METHODOLOGY AND SURVEY OF ORGANIC POLLUTANTS IN SOUTH AFRICAN SEWAGE SLUDGES

VOLUME 1

D Jaganyi

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METHODOLOGY AND SURVEY OF ORGANIC POLLUTANTS IN SOUTH AFRICAN SEWAGE SLUDGES

VOLUME 1

by

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EXECUTIVE SUMMARY

Large quantities of sludge are generated in sewage treatment plants. It contains both compounds of agricultural value, which include organic matter, nitrogen, phosphorus and potassium, and to some extent, calcium, sulphur and magnesium. Sludge is also composed of highly polluting substances which consist of pathogens (viruses, bacteria, protozoa, eggs of parasitic worms), toxic heavy metals and toxic organic substances. Sludge undergoes various treatments at sewage works in order to render it suitable for disposal or reuse. This is done in accordance with the rules set by legislative bodies so that it does not cause an adverse impact on the environment. The ultimate disposal of sewage sludge includes soil application, landfill, lagooning, incineration and disposal at sea. The disposal process continues to be one of the most challenging problems for wastewater treatment plants.

A well-treated sludge can be used as a nutrient source for vegetation. This includes agricultural application for crop cultivation, soil reclamation in areas where mining activities take place and application in gardens. This is of economic importance to the sewage works as a source of income and to the farmers as a source of cheap fertilizer. The long-term benefits of application of sewage sludge to land are limited due to the presence of toxic heavy metals and toxic organic substances. The other limitation is the National Guidelines for the disposal of sewage sludge, which are sometimes very conservative.

The aims and objectives of this project were to:
a) carry out a literature study so as to determine the most suitable method(s) for extraction and analysis of potentially harmful organic compounds in sewage sludge,
b) establish standardised methods for sampling and preservation of sludge samples,
c) test the selected methods for extraction efficiency and reproducibility using standards and spiked samples,

d) carry out a screening process on sewage sludge samples for the purpose of determining the existence of the most persistent organic pollutants,

e) quantify the selected organic contaminants, and

f) compare the values obtained in this work with the current Sludge Guidelines and make recommendations based on risk and suggest maximum permissible concentrations of organic pollutants in sewage sludge.

The study provides the much needed information on the quality of the South African sewage sludge in relation to organic pollutants. On a bigger picture the project assesses the current South African legislation (Guideline) on permissible utilization and handling of sewage sludges by comparing the findings with the guideline and with the international limits. The information is expected to support decision making at national level and help with Edition 2 of the Permissible utilisation and disposal of sewage sludge.

A comprehensive literature survey, looking at different aspects of organic pollutants in sewage sludge, is incorporated in the report. It is clear from the data available that most of the organic pollutants are not taken up by plants. However, a risk of contamination of the food chain exists when sludge is spread directly onto crops that are to be consumed raw or semi-cooked. The major source of human exposure to sludge-borne organic pollutants is through the consumption of animal products such as meat and milk through the bioaccumulation of compounds such as PCDD/Fs, PCBs or PAHs. This is due to the ingestion of soil and sludge by livestock due to the spreading of sludge on the land used for grazing. Currently little is known about the plant uptake of phthalates and nonylphenols which are present in relatively high levels in sludge.

Included in the literature survey is a list of the most common methods normally used for extraction of organic compounds and the possible methods of analysis. What is noted is that there is no universally accepted and validated analytical method for analysing most of the organic compounds. In addition, data concerning levels of organic pollutants is scarce worldwide.

The methods selected for this project were EPA Methods 3510C (Liquid-liquid extraction) and 3540C (Soxhlet extraction) for the aqueous and solid sewage sludge. These two methods were chosen because they are simple, inexpensive and effective. The chosen purification method was the sulfur clean-up process (EPA Method 3660B). This is because sulfur precipitates were observed in most of the concentrated extracts, especially from the solid samples.

Details regarding sampling process, type of containers, transport and storage of sludge samples are reported. In brief, 1-liter bottles made of glass having polytetraflouroethylene (PTFE) lined screw caps were used. These were transported from the sampling sites using cooler boxes designed to maintain a temperature of $4^{\circ}C$ for a minimum period of 24 hours using ice blocks. On arrival in the laboratory, the samples were immediately wrapped in aluminium foil to stop any possibility of photo-degradation, before being stored in a chest freezer that had been converted to maintain a temperature of between 2.5 and $3.5^{\circ}C$.

A total of 109 samples from 78 sewage works were extracted, using Soxhlet extraction for solids and liquid-liquid extraction for liquid samples. All the extracts were analysed using GC-MS. The identification of the organic compounds using GC-MS Wiley library was carried out and the data is presented. A total of 712 organic compounds were identified in the South African sewage sludge. These included Phenols, Pesticides, PAHs, Phthalates, PCBs, Furans, Amines, Aldehyde, Esters, Acids, Chlorinated Hydrocarbons, Alcohols, Hydrocarbons and others (all sorts of organic compounds that did not belong to the named categories). A detailed information for each WWTP is presented in volume two of this report (see CD at back).

To test the for extraction efficiency and reproducibility, a "clean" sludge matrix was prepared from Heidelberg sludge by extracting it five times to remove the extractable organic material. The process did not remove all of the organic acids. The sludge was then spiked with a mixture of 6 chlorinated pesticides (aldrin, DDT, dieldrin, heptachlor, hexachlorobenzene and lindane) at half the regulatory limits (WRC, 1997). Analysis was by GC-MS at SIM and GC attached to ECD. In addition, the

solvent mixture (Hexane/Dichlomethane) used in the extraction was also spiked with the same mixture of pesticides. This was diluted into $\frac{1}{4}$, $\frac{1}{2}$, $\frac{1}{8}$, and $\frac{1}{16}$th of the guideline limit and the sample analysed using GC and GC-MS.

The results showed that the method chosen for extraction i.e. Soxhlet method had an efficiency of over 80% for all the pesticides investigated. In terms of the instrument, using the GC-MS operated at SIM mode and GC attached to ECD made it possible to detect the 6 pesticides to $\frac{1}{16}$th of the guideline limit.

A total of 14 samples were selected for the quantification of p-cresol, nonylphenol and pesticides listed in the current guideline, while 32 WWTPs were used to determine PAHs. The results showed negative results for pesticides, confirming that the pesticides listed in the guideline are not the compounds of interest as far as organic pollutant is concerned. The reasons for this is most likely due to the fact that most of the pesticides listed are banned or their use is severely restricted. The pesticide classes that have been recorded to be in use in order of sales are triazines, organometallic compounds, carbamate/thiocarbamate, organophosphates, and under restriction organochlorine pesticides (DDT).

The quantification of phenols; p-cresol, Nonylphenol, and PAHs was based on the outcome of the screening process. Apart from just having been detected in the majority of the sludge samples, these pollutants are known to have detrimental effects on marine and human life. In addition the compounds are listed in the EU and USEPA list of priority pollutants.

Comparing the liquid and the solid extracts of the liquid sludge, the results show that 99% of p-cresol is concentrated in the liquid phase. The opposite is true when looking at the NP where 90% of it is trapped in the solid matrix leaving 10% in the liquid phase. It is also noted that liquid sludge contains high values for the two organic compounds when compared to the solid sludge.

In the case of PAHs, two compounds namely Benzo(b)anthracene and Benzo(k)fluoranthene were found to exist in all the samples analysed. Using the concentration of the indicator PAH (i.e. benzo(a)pyrene), as stipulated in the South African guideline, is misleading. Using the EU limit, the current results show that most of the sludge being produced in this country exceeds the set limit. This is also true for most of the EU member countries.

PCBs were only detected in Gauteng province.

Based on this study the following recommendation can are made:

- The recommended methods of analysis are EPA Methods 3510C (Liquid-liquid extraction) for liquid sludge, 3540C (Soxhlet extraction) for solid sludge and EPA Method 3660B for sulfur clean-up.

- There is clear evidence that organochlorine pesticides are not the group of organic pollutants that need to be monitored because of their low level of occurrence. These should therefore be removed from the guideline.

- The three compounds that require regular monitoring are p-cresol, nonylphenol and PAHs (group of 9 as in the EU 2000 draft).

- The liquid samples that leave wastewater plants need to be analysed for nonylphenols.

- PCBs should be quantified and regularly checked especially where it was identified to exist (e.g. Gauteng). This is because of their toxicity. Also, internationally these compounds have very low limits. The presence of the other listed compounds namely PCDD/F, DEHP, LAS and AOX should be quantified in only a few areas to gauge their level of pollution. There is no need to do regular checks on LAS and AOX compounds because, based on EU limits, their toxicity levels are not so critical.

- There is a need for carrying out a five year screening process. This will update the legislator of the dynamic changes of the restricted compounds and will also bring into light new compounds that may need to be introduced into restriction category (e.g. LAS or AOX).

Therefore the recommended organic pollutants that should be monitored together with the relevant limits are:

Pollutant	Limits (mg/kg)	
Nonylphenol	20	EU limit
PAH	6* OR	EU limit

*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.

The government should 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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AOX	sum of adsorbable organic halogen compounds
BaP	Benzo[a]pyrene
BHC	Benzene hexachloride
CB	Chlorobenzenes
CH	Chlorinated hydrocarbon
dm	Dry mass
dw	Dry weight
DCB	Dichlorobenzene
DDT	Dichlorodiphenyltrichloromethane
DEHP	Di-(2-ethylhexyl)phthalate
EC	Eastern Cape
ECD	Electron capture detector
EU	European Union
FID	Flame ionisation detector
FS	Free State
GC	Gas chromatography
GC-MS	Gas Chromatography-Mass Spectrometry
HCB	Hexachlorobenzene
HCH	Hexachlorocyclohexane
HPLC	High performance liquid chromatography
K_{ow}	Octanol/water partition coefficient
KZN	KwaZulu-Natal
LAS	Linear alkyl benzene sulfonate
LC_{50}	Concentration expected to kill 50% of the organisms tested
LD_{50}	Dose expected to kill 50% of the organisms tested
MSDS	Material safety data sheet
NC	Northern Cape
NDMA	N-nitrosodimethylamine
NP	Nonylphenol
NPE	Nonylphenol ethoxylate
NW	North West Province
OECD	Organisation for economic cooperation and development
PAH	Polynuclear aromatic hydrocarbons
PCB	Polychlorinated biphenyl
PCDD/F	Polychlorinated dibenzo-p-dioxins and -furans
PCP	Pentachlorphenol
PTFE	Poly(tetrafluoroethylene)
PVC	Poly(vinyl chloride)
TCB	Trichlorobenzene
TCDD	Tetrachlorodibenzodioxin
TCE	Trichloroethylene
USEPA	United State Environmental Protection Agency
VOC	Volatile organic compound
WWTP	Wastewater treatment plant

1 INTRODUCTION

1.1 PURPOSE OF THIS STUDY (Problem identification)

Large quantities of sludge are generated in wastewater treatment plants. Approximately 1-2% of the wastewater ends up as a wet sludge and about 2-3 L of sludge are produced per person per day. The total dry solids content of sludge varies between 0.25 and 12%, and 60-70% of these solids consist of organic matter. Sludge is composed largely of highly polluting substances and it undergoes various treatments at sewage works in order to render it suitable for disposal or reuse. Among the more harmful components of sludge are pathogens (viruses, bacteria, protozoa, eggs of parasitic worms), toxic organic substances and toxic heavy metals. (Ross *et. al.*, 1992). Concentrations of pollutants can be extremely high, especially for heavy metals, which can exceed 1000 mg kg^{-1}. Sewage sludges are contaminated with a wide array of organic compounds. The source of these pollutants originates from a wide variety of organic compounds used in households and industries. These find their way unchanged or metabolised into sewage sludge via wastewater treatment.

The ultimate disposal of sewage sludge includes soil application, landfill, lagooning, incineration and disposal at sea. Owing to the high concentration of many harmful substances present in sludge, many countries have banned disposal at sea. The disposal process continues to be one of the most difficult and expensive problems in the field of wastewater engineering (Tchobanoglous & Burton, 1991). In the long term, the ability to continue these dumping practices will depend on the capacity of the receiving system to dilute, disperse or degrade and ultimately accommodate the associated contaminants at acceptable levels. The use of sewage sludge for soil improvement is attractive because the high content of organic materials, nitrogen and phosphorous in the sludge suggests that it would be a good soil conditioner and fertilizer. Instead of being dumped as a waste material, then, the sewage sludge could become a useful product. However a wide variety of undesired chemicals may be found in sludge which could have adverse effects on the environment. These compounds may also affect soils, plant, animals and human health, and have impacts on the environment (Langenkamp & Marmo, 2000). The United State Environmental

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Protection Agency (USEPA) has compiled a priority list of pollutants considered as having the greatest potential to harm human health or to be detrimental to the environment. The list includes 129 substances of which 13 are metals, 2 are miscellaneous and the remaining 114 are organic compounds including pesticides and polychlorinated biphenyls (PCBs).

The fate of these compounds when sewage sludge is applied to agricultural soil or grassland is, however, still largely unknown. Uncertainties remain over soil persistence and potential groundwater as well as surface water contamination, plant uptake and livestock ingestion. All these fates can potentially lead to human exposure. There is enough evidence from literature confirming that applying sludge to land normally increases soil polycyclic aromatic hydrocarbon (PAH) concentrations. Container experiments have shown that an increase of PCB content also takes place, according to the load of sludge. Some of these compounds are known or suspected carcinogens/mutagens.

Ecological consequences of the disposal of urban wastewater or sewage sludges are a question of major concern (Korentajer, 1991; Ross et al., 1992). As a result, there is a growing interest in the establishment of analytical methodologies for the detection of contaminants in both wastewater and coastal water (Snyman et al., 1999; Tchobanoglous and Burton, 1991), and in the development of predictive models for assessing the environmental fate and the distribution of these contaminants in the environment (Perez et al., 2001; Albiach et al., 2001; Sanchezmonedero et al., 2001).

A large body of knowledge has been obtained and is still being generated concerning the problems resulting from the agricultural use of sewage sludge contaminated with heavy metals. However, there is not yet the same level of knowledge about the problems associated with potentially harmful organic substances in sewage sludge. For example, no adequate explanation has yet been put forward as to how such substances applied with sewage sludge may behave in the long run in the soil and whether they may be transferred to crops.

In South Africa an estimated 28% of the sludge generated at the sewage plants is used beneficially (Du Preez et al., 1999). This includes agricultural application for crop cultivation, soil reclamation in areas where mining activities take place and application in gardens. As the population of South Africa grows, so will the number of sewage treatment plants and the amount of sewage sludge that has to be treated and disposed of.

The characteristics of sewage sludge are specific to a country. It is therefore important that each country develop its own National Guidelines for the disposal of sewage sludge based on the knowledge about the nature and content of metal and organic pollutants in their sewage sludge and taking into account the long-term impact on groundwater as well as surface water quality, and on the sustainability of the soil for crop production if sewage sludge is land disposed. The South African Sludge Guidelines (WRC, 1997) stipulates limits for organic pollutants. The maximum concentration limits as stipulated in the document are based on lethal concentration (i.e. LC_{50}) calculations and not on researched values.

Due to the presence of toxic organic substances and toxic heavy metals, the long term benefits of application of sewage sludge to land are limited (Korentajer, 1991) and tt is therefore the responsibility of every government to protect its people by regulating the disposal of sewage sludge.

1.2   AIMS AND OBJECTIVES

The aims and objectives of this study were as follows:
   a) to do a literature study to determine the most suitable method(s) for extraction and analysis of potentially harmful organic compounds in sewage sludge,
   b) to establish standardised methods for sampling and preservation of sludge samples,
   c) to test the selected methods for extraction efficiency and reproducibility using standards and spiked samples,
   d) to carry out a screening process on sewage sludge samples for the purpose of determining the existence of the most persistent organic pollutants,

e) to quantify the selected organic contaminants, and

f) to compare the values obtained in this work with the current Sludge Guidelines and make recommendations based on risk and suggest maximum permissible concentrations of organic pollutants in sewage sludge.

It is worth mentioning that the project only looked at the sewage sludge and not any other type of sludges (i.e. sludge from wastewater treatment plants not pit latrines).

It is envisaged that the results of this study will provide the needed statistical information on the types of organic pollutants that can be found in South African sewage sludge. The data from this study will also be used to assess the validity of the current stipulated limits for organic pollutants in the South African Sludge Guidelines (WRC, 1997). In addition the results will be used to assess whether the presence of organic compounds in sludge applied to agricultural land is a cause for concern and to direct future research.

The inorganic pollutants (metal content) are currently being investigated (WRC K5/1285) with the aim of revising the current Guideline limits. A study to determine the organic pollutants in South African Sludge is underway so as to provide the necessary scientific backing to the selected compounds and the stipulated limits in the current Guideline.

1.3   THE APPROACH TO THE STUDY

The study is base on the following steps:

1   A literature review was conducted to find out what had been done with respect to organic pollutants worldwide. The search was also done to find out the best method(s) of extraction and analysis. A total of 152 references were selected for use in this study.

2   Samples were collected from different parts of the country. Care was taken to make sure that all the samples arrived in the laboratory in the same condition as there were in the field.

3   The samples were then subjected to different extraction methods depending on the nature of the sample. The methods used had earlier been tested and found to have reproducibility of over 80%.

4   The extracted samples were then analysed using GC-Ms for qualitative analysis and GC for quantitative analysis. The qualitative analysis provided the broader picture of what type of organic compounds were present in the sludge samples. This made it possible to identify pollutants of concern and to focus the quantification process on these compounds.

5   The results obtained were then compared with what has been published in literature in other countries before arriving at our conclusions and recommendations

2 LITERATURE REVIEW

2.1 INTRODUCTION

The objective of wastewater treatment is to prevent large quantities of substances reaching and impacting on the environment in high doses and concentrations. Areas of high population density naturally are areas where production of sewage sludge is high. Sewage sludge has a high content of organic materials, of nitrogen and phosphorous indicating that it can be useful as a soil conditioner and fertilizer in agriculture. Consequently, it should be one of the South Africa's policies to enhance sludge use in agriculture as it is in the European Union (EU) (Marmo, 2000).

However, a wide variety of undesired substances may be found in sludge, which could have adverse effects on the environment. They also may affect soils, plant, animals and human health, and have impacts on the environment (Langenkamp & Marmo, 2000). Due to these potential toxicological properties the public expects and demands the implementation of the guidelines to control the problems of environmental contamination.

The term "Biosolids" has been used to designate sludge that meets the U.S. Environmental Protection Agency's (US EPA) standards for land application (Lue-Hing, 1992). The moisture content of the sludge is regarded as the most significant characteristic affecting the design and operation of the stabilisation and disposal processes. Sludge meeting South African standards for land disposal is categorised as Class C and D (WRC, 1997[*]). Class C sludge has been treated in a manner to reduce the number of pathogens. While the Class D sludge has been treated in a manner to further reduce the number of pathogens, so that it can be applied without restrictions. The Class A and B sludges are considered as environmentally unfriendly because they have the ability to cause an uncomfortable smell and a high rate of fly-breeding. In addition they are capable of transferring pathogens to humans and their environment (WRC, 1997; Snyman et al., 2000). The classification of South African sewage sludges is represented in Table 2-1.

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[*]These guidelines are currently under review

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Table 2-1: The classification of sewage sludge to be used or disposed on South African land (WRC 1997*).

Type of Sewage Sludge	Treatment	Characteristics-Quality of Sewage Sludge
Type A sludge	- Raw sludge. - Cold digested sludge. - Septic tank sludge. - Oxidation pond sludge.	- Unstable and can cause odour nuisances. - Contains pathogenic organisms and variable metal and inorganic content.
Type B Sludge	- Anaerobically digested sludge. - Surplus activated sludge. - Humus tank sludge.	- Fully or partially stabilised (i.e. 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 quality requirements:
		  i. Stabilised (i.e. should not cause significant odour nuisance or fly breeding).
		  ii. Contains no viable Ascarsis ova per 10g dry sludge.
		  iii. Maximum zero Salmonella per 10g dry sludge.
		  iv. Maximum 1000 Faecal coliform per 10g dry sludge immediately after treatment.
		- Variable metal and inorganic content.

Type D Sludge
 	
This is a sludge product produced for unrestricted use on land with or without the addition of plant nutrients or other materials. This type of sludge 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
	- Irradiated sludge
		- Certified to comply with the following approved requirements:
		  i. Stabilised (i.e. should not cause significant odour nuisance or fly breeding).
		  ii. Contains no viable Ascarsis ova per 10g dry sludge.
		  iii. Maximum zero Salmonella per 10g dry sludge.
		- Maximum 1000 Faecal coliform per 10g dry sludge immediately after treatment.
		- Maximum metal and inorganic content in dry sludge.
		- User must be informed about the moisture and nitrogen (N), Phosphorus (P) and potassium (K) content.
		- User must be warned that not more than 8 t/ha/year may be applied to the soil. In addition it should be noted that the pH of the soil should preferably be higher than 6.5.

*These guidelines are currently under review

Studies on the occurrence of organic pollutants in soil and effects in plants including transfer mechanisms are scarce. Sludge may contain volatile organic compounds (VOCs) such as benzene, toluene, and xylenes (Quaghebeur, 1989). These compounds

are generally volatile, so most of them are lost to the air fairly quickly following the spreading of sludge on the soil surface (EU, 2000). As a result of these uncertainties a strategy for scientifically-based handling of sewage sludge utilization is difficult to make.

2.2   DEFINITIONS

The terminology has been defined following the definitions given in the European Union Working Document on Sludge, 3rd draft (EU, 2000):

Sludge: "mixture of water and solids separated from various types of water as a result of natural or artificial processes."

Sewage sludge: "sludge from urban water treatment plants", whereby 'urban wastewater' is understood as: "domestic wastewater or the mixture of domestic wastewater with industrial wastewater and/or run-off rain water". The definition of "domestic wastewater" is: "wastewater from residential settlements and services, which originates predominantly from the human metabolism and from household activities".

Treated sludge: Sludge which has undergone a treatment process so as to significantly reduce its biodegradability and its potential to cause nuisance as well as health and environmental hazards when it is used on land.

2.3   SEWAGE SLUDGE PRODUCTION AND TREATMENT

Sewage sludge, a mixture of solids and water, is a waste product formed during conventional wastewater treatment. The bulk of sewage sludge derives mainly from human wastes, although discharges of industrial effluents and storm water runoff within the treatment works catchment may also be significant (Langenkamp and Marmo, 2000). Sludge characteristics vary depending on each treatment facility's waste stream and the processes that are used. Hence it is necessary that every country establish its own sewage sludge composition legislation. This is not only because of the different pollutants in different countries but because if sludge is to be applied to land the total input rate of organic pollutants should not exceed the rate of

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degradation. This is determined by the local factors that control the physical, chemical, and biological properties. Most of the countries base their legislation limits purely on precautionary measure as detailed in section 2.7.

The wastewater treatment process involves preliminary screening to remove larger floating and suspended materials, followed by primary sedimentation where approximately 55% of the suspended solids settle out and are concentrated into primary sludge. Where the water treatment works has primary setting tanks, primary settlement produces the majority (60-75%) of the final sewage sludge. The wastewater may then undergo secondary (biological) treatment, usually consisting of a percolating filter or activated sludge treatment with further settling, from which secondary sewage sludge is produced. In some cases, a further tertiary treatment is required to "polish" the effluent prior to final discharge. The aim of sewage treatment is to produce a final effluent suitable for discharge to the selected receiving water.

The sludges produced during wastewater treatment are combined and usually treated to some extent prior to disposal. The extent of sludge treatment frequently depends on the final use/disposal option selected and is generally intended to thicken and reduce the sludge water content, reduce the microbiological hazard potential and also reduce the nuisance value from odour (Bruce & Davis, 1989). Essentially five processes may be employed either alone or in combination as follows:

a)   screening to remove rags and litter,

b)   thickening to reduce volume,

c)   stabilisation to reduce pathogens and improve odour,

d)   positive disinfection to destroy pathogens, and

e)   de-watering to form a solid cake.

2.4   SEWAGE SLUDGE USE/DISPOSAL

Smith and Vasiloudis (1991) approximated that the production of sludge per person was 16.5 kg of dry sludge per year. The most widely used sludge disposal options include ploughing the sludge into land specially designated for this purpose or

stockpiling at the sewage treatment plants in dry heaps or liquid lagoons (paddies) (Ekama, 1993). A list of some of these options is shown in Table 2-2 with the relative percentage of sludge disposed of by each option. It is obvious that "beneficial uses" which include agricultural application, soil reclamation and application in gardens is not a major route (28%). Almost half of the sludge produced is disposed to land in a non-beneficial way. This can be contrasted with the situation in Europe and the United States where application of sludge to agricultural land is practised extensively and accounts for >40% of the sludge produced (DoE, 1993; WPCF Residual Management Committee, 1989; Anderson, 1992; Agg et al., 1992; Matthews, 1992; Sieger & Hermann, 1993).

Table 2-2:   **Sludge disposal options in South Africa (Du Preez et al., 1999)**

Beneficial uses	28%
Accumulation at plant	20%
Landfill	3%
Non-Beneficial land application	47%
Unspecified	2%

2.5   THE ORGANIC CONTAMINANTS IN SEWAGE SLUDGE

2.5.1   Priority Lists Produced By Various Organizations

Many thousands of organic chemicals are now produced for industrial and domestic use which may occur in wastewater and sewage sludge. Various so-called 'priority pollutant' lists have been produced by international organizations aimed at identifying those compounds which may require regulation. These lists are not specific to wastewater and sludge contaminants but are illustrative of the range of types of organic contaminants that may occur. Various priority lists for organic and inorganic pollutants for water, sewage sludge and other media have been produced by the United States Environmental Protection Agency (USEPA), the European Community (EC) or the European Union (EU) and UK government agencies. (A priority list set

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according to UMK-AG 2000 is presented in Appendix A.) The lists produced by the different organisations are likely to differ from each other, highlighting the different purposes and reasons for which the lists were produced in the first instance.

Pollutants such as PAHs and PCDD/Fs have been reported to have relatively high rates of deposition from air (Jensen & Endres, 1999). This has resulted in a discussion about the significance of atmospheric deposition of pollutants onto soils versus introduction via sludge.

Table 2-3: **Priority pollutants identified most frequently by US, European Union and UK organizations (US EPA).**

Monocyclic aromatics	Benzene Ethylbenzene Toluene Chlorobenzene Dichlorobenzenes Trichlorobenzenes (specially 1,1,4- TCB) Hexachlorobenzene Pentachlorophenol
Halogenated aliphatics	Carbon tetrachloride Chloroform 1,2-Dichloroethane Trichloroethene Tetrachloroethene Hexachloro-1,3-butadiene
Polycyclic aromatic hydrocarbons (PAHs)	Naphthalene
Organochlorines	Polychlorinated biphenyls (PCBs) Polychlorinated dibenzo-p-dioxin and furans (PCDD/Fs) Aldrin Dieldrin Endrin DDT (and isomers) Alpha-&-beta-endosulfan Gamma-HCH (lindane)

In 1976 the USEPA initiated a scheme for establishing drinking water quality standards and priority lists. The USEPA priority list for water includes those substances:

a) for which there is substantial or some evidence of carcinogenicity, mutagenicity or teratogenicity or which have a similar molecular structure to the aforementioned compounds,

b) known to have toxic effects on humans or aquatic organisms at sufficiently high concentrations and which are present in industrial effluent,

c) known to be chemically or biologically stable and which are, therefore, persistent in the environment and

d) which have been identified a significant number of times in waste or potable water and which are produced in quantity by industry and are available as analytical standards.

This list comprises 129 priority pollutants, of which 114 are organic compounds (Appendix A) and the rest comprise 13 metals and metalloids, cyanide and asbestos.

2.5.2 Fate Of Organic Contaminants In Sludge-Amended Agricultural Soils

Base on sustainability, the total input rate of organic pollutants to soils should not exceed the rate of degradation or removal. Once added to the soil, sludge-borne persistent organic pollutants are subject to a variety of processes such as:

- adsorption/desorption,
- degradation (biotic and abiotic),
- volatilization,
- erosion/runoff and
- leaching.

Thus the actions of these processes reduce the concentration of persistent organic pollutants potentially available for plant uptake (O'Connor, 1996). There is an accumulation in soils, but the persistence varies between different groups and specific compounds within each group.

Soil sorption is now widely recognized to affect microbial degradation of many compounds. Strongly adsorbed species are apparently unavailable to microbes because only low concentrations are desorbed into solution and become available for microbial uptake and intercellular metabolism (O'Connor, 1996). These species will also be less available for leaching and plant uptake.

Adsorptions to humus and clay particles as well as biological degradation (anaerobic and aerobic) are decisive factors for the persistency of organic contaminants in soils. Microbial degradation is the most important loss mechanism for many organic chemicals in soils. The rate of degradation of a particular compound is influenced by many environmental factors such as temperature, water content and soil pH. Biodegradation of organic compounds can generally be described by a first order rate constant. Half-lives of many organic compounds have been published and reported values show enormous variations between soil types and with experimental conditions.

Relating the results obtained from spiking soil with organic compounds to sludge-applied organic compounds may be problematic due to influences of the sludge matrix, as sludge applications stimulate soil microbial activity through the addition of nutrients and bulky organic matter. Sludge also contains surfactants, which may enhance the solubility and availability of recalcitrant compounds for microbial breakdown. Alternatively, the sludge matrix may also bind the compounds, excluding them from degradation. Behaviour of organic compounds may also differ significantly between laboratory and field experiments due to different environmental conditions (Wild and Jones, 1992). Compounds such as linear alkybenzene sulfonates (LAS), di(2-ethylhexyl)phthalate (DEHP) and nonylphenols (NPs) are less likely to absorb to humus and are more easily degraded than are polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs) or polychlorinated dibenzo-p-dioxins and –furans (PCDD/Fs).

2.5.3 Risk Assessment (Exposure Pathways)

Besides direct ingestion of sludge by children, the greatest risk from persistent lipophilic organic compounds arises when fluid sludges are applied so that they adhere to forage/pasture crops and are subsequently ingested by livestock used as human food (Madsen et al., 1997; Chaney et al., 1998). It is also stated (Smith, 2000) that the uptake of organic pollutants through direct ingestion of sludge adhering to grass and/or sludge-treated soil by grazing livestock and subsequent accumulation in the animal is the main route of human exposure from agricultural use of sludge.

However, it is also summarized that the total human intake of identified organic pollutants from sludge application to land is minor and is unlikely to cause adverse health effects.

In view of the variety of sources, many different organic compounds may be present in sludge, all of which will behave differently when applied to soil, depending on their individual properties as well as the sludge-amended soil system (Dean & Suess, 1985; Jacobs et al., 1987). The principal pathways for transfer of substances to man from sludge amended agricultural land are listed below (Dean & Suess; 1985 Jacobs et al., 1987; Wang & Jones, 1994).

1)   direct ingestion of sludge-contaminated soil by children, a behavioural attribute known as "pica" (Eikmann et al., 2000),

2)   direct application to edible parts of plants as sludge, dust or mud when sludge is mixed with soil and subsequent consumption by humans (Duarte-Davidson et al., 1996),

3)   uptake via plants used as feed or fodder for animals, transfer to animal food products and consumption by humans (Stark and Hall, 1992; McLachlan et al., 1994, 1996; Fries 1996; Chaney et al., 1996; Jones and Alcock, 1997),

4)   uptake by plant roots in sludge-treated soil, transfer to edible parts of plants and consumption by humans (Wild and Jones, 1992; O'Connor, 1996, Topp et al., 1986; Smith, 2000),

5)   direct atmospheric deposition to edible parts of plants and consumption by humans (Hembrock-Heger, 1992; McLachlan et al., 1994),

6)   direct ingestion of soil or sludge by grazing animals and transfer to animal food products with subsequent consumption by humans,

7)   direct intake of airborne dust (soil or sludge),

8)   surface runoff/erosion to streams, rivers used as drinking water sources,

9)   leaching to a groundwater aquifer used as a drinking water source (Madsen et al., 1997),

10   direct intake of vapours containing volatile pollutants in sludge (Beck et al., 1996; McGrath 2000),

11) direct handling of sludge during treatment or application of sludge to land (Legeas, 2000; Andersen, 2001).

The individual exposure pathways vary in importance for each substance, again depending on its characteristics and the location, use and type of soil on which application occurs. As a result, human exposure to some compounds may be minimal in view of the concentrations detected in sludge and respective physico-chemical properties, whereas that of others may be higher.

Although it is difficult to predict every agricultural sludge-amendment situation, there have been some attempts to systematically prioritise those compounds of most concern with regard to exposure from sludge application to agricultural land. Recently there have been attempts by MAFF with regard to contamination of food products, and also by the USEPA under the review of the 503 rule. This has become an area of some importance in view of the array of compounds detected in sludge.

2.6 INFORMATION ABOUT CONTAMINANTS AND THEIR BASIC TOXICOLOGICAL DATA

There are a wide range of organic contaminants that are present in sewage sludge, having originated mostly form commercial as well as domestic activities. Compared to metals, organic pollutants have only recently been identified as having potential adverse human health effects. Most organic pollutants are present in the environment at very low concentrations. However, as some of these compounds may bioaccumulate or have effects at low concentrations, chronic health effects are starting to be investigated for some of the major organic pollutants. This section briefly describes some of these organic pollutant groups that are of concern and their toxicological effects.

2.6.1 Organic Contaminants and their Sources in Sewage Sludge

A literature review with 900 references to papers published between 1977 and 1992 revealed that German sewage sludges contained 332 organic compounds (Drescher-Kaden et al., 1992). Some of these compounds are known to have or are suspected of having toxic effects, 42 of the compounds appeared regularly; most of them within the

range of g/kg to mg/kg dry weight (dw). It was found that the residue level increases from raw to digested sludge with the exception of the volatile and easily degradable chemicals. Samples from rural treatment plants were reported to have a more balanced residue pattern than those from urban origin where the highest and the lowest concentration values were found. In general, the residues in rural sludges were found to be slightly lower than in urban sludges, particularly for typical industrial chemicals (Drescher-Kaden et al., 1992).

Five main industrial categories were considered as the major sources of organic pollutants in sewage works. These sources include petroleum refining, organic chemicals and synthetic industries, steel milling and coal conversion, textile processing as well as pulp and paper milling (Rawlings & Bamfield, 1979; Wise & Fahrenthold, 1981). The sources of some of the organic compounds that are more likely to be encountered in sewage sludges as well as the target compounds are briefly explained in the following sections.

2.6.2 Organochlorine Pesticides

These are pesticides, which can be defined as substances or mixtures that are employed for the destruction, prevention, repelling or mitigating of any pest (Andersen and Milewski, 1999). It has been suggested that a number of these substances are a potential hazard to plants and possibly humans as well as animals since they are known to be extremely persistent in the environment. In addition, the continuous utilization of these pesticides has resulted in more insects becoming resistant to them. Furthermore, they can be non-specific, killing both useful and hazardous insects (Carson, 1963).

As a result organochlorine pesticides are now only employed for particular purposes, and have been replaced by organophosphorus and carbamate insecticides in various aspects of crop protection in several countries. The target pesticides for this project included DDT, aldrin, chlordane, dieldrin, heptachlor, hexachlorobenzene and lindane. This is because these compounds are included in the South African guidelines on disposal and utilization (WRC, 1997). Moreover, they form part of the

priority pollutants list identified by USEPA and UK organization. A brief description and structures (Figure 2-1) of the SA target pesticides are described.

DDT was mainly designed to control the spread of life-threatening diseases such as malaria and the regulation of pests that feed on agricultural crops (Hassal, 1982). It has multiple applications and hence caused universal pollution of water and soil resources, significantly affecting the well-being of animals. As a result of the known adverse effects, DDT has been banned in most countries although it is still used for residual indoor spraying in several countries, including some parts of South Africa (UNEP, 2000, http://pops.gpa.unep.org/14ddt.htm). Indoor residual spraying of DDT is mainly used to destroy insects responsible for the spreading of life-threatening diseases such as malaria where the application is approved by governments and supported by the World Health Organisation (WHO) (WFPHA, 2000). DDT is still considered to be the best and most cost-effective insecticide against the malaria-carrying mosquito (htt:/www.environment.gov.za/ParliamentUpdate/eqp_questions.html). Exposure to DDT in humans is associated with reproductive abnormalities including low fertility rate, stillbirths, neonatal deaths and congenital defects in babies (WFPHA, 2000).

The long-term health effects in birds and mammals involve estrogenic properties and anti-androgenic sexual development (*i.e.* feminization of males in alligators and Florida panthers) as well as eggshell thinning of offspring (WFPHA, 2000).
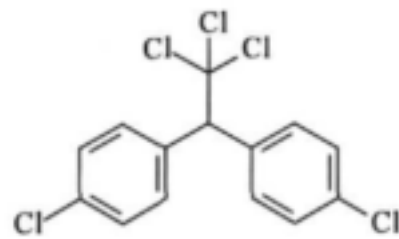
Dichlorodiphenyltrichloroethane (DDT)   **Lindane**   **Aldrin**
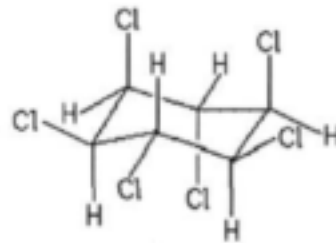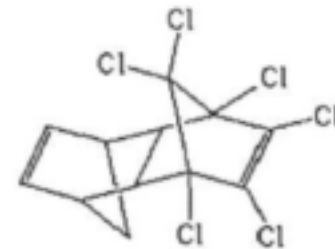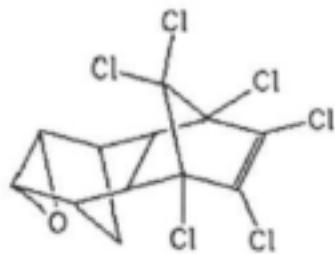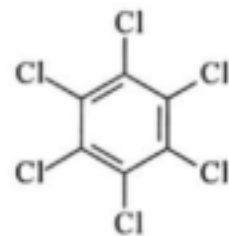
Dieldrin   **Hexachlorobenzene**   **Heptachlor**   **Chlordane**
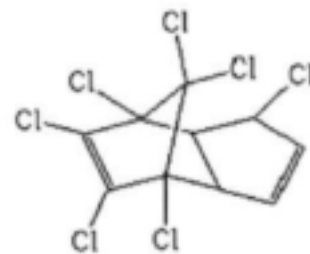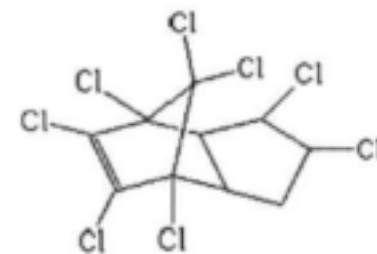
Figure 2-1: Structural representation of organochlorine pesticides.

Lindane, which is also known as γ-BHC is generally employed on a broad range of crops, in warehouses, in public health to regulate insect-borne diseases and as a seed treatment when used in conjunction with fungicides (EXTOXNET). Currently lindane is available in the form of lotions, creams and shampoos in order to regulate lice and mites in people. In addition, it is preferable to DDT in situations where a fumigant action is required. This is because lindane has a vapour pressure approximately fifty times greater than that of DDT and is generally less persistent on crops (Hassal, 1982; WFPHA, 2000). Acute exposure as a result of the inhalation of lindane can cause nasal discomfort and results in some skin deformations or anaemia. Oral exposure in humans can results in nervous system disorder causing seizures and vomiting (ATSDR, 1997). On the other hand, chronic exposure can result in the destruction of the liver and kidney according to studies performed on animals.

Aldrin is similar to lindane insofar as it has a moderately high vapour pressure and hence is desirable in cases where fumigant action in the soil is required (Hassal, 1982; EXTOXNET; WFPHA, 2000). Fumigant action is employed for the regulation of wireworms on potatoes as well as larvae of root flies.

Dieldrin is mostly efficient in the regulation of specific insect bugs found on animals such as lice, blowfly larvae and ticks and it is 40-50 times more toxic than DDT (Hassal, 1982; WFPHA, 2000). Its application in Britain has been restricted mainly to crop protection as a dip for cabbage roots during transplanting. The health effects of both aldrin and dieldrin are basically the same in the environment since the two are closely related (UNEP, 2000, http://pops.gpa.unep.org/11aldi.htm). It has been recorded that short-term exposure of these compounds in humans can result in neurological symptoms such as severe convulsions (WFPHA, 2000), these effects can last for several weeks. Prolonged exposure can result in headaches, dizziness, nausea and vomiting, anorexia, muscle twitching, physiological illness and Parkinson's disease.

Chlordane is a combination of several chlorinated dicyclopentadienes. Pure chlordane in its technical form consists of two geometric isomers each containing eight chlorine

atoms (Hassal, 1982; WFPHA, 2000). It is more efficient in regulating aphids, Colorado beetle larvae as well as grasshopper than is DDT. The other functions for chlordane include regulation of ants, earthworms, earwigs, household insects, moth larvae, termites and wireworms. It has been suspended in the US when it was found that 90% of all Americans contain chlordane metabolite residues in their tissues and there was a possibility that it can be transferred from mother to child through the placenta and also during breastfeeding (UNEP, 2000, http://pops.gpa.unep.org/13chlo.htm). Chlordane is considered fairly toxic and hazardous. Generally, people who are exposed to chlordane show respiratory illnesses, bronchitis, sinusitis and migraines (WFPHA, 2000; UNEP, 2000, http://pops.gpa.unep.org/13chlo.htm).

Hexachlorobenzene (HCB) was widely used as a pesticide to protect onions and sorghum seeds, wheat, and other grains against fungus until 1965 (ATSDR). It was also used in the chemical industry to make fireworks, ammunition, and synthetic rubber. Practically, HCB is no longer manufactured but it is still produced as by-product during the production of several chlorinated chemicals. It has been found in the flue gas as well as the fly ash of municipal incinerators and other thermal processes (UNEP, 2000 http://pops.gpa.unep.org/16hexac.htm). Short-term exposure of elevated concentrations of HCB is linked with *porphyria cutanea tarda* since it is very poisonous to the liver (WFPHA, 2000). In addition, mothers who have been accidentally exposed to HCB gave birth to babies with enlarged thyroid glands and arthritis. On the other hand, animals exposed to high HCB contents exhibit acute neurological toxicity with symptoms such as tremors, paralysis, lack of coordination, weakness and seizures (WFPHA, 2000).

Heptachlor is an insecticide used on seed grain and crops and can be detected in chlordane as an impurity (UNEP, 2000, http://pops.gpa.unep.org/15hept.htm). The use of heptachlor has been banned in Cyprus, Ecuador, the European Union, Portugal, Singapore, Sweden, Switzerland and Turkey. Its use is severely restricted in Argentina, Israel, Austria, Canada, Denmark, Finland, Japan, New Zealand, the Philippines, the U.S., and some countries of the former Soviet Union (UNEP, 2000 http://pops.gpa.unep.org/15hept.htm). Animals metabolise heptachlor into heptachlor

epoxide. Heptachlor is very poisonous to human beings and results in hyperexcitation of the central nervous system and liver damage. It has been observed that heptachlor can cause liver damage and a change in progesterone and oestrogen levels (WFPHA, 2000).

In South Africa the agricultural sector is the main consumer of pesticides and is responsible for a considerable amount of sales (Naidoo & Buckley, 2002). The agricultural sector includes the emerging farmers, small-scale subsistence farmers, large scale commercial farmers and co-operatives (i.e. food plots or farm groups). There are other sectors that consume pesticides, which include industrial, public and governmental sectors. The government sector uses pesticides to regulate disease or pests such as malaria, lice and rats. Usually industries employ the pesticides for sterilization and management of pests, which is vital to sustain quality standards of their products and processes. The domestic sector includes homes and gardens. This sector obtains pesticides from supermarkets and in small quantities. However, there is basically no information concerning the dumping of wastes after the use of pesticides in public and government sectors. Nevertheless it has been suggested that pesticide wastes from homes and businesses are likely to end up in sewage works (Naidoo & Buckley, 2002).

2.6.3 Trichloroethylene (TCE)

Trichloroethylene is generally employed as a solvent for metal parts degreasing operations and it is also used to produce other chemicals (ATSDR, 1989; McNeill, 1979). The main route through which TCE can be introduced into the environment is through evaporation into the atmosphere during the removal of grease from the metal. The other ways that TCE can be released into the environment include (ATSDR, 1989):

(i)   evaporation from adhesive glues, paints, coatings and other chemicals,

(ii)   burning of community and harmful waste,

(iii) air-cleaning processes at publicly-owned waste treatment plants that receive wastewater with trichloroethylene

The structural representation of trichloroethylene is provided in Figure 2-2.
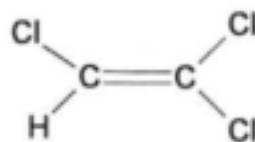
Figure 2-2:   Chemical structure of trichloroethylene.

Human beings can be exposed to trichloroethylene at their working places. It has been found that employees working with trichloroethylene-containing products in small, poorly ventilated places or those that breathe these compounds have several side effects. These include dizziness, headaches, slowed reaction times, sleepiness and facial numbness (ATSDR, 1989; ATSDR, 1997). Studies have also shown that breathing higher amounts than is recommended may damage the liver and kidneys, resulting in tumours of the liver, kidney, lung and male sex organs as well as leukaemia.

2.6.4   Polynuclear Aromatic Hydrocarbons (PAHs)

Polnuclear Aromatic Hydrocarbons (PAHs) are hydrocarbons with multiple ring structures. These are ubiquitous environmental contaminants found in air, soil and water (Liu & Korenaga 2001). Many human activities result in the formation of PAHs (Stevens et al., 2003), 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 is the primary source of PAHs in densely populated areas (Langenkamp & Pärt, 2001). The replacement of coal with oil in Germany has significantly lowered the quantities of PAHs in sewage sludges as reported in Germany (UMK-AG, 2000; McLachlan et al., 1996). However, there are other natural sources such as forest fires and volcanoes. Some of the lighter PAHs such as acenapthene, fluorene and anthracene are produced from wood treatment (http://dsp-dsp.communication.gc.ca/Collection/H48-10-1-16-1988E.pdf). The most extensively-studied PAH is benzo(a)pyrene and is included in SA Guidelines on the utilization and disposal of sewage sludge. The structural representations of the 16 priority PAHs are given in Figure 2-3.

(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
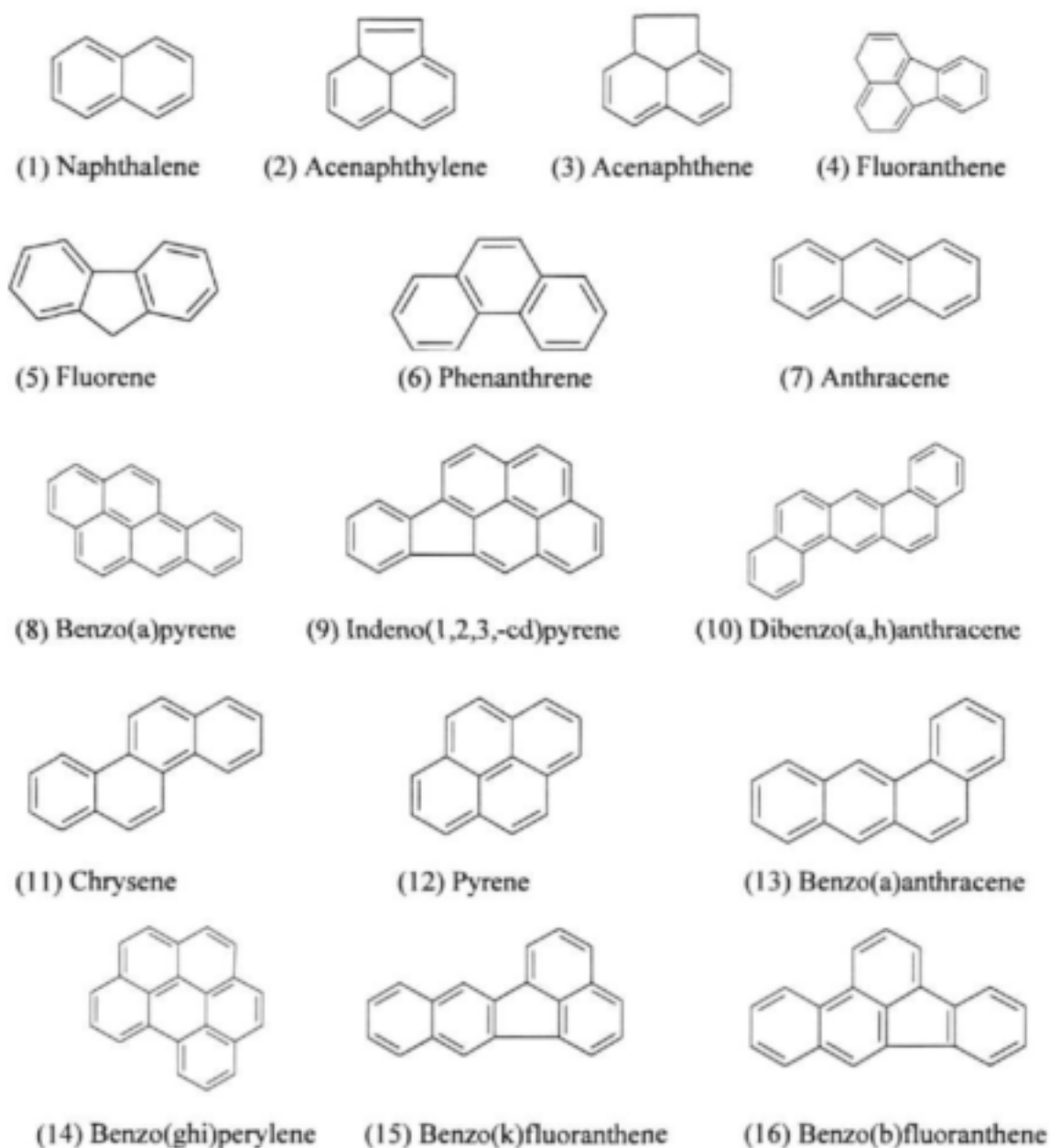
Figure 2-3:   **Structures of 16 polynuclear aromatic hydrocarbons.**

The oral toxicity of PAHs on a short-term basis seems to be from low to moderate while chronic exposure in experimental animals has resulted in detrimental haematological effects. Immunosuppressive effects, irritation, sensitising activity, reproductive and foetal effects are some of the adverse effects that can be caused by exposure to PAHs (Frijus-Plessen & Kalberiah, 1999). In addition, experiments on

animals and epidemiological studies have shown that inhalation and dermal exposure of PAH mixtures can lead to respiratory tract and skin tumours (Langenkamp & Pärt, 2001). Although most of the PAHs are suspected or known carcinogens, their carcinogenic activity depends on specific structure of the PAH. The LD_{50} and LC_{50} of some of the known PAHs are recorded in Table 2-4.

The most potent carcinogens have been shown to be benzo[a]pyrene, dibenzo[a]pyrene and dibenzo[ah]anthracene (WRC, 1997). Benzo(a)pyrene is considered to be an indicator substance for PAHs in sewage sludge, since its presence signifies the probable presence of other PAHs (http://dsp-dsp.communication.gc.ca/Collection/H48-10-1-16-1988E.pdf). 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 (http://cira.ornl.gov/documents/Benzoapyrene.pdf). As a product of incomplete combustion it gets released into air and gets removed from the atmosphere by photochemical oxidation and dry deposition to land or water (http://cira.ornl.gov/documents/Benzoapyrene.pdf). The semivolatility of PAHs makes them highly mobile through the environment via deposition and revolatilization between air, soil and water bodies.

For these reasons PAHs have become one of the most crucial organic pollutants in sewage sludge concerning possible human exposure (Connor, 1984; Dean & Suess, 1985). However, the concentration of the PAHs following the application of sludge to land decreases with time. The higher molecular weight PAHs are more persistent than ones of lower molecular weight. 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 the presence of air. In sewage sludge that was stored in a container, there was a reduction in the organic contaminants in the top 20 cm surface only. Whilst where the sludge was being turned mechanically to aerate it, a 32% reduction in the amount of PAH was observed (Peterson et al., 2003).

Table 2-4: The LD_{50} and LC_{50} for some of the known PAHs.

PAHs	LD_{50} (mg/kg) (ORL-Rat)	LC_{50} (mg/L)
Acenaphthene	IPR-RAT 600 (The Physical and Theoretical Chemistry Laboratory)	
Anthracene	18000 in rat (UNEP, 2000)	
Benzo(a)pyrene	250 in mouse[44] 50 in rate[45]	
Benzo(a)anthracene	10 in mice (UNEP, 2000)	
Fluoranthene	2000 (Smyth, 1962)	
Naphthalene	490 in rat (The Physical and Theoretical Chemistry Laboratory)	*Daphnia pulex* 1.00 (UNEP, 2000))
Phenanthrene		*Daphnia pulex* 0.10 (UNEP, 2000)
Pyrene	2700 (The Physical and Theoretical Chemistry Laboratory)	
1,2,3,4-tetrahydronaphthalene	2860 (The Physical and Theoretical Chemistry Laboratory)	

2.6.5 DimethylNitrosamines

Dimethylnitrosamines also known as N-Nitrosodimethylamine (NDMA) can be generated through several routes. It has been reported that one of the routes through which NDMA can be produced is through a reaction of nitrous acid and trimethylamine (Smith and Loeppky, 1967). NDMA was commonly employed in the production of the rocket fuel, 1,1-dimethylhydrazine, in the 1950's. In addition, NDMA can be produced as by-product in the rubber industry during compounding and curing operations (Verscheunsen, 1983).

The most likely source for the contamination of water supplies with NDMA was thought to be bacterial action or chemical reactions. It has been recorded that bacterial action has resulted in the formation of NDMA in soil, water and sewage (Ayanaba et al., 1973; Calmels et al., 1988). The structural composition of NDMA is given in Figure 2-4.
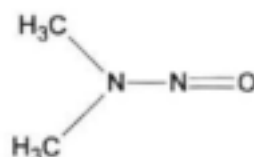
Figure 2-4: The chemical structure of N-Nitrosodimethylamine.

Generally nitrosamines are known carcinogens and mutagens with NDMA being specifically more hazardous (Loeppky et al., 1994). It has been confirmed that NDMA is capable of causing cancer in rats (Magee and Barnes, 1956). The tests were specifically performed on laboratory animals and species of mammals, birds, fish and amphibian have shown no resistance (NIOSH, 1983).

2.6.6 Polychlorinated Dibenzo-p-Dioxins and –Furans (PCDD/Fs)

A group of polychlorinated dibenzo-p-dioxins (PCDDs) and dibenzofurans are commonly known as dioxins (Langenkamp and Pärt, 2001). Generally dioxins are undesirable products of thermal processes and of chemical formulations. There are several ways through which dioxins can be generated during incineration processes such as municipal waste combustion, cigarette smoking and combustion of wood. Moreover dioxins can be generated as by-products in industrial processes during the manufacturing of pesticides and in the pulp and paper industry.

The level of chlorination and location of chlorine atoms in PCDDs and PCDFs vary and there are 75 and 135 congeners of PCDD and PCDF respectively (Langenkamp and Pärt, 2001). Household wastewater is considered to be the main source of PCDD/Fs due to significant generation of PCDDs from laundry wastewater (Horstmann & McLachlan, 1994.). Another source of PCDD/Fs in sewage sludge is by conversion from pentachlorophenol (PCP) which is used as a fungicide on cotton textiles (McLachlan et al., 1996; Horstmann & McLachlan, 1994). It has been shown that ^{13}C-PCP (pentachlorophenol) is biologically converted to ^{13}C-PCDDs. Furthermore, data found from samples collected prior to the introduction of pentachlorophenol and other organochlorine pesticides in industry support the idea that PCP can be a source of dioxins (Rappe et al., 1989). It is suggested that another source of PCDDs and PCDFs is the chlorine treatment of sludge (Nestrick and Lamparski, 1983.).

The presence of the polychlorinated PCDD/Fs in the inlet wastewater depends on the plant uptake area (Naf et al., 1990). There are several possible sources for the presence of PCDD/Fs in the wastewater treatment plants, which include municipal

incineration, hospital waste incineration and vehicles exhausts. Another possible source of the PCDD/Fs can be industrial wastewater effluents, for example, minor industries with combustion of chlorine containing material or with production of chemicals. The general molecular structures of PCDDs and PCDFs are provided in Figure 2-5.
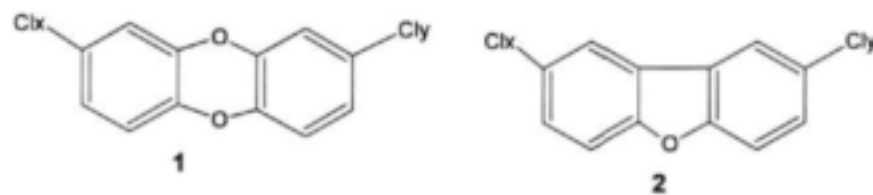
Figure 2-5: **Typical molecular structures of PCDD (1) and PCDF (2) respectively.**

A compound representing PCDD/PCDF is 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD) as it is the most poisonous and the best-investigated compound (Langenkamp and Pärt, 2001). There are various adverse effects associated with the exposure of high and low quantities of TCDD. Chloracne, porphyria, hepatotoxic effects as well as neurological symptoms are some of the adverse effects that can be caused by the exposure to high quantities of TCDD. On the other hand, low quantities of TCDD result in reproductive and foetotoxicity (Schneider and Kalberlah, 1999; Schrenk & Fürst, 1999; EPA, 2000). It has been shown that the oral and dermal exposure of TCDD to rats and mice results in cancer (Schneider and Kalberlah, 1999). In addition TCDD is regarded as a chemical with the potential to cause cancer in humans (IARC, 1997).

Generally, the polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzo-p-furans (PCDFs) environmental content is enhanced in sewage sludge (Wild et al., 1994). Hence the human population is more exposed to PCDD/Fs through transfers by means of food chain as the sewage sludge is intentionally applied on the agricultural land.

2.6.7 Polychlorinated Biphenyls (PCBs)

PCBs were first introduced to the market in 1929 and because of their chemical and physical features have broadened their applications in heavy-duty transformers and capacitors (Jones, 1989). Other industrial PCB uses include the formulation of hydraulic and heat-exchange fluids, incorporation into protective coatings for wood, metal and concrete, usage in plastics, printing inks, plasticisers, adhesives and lubricating additives. The attractive characteristics of PCBs are their electrical resistance, high chemical stability, low volatility, poor tendency to combustion and resistance to degradation at elevated temperatures. PCBs are generated by the chlorination of biphenyl, which possesses 10 sites accessible for chlorine atoms. Hypothetically a mixture of up to 209 potential compounds, which can be scattered among 10 levels of chlorination, is formed from the biphenyl chlorination (Rogers et al., 1989). The general molecular structure for a PCB is shown in Figure 2-6.
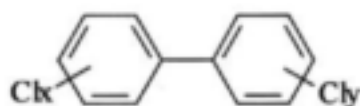
Figure 2-6:   General structure for a PCB.

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 (Chaudri et al., 2001). They have low water solubility but are readily soluble in hydrocarbon solvents.

Exposure to PCBs can cause discomfort to the skin and eyes, which can result in chloracne, neurotoxicity, hepatotoxicity and high blood pressure as well as reproductive effects in both animals and humans. It has been seen in laboratory animals, especially in rhesus monkeys, as well as in humans that immunological changes represent one of the crucial sensitive endpoints of PCB toxicity (Hassauer & Kalberlah, 1999). Oral exposure of PCB to rats and mice can result in liver tumours.

There is not sufficient proof that the same effects can be observed in humans (IARC, 1987). Hence safety measures need to be exercised when sewage sludge is applied to surface soils in public as the heavily chlorinated PCBs in the sludge are very stable (Amundsen et al., 1997).

In addition, it has been recorded that humans are exposed to PCBs and dioxins mainly through accidents, at their place of work and the environment in general. PCBs chemicals can be found many parts of the human body, such as adipose tissue and lipids (Jensen, 1987). Furthermore, they can be detected in the fat of human breast milk and they are capable of passing through the placenta (Jensen, 1987; Ando et al., 1985; Masuda et al., 1978; Rogan, 1983). The lethal dose and concentration capable of killing 50% of the population once exposed to PCBs (LD_{50} and LC_{50}) are provided in Table 2-5.

Table 2-5: Polychlorinated Biphenyls' LD_{50} and LC_{50}.

PCBs	LD_{50} (mg/kg) (ORL-Rat)	LC_{50} (mg/L)
1,1'-Biphenyl	3280 (The Physical and Theoretical Chemistry Laboratory)	4.7 and 2.1 mg/L (per 48 hr) (Gersich 1989)

2.6.8 Phenols

Phenols can be generated through normal human metabolism from tyrosine and applied pharmaceuticals by means of arene oxides. Phenols are useful substances in natural defence mechanisms for biological systems, hence phenols are used as disinfectants. However, these properties are no longer of such interest, and the usage of phenols as disinfectants has declined as a result of their toxicity. Nevertheless, the use of phenol in cosmetics is still permitted when the relevant restrictions are observed (Gomez et al., 1985). Some of the most common phenols in sewage sludge are nonylphenol (NP) and nonylphenol ethoxylates (NPEs), which are considered to be toxic organic compounds formed as a result of the degradation of alkylphenol polyethoxylates (Jones & Northcott, 2000). These degradation products have short chain lengths, formed under aerobic and anaerobic conditions and tend to adsorb on sludge particles (Grüttner et al., 1997).

In most cases the nonylphenol ethoxylates and nonlyphenol content in sewage sludges is high in anaerobic digestion as their degradation rate is very slow. NPEs are mainly employed as surface active agents in cleaning products, cosmetics and hygiene products as well as in emulsifications of paints and pesticides (Langenkamp and Pärt, 2001). Another commonly encountered phenol in sewage sludge is *para*cresol (p-cresol). The structures of nonylphenol and *para*cresol are illustrated in Figure 2-7.
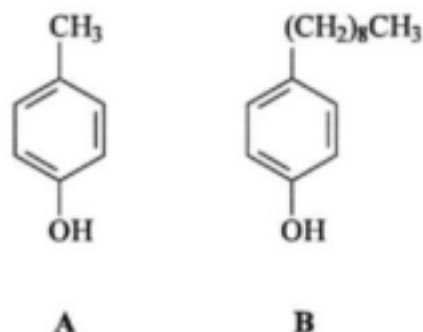
Figure 2-7:   The structural representation of para-cresol (A) and nonylphenol

Environmental problems caused by phenolic compounds are attributed to their long-term, large-scale uncontrolled release, as well as to their persistence and, above all, their toxicity (Lue-Hing et al., 1992). The toxicities of individual phenols vary depending on the type, number and position of substituents. In human exposure studies, phenol itself has been shown to be rapidly absorbed into the body via ingestion, skin absorption or inhalation and rapidly excreted (Lue-Hing et al., 1992). Exposure to phenol vapour may cause severe irritation, neurosis, affect the central nervous system and damage the liver and kidneys. Since evidence of the carcinogenicity of phenol in humans is inadequate, it cannot be classified as carcinogenic.

NP is considered harmful, as it is corrosive in rats following acute oral exposure (LD_{50} approx. 1900 mg/kg, OECD guideline 401) (BUA, 1998; ECB, 2000). It is widely known that NP is a reproductive toxicant, for instance NP illustrated affinity for binding to the oestrogen and progesterone receptors (Laws et al., 2000).

The toxicity of p-cresol in humans is relatively the same as the phenols but shows less severe health effects. Its main route of exposure is through skin absorption and

ingestion. (MSDS, 1999). The inhalation of p-cresol can result in side effects such as vomiting, swallowing problems, diarrhoea and loss of appetite. Severe effects relating to consumption of p-cresol are abdominal pain, headache, dizziness, muscular weakness, irregular breathing, weak heartbeat, coma, burning pain in mouth and throat as well as the lung, pancreas, kidney and liver damage. In addition, there is a likelihood of death from circulatory or cardiac failure. p-Cresol is corrosive and if it comes into contact with the skin it can cause fierce pain followed by lack of feeling in the skin and results in fierce pain in the eyes as well as long-term damage to the eye. Long-term exposure can result in liver damage as well as symptoms described above (MSDS, 1999). In addition, the LC_{50} and/or LD_{50} of some of the phenolic compounds expected to be present in most sewage sludges and considered to be capable of causing severe animal health effects are provided in Table 2-6.

Table 2-6: **The LD_{50} and LC_{50} of some selected phenols.**

Phenols	LD50(mg/kg) (ORL-Rat)	LC50(mg/L)
2-Methylphenol (o-cresol)	121 (Papa, 1995)	5.00 in *Daphnia* (Parkhurst et al., 1979)
3-Methylphenol (m-cresol)	207 (Papa, 1995)	1.60 in *Daphnia* (Bringmann et al., 1977)
4-Methylphenol (p-cresol)	242 (Papa, 1995)	1.40 in *Daphnia* (Parkhurst et al., 1979)
Nonylphenol	1300 (The Physical and Theoretical Chemistry Laboratory)	0.13-1.4 (per 96 hr) Fish (The Physical and Theoretical Chemistry Laboratory)
Phenol		3.90 (Bringmann et al., 1977)
4-(1,1,3,3-Tetramethylbutyl)-phenol	4600 (The Physical and Theoretical Chemistry Laboratory)	5.15 in fathead minnow (Geiger et al., 1984-1988)

2.6.9 Di-(2-ethylhexyl)phthalate (DEHP)

Phthalates are mainly used in plastics as plasticisers. However, there are several other uses of these compounds, which include additive roles in paints, lacquers, glues and inks (Langenkamp and Pärt, 2001). 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 (ICON, 2001). The most commonly encountered phthalate ester is di-(2-ethylhexyl)phthalate.
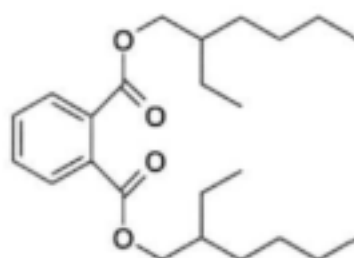
Figure 2-8:   The structural representation of di-(2- ethylhexyl)phthalate.

The human activities contributing to DEHP emissions include 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 to agricultural land there is a very small possibility of these compounds being taken up by plants, since they are likely to degrade (Aranda et al., 1989: Futsum et al., 1986) In addition, these compounds have very high $logK_{ow}$ of 7.6 meaning they are less likely to be taken up and translocated by plants(Petersen et al., 2003),[35] since compounds with $logK_{ow}$ > 4 are said to have a high potential for root retention and low potential for uptake and translocation (Roslev et al., 1998). In the event of these compounds being in sludge applied as a soil fertilizer, they show no adverse effects on crop yields, soil fertility or biological activity (Petersen et al.,, 2003).[35]
The primary concern with regard to phthalates is the transfer up the food chain, which might end up affecting humans and animals (Duarte-David et al., 1996).

The rate of actual degradation of phthalates is significantly decreased by their sorption onto sludge particles. Phthalates are however known to degrade readily under both aerobic and anaerobic conditions. It has been found that phthalates are harmful to soil organisms and certain phthalates are alleged to have hormone-mimicking properties

(Madsen et al., 1997). In addition, there is a possibility that plants can absorb these phthalates once sewage sludge has been applied to land (http://europa.eu.int/comm./environment/waste/sludge/organics.in.sludge.pdf).

The LD_{50} of DEHP is fairly high (*i.e.* greater than 25000 mg/kg) in rats after short-term exposure (Langenkamp and Pärt, 2001). Laboratory animals develop hepatotoxic and nephrotoxic effects following chronic exposure to DEHP. In addition, it is likely that the exposure to DEHP can have adverse effects on the developing foetus and decreases the fertility in both male and female rats (Langenkamp and Pärt, 2001). A recent study has shown that long-term exposure of DEHP in mice resulted in various changes including change in kidney, liver and testis weights in male mice (David et al., 2000). The LD_{50} and LC_{50} of the common phthalates (*i.e.* diethylphthalates & DEHP) as provided by various sources are recorded in Table 2-7. There is no concrete evidence to declare this compound as a potential carcinogen for humans (IARC, 2000). According to World Health Organisation an oral exposure of 25 mg kg^{-1} can be tolerated by humans (WHO, 1996).

Table 2-7: The LD_{50} and LC_{50} of diethylphthalates & DEHP.

Phthalates	LD50(mg/kg) (ORL-Rat)	LC50(mg/L)
Diethylphthalates	9000 (The Physical and Theoretical Chemistry Laboratory)	>100 mg/L for fish
DEHP	27 000 (Product Safety Data Sheet Number 8110)	>0.24mg/ in fathead minnow (Environmental Health and Safety, 1998)

2.6.10 Adsorbable Halogenated Organic Compounds (AOX)

The term "Adsorbable Halogenated Organic compounds (AOX)" does not signify any specific organic compounds but an analytically determined parameter, which is the sum of all halogen-containing (*i.e.* chlorine, bromine, iodine) chemicals that are determined by a particular method (Langenkamp and Pärt, 2001). The main sources of AOX in municipal wastewater are household, hospital and self-service restaurant cleaning agents and disinfectants (Schulz and Hahn, 1998). These chemicals are capable of giving off activated chlorine. An industrial source of AOX that was mainly

observed in Finland was the use of chlorine dioxide and non-chlorine chemicals for bleaching in modern pulp mills, where 2-4% of organic chlorine is found as AOX in the recipient water ecosystem (Salkinoja-Salonen et al., 1998). The structural composition of some of the chlorinated hydrocarbons that have been detected in bleaching effluent from an elemental chlorine free (ECF) bleaching process are shown in Figure 2-9 (McKague and Grey, 1996; Smith et al., 1994).
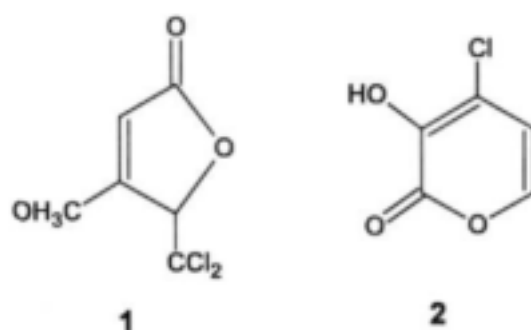
Figure 2-9: **AOX detected from EFC: dichloromethylene-furanones (1) and 4-chloro-3-hydroxy-2H-pyran-2-one (2).**

The actual production of AOX is due to the reaction between organic compounds in wastewater and activated chlorine. Studies have shown that the addition of hypochlorite at the normal disinfectant level will raise AOX content in municipal wastewater by a factor of thirteen (Schulz and Hahn, 1998). A significant amount of AOX in municipal wastewater can be generated in thirty minutes while it can take up to numerous days in sewage containing large quantities of solid compounds. Some of the AOX that are formed as a result of chlorination are trihalomethanes (THM). The German drinking-water directive has mentioned compounds such as chloroform, bromodichloromethane, dibromochloromethane and bromoform as analytical parameters for THM.

Another crucial source of the AOX is paper pulp industry, production of polyvinyl chloride (PVC) as well as waste incineration (Langenkamp and Pärt, 2001). There is a possibility that a more toxic compound such as vinyl chloride, which is a known human carcinogen can be formed as a result of the transformation of organic halogens

(Salkinoja-Salonen et al., 1995; AURAS, 2001). Since AOX is a parameter that represents various halogenated organic compounds with different chemical structures and toxicological profile it cannot be used to indicate the toxicity of various compounds (Langenkamp and Pärt, 2001).

2.6.11 Linear Alkyl Benzene Sulfonates (LAS)

LAS is manufactured from alkybenzene sulfonates (ABS). It is considered to be the world's number one surfactant due to its effectiveness, versatility, low-cost and biodegradability (http://www.cler.com/facts/sludge.html). It has several applications, which make use of its detergent, emulsifying, dispersing, wetting and foaming capabilities. LAS is mainly found in laundry and dishwashing detergent as well as in cleaning liquids and pastes. ABS was initially used as a detergent surfactant over a period of 45 years however, its popularity decreased when it was discovered that it was resistant to biological break down. In addition, foam-related environmental problems were observed in surface waters, groundwater, and drinking water as well as in wastewater treatment plants. These problems gave impetus to the search for easily biodegradable and environmentally friendly detergents (Cognis Benelux, http://www.blx.cognis.com/framescout.html?/oleochemicals/LinearAlkylbenzeneSulfonates.htm). A typical structural formula for a linear alkylbenzene sulfonate is as shown in Figure 2-10.

Figure 2-10:   A general structural formula of linear alkylbenzene sulfonate.

There are no side effects that have been observed on tested soil living organisms (i.e. earthworm) and crops (i.e. sorghum, wheat, corn, sunflower) that were exposed to

high LAS concentrations as a result of sludge application. The earthworms were exposed to LAS concentrations of 250 mg/kg and 615 mg/kg while crops were exposed to concentrations of between 167 mg/kg and greater than 407 mg/kg (Mieure et al., 1990). In addition, large quantities of LAS are allowed to vanish from sludge-amended soil as it applied to soil at least a month prior to planting of crops. The rest of the LAS are biologically completely broken down during the growing season (Giger et al., 1989 and Berna et al., 1989).

It has been reported that from acute oral exposure of LAS to rats the $LD_{50}=500\text{-}200$ mg/kg (Langenkamp and Pärt, 2001). An exposure to LAS has resulted in irritation to the skin and the eyes of animals under the study, where test were performed according to OECD guidelines. The adverse effects that have been seen in humans are skin and mucous membrane irritation, a long-term dermal and oral exposure of LAS can result in hepatoxicity and nephrotoxicity (Langenkamp and Pärt, 2001).

The rate of chemical uptake by plants is dependent upon the type of chemical species present, with only those of moderate solubility being effectively transported to plant shoots. As a result, low solubility compounds like PCBs and DDT are more likely to bioconcentrate in roots. For example high contents of PCBs have been detected in plants like carrots (Iwata & Gunther, 1976). However, it has been proposed that the PCBs detected in carrots do not infiltrate the root and are only adsorbed to the outer cell wall.

Table 2-8:   A summary of major organic pollutants and their sources of origin

Name of compound	Origin
Petroleum hydrocarbons	Petrochemical industry, Domestic refuse.
Organochloride pesticides	Agricultural runoff, Domestic usage, Wood industries, Pesticide manufacture.
DDT, derivatives	Insecticides
Lindane (BHC)	Insecticides
Aldrin, Dieldrin	Insecticides
Chlordane	Insecticides
Trichloroethylene (TCE)	Paints, Coating
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)
DimethylNitrosamines	Rubber industry,
Polychlorinated dibenzo-p-dioxins and furans (PCDD/Fs)	Thermal processes, Municipal waste combustion, cigarette smoking, Combustion of wood, By products in the manufacturing of pesticides and in pulp nd paper industry.
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.
Phenols, derivatives	Fungicides, herbicides, domestic effluent
Phthalate esters	Rubber and paint manufacture, Synthetic raindrops.
Halogenated aliphatic and aromatic hydrocarbons (HAHs)	Dry-cleaning effluent, Aerosol propellants, Fumigants, Water disinfectants.
Detergents	Domestic effluent

2.7   REGULATORY GUIDELINES

As a guide to assist and give direction, a National Guidelines to promote safe handling, disposal and utilisation of sewage sludge was developed in 1991 (The South African Sludge Guidelines of 1991). These guidelines were revised in 1997 (Permissible Utilisation and Disposal of Sewage Sludge) stipulating the maximum

annual loading limits for some organic chemicals. The limits as presented in Table 2-9 were based on LC_{50} calculations (Private communication H. Snyman).

Table 2-9: Maximum limits for organic pollutants in South African Sewage Sludge (WRC 1997)

Pollutants	Dry sludge concentration (mg/kg)	Group
Aldrin	0.202	Pesticide
Benzo(a)pyrene	2.53	PAH
Chlordane	3.5	Pesticide
DDT	0.35	Pesticide
Dieldrin	0.303	Pesticide
Dimethyl nitrosamine	2.9	
Heptachlor	0.35	Pesticide
HCB	16.2	CB-Chlorobenzene
Lindane	1.36	Pesticide
PCB	1.0	PCB
Trichloroethylene	2020.0	VOC

For comparison purposes legislation from other countries is as shown below. Table 2-10 shows limit values for concentrations of organic compounds in sludge of different countries as suggested in the 3rd draft of the EU "working paper on sludge"

Table 2-10: Standards for concentration of organic contaminants in sewage sludge in different countries of the EU (EU 2000)

	Organic Contaminants						
	AOX mg/kg dm	DEHP mg/kg dm	LAS mg/kg dm	NP/NPE mg/kg dm	PAH mg/kg dm	PCB mg/kg dm	PCDD/F ngTEq/kg dm
EU 2000 (3rd draft)	5000	100	2600	20	6[1]	0.8[2]	100
Denmark (Danish Ministerial Order No. 823, 16 Sept 1996, cit in MADSEN et al., 1997)	-	50	1.300	10	3[1]	-	-
Sweden (LRF & SEPA & VAV; 1996)	-	-	-	50	3[3]	0.4[4]	-
Austria (NÖ, 1994 cit. FÜRHACKER & LENCE 1997)	500	-	-	-	-	0.2[5]	100
Germany (Sauerbeck & Leschber 1992)	500	-	-	-	-	0.2[5]	100

[1] Sum of acenapthene, 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 the six congeners PCB 28,52,101,138,153,180.

Table 2-11: French guide values for PAH concentrations in sewage sludges and maximum amounts in pasture soils (CSHPF, 1997)

Compound	Concentration in sludge to be used in agriculture at a rate of no more than 30 tons/ha/10a (mg/kg dw)	Maximum permissible cumulated input on pasture soils per hectare in 10 years (g/ha dw)
fluoranthene	4	60
benzo(b)luoranthene	4	60
benzo(k)luoranthene	4	60
benzo(ghi)perylene	4	60
benzo(a)pyrene	1.5	20
indeno(1, 2, 3-c,d)pyrene	4	60

Table 2-11 gives the **French** guide values for concentrations of PAH and for the maximum accumulated input over a period of ten years.

In 1995, a working group of the **Danish** Ministry of Environment and Energy identified organic chemical residues, for which limit values should be elaborated (Madsen, 1997). Until 1997, the use of sludge in Denmark was regulated with respect to the maximum content of selected heavy metals, maximum of phosphorus, nitrogen and dry matter of waste to be applied per hectare per year and regulations regarding the use of waste-treated farmland (no root crops, cattle grazing or other direct non-processed use for consumption until one year after application (Madsen, 1997).

In **Germany** the fertilizer effects of sludge have to be taken into account according to the rules of the German Fertilizer Act and its respective ordinances when sewage sludge is to be used in agriculture (Leschber, 1997). It is prohibited to use sludge in fruit and vegetable cultivation, on grassland, in nature conservation areas, in forests and near water catchments/wells in water protection areas. The German regulation comprises limits for AOX, PCB and PCDD/F. The German Ministry of the Environment set these limit values as a purely precautionary measure; they were not based on scientific evidence of imminent toxicological implications. Instead the limit values were based on the current concentrations of the respective compounds in German sewage sludges (Sauerbeck and Leschber, 1992). Concentrations of AOX in sludges do not really give information about the absence or presence of hazardous substances, this could mean a measure of careful soil protection to prevent the input of high amounts of anthropogenic compounds into soils, some of which may be persistent pollutants (Leschber, 1997).

Surface application of undigested or digested sludges on grazing land was banned in the **UK** in January 1999, although the injection of digested sludge into grazed pasture soils is currently allowed (Smith, 2000).

There are, actually, no formal **Swedish** regulations for organic contaminants in sludge. There is an informal agreement between the Swedish EPA, the Farmers Union and the Water and Wastewater Association, which includes the recommendations in Table 2-10. These agreements are based more on practical experience than on

scientific data. Sweden also used to have a recommended limit value for toluene, but this has been omitted.

The **US** regulations on the use of sewage sludge in agriculture do not establish numerical pollutant limits of any organic pollutants except under certain circumstances (USEPA, 1995; Smith, 2000).

2.8   POLLUTANT-SPECIFIC DATA

In this section, a summary of data as reported in the current literature is presented, in the form of tables. The tables are arranged according to different groups of organic pollutants. The concentration data is given on the basis of a dry mass of sewage sludge (mg/kg dm).

AOX

Table 2-12:   AOX content in sewage sludges from Germany (UMG-AG 2000)

Year	Mean mg/kg dm	Highest 90-percentile among German Bundeslaender mg/kg dm
1994	206	370
1995	201	400
1996	196	363

NPE

Table 2-13:   **Overview of concentrations of Nonylphenols (+ethoxylates) in Scandavian sewage sludges**

Investigations	Number of samples	Range mg/kg dm	Median mg/kg dm	References
Norwegian (1989)	19	25-2298	189	Vigerust, 1989
Swedish (1993)	23	23-171	82	National Swedish Environmental Protection Board, 1995 cit in Paulsrud et al., 2000
Swedish (1989-91)	27	44-7214	825	National Swedish Environmental Protection Board, 1992 cit in Paulsrud et al., 2000
Danish (1995)	20	0.3-67	8	Törslöv et al., 1997
Danish (1993-91)	9	55-537	-	Törslöv et al., 1997

LAS

Table 2-14   Concentrations of LAS in sewage sludge from selected countries (Jones 2000).

Country	No. of WWTP	Sludge description	Range mg/kg
Denmark	19	Various	11-16100
Germany	8	Anaerobically Digested	1600-11800
Germany	10	Aerobic	182-432
Italy	1	Anaerobically Digested	11500-14000
Spain	3	Anaerobically Digested	12100-17800
Spain	2	Non-treated	400-700
Switzerland	10	Anaerobically Digested	2900-11900
UK	5	Anaerobically Digested	9300-18800

Table 2-15:   Concentrations of LAS in sewage sludge from Norway and Denmark

Country	No. of samples	Range mg/kg	Median mg/kg	References
Norway (1996-97)	36	<1-424	54	Pualsrud et al., 2000
Danish (1995)	20	11-16100	530	Törslöv et al., 1997
Danish (1993-94)	6	200-4640	455	Törslöv et al., 1997

DEHP

Table 2-16:   Concentration of DEHP in sewage sludges of various countries

Investigations	No. of samples	Range mg/kg dm	Median mg/kg dm	References
Norway	36	<1-140	58	Pualsrud et al., 2000
Norwegian (1989)	19	27-1115	83	Vigerust, 1989
Swedish (1989-91)	27	25-661	170	National Swedish Environmental Protection Board, 1992 cit in Paulsrud et al., 2000
Danish (1995)	20	3.9-170	24.5	Törslöv et al., 1997
Danish (1993-94)	9	17-120	38	Törslöv et al., 1997

PAHs

Table 2-17: Concentrations of PAH in sewage sludges of various countries

Investigations	No. of samples	Range mg/kg dm	Median mg/kg dm	References
Danish (1995) (Sum of 18 compounds)	20	<0.01-1.85	-	Törslöv et al., 1997 (cit. in Paulsrud 2000)
Danish (1993-94) (Sum of 18 compounds)	9	0.42-2.4	-	Törslöv et al., 1997 (cit. in Paulsrud 2000)
Norway	36	0.7-30	3.9	Paulsrud et al., 2000
Sweden (sum of 6 compounds)	-	-	1.6	Tideström 1997
Parts of Germany (sum of 6 compounds)	124	0.4-12.83	-	UMK-UG 2000
Parts of Germany (sum of 16 compounds)	88	0.25-16.28	-	UMK-UG 2000

PCBs

Table 2-18: Concentrations of PCB in sewage sludge of various countries.

Investigations	No of samples	No of congeners	Range mg/kg dm	Mean mg/kg dm	References
Norway	36	7	0.017-0.10	0.0422	Paulsrud et al., 2000
Swedish (1993)	23	7	0.0006-0.232	0.113	National Swedish Environmental Protection Board, 1995 cit in Paulsrud et al., 2000
Swedish (1989-91)	27	7	-	-	National Swedish Environmental Protection Board, 1992 cit in Paulsrud et al., 2000
Sweden (sum of 7 congeners)	-	7	-	(0.1)	Tideström, 1997
Germany	-	Each of 6 congeners	<0.2	-	UMK-AG, 2000

Table 2-19: Mean PCB-concentrations in sewage sludge in Germany (UMK-AG 2000)

Year	PCB congener no. (mg/kg dm)						
	28	52	101	138	153	180	Sum
1989	0.041	0.028	0.052	0.082	0.084	0.053	0.340
1994	0.015	0.015	0.024	0.039	0.039	0.026	0.158
1996	0.016	0.017	0.020	0.037	0.038	0.026	0.154

PCDD/F

Table 2-20: Comparison of Investigations of PCDD/F in sewage sludge (AEA Technology 1999)

Country	Austria	Denmark	Germany	Spain	Sweden	UK
Range NgTEq/kg dm	8-38	0.7-55	0.7-1207		0.02-115	9-192
Average ngTEq/kg dm	14.5	21	20-40	64	20	

3   METHODOLOGY AND STUDY PROCEDURES

Organic compounds are formed by the union of carbon with hydrogen, oxygen, nitrogen, phosphorus, sulphur and the halogen elements. The unique property of carbon is its ability to form chains and rings of atoms of high stability, accounting for the very large number of organic compounds which are known to exist. In fact, over 8 millions of different organic compounds have been characterized, and every year tens of thousands of new substances are added to the list, either by discovery in nature or by preparation in the laboratory (e.g. polyethylene and other plastics and film, most dyes and pigments, medicinal drugs, gasoline, pesticides, insecticides, paints, and surface coatings). The chief sources of organic compounds are crude oil, natural gas, coal and living materials. The simple compounds from crude oil and coal are used as building blocks from which large and more complicated compounds are made.

On the basis of structure, organic compounds are divided into two main classes-aliphatic and aromatic. Aliphatic compounds are further divided into alkanes, alkenes, alkynes. Each organic compound has its own characteristic set of chemical and physical properties. Particular groups of atoms present in organic compounds impart specific types of chemical reactivity to the molecules. These different groups are called functional groups which include alcohols, phenols, amines, ethers, aldehydes, ketones, carboxylic acids etc.

The type of analysis and quantification of the different organic compounds is based on the characteristic of the compounds. Therefore in this study, before any quantification from the 13 sites could be carried out, a screening process had to be done to identify all possible organic pollutants present in the sludge.

3.1   MATERIAL AND METHODS

3.1.1   Sample Collection

Sampling forms a very important part of environmental analytical studies as it can limit the overall accuracy of the results. The sewage sludge sample depict high degree of heterogeneity, thus during sampling and when preparing the sample for analysis

great care should be exercised to ensure that the sample taken is a true representative of the source.

In this study the solid samples from drying beds and lagoons were taken randomly in small amounts from different spots through out the bulk, approximately 2 cm beneath the surface using a metal hand shovel. This was also true for compost heaps. The composite sample was mixed within the container to obtain a uniform composition. For liquid samples from the return flow, these were sampled using a small metal bucket attached to a long metal rod so as to reach below the surface level of the flow. All the samples were collected in a 2-litre glass bottles having polytetraflouroethylene (PTFE) lined screw caps.

The selection of sampling sites (Appendix A) was based on the work done for the Water Research Commission (WRC) project K5/1283 (A detailed metal content survey of South Africa sewage sludge and an evaluation of analytical methods for metal determination). The first phase, which was the identification of all possible organic pollutants, involved sampling 69 wastewater treatment plants (WWTPs) located across the nine provinces of South Africa. The samples were collected from July to August 2002. A total of 78 samples were collected, of which 71 were solid and 7 were liquid sludge samples.

A total of 23 samples were taken in Gauteng, 15 in Western Cape, 11 in KwaZulu-Natal (KZN), 7 in Limpopo, 7 in North-West (NW), 5 in Free State (FS), 4 in Eastern (EC), 4 in Northern Cape (NC) and 2 in Mpumalanga.

Sampling for the second phase of the study was reduced to 13 sites. These were class D sludge of which 7 had been found to have the highest metal content and 5 had the lowest as reported in WRC Project K5/1283. One extra site (Gauteng/22) was added to the list because, from the screening results, it was found to contain a large variety of organic pollutants. The selected sites for the second round of sampling are tabulated in Table 3-1.

Table 3-1: **List of the selected sites for second round of sampling based on the lowest and the highest metal content as found by WRC project 5/1283**

*Lowest metal content sites	*Highest metal content sites
KwaZulu Natal Province (KZN/41)	Gauteng Province (Gauteng/1/2)
KwaZulu Natal Province (KZN/75)	Gauteng Province (Gauteng/4)
North West Province (NW54)	Gauteng Province (Gauteng/6)
Western Cape Province (WC/28)	Gauteng Province (Gauteng/15)
Western Cape Province (WC/37)	Gauteng Province(Gauteng/21)
	North West Province (NW/55)
	Western Cape Province (WC/30)
Gauteng Province (Gauteng/22) based on the preliminary organic analysis	

*Names of the WWTP are not given for confidentiality reasons

The samples were stored and transported from the sampling location in cooler boxes designed to maintain a temperature of 4°C for a minimum period of 24 hours. This was achieved by lining the inside of the cooler boxes with foam material for insulation. A total of eight ice blocks per cooler box provided the low temperature. The samples were then transported overnight by courier service (TNT) to Pietermaritzburg. On arrival the samples were immediately wrapped in aluminium foil to stop any possibility of photo-degradation and stored in a chest freezer that had been converted to maintain a temperature of between 2.5 and 3.5°C. Photographs showing the sample bottle, the cooler box and the chest freezer are shown in Figures 3-1, 3-2, and 3-3 respectively.

Figure 3-1:   Sampling bottle

Figure 3-2:   Cooler box for transporting sludge samples

Figure 3-3:   Chest freezer for storing sludge samples

3.2 EXTRACTION METHOD

The United States Environmental protection Agency (USEPA) recommends a number of different methods for the extraction of organic compounds from solid or liquid matrices. A list of these USEPA methods is shown below. In addition Table 3-2 details the type of analytes amenable to each method as well as advantages and disadvantages of each method.

- Method 5035   Closed-System Purge-And-Trap and Extraction for Volatile Organics in Soil and Waste Samples
- Method 5030 B   Purge-and-Trap for Aqueous Samples
- Method 3561   Supercritical Fluid Extraction of PAHs
- Method 3541   Automated Soxhlet Extraction.
- Method 3535   Solid-Phase Extraction.
- Method 3546   Microwave extraction.
- Method 3540 C   Soxhlet Extraction.
- Method 3520 C   Continuous Liquid-Liquid Extraction.
- Method 3545   Pressurised Fluid Extraction.
- Method 3562   Supercritical Fluid Extraction of PCBs and organochlorine pesticides.
- Method 3560   Supercritical Fluid Extraction of Total Recoverable Petroleum Hydrocarbon.
- Method 3510 C   Separatory Funnel Liquid-Liquid Extraction.
- Method 3550 C/B   Ultrasonic Extraction.
- Method 3580 A   Waste Dilution.

Table 3-2: USEPA Methods for extracting organic compounds from sewage sludge (USEPA, 2003)

Extraction Method	Analytes	Advantages	Disadvantages
SOLID SAMPLES			
Soxhlet Extraction (**Method 3540C**)	Semi-volatile and non-volatile water insoluble and slightly water-soluble organics.	-Ensures intimate contact of sample with the extraction solvent, providing efficient extraction. - Uses relatively inexpensive glassware.	Extraction time is very long (18-24 hours).
Automated Soxhlet (**Method 3541**)	Semi-volatile and non-volatile water insoluble and slightly water-soluble organics.	-Intimate contact of sample with the extraction solvent, providing efficient extraction. - Extraction complete in 2 hours.	Require expensive devices.
Microwave Extraction (**Method 3546**)	Semi-volatile organics e.g. organophosphorus pesticides, organochlorine pesticides, chlorinated herbicides, phenoxyacid herbicides, substituted phenols, PCBs and PCDD/PCDFs.	Faster than Soxhlet method and uses less solvent with comparable recoveries.	Requires the use of expensive apparatus.
Pressurized Fluid Extraction (**Method 3545**)	Semi-volatile and non-volatile organic compounds that are insoluble or slightly water-soluble, such as organophosphorus pesticides, organochlorine pesticides, chlorinated herbicides and PCBs.	Equivalent to Soxhlet but uses less solvent and it is much faster.	Requires the use of expensive apparatus.
Ultrasonic Extraction (**Method 3550C**)	Non-volatile and semi-volatile organic compounds.	- Fast, extraction takes about 2-3 minutes. - Intimate contact between sample matrix and extracting solvent.	-Extraction method not very rigorous; hence choice of extraction solvent is very critical. - Clean-up highly recommended. - Not validated for organophosphorus compounds
Supercritical Fluid Extraction of Total Recoverable Petroleum Hydrocarbons (TRPH) (**Method 3560**)	Total recoverable petroleum hydrocarbons	No organic solvents required for extraction.	- Expensive apparatus. - Not suitable for extraction from liquid samples.
Supercritical Fluid Extraction of Polynuclear Aromatic Hydrocarbons (PAHs) (**Method 3561**)	PAHs,	No organic solvents required for extraction.	- Expensive apparatus. - Clean-up is required prior to analysis. - Not suitable for liquid samples.
Waste Dilution (**Method 3580A**)	Non-volatile and semi-volatile organic compounds.	For wastes with organics greater than 20 000 mg/kg and soluble in dilution system.	
Closed-System Purge-And-Trap (**Method 5035**)	VOCs	Sample is never exposed to atmosphere, VOC losses are negligible.	Cannot be used for samples with organics greater than 200μg/kg.

Table3.2: cont.

AQUEOUS SAMPLES			
Extraction Method (EPA)	**Analytes**	**Advantages**	**Disadvantages**
Solid-Phase Extraction (**Method 3535**)	Semi-volatile and non-volatile organics, especially: organochlorine pesticides and phthalates.	It is relatively fast and uses small volumes of solvent.	-May not be appropriate for aqueous samples with suspended solids greater than 1% since these samples can be difficult to filter hence reducing the extraction efficiency. - It requires specialized equipment.
Continuous Liquid-Liquid Extraction (**Method 3520C**)	Semi-volatile and non-volatile organics, which are water-insoluble or slightly water-soluble.	It is excellent for samples with particles (of up to 1% solids) that cause emulsion and it provides more efficient extraction of analytes that are more difficult to extract.	- Requires expensive glassware, uses fairly large volumes of solvent and extraction time is rather lengthy (18-24 hours).
Supercritical Fluid Extraction of PCBs and Organochlorine Pesticides (**Method 3562**)	PCBs and Organochlorine Pesticides		- It is applicable without any liquid treatment prior to extraction in order to stabilize it.
Purge-and-Trap for Aqueous Samples (**Method 5030 B**)	- Volatile Organic Volatiles (VOCs) that have boiling points below $200^{\circ}C$ and are insoluble or slightly soluble in water. This includes low molecular weight halogenated hydrocarbons, aromatics, ketones, nitriles, acetate, acrylates, ethers and sulfides.	- Purging time is relatively short (about 15 minutes).	- This method can also be used for water-soluble compounds, but quantitation limits (by GC or GC/MS) are approximately ten times higher because of poor purging efficiency. - Solids and waste samples require screening prior to extraction and GC analysis.
Volatile, nonpurgeable, water soluble compounds by azeotropic distillation (**Method 5031**)	Volatile Organic Volatiles (VOCs)	An alternative to Method 5030 A/B	Clean-up is required if significant interferences occur.
Separatory Funnel Liquid-Liquid Extraction (**Method 3510C**)	Water-insoluble and slightly water-soluble organic compounds	Uses relatively inexpensive glassware and is fairly rapid (2-3 minute) extractions.	It is labour intensive, uses a large volume of solvent and is subject to emulsion problems.
VOCs by Vacuum Distillation (**Method 5032**)	VOCs with boiling point less than $180^{\circ}C$ and insoluble or slightly soluble in water.	-It is applicable to almost all types of matrices regardless of water, soil, sediments, sludge, oil and	

The techniques that were selected for the extraction of the solid and the aqueous sewage sludge samples were methods 3540C and 3510C respectively. These two methods were chosen because they are inexpensive, simple and effective. Sewage sludge samples that had multiple phases were centrifuged such that the solid and aqueous phases were separated. The separated phases (*i.e.* solid & aqueous) were then subjected to the appropriate extraction techniques.

3.2.1 Soxhlet Extraction

In cases where the solid sludge was still very wet it was allowed to air-dry undercover in the laboratory at room temperature for several days prior to its extraction. If the solid sludge was without water, unwanted materials like grass, fibre and sticks were removed from the solid sludge prior to grinding. The hard solid material was reduced to small particles by conventional grinding using mortar and pestle or/and a motorised mortar grinder (Glen Creston, Stanmore UK). The purpose of grinding was to increase the extraction efficiency by increasing the surface area of the sample, as well as to decrease the particle size to make sub-sampling more representative. Since the results were to be expressed on a dry weight basis, two portions of sludge were weighed. One portion was used for the determination of moisture content while the second was extracted in the Soxhlet extractor. For the moisture determination, an accurately-weighed 10 g sludge sample was dried in an oven set at 106°C for 24 hours. The samples were cooled in a desiccator having silica gel as drying agent before re-weighing to a constant weight. The moisture content of the sample was then determined as a percentage of the dry mass.

The second accurately weighed portion of the sample (10 g) was thoroughly mixed with an equal amount of dried anhydrous sodium sulfate. This was done so that any remaining moisture in the sludge is absorbed by the sodium sulfate and the sludge particles are then only loosely attached to each other, allowing the easy flowing of the extraction solvent through the particles, thereby enhancing the extraction process. The mixture was then transferred into a cellulose extraction thimble, which was then placed in the Soxhlet extractor. The extraction solvent (300 ml, 1:1v/v) was a mixture of hexane and dichloromethane, which was added into the round bottom flask

containing three clean boiling chips. Hexane and dichloromethane were both used as the extraction solvent as recommended by the EPA method. The flask was attached to the extractor and the extractor attached to the condenser. The extraction set up is illustrated in Figure 3-4.
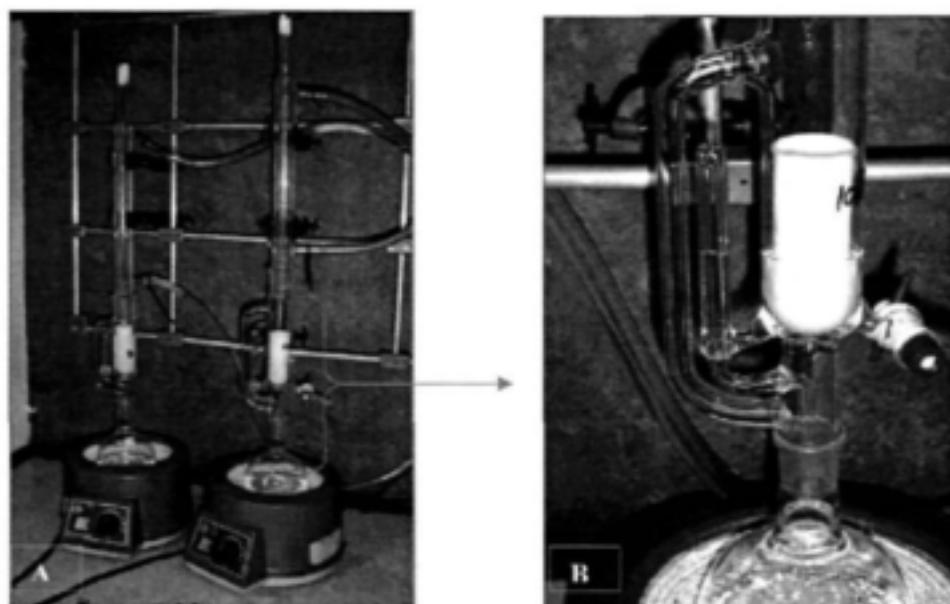
Figure 3-4: (A) The Soxhlet extractor placed in the heating mantle and (B) enlarged view of cellulose extraction thimble.

The extraction process was completed in 24 hours and the extract was allowed to cool to room temperature (~ 23°C) before it was dried (section 3.2.3). The procedure is summarized in the flow diagram in Figure 3-5.
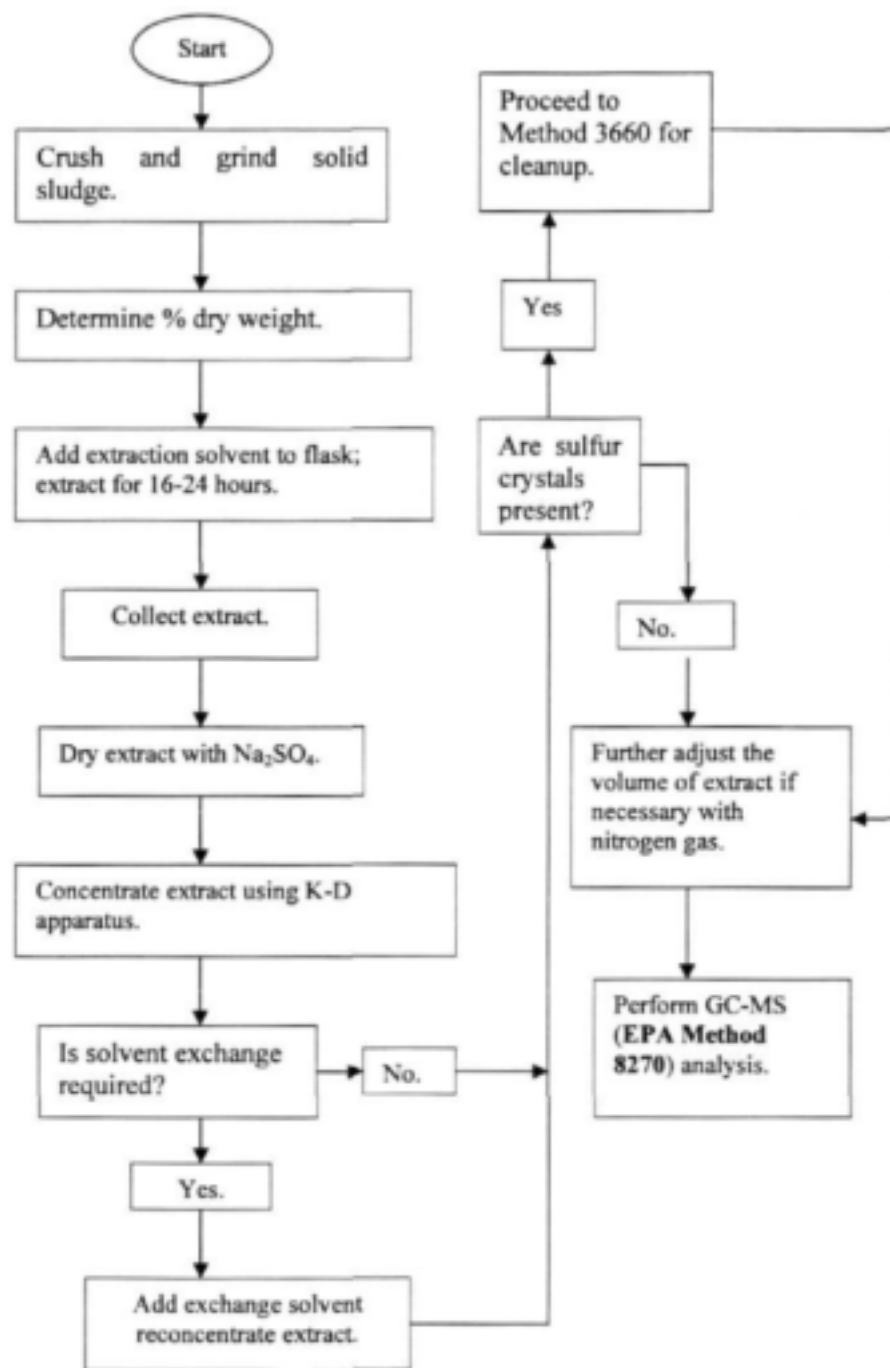
Figure 3-5: The schematic representation of Soxhlet extraction (Method 3540C).

3.2.2 Separatory Funnel Liquid-Liquid Extraction (Method 3510C)

All the aqueous sludge samples were extracted at neutral, acidic and basic pHs as recommended by the EPA methods. When using this method it is important to recognise that   some of the organic compounds of interest may undergo some decomposition at high pH values. For example, some organochlorine pesticides may become dechlorinated, phthalate esters may undergo exchange and phenols may react to produce tannates (USEPA, 2003).

The extraction procedure involved measuring 1 litre of sample by transferring the contents in the glass bottle into a 2 litre graduated glass measuring cylinder. The sample was quantitatively transferred from the measuring cylinder into a separating funnel. The samples were extracted at neutral pH, which was the pH of the samples.

The extraction solvent recommended by the EPA method for aqueous samples is dichloromethane. The cylinder was rinsed with dichloromethane (60 ml) and the rinsate transferred into the separating funnel. The separating funnel was sealed and shaken vigorously for five minutes with periodic venting to release excess pressure. The mixture was left to separate for ten minutes. The organic layer was collected into an Erlenmeyer flask. This procedure was repeated twice using fresh portions (60 ml) of the solvent and all the three extracts were collected into one Erlenmeyer flask. The combined extract was then transferred into a glass beaker (1 litre) ready for drying (section 3.2.3). The flask was rinsed with dichloromethane (60 ml) and the rinsate was added into the beaker to complete the quantitative transfer.

After the extraction of the sample at neutral pH, the pH of the aqueous layer was adjusted to pH 1 by addition of sulfuric acid. The acidic sample was extracted three times with fresh portions of dichloromethane (60 ml). The three extracts were combined then transferred into a 1 litre glass beaker ready for drying (section 3.2.3). Thereafter, the acidic aqueous layer was adjusted to pH 13 using NaOH (10 M) and the sample was extracted three times as in the previous cases. The combined extracts were transferred into glass beaker for drying. In each case, the pH was measured

using a wide-range pH paper. The summary of this extraction method is represented in Figure 3-6.
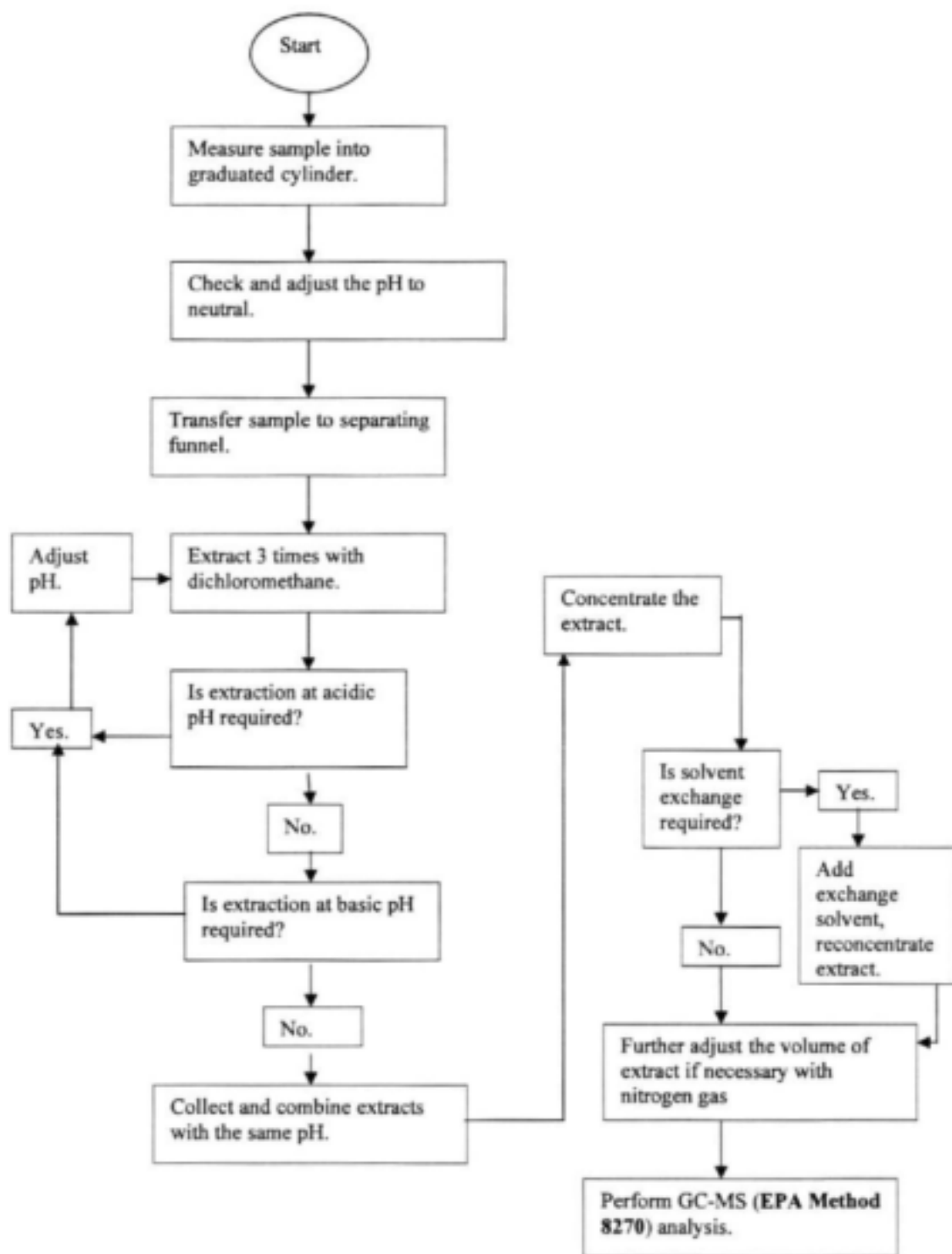
Figure 3-6:   Schematic Representation of Liquid–Liquid Extraction (method 3510C)

3.2.3 Drying of the Extract

The extracts from the solid and aqueous sludge samples were dried using two different processes. Extracts from aqueous samples were dries by the direct addition of solid sodium sulfate, whereas extracts from solid samples were dried using a drying column.

The sewage sludge extracts obtained from the aqueous samples were dried by the addition of sodium sulfate to the extract. Prior to the drying process, 120 ml of the extraction solvent was added to the extract. This was to increase the amount of the solvent in the extract and hence enhance the drying process. A drying column was not used in this case because the extract contained some emulsion. This meant that there was a possibility that some of the target compounds were contained within the oily emulsion layer. Hence significant quantities of solvent were required to increase the chances of dissolving organic compounds in organic layer (*i.e.* dichloromethane). The mixture was continuously stirred with a glass rod during the addition of sodium sulfate until the emulsion was broken and a clear organic layer persisted above the sodium sulfