sludge process is usually a long, deep channel.[6] The sewage is mixed with returned sludge to produce a mixed liquor before it enters into the channel. This liquor is aerated for about six hours as it passes through the channel, prior to secondary sedimentation. In the channel organisms use the organic matter as a source of food to maintain life and synthesize new cells. The treated mixed liquor then reaches the secondary settling tank, which under normal circumstances settles the activated sludge quite readily leaving a clear supernatant liquid.[4]

1.3.4 Outflows from a wastewater treatment plant

When the wastewater has been treated to environmentally acceptable levels, it is also necessary to treat and dispose of the sludge produced in such a way that mankind, animals and plants in the environment are not harmed. The sludges produced at the wastewater treatment plants are very active biologically and this causes uncontrolled biodegradation, which can create very unpleasant odours. It also provides a breeding site for insects and vermin, which have the potential of spreading diseases as they carry the pathogens present in the sludge. Most of the pathogens found in sludge such as viruses, bacteria and worms are of human and animal origin.[7,8]

The challenge imposed by the increase in the quantities of sewage sludge is that of the effective handling of sludge by wastewater treatment personnel in a cost effective, and in community-approved manner. Some of the reasons causing the handling of sludge to be a difficulty include the following:[9]

- High concentrations of substances that are responsible for offensive odours in untreated wastewater.
- The presence of high heavy metal concentrations.
- Presence of organic matter that can decompose to give offensive odours.
- Presence of high nutrient concentrations such as nitrogen and phosphorous, these can lead to harmful effects on surface and underground waters.

Thus, before disposal of the sludge, it is necessary to treat it to convert it to produce sludge of acceptable nature. The treatment processes that are used vary depending on the plant mandate and the intended use of the sludge.

When the sludge has been separated from wastewater the primary function becomes that of reducing the amount of water and stabilising the sludge for disposal.[10] The sludge treatment process can be divided into the following non-prescriptive functions: thickening, stabilisation, conditioning, disinfections, dewatering, composting, and thermal processes. The selected combination of these steps may be different from plant to plant.

Sludge thickening is performed with the aim of reducing the volume of sludge by reduction of its water content. The treatment results in the reduction in the operating and capital costs of the remaining sludge treatment. Stabilisation reduces the number of pathogens and the amount of odours emitted by the sludge. Conditioning is performed prior to dewatering with the purpose of improving the de-waterability of sludge. Disinfection is the process where the pathogens are either destroyed or deactivated so that they stop reproducing.

Dewatering is a process designed to remove a substantial amount of water such that the sludge solid concentrations of about 20-40% are reached.[10] The significance of water is of high importance especially prior to incineration and composting of sludge. Dewatering is also important when the sludge is to be landfilled as it reduces the amount of leachates, and this also reduces volumes and consequently transport costs. There are many dewatering methods that are employed around the world, the most commonly used are: drying beds, lagoons, pressure filters, belt filter press, perched beds, solar drying and centrifuges.

The sludge produced by South African wastewater treatment plants can be classified into four categories ranging from A to D as shown in Table 1.1. Type D sludge is recommended for unrestricted use on land and this is the sludge of high quality.[11]

Table 1.1 Classification of sewage sludge to be disposed of on land [11]

Type of sewage sludge	Origin/treatment	Characteristics Quality of Sewage Sludge.
Type A Sludge	Raw sewage; Cold digested sludge; Septic tank sludge; Oxidation pond sludge	Unstable and can cause odour nuisances and fly breeding. Contains pathogenic organisms and variable metal and inorganic content.
Type B Sludge	Anaerobic digested sludge; Surplus activated sludge; Humus tank sludge.	Fully or partially stabilized. Should not cause significant odour nuisance or fly breeding. Contains pathogenic organisms and variable metal and inorganic content.
Type C Sludge	Pasteurised sludge; Heat-treated sludge; Lime-stabilised sludge; Composted sludge; Irradiated sludge.	Certified to comply with the following qualified requirement: Stabilised, should not cause odour nuisances or fly-breeding; Contains no variable *Ascaris ova* per 10 g dry sludge; Maximum 0 *Salmonella* per 10 g dry sludge; Maximum 1000 Faecal coliform per 10 g dry sludge immediately after treatment; Variable metal and inorganic content.
Type D Sludge A sludge product for unrestricted use on land with or without the addition of plant nutrients or other materials. Must be registered in terms of Act 36 of 1947 if used for agricultural activities.	Pasteurised sludge; Heat-treated sludge; Lime stabilised sludge; Composted sludge; Irrigated sludge.	Certified: Stabilised- should not cause odour nuisances or fly breeding; Contains no viable *Ascaris ova* per 10 g dry sludge; Max 0 *Salmonella* per 10 g dry sludge; Max 1000 Faecal coliform per 10 g dry sludge immediately after treatment; Maxi metal and inorganic content in dry sludge; User must be informed about the moisture and N, P and K content; User must be warned that not more than 8 t/ha/year may be applied to soil and that the pH of the soil should be preferably be higher than 6.5.

The presence of heavy metals such as cadmium, lead, manganese, chromium and cadmium and toxic organic compounds such as pesticides, polychlorinated biphenyls (PCBs), phenolic compounds and polynuclear aromatic hydrocarbons (PAHs) can be attributed to local industries. As can be deduced, sewage sludge is a potential nuisance and a health hazard which when disposed without caution can contaminate land, sea, surface and ground waters with pathogens, heavy metals and toxic organisms.

1.4 Methods of sewage sludge disposal

Over the past decades the four main disposal routes have been landfilling, incineration, land spreading (agricultural use) and ocean dumping. However, ocean dumping has recently been abandoned in most countries due to the impact this route has on the aquatic environment. Effects such as algal bloom and the accumulation of heavy metals in the ocean environment have been attributed to this disposal route and is said to harm the environment.[12]

1.4.1 Land filling

Land filling is one of the most popular methods of sewage sludge disposal, which has been in use for many years.[13] In this route volumes of sludge are buried under the land for disposal. The appealing factor about this route is that there are no strict regulations on the contents of contaminants that should be present in the sludge prior to disposal.[12] There are generally two types of landfilling that are used: mono-deposits, where only sludge is disposed of, and mixed deposits where the landfill is also used for municipal wastes.

The advantage with dedicated disposal sites is that sludge can be applied regularly at high application rates. Also there are no crops to be planted on the area and the public will have limited access to the sites and thus there is minimum risk of human infections. No attempts are made to utilise the sludge nutrient content or the soil conditioning properties of sludge. Landfilling in dedicated disposal sites is usually recommended for sewage works receiving heavy industrial inputs and those that produce sludge with high metal and organic contents.[13]

In a landfill sludge is concentrated in one location and this minimises the risks associated with sludge borne pollutants and pathogens. From a management and materials handling perspective landfilling provides a simple solution to disposal. On an economic standpoint it compares favourably with other options, since there are environmental and transport costs.

For a properly constructed landfill, minimal risks to the environment are posed by this practice.[14] The main observed risks associated with a landfill are due to the fact that organic waste in the landfill might undergo anaerobic decomposition resulting in production of gases such methane and carbon dioxide. Both of these gases are greenhouse gases, which have been associated with global warming.[14]

In addition, there is always a possibility of material leaching, such as oils, heavy metals, organic compounds and microorganisms. These leachings pose a major threat to the underground water system, since they are likely to contaminate these waters. Moreover, the operation of the landfill will generate impacts such as noise, and dust from delivery vehicles, as well as odours, land use disturbance of vegetation and landscape.

Landfilling in municipal solid waste landfills was once the method of choice for disposal of sludge. However, there has been a decline in the use of this method of disposal as result of many countries encouraging the beneficial disposal such as in the reclamation of soils, fertilizer, and material for construction.

1.4.2 Incineration

Incineration is a process where sewage sludge is burnt as a way of disposal. Incineration reduces the volume of the material to be disposed of, completely destroys pathogens, decomposes most organic substances and recovers the small amount of heat contained in sewage sludge.[14] This process however generates emissions in air such as particles, acidic gases, greenhouse gases, heavy metals, volatile organic compounds, and ashes that need to be disposed of. Sometimes the ashes produced from incineration are used in construction material.[14]

If this process is performed properly it can be the least harmful to the environment since no organic nor pathogens will result from the procedure while the metals will only concentrate in the ashes.[14] The process requires sophisticated systems to remove fine particulate matter and volatile pollutants from stack gases. Due to the process, benefits associated with organic matter and plant nutrients are lost. Incineration represents one of the most expensive methods of sludge disposal.

1.4.3 Ocean dumping

In ocean dumping procedures, sewage sludge is dumped into the ocean with the hope that toxic contaminants will be diluted to an extent that their concentrations will be insignificant. This method of disposal has been having observed effects in some of the US oceans, resulting into a ban of ocean dumping in 1992 in USA.[15]

1.4.4 Agricultural use of sewage sludge

Agricultural use is one of the longest used and remains as one of the reasonable and cost effective methods of disposal. The idea is to use the sludge as a resource in agriculture. This method has been under tremendous criticism from environmentalists who are concerned about the danger that might be posed by contaminants on the environment.

Land application, which is the controlled spreading of sewage sludge onto the soil surface, is by far the most popular means of sludge disposal, not least for its great economy. The benefits of applying sludge to land have long been recognised; it improves fertility and physical properties of the soil in the following ways:[16]

- Improves soil fertility
- Improves moisture holding capacity and ameliorates erosion
- Improves soil structure
- Encourage symbiotic micro-organism activity and
- Adds trace metals and elements.

There are, however three major concerns in application of sewage sludge to agricultural land

- Ground water pollution
- Odour production and
- Food chain contamination with metals, elements, pathogens and toxic organics.

The disposal methods already mentioned above are the most widely utilized disposal routes worldwide, however each country would have its own pattern with regard to the popular disposal route. At present only 28 % of the sludge produced in South Africa is used beneficially (Figure 1.3). This value is relatively low when compared to other countries such as Japan, United Kingdom, and the USA that are estimated to use about 42, 50 and 54% respectively.[17]

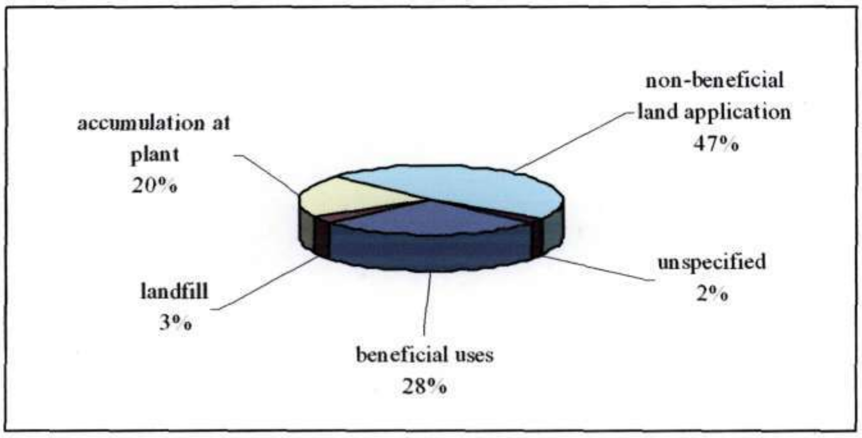

Figure 1.2 Sludge disposals in South Africa.[18]

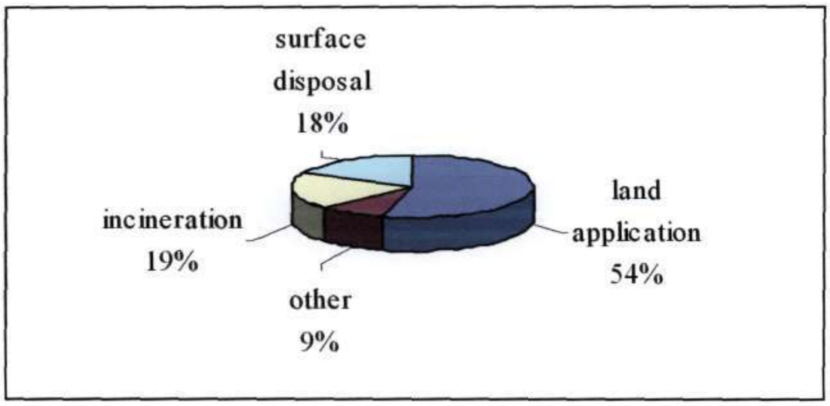

Figure 1.3 Use and disposal of sewage sludge in the Unites States[15]

Foster reported that conditions that are likely to influence land application of sewage sludge include: community size, soil properties, distance to sites, sludge properties and local cropping practices.[19] He also reported land spreading of sludge to be the low-cost alternative. Also, the dewatering was found to be beneficial only when sludge would have to be transported to relatively long distances. The wastewater treatment plants produce less than 1% of the effluents in the form of sludge, but about half of the total costs of wastewater treatment process are directed towards sludge treatment.[20] The recently increased interest in land application of sewage sludge among farmers and sewage sludge treatment operators is mainly due to economic benefits provided by this disposal route. This method of disposal is a challenge as it may not have been considered a viable option in design of other treatment plants. Thus the future challenge would be to try and incorporate this cheap disposal procedure to the already existing sewage treatment plants and to spread sludge such that the environment is not damaged by this practice.

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Chapter 2

Contaminants in Sewage Sludge

CHAPTER 2

2 CONTAMINANTS IN SEWAGE SLUDGE

Sewage sludge is basically composed of microbial and chemical contaminants. Chemical contaminants include organic compounds, inorganic materials, plant nutrients and trace elements such as heavy metals. These have been detected in sewage sludges around the world in countries such as Canada, Germany, USA, UK, Zimbabwe and South Africa just to mention a few.[1] Pathogens such as bacteria, viruses, protozoa, parasitic worms and fungi have also been found in many sewage sludges.[1] Table 2.1 classifies some of the typical substances, which have been found in the sewage sludge of USA.

Table 2.1 Substances found in sewage sludge in USA[1].

Group	Examples
Polychlorinated biphenyls (PCBs)	
Chlorinated pesticides	DDT, dieldin, aldrin, endrin, lindane, heptachlor, mirex, kepone, 2,4,5-T, 2,4-D
Chlorinated compounds	Dioxin, dichlorobenzene, trichlorobenzene, tetrachlorobenzene, chloroaniline, dichloroaniline, dichloronaphthalene, trichlorophenol, pentachlorophenol, chlorobiphenyl.
Polynuclear aromatic hydrocarbons	Benzo(b)fluoranthene, benzo(k)fluoranthene, dibenzo(a,j)anthracene, perylene, chrysene, indo(1,2,3,c,d)pyrene, benzo(a)pyrene.
Heavy metals	Antimony, arsenic, cadmium, chromium, copper, lead, mercury, selenium, thorium, uranium, vanadium and zinc.
Pathogens	Bacteria, viruses, protozoa, parasitic worms, fungi.

2.1 Sources of pollution in the sewage sludge

The three main sources of pollution in wastewater entering a waste treatment plant are domestic and commercial discharges as well as urban runoff. Figure 2.1 represents a summary of the various inputs, outputs and the pathways followed by water and associated contaminants from both anthropogenic and natural sources in the environment.

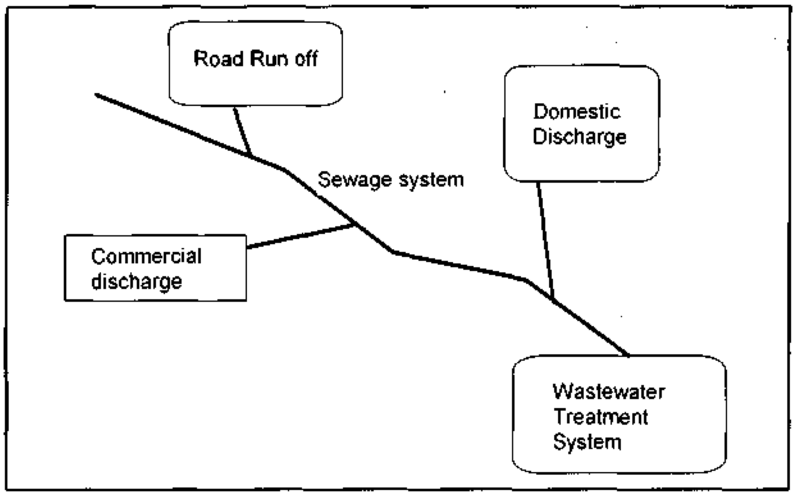


Figure 2.1 Sources and pathways of contaminants in urban wastewaters.

2.1.1 Domestic discharges

The domestic source of pollution is constituted by the following sub-sources: discharge from households, corrosion from materials used in distribution and plumbing networks,[2] tap water and detergents. Most of the discharges will be containing pollutants originating from cosmetics, hobby materials and medicines.

2.1.2 Commercial discharges

This section represents a significant fraction of the sources of pollutants. Most of the contaminants in the wastewater originate from effluent of the industries in that area. Metal industries are the main sources of heavy metals, while chemical industries such as those producing organic and petrochemicals, fertilizers, textile and leather industries contribute a significant amount of organic pollutants. Some chemicals are used as detergents during clean-up procedures while others will be the remnants in the vessels or reaction tanks, others come as dirt, dust or spillages being cleaned and washed from factory floors.

2.1.3 Runoff

Water originating from surfaces of roads and highways may end in sewage with all pollution types such as vehicle lubricant loss, load loss, tyre degradation, exhaust emission, road-surface degradation, road cleaning and atmospheric precipitation. Numerous studies have shown very high concentrations of heavy metals in the soils, plants, soil animals and air that can be correlated to traffic densities, and distances from the highway.[3]

According to the studies, which had been conducted previously, the main sources of pollution in urban precipitation runoff can be summarised as follows:[4]

- Road and vehicle related pollution
- Degradation of roofing materials
- Construction
- Litter, vegetation and associated human activities
- Erosion of soil

The atmospheric inputs to the urban runoff depend on the nature of the surrounding industries; on the proximity of the major emission sources such as smelters and coal fired power stations as well as the directions of the prevailing winds. The contributions from the industries can be so significant that, in some cases, the concentrations are five times higher in runoffs near commercial activities than in residential areas far from industrial areas.[4] Other significant runoffs are from roof runoffs and building runoffs, especially during storm events. It is important to note that the metal species released are usually in bioavailable form.

2.2 *Inorganic contaminants in sewage sludge*

Inorganic contaminants entering the wastewater treatment plant can be classified into two categories; plant nutrients and trace elements. These contaminants accumulate in sewage sludge, and hence constant monitoring and analysis of the sludge is undertaken to ensure that contaminants are kept at levels below those required by the legislations prior to land disposal of the sewage sludge. The contaminants present in sewage sludge can have detrimental effects on the treatment process of sludge as well as on the growth of plants and health of animals and marine life.[5]

The use of sewage sludge for agriculture and horticulture has been in practice for a number of years, since sewage sludge represents a good source of nutrients and soil conditioners to improve soil physical properties.[6] The agricultural land use comes as a result of nutrients such as nitrogen and phosphorous which are contained in significant amounts in sewage sludge. There are other trace elements in sewage sludge that might be beneficial to crops such as sodium, potassium and magnesium.[5]

The occurrence of metals in sewage sludge is due to the presence of metals in the incoming raw sewage. Sewage inherits metals from a number of sources such as industrial operations (e.g. metal finishing and printed circuit board production), corrosion of water pipes and urban storm water in combined sewered areas.[7] The metals that are of major concern are cadmium, chromium, copper, lead, manganese, nickel and zinc. This is because of wide spread occurrence in WWTP influent.

The minority of metals is removed in the primary settling tank while the majority is removed in the secondary settling tank by adsorption onto the biological flocs. The removal varies with the metal type but data shows that about 5-50% of metals can be removed in primary tank; while further removal of about 15-80% of the metal may occur during the secondary treatment.[7] Secondary treatments produce sludge that is used for beneficial purposes. There is, however, an obvious danger associated with this sludge since most of the metals will be concentrated in it.

Elements such as phosphorous, potassium, sodium, calcium, magnesium, barium, iron, aluminium, manganese, boron, arsenic, cobalt, molybdenum, mercury, lead, copper, nickel, cadmium, chromium and selenium have been detected in sewage sludges around the world.[8,9] The presence of these elements (which include heavy metals) in sludge is of major concern since most of the studies have shown a significant increase in the amount of heavy metals found in the soil as well as those that are mobile and bioavailable to crop uptake.[10]

The concentrations of toxic substances found in sewage sludge are generally higher than those found in typical soils. The continued use of sludge might thus result in adverse crop and food chain effects, due to plant uptake of certain trace metals and other contaminants which might be present in sludge; such as pathogens, organic and other inorganic pollutants.[8] Entry of these contaminants into the food chain might have serious health implications in the people consuming the foodstuffs. Entry of cadmium, for an example, might cause chronic health problems such as bone diseases, lung oedema, liver damage, renal dysfunctions and hypertension.[10] Apart from human health concerns, the presence of nonessential and potentially toxic metals in agricultural produce can have serious implications for international trade. The strict quality issues might end up becoming non-tariff barriers to trade.

2.2.1 Nutrients in sewage sludge

The utilization of sewage sludge as a fertilizer is mainly due to the high nutrient content that would be available for plant uptake. Some of the major nutrients present in sludge include nitrogen (N), phosphorous (P), calcium (Ca), magnesium (Mg), potassium (K) and sulfur (S).[12,13] These elements are essential to growth of vegetation; however, at elevated concentrations they are likely to contaminate other systems in the environment.

2.2.1.1 Nitrogen [14]

Nitrogen content in sewage sludge has been found to vary considerably in the ranges <1 to 176 g kg^{-1} for the total nitrogen (N); 5 to 67600 mg kg^{-1} for ammonium nitrogen (NH_4-N); 2 to 4900 mg kg^{-1} for NO_3-N. In the sludge only the inorganic nitrogen will be available for plant uptake (i.e. NH_4-N and NO_3-N). When the value of total N is reported it engulfs NO_3-N, NH_4-

N and organic N. Thus not all of the nitrogen gets to be available for plant uptake, some is volatilised to the atmosphere while some just remain as organic nitrogen and thus is unavailable to plants. Organic nitrogen can be converted to NH_4-N through a process called mineralisation.

2.2.1.2 Phosphorous

Phosphorous is an essential nutrient for plants which, when deficient, creates serious fertility problems in soils.[13,15] Excessive amounts, however in soils can result in immobilisation of other elements such as Zn and Cu.[16] Moreover plant uptake of phosphorous will generally increase with increasing available phosphorous contents from sewage sludge application.[17] Other consequences might include water eutrophication as a result of increased phosphorous concentrations.[18]

Sewage sludge provide a good source of phosphorous since phosphorous levels of about <1 to 143 g kg^{-1} for total phosphorous have been reported. These high phosphate contents have been attributed to phosphate in soaps and detergents.[19] The phosphorous in sewage sludge exists as organic and inorganic forms; the inorganic is generally the predominating form.[15] Only the inorganic form is available for plant uptake the organic phosphorous must first undergo mineralisation before it become available.[15] Hence sewage sludge applications will result in increased plant phosphorous and this will increase even further at high irrigation rates.[18]

The amounts of phosphorous present in sludge have been increasing very significantly owing to improved efficiencies in tertiary treatments.[17] The results are sewage sludges of high inorganic phosphorous content. When these sewage sludges are land applied the application rates are based on available nitrogen and this leaves a potential for phosphorous accumulation. Such accumulations might result in a serious impact on surface waters and eutrophication of lakes.[15] Phosphorous availability can be regulated by the addition of other elements such as Ca in sludge.[20]

2.2.1.3 Potassium

Potassium is an essential element to both man and plants. It has a physiological importance to man for the functioning of most of human body functions such as digestive, renal, endocrine, respiratory, neurological and cardiovascular systems.[21] Soil potassium is divided into non-exchangeable, exchangeable, and water soluble fractions. Almost all soil potassium is non-exchangeable (>99%), whereas plants can only draw the water soluble and exchangeable fractions. The general potassium demand for plants exceeds supply from soils[22] and as a result the use of fertilizers becomes a necessity if plant growth is to be kept at an optimum. Application of sewage sludge will generally contribute to crop available potassium since it contains small amounts of potassium.[15]

Potassium is one of the major plant nutrients that has been reported to be present in sewage sludge.[12] Usually the sewage sludge will contain only small amounts of potassium due to it being water-soluble. As a result, most of the potassium will be discharged with the sewage treatment effluent. Thus only small concentrations will be present in sludge at normal application rates.[8]

When the nutrient value of sewage sludge was compared to other fertilizers and soil amendments such as urea, rock phosphate, commercial phosphate, potassium, and nitrogen based fertilizers, it was found that they carry similar values.[23] However, sewage sludge and rock phosphate bear higher concentrations of heavy metals such as Cr, Cs, Cu, Fe, Pb, Se. Ti, Ag and Zn.[23]

2.2.2 Metallic elements found in sewage sludge

Potentially toxic elements are a primary concern since they have the potential to accumulate in soils and sediments for very long periods. The clear goals of all municipal wastewater treatment systems, as mentioned, are to reduce the levels of pollutants to background levels. However, the consequence is the transfer of these pollutants into sewage sludge.

It therefore becomes a necessity to treat these metal elements to acceptable levels to minimise the risk of contaminating the environment on which the sludge is dispersed. Shown in Table 2.2 is a list of inorganic pollutants, which are found in sewage sludge that are supposed to be regulated for proper disposal of sewage sludge in Southern Africa.

Table 2.2 Allowable Concentrations in a Type D Sludge in South Africa.[24]

Element	Leachable fraction Concentration (mg kg^{-1} ds)	Total concentration (mg kg^{-1} ds)
Cadmium	15.7	20
Cobalt	-	100
Chromium	-	1750
Copper	50.5	750
Mercury	-	10
Molybdenum	-	25
Nickel	-	200
Lead	50.5	400
Zinc	353.5	2750
Arsenic	-	15
Selenium	-	15
Boron	-	80
Fluoride	-	400

ds – dry solid

2.2.2.1 Zinc

Zinc is a metal readily taken up by plants from soil and translocated to leaves and shoots, it is an essential metal for plant life.[19] Although essential, zinc can be phytotoxic if present in excessive amounts.[8,15] Sludge exhibits a wide range of Zn concentrations, which are generally higher than the background levels found in soils.[14] Thus, it is clear that the uncontrolled use of sewage sludge on agricultural land will lead to accumulation of Zn in the soil and consequently creates a risk for plants and animals. Different plants have different tolerance levels to zinc toxicity.[14] Toxic levels in plants cause a reduction in root growth and leaf expansion that is then followed by chlorosis.

Zinc is essential to animals and humans and is an indispensable component of more than 200 enzymes and proteins.[25] In humans and livestock, toxicity is observed after intake of several grams, with 6 grams being considered as a lethal dose.[14] Ingestion of excessive amounts of zinc by live stock result in gastrointestinal disorders, decreased food consumption, and growth by these animals, while resulting to vomiting and diarrhoea for humans.[14]

The sources of zinc can be both domestic and industrial. Domestic sources include corrosion and leaching of plumbing, anti pest products such as rat poisons, wood preservatives, deodorants and cosmetics, medicines and ointments, paints and pigments.[2] The industries that use zinc involve the following processes:

- production of brass and bronze alloys, tyres, batteries, paints, plastics, rubber, fungicides, paper, textiles, building materials and special cements. It is also used in galvanizing processes and in cosmetics and pharmaceuticals.[60]

2.2.2.2 Copper

Copper is an essential element to plants, animals and man. In large quantities phytotoxicity is possible in plants and copper can be toxic to animals as well.[8] The chemistry of copper shows that it can be specifically adsorbed or fixed with soil. Thus continuous use of sewage sludge is capable of increasing the copper content of soil.

Copper levels of 21 mg kg^{-1} and above could indicate excessive accumulation in plants.[14] Copper is capable of replacing other metals such as iron from physiologically important centres, and this might lead to chlorosis.[14] Its toxicity may lead to reduced branching, thickening and abnormally dark coloration in rootlets of many plants. Copper poisoning is also found in animals, especially sheep where the main accumulation site will be in the liver and kidneys of the infected animal.[8] Acute copper toxicity in humans is rare and it is associated with gram quantities and includes haemolysis and renal damage.[14] A single dose of 0.1 to 0.2 mg kg^{-1} body weight can lead to gastrointestinal disturbances in sensitive people.

The main sources of copper include corrosion and leaching of plumbing, fungicides (copper(I) chloride), pigments, wood preservatives, and antifouling paints. Copper is used in electronics, plating, textile, rubber, printing, plastic and brass and other alloy industries.

2.2.2.3 Nickel

Nickel is an essential element for plants, animal and man. It can be highly toxic to most plants, where toxicity manifests itself in chlorosis and yield reduction.[15] It is taken up by the roots and translocated to shoots and leaves. The metal can be toxic to animals or humans at very high concentrations.

Nickel can be found in alloys used in food processing and sanitary installations; in rechargeable batteries and protective coating. Nickel is used in the production of alloys, electroplating, catalysts and nickel-cadmium batteries. Some of the main sources of nickel emission include launderettes, small electroplating plants, old pigments and paints.[8]

2.2.2.4 Cadmium

Cadmium is a natural element in soils and geological materials, it can also enter the environment from fertilizers, zinc-associated compounds, plastics, batteries, coated metals, paints and smelting and purification of metal ores.[15] The metal is phytotoxic and even highly toxic to humans.[14] It is readily absorbed from soils and translocated to plants.

Cadmium concentrations of about 3 mg kg^{-1}, depress growth in plants.[14] It interferes with photosynthesis as well as uptake and transportation of nutrients. Cadmium is considered to be one of the most mobile pollutants, thus its plant concentrations are correlated to the concentrations in soil.[17] Cadmium can accumulate in certain tissues of the plant without showing any toxic effect, however these might cause some harmful effects to humans and animals. It is a cumulative poison in animals as it accumulates in their kidneys, liver and spleen. In humans it is known to cause hypertension, diarrhoea, cancer, immune disorders, coughing, headaches, brown urine and renal failure.[14] Man is usually exposed to this metal through food intake of cereals and vegetables.[17]

Substantial amounts of cadmium can be found in batteries and paints. Nevertheless, the main sources in wastewater are food products, detergents, body care products and storm water.[2] The various sources in sewage sludge include human excretion, domestic production, and storm waters containing particles of rubber tyres and various industrial effluents.

2.2.2.5 Chromium

Chromium is present in sewage sludge as trivalent chromium (Cr^{3+}) this form is relatively non-toxic as compared to hexavalent form (Cr^{6+}).[8] The hexavalent form has been reported to demonstrate some carcinogenic properties. Cr^{6+} is readily reduced in soil to chromic (Cr^{3+}) a less mobile and less toxic species.[15] The highly toxic form, Cr^{6+}, is not usually found in sludge in any significant amounts.

Chromium sources include products and activities such as preservatives, dying and tanning. It is widely used as a tanning agent in leather processing, chromium^{3+} is the species that is used in this industry.[2] In many industries the use of the carcinogenic chromium^{6+} has found high restrictions.

In a study conducted in Finland[2] (Table 2.3) to investigate the sources of chromium in their wastewater, it was found that metal, chemical and leather industries are the major sources of chromium.

Table 2.3 Chromium emissions to water in Finland[2]

Source category	Emissions to water (not exclusively UWW)	
	Tonnes per annum	% of total contribution
Chemical industry	14.3	58.1
Paint Manufacture	0.01	<0.1
Electroplating	0.1	0.4
Ferro-chrome and stainless steel plants	4.6	18.7
Leather processing	5.5	22.5
Total	24.6	100.0

The figures in Table 2.3 cannot be used in SA, as a general trend for the chromium sources around the world because significant differences might be observed for different countries. Thus research with respect to a particular country is necessary for such trends.

2.2.2.6 Lead

Lead is a non-essential element, which can be very insoluble and thus plants do not readily take it up. It has the longest residence time compared to other elements.[14] This is due to its strong binding capacity to the particles and the formation of highly insoluble phosphate precipitates in the roots, resulting in a very small plant uptake. The possible routes towards human are through ingestion of contaminated sludge or soil by grazing animals. Sewage sludge can have variable lead contents, with concentrations at less than 1000 mg kg^{-1}.[14]

This metal has not been shown to be phytotoxic, but is toxic and cumulative in humans and animals. Lead can accumulate in some plants to levels of 350 mg kg^{-1} without visible harm. Plant roots readily take up this metal element, the amount varies with species and type, but less than 3% is translocated to the plant tops.[15]

Ingestion and inhalation represent the major routes of exposure to animals and humans. The toxicity effects in man include cancer, brain damage, anaemia, and many neurological symptoms. These are caused because lead mimics the calcium behaviour and inhibits many of the enzyme activities and also accumulates in the skeleton.[64]

Domestic sources of lead include old lead piping in water distribution system, old paint pigments, certain cosmetics and on ceramic dishes as glazes. Lead is also used in the fuel industry, batteries, pigments, solder, roofing cable covering, lead jointed waste pipes, ammunition, and other sources.[41]

2.2.2.7 Selenium

Selenium is found in geological materials on earth and is a component of soil due to weathering of rocks. It enters the atmosphere and the environment from volcanic activities and burning of fossil fuel, especially coal.[15] It is an essential element for livestock but can be toxic at high amounts. Its availability increases with pH of the soil. In alkaline soils, a total content of 5 mg kg^{-1} would have adverse effects.[14] It is however marginally available to plants due to adsorption in soil.[15] Selenium sources are food products and food supplements, shampoos and other cosmetics, old paint and pigments.

2.2.2.8 Molybdenum

Molybdenum is an essential element to plants, animals and man.[14] This metal is not phytotoxic; however, high intakes by animals can result in copper deficiency problems. In the soil it is associated with both the organic and inorganic fractions.[14] Clays and hydrous oxides absorb it and the amount absorbed will decrease with increasing soil Ph.[15] The metal becomes more available with increasing soil pH.

2.2.2.9 Boron

Boron is a metalloid widely distributed mainly as a sodium salt, borax (sodium tetraborate $Na_2B_4O_7$). It is an essential nutrient for plant growth but can be toxic if in excess. It is not toxic to animals at levels commonly found. Boron finds use in agriculture and in industries such as steel, glass, enamel and ceramic making [26]

2.2.2.10 Arsenic

Arsenic is a toxic element to animals and man, while being non-essential to plants. In treated sewage sludge the levels of arsenic are very small, and in sludge it is mostly present in its organic form, which is the less available form.[15] Under aerobic conditions ersenic will be strongly bound to the clay fraction making it less available for plant uptake, in addition it is not readily taken up by plants. Where taken it will be concentrated in the roots.[15]

Major sources of arsenic include natural sources and household products such as washing products, medicines, garden products, wood preservatives, old paint and pigments.[15]

2.2.2.11 Calcium

Calcium is an essential nutrient for plants, animals and man. It is not associated with any environmental or human health problems.[12] Deficiency of this nutrient in man is associated with bone defects. Sludge application in soils would generally increase the amount of mobile calcium and hence increase soil quality.[27]

2.2.2.12 Iron

Iron (Fe) is silver, malleable metal found in group VIII of the Periodic Table. It comprises about 4.7% of the earth's crust it can be extracted from ores such as hematite (Fe_2O_3), magnetite (Fe_3O_4), limonite (FeOOH), and siderite ($FeCO_3$). It is used in the manufacture of grades of steel such as soft steel used in electrical transformers and shipbuilding and hard steel used for metal cutting.[28]

Iron is an essential element for man, animal and plants.[14] It is macronutrient for plants where it is required for photosynthesis, respiration and nitrogen fixation. Deficiency results into chlorosis, a process shown by yellowing, blanching of leaves and limited growth. When present at too high concentrations it becomes toxic to plants. It is a micronutrient in humans and animals and is central in the transportation of oxygen; it is also a component of the proteins that play a role in energy metabolism. Deficiency of this element results in anaemia while excessive intake can result into heartburn, diarrhoea, as well as cardiovascular and carcinogenic risks.[22]

2.2.2.13 Manganese

Manganese is an essential element to man, animals and plants. In plants it is a micronutrient responsible for plant growth.[15] Manganese deficiency results into reproductive failure, skeletal defects and ataxia in humans and animals. A high intake in animals however results in growth retardation, anemia and gastrointestinal lesions.[22]

2.2.2.14 Cobalt

Cobalt is a transition element ranked 32nd in the abundance list on the earth's crust.[22] It exist on the earth crust as sulfidic copper ores and pyrites, the sulfidic ores are used to prepare metallic cobalt. Cobalt is used industrially to prepare metal alloys used in jet engines and gas turbines; it is also used in paints, fuel synthesis as a catalyst and in glass industry.

In soils the mobility of Co is pH dependent.[14] It is more mobile in acidic soils than in alkaline soils. Plant uptake of this element is species dependent; it shows a positive growth effect on some plants. Cobalt forms part of vitamin B_{12} and thus its classified as an essential element for animals and man. However, at high concentrations, it might result in allergic reactions and anaemia.[28]

2.2.2.15 Silicon

Silicon is among the most abundant elements on the earths' crust. It is a micronutrient essential for body functions of most animals.[29] It usually show low toxicity to most animals, even at high concentrations[28]. It is also an essential element for plants as it is responsible for control of the root system.[30] It has a number of industrial applications such as in glass manufacturing, computer chips, lubricants, and use in concrete and bricks.[31]

2.2.2.16 Aluminium [2,28]

Aluminium is the third most abundant element making up to 8.8% of the earth's crust and highly reactive metal, hence in nature does not appear as a free metal but compounds of oxygen, silicon and fluorine. It is used in structural materials in buildings and construction, in transportation, packaging and containers. It is used domestically as a household foil and its compounds are used in water purification, sugar refining, wood preservation, alloy making and in heat resistant paints.

The availability of the metal in soil decreases with increasing pH, at pH greater that 5.5 it becomes insoluble. Aluminium can have unfavourable effects such as inhibiting plant growth, reducing survival and impairment of reproduction in aquatic invertebrates, fish and amphibians. It is also toxic to human at high concentrations causing bone diseases, pulmonary and impairment of motor and memory functions.

2.2.2.17 Magnesium

Magnesium is one of the abundant elements on the earth's surface; it is a product of magnetic and metamorphic rocks and their weathering products.[22] It is an essential element with minor nutritional effects on plant and man. It shows low toxicity at high concentrations, but deficiencies of magnesium result in great risks on living organisms.[14] In sewage sludge it is present in concentrations around 1% of the dry solid.[8]

2.2.2.18 Beryllium [14]

Beryllium (Be) is an alkaline earth metal that forms compounds, which show poor solubility in water. Be occurs in some specific ores, but there is generally very little beryllium in the soil. However, it is present in coal and coal ashes may contain from 45 to over 1000 mg kg^{-1} Be. The solubility of Be compounds decreases with increasing soil pH, thus acidic soils promote plant uptake of Be.

Beryllium in water soluble form can be toxic to plants, this is of minimal concern since soil can fix it in forms that are unavailable to plants. Oral uptake by animals and humans has not shown any abnormalities, however inhalation can cause acute to chronic toxic reactions such as tumours and lung cancer.

2.2.2.19 Sodium [28]

Sodium is among the most abundant elements on the earth's crust. It is present in its deposits such as sodium chloride, sodium borate, sodium nitrate and sodium sulfate. Sodium is an important element affecting growth and development of a few plant species. At high concentrations sodium can be toxic to plants. Sodium is an essential element for man and animals. Deficiencies to man may lead to premature deaths.

2.2.2.20 Strontium

Strontium is an alkaline earth metal that occurs naturally as two mineral forms strontianite ($SrCO_3$) and selestite ($SrSO_4$). Strontium is used mainly in the manufacture of glass faceplates for colour television and computer tubes. It is also used in the automobile industry and in ferrous metallurgy. Strontium is an essential element for man with some physiological relevance; it also has some beneficial effects on plants. It is relatively low toxic to man and animals.[28]

2.3 Availability of metal in soil for plant uptake

The most important route of human exposure to trace elements from sewage sludge when it is applied on land is through plant uptake. Interestingly, the studies conducted on this subject have revealed the following findings.[32,33]

- Plant uptake is a function of plant species, individual trace elements, soil characteristics and sludge characteristics.
- Sludge acts as a source of trace elements while at the same time it acts as a sink of these elements.
- Trace element uptake by plants does not obey a specific rate response function; it may obey different rate response functions such as linear, asymptotic, no response or even negative response.
- There is a general increase in the bioavailable metals (EDTA-extractable) with increasing sludge application rates.

There has been a general understanding about the nature of trace element uptake by crops. The uptake by most crops is not necessarily linear with trace elements or sludge application, rather there is a maximum that can be reached (Plateau response).[15] This plateau is not a result of physiological maximum, and it becomes more pronounced and the maximum values decrease with sludge trace element concentrations. This indicates that sludge chemistry and trace elements concentrations have some effects on plant uptake. This plateau response has been observed for Cd, Cu and Zn in previous studies.[32,34]

The plateau findings suggest and validate the claim that sludge is both a source and a sink of trace elements. This is the case since, at low sludge application rates, soil binding of trace elements would predominate and linear uptake would be expected. However, at high application rates sludge matrix would begin to have some impact on metal availability, and the uptake would be similar to that depicted in the sludge matrix.[32]

Organic matter decomposition and sludge effects on soil pH largely govern the concept of a plateau. The idea is that most of the trace metals are absorbed on the organic part of sludge, thus when sludge decomposes it will start to release some of these trace elements to be available for plant uptake. However, no evidence has been gathered yet to support the idea of increased trace metal availability with time. The evidence currently available indicates that there is a substantial increase in bioavailable metals in the first two to three years after sludge application, this the same period increased plant uptakes of trace elements are observed.[32]

Sludge tends to slightly increase soil pH.[34] Well-decomposed, low molecular weight organic compounds may transport the metals down the soil profile.[33] These dissolved organic carbon (DOC) affects the movement of heavy metal down the soil, thus at high sludge application rates and high irrigation rates and rainfalls heavy metals are likely to leach to deeper levels of the soil profile.[33]

When the sewage sludge is applied as a soil conditioner it is vital to monitor the pH of soil as well. This is because soils at low pH (acidic soils) tend to increase the plant uptake of Zn, Cd, Ni, Mn and Co and increase the potential for phytotoxicity from Zn, Cu, and Ni; while alkaline soil pH increases the potential of Mo and Se phytotoxicity.[19]

2.4 Organic compounds in sewage sludge

The idea of using waste as a resource by landfarming sewage sludge is appealing. Nevertheless, this is a narrow view since only the inorganic substances are being considered to act as nutrients and fertilizers. The presence of substantial amounts of organic compounds such as very toxic dioxin and DDT in sewage sludge makes the analysis of sewage sludge for organic compounds a necessity. The understanding of these compounds concentrations in sludge, their mobility in soil and effects on the environment will be invaluable since sludge should be applied with caution.[14]

Most of the toxic organics bear similar characteristics such as the following:

1. They are chemically stable and resist chemical and microbiological oxidation.
2. They are lipophilic.
3. They have very low solubility in water.
4. They are mainly associated with solid phase (sludge) of water treatment works.
5. They bio-accumulate and consequently migrate upwards through the food chain.

The organic compounds present in sewage sludge can be classified into three categories, which are volatile, semivolatile and non-volatile organic compounds. This type of classification is based on the stability of compounds with the changing temperatures and time. The compounds that evaporate readily at room temperatures (~25°C) and one atmosphere pressure are of little concern. However, those that are semi-volatile and non-volatile are of great concern, because they show the potential to accumulate in the soil for plant uptake.[35]

The persistent organic pollutants (POPs) include a variety of compounds such as polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), phthalate esters, phenols and their derivatives and organochlorine pesticides.

2.4.1 The origin and occurrence of toxic organic compounds in sewage and waste water

The three major sources of POPs are industry, agriculture and domestic works.[36] Most of the time municipal wastewater is a combination of water from suburban area homes and businesses. Domestic wastewater is derived from washing, bathing and flushing toilets. These wastewaters may also contain water from industrial sources. A variety of chemicals are possible from different industries, thus inputs by industries are likely to differ significantly. The persistent organic contaminants enter the wastewater stream via aerial deposition and runoff into urban drains, household domestic wastewaters, and industrial effluent or possibly through formation in wastewater treatment plant.[37]

The POP's lipophilicity results in them partitioning onto the solid part of sewage sludge during the wastewater treatment process. In the soil POPs tend to associate with the organic, mineral and amorphous phases of the soil and they have slow biodegradation rates. As a result, they tend to remain in soil for long periods ranging from months to years.[37] Studies that have been conducted have shown that sludge-derived organic compounds in the soil have the potential to be taken up by plants and animals and thus can accumulate in the terrestrial food chain. [38,39]

Table 2.4 lists possible organic compounds that can be found in a sludge sample of and their origin. In a study conducted in 2003 at the University of Natal, where qualitative analysis of 78 South African sewage sludges took place, over 300 possible organic compounds were detected to be present in these sludges. Because of the expensive nature of analysis of these compounds, different countries select particular group of compounds and specific number of compounds within the group that must be monitored. The general trend is to select those compounds that are known to persist in the environment, since the non-persistent compounds biodegrade and hence impose less danger to the environment.

Table 2.4 Origin of some of the organotoxins.[36]

Name of compound	Origin
Polychlorinated biphenyl's(PCBs)	Electrical industry (capacitors and transformers), Paper industry (self-copying paper), Metal foundries, Chemical industry, PCB manufacture, Insecticides, Aluminium foil (domestic), Hydraulic fluids, Flame retardants.
Petroleum hydrocarbons	Petrochemical industry, Domestic refuse.
Phthalate esters	Rubber and paint manufacture, Synthetic raindrops.
Halogenated aliphatic and aromatic hydrocarbons(HAHs)	Dry-cleaning effluent, Aerosol propellants, Fumigants, Water disinfectants.
Polynuclear aromatic hydrocarbons (PAH's)	Domestic effluent, Petrochemical industries, Bitumen production, Incomplete combustion processes (e.g. tobacco smoking, burning of fossil fuels, exhaust gases of combustion engines, etc)
Organochloride pesticides	Agricultural runoff, Domestic usage, Wood industries, Pesticide manufacture.
Phenols, derivatives	Fungicides, herbicides, domestic effluent
Lindane (BHC)	Insecticides
DDT, derivatives	Insecticides
Aldrin, Dieldrin	Insecticides
Chlordane	Insecticides
Detergents	Domestic effluent

In Europe, regulations for the concentrations of the following group of compounds have been suggested for sludge users (AOX, LAS, DEHP, NP(E), PAH, PCB and PCDD/F) as shown in Table 2.5. Various countries have different regulations, depending on a number of factors such as the frequency of occurrence, nature of industries in the country and degradation patterns. In

South Africa the guidelines also exists, the limits for PAH and PCB have been inserted in Table 2.7 for comparison reasons.[40] The complete list is discussed in later section. There is a need to benchmark these guidelines against those of other countries.

Table 2.5 Recommended concentrations (mg kg^{-1}) for organic contaminants in sewage sludge in different countries in the EU [41] and SA

	AOX	DEHP	LAS	NP/NPE	PAH	PCB	PCDD/F
EU 2000	500	100	2600	50	6[1]	0.8[2]	100
Denmark	-	50	1.300	10	3[1]	-	-
Sweden	-	-	-	50	3[3]	0.4[4]	-
Lower Australia	500	-	-	-	-	0.2[5]	100
Germany	500	-	-	-	-	0.2[5]	100
S.A.	-	-	-	-	2.53	1	-

[1] Sum of acenaphthene, phenanthrene, fluorene, fluoranthene, pyrene, benzo(b+j+k)fluoranthene, benzo(a)pyrene, benzo(ghi)perylene, indeno(1,2,3-c,d)pyrene.
[2] Sum of 6 congeners PCB 28, 52, 101, 138, 153, 180.
[3] Sum of 6 compounds.
[4] Sum of 7 congeners.
[5] Each of 6 congeners PCB 28, 52, 101, 138, 153, 180.

2.4.2 Polychlorinated Biphenyls (PCBs)

The production of polychlorinated biphenyls (PCBs) is said to have begun in 1929, where they were produced by chlorination of biphenyl.[41] The biphenyl molecule contains ten sites for the binding of chlorine atoms, this leads to a theoretical mixture of 209 possible compounds (congeners). The popularity of this group of compounds is attributed to properties such as physical and chemical stability, electrical resistance, low volatility and resistance to degradation.

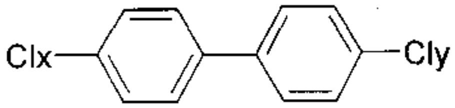


Figure 2.2 Schematic representation of PCBs general structure.

The list of the possible sources for PCBs in wastewater is given in Table 2.4. Nevertheless some of the PCB's are formed from chlorination of drinking water and waste. There are generally two main sources of PCBs:[2]

- One group is that of directly manufactured PCBs these include those used as hydraulic liquids, lubricants, impregnating agents for wood and paper, flame protective substances, carrier substances for insecticides and transformers
- The other group are those produced from combustion processes such as waste incineration, fossil fuel burning, and other incomplete burning processes.

These compounds (PCBs) are chemically stable and have the tendency to be resistant to biological degradation. They are adsorbed on solid particles and thus accumulate in sewage sludge and are highly resistant to heat treatment. They remain stable for long periods at 150°C.[11] They have low water solubility but are readily soluble in hydrocarbon solvents. The recycling of PCBs from the environment is one of the important procedures and this can be done by remediation of the historically polluted areas.

2.4.3 Polynuclear Aromatic Hydrocarbons (PAHs)

Polnuclear Aromatic Hydrocarbons (PAHs) are ubiquitous environmental contaminants found in air, soil and water.[42] These are hydrocarbons with multiple ring structures. Within the group are compounds such as naphthalene, acenaphthylene, fluorene, anthracene, pyrene, chrysene, benzo(a)pyrene, fluoranthene, dibenzo(a,h)anthracene, chrysene, pyrene, benzo(a)anthracene, benzo(g,h,I)perylene, benzo(k)fluoranthene, benzo(b)fluoranthene and indeno(1,2,3-cd)pyrene. These compounds are produced from incomplete combustion of organic material such as wood and mineral oil. They are considered to be potential mutagens and carcinogens, especially benzo(a)pyrene.

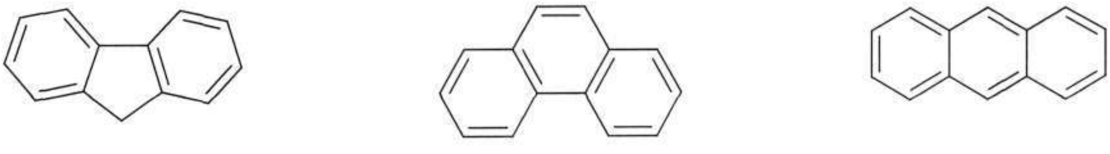
Many human activities result in the formation of PAHs,[37] activities such as industrial processes, vehicle emissions, waste incineration and biomass burning. The burning of coal in power stations or petrol in cars, trains, and trucks leaves residual tar and this is the primary source of PAHs in densely populated areas.[2] However, there are other natural sources such as forest fires and volcanoes. In the UK anode baking carried out in the aluminium industry was the major source of PAH emissions, contributing about 39% of the total in 1995 and 1996.[43] Other major sources in the UK are domestic and industrial coal combustion and wood combustion. Some of the lighter PAHs such as acenapthene, fluorene and anthracene are produced from wood treatment. [43]

Various compounds have been monitored within the PAHs group in different countries, with different countries within the same continent imposing different limits for different groups of compounds (as shown in Table 2.5). For an example in USA USEPA has a total of sixteen PAHs compounds that they regard as priority pollutants while EU proposed a limit for a total of only nine compounds.

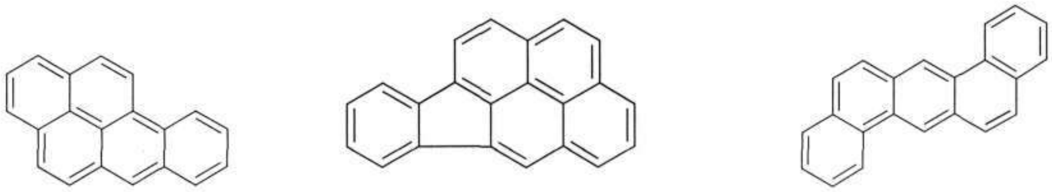
In the most recent studies conducted within the EU countries the total concentrations of the six PAHs proposed for monitoring have been found to exceed the limits.[37] The proposed limit is 6 mg kg^{-1} while the studied concentrations range between 18 and 50 mg kg^{-1}. This was a likely consequence since they're no clear criteria for the selection of these compounds as well as setting of the limit values.[37] In most countries, including South Africa, there are no clear criteria for the selection of these organic compounds for monitoring, this is mainly due to scarcity of the data about these compounds.

The USEPA methods of environmental monitoring list 16 priority compounds under PAHs, these will be listed in figure below.

(1) Naphthalene (2) Acenaphthylene (3) Acenaphthene (4) Fluoranthene

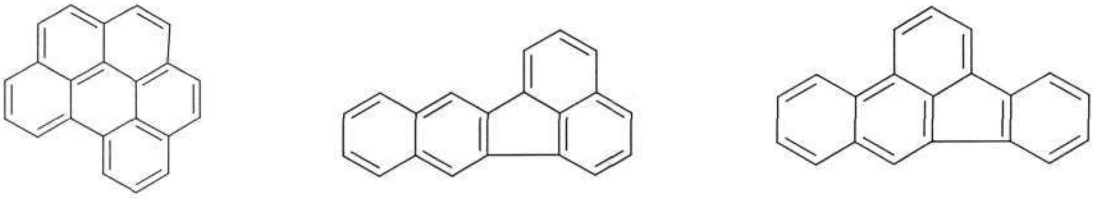


(5) Fluorene (6) Phenanthrene (7) Anthracene



(8) Benzo(a)pyrene (9) Indeno(1,2,3,-cd)pyrene (10) Dibenzo(a,h)anthracene

(11) Chrysene (12) Pyrene (13) Benzo(a) anthracene



(14) Benzo(ghi)perylene (15) Benzo(k)fluoranthene (16) Benzo (b)fluoranthene

Figure 2.3 Polynuclear aromatic hydrocarbons regarded as priority pollutants in US

The most potent carcinogens have been shown to be benzo[a]pyrene, and dibenzo[a,h] anthracene.[40] Benzo(a)pyrene is considered as an indicator substance for PAHs in sewage sludge, since its presence signifies a probable presence of other PAHs.[44] There is currently no known commercial production of benzo(a)pyrene, and yet it has been identified in surface water, tap water, rain water, ground water, waste water and sewage sludge.[45] As a product of incomplete combustion it gets released to air and gets removed from the atmosphere by photochemical oxidation and dry deposition to land or water.[45]

The semivolatility of PAHs makes them highly mobile throughout the environment via deposition and revolatilization between air, soil and water bodies. In a study conducted to measure the rate of degradation of organic compounds in wastewater sludge, it was found that degradation of some contaminants is facilitated by presence of air.[13] In the sewage sludge that was stored in a container, there was a reduction in the organic contaminants in the top 20 cm surface only. While in the other experiment where the sludge was being turned mechanically a 90, 43, 47 and 32% reduction in the amounts of LAS, NPE, DEHP, and PAH, respectively, was observed .[13]

The intraperitoneal LD_{50} for benzo(a)pyrene for mouse[44] is 250 mg kg^{-1}, and the subcutaneous LD_{50} for the rat[45] is 50 mg kg^{-1}. The acute oral toxicity of PAHs appears to be low to moderate, however long-term experiments results to adverse haematological effects. Also, dermal, immunosuppressive and reproductive and fatal effects have been observed with the most important being carcinogenicity.[45]

2.4.4 Phthalates

Generally phthalates are incorporated into plastics as plasticisers. One of the mostly used phthalates is di-(2-ethylhexyl)phthalate (DEHP), which is used as an emollient in synthetic materials.[1] It is a common procedure to use DEHP as an anti fouling agent in paper production, as an emulsifier for cosmetics, in perfumes and pesticides; phthalates also substitute PCBs in the production of different synthetic materials.[2] Many of these compounds are degradable under anaerobic and aerobic conditions; however, the degradation rate decreases significantly when they are absorbed to particles. They show great potential for plant uptake and are toxic to some soil organisms.[41]

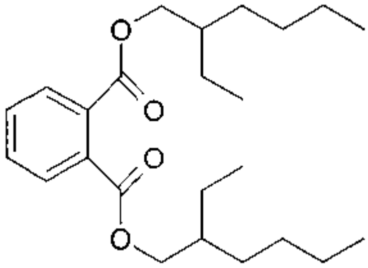


Figure 2.4 Structural representation of di-(2-ethylhexyl)phthalate

The human activities contributing to DEHP emissions include the following:

- Cellulose and paper production
- DEHP production
- PVC production and processing, leaching from PVC products
- Leaching from waste in landfills
- Waste incineration and uncontrolled combustion

DEHP is common in municipal wastewaters and because of its lipophilic property it concentrates in sewage sludge during wastewater treatment. When sewage sludge is applied on agricultural land there is a very small possibility of these compounds uptaken by plants, since they are likely to degrade. [57,61]In addition, these compounds have very high logK_{ow} of 7.6 meaning they are less likely to be uptaken and translocated by plants,[35] since compounds with log$K_{ow} > 4$ are said to have a high potential for root retention and low potential for uptake and translocation.[62] In the event where these compounds are applied as a soil fertilizer, they show no adverse effects on crop yields, soil fertility or biological activity.[35]

The primary concern with regard to these compounds is the transfer up the food chain which might end up affecting humans and animals.[63] DEHP has an LD_{50} value of 25000 mg kg^{-1} for rats and results in hepato- and neuphrotoxic effects in animals, it also reduces fertility in rats.[41] There is however, no concrete evidence to declare this compound as a potential carcinogen for humans'.[46] An oral exposure of 25 mg kg^{-1} can be tolerated by human beings according to World Health Organisation.[47]

2.4.5 Chlorinated compounds

These are organic compounds with one or more chlorine atom in their structure. The group contains compounds such as dioxin, dichlorobenzene and pentachlorophenol. Dioxin is one of the most highly toxic substances known to man; it is a known carcinogen and teratogen.[36] The most well-known and hazardous dioxin, is the tetrachlorodibenzo-p-dioxin (TCCD). The main sources of polychlorinated dibenzo-*p*-dioxins and furans are as follows.[20,2]

- Chemical reactions and chemical reaction processes; dioxins arise as unwanted products from production or use of many organo-chlorine compounds such as chlorine bleaching.
- Combustion processes or thermal processes
- Dioxins can also arise from incomplete combustion processes involving chlorine containing organic compounds.

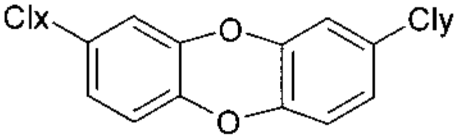


Figure 2.5 A typical chemical structure of PCDD

TCCD is one of the most studied compound in this group and it can result in a number of effects such as chloracne, hepatotoxic effects, neurological symptoms, diabetes, immunotoxicity and reproductive effects on man.[41] TCCD is carcinogenic when applied orally and dermally on rats and mice.[41]

2.4.6 Pesticides and herbicides

The origin of these compounds is mainly from agricultural runoffs, road and rail weed treatment, parks and urban woodland areas. Examples of these compounds include DDT, dieldrin, aldrin, andrin, lindane and heptachlor. The use of pesticides such as DDT was stopped many years ago due to the potential danger imposed by the compound since it causes tumours in mice.[48,59] However, the main worry is the traces of these chemicals in the environment since these are very persistent organic compounds.

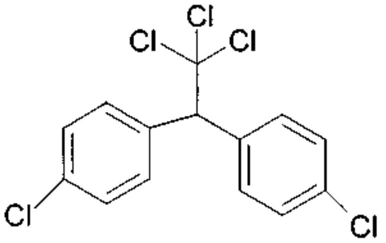


Figure 2.6 Structural representation of DDT

2.4.7 Phenols

An important compound in this group is 4-nonylphenol (NPE), a degradation product of non-ionic alkylphenol polyethoxylate surfactant. NPEs are used as surface-active agents in cleaning products, cosmetics and hygiene products and in emulsification of paints and pesticides.[41] NPE is harmful in rats after an acute exposure and is classified as corrosive in these animals.[49] In humans and most animals it tempers with the reproductive system.[50]

2.4.8 Other compounds[49]

In sewage sludge there are other contaminants, which might be harmful such as linear alkylbenzene sulphonates (LAS), musk, ketones and detergents. These can have detrimental effects on the environment if improperly managed. LAS is a skin irritant and can lead to increased skin penetration of other compounds due to damage of lipid layer.

2.5 Mobility and fate of pollutants in sewage sludge

2.5.1 Soil Profile[51,52]

The process of efficient use of sludge on land cannot be fully understood unless the effects from the soil type and characteristics are understood. Soil is a three-component composition, being made of water, solid matter and air. Solid matter can generally be categorised into two: organic and inorganic components. Inorganic minerals are derived from weathering of rocks and accounts for about 50-60% of soil. The organic matter is mainly derived from plants and microorganisms and accounts for about 0-10% of soils.

Soils are packed in horizons with distinct characteristics. There can be about six horizons with a variety of thickness. The layer on the surface is called the 'O' horizon and it contains fresh and decaying organic materials such as leaves, dead plants and animal remains. The horizons that are close to the surface contain mostly humus while those deeper down contain mainly rocky materials.

The 'O' horizon is of high interest because when sludge is applied on land it interacts with this soil layer. Due to its composition sludge application will eventually increase the concentrations of organic and inorganic pollutants as well as that of pathogens. When these pollutants are dumped on the soil they can either accumulate, taken up by plants or infiltrate to contaminate the underground water system.

Accumulation in soil can have serious environmental impacts such as changing soil character or contaminating surface water during runoffs. Processes such as eutrophication might result. Eutrophication refers to a process of excessive addition of nutrients, usually with reference to anthropogenic activities and the addition of phosphorous and nitrogen to natural waters. Addition of nutrients results in excessive growth of plants including phytoplankton, periphyton and macrophytes.

Eutrophication is a natural process that is, however, accelerated by human activities. As a natural process, eutrophication results from soil erosion and biological production, this is a slow process and might take thousand of years to fill the lakes. However, with the addition of anthropogenic nutrients the process might take decades hence lakes becoming overly productive biologically. The process results to processes in water such as the following:[51]

- Excessive plant growth
- Taste and odour problems
- Loss of species diversity
- Hypolimnetic loss of dissolved oxygen

The compounds that are located in the zone below the plant root zone are no longer subject to decomposition by ultraviolet radiation (UV) and both volatilisation and microbial degradation of chemicals reduce as chemicals move down the soil profile. Moreover, the soil organic content diminishes with depth leading to less chemicals being sorbed and hence more becoming mobile.

2.5.2 Organic transformations

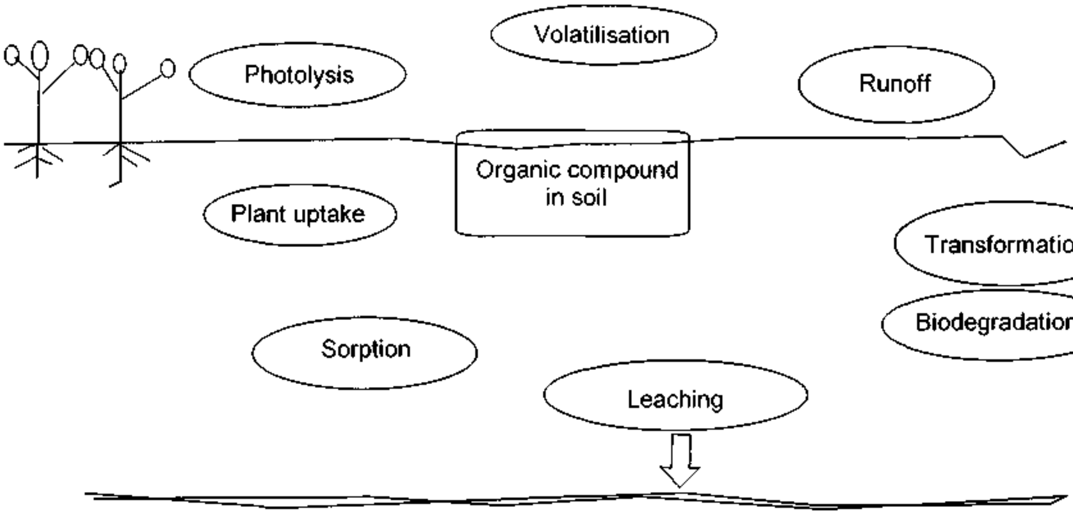


Figure 2.7 Various processes determining the fate of organic compound in the soil environment.

Organic chemicals may undergo a variety of chemical reactions ranging from biological transformations, chemical hydrolysis, oxidation/reduction, photo-degradation, volatilisation and wind erosion, leaching to ground water, run off and erosion to surface water, sorption and bio-concentration to mention but a few.

2.5.3 Degradation

Organisms such as fungi and bacteria can degrade organic compounds under aerobic conditions. Organic compounds, such as those in the following list, have been shown to be degraded by the rot fungus *Phanerochaete* chrysosporium:[53]

Chlorinated aromatic compounds

- Pentachlorophenol
- 2,4,5-trichlorophenoxyacetic acid
- Polychlorinated biphenyls (PCBs)
- Dioxins

Polycyclic aromatic hydrocarbons

- Benzo(a)pyrene
- Pyrene
- Anthracene
- Chrysene

Pesticides

- 1,1,1-Trichloro-2,2-bis(4-chlorophenyl)ethane (DDT)
- Lindane
- Chlordane
- Toxaphene

Many organic compounds added to soil will degrade. The addition of organic matter can accelerate or possibly inhibit the biodegradation process. The acceleration can be a result of enhancement of the microbial population and its activities, while on the other hand organic matter can tie up the organic compounds and thus delay their assimilation by the microbial population.[54]

Biological transformation refers to those transformations of organic chemicals, which are facilitated by microbes such as bacteria, fungi or algae. The transformations may be intracellular or extra cellular taking place under aerobic or anaerobic conditions.[51]

When organic compounds are spread on or incorporated into the soil they eventually exert a vapour pressure due to partitioning between gas and liquid phases. The vapour may be rapidly lost when the vapour pressures are sufficient. Many of the organic compounds e.g. toluene and benzene will exert enough pressure to be rendered volatile while increasing bulkiness in a structure will decrease the volatility of a compound. The increase in the organic matter of the soil will also decrease the volatilisation of the hydrophobic nonpolar aromatic compound.[15]

Some studies have indicated that there is a substantial decrease in the amount of volatilisation of organic compounds with the addition of sewage sludge to soil.[55] The addition of sewage sludge decreased the amount of volatilisation and environmental transport of PCBs.[55] The indication was that the addition of sewage sludge could decrease plant uptake of PCBs since the contamination from sorption is the primary source of contamination in some plants. Furthermore there was increased complete degradation or detoxification of PCBs with the addition of sludge.

Plant uptake of the organic compound depends on a number of issues such as chemical and physical properties of the compound, reactions in the soil that affect the availability, and the rate of uptake by plant. The organic compounds of concern in sewage sludge are the persistent compounds such as PAHs, PCBs dioxins, phthalates and other compounds of similar nature.[36]

There are basically two routes of entry for an organic compound in a plant, the first is through translocation in xylem. The compounds transported through the xylem need to be water-soluble since the xylem transports water. The second route is through phloem from leaves.

The studies have shown that some of the organic contaminants can be adsorbed by root crops such as carrot.[56] The PAHs are, however, less likely to be found in plants as a result of sludge application. Due to their hydrophilic nature they will adsorb onto the organic matter of the soil. Furthermore the addition of sludge will increase the adsorption potential of soil thus making PAHs even less available to plants. Phthalates such as DEHP are strongly adsorbed by the soil organic matter, thus the presence of sludge will decrease the availability of the compound.[57]

The plant uptake of PCDD/F was studied in the aboveground portion of the plant the results showed that the concentrations on plants are not affected by the changes in the soil concentrations.[58] The conclusion that sludge application will have ignorable effects on the aboveground plant tissues concentrations of PCDD/F can then be made.

The limits for organic contaminants in South African sewage sludge have been set based on lethal dose calculations (LD_{50}) these limits are presented in Table 2.6.

Table 2.6 Limits for organic pollutants in South African sewage sludge[40]

Pollutant	Dry sludge concentration (mg/kg)	Group
Aldrin	0.2020	Pesticide
Chlordane	3.500	Pesticide
DDT	0.3500	Pesticide
Dieldrin	0.3030	Pesticide
Heptachlor	0.3500	Pesticide
Hexachlorobenzene (HCB)	16.20	CB-Chlorobenzene
Lindane	1.360	Pesticide
Benzo(a)pyrene	2.530	PAH
Dimethyl nitrosamine	2.900	
Trichloroethylene	2020.0	VOC
PCB	1.000	PCB

The comparison of these guidelines with those of other countries is a necessity to evaluate the practicality of these limits.

2.6 The aim of the study

The main objective of a wastewater treatment plant is to prevent large quantities of pollutants to reach and impact the environment in high doses and concentrations. Substances such as organic and inorganic chemicals and pathogenic organisms are removed from sewage and they accumulate in sewage sludge. The chemicals that are found in sludge could have adverse effects on soil, plants, animals and human health as well as the environment.[41] The challenge to waste water treatment plants becomes that of disposing sludge in a manner abiding to the legislative bodies without causing adverse effects on the environment. Some of the main disposal routes include disposal to land, sea and incineration. The most desirable disposal route is that of using well treated sewage sludge as a fertilizer, where it acts as a nutrient source for vegetation, improves soil physical properties such as soil structure, water retention capacity and transmission characteristics. Limiting the use of sludge as bio-fertilizer is the presence of high concentrations of organic and inorganic substances and some harmful microorganisms. Inorganic chemicals such as heavy metals, in particular, may have adverse effects on the environment by accumulating on soil and plants and consequently resulting into phytoxic, zootoxicity and end up affecting human health effects.

The same accumulation for organic compounds can take place mostly on plants surface during application of sludge to land consequently can be transmitted through the food chain to man, this might result to carcinogenic and mutagenic effects to man. Toxicity of sewage sludge when applied on land is largely influenced by the nature and metal and organic compounds content of the soil, the rate and frequency of sludge application the types of crops grown and the part of a plant to be consumed. The use of sludge as a bio-fertilizer is now a global practise. In South Africa, 28% of the sludge produced is used as a bio-fertilizer.

Sludge application to agricultural land is of economic importance since it provides an alternative route for sludge disposal in a beneficial way; at the same time it provides a source of income to sludge producers. To the farmers it provides a source of cheap fertilizer. Because of the potential dangers associated with sludge disposal it becomes necessary to analyse sludge for both organic and inorganic pollutants present. The findings are of high importance since they would give an indication of pollutant type and concentrations. Hence a guide towards a suitable disposal route can be adapted.

The aim of this project was therefore to identify and quantify the amounts of inorganic metals, nutrients and polynuclear aromatic hydrocarbons (PAHs) in South African sewage sludge. A total of 34 waste water plants were sampled from Gauteng, KwaZulu-Natal, Western Cape and North West provinces and these were analysed using suitable procedures.

Therefore the specific targets of this project were:

- To carry a detailed literature survey relating to sewage sludge.
- To understand the impact of contaminants present in the sewage sludge to the environment.
- To sample sewage sludge from different wastewater plants and analyse for inorganic substances and PAH compounds present in the sludge.
- To quantify these inorganic and the organic compounds (PAH) present in the sludge samples.
- Make recommendations in as far as the use of sludge in agriculture is concerned.

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Chapter 3

Experimental

CHAPTER 3

3 EXPERIMENTAL

3.1 *Reagents*

Analytical Reagent (AR) grade reagents were used for the determination of metal ions in sludge samples. These included nitric acid (65%, Fluka), hydrochloric acid (30%, Fluka) and hydrogen peroxide (30%, SMM Chemicals). The ICP standards packed in 1000 mg/L were obtained from Fluka supplied in 100 ml plastic bottles.

For organic determinations all the solvents used were of HPLC grade. These included Hexane (97% purity, BDH), dichloromethane (99.8%, BDH) and 2-propanol. The water that was used was ultra pure de-ionized water (MilliQ). Granular, anhydrous sodium sulfate (99% purity, Merck) was dried in an oven set at 400 °C for 4 hours in a shallow tray, to remove possible organic contaminants. The pure sodium sulfate was then cooled and stored in a desiccator before use.

The tetrabutylammonium solution (TBA) (Aldrich) was prepared by dissolving 3.39 g of solid TBA in 100 ml of ultra pure water using a 100 ml volumetric flask. This solution was purified by extracting with 3-portions of 20 ml hexane and into the aqueous extract 25 g sodium sulfate was added. The solution was stored in an amber bottle.

3.2 *Apparatus for the extraction of organic compounds*

The extraction of solid sewage sludge involved the use of Soxhlet extraction apparatus mad up of a condenser having a 40 mm internal diameter connected to a round bottom flask (50 ml) that contained the extracting solvent. The sample was loaded into a cellulose extractio thimbles (28 mm internal diameter, 80 mm height) and the setup heated using a mantle. Th picture of an experimental set up is shown in Figure 3.1.

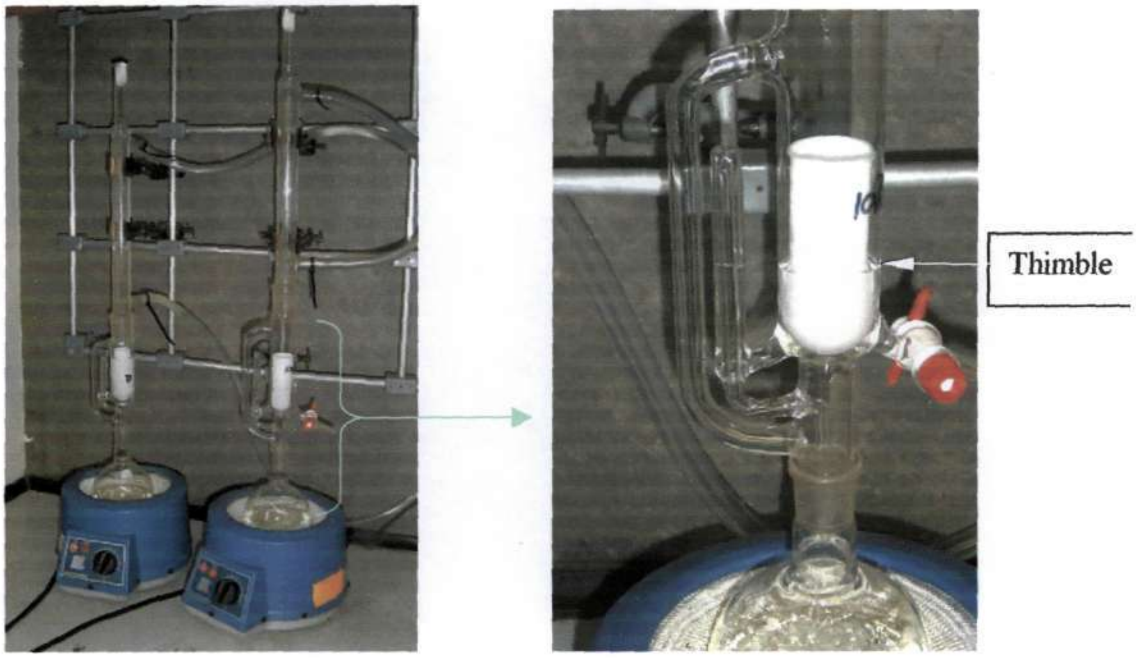


Figure 3.1 Soxhlet extraction apparatus assembly used in the current study.

3.3 Sampling

Sampling forms a very important part of environmental studies as it can limit the overall accuracy of the whole analytical process[1]. The samples taken from sewage sludge usually depict a high degree of heterogeneity, thus great care was exercised during sampling and preparation of these samples to ensure that the samples were a true representative of the site.

In sampling sewage sludge these were first agitated to afford a representative and a more homogenous sample. The solid samples from drying beds and lagoons were taken in small amounts from different points through out the bulk beneath the surface by using a hand shovel. This was also true for compost heaps. The return flow was sampled by using a small bucket elongated with a long metal rod to reach below surface level of the flow. The majority of the samples were collected from Gauteng and KwaZulu-Natal provinces. Samples from Gauteng province were collected in July and those from KwaZulu-Natal in August. A total of 20 samples were collected from Gauteng and 9 samples from KwaZulu-Natal. In additional 5 samples were collected from other South African provinces. In total 34 samples were collected from around South Africa, for both metal and organic analysis

Table 3.1 A table showing the different sampling points.

Sampling point	Drying beds	Compost heap	Belt Press	Peddies	Others	Return Flow	Wet sludge	Digesters
Number of samples	4	5	5	3	5	3	6	3

Samples were collected from different sampling points as listed in Table 3.1. These samples were collected in a 2-litre glass bottles having a Teflon-screw top, after which they were transported over night in modified cooler-box. Preservation of samples was achieved at 4 °C using ice blocks and on arrival to the laboratory they were placed in a freezer modified to maintaining a temperature between 3.5 and 4 °C. These samples were protected from any photo degradation by wrapping the bottles in aluminum foil.

The samples were immediately subjected to Soxhlet extraction after arrival in the laboratory The extracts were placed in 3 ml bottles that were stored in the freezer and later analyzed fo PAHs within 7 days. Once the extraction of PAHs was complete, the digestion of sludge fo metal ions was conducted.

3.4 Sample preparation for analysis of metal elements

Sample preparation is usually conducted so as to extract the analytes of interest from th sample matrix. The matrix is the portion of the sample that is not of interest; these are usuall non-target elements and compounds present in a sample. It usually constitutes the va majority of the sample mass, and can interfere with digestion or extraction of target analytes.

Samples can contain wide ranges of moisture and must often be dried prior to analysis. This done for variety of reasons: one is so that comparisons between samples are more realistic an not skewed by moisture content. Drying can also make other sample preparation procedure such as milling and sieving, easy. Finally, some of the analytical procedures are sensitive to moisture content and so, by removing moisture, the samples are more comparable to the calibration standards.

Milling is generally performed to make particle sizes to be more or less uniform and thus making sieving easy. These two treatments help in homogenizing the sample especially for samples with heterogeneous distribution of analytes. All the sludge samples obtained were dried and ground prior to analysis, using the procedure discussed in section 3.4.1.

3.4.1 Determination of moisture content and sample preparation

The samples chosen for analysis in this research included a combination of wet solid and liquids. All solid sludge samples were weighed in a four decimal place balance (Mettler Toledo) and dried for three days in an oven set at 105 °C. The dried sludge samples were later cooled to room temperature (~23 °C) in a dessicator packed with silica gel before re-weighing to a constant weight. The percentage differences in the two masses represented the moisture content in the original sample. The sample was then crushed into powder and sieved through a 0.60 mm stainless steel and brass-coated Endecott sieve. This dry sample was then used in the digestion process for metal ion determination.

3.4.2 Digestion of sewage sludge

Most of the techniques used in environmental determination of metal elements require tha sample be in liquid form and that suspended solids be removed to prevent clogging of th instrument during analysis. Solid samples such as sludges, are digested so as to extract th metals of interest from the solid and resulting digestate filtered, centrifuged or allowed t settle for the removal of solids prior to analysis.

A universal dissolution procedure that is good for all samples matrices does not exis However, the most desirable features in a digestion procedure include the following:

- The ability to dissolve the sample completely
- Reasonably quick and safe procedure at all times
- No sample loss through volatility or adsorption in the digestion vessel and
- Limited sample contamination from reagents used

The two main digestion procedures that are usually used for the solid sample digestion, are dry ashing and wet digestion. In dry ashing the sample is placed in a hot oven (500-550 °C) for about 24 hours to allow for the decomposition of most of the organic matter. Problems such as the volatilization of Hg, As, Sn, Se, Pb, Ni and Cr might be encountered when this method is used. Alternatively, wet digestion can be used where acids are used for the decomposition of organic matter. The problem with the method is that the use of mineral acids might be a source of some elements; hence the method requires the use of reagents as a blank.

In acid digestion elements of interest are removed from the sample matrix and transferred into the liquid matrix for analysis. The most common approach is to use hot acids to destroy chemical and physical bonds between elements of interest and the sample matrix and to convert the elements into water-soluble forms. This procedure generally leaves the bulk of non-target elements, especially silicaceous materials, such as solids that can be filtered out.[2]

The selection of a digestion procedure for a particular operation depends on two importan factors:

(1) The acid aggression towards breaking the bonds between the element and matrix,

(2) The solubility of elements in the acid chosen for use. Among the list of oxidants that are commonly used are nitric acid, hydrochloric acid, sulfuric acid, perchloric acid hydrofluoric acid, potassium permanganate and hydrogen peroxide.[4]

The USEPA recommends method 3050B for ICP-OES analysis of sludge samples. Thi method which involves using a combination of nitric acid and hydrochloric acid, was used i the current study as described in Section 3.4.3.

3.4.3 Acid digestion of sludge for ICP-OES analysis (USEPA method 3050B)

The homogeneous powder obtained by drying the solid sludge and grinding was used in acid digestion. Four 1.00 g samples per site were used for reproducibility purposes. These were weighed and transferred into digestion vessels.

10 ml of a 1:1 HNO_3 (65%) was added into the digestion vessel and the contents mixed and covered with a watch glass. The mixture was then heated to 95±5°C using a water bath and refluxed for 15 minutes without boiling. The sample was then allowed to cool to room temperature before adding 5 ml of conc. HNO_3 (65%) and then heating the sample for a further 30 minutes in a steam bath. The addition of 5 ml of concentrated HNO_3 (65%) was repeated every 30 minutes until no brown fumes were generated, indicating the completion of the oxidation process by nitric acid. The resultant solution was then evaporated to approximately 5 ml without boiling at 95±5°C. This solution was then allowed to cool to room temperature (~23 °C). To the cool solution, 2 ml of water and 3 ml of 30% H_2O_2 were added. The vessel was then covered with a watch glass and heated as usual until the effervescence subsided. The vessel was cooled to room temperature (~23 °C) before any further 1 ml of 30% H_2O_2 aliquots were added with continuous warming until the effervescence had subsided or sample appearance was not changing. The acid-peroxide digestate was then steam heated until the volume had reduced to about 5 ml.

Into the resultant sample (~5 ml) 10 ml of concentrated HCl was added and refluxed for 1 minutes at 95±5°C. The digestate was then allowed to cool to room temperature (~23 °C before filtering it through a Whatman No. 41 filter paper into a 100 ml volumetric flask. The filter paper was washed with deionized water as the volumetric flask was made to the mark The solution was mixed thoroughly before analysing for mineral ions using ICP-OES. A flov chart representing the process description is shown in Figure 3.2.

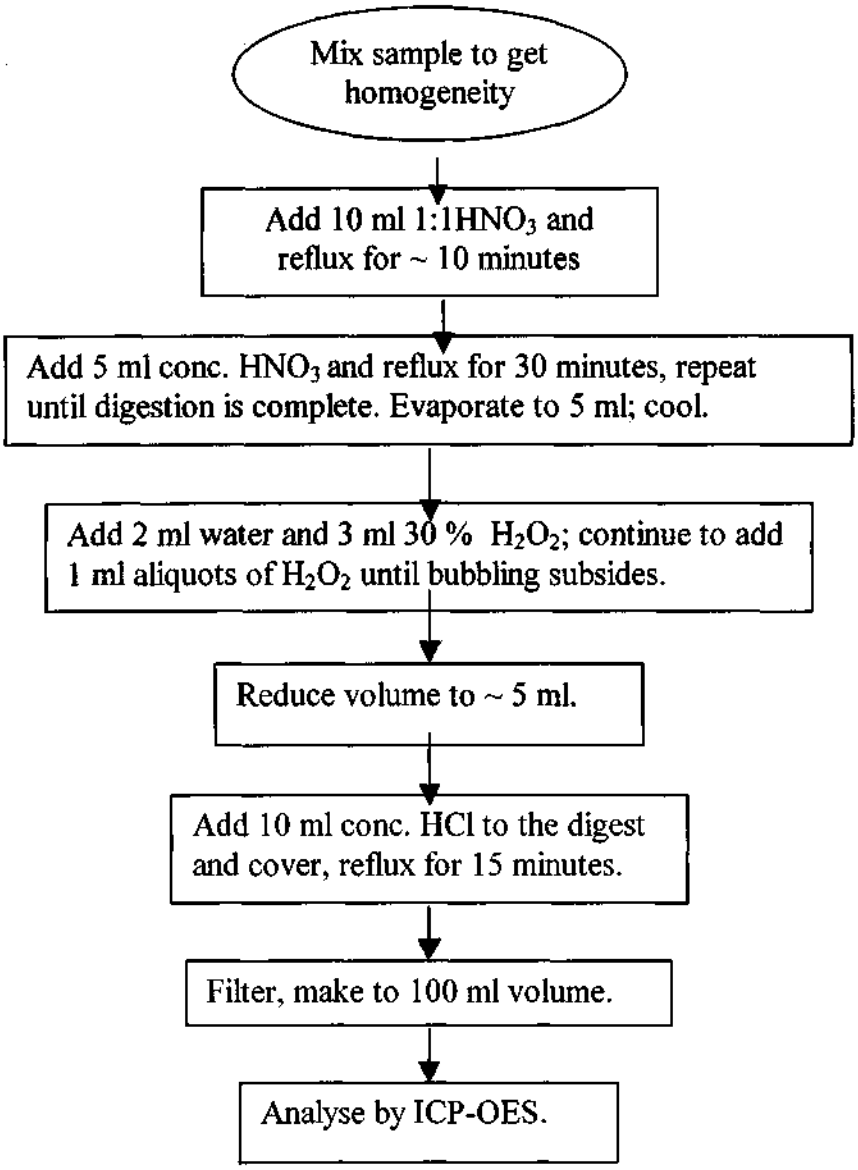


Figure 3.2 Digestion process for solid sludge (EPA Method 3050B).

3.5 *Analysis of mineral ions*

3.5.1 Introduction

Metal analysis can be performed using a number of techniques; these include coulorimetry, atomic absorption and emission spectroscopy, ion selective electrodes, redox titrations, electrophoresis and gravimetry. Each and every technique has its advantages as much as disadvantages. However, spectroscopic methods of determination come in handy when it comes to elemental analysis of the environmental samples. This is because of their lower detection limits as well as the ability to interact with most of the elements in the periodic table.

Spectrometry represents a range of analytical techniques where there is an interaction of matter with energy such as electromagnetic radiation, acoustic waves and beams of particles such as ions and electrons.[5] However the most widely used spectrometric methods are based on the electromagnetic radiation, which is a type of energy that takes several forms the most readily available being light and radiant heat.[1] Others that are not so obvious include gamma rays, X-rays, ultraviolet, infrared, microwaves and radiowaves.[6]

Spectroscopy is a very old technique dating back to the 1860s, when Kirchoff and Bunsen first introduced it into the scientific community.[5] During the initial stages of the development of this technique, only the visible part of the electromagnetic spectrum was being utilized for analysis, however, technological breakthroughs have resulted in the other parts of the spectrum being incorporated into spectroscopy. To date, there are three major types of spectrometric methods for the identification of elements and determination of their concentrations in samples of matter namely: (1) optical spectrometry, (2) mass spectrometry, and (3) X-ray spectrometry.[5]

In optical spectrometry the elements in the sample are converted into gaseous atoms and elementary ions by atomization processes. This is then followed by measurement of ultraviolet/visible absorption, emission or fluorescence of the atomic species in the vapour. In atomic mass spectrometry, samples undergo the same atomization but this time gaseous atoms get converted to positive ions and get separated on the basis of their mass to charge ratio. For

X-ray spectrometry, atomization is not required since X-ray spectra for most elements are largely independent of how they are chemically combined in a sample.

All the optical spectroscopic techniques depend upon the emission or absorption of electromagnetic radiation.[6] At room temperature, essentially all atoms in a sample of matter are in the ground state. When an atom is supplied with enough energy (thermal or electrical) an electron can be raised from low energy to a higher energy level called the excited state. Additionally, the excited state is unstable and has a short lifetime, and this results in the electron returning to the ground state. The return to the ground state is accompanied by emission of a photon.

Alternatively, an atom can be excited by the absorption of a photon of electromagnetic radiation. Fluorescence occurs when the excited state produced by the absorption returns to the ground state by the emission of electromagnetic radiation. Both absorption and emission will only take place at specific and selected wavelengths or energies. According to quantum theory, atoms, molecules or ions have only a limited number of discrete energy levels. Thus for absorption to occur the energy of the excited photon must match, exactly, the energy difference between the ground state and the one of the excited state of the absorbing species.[5]

Atomic line width in atomic spectroscopy is of high importance. For example narrow lines are desirable for absorption and emission spectroscopy since they reduce the chances of spectral interference because of overlapping spectra. Furthermore, line width is of considerable importance when designing instruments for atomic absorption spectroscopy. The four sources of band broadening are: (1) the uncertainty effect, (2) the Doppler effect, (3) pressure effects due to collision between atoms of the same kind with foreign atoms, and (4) electric and magnetic effects. The Doppler effect is a result of thermal motion of atoms in a gas.

Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES) was the method of choice for the analysis in the current work because of the following advantages over atomic absorption (flame) spectroscopy (AAS).

- Lower inter-element chemical interference, which is a direct consequence of their higher temperatures.[8]

- Secondly, good emission spectra are obtained for most elements under a single set of excitation conditions and, as a consequence, spectra for many elements can be recorded simultaneously. This property is of particular importance for multi-elemental analysis of very small samples. Flame sources are less satisfactory in this regard because optimum excitation conditions vary widely from element to element. Further disadvantages of AAS are that high temperatures are required for the excitation of some elements and low temperatures for others, and finally, the regions that give rise to optimum line intensities vary from element to element.

- Another advantage is the energetic plasma sources that permit the determination of low concentrations of elements that tend to form refractory compounds. These compounds, include oxides of boron, phosphorus, tungsten, uranium, zirconium, and niobium that are highly resistant to thermal decomposition.

- Finally, methods based upon plasma sources usually have a much larger range of concentrations in contrast to two or three for the absorption methods.[1] This is important since the mineral ions in sewage sludge vary quite significantly in concentrations, requiring a large calibration range.

Among the other advantages of atomic absorption methods are simple and relatively less expensive equipment requirements, lower operating costs, somewhat greater precision and procedures that require less operator skill to yield satisfactory results.[1]

3.5.2 The principles of ICP-OES

The ICP-OES instrument comprise of many components such as a nebulizer, spray chamber, torch, RF generator, monochromator, photomultiplier, detector, and a computer. A schematic diagram representing the components is shown in Figure 3.3. Sample introduction into the instrument involves pumping of the sample from the container (by the pump) into the nebulizer where it gets turned into an aerosol, then into the torch for vaporization, atomization or ionization, detection and data processing.

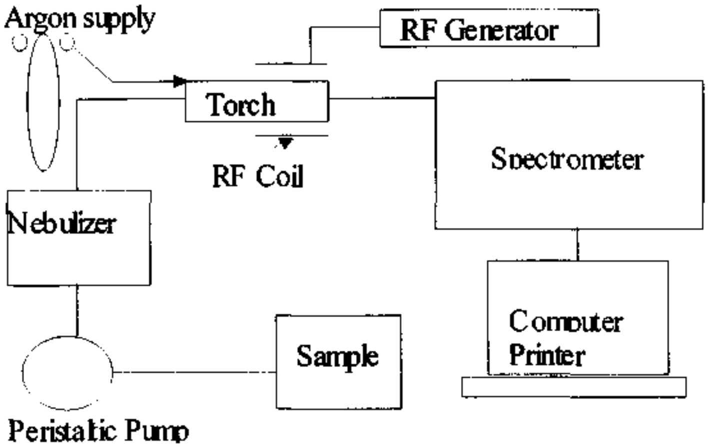


Figure 3.3 Schematic Diagram of ICP-OES

One of the most important processes in the ICP-OES is that of sample introduction, this process involves the utilization of the nebulizer. The sample introduction step can limit the accuracy, the precision, and the detection limit of the spectroscopic measurements.[5] The goal of the sample introduction system is to transfer a reproducible and a representative portion of a sample into the atomizer with high efficiency and with no adverse interference effects.

One of the most commonly used devices when introducing a sample in ICP-OES is the nebulizers.[6] These devices convert a liquid sample into an aerosol. Most of the nebulizers available have a transport efficiency of 1-2%.[6,7] Ideally the droplets in the aerosol produced by the nebulizer should have a diameter of 10 μm. This ideal diameter reduces the possibilities of the aerosol cooling or distinguishing the plasma. The commonly used nebulizers are the pneumatic nebulizers, however, other types are available such as ultrasonic, glass frit, and the Babington type of nebulizers.[7]

The commonly used type of pneumatic nebulizers is the concentric type, called Meinhard nebulizers.[7] These are constructed from standard glass-blowing techniques to form a concentric glass-tube fitted with a capillary tube. The sample is drawn through this capillary tube by the action of the carrier gas. The flow of gas then carries the sample into the region where atomization takes place. A spray chamber is placed in between the nebulizer and the ICP torch in order to remove large droplets from the aerosol and to dumpen the pulses that may occur during nebulization. This is the reason that only a maximum of about 5% of the sample reaches the plasma, the other 95% is lost down the drain in the spray chamber.

The sample that is transported into an atomization section made up of a plasma torch where the elements present in a sample are converted into gaseous atoms or ions. The process of atomization will take place in a plasma torch. Greenfield *et al.* developed the first plasma torch specifically designed for spectroscopy in 1964.[7] The plasma formed was toroidal, with the sample material being injected by the innermost tube through the hole punched into the flat-bottomed plasma. The outer gas flow was introduced tangentially to the axis of the torch and this feature has been retained in all the subsequent models.

A typical modern plasma source (torch) usually consists of three concentric quartz tubes through which a stream of argon gas flows. Surrounding the top of this tube is a water-cooled induction coil that is powered by a radio frequency generator. A spark from a Tesla coil initiates ionization of the flowing argon. The resulting ions, and their associated electrons, then interact with the fluctuating magnetic field produced by the induction coil. This interaction causes the ions and electrons within the coil to flow in the closed annular paths; ohmic heating is the consequence of the resistance of the ions and electrons to the movement.[1]

The temperature of the plasma formed in this way is high enough (6000 K-10 000 K)[8] enough to require thermal isolation of the outer quartz cylinder. The isolation is achieved by flowing argon tangentially around the walls of the tube. The tangential flow cools the inside walls of the center tube and centers the plasma radially.

The collisions due to excitation in the plasma lead to atoms emitting photons, the amount of which is directly proportional to the amount of the originating element in the sample. The spectrometer/detector then monitors the emitted photons. The spectra emitted at these high temperatures have two dimensions. The first is the wavelength at which atomic emission occurs. This wavelength is characteristic of the elemental composition of the sample. Secondly, the intensity of the emitted photon is proportional to the concentration of the elements in the sample. A photomultiplier tube measures the intensity of the lines. The selection of the wavelength line is performed by the monochromator. The computer finally integrates and gives spectral data with all the required information. The ICP-OES instrument that was chosen for analysis in the current study and is shown in Figure 3.4.

Figure 3.4 A photo of the ICP-OES (Varian Liberty AX150) used in the study.

3.5.3 Optimization of conditions for the ICP-OES

The optimization of the operating conditions for the ICP-OES involves the adjustment of the instrument's operating conditions such as pump speed, nebulizer pressure, auxiliary argon flow, plasma argon flow, nebulizer pressure, and RF power. The optimization of these conditions results in the desired results of signal to background ratio and signal to noise ratio in the results.

When the condition are optimal the signal to noise ratio (SNR) is at its highest as well as the highest signal to background ratio (SBR), this means lower interferants and minimun matrix effects caused by the easily ionizable element (EIE) signals such as sodium. These EIEs can suppress or enhance the emission signals at high concentrations. In this project, the EIE interference was remedied by the dilution of the samples. The operating conditions adapted in this project, including the type of the instrument are reflected in Table 3.2.

Table 3.2 Operating conditions utilized in ICP-OES analysis

Instrument	Liberty 150 AX Turbo (Varian)
Torch mounting	Axial, low flow
Nebulizer	Pneumatic (Concentric)
Nebulizer pressure	240 kPa
Pump Speed	15 rpm
RF power supply	40.68 MHz
Operating power	1.00 kW
Photon multiplier voltage	800 V
Plasma argon flow	15.0 L/min
Auxiliary argon flow	1.50 L/min

The elements identified in sludge extracts, using the rapid scan function of the instrument are shown in Table 3.3. Included, are the respective lines that were chosen according to their prominence, freedom from spectral interference and range of calibration curve linearity. The peak search window is the wavelength range scanned for a peak for that particular species. The window was made narrow enough to ensure that the correct intensity was measured.

Table 3.3 Elements that were chosen for analysis using ICP-OES.

Element	Wavelength (nm)	Search Window (nm)
Aluminium (Al)	237.312	0.080
Barium (Ba)	455.403	0.080
Beryllium (Be)	265.045	0.040
Boron (B)	249.773	0.027
Cadmium (Cd)	228.802	0.027
Calcium (Ca)	393.366	0.080
Chromium (Cr)	267.716	0.040
Cobalt (Co)	228.616	0.027
Copper (Cu)	324.754	0.040
Iron (Fe)	259.940	0.040
Lead (Pb)	220.353	0.027
Magnesium (Mg)	279.553	0.040
Manganese (Mn)	257.610	0.080
Nickel (Ni)	231.604	0.040
Phosphorous (P)	213.618	0.027
Potassium (K)	769.896	0.080
Selenium (Se)	203.985	0.080
Silicon (Si)	251.611	0.040
Sodium (Na)	588.995	0.080
Strontium (Sr)	407.771	0.080
Zinc (Zn)	213.856	0.027

Frequent cleaning of the torch is one of the recommended procedures if the optimum performance of the instrument is to be maintained. Therefore, the torch was cleaned once a week depending on the number of samples analysed. The cleaning process was as per instructional manual. This involved submerging the torch in aqua-regia overnight, and then rinsing it with ultra pure deionized water and oven drying at 105 °C overnight. In cases of extreme soiling HF was used to soak only the soiled section for a few minutes and the torch was rinsed as before. At the same time, the optical window was cleaned using lint free tissue moistened with ethanol. Brasso was used to polish the base plate, which was later rinsed thoroughly with MilliQ water before putting it back into its place. To ensure that sample introduction did not fluctuate, the peristaltic pump tubing was replaced when necessary.

3.5.4 Calibration curves for cations and phosphorous

ICP-OES standard solutions were obtained from Fluka with the exception of phosphorous. The solutions were supplied in 100 ml plastic bottles of 1000 ppm concentration. The standards were prepared in 100 ml volumetric flasks (grade A), and stored in plastic containers to avoid analyte absorption into the glass walls. The micropipette used to prepare the stock standard solution was calibrated by weighing ten 1 ml aliquots of water on a four decimal place balance. The temperature of water was measured using a thermometer and its density determined by interpolation of data provided by Robinson and Stokes.[10]

A total of 22-elements were selected for analysis and for each element standards were prepared. Two different sets of mixed standards were prepared to avoid the possibility of precipitation. The first set (SET-1) consisted of the following elements: aluminum, barium, beryllium, calcium, cobalt, iron, magnesium, manganese, phosphorous, silicon and sodium. The second set (SET-2) was composed of boron, cadmium, chromium, copper, lead, molybdenum, nickel, potassium, selenium, strontium and zinc.

The procedure for the preparation of five standards for Set-1 group of elements involved pipetting (10, 20, 50, 70 and 100 ml of the sock solution) into a 100 ml volumetric flask and diluting the solutions with a 0.1 M HNO_3 solution. For Set-2 elements, a similar approach was followed but different volumes (12.5, 25, 50, 75, and 100 ml) were pipetted. The acid was used so as to match the sample matrix and to preserve the standard solutions. The blank solution was that of 0.1 M HNO_3.

The phosphorous solution that was used for this analysis was prepared in the laboratory, b dissolving 4.2640 g of dibasic ammonium phosphate. The compound was first dried in a oven set at 105 °C before dissolving it in ultra pure deionised water using a 1 litre volumetri flask. The different concentrations for the elements in the two sets are summarized in Table 3.4 and 3.5.

Table 3.4 Set-1 analytes and standard concentrations (ppm) used for ICP-OES calibration.

Element	Standard 1 (ppm)	Standard 2 (ppm)	Standard 3 (ppm)	Standard 4 (ppm)	Standard 5 (ppm)
P	10	20	50	70	100
Al	5	10	25	35	50
Ca	2	4	10	14	20
Fe	1.5	3.0	7.5	10.5	15
Na	1	2	5	7	10
Ba	0.1	0.2	0.5	0.7	1
Be	0.1	0.2	0.5	0.7	1
Co	0.1	0.2	0.5	0.7	1
Mg	0.1	0.2	0.5	0.7	1
Mn	0.1	0.2	0.5	0.7	1
Si	0.1	0.2	0.5	0.7	1

Table 3.5 Set-2 analytes and standard concentrations (ppm) used for ICP-OES calibration

Element	Standard 1 (ppm)	Standard 2 (ppm)	Standard 3 (ppm)	Standard 4 (ppm)	Standard 5 (ppm)
K	0.625	1.25	2.5	3.75	5.0
Zn	0.625	1.25	2.5	3.75	5.0
B	0.125	0.25	0.5	0.75	1
Cd	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
Mo	0.125	0.25	0.5	0.75	1
Ni	0.125	0.25	0.5	0.75	1
Pb	0.125	0.25	0.5	0.75	1
Se	0.125	0.25	0.5	0.75	1
Sr	0.125	0.25	0.5	0.75	1

The standards were run in the ICP-OES as per conditions given in Table 3.2. In addition, the instrument was programmed to perform a background correction and to plot calibration curves for each element rejecting those with a correlation coefficient (R) value less than 0.995. The running of the standards involved the use of a 0.1 M HNO_3 solution as a blank followed by the standards from the least to the most concentrated.

The instrument was calibrated each time before use to ensure optimum operating conditions. The standard concentrations were plotted against their respective intensities to generate calibration curves using Origin 5.0, a data analysis and technical graphics software. Linear plots in the form of **y** = **mx** + **c**, where **y** represent the intensity, **m** the slope, **x** the concentration and **c** a constant (intercept) were developed. The details for each calibration curve are presented in the in Table 3.6, included are the corresponding regression coefficients (R). The respective calibration curves are shown in Figures 3.5 –3.8.

Table 3.6 Calibration curves parameters (y = mx + c) and their respective regression coefficients (**R**) values

Element	*Slope (**m**)*	*Constant (C)*	*Regression (**R**)*
Selenium (Se)	21361	0.5754	1
Strontium (Sr)	10000000	142435	0.9996
Nickel (Ni)	8192.6	78.575	0.9991
Boron (B)	28845	322.56	0.9991
Chromium (Cr)	29209	290.37	0.9994
Zinc (Zn)	528165	135.93	0.9998
Copper (Cu)	10500	-0.9425	1
Lead (Pb)	31540	165.97	0.9997
Cadmium (Cd)	317082	8.393	1
Potassium (K)	25491	-883.89	0.9998
Calcium (Ca)	5000000	1000000	0.9991
Barium (Ba)	4000000	420.71	0.9998
Aluminum (Al)	583.41	82.773	0.9998
Silicon (Si)	22856	-0.5612	1
Manganese (Mn)	92257	-0.4232	1
Iron (Fe)	15254	-1703.9	0.9997
Beryllium (Be)	8312.3	1.0535	1
Magnesium (Mg)	353468	-980.76	0.9999
Sodium (Na)	9970.3	7.1269	1
Phosphorous (P)	4907.3	-821.09	1
Cobalt (Co)	82977	-0.5345	1
Molybdenum (Mo)	162169	904.21	0.9992

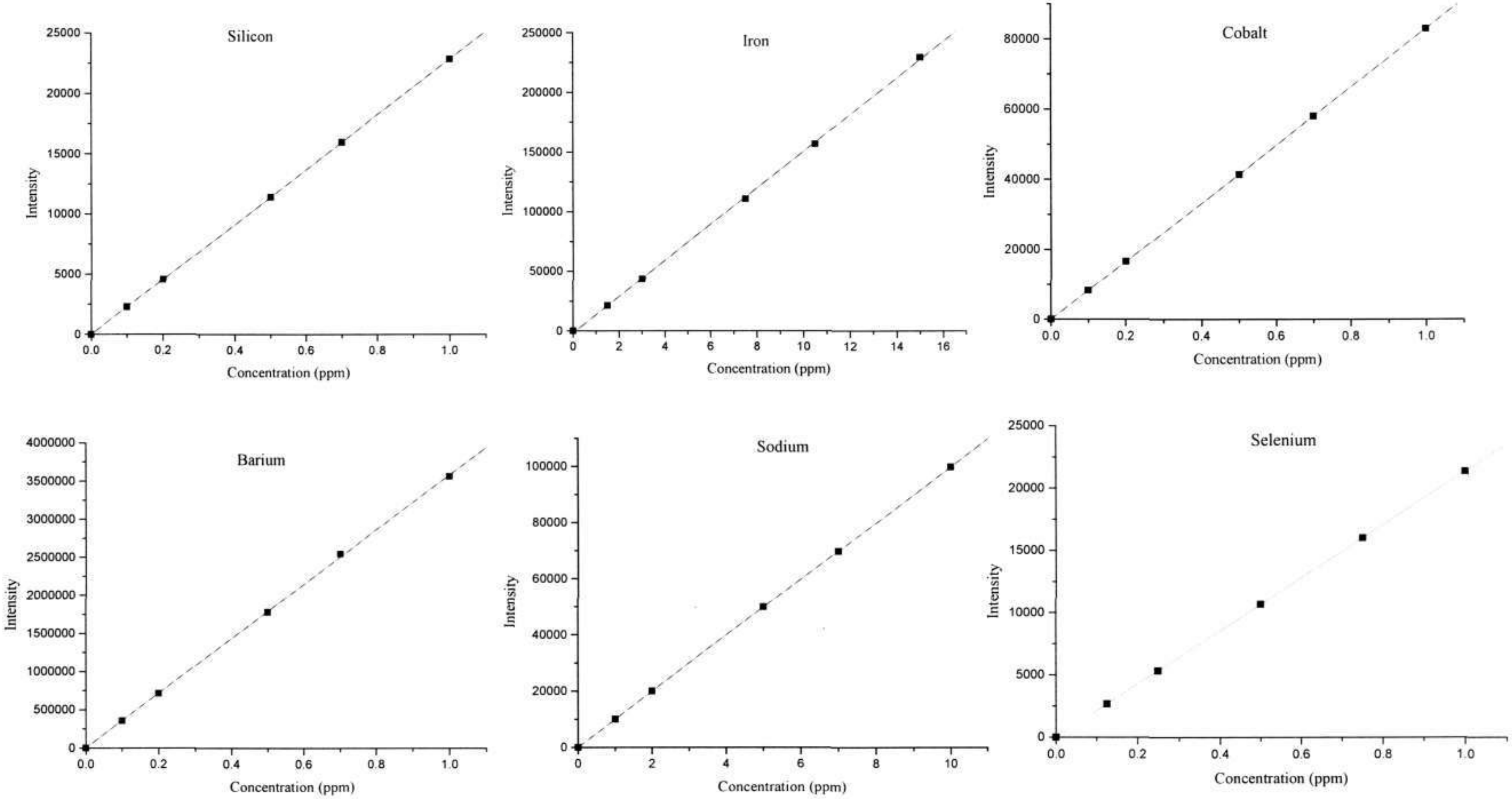


Figure 3.5 Calibration curves for Silicon, Iron, Cobalt, Sodium, Barium and Selenium.

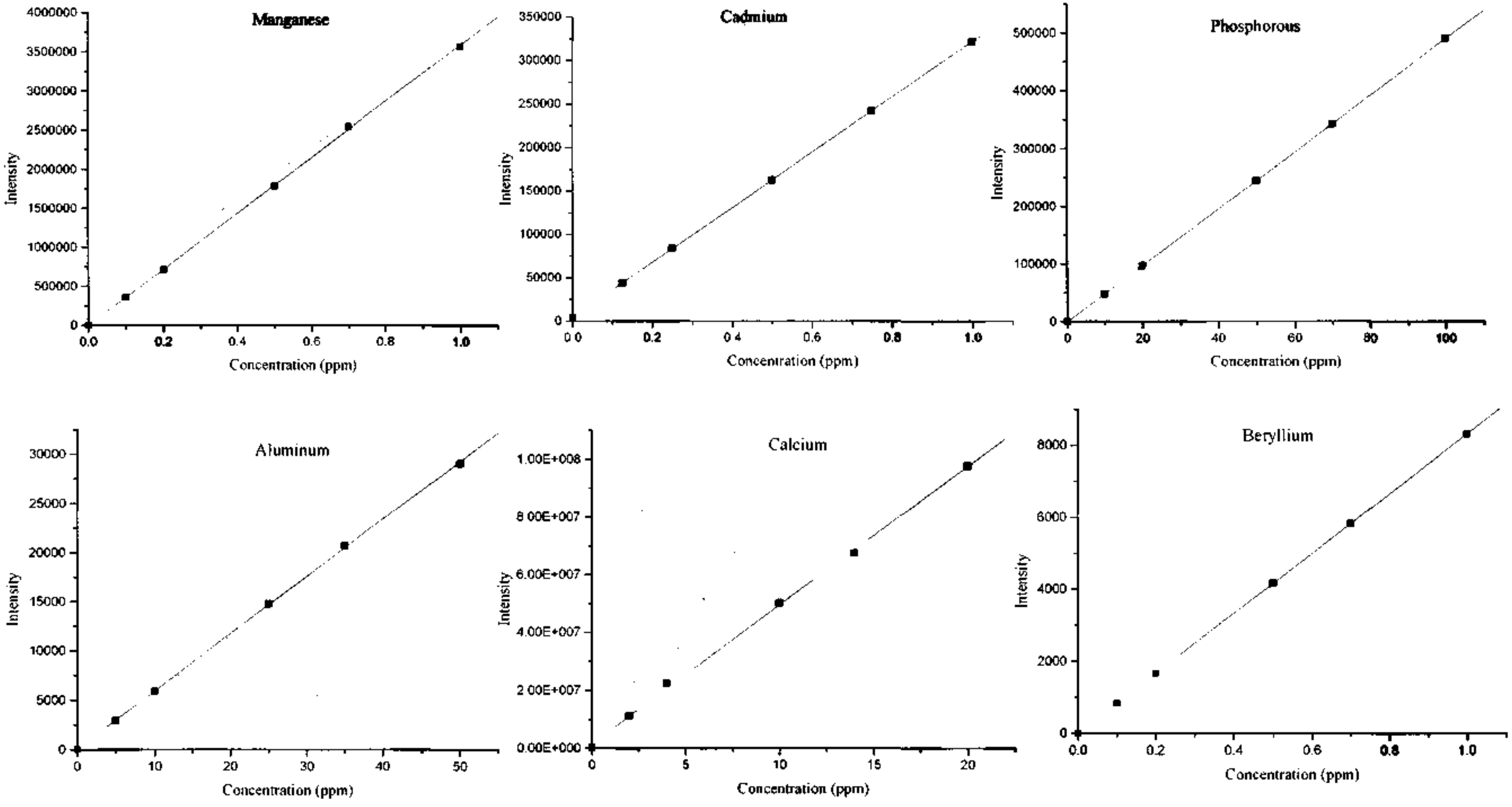


Figure 3.6 Calibration curves of Manganese, Cadmium, Phosphorous, Aluminum, Calcium and Beryllium.

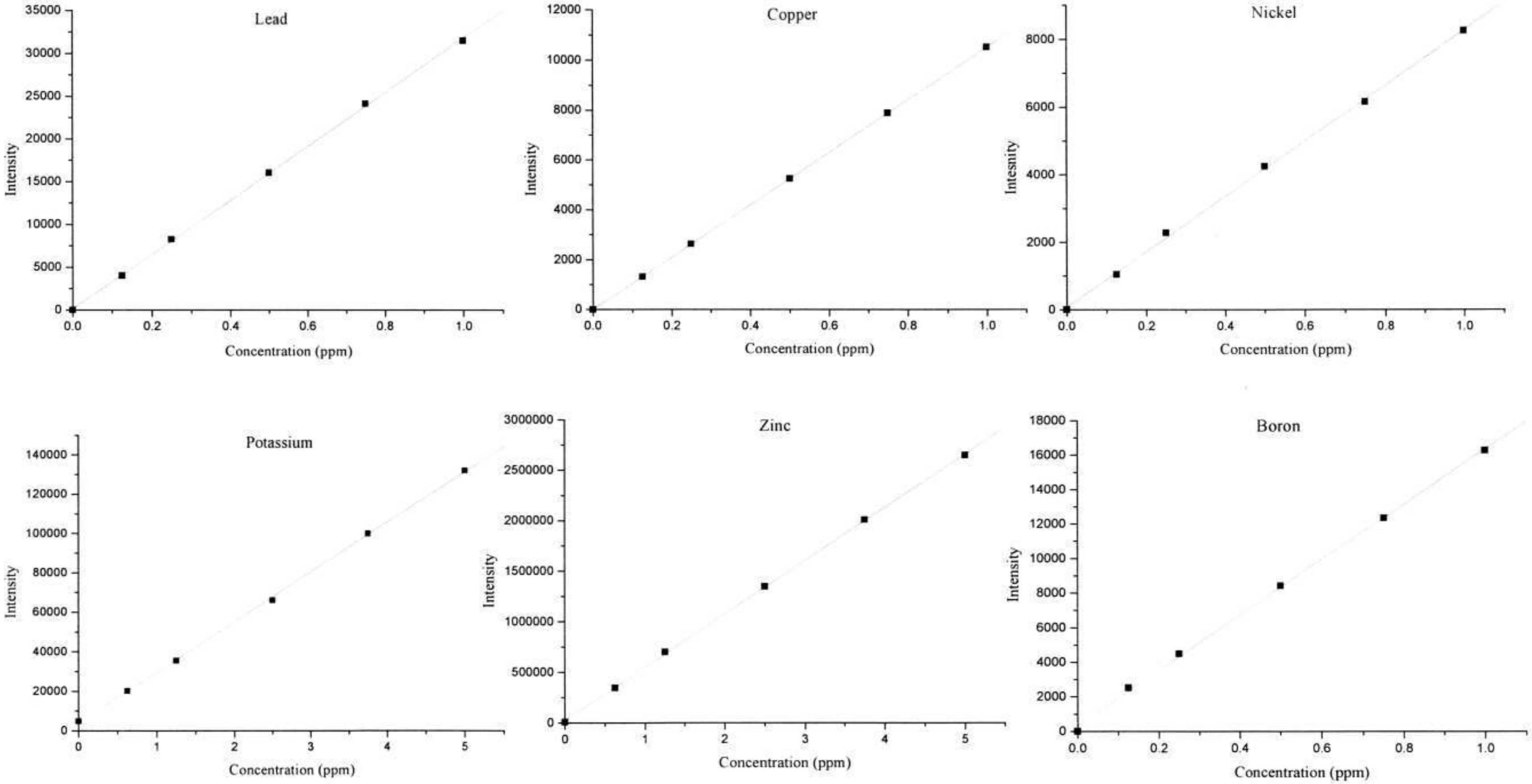


Figure 3.7 Calibration curves of Lead, Copper, Nickel, Potassium, Zinc and Boron.

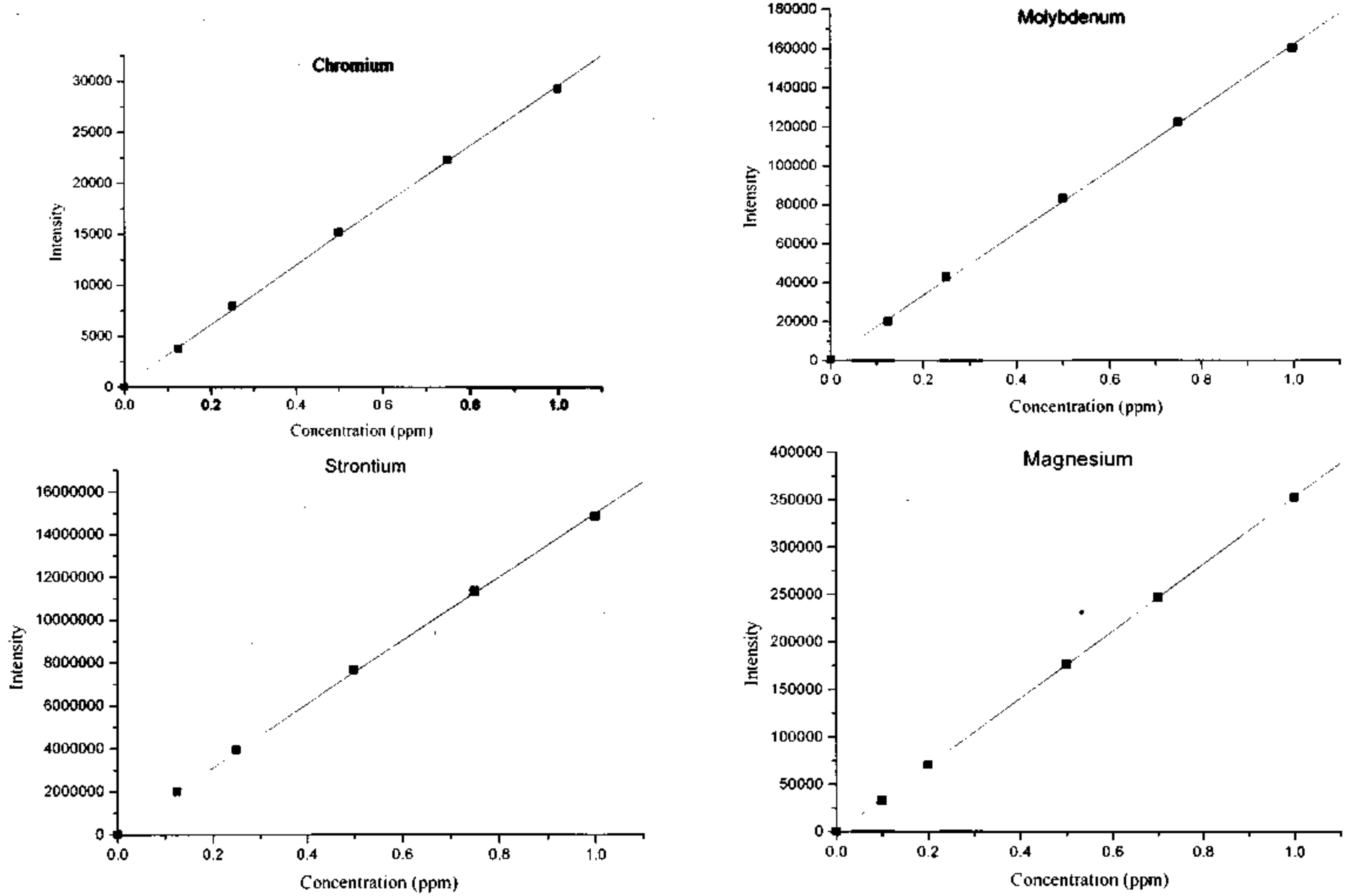


Figure 3.8 Calibration curves for Chromium, Molybdenum, Strontium and Magnesium.

3.6 Extraction of Polynuclear Aromatic Hydrocarbons (PAHs)

3.6.1 Sample handling

The sludge samples that had too much water were centrifuged to separate the solid and the aqueous phases. These samples were covered and left to dry at room temperature (~23 °C). Foreign materials such as wood and leaves were removed from the solid sludge before grinding, to achieve a homogenous sample having a bigger surface area for extraction efficiency. Two 10 g samples were weighed using a four decimal place balance (Mettler Toledo). One sample was for PAH extraction using Soxhlet method and the second one was for the determination of moisture content.

3.6.2 Soxhlet Extraction (USEPA method 3540C)

This is a method for the extraction of non-volatile and semi-volatile organic compounds from solid matrices such as sludge and wastes. The process ensures intimate contact of the sample with the extraction solvent. The method is applicable to the isolation of water-insoluble and slightly water soluble organic compounds for chromatographic methods of analysis.

A 10 g sample was weighed into a 100 ml beaker to which an equivalent amount of anhydrous sodium sulfate was added. Before blending of the two masses, 3 ml of surrogate standard solution was spiked into the sample, and allowed to age for an hour. The two masses were then blended together before being transferred into the extraction thimble, which was then placed in the Soxhlet extractor. A total of 300 ml of extracting solvent (1:1 dichloromethane: hexane) was placed into the 500 ml round bottom flask. The Soxhlet apparatus was then assembled (Figure 3.1Ssection 3.2) before the extraction process was allowed to proceed for 24 hours. After cooling the sample to room temperature (~23 °C), the sample was then dried by passing the extract through a 10 cm drying column containing anhydrous sulfate. The column was then washed with 125 ml of the extracting solvent. The dried extract and rinsate were transferred into the Kuderna-Denish (K-D) concentrator to reduce the solvent content. The concentration process was allowed to proceed until the volume had reduced to 2 ml. The concentrate was allowed to cool to room temperature before 50 ml of hexane (exchange solvent) was added, and the concentration process repeated. The extract was then allowed to cool to room temperature before being subjected to a sulfur clean-up process. The final volume of the extract was thus reduced to 3 ml using the nitrogen blowing technique and was stored in a refrigerator at 4 °C while waiting to be analysed.

3.6.3 Sulfur clean-up (USEPA method 3660B)

Elemental sulfur is found in many samples such as sediments and sewage sludge. The presence of elemental sulfur becomes evident in chromatograms produced in gas chromatography analysis. Elimination of sulfur by tetrabutylammonium (TBA) sulfite is recommended since it causes the least degradation of a broad range of pesticides and some organochlorine pesticides including PAHs.

The concentrated sample extract (3 ml) was transferred into a 50 ml clear glass bottle having a PTFE-lined screw-cap. The concentrator tube was then rinsed with 1 ml of hexane and the rinsate added to the 50 ml bottle. 1 ml of TBA sulfide reagent and 2 ml of 2-propanol were added to the extract and the bottle capped and shaken for 3 minutes. The presence of clear crystals indicated the presence of sufficient sodium sulfate in the sample extract. In the absence of a precipitate more crystalline sodium sulfite was added until crystals remained after repeated shaking. Thereafter, 5 ml of ultrapure water was added and the contents shaken for a minute to dissolve all the solid residues. The resultant solution was allowed to stand for ten minutes to separate the organic layer from the aqueous layer. The organic layer was then transferred into a 10 ml measuring cylinder where it was reduced to 3 ml using nitrogen-blowing techniques. The 3 ml extract was stored in a 3 ml Teflon sealed screw capped vial and refrigerated at 4 °C. This sample extract was analysed using a GC as recommended by USEPA method 8100 for PAH.

3.7 Analysis of Polnuclear Aromatic Hydrocarbons (PAHs)

3.7.1 Introduction to chromatography[11-19]

Chromatography can be defined as a technique in which components of a mixture of organic compounds are separated as the mobile phase transports the sample components through or across the stationary phase. Separation is based on the rate at which sample components are carried through the stationary phase by a gaseous or liquid mobile phase.

Gas chromatography (GC) represents a method for separating and detecting volatile organic compounds. As an instrumental technique it was first introduced in 1950's and has evolved to be one of the widely used tool in many laboratories. The technique is utilized in most of the industries such as environmental, pharmaceutical, petroleum, chemical manufacturing, food science and chemical forensics.

Separations in chromatography are determined by the extent at which a solute is partitioned between stationary and the mobile phases. For a solute A, the equilibrium involved is described by equation (3.1).

$$A_{mobile} \leftrightharpoons A_{stationary} \qquad (3.1)$$

The equilibrium constant for the reaction is called partition coefficient (K) or partition ratio and is defined by equation (3.2). In the equation C_s and C_m represents molar analytical concentrations in the stationary and mobile phases respectively.

$$K = C_s / C_m \qquad (3.2)$$

Ideally, K remains constant over a wide range of solute concentrations, and those compounds with low K values will spend most of their time in the mobile phase and hence, elute first; while those with high values will spend most of their time in the stationary phase and elute last as a result of higher retention.

When the bands elute a peak representative of the amount of the solute in the sample can be plotted as a function of time. For qualitative identification of peaks, retention times of individual peaks are used, these represent times required for peak to reach a detector after sample injection. The choice of a chromatographic column largely determines the success of the separation procedure. Efficiency can, however, be affected by band broadening. This results in a symmetric spread of velocities around mean value, which represent the behaviour of the average analyte molecule.

Column efficiency can quantitatively be evaluated using equation (3.3), where N represents the number of theoretical plates H the plate height, and L the length of the column.

$$H = L/N \tag{3.3}$$

The column efficiency increases with the N value and decreases with increasing H values. The efficiency of a column decreases with increasing band broadening. The various factors affecting band broadening can be summarized by a Van Deemter equation (3.4);

$$H = A + B/u + C_s u + C_m u \tag{3.4}$$

where H is the plate height in centimeters, u is the mobile phase velocity, the A term is the Eddy diffusion, C_s and C_m are mass transfer coefficients for mobile and stationary phases respectively and B is the longitudinal diffusion.

Eddy diffusion, defined by equation (3.5) is present only in the packed columns as a result of different flow paths around packing particles.

$$A = 2\lambda d_p \tag{3.5}$$

The term λ is the packing constant while d_p is the particle diameter.

The longitudinal diffusion term, B/u, represents a process by which molecules move from a more concentrated region to a more dilute region in the column. The rate of movement is directly proportional to the concentration difference in the regions and the diffusion coefficients (D_m) of the species. D_m is a measure of mobility of a substance in a given medium. The B term decreases as the velocity of the mobile phase increases because, at high velocities, analytes have less time in the column than at low velocities and, hence, less time for diffusion.

The mass transfer coefficients, C_s and C_m, can mathematically be expressed as in equations (3.6) and (3.7)

$$C_s = d_T^2/D_s \tag{3.6}$$

$$C_m = d_p^2/D_m \tag{3.7}$$

where d_T = film thickness of packing material

d_p = particle diameter

D_s = diffusion coefficient of solute in solid phase

D_m = diffusion coefficient of solute in mobile phase

These C terms represents the resistance to mass transfer at the solute/solid phase interface and resistance to radial mass transfer by the packing material. The effects by this term are more pronounced at low mass transfer rates and at increased mobile phase velocities.

The constant improvements in column technologies, detector efficiencies and sensitivities have made the difficulties presented by band broadening to be a minor impediment in chromatographic separations. The selection of the relevant program coupled with a carefully selected column can produce reasonably good separations. The latest discoveries have resulted in detection of even smallest concentrations, especially in environmental samples. Breakthroughs such as the recently discovered 2-dimensional analysis (GC-GC) promise to be a new window of opportunities for chromatography.

3.7.2 Fundamentals of Gas Chromatography

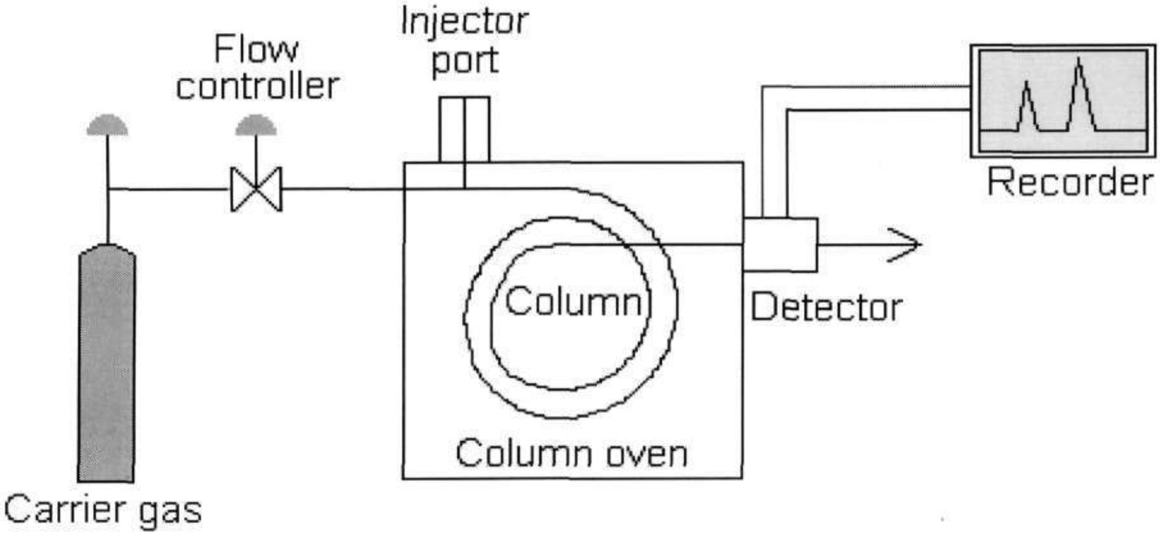


Figure 3.9 Schematic representation of a gas chromatography

The basic components of a GC include a carrier gas (N_2, He or Ar) supply and control unit, an injection port at one end of the column, a column housed in an oven equipped with a fan, a detector on the other end of the column, amplifier and signal processor. A sample introduced on the injection port by a syringe gets vapourized in the injector and the carrier gas carries this sample throughout the column into the detector where a response is generated for each and every compound in the sample.

The carrier gases that are most commonly used are helium and nitrogen. These must be of sufficient pressure and quality, as the use of high quality carrier gases (those that are inert, dry and free of oxygen) prevents column degradation.[2] When the GC system uses a flame ionization detector (FID), two more gas supplies, namely air and hydrogen, are required. The injection port serves the main function of introducing the sample onto the carrier gas/column system in a gaseous form. Sample injection in packed column chromatography is normally a simple septum injection, while in capillary columns chromatography it can either be 'split/splitless' injector or the 'on-column' injector. In a split/splitless injector the sample is vapourized and a portion allowed to pass into the capillary column for separation while the remainder is purged out.

The components of the sample starts to separate as the sample reaches the column. As already mentioned, there are two types of columns for GC: packed and capillary columns. These would be housed in the oven to increase and/or decrease the temperature to desired levels. The GC ovens can respond rapidly to small temperature changes. As the compounds leave the column they reach a detector. The most popular detector due to its non specificity is the FID invented by Dr. RPW Scott in late 1960s.[12]

The FID was chosen in this investigation since it can detect almost any type of hydrocarbon organic compounds except for carbon monoxide, carbon dioxide, hydrogen cyanide, formaldehyde, formic acid and water.[11,16] In addition, the detector has very low detection limits (ppb or pico-grams).[15] Generally, organic compounds' response differences are very small, this means that one can compare peaks to get a general idea of the compound concentrations in the sample.

The detectors used during early stages of GC application included hot wire detectors, the gas density balance and the flame thermocouple detector. These detectors were effective, however low in the sensitivity scale. With improving technologies more sensitive detectors such as (FID), electron captured detector (ECD) and argon ionization (AI) were invented. Nowadays detectors for a specific group of compounds have been made such as ECD for the detection of halogenated compounds.

3.7.3 Optimisation and the GC conditions for the current work

The selection of the optimum conditions for GC involves choosing an appropriate column for a particular separation. The search for the best columns for separations is an ever-continuing process. As new and efficient columns get discovered, a need to have operating condition adaptable to separations is created. The column used in the current study was VF-5ms. When this column (VF-5ms) was obtained different conditions were essayed on the instrument until the optimum conditions were obtained, these are given in the Table 3.7.

Table 3.7 GC condition used in the current study

Instrument	Varian 3800 GC			
Column Specifications				
Part No.	CP8944			
Column type	WCOT Fused Silica			
Length	30 m			
Stationary phase	VF-5ms			
Inside diameter	0.25 mm			
Outside diameter	0.39 mm			
Film thickness	0.25 μm			
Oven temperature program:	Temperature (°C)	Rate (°C/min)	Hold (min)	Total (min)
	65	0.0	5.00	5.00
	140	25.0	5.00	13.00
	240	10.0	5.00	28.00
	300	2.0	2.00	60.00
Column flow	1.0 ml/min			
Detector	Flame Ionization Detector (FID)			
Temperature	250 °C			
Range	12			
Injection system	8400 Auto sampler			
Syringe Size	10 μL			
Injection mode	Standard split/splitless			
Solvent penetration depth	90%			
Sample penetration depth	90%			
Injector type	1177			
Operating temperature	300 °C			

The column was conditioned by heating at 320 °C for three days with the injector end connected while the detector was detached. The carrier gas (nitrogen) was allowed to flow through the column throughout the conditioning procedure. This was to sweep all the dirt from the column.

The environmental samples are known to contaminate the column and hence reduce the column resolution. When that happens strict quality control measures need to be implemented. For the current work small pieces (~10 cm) of the column ends were cut to remove the contaminated end, and the injector liner was frequently cleaned. Between runs the syringe was cleaned with a solvent (hexane) to prevent contamination. Calibration runs were periodically conducted in order to detect possible losses in instrument sensitivity and resolution.

3.7.4 Calibration of GC-FID instrument for PAH analysis

A mixed standard was obtained from Sigma-Aldrich containing a combination of sixteen compounds, namely: naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo(a)anthracene, chrysene, benzo(b)anthracene, benzo(k)flouranthene, benzo(a,h)anthracene, benzo(g,h,I)perylene, benzo(a)perylene, and indeno(1,2,3-cd)pyrene.. These compounds were present in different concentrations in the mixed standard as indicated in Table 3.8.

Table 3.8 Concentration of each PAH in the composite standard.

Compound Name	Concentration in the stock (ppm).	Formula weight (g/mol)	Retention time (minutes)
Naphthalene	1000	128.2	10.48
Acenaphthylene	2000	152.0	15.90
Acenaphthene	1000	154.0	16.47
Fluorene	200	166.2	18.09
Phenanthrene	99.8	178.2	20.81
Anthracene	100.4	178.2	20.95
Fluoranthene	200	202.3	23.98
Pyrene	100.2	202.2	24.70
Benzo(a)anthracene	100.4	228.2	30.56
Chrysene	99.8	228.2	30.78
Benzo(b)fluoranthene	200	252.3	37.13
Benzo(k)fluoranthene	99.8	252.3	38.34
Benzo(a)pyrene	100	252.3	40.52
Indeno(1,2,3-cd)pyrene	100.2	276.3	48.98
Dibenzo(a,h)anthracene	200	252.3	49.36
Benzo(g,h,I)perylene	199.6	276.3	50.82

The standards were prepared by pipetting 1ml from the stock solution and diluting this in a 10 ml volumetric flask with isooctane as recommended by EPA method 8100 for PAH analysis. An average of five standard solutions were prepared from the supplied stock solution. These were always refrigerated at 4 °C when not in use. The precaution was undertaken to curb any possible reaction that could lead to degradation of the samples. The standard concentrations (ppm) and their respective peak areas (µV.sec) are shown in Table 3.9 and Table 3.10 respectively.

Table 3.9 Concentrations of calibration standards used for PAHs.

Compound Name	Standard 1	Standard 2	Standard 3	Standard 4	Standard 5	Standard 6
Acenaphthylene	0.4	4.0	20	40	100	-
Acenaphthene	0.2	2.0	10	20	50	-
Naphthalene	0.2	2.0	10	20	50	-
Indeno(1,2,3-cd)pyrene	-	2	5	12.5	25	50
Pyrene	0.19	1.9	9.61	19.2	48.1	-
Benzo(b)fluoranthene	0.04	0.4	2.0	4.0	10.0	-
Dibenzo(a,h)anthracene	0.04	0.4	2.0	12.5	25.0	50.0
Fluorene	0.04	0.4	2.0	4.0	10.0	-
Fluoranthene	0.04	0.4	2.0	4.0	10.0	-
Benzo(g,h,I)perylene	2	4	5	12.5	25	50
Anthracene	0.0201	0.201	1.0	2.01	5.02	-
Benzo(a)anthracene	0.020	0.20	1.00	2.01	5.02	-
Benzo(a)pyrene	1	2	4	12.5	25	50
Benzo(k)fluoranthene	1.	2	5	5	12.5	25
Chrysene	0.02	0.2	1.00	2.0	4.99	-
Phenanthrene	0.02	0.2	1.00	2.0	4.99	-

Table 3.10 Area count(μV-sec) for PAH standard, used for preparation of calibration curves

Compound Name	Standard 1	Standard 2	Standard 3	Standard 4	Standard 5	Standard 6
Napthalene	19823	20018	104749	205933	513829	--
Acenaphthylene	7004	36763	202187	399375	1019344	--
Acenaphthene	3886	16046	86228	182736	473338	--
Fluorene	4125	3150	15998	34274	88841	--
Phenanthrene	602	1186	7156	14709	40367	--
Anthracene	250	878	5562	12401	35901	--
Fluoranthene	893	1476	10611	23551	68877	--
Pyrene	119	1063	5361	11399	28902	--
Benzo(a)anthracene	21	104	1347	3725	13114	--
Chrysene	24	60	1447	3720	13247	--
Benzo(b)fluoranthene	-	51	854	4256	15943	--
Benzo(k)fluoranthene	512	1894	6995	77032	219846	402664
Benzo(a)pyrene	850	1503	5613	72873	202394	384535
Indeno(1,2,3-cd) pyrene	1500	6995	135186	384692	746013	--
Dibenzo(a,h)anthracene	-	1434	4402	135186	384692	746013
Benzo(g,h,I)perylene	302	1937	6237	146957	392311	757265

- concentration of the standard was below the detection limit of the instrument.

-- no standard was prepared.

A composite standard was run in a GC-MS instrument with a column having a stationary phase similar to the one that is used on the GC. From the GC-MS results a sequence of peak appearance was established and the sequence agreed satisfactory with data reported from previous works on PAH analysis. The instrument type and the conditions for GC-MS are summarized in Table 3.11. The sequence of these compounds in terms of retention times is presented in Table 3.8.

Table 3.11 GC-MS conditions used in the qualitative analysis study PAH standards

Instrument Parameters	ThermoFinnigan, Model K07300000000080, S. No. 200031445, Milan.
Injector	
Split mode	Split-less mode
Split flow (ml/min)	50
Splitless time (min)	0.75
Injected volume (μL)	1.0
Wash solvent	Hexane
Carrier gas	Helium (99.995%, Afrox, South Africa)
Carrier gas flow (ml/min)	2.0
Column	EC-5, Serial No. 306187, Alletech Associates, USA. (5% phenyl, 5% methyl polysiloxane)
Length (m)	30
Internal diameter (μm)	0.32
Film thickness (μm)	1.00
Mass Spectrometer	PolarisQ A1/AS 3000.
Source temperature (°C)	200
Damping gas flow (ml/min)	0.3
Micro scans	3
Max ion time (ms)	25
Polarity	Positive
Ionization mode	EI
Scan mode	Full Scan
Mass range (amu)	50.0-600.0

Representative chromatograms for the 16 PAHs are shown in Figure 3.10. The expanded portions of the chromatogram, showing increase in peak height with increasing standard concentrations for the individual PAH, are shown in Figures 3.11 and 3.12.

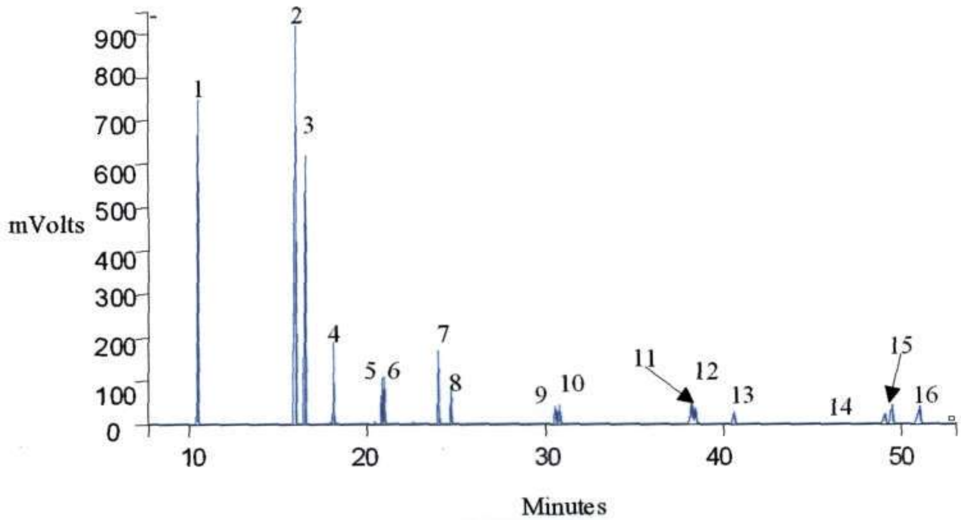


Figure 3.10 PAH peaks obtained from the mixed standard as they appeared from the GC.

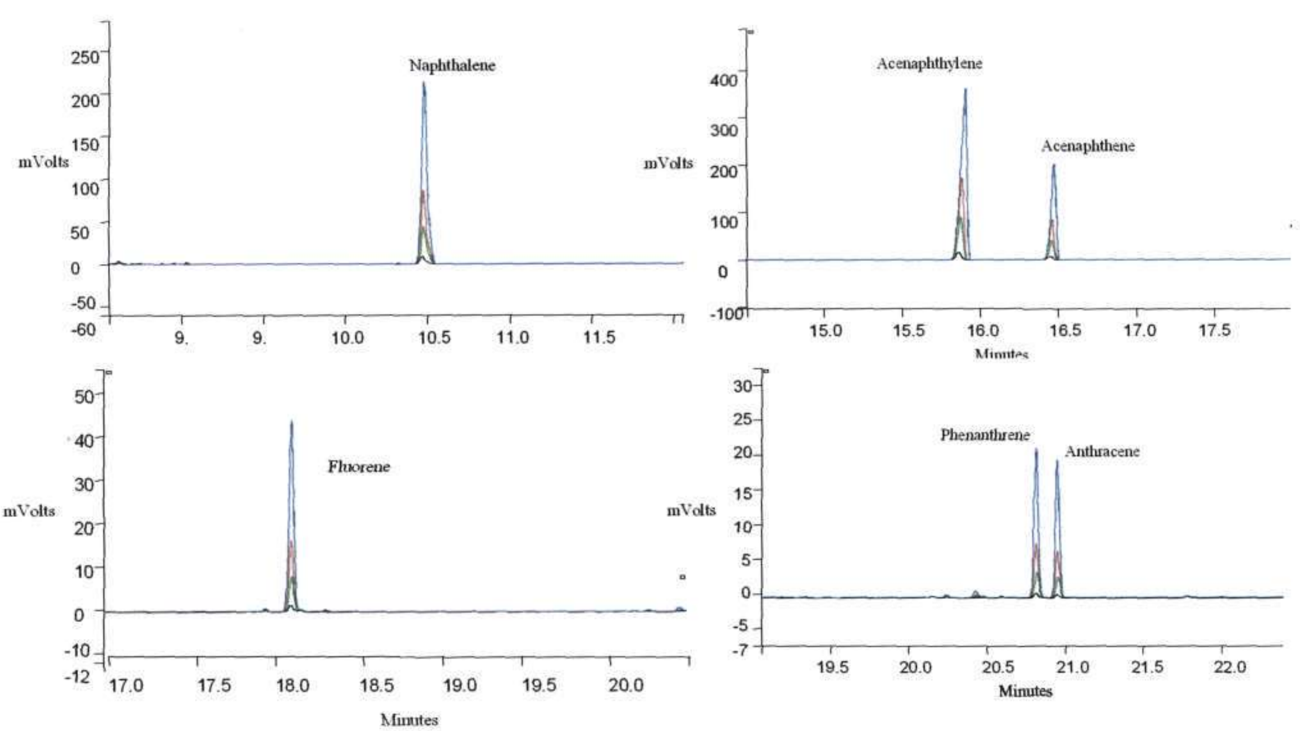


Figure 3.11 A zoomed view of standard peaks as they were observed in the GC.

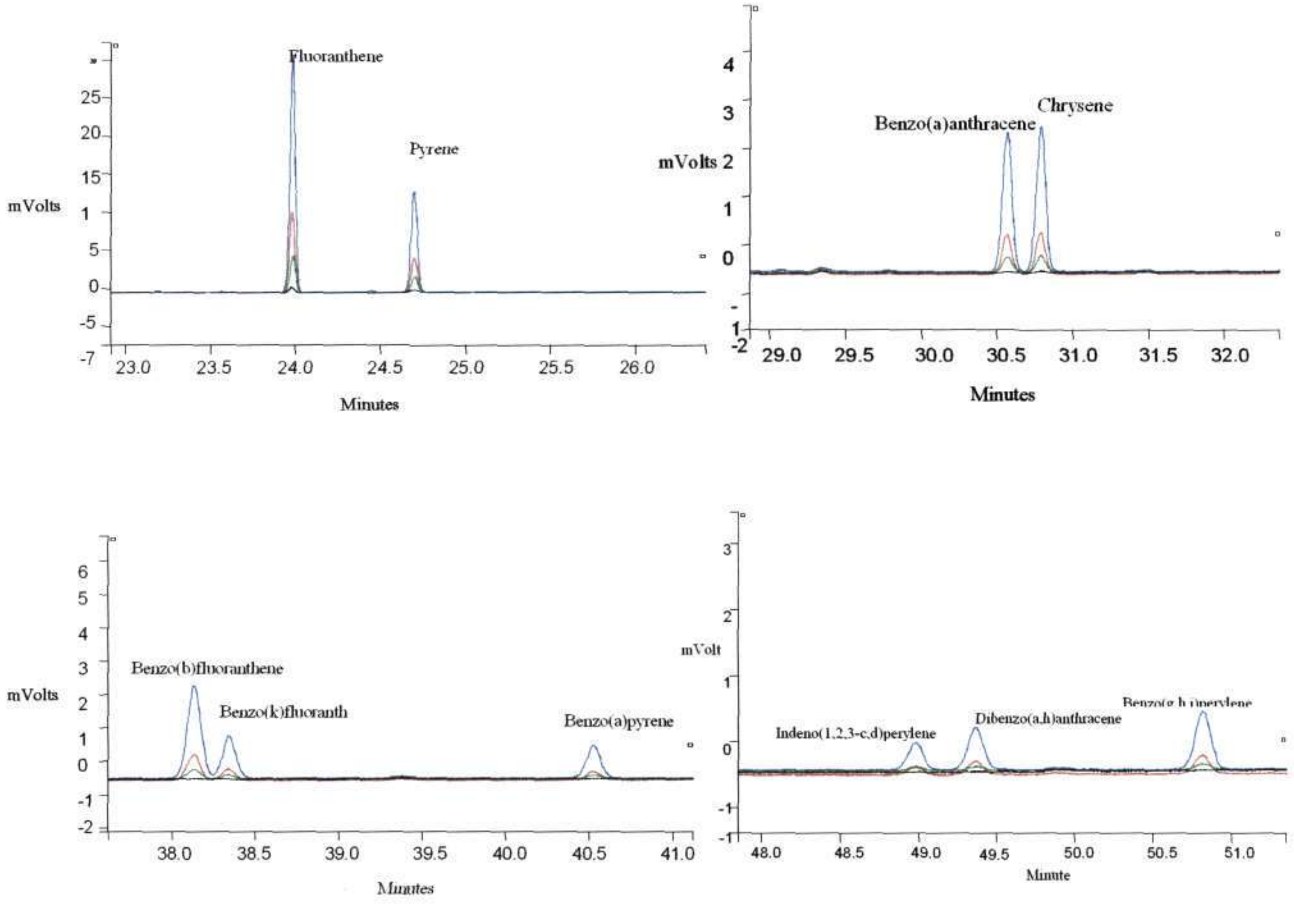


Figure 3.12 A zoomed view of standard peaks as they appeared in the GC.

The peak areas corresponding to each PAH were therefore plotted against concentrations to generate calibration curves shown in Figures 3.13 to 3.16.

3.7.5 Calibration curves for PAHs.

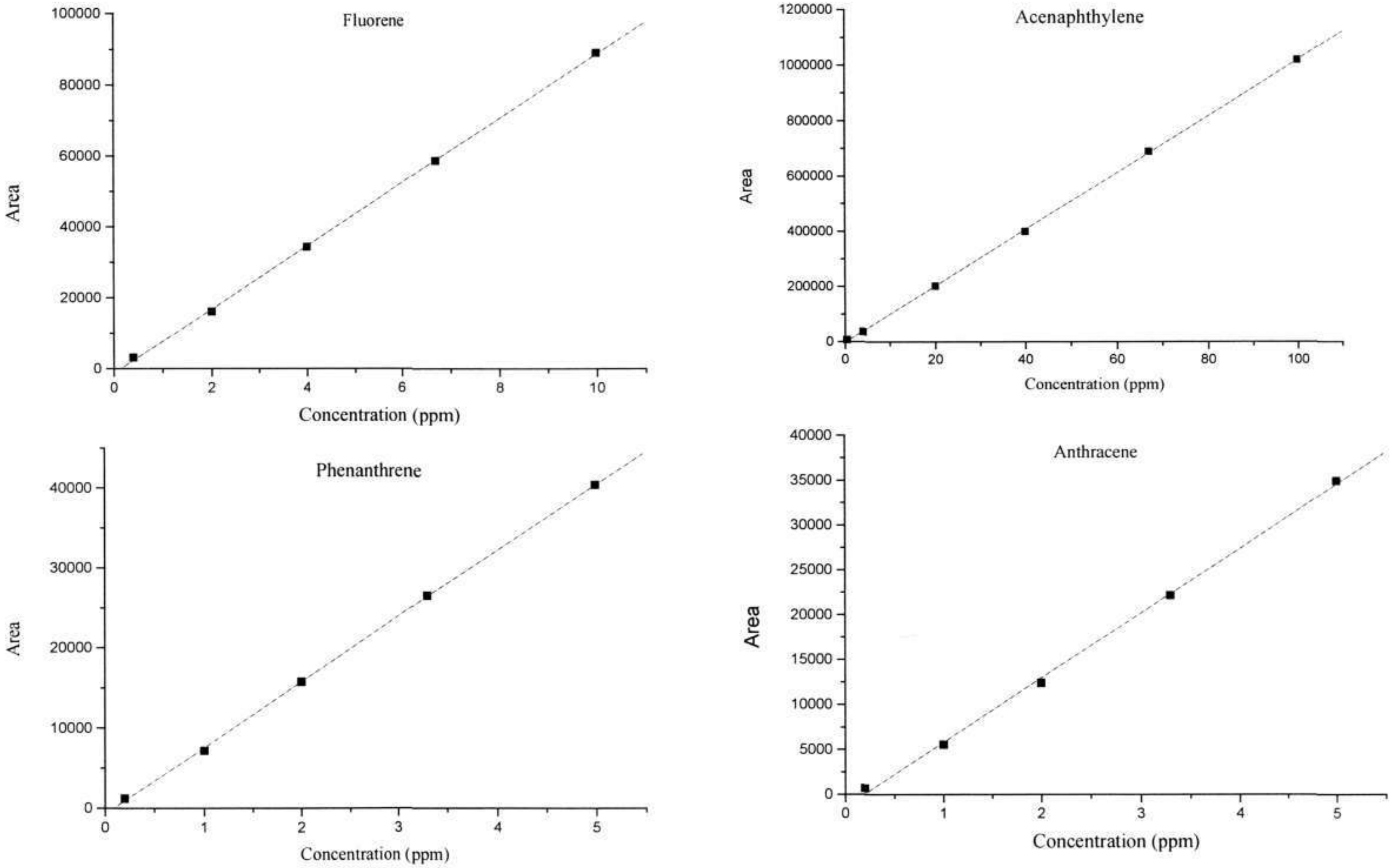


Figure 3.13 Calibration curves for Acenaphthylene, Anthracene, Fluorene and Phenanthrene.

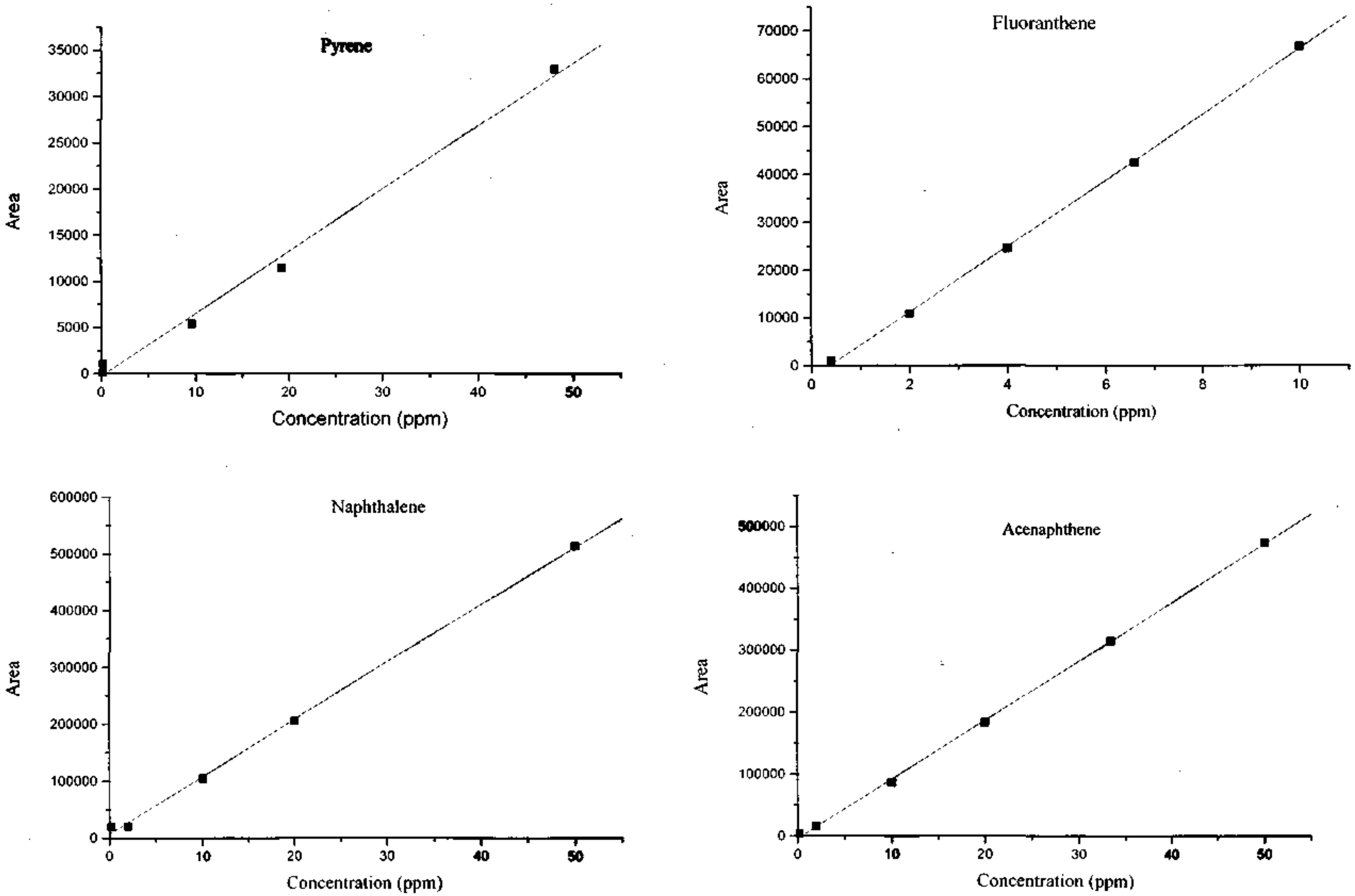


Figure 3.14 Calibration curves for Acenaphthene, Fluoranthene, Naphthalene and Pyrene.

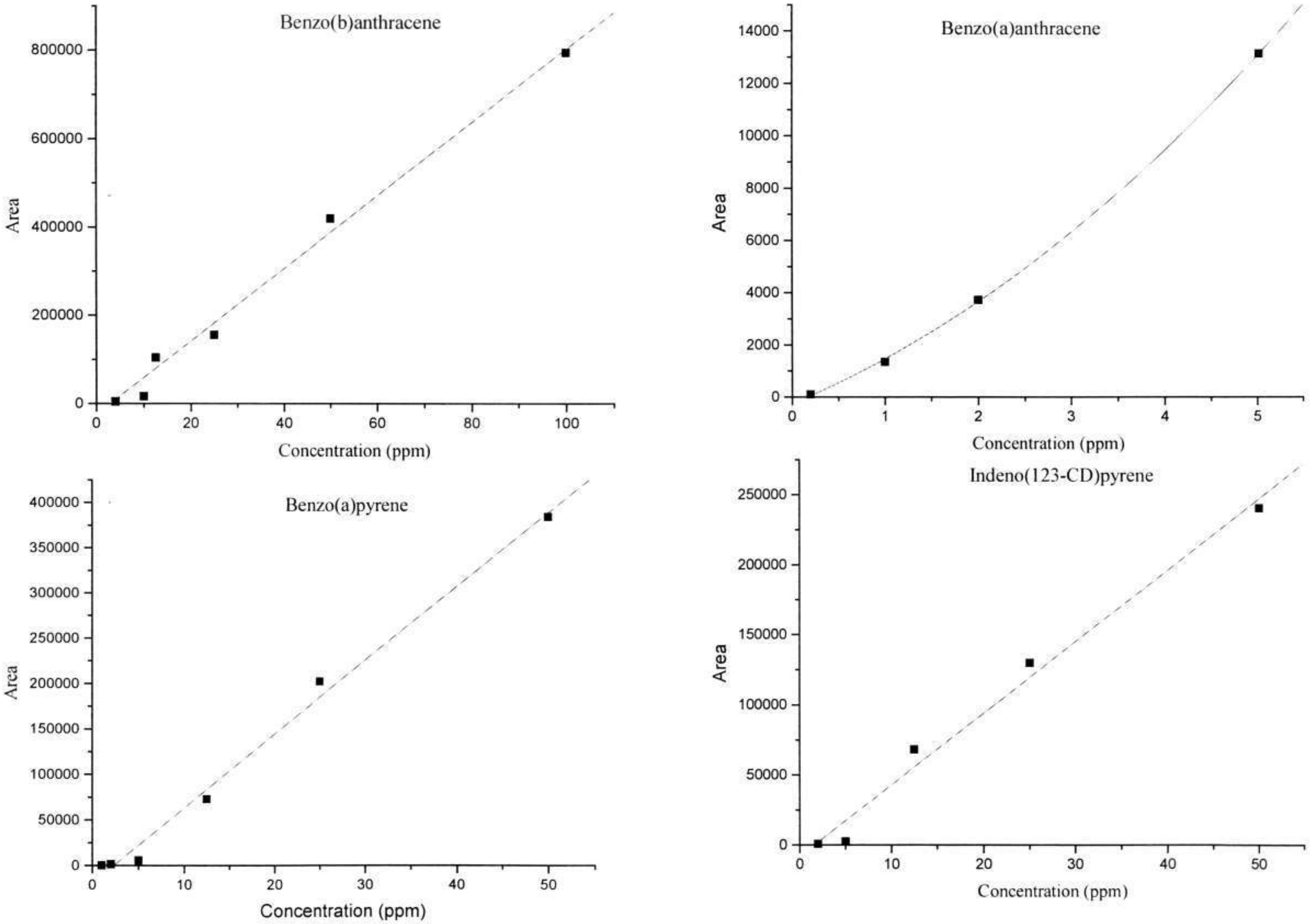


Figure 3.15 Calibration curves for Benzo(a)anthracene, Benzo(b)fluoranthene, Benzo(a)pyrene, and Indeno(1,2,3-CD)pyrene

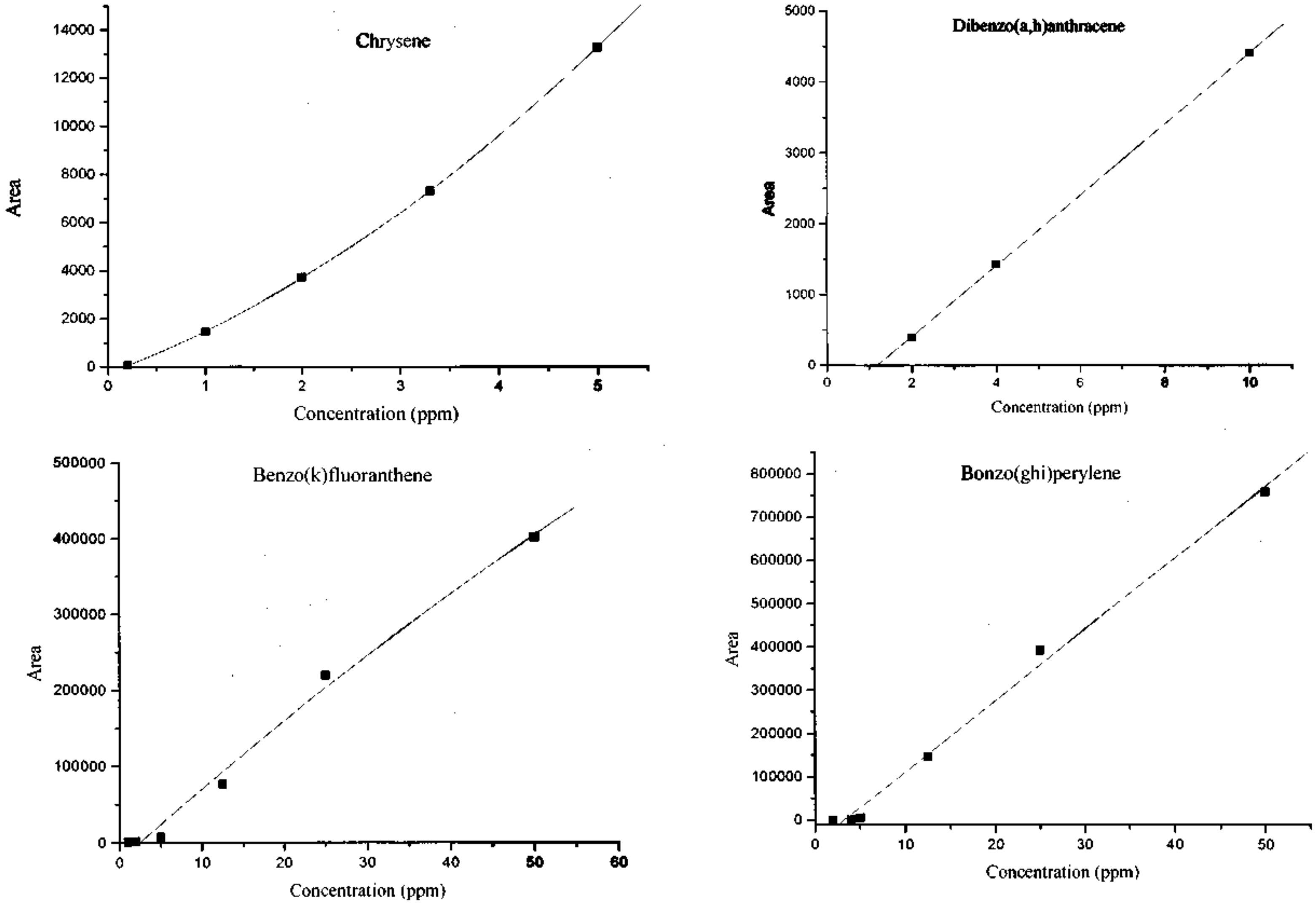


Figure 3.16 Calibration curves for Benzo(k)fluoranthene, Benzo(ghi)perylene, Chrysene and Dibenzo(a,h)anthracene

The calibration curve parameters generated using Origin 5.0 software for each compound are tabulated in Table 3.11 and 3.12. The compounds listed in Table 3.11 were those that produced a straight line with satisfactory correlation coefficients in the form of y = mx + c, while those in Table 3.12 were those that produced a curve with the equation $y = ax^2 + bx + c$. Not all the plots passed through the origin. As a result, an intercept term (c) including the slope (m) and correlation coefficients (R^2) are included in Table 3.11. These parameters were used to quantify the respective PAHs in the sludge extracts.

Table 3.12 Calibration equations for PAHs in the form of y = mx + c

Compound	m	C	R^2
Naphthalene	10099	6829	0.9988
Acenaphthylene	10190	-2141	0.9999
Acenaphthene	9491	-3586	0.9998
Fluorene	8836	508	0.9993
Phenanthrene	8073	-468	0.999
Anthracene	7239	-903	0.999
Fluoranthene	6932	-1710	0.998
Pyrene	580	-168	0.9999
Benzo(b)fluoranthene	16636	-31108	0.991
Benzo(a)pyrene	15299	-18190	0.9932
Dibenzo(a,h)anthracene	76991	1198	0.9925
Indeno(1,2,3-cd) pyrene	16073	-39734	0.9911
Benzo(g,h,I)perylene	7275	-6751	0.9934

Table 3.13 Calibration parameters for the plots in the form of $y = ax^2 + bx + c$

Compound	a	b	c	R^2
Benzo(k)fluoranthene	-7.5	8809	-15352	0.9902
Benzo(a)anthracene	268	1299	-64.6	0.9995
Chrysene	201	1717	-179	0.9958

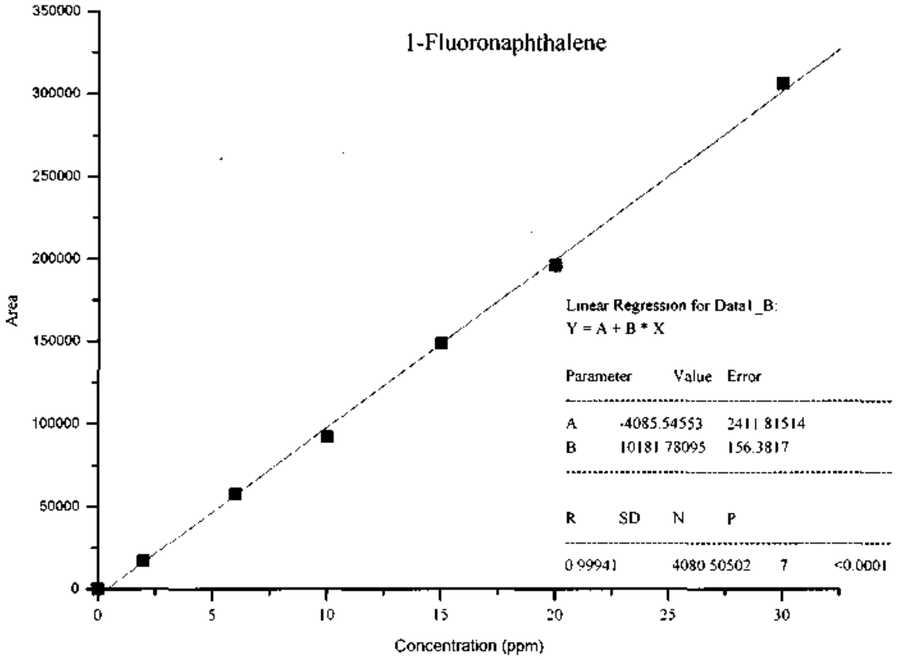
3.7.6 Preparation of calibration curves for surrogate standards

A surrogate standard is a compound that has properties similar to the target analyte(s) that a particular analytical method is designed to identify and measure. The surrogate compound is not, expected to be in an environmental field sample and should not therefore, interfere with the identification or quantification of the target analytes. By demonstrating that the surrogate compound can be recovered from the sample matrix with reasonable efficiency, the surrogate standard performs a quality control function on the suitability of the analytical method for the intended analyses and on the ability of the laboratory to execute that method with reasonable proficiency. If a surrogate compound is not recovered, an analyte of concern also may not be recovered.

The two surrogate standards that were selected for this determination were 2-fluorobiphenyl and 1-fluoronaphthalene. Pure standards obtained from Aldrich were used to prepare a series of concentrations six in total as shown in Table 3.13. The area counts used in the construction of the calibration curve are included in Table 3.13. The concentrations were prepared from a stock standard solution of 100 ppm by dilution process. The linear plots that were obtained by using Origin 5.0 software can be seen in Figure 3.17 and 3.18. The linear equations for each graph have been inserted in the plots. These were used to calculate the amount of surrogate standards recovered in the extracted samples.

Table 3.14 Concentrations and the corresponding area counts for surrogate standards.

Concentration (ppm)	1-Fluoronaphthalene [Area in (μV.sec)]	2-Fluorobiphenyl [Area in (μV.sec)]
0	0	0
2	16876	52656
6	57728	185624
10	91903	297834
15	148385	485053
20	195927	631752
30	305670	987628

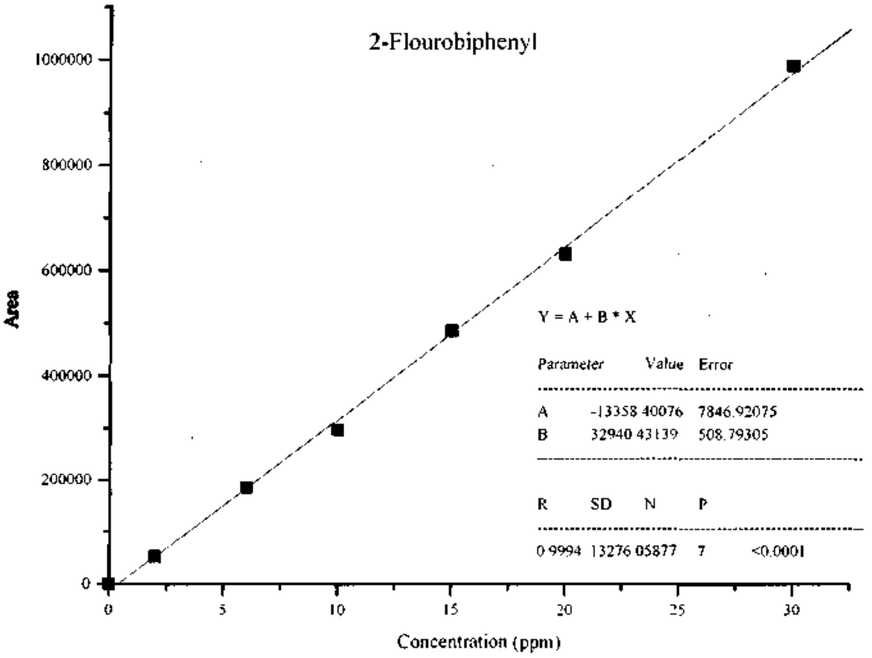


```
Linear Regression for Data1_B:
Y = A + B * X

Parameter      Value       Error
------------------------------------------------
A         -4085.54553    2411 81514
B          10181 78095   156.3817
------------------------------------------------

R         SD         N      P
------------------------------------------------
0 99941        4080 50502    7        <0.0001
```

Figure 3.17 Calibration curve for surrogate standard 1-Fluoronaphthalene



```
Y = A + B * X

Parameter      Value       Error
------------------------------------------------
A         -13358 40076   7846.92075
B         32940 43139    508.79305
------------------------------------------------

R       SD          N      P
------------------------------------------------
0 9994  13276 05877  7        <0.0001
```

Figure 3.18 Calibration curve for surrogate standard 2-Fluorobiphenyl

The USEPA method 3500 recommends that the concentration of the surrogate should be 10 times the average concentration of the analytes to be evaluated. In this investigation the concentration of the surrogate used for spiking the sludge samples was 10 ppm. A total of 34 samples were spiked with 3 ml of surrogate standard solutions of 10 ppm. The spiked samples were left to age for over an hour before subjecting it through the Soxhlet extraction process as indicated in Section 3.6.2.

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Chapter 4

Discussion of Results

CHAPTER 4

4 DISCUSSION OF RESULTS

4.1 Moisture content in sewage sludge

The sewage sludge moisture content was determined following the procedure explained in section 3.4.1. The sample was dried at 105 °C and then cooled in a dessicator. The change in mass was then calculated in terms of percentage as shown in Appendix A. The results that were obtained are presented in Table 4.1.

Table 4.1 Moisture content (%) found in the South African sewage sludge.

Plant Number	Moisture Content (%)	Sampling Point	Sample Description
01	90.59	Wet sludge	Anaerobic digested
02	25.90	Compost	Anaerobic digested
04	73.05	Peddies	Anaerobic digested
05	67.69	Peddies	Anaerobic digested
06	62.24	Peddies	Anaerobic digested
07	99.02	Return flow	WAS
08	90.50	Digesters	Anaerobic digested
09	99.40	WAS	WAS
10	73.99	Digesters	Anaerobic digested
11	4.51	Pit	WAS
13	89.80	Wet sludge	Anaerobic digested
14	95.23	Wet sludge	Aerobic digested
15	92.44	Wet sludge	Aerobic digested
16	85.75	Belt press	Anaerobic digested
17	26.07	Drying beds	Anaerobic digested
18	21.07	Compost heap	Compost
19	84.34	Belt press	WAS
20	17.83	Compost heap	Compost
21	97.76	Wet sludge	Anaerobic digested
22	93.08	Wet sludge	Anaerobic digested
28	88.08	Return flow	WAS
30	97.42	Drying lagoons	WAS
37	40.53	Compost heap	Compost
41	89.12	Centrifuge	WAS
42	95.89	Return flow	WAS+Digested
44	70.81	Drying beds	Digested sludge
45	93.64	Belt press	Digested sludge
54	72.60	Return flow	WAS
55	68.68	Drying beds	Anaerobic digested
57	95.76	Belt press	WAS
58	76.35	Belt press	WAS & Digested
59	4.49	Bins	Pellets
75	74.42	Heaps	WAS
76	71.37	Drying beds	Petro sludge

The results in Table 4.1 show a great variability in terms of moisture content with the values ranging between 4.5 and 99.4%. The variability can be explained by the difference in sampling points and the amount of time samples spent in the respective sampling points. When samples are classified in terms of their sampling points (Table 4.2) a clear picture emerges, which shows that fresh samples such as those from belt press, centrifuge, return flow, and wet sludge (Table 4.1) contained higher moisture contents of similar percentage. The other group of sludge that had not been collected immediately after being produced and had possibly stayed in their respective sampling points for unknown length of time had a slightly lower moisture content. This is possibly due to the fact that these samples had been exposed to the sun and had undergone evaporation and leaching of water to the ground. This point is clearly demonstrated by looking at the variation in the moisture contents at plant numbers 17, 44, and 76 which are all different, ranging between 26 to 71% moisture yet are all from drying beds.

Table 4.2 represents average values for different sampling points. An overall analysis of samples according to sampling points indicated that the minimum content of 26 ± 10% moisture was present in samples from compost heap while a maximum of 94 ± 3.0% was detected from wet sludge samples. The sample that had the lowest moisture content looking at Table 4.1 were samples collected from pit and bins with moisture content of 4.5%.

Table 4.2 Moisture content (%) according to sampling points.

Sampling Point	Mean (±SD)	No. of sewage works
Wet sludge	94 ± 3.0	7
Return flow	89 ± 12	4
Belt Press	87 ± 8.0	5
Digesters	82 ± 12	2
Peddies	68 ± 5.0	3
Drying beds	53 ± 24	5
Compost Heap	26 ± 10	4
Others*	45 ± 48	4

* - Others categories include four samples from pit, drying lagoons, heaps and bins.

4.2 Concentrations of mineral ions detected in sewage sludge

The sludge was analysed for mineral ions using the procedure explained in section 3.4.3 of the experimental procedures. Four dried 1.0 g samples of sewage sludge were digested following USEPA procedure method 3050B for solid sludge. The resultant digestate was analysed for mineral ions using ICP-OES. A total of 22 mineral ions were detected, namely: Al, B, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, P, Pb, Se, Si, Sr, and Zn. Each sewage sludge sample was analysed for all 22 mineral ions and the concentrations obtained (mg kg^{-1} dry basis) are presented in Appendix C. In almost all of the samples analysed phosphorous was the most abundant mineral ion while Be was the least; in other cases Be was below the detection limits of the instrument. The following general trend of abundance was the most common:

P>Ca>Fe>Al>Mg>K>Zn>Na>Mn>Cu>Ba>Cr>Pb>Si>Se>Sr>B>Ni>Mo>Co>Cd>Be.

However, in a few samples calcium was the most abundant and sometimes cadmium was the least abundant instead of Be. The variability in abundance can be explained in terms of sewage sludge composition, which is largely dependent on the source of the inflow that is received by the wastewater treatment plant.

The heavy metals pollutants order of abundance was Zn>Pb>Ni>Cd was consistent throughout all the samples analysed. The concentrations of other metals such as Cu, Se, B, Cr, Co and Mo varied among the samples.

4.3 Classification according to different provinces

Since the samples were from different provinces, it is appropriate to analyse the data provincially. This is because each province has its own identity in terms of population dynamics and industry variations. The provincial average values tabulated in Table 4.3 were obtained by adding up all the concentration values of each sewage work in the province and taking the mean. The provincial concentrations are important in assessing the variability of the sewage sludge pollution in terms of content and quantity with respective to provinces, since the type of industries and population dynamics differ from one province to another. This information is likely to shed some light on the source of pollution. The standard deviation was also calculated to show the variability within a province.

Table 4.3 Mean concentration (mg kg^{-1}) classified according to provinces.

	KwaZulu-Natal **(9 samples)**	**Gauteng** **(20 samples)**	**WC + NWP** **(5 samples)**
P/10^4	5.2±1.5	5.3±2.7	4.7±2.8
Ca/10^4	1.3±7.1	2.9±2.2	1.9±0.7
Fe/10^4	1.2±0.7	2.5±2.3	1.1±0.6
Al/10^4	1.6±0.8	2.1±4.3	1.0±0.6
Mg/10^3	2.8±1.8	3.6±1.4	3.4±1.2
K/10^3	4.3±2.5	3.8±2.5	3.1±1.0
Zn/10^3	1.0±0.7	2.6±2.8	2.0±2.2
Na/10^3	1.5±1.8	6.8±13	3.1±2.3
Mn/10^2	22±57	4.3±4.1	2.5±2.4
Cu/10^2	3.0±1.4	4.5±2.6	3.7±3.6
Ba/10^2	1.9±1.0	2.4±2.5	1.5±0.8
Cr/10^2	1.5±2.2	4.3±7.8	1.1±0.8
Pb/10^2	2.6±1.9	2.4±2.0	1.3±1.4
Si/10^1	2.1±2.3	3.2±1.9	1.3±1.2
Se/10^1	3.1±2.6	9.8±17	2.7±3.3
Sr/10^1	5.6±1.9	8.8±9.4	7.8±1.5
B/10^1	1.3±0.9	2.5±2.4	1.8±1.3
Ni/10^1	5.2±3.0	17±15	17±20
Mo/10^1	3.3±5.4	2.7±5.2	1.7±0.5
Co	4.8±3.5	20±23	17±8.7
Cd	2.8±2.1	6.9±8.5	4.5±2.9
Be	1.4±1.3	9.9±15	1.3±1.9

WC + NWP – North West 2 samples and Western Cape 3 samples.

In Table 4.3 only 3 categories can be seen these are concentrations for KwaZulu-Natal, Gauteng and North West plus Western Cape provinces. The concentration values were arranged in a descending order of abundance. The results show that on average the Gauteng values are slightly higher than those in the other provinces, this can be due to an established mining industry within this province. However, when the results were subjected to statistical analysis (ANOVA) the outcome was that the concentration ranges for the elements within the provinces were not statistically different, since the p-factor obtained were all greater than 0.05. For the difference to be significant the p-factor must be less than 0.05. Phosphorous proved to be the most abundant mineral ion with beryllium the least in all the provinces. There is also a general trend established within the major pollutants of concern, also to the South African legislator, where Zn is the most abundant and Cd the least with the concentrations ranging from 5.3×10^3 mg kg^{-1} to 1.3 mg kg^{-1}. The common order was found to be:

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

The results show very high standard deviations in and between provinces. This is expected since sludge composition is dependent on the inflow in a sewage treatment plant. Therefore one would expect these to be different depending on the type of industries and population within the province. It is therefore not surprising that the standard deviation varies as in the table.

4.4 Effect of sewage sludge origin and its effect on the mineral ion concentrations

The treatment and disposal of sewage sludge is one of the more tedious and costly exercises undertaken in a waste water treatment plant. As a way to reduce pollution levels in sewage sludge one needs to know the type and amount of pollutants in the original influent sewage. The main reason for this is that almost all of the inorganic pollutants present in the sludge are a result of original sewage. Thus it becomes necessary to distinguish between the influence that might be due to industrial origin and one that might be due to domestic sources. Because of this the sewage plants were categorized into two groups: those that receives more than 10% of industrial effluent and ones that receives more than 90% of domestic effluent. The data showing the mean concentrations including the standard deviations is presented in Table 4.4. From the table it can be seen that the samples that received over 10% of industrial sewage had a slightly higher levels of pollutants as compared to those that received over 90% of domestic sewage. The only exception was with the magnesium and potassium concentrations. However, both the domestic and industrial values fell within the same magnitude. Hence one can conclude that the levels of pollution from both domestic and industrial sewage are comparable, with industrial effluents having slightly higher levels. This can possibly be attributed to in-house treatment processes in industries prior to sewage discharge. The conclusion arrived at here was substantiated by the statistical analysis that was carried out using ANOVA where a t-test was performed at 95% confidence levels. The p-factor of > 0.05 was obtained indicating that the comparison between industries to domestic was not statistically different since the p-factor was greater than 0.05. This conclusion is in agreement with the comparison of data within the provinces. One can therefore conclude that domestic pollution might be the major source of pollutants.

Table 4.4 Mean concentrations (mg kg^{-1}) of mineral ions classified according to sources of pollution in sewage sludge

Mineral ion	≥90% Domestic	≥10% Industrial
P/10^4	4.7±1.9	5.4±2.8
Ca/10^4	2.3±1.0	2.7±2.2
Fe/10^4	1.3±0.6	2.3±2.2
Al/10^4	1.2±0.9	2.1±4.0
Mg/10^3	3.5±1.3	3.2±1.5
K/10^3	4.9±3.4	3.3±2.0
Zn/10^3	1.2±1.6	2.5±2.6
Na/10^3	2.8±2.9	5.8±12
Mn/10^2	2.9±1.6	3.9±4.0
Cu/10^2	3.2±2.5	4.3±2.5
Ba/10^2	1.6±0.6	2.4±2.4
Cr/10^2	1.3±2.0	3.9±7.3
Pb/10^2	2.0±1.8	2.4±1.9
Si/10	1.7±1.4	3.1±2.2
Se/10	3.0±3.1	9.0±16
Sr/10	5.8±2.1	8.9±7.7
B/10	1.5±0.9	2.4±2.3
Ni/10	11±16	16±14
Mo/10	1.3±0.7	3.4±4.7
Co	5.9±4.8	19±23
Cd	2.8±2.3	6.6±8.0
Be	2.9±4.4	8.0±15
No of samples	11	23

The data obtained was also analysed in terms of treatment processes as shown in Table 4.5 using the raw data in Appendix C. It is clear from the table that the order of abundance is the same for all the methods. One may say that to determine the effect of the treatment method one needs to use the same sewage. This is true but not possible in this case. The comparison between the industrial and domestic contribution indicated that there is no statistical difference between the two. Therefore one can treat the sample as being of similar origin. The results in Table 4.5 shows that there is not much difference between the treatment processes with the exception of concentrations for nickel and cobalt where the mean value for individual treatment processes varied by a factor of ten. The slight variation in all the other elements is most likely due to the difference in the influent.

Table 4.5 Classification of sewage sludge concentrations (dry basis, mg kg^{-1}) according to treatment processes.

Mineral ion	Anaerobic digested	WAS	Aerobic digested	Compost	Digested sludge	Others*
P/10^{4}	5.2±3.1	5.3±2.3	7.6±0.99	4.8±1.2	4.6±0.85	5.1±0.99
Ca/10^{4}	2.5±1.3	2.5±2.8	1.6±0.21	3.1±0.2	3.0±0.71	2.8±2.3
Fe/10^{4}	2.5±2.4	1.0±0.65	1.98±1.9	3.4±2.9	1.4±0.88	1.8±0.42
Al/10^{4}	2.8±5.3	1.1±0.84	0.7±0.51	1.2±0.2	1.0±0.69	2.1±0.42
Mg/10^{3}	3.2±1.5	3.5±1.3	4.3±0.14	3.9±1.7	2.0±0.28	2.6±1.8
K/10^{3}	3.1±2.3	4.1±2.4	5.4±1.5	3.6±1.2	2.1±1.06	7.4±6.6
Zn/10^{3}	3.2±2.7	0.79±0.38	5.8±5.8	1.5±0.3	0.59±0.26	1.8±1.3
Na/10^{3}	8.1±16	2.8±3.0	2.4±0.64	5.6±4.5	0.60±0.07	0.94±0.23
Mn/10^{2}	4.5±4.3	2.0±1.3	2.6±1.8	6.5±6.2	3.9±1.4	3.0±0.99
Cu/10^{2}	5.4±3.0	2.5±1.9	5.6±0.71	3.7±1.2	2.8±0.57	3.5±1.5
Ba/10^{2}	2.7±3.0	1.5±0.71	1.8±0.45	2.3±0.85	1.6±0.42	3.0±0.92
Cr/10^{2}	5.4±9.5	1.3±1.9	3.4±1.1	2.0±0.91	0.46±0.12	1.8±0.99
Pb/10^{2}	2.9±2.1	1.3±1.6	2.6±0.28	2.1±1.6	2.5±2.5	3.6±0.92
Si/10	3.5±2.1	2.2±2.3	4.0±0.42	1.5±1.0	0.94±0.94	1.4±0.07
Se/10	9.9±14	2.2±2.5	4.0±3.8	21.6±33	0.67±0.47	4.3±0.85
Sr/10	10±11	6.2±2.4	6.3±2.6	8.3±6.4	4.5±0.07	5.9±1.4
B/10	2.4±2.6	1.5±1.0	3.3±0.71	3.1±3.5	0.58±0.09	1.2±0.7
Ni/10	21±19	6.9±7.4	15±0.0	22±10	3.4±0.49	8.9±4.5
Mo/10	1.9±1.6	1.2±0.62	1.7±0.85	9.2±13	1.1±0.28	9.7±11
Co	20±27	6.9±6.7	11±11.8	23±16	3.3±0.76	10±4.4
Cd	6.8±7.5	2.4±2.0	18±18.5	5.3±1.7	2.1±1.1	4.8±3.3
Be	7.5±12	3.4±4.3	32±40.	2.8±2.4	1.2±1.7	2.3±0.01
No of samples	13	11	2	3	3	2

* - Others include both Pellets and Petro sludge.

The data was subjected to ANOVA analysis and the outcome showed that the differences in all the element concentrations were not significant and only the concentrations of Nickel were significantly different with the p-factor value of 0.03. The nickel concentrations for compost, aerobic and anaerobically digested sludge had higher concentrations when compared to other processing methods. This might indicate that these treatment procedures are possibly more effective in removing nickel than other treatment procedures. However, for one to reach that conclusion a standardized influent to all treatment processes need to be used. It can therefore be concluded that the treatment processes are equally effective in removing the mineral ions from sewage with the exception of nickel. A statistically significant difference in the abilities of the treatment processes to remove nickel was observed. The concentrations for Co, Cd, Se, and Be varied among different treatment processes, however the differences were not statistically significant.

The treatment processes have different advantages and disadvantages. Composting has the advantage of producing a stabilized, humus like product that is low in odour and volatile organic content scale.[1] Aerobic digestion reduces the volatile solid content by 50% and total solid by 30%, in addition to that it reduces the odours associated with raw sewage.[2] However, the sludge produced in this process usually contains high water content and hence would require some form of dewatering prior to dispersal. WAS and aerobic digestion processes also produce sludge that is very high in water content and this means that this sludge can be transported by pipes to a nearby site of dispersal. However, the sludge produced in these processes has high contents of microorganisms hence would require some form of stabilization before it is disposed-of.[1,2] Pellets are easy to handle and contain the least moisture content, in addition they have the least odour than all other sludge types.

The information generated so far shows that the different wastewater treatment plants produce sludge that has very similar types and abundance of mineral ions. Because of this a summary of the pollution status of the South African sewage sludge was generated and results are presented in Table 4.6. The table was generated by calculating the mean concentrations of mineral ions for all sewage works that were analysed.

Table 4.6 Overall statistical results of the concentrations (dry basis, mg kg^{-1}) of the mineral ions in South African sewage sludges.

Mineral ions	Mean (mg kg^{-1})	Median	Range
$P/10^4$	5.3 ±2.4	5.1	0.3-11
$Ca/10^4$	2.6±1.9	2.2	0.80-11
$Fe/10^4$	1.9±1.9	1.5	0.07-7.4
$Al/10^4$	4.2±14.5	1.1	0.30-8.2
$Mg/10^3$	3.3±1.4	3.6	0.86-5.3
$K/10^3$	3.8±2.6	3.1	0.62-12
$Zn/10^3$	2.1±2.4	1.3	0.40-10
$Na/10^3$	4.8±10.3	2.0	0.03-59
$Mn/10^2$	3.6±3.4	2.5	0.54-16
$Cu/10^2$	4.0±2.6	3.9	0.85-10
$Ba/10^2$	2.2±2.0	1.8	0.37-12
$Cr/10^2$	3.0±6.2	1.1	0.25-36
$Pb/10^2$	2.3±1.9	2.0	0.14-6.5
Si/10	2.6±2.1	1.9	<0.06-8.2
Se/10	7.1±13	2.7	0.019-53
Sr/10	7.9±7.4	6.2	1.4-45
B/10	2.1±2.0	1.7	<0.6-7.8
Ni/10	14.1±14.6	8.4	2.1-55
Mo/10	2.7±4.8	1.6	0.1-24
Co	13.3±18.8	5.4	1.9-90
Cd	5.4±6.9	3.6	0.36-31
Be	6.4±12.3	3.5	<0.16-60

The results show that there is no significant change in the order of mineral ions in terms of abundance. There is however, a very wide concentration range which can be due to the variability of concentrations in different sewage works in different provinces. The variability is most likely due to difference in sources of pollution that is received by the individual sewage works. This is largely influenced by the industries found in the sewage work region as well as the population dynamics feeding the sewage work.

The high abundance of Ca, Fe and Al might be a result of the use of lime, alum and iron compounds in the stabilization of sewage sludge.[1] The addition of these chemicals in sludge is one of the contributing factors resulting in high concentrations of these elements. Other factors might be the industries (such as mining industry, steel industry and power plants) releasing effluents that are rich in these elements. The elements such as P, Ca, Mg and K are the major nutrients for plants. Their high concentrations in sewage sludge means that sludge is a potential source of these elements and hence a good candidate for use as a bio-fertilizer for agricultural applications. The major concern for this practice is the presence of heavy metals in the sludge.

The inorganic pollutants that are of major concern in South African sewage sludge according to the legislation guidelines[3] include Cd, Co, Cr, Cu, Hg, Mo, Ni, Pb, Zn, As, Se, B and F. Elements that were detected during this study were Cd, Co, Cr, Cu, Mo, Ni, Pb, Zn, Se and B. The order of abundance for these mineral ions was:

Zn>Cu> Cr >Pb >Ni>Se>Mo>B>Co>Cd

The order of abundance for Zn, Cr, Cu, Pb and Ni was **Zn>Cu>Cr>Pb>Ni** this order was similar to that found in the survey conducted by Smith for inorganic chemicals in South Africa in 1989.[4] However, there was a difference in the concentrations order for Se, Mo, B, Co and Cd. The differences in these values can be attributed to the values that were outliers and hence omitted in the mean. These were either too high up or low and since these values are of low orders of magnitude small change in concentration result in a significant change in the mean value. For the heavy metals the highest value was that of zinc and copper which were 1880 mg kg^{-1} and 372 mg kg^{-1} followed by chromium, lead and nickel with 227 mg kg^{-1}, 209 mg kg^{-1} and 131 mg kg^{-1} respectively. The metals on the lower end were selenium, molybdenum, boron, cobalt and cadmium with concentrations of 52 mg kg^{-1}, 25 mg kg^{-1}, 19 mg kg^{-1}, 13 mg kg^{-1} and 4.7 mg kg^{-1} respectively.

4.5 Comparing of mineral ions between 1989 and 2003

The analysis of the change in the mineral ion concentrations over a period of time is important since it gives an idea of the behaviour patterns of the country with respect to pollution levels in their effluents. For this purpose the data obtained in 1989 was compared to the current data to formulate a pattern in the country. The concentration of mineral ions Ca, P, Mg, Zn, Cr, Cu, K, Pb, Se, B, Ni, Mo and Cd were selected for comparison and these are shown in Table 4.7.

Table 4.7 Concentrations of mineral ions in sewage sludges from sewage treatment works in South Africa.

Mineral ions		1989[a] survey[5]			2003[b] survey		
		Range	Mean	Median	Range	Mean	Median
Conc. (g kg^{-1})	P	4-41	16	14	3-110	51	50
	Ca	11-79	32	29	8-110	21	22
	Mg	2-13	6	5	0.86-5.3	3.2	3.3
	K	1-11	3	2	0.62-12	3.7	3.1
Conc. (mg kg^{-1})	Zn	237-17680	2054	1432	400-10000	1900	1200
	Cu	80-17217	654	355	85-1000	370	380
	Cr	25-10015	551	220	25-3600	230	110
	Pb	67-10137	452	214	14-650	209	240
	Se	<1-107	4	2	<3.9-530	52	27
	B	6-78	31	28	<0.6-78	19	17
	Ni	6-2660	154	55	20-550	131	91
	Mo	1-24	6	5	<0.1-24	2.5	15
	Cd	<1-122	12	3	<0.1-31	4.7	3.6

a- represents an average of 77 sewage sludge samples
b- represents an average of 34 sewage sludge samples
The upper section of the table represents the nutrient concentrations in g mg^{-1} and the lower part to heavy metals in mg kg^{-1}

The analysis in Table 4.7 was divided into two categories that of major nutrients such as phosphorous, calcium, potassium, magnesium and major pollutants. Looking at the mean in the table values it can be seen that there is no significant difference in the concentration of the major nutrients, with the values remaining within a constant range. However, there has been a big increase in the amount of phosphorous from 16g kg^{-1} in 1989 to 51g kg^{-1} in 2003. The number of samples analysed in 2003 is less than that of 1989 being 77 and 34 respectively, but the concentration ranges are wide in 2003. The lower limits being similar to those of 1989 but the upper limits are bigger. This indicates the variability in the influents that gets to the wastewater plants. The data for the heavy metals show that there is a general decline in the concentrations of heavy metals from the levels that were observed in 1989 analysis. The mean concentrations of Cu, Cr Pb, B, Mo and Cd showed a reduction of approximately 50% with the other elements having similar values. The only exception was the mean for Se that showed a huge increase in the mean concentration from 4 mg kg^{-1} in 1989 to 52 mg kg^{-1} in 2003 analysis.

The information above indicates that there are no dramatic increases in terms of the sludge pollution levels; however, it is interesting to note that there is a general increase in sludge quality since there is a decrease in heavy metal concentrations. The slight increases in the phosphorous and selenium concentrations are major concern. This is because high phosphorous content means that some of it might pass with the released effluent which end up in rivers and dams promoting excessive plant growth and as a result eutrophication occurs causing a decline in species diversity.[6] Selenium is toxic to plants.[7] There is, therefore, a need to control the amount of phosphates and all phosphorous based compounds that are added in washing detergents and dental materials. To control selenium, the industries using the element need to treat their effluent before releasing it.

4.6 Comparison of current guidelines with the concentrations obtained

In the South African guideline document[3] for disposal of sewage sludge there are thirteen inorganic elements, which are regarded as priority pollutants and have their concentration limits set. In the latest document with the concentration limits there are basically two categories of limit concentrations: the leachable fraction and the total concentration. In this study only the total concentration limits will be used for comparison because only the total concentrations were determined in the study.

Table 4.8 Comparison between the 2003 survey and the maximum limit permitted in the sludge (dry mass, mg kg^{-1}) for land applications in the current South African legislation guidelines (2002)[3].

Element	Cd	Co	Cr	Cu	Hg	Mo	Ni	Pb	Zn	As	Se	B	F
Maximum Limit legislation	20	100	1750	750	10	25	200	400	2750	15	15	80	400
Mean 2003 survey	4.7	12.6	227	372	-	25.4	131	209	1900	-	52	19	-

- element not analysed for in the study.

The results in Table 4.8 shows that most of the samples that were analysed for inorganic substances had these substance concentrations below the maximum limits. The exception were Se which gave a mean of 52 mg kg^{-1} while the maximum limit is 15 mg kg^{-1}. For molybdenum a mean of 25.4 mg kg^{-1} was calculated and this was slightly higher that the recommended maximum limit of 25 mg kg^{-1}.

Table 4.9 Comparison of individual sewage work with South African limits of inorganic compounds in sewage sludge.

Sample No.	B	Cd	Co	Cr	Cu	Mo	Ni	Pb	Se	Zn
1									*	
2									*	
4					*	*		*	*	*
5									*	
6		*				*	*	*	*	*
7									*	
8				*	*			*	*	*
9							*			
10										
11										
13							*		*	
14										
15		*							*	
16									*	*
17									*	
18						*	*		*	
19									*	
20									*	
21							*		*	
22							*		*	*
28										
30										
37							*		*	
41									*	
42									*	
44										
45								*		
54									*	
55					*		*		*	*
57								*		
58									*	
59								*	*	
75								*	*	
76						*			*	

Table 4.9 gives a more informative picture by linking individual sewage works with legislatio limits. The results show that 74% of wastewater plants produced sludge having a selenium content above the set limit. This is followed by nickel and lead where 24% and 21% respectively of the plants exceeded the limits. The possible source of pollution in terms of selenium could be domestic since the compound is used in making of deodorants and shampoo

products.[21] Nickel also showed a significant tally this might be attributed to metal alloy industries that are very common in South Africa.

The results in Table 4.9 shows that most of the sewage works are able to meet the limits set by the South African legislation, the exception is selenium which showed a high concentration in 75% of the samples analysed. This then means that the prospects of using South African sewage sludge as a cheap fertilizer are very high.

To have a global perspective of how South African legislation limits compares with international limits and to see how the survey fits within these limits Table 4.10 was generated. Making reference to the table the current South African limits are in line with those of the international communities such as USA and EU. There are small differences but the overall picture is that they are similar. South African guidelines still include elements such as boron and fluorine, which are not restricted internationally. When comparing the current survey, it can be seen that all elements falls within the limits of the international community with the exception of selenium as it was found with the South African guideline limits. These mean values show that the technologies used in South Africa for treatment of wastewater are able to produce sludge with internationally acceptable mineral ion concentrations.

It can therefore be recommended that the government looks at introducing strict measures to control the use of phosphates and phosphorous-based compounds including selenium so as to promote the use of sewage sludge a source of bio-fertilizer in an agricultural industry.

Table 4.10 Comparison of South African limits with those of international community.

Element	SA[3]	Canada[8]	Australia[9]	USA[26]	EU[20]	Mean
Cd	20	20	20	39	20-40	4.7
Co	100	150	-	-	-	12.6
Cr	1750	-	500-3000	1200	200-1200	227
Cu	750	-	2500	1500	1000-1750	372
Hg	10	5	**15**	17	16-25	--
Mo	25	20	-	18	**20**	25.4
Ni	200	180	270	420	300-400	131
Pb	400	500	420	300	750-1200	209
Zn	2750	1850	2500	2800	2500-4000	1880
As	15	75	**60**	41	10-75	--
Se	15	14	**50**	36	14-100	52
B	**80**	-	-	-	-	19
F	400	-	-	-	-	--

-- element not analysed in the current study
- limit not supplied for the element.

4.7 Concentrations of PAH in the individual sewage works

Polynuclear aromatic hydrocarbons in the sewage sludges, were identified using GC-MS and their concentration determined through GC-analysis as explained in the experimental chapter in section 3.6.2. The different PAHs that were determined were benzo(b)fluoranthene, benzo(k)fluoranthene, phenanthrene, acenaphthylene, fluorene, naphthalene, penzo(a)anthracene, chrysene, acenaphthene, benzo(a)pyrene, fluoranthene, anthracene ~ pyrene, benzo(g,h,i)perylene, indeno(1,2,3-cd)pyrene, and dibenzo(a,h)anthracene. All concentrations and their sums are expressed in mg kg^{-1} on dry mass basis and are tabulated in Table 4.11. Included in the table is a sum of the nine compounds regarded by the European Union (EU) as the priority PAH pollutants. According to EU guidelines[20] the sum of concentrations for nine specific PAHs should not exceed 6 mg kg^{-1}, these compounds are acenaphthene, fluorene, phenanthrene, fluoranthene, pyrene, benzo(b+j+k)fluoranthene, benzo(a)pyrene, benzo(g,h,I)perylene, and indeno(1,2,3-cd)pyrene. In Table 4.11 it can be seen that, out of 32 samples that were analysed for PAHs, only eleven had their concentrations below the EU limit. Most of the samples that had values above the limit were from the Gauteng province, which had 88% of its wastewater plant samples being above the limit. This can be explained in terms of the type of industries found within the province. Gauteng is a leader in mining activities and these involve the use of coal and other fossil fuels as energy source, thus high contents of PAHs are likely to be present in this province. In addition, a significant number of residents in the province rely on coal for energy, hence smoke emissions that might contribute to PAH concentrations.

The EU limits are among the most conservative limits and due to that most of the sewage sludges will have the PAH concentration above these limits. The recent results from 14 sewage works in UK had PAH concentrations above 6 mg kg^{-1} with concentrations ranging between 18 and 50 mg kg^{-1}.[10] Interestingly, the most abundant compounds being lighter PAHs such as fluorene and phenathrene while the lower molecular weight PAHs were not the most abundant in this study. The most likely reason for this is because these samples might have degraded and volatilized due to weather differences between UK and SA.

A general look at the results reveals that there is no general trend in terms of abundance. The concentration values for the individual PAHs vary from one province to another and within each province. Of the samples that had the sum of the nine PAHs within the EU limits, 10 out of 11 receives over 90% of domestic sludge. Table 4.11 also show that indeno[1,2,3-cd]pyrene is not present in any province except Gauteng and dibenzo (a,h)anthracene was below the detection limit in all the provinces. South African legislation[11] has a limit that requires that the level of benzo(a)pyrene should not exceed 2.53 mg kg^{-1}. Using this limit means that all the samples analysed do meet the requirement with the exception of sample number 6 in Gauteng with a concentration of 3.45 mg kg^{-1}.

Table 4-11: Concentrations of PAHs in South African sewage sludge in mg kg dm, arranged in terms of provinces.

	PAH Conc. (mg/kg dm)																	
	Samples from North West and Western Cape Provinces																	
Sample	3	4	5	7	8	12	13	14	15	**Sum of 9**	1	2	6	9	10	11	16	**Sum of 16**
28	0.29	0.12	0.17	-	-	1.24	-	-	0.14	**1.96**	0.36	0.08	0.10	-	0.18	2.04	-	**4.72**
30	5.37	2.15	3.40	-	0.39	0.97	1.00	-	-	**13.28**	-	1.78	6.86	0.83	11.5	0.97	-	**34.84**
37	0.05	0.23	0.30	-	0.71	1.24	-	-	0.08	**2.61**	0.23	-	0.24	-	-	2.10	-	**5.18**
54	-	-	0.73	-	0.75	1.23	0.49	-	-	**3.20**	0.09	-	4.40	-	-	2.56	-	**10.25**
55	0.72	0.04	1.56	-	-	1.25	-	-	-	**3.57**	1.02	0.12	-	-	-	1.24	-	**5.95**
MEAN	**1.61**	**0.64**	**1.23**	-	**0.62**	**1.19**	**0.75**	-	**0.11**		**0.42**	**0.66**	**2.9**	**0.83**	**5.84**	**1.78**	-	
	Samples from KwaZulu-Natal Province																	
41	0.23	0.06	0.44	0.57	-	1.24	-	-	0.28	**2.82**	0.14	0.07	-	5.57	-	2.11	-	**10.7**
42AD	-	-	0.85	-	-	2.93	0.56	-	-	**4.34**	-	-	1.06	2.93	-	1.30	-	**9.63**
42WAS	-	-	1.64	4.61	-	1.89	0.52	-	1.37	**10.03**	-	-	-	1.89	0.28	1.28	-	**13.5**
44	-	0.37	1.05	-	-	1.24	-	-	0.10	**2.76**	0.30	0.06	0.16	-	-	2.15	-	**5.43**
45	0.21	0.08	0.21	1.51	6.80	1.24	-	-	0.10	**10.15**	0.71	0.17	0.12	-	2.28	4.80	-	**18.3**
57	3.20	5.20	0.33	-	-	2.69	0.58	-	1.06	**13.06**	-	0.67	-	1.17	0.69	1.38	-	**17.0**
58	-	0.24	2.08	-	-	1.24	-	-	1.84	**5.40**	2.92	0.40	-	23.1	0.12	1.24	-	**33.2**
59	1.06	1.91	-	-	-	1.34	0.04	-	-	**4.35**	0.73	1.27	0.58	1.55	0.36	1.29	-	**10.1**
75	-	2.59	2.91	21.6	30.4	22.8	0.02	-	-	**80.32**	4.74	0.25	-	0.30	0.24	1.23	-	**87.6**
76	-	1.75	6.40	0.92	-	1.24	0.06	-	1.54	**11.91**	1.50	0.38	-	1.88	0.27	1.23	-	**17.2**
MEAN	**1.18**	**1.52**	**1.77**	**5.84**	**18.6**	**3.78**	**0.30**	-	**0.90**		**1.6**	**0.41**	**0.48**	**4.8**	**0.75**	**1.8**	-	

1-naphthalene, 2-Acenaphthylene, 3-Acenaphthene, 4-Fluorene, 5-Phenanthrene, 6-Anthracene, 7-Fluoranthene, 8-Pyrene, 9-Benzo(a)anthracene, 10-Chrysene, 11-Benzo(b)fluoranthene, 12-Benzo(k)fluoranthene. 13-benzo(a)pyrene, 14-indeno(1,2,3,-c,d)pyrene, 15-benzo(g,h,I)perylene, 16-Dibenzo(a,h)anthracene.

- AD – Anaerobic digested, WAS- Waste Activated Sludge.

Table 4-11 (cont):

	PAH Conc. (mg/kg dm)																
Samples from Gauteng Province																	
Sample	3	4	5	7	8	12	13	14	15	**Sum of 9**	1	2	6	9	10	11	16	**Sum of 16**
01	-	-	21.6	-	-	40.7	0.51	0.29	-	**63.10**	-	2.89	-	-	37.1	13.2	-	**116.3**
02	6.80	0.20	5.60	-	-	1.28	0.55	17.3	-	**31.73**	0.36	0.20	4.00	-	0.40	1.28	-	**37.94**
04	0.70	0.62	-	-	-	1.24	0.51	-	-	**3.07**	1.37	0.21	5.60	-	-	1.32	-	**11.57**
06	0.83	0.16	8.99	12.5	1.16	0.79	3.45	-	-	**27.88**	-	1.02	5.97	14.2	0.31	0.79	-	**50.19**
07	0.44	0.75	2.50	5.48	1.90	1.23	-	-	0.83	**13.13**	0.24	0.12	-	5.19	2.06	2.7	-	**23.41**
08	0.12	0.48	2.47	21.2	-	2.92	-	0.04	0.54	**27.77**	2.26	0.32	-	-	6.79	1.23	-	**38.40**
09	-	2.88	11.6	-	0.58	4.39	-	-	-	**19.45**	1.03	0.39	-	19	1.65	3.98	-	**45.45**
11	0.69	0.22	0.58	1.97	0.28	1.24	0.04	-	2.47	**7.49**	1.99	0.26	0.42	1.51	-	1.62	-	**13.29**
13	-	0.87	2.63	-	3.54	9.53	0.18	-	-	**16.75**	0.32	0.05	-	12.4	0.23	0.03	-	**29.83**
14	0.61	0.18	2.36	-	-	6.35	0.06	-	-	**9.56**	1.04	0.15	-	-	0.53	2.00	-	**13.28**
15	1.19	0.55	0.36	-	-	2.88	-	6.01	-	**10.99**	0.28	2.41	1.61	12.5	5.84	2.88	-	**36.51**
16	0.08	0.58	1.61	18.4	-	1.24	-	-	-	**21.91**	4.00	0.08	-	12.6	-	1.23	-	**39.81**
17	-	1.21	13.6	4.94	-	1.38	0.06	8.42	0.02	**29.63**	0.63	0.22	-	1.06	0.98	1.36	-	**33.88**
18	0.89	-	4.30	13.5	0.71	1.42	0.07	0.05	0.05	**20.99**	0.24	1.68	-	1.38	0.55	1.35	-	**26.2**
19	1.25	0.44	1.05	-	2.61	1.24	-	-	-	**6.59**	1.40	0.14	6.80	10.2	0.46	1.23	-	**26.82**
20	0.24	0.52	1.83	0.65	0.12	1.35	0.09	0.22	0.04	**5.06**	0.23	0.24	1.43	1.78	0.56	1.23	-	**10.53**
22	0.76	1.64	6.40	-	0.32	1.24	0.57	-	-	**10.93**	0.60	0.44	-	-	0.80	5.60	-	**18.34**
MEAN	**1.12**	**0.75**	**5.47**	**9.83**	**1.25**	**4.73**	**0.55**	**4.62**	**0.66**		**1.07**	**0.64**	**3.69**	**8.35**	**4.16**	**2.55**	-	

1-naphthalene, 2-Acenaphthylene, 3-Acenaphthene, 4-Fluorene, 5-Phenanthrene, 6-Anthracene, 7-Fluoranthene, 8-Pyrene, 9-Benzo(a)anthracene, 10-Chrysene, 11-Benzo(b)fluoranthene, 12-Benzo(k)fluoranthene, 13-benzo(a)pyrene, 14-indeno(1,2,3,-c,d)pyrene, 15-benzo(g,h,l)perylene, 16-Dibenzo(a,h)anthracen.

4.8 A summary of PAH content classified according to provinces

The mean values calculate in Table 4.11 are compiled in Table 4.12 These values are used to compare the level of PAH pollution between the provinces. The standard deviation of the mean has also been included in the table. The results show that Gauteng leads in terms of abundance with 50% of the compounds being higher in the province compared to the other provinces. As already explained in section 4.7, this is due to activities that involve the burning of fossil fuels.

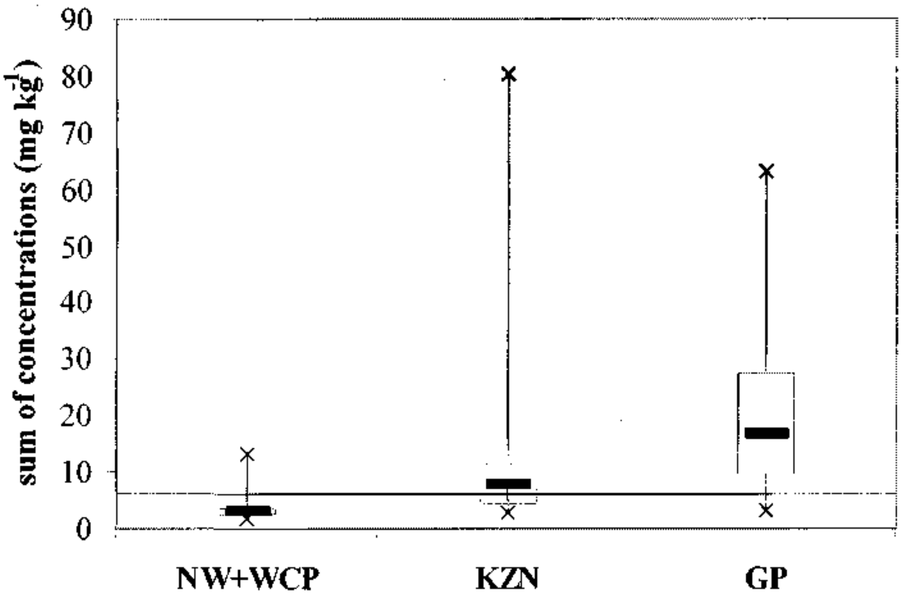
Table 4.12 Mean concentrations of PAHs in mg kg^{-1} classified according to provinces.

Compound	**Gauteng (19 samples)**	**KwaZulu-Natal (10 samples)**	**NWP + WCP (5 samples)**
Naphthalene	1.07±1.0	1.6±1.68	0.42±0.41
Acenaphthylene	0.64±0.9	0.41±0.38	0.66±0.97
Acenaphthene	1.12±1.71	1.18±1.43	1.63±2.52
Fluorene	0.75±0.73	1.52±1.84	0.64±1.01
Phenanthrene	5.47±5.79	1.77±2.02	1.2±1.34
Anthracene	3.69±2.48	0.48±0.44	2.9±3.28
Fluoranthene	9.83±7.72	5.84±9.03	-
Pyrene	1.25±1.23	18.6±16.71	0.62±0.18
Benzo(a)anthracene	8.35±6.45	4.8±7.56	0.83±0.0
Chrysene	4.16±9.74	0.61±0.76	5.8±8.01
Benzo(b)fluoranthene	2.55±2.96	1.8±1.13	1.8±0.66
Benzo(k)fluoranthene	4.37±9.62	3.78±6.74	1.2±0.12
Benzo(a)pyrene	**0.55±1.03**	**0.30±0.28**	**0.75±0.36**
Indeno(1,2,3-cd)pyrene	4.62±6.53	-	-
Benzo(g,h,I)perylene	0.66±0.92	0.90±0.73	0.11±0.04
Dibenzo(a,h)anthracene	-	-	-

- Sample concentrations were below the detection limits of the instrument.
- The bolded compound is the PAH recommended by SA legislation to be monitored.[11]

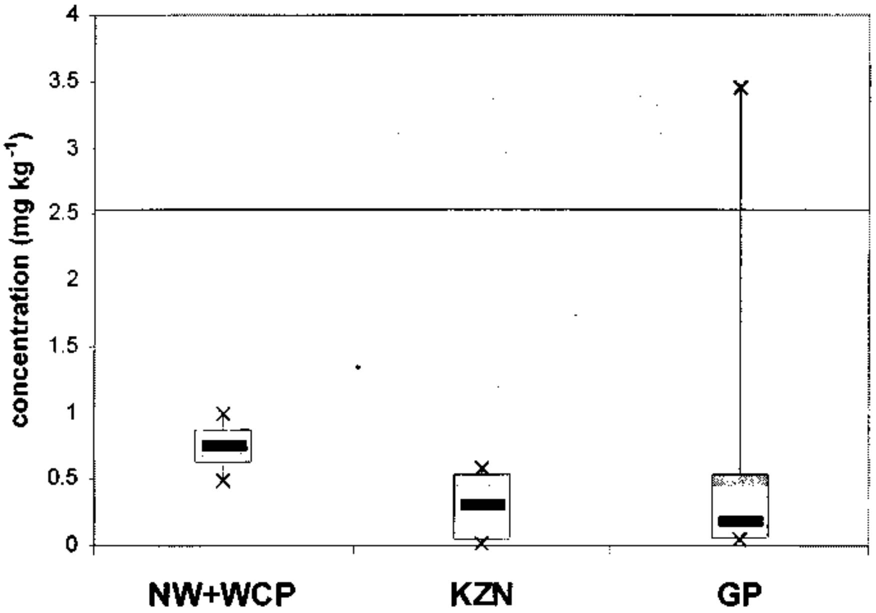
There is no trend that can be formulated from the data obtained, since the abundance is varying in different provinces. To amplify on this point, the most abundant PAH in Gauteng is fluoranthene while the most abundant PAHs in KwaZulu-Natal and NWP + WCP it is pyrene and chrysene respectively-indeed, fluoranthene was not even detected in any of the NWP + WCP samples.

With such a small data set it is obviously impossible to do a rigorous statistical analysis of the results. Furthermore, the results for each of the PAHs do not appear to be normally distributed. However, in such circumstances, box and whisker plots can be useful for summarising the data--the box is bounded by the upper and lower quartiles and the whiskers stretch out to the extreme values whilst the bar in the box represents the median. Box and whisker plots for the combination of the nine priority PAHs (as defined by the EU – see above) and for the sum of all 16 determined PAHs as well as for the concentration of benzo(a)pyrene are shown in Figures 4-1, 4-3and 4-2 respectively.



Note: the red horizontal line represents the EU limit - see text for details.

Figure 4-1: Box and Whisker plot for the sum of 9 priority PAHs by province.



Note: The red horizontal line represnts the SA limit - see text for details.

Figure 4-2: Box and Whisker plot for benzo(a)pyrene by province.

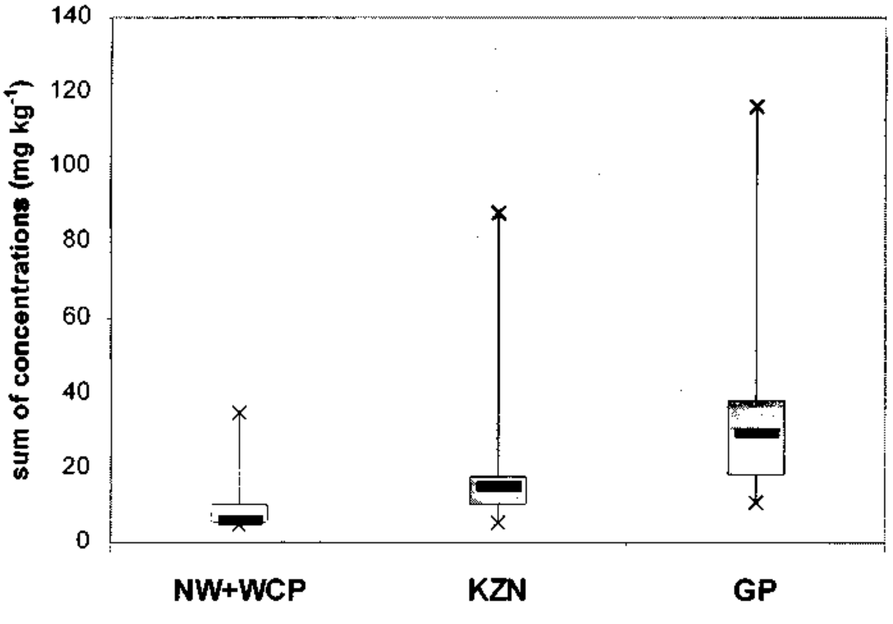


Figure 4-3: Box and Whisker plot for the sum of 16 PAHs by province.

The general conclusion from these results is that, overall, the total PAH contamination is higher in Gauteng than in the other provinces. However, when considering benzo(a)pyrene alone, the picture is different and the samples from North West and Western Cape are generally higher than those from Gauteng – even though Gauteng has one extremely high value. The long whiskers on some of the plots indicate the existence of outliers – abnormally high values. Furthermore, the data also show that, whilst many of the samples exceed the EU limit for the sum of 9 priority PAHs, almost all of the samples are within the SA limit for benzo(a)pyrene.

Finally, the very high intra-provincial standard deviations, which in many cases are greater than the mean values, show that there is a large variation of concentrations within each province.

4.9 PAHs in South African Sewage sludge

To have a general picture of the sewage sludge within the country, the data in Table 4.11 was combined and average values are shown in Table 4.13. What is noteworthy is that the standard deviations are either bigger or equal to the mean values. The range is also wide taking in account the magnitude of the mean. This variation is in agreement with what has been observed at the individual level of wastewater plants. The deviation and the range, points to the fact that the level of these pollutants differs a great deal from one sewage work to another. A reflection that the inflows of the effluent to the wastewater plants differ depending on the type of industries and population that feeds the plants.

Table 4.13 National mean±standard deviation concentrations (mg kg^{-1}, dry basis) for PAHs in South Africa.

Compound	Mean	Median	Range	No. of samples that were below the detection limit
Benzo(b)fluoranthene	2.2±2.3	1.4	0.03 – 13.2	0
Benzo(k)fluoranthene	3.9±7.9	1.2	0.79 – 40.7	0
Phenanthrene	3.7±4.8	1.8	0 – 21.6	2
Acenaphthylene	0.57±0.75	0.22	0 – 2.89	4
Fluorene	0.96±1.2	0.48	0 – 5.20	5
Naphthalene	1.1±1.2	0.48	0 - 4.47	6
Benzo(a)anthracene	6.6±6.6	4.3	0 – 19.0	7
Chrysene	3.2±7.9	0.63	0 – 76.0	8
Acenaphthene	1.2±1.8	0.61	0 – 6.80	11
Benzo(a)pyrene	0.49±0.77	0.18	0 – 3.45	14
Fluoranthene	8.3±8.1	2.2	0 – 21.6	16
Anthracene	2.6±2.7	1.06	0 – 6.86	17
Pyrene	3.6±7.9	0.71	0 – 30.4	17
Benzo(g,h,i)perylene	0.70±0.79	0.28	0 – 2.47	18
Indeno(1,2,3-cd)pyrene	4.6±6.5	0.29	0 – 17.3	26
Dibenzo(a,h)anthracene	-	-	-	33

- Concentration was below the detection limit of the instrument.

The table also shows that benzo(b)fluoranthene and benzo(k)fluoranthene are the most common PAHs in South African sewage sludges, since both of these compounds were present in all the samples that were analysed. The least abundant compound was dibenzo(a,h)anthracene, which was not detected in any of the samples. The complete order of occurrence (using the detection limit in Table 4.13) was as follows:

benzo(b)fluoranthene ~ benzo(k)fluoranthene> phenanthrene> acenaphthylene> fluorene> naphthalene> benzo(a)anthracene> chrysene> acenaphthene> benzo(a)pyrene> fluoranthene> anthracene ~ pyrene> benzo(g,h,i)perylene> indeno(1,2,3-cd)pyrene> dibenzo(a,h)anthracene.

This order is based on the frequency of occurrence of the compounds in the sludge and not on the concentration of the compounds. For considering a ranking according to concentration, either the mean or the median could be used – since the data are not normally distributed and since there appear to be outliers it was thought that the median would be a better measure to use. When the PAHs are ranked according to national median concentration a completely different order is generated:

benzo(a)anthracene > fluoranthene > phenanthrene> benzo(b)fluoranthene > benzo(k)fluoranthene > anthracene > pyrene > chrysene > acenaphthene > naphthalene > fluorene > indeno(1,2,3-cd)pyrene > benzo(g,h,i)perylene > benzo(g,h,i)perylene > benzo(g,h,i)perylene > benzo(a)pyrene > dibenzo(a,h)anthracene

Because the trend above is based on median concentrations of those sewage works in which the compounds were detected, it does not reflect how often the compound was detected in sewage sludge but how high the median concentrations were in the event that they were detected. In the case of benzo(a)anthracene for example, it appears to have the highest median but was only ranked seven according to frequency of appearance. Table 4.14 compares the rankings by occurrence and by concentration for the 16 target PAHs.

Table 4.14 shows that there is no significant correlation between median concentrations and frequency of occurrence trends. The analysis that is relevant is the frequency of occurrence since it gives a picture of which PAHs are widely spread across the country. This information will certainly help in formulating the guidelines for the disposal of sewage sludge.

The primary concern about sludge is its use as a bio-fertilizer in pastureland where PAHs might transfer to and bio-accumulate in grazing animals since these animals can ingest surface soil as they feed.[12-15] Uptake of PAHs by roots and translocation through plants is an inefficient process since PAHs are hydrophobic compounds. Thus exposure associated with this route is thought to be of little danger to man[16-19]

Table 4.14 Ranking of PAHs according to frequency of occurrence and concentration.

Compound	Rank by occurrence	Rank by National median concentration
Benzo(b)fluoranthene	1=	4
Benzo(k)fluoranthene	1=	5
Phenanthrene	3	3
Acenaphthylene	4	14
Fluorene	5	11
Naphthalene	6	10
Benzo(a)anthracene	7	1
Chrysene	8	8
Acenaphthene	9	9
Benzo(a)pyrene	10	15
Fluoranthene	11	2
Anthracene	12=	6
Pyrene	12=	7
Benzo(g,h,i)perylene	14	13
Indeno(1,2,3-cd)pyrene	15	12
Dibenzo(a,h)anthracene	16	16

4.10 Influence of source and treatment of sewage sludge

To control the pollution that ends up in the wastewater plants it is important to try and ascertain the source of pollutants. It is for this reason that the data in Table 4.11 was re-analyzed and grouped according to two categories of sewage works. These categories are those sewage works that received at least 10% of industrial effluent and those that received more than 90% of domestic sewage effluent. The data including the standard deviations, arranged in order of frequency of occurrence as in Table 4.14 is shown in Table 4.15.

Table 4.15 Mean±standard deviation of PAHs concentrations (mg kg^{-1} dm) according to the sewage origin, arranged in the order of frequency of appearance.

Compounds	≥ 10% Industrial	≥ 90% Domestic
Benzo(b)fluoranthene	2.20±2.71	2.07±1.23
Benzo(k)fluoranthene	4.72±9.41	4.80±11
Phenanthrene	3.84±5.22	2.17±3.15
Acenaphthylene	0.52±0.79	0.42±0.57
Fluorene	0.58±0.67	1.14±1.62
Naphthalene	1.00±1.28	0.59±0.84
Benzo(a)anthracene	5.72±7.39	4.64±7.86
Chrysene	5.97±18	2.71±4.69
Acenaphthene	0.72±1.41	0.92±1.68
Benzo(a)pyrene	0.19±0.73	0.23±0.35
Fluoranthene	6.04±11.2	1.01±1.94
Anthracene	1.20±2.17	1.10±2.20
Pyrene	2.88±7.96	0.87±1.95
Benzo(g,h,i)perylene	0.87±3.30	0.44±0.66
Indeno(1,2,3-cd)pyrene	4.91±18.1	-
Dibenzo(a,h)anthracene	-	-

The statistical analysis of the two groups of data using a Genstat in ANOVA mode showed that there is no statistical difference between the two categories. This is because the p-factor obtained was greater than 0.05 for all the compounds at 95% confidence levels. It can therefore be concluded that industrial influence on the levels of PAHs in sewage sludge is not significantly greater than that from the domestic effluents. A possible exception to this is indeno(1,2,3-cd)pyrene which was only detected in samples from sewage works that received at least 10% of industrial effluent.

Another way of categorising the sewage works is by treatment process type. The sewage works were grouped into the following categories: anaerobic digestion, waste activated sludge (WAS), aerobic, composted, digested sludge and others. The data in Table 4.11 were re-analysed in order to determine if the method of sewage treatment had any significant effect on the PAH content of the final sludge. The mean and standard deviations of the PAH concentrations grouped according to treatment process are shown in Table 4.15.

The results show that there is no single treatment procedure that had consistently higher mean values than the others – there appears to be no correlation between the sewage treatment process and the PAH concentration. Two compounds namely benzo(b)fluoranthene and benzo(k)fluoranthene were singled out for particular consideration. This is because they appeared across the country in the sludge from each and every wastewater treatment plant. It was therefore thought best to use these two compounds as indicators of the influence of the processing methods. These compounds are shown in bold in Table 4.16. When looking at these results, a picture emerges, showing that the anaerobic, aerobic digested and waste activated methods produce sludges with the highest concentrations of benzo(k)fluoranthene. The same treatment processes also produce the highest concentrations of benzo(b)fluoranthene. Of course, care must be taken in analysing the results in this way as factors other than the treatment process may be determining – for example the source of the effluent received by each plant.

Table 4.16 Mean±standard deviation of PAH concentrations (mg kg^{-1} dm) according to the sewage treatment type, arranged in the order of frequency of appearance.

Compound	Anaerobic Digested	WAS	Aerobic	Compost	Others
Benzo(b)fluoranthene	**1.32±3.49**	**2.02±0.96**	**2.44±0.62**	**1.56±0.47**	**1.26±0.04**
Benzo(k)fluoranthene	**1.24±10.97**	**4.11±7.09**	**4.61±2.42**	**1.33±0.14**	**1.29±0.07**
Phenanthrene	2.55±6.41	2.62±3.65	1.36±1.42	2.14±2.03	6.40±0.0
Acenaphthylene	0.20±0.75	0.44±0.64	1.28±1.62	0.96±1.01	0.83±0.63
Fluorene	0.37±0.49	1.80±1.81	0.37±0.26	0.37±0.22	1.8±0.11
Naphthalene	0.62±1.13	1.15±1.72	0.66±0.54	0.24±0.01	1.11±0.55
Benzo(a)anthracene	5.76±3.33	5.55±6.32	12.50±0.0	1.26±0.61	1.72±0.23
Chrysene	1.63±24.65	2.40±4.11	3.18±3.84	0.55±0.003	0.31±0.06
Anthracene	0.42±2.67	4.54±3.22	1.61±0.0	0.83±0.80	0.58±0.0
Acenaphthene	0.60±2.03	1.80±2.11	0.90±0.41	0.53±0.43	1.06±0.0
Benzo(a)pyrene	0.06±1.13	0.41±0.5	0.06±0.0	0.08±0.02	0.05±0.01
Fluoranthene	1.53±15.22	3.02±3.51	-	7.07±9.1	0.92±0.0
Pyrene	1.16±11.59	4.61±8.40	-	0.51±0.34	-
Benzo(g,h,i)perylene	0.10±0.24	0.58±0.41	-	0.06±0.02	1.5±0.0
Indeno(1,2,3-cd)pyrene	0.17±7.17	-	6.01±0.0	0.14±0.12	-
No of sewage works	14	11	2	3	2

Others- include pellets and petro sludge.

Bold – PAH that appeared in all the sewage works that were analysed.

- = compound not detected.

4.11 *Comparison of the current results with the SA guidelines and other countries*

The SA guidelines on permissible utilization and disposal of sewage sludge for organic compounds[11] recommend that the concentration of PAHs in sewage sludge should not exceed 2.53 mg kg^{-1} for benzo(a)pyrene, the indicator substance. In all the samples that were analysed, the concentration for this compound was below the threshold value. The sludge in Gauteng province had an average benzo(a)pyrene concentration of 0.55 mg kg^{-1} with only one sample exceeding the regulatory limit. In KwaZulu-Natal the average was 0.30 mg kg^{-1} and 0.75 mg kg^{-1} was the mean value for NW and WCP. Using the legislation limit as a criterion the results indicate that the sewage sludge produced in SA contains concentrations at levels that are acceptable. However, the South African guideline[11] does not cater for other PAHs that might be harmful to the environment. The guidelines for other countries require that the limit include a total of more than just one PAH as shown in Table 4.17. The EU limits, for example, insist that a total of nine PAHs be monitored in their sewage sludge with the limit set at 6 mg kg^{-1} while in USA 16 PAHs are regarded as priority pollutants but no limits are set.

Thus it is therefore necessary to compare the levels of pollutants detected in the current survey to the limits of other countries to access our status in comparison to the international community.

Table 4.17 Limit value (mg kg^{-1} dry mass) for PAHs in various countries

Country	**EU 2000[20]**	**Denmark[21]**	**Sweden[22]**	**South Africa[11]**
Limits	6[a]	3[a]	3[b]	2.53[c]

[a] Sum of acenaphthene, phenanthrene, fluorene, fluoranthene, pyrene, benzo(b+j+k)fluoranthene, benzo(a)pyrene, benzo(ghi)perylene, indeno(1,2,3-c,d)pyrene.
[b] Sum of 6 compounds.
[c] Benzo(a)pyrene

Making reference to Table 4.11 and using the EU limits in Table 4.16, the data shows that South African sludge does not fair very well according to international standards in terms of

PAHs. In Gauteng only 2 out of 17 sewage works meets the limit while in KwaZulu-Natal 5 out of 10 and in NW + WC 4 out of 5.

Table 4.17 shows PAH concentrations found in sewage sludges from various countries. The values found in South Africa are high compared to those found in other the countries listed. The only country that came close is Norway on the upper limit.

Table 4.18 Concentrations of PAH in sewage sludge for various countries

Investigations	**No. of samples**	**Range mg/kg dm**	**Median mg/kg dm**
Danish (1995) (Sum of 18 compounds)[23]	20	<0.01-1.85	-
Danish (1993-94) (sum of 18 compounds)[23]	9	0.42-2.4	-
Norway[24]	36	0.7-30	3.9
Sweden (Sum of 6 compounds)[25]	-	-	1.6
Parts of Germany (sum of 6 compounds)[26]	124	0.4-12.83	-
Part of Germany (Sum of 16 compounds)[26]	88	0.25-16.28	-
South Africa 2004 (sum of 16 compounds)	34	4.72-116.3	18.31
South Africa 2004 (sum of 9 compounds)	34	1.96-80.8	10.55

For results with * only 32 samples were considered and two values that appeared as outliers were not included in this analysis.

It can therefore be concluded that the values that were obtained in the current study are higher than those that are typically found in some European countries. The data also shows that the sewage sludge produced by South African wastewater treatment plants is contaminated with

PAHs. It is therefore recommended that SA guidelines be reviewed to include more PAHs in its limits taking into account the frequently common PAHs. As a country it will be best to look at the benefit versus the risk posed by PAHs before coming up with a limit that sludge producers must meet.

4.12 Conclusions and recommendations

The conclusions and recommendations that can be arrived at from this survey is that a majority of wastewater treatment plants in South Africa are producing quality sludge that meets the legislation requirements in terms of inorganic pollutants set in the permissible utilization and disposal of sewage sludge. One element that needs close monitoring is selenium, which was found to be higher than the set limits in most of the sludge analysed. The level of phosphorous, though might be a good plant nutrient, it poses danger of eutrophication. Therefore, there is a need for the government to control the amount of phosphorous and all phosphorous-based compounds that are added in washing detergents and dental products. Since these are likely to be the source of phosphorous in the sewage sludge.

The PAH analysis has revealed that SA sewage sludge contains a number of PAH compounds at a significant level. Using the quantity of the indicator PAH i.e. benzo(a)pyrene as stipulated in the South African legislation is misleading, as shown in the discussion. Using the EU limit, the current results show that most of the sludge being produced in the country exceeds the set limit. This is also true for most of the EU member countries. It is therefore recommended that the government to revise the current limit and increase the number of PAHs that must be monitored. But must look into the benefit of using sludge as bio-fertilizer against the risk posed by PAHs before setting a regulatory limit.

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Appendices

APPENDIX A Calculation of moisture Content

Moisture of the solid sewage sludge was calculated in the following manner:1

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

where: Loss in weight on drying (g) = initial sample weight (g) – dried sample weight[1]

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

APPENDIX B Calculation of Concentration

Sample concentration[2] = $\frac{V\,(W - B)}{M}$ mg kg-1

Where

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

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[2] Department of the environment, Methods for the Determinations of Metals in Soils Sediments, and Sewage Sludge and Plants by Hydrochloric- Nitric Acid Digestion, with a note on the Determination of the insoluble Metal Contents 1986, Methods for the Examination of Water and Associated Materials, Her Majesty's Stationary Office, London, 1986, p15.

APPENDIX C 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
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
13	Rooiwal Northern	Anaerobic Digested	Pretoria	Wet sludge	Gauteng
14	Rooiwal West/East	Anaerobic Digested	Pretoria	Wet sludge	Gauteng
15	Zeekeogat	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
28	Borcherds Quarry	WAS	Cape Town	Return flow	Western cape
30	Athlone	WAS	Cape Town	Dryign beds	Western cape
37	Oudshoorn	Compost	Oudshoorn	Compost heap	Western cape

APPENDIX C Continues… Details about sewage works of South Africa continues.

Plant No	Wastewater plant name	Sample description	Town	Sampling point	Province
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	KwaMashu	Digested Sludge	Durban	Belt press	KwaZulu-Natal
54	Boitekong	WAS	Rustenburg	Return flow	North West
55	Brits	Anaerobic Digested	Brits	Drying beds	North West
57	Phoenix	WAS	Durban	Belt press	KwaZulu-Natal
58	Durban Northern	WAS/Digested	Durban	Belt press	KwaZulu-Natal
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

APPENDIX D Concentration (mg kg^{-1}, dry basis) of mineral ions in South African sewage slugdes.

D1 Gauteng Province

Sewage work Name	Vlakplaats	Vlakplaats	Dekema	Waterval	Rondebult	CF Grundlingh	Herbert Bickley	Tsakane WWTP	Heidelderg	Heidelderg	Rooiwal Northen
Sample Number	**1**	**2**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**13**
P/104	5.1±0.7	7.9±0.3	7.5±2.8	0.3±0.2	11.±2.8				0.53±0.33		3 0±0.8
Ca/104	1.6±0 01	2.6±0.1	2.7±0.04	1.6±0.02	1.8±0.3	2.6±0.03	2.1±0.3	1.9±0.2	6.7±0.1	11±0.1	1.7±0.02
Fe/104	0.73±0.008	2.4±0 1	7.3±0.2	1 9±0.08	7.4±1.3	1.9±0.04	1.1±0.03	0.84±0.008	0.33±0.008	0.32±0.2	4.7±0 06
Al/104	0.39±0.01	1.5±0.1	8.2±0.2	19±0.06	0.84±0.1	0 44±0.03	1.1±0.05	0.76±0 3	0.45±0.01	0.53±0.01	0.32±0.009
Mg/103	4.4±0.008	5.1±0.3	3.0±0.09	2.9±0.07	1.7±0.3	2.8±0.03	0.86±0.01	4.9±0 05	3.3±0.09	3 8±0.2	0.86±0.02
K/103	6.8±0 1	1.2±0.08	2.3±0.03	2.8±0.07	1.6±0.3	5.9±0.1	7.9±1.3	9.0±0.3	0 7±0.07	0.9±0.08	0.62±0.01
Zn/103	1 5±0.04	1.3±0.07	4.6±0.05	2.7±1.4	5.2±0.9	0.48±0.1	10±1.5	0.53±.0.02	0.88±0.06	0.40±0.004	2.2±0.04
Na/103	3.4±0.04	0.51±0.03	3.0±0.07	15.±0.09	1.7±0.3	9.9±0.1	1.4±0.08	6.6±0.5	59±7.0	0.55±0 08	2.0±0.02
Mn/102	1.4±0.01	1.8±0.1	8.8±0.3	7.3±0.44	16±2.9	1.3±0.0007	2.0±0.4	2.9±0.5	0.54±0.02	1.1±0.02	4.2±0 07
Cu/102	4.1±0.2	4.1±0.4	9.8±0.3	2.4±0.4	5.7±1	1.4±0 1	10±1.4	1.0±0.04	1.8±0.2	1 1±0.01	3.8±0.04
Ba/102	1.8±0.3	3.6±7.0	4.9±0 7	2.0±0.05	1.8±0.3	1.1±0.7	1.3±0.04	1.9±1.1	0.68±0.03	0.77±0.005	0.7±0.01
Cr/102	0.98±0.03	0.58±0.03	5.9±0.3	2.5±0.3	5.4±1.1	2.7±0.1	36±5	0.25±0.005	0.95±0.03	0.48±0.01	3.2±0.07
Pb/102		1.0±0.07	6.5±0.2	2.9±0.4	4.1±0.4	0.64±0.06	7.2±1	0.19±0.1	0.41±0.008	0.14±0.005	1.6±0.04
Si/10	4.0±0.2	6.9±0.4	4.4±0.4	2.4±0.1	7.1±1	4.2±0.4	2.0±0.1	0	1.0±0.5	3.1±0.2	1.5±0.8
Se/10	1.6±0.1	5.8±2	26±2	4.9±0.3	9.9±2.1	2.5±0.7	53±9 4	0	0	0	4.3±0.3
Sr/10	4.9±0.1	45±2	18±0.2	6.9±0.07	5.8±1 0	3.1±0.05	2.9±0 07	4.8±0.09	12±0.3	8.9±0 2	6.8±0.2
B/10	0.86±0.1	1.6±0.1	7.8±0.1	1.7±0.07	7.6±2	3.0±0.2	1 5±0.09	1.4±0.3	0	0.19±0.05	4.3±0.2
Ni/10	7.2±0.6	6.8±0.3	15±6.7	12±1.2	48±11	4.0±0.2	2.9±0.06	29±0.05	3 5±0.3	2.1±0 09	22±4.9
Mo	11±1.2	16±3.0	65±1	18±2	37±6 0	0.91±0.42	4 1±0.45	1.7±2.0	10±0.8	3.8±0.08	18±0.9
Co	2.1±0.2	58±3	45±1.0	9.0±0.1	90±12				3.3±0.2		13±0.4
Cd	5.2±0.3	2.7±0.4	18±0.1	7.1±0.9	26±5.0	3.9±0.4	0.38±0.04	0.36±0.3	1.2±0.1	0.71±1.0	9.8±0.3
Be	3.6±0.3	3.7±0.08	2 7±1.3	3.9±0.4	46±12	13±3	4.6±4	9.3±1.5	4.2±0.07	6.8±0 5	3.0±0.08

APPENDIX D1 Continues… Gauteng Province

Sewage work	Rooiwal West/East	Zeekoegat WCW	Centurion WCW	Daspoort WCW	Olifantsvlei	JHB Northern Works	JHB Northern Works	Percy Steward	Flip Human
Sample Number	**14**	**15**	**16**	**17**	**18**	**19**	**20**	**21**	**22**
P/104	8.3±0.14	6.9±0.2	3.4±1	8.7±0.2	6.1±1.2	4.0±0.2	3.7±0.4	3.4±0.07	
Ca/104	1 5±0 02	1.8±0 06	2.0±0.02	2.6±0.07	3.0±0.04	2.9±0.05	3.3±0.09	3.1±0 04	2 3±0.1
Fe/104	0.65±0.01	3.3±0.2	1 2±0.03	2.2±0.09	6.5±0.1	2.0±0.03	3.0±0.06	1.6±0.05	0.07±0.04
Al/104	0 38±0.008	1.1±0.05	1.3±0.02	1 3±0.03	1.4±0.009	0.49±0.01	1.2±0.02	0.3±0.01	0 97±0.06
Mg/103	4.2±0.08	4.4±0.1	5.1±0.09	5.3±0.2	5.3±0.2	4.0±0.04	4.4±0.1	2.3±0.03	2.5±0.1
K/103	6.4±0.2	4.3±0.2	4.6±0.1	1.3±0.05	4.0±0.03	3.3±0.08	4.6±0.06	3 8±0.1	4.3±0.2
Zn/103	1.7±0.05	9.96±0.5	1.2±0.03	2.1±0.06	1.5±0.06	1.2±0.04	1.2±0.03	0.51±0.02	2.8±0.1
Na/103	2.8±0.1	1.9±0.04	1.3±0.03	0.6±0.008	9.1±0.005	0.75±0.03	0.57±0.005	13±0.2	2.1±0.2
Mn/102	1.3±0.01	3.9±0.2	2.3±0.03	1.6±0.05	13±0.2	4 2±1	5.6±0.2	3.7±0.2	2 6±0 2
Cu/102	5.1±0.9	6.1±0.3	6.0±0.09	6.8±0.3	3.6±0.04	6.4±1.1	5.0±0.5	4.3±0 7	1.0±0.03
Ba/102	1.46±0.2	2.1±0.08	2.0±0.04	2.5±0.03	3.2±0.02	1.9±0.02	2.2±0.1	0.77±0.01	12±0.6
Cr/102	2.6±0.1	4 2±0 3	0.98±0.04	0.7±0.009	2.7±0.2	1.4±0.2	1.0±0.05	8.4±0.6	4.1±0.2
Pb/102	2.4±0.6	2.8±0.3	3.1±0.07	3.1±0.3	3.0±0 002	0.79±0 04	3.1±0.1	2.8±0 6	0.36±0.009
Si/10	3.7±0.03	4.3±0.5	6.0±0.7	2.7±0.1	2.6±0.2	1.8±0.07	1.4±0.2	1 9±0.5	1.9±0.3
Se/10	1.3±0.3	6.6±1	2.2±0.2	2.6±0.9	60±0.2	1.6±0.5	2.0±0.07	4 4±0.3	6.9±0.1
Sr/10	4.5±0.05	8.1±0.4	6.9±0.2	2.4±2	14±0.2	9.6±0.2	1.4±0.3	4.6±0.1	6 0±0.06
B/10	2.8±0.1	3.8±0.4	0.85±0.1	1.8±0.05	6 9±0.08	0.9±0.2	2.4±3	0.86±0.1	0 44±0.2
Ni/10	15±1.3	15±5	10.±0.5	7.4±0.6	32±10	9.3±0.2	11±0.5	55±37	33±0 8
Mo	11±1	23±2	17±0.6	16±2	235±20	14±0.2	12±0.7	8.4±0.5	5.5±0.2
Co	2.3±0.2	19±1	9.0±0.7	7.2±0.5	36±0.8	3 7±0.2	5.6±0.2	1.9±0.4	
Cd	4.8±0.1	31±2	7 1±0.8	3 5±0.2	3.7±0 2	4.7±0.2	5.5±0.5	1.1±0.02	0.41±0.03
Be	3.3±0.06	60±12	8 9±10	4.1±0 09	4.2±0.1	3.9±0 3	4.1±0.1	3.4±0.3	5.7±1

APPENDIX D2 KwaZulu-Natal Province

Sewage work	Hammarsdale	Darvill WCW	Isipingo	KwaMashu	Phoenix	Durban Northern	Durban Northern	Klipfontein	New Castle
Sample Number	**41**	**42**	**44**	**45**	**57**	**58**	**59**	**75**	**76**
P/104	6.6±0.2	4.9±1	4.0±0.2	5.2±0.3	8.3±0.4	4.1±0.1	5.8±0.2	3.6±0.2	4.4±1.3
Ca/104	0.80±0.08	1.3±0.01	2.5±0.06	3.5±0.05	0.84±0.02	2.3±0.06	4.4±0.1	1.7±0.06	1.1±0.03
Fe/104	0.35±0.01	0.62±0.007	2.0±0.04	0.76±0.3	0.47±0.02	1.2±0.04	1.5±0.06	2.0±0.06	2.1±4.3
Al/104	1.9±0.09	2.9±0.02	1.5±0.07	0.52±0.008	0.34±0.02	1.0±0.04	2.4±0.1	1.8±0.07	1.8±0.03
Mg/103	1.7±0.07		1.8±0.05	2.2±1	5.0±0.2	2.5±0.1	3.9±0.2	1.5±0.05	1.3±0.04
K/103	3.8±0.1	7.3±1	1.3±0.05	2.8±0.05	5.3±0.05	1.3±0.04	12±1	2.1±0.09	2.7±0.07
Zn/103	0.44±0.02	0.65±0.1	0.77±0.02	0.40±0.02	0.73±0.03	1.3±0.04	0.88±0.03	1.4±0.06	2.7±1.4
Na/103	5.9±0.2	2.0±0.05	0.55±0.1	0.65±0.04	2.0±0.1	0.69±0.03	1.1±0.07	0.03±0.0006	0.77±0.02
Mn/102	0.68±0.02	1.6±0.03	4.9±0.2	2.9±0.03	173±8.0	2.0±0.08	3.7±0.2	2.8±0.1	2.3±0.06
Cu/102	1.0±0.02	1.2±0.5	2.4±0.2	3.2±0.3	3.2±0.2	4.2±0.2	4.5±0.1	4.7±0.1	2.4±0.4
Ba/102	0.37±0.01	1.7±0.01	1.9±0.07	1.3±0.01	1.1±0.04	1.7±0.06	2.3±0.05	3.0±0.1	3.6±0.07
Cr/102	0.43±0.02	7.0±0.9	0.54±0.01	0.37±0.02	0.16±0.01	0.62±0.008	1.1±0.02	0.51±0.03	2.5±0.3
Pb/102	0.18±0.02	0.50±0.01	0.70±0.01	4.2±0.2	4.7±0.02	1.4±0.04	4.2±0.7	4.6±0.05	2.9±0.4
Si/10	8.2±0.4		1.6±0.2	0.27±0.05	3.3±0.2	1.3±0.1	1.4±0.2	1.4±0.4	1.3±0.1
Se/10	2.1±0.2	8.1±0.3	1.0±0.4	0.34±0.4	0.037±0.07	2.2±0.8	5.2±0.3	3.7±2	4.9±0.2
Sr/10	4.6±0.07	5.9±0.1	4.9±0.08	5.0±0.1	3.0±0.09	5.6±0.2	9.7±0.2	4.9±0.3	6.9±0.07
B/10	2.7±0.1	0.15±0.09	0.51±0.05	0.64±0.05	1.8±0.2	1.2±0.04	2.1±0.1	0.71±0.09	1.7±0.07
Ni/10	2.9±0.1	3.3±0.2	3.7±0.1	3.0±0.4	3.0±0.4	5.3±0.2	7.7±0.2	5.7±0.2	12±1
Mo/10	1.3±0.7	1.6±0.1	1.3±0.9	0.9±0.1	0.92±0.06	1.6±0.06	2.4±0.08	1.7±0.05	17.6±1.9
Co	2.7±0.2	3.3±0.05	3.81±0.76	2.74±0.07	2.21±0.2	3.0±0.14	5.21±0.1	6.93±0.34	13.1±0.29
Cd	0.78±0.2	1.31±1.8	1.15±0.1	2.91±0.14	1.7±0.054	2.5±0.1	4.95±0.2	2.4±0.05	7.12±0.91
Be	2.8±0.4		2.5±0.05	2.4±0.06	0	0	0	2.34±0.07	2.35±0.03

APPENDIX D3 Western Cape Province

Sewage work	Borcherds Quarry	Athlone	Oudtshoorn
Sample Number	**28**	**30**	**37**
P/104	9.1±0.3	1.4±0.05	4.5±0.09
Ca/104	1.4±0.06	1.2±0.02	2.9±0.09
Fe/104	0.47±0.02	0.94±0.04	0.79±0.004
Al/104	0.35±0.02	0.66±0.02	1.0±0.009
Mg/103	4.2±0.2	2.3±0.06	2.0±0.05
K/103	4.7±0.1	2.9±0.05	2.2±0.06
Zn/103	0.94±0.04	0.33±0.3	1.8±0.06
Na/103	1.6±0.08	1.6±0.08	7.1±0.04
Mn/102	0.56±0.02	1.2±0.05	0.76±0.004
Cu/102	1.1±0.1	0.85±0.02	2.6±0.2
Ba/102	1.4±0.04	0.5±0.04	1.5±0.01
Cr/102	1.3±0.04	0.32±0.02	2.4±0.1
Pb/102	0.78±0.02	0.50±0.1	0.2±0.2
Si/10	0	1.1±0.3	0.53±0.06
Se/10	0.23±0.4	0.56±0.8	2.9±0.6
Sr/10	10±0.3	6.4±0.1	9.4±0.2
B/10	3.0±0.2	0.74±0.1	0
Ni/10	5.6±0.4	2.9±0.2	22±5.8
Mo/10	1.2±0.05	1.5±1.7	2.3±0.1
Co	24±5	17±3	27±5
Cd	2.3±0.09	0.58±0.2	6.6±0.2
Be	0	0	0

APPENDIX D4 Northern Province

Sewage work	Boitekong	Brits
Sample Number	**54**	**55**
P/104	3.7±0.2	5.0±0.04
Ca/104	2.0±0.03	2.2±0.02
Fe/104	1.4±0.08	2.1±0.05
Al/104	2.0±0.2	0.96±0.03
Mg/103	4.5±4	3.9±0.05
K/103	2.7±0.1	2.8±0.03
Zn/103	1.1±0.08	5.9±4
Na/103	2.7±0.1	2.7±0.01
Mn/102	4.3±0.4	5.9±0.07
Cu/102	4.0±0.4	9.7±0.3
Ba/102	2.7±0.17	1.4±0.03
Cr/102	0.74±0.5	0.72±0.006
Pb/102	1.1±1	3.7±1
Si/10	1.7±0.2	3.1±0.2
Se/10	5.7±3.1	7.7±4.4
Sr/10	7.4±3.8	8.4±0.2
B/10	2.2±1	2.4±0.3
Ni/10	9.1±5.1	52±15
Mo/10	1.9±0.04	2.1±0.3
Co	7.25±0.3	9.4±0.6
Cd	7.11±8.6	5.64±0.6
Be	2.57±0.01	4.1±0.12

APPENDIX E Detection limits for ICP-OES.

Sample Number	Detection limit mg k^{-1}
P/10^4	420
Ca/10^4	0.26
Fe/10^4	0.55
Al/10^4	2.8
Mg/10^3	0.08
K/10^3	0.90
Zn/10^3	6.1
Na/10^3	0.10
Mn/10^2	0.04
Cu/10^2	1.7
Ba/10^2	0.013
Cr/10^2	0.60
Pb/10^2	0.77
Si/10	0.60
Se/10	2.9
Sr/10	0.04
B/10	0.6
Ni/10	2.2
Mo/10	0.1
Co	0.08
Cd	0.11
Be	0.16

The detection limits were calculated using (3 x sd) of the reagent blank, with $n = 14$.

APPENDIX F Spike recovery data for the surrogate standards fluoro-naphthalene and fluoro biphenyl.

	Fluoro-naphthalene		**Fluoro-biphenyl**	
Sample No.	**Concentration (ppm)**	**Percentage recoveries**	**Concentration (ppm)**	**Percentage recoveries**
Vlaakplats(01)	10.09	100.9	2.55	25.5
Vlaakplats(02)	77.2	77.2	6.52	65.2
Dekema(04)	8.92	89.2	11.73	117.3
Waterval(05)	8.01	80.1	12.61	126.1
Rondebuilt(06)	6.16	61.6	1.22	12.2
C.F. Grundlight(07)	4.88	48.8	3.74	37.4
C.F. Grundlight(7L)	13.5	135	11.26	112.6
Herbert Bickley (08)	11.2	112	2.69	26.9
Tshakane(09L)	8.05	80.5	12.79	127.9
Heidelberg(10)	-	0.0	-	0.0
Heidelberg(11)	6.3	63.0	9.23	92.3
Rooiwal Northern(13L)	9.8	98.0	7.80	78.0
Rooiwal Northern (13)	4.5	45.0	8.19	81.9
Rooiwal E/W(14)	-	-	-	-
Zeekoegart(15)	2.22	22.2	3.80	38.0
Centurion(16)	50.9	50.9	3.57	35.7
Daspoort(17)	5.95	59.5	4.10	41.0
Olifantsvlei(18)	6.51	65.1	5.07	50.7
JHB Northern(20)	5.34	53.4	4.40	44.0
Flip Human(22)	5.01	50.1	3.99	39.9
Borchards Quarry(28)	2.43	24.3	2.06	20.6
Athlone(30)	9.52	95.2	6.66	66.6
Oudshoorn(37)	16.09	160.9	12.26	122.6
Isipingo(44)	9.98	99.8	8.99	89.9
KwaMashu(45)	4.29	42.9	1.07	10.7
Boitekong(54)	1.43	14.3	3.01	30.1
Brits(55)	7.9	79.0	4.38	43.8
DBN Northern(58)	9.12	91.2	10.5	105.0
DBN Northern(59)	12.5	125.2	4.71	47.1
Klipfontein(75)	10.7	107.2	8.10	81.0
Newcastle(76)	9.23	92.3	7.77	77.7

SURVEY OF ORGANIC AND INORGANIC POLLUTANTS IN SOUTH AFRICAN SEWAGE SLUDGE

UNIVERSITY OF KWAZULU-NATAL

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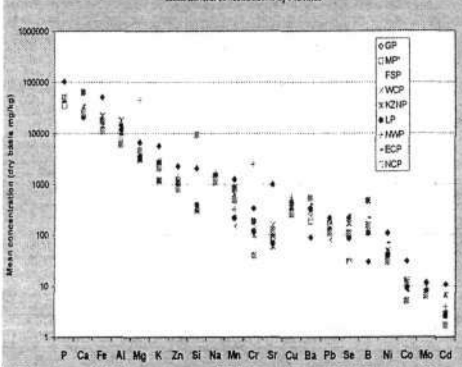
ntroduction

.and disposal of sewage sludge has become a common practice in many countries for both practical and economic reasons. However, ewage sludge as a Waste Water Treatment Plants (WWTPs) by-product is made up of highly hazardous components which includes athogens (viruses, bacteria, protozoa etc), toxic organic substances and toxic heavy metals. The type of sludge from a WWTP is ependent upon the inflow into the plant. The purpose of the study was to investigate the type and quantity of some inorganic and rganic pollutants found in South African sludge.

Summary of Results

:oncentration of minerals ions found in the 71 SA sewage sludge re presented in Graph 1, and a statical average is presented in Table 1.

Graph 1: Conc (dry basis mg/kg) in SA sewage sludge



3P-Gauteng, MP-Mpumalamga, FSP-Free State, WCP-Western Cape, KZNP-KwaZulu-Natal, .P-Limpopo, NWP-North West, ECP-Eastern Cape, NCP-Northern Cape.

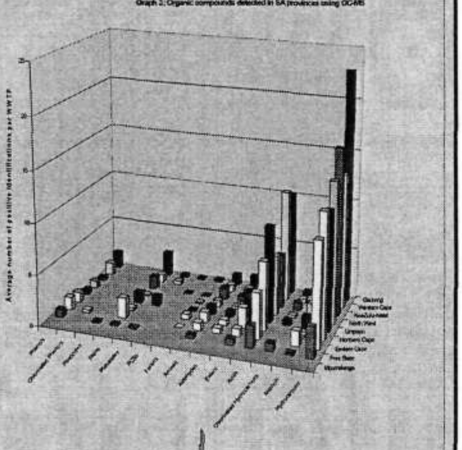
Experimental

Samples were acid digested with nitric acid and hydrogen peroxide as stated in US-EPA method 3050B for elemental analysis.

For organic compound analysis, samples were soxhlet extracted using hexane-dichloromethane solvent system.

78 sewage works were sampled and a GC-MS study conducted to detect a range of organic pollutants found in SA sewage sludge. The result in the form of average number of positive identification are presented in Graph 3 below.

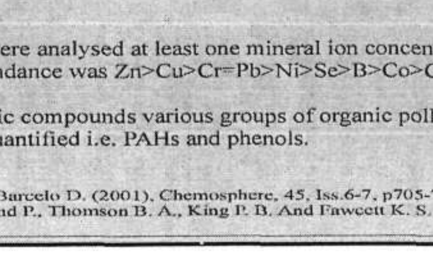
Graph 3: Organic compounds detected in SA provinces using GC-MS



'able 1: Concentrations (dry basis mg/kg) in SA sewage sludge

	Mean	Median	Maximum
P	$6.0x10^4$	$5.1x10^4$	$1.7x10^5$
Ca	$3.8x10^4$	$2.5x10^4$	$3.7x10^5$
Fe	$2.4x10^4$	$1.4x10^4$	$2.5x10^5$
Al	$1.2x10^4$	$1.0x10^4$	$7.0x10^4$
Mg	$4.5x10^3$	$3.7x10^3$	$31x10^3$
K	$3.4x10^3$	$1.9x10^3$	$33x10^3$
Zn	$1.4x10^3$	$9.0x10^3$	$13x10^3$
Si	$1.3x10^3$	$3.0x10^3$	$38x10^3$
Na	1200	1100	4000
Mn	600	250	.10000
Cr	510	1.1	17000
Cu	370	2.9	2500
Ba	250	2.5	700
Pb	150	1.0	900
Se	140	0.004	1300
Sr	110	0.009	400
B	90	0.005	400
Ni	60	0.4	600
Co	14	8.3	230
Mo	8.9	8.0	25
Cd	5.4	2.8	50

Graph2: No of sewage works with inorganics exceeding maximum concentration limits as stipulated in 1997 Guidelines.



The organic pollutants for quantification were PAHs and Phenols whose values are shown in Table 2.

Table 2 : Concentrations in mg/kg of organic pollutants quantified using GC.

	Phenols (mg/kg)		PAHs Concentration (mg/kg)					
Sample	1*	2*	3*	4*	5*	6*	7*	8*
Gauteng 01	5.73	350	-	2.41	-	-	18.1	-
Gauteng 02	0.35	203	0.51	0.53	1.85	0.53	13.8	9.98
Gauteng 04	-	0.30	3.42	0.53	1.74	1.57	-	13.7
Gauteng 06	-	0.45	14.0	6.77	12.5	2.31	15.8	9.42
Gauteng 15	-	0.15	2.52	0.86	2.41	6.35	23.0	42.8
Gauteng 22	1.70	2079	1.50	1.15	1.94	4.08	15.76	-
Western Cape 28	14.1	232	0.17	0.13	0.73	0.46	0.86	0.25
Western Cape 30	2.57	821	21.96	3.66	-	18.3	28.5	-
Western Cape 37	-	-	0.58	-	0.25	0.58	0.75	0.59
KwaZulu-Natal 44	12.2	1.82	0.37	0.17	0.57	0.145	1.10	-
North West 54	1.67	2.36	0,24	-	-	-	1.83	1.79
North West 55	-	-	11.9	0.64	-	6.47	7.27	-

1*-p-Cresol, 2*-Nonylphenol, 3*-naphthalene, 4*-Acenaphthylene, 5*-Acenaphthene, 6*-Fluorene, 7*-Phenanthrene, 8*-Anthracene.

Conclusion

In all the 71 sewage sludge that were analysed at least one mineral ion concentrations was above the stipulated guidelines. The order of the heavy metal abundance was Zn>Cu>Cr=Pb>Ni>Se>B>Co>Cd.

In the samples analysed for organic compounds various groups of organic pollutants were detected, concentrations of some of these pollutants groups were quantified i.e. PAHs and phenols.

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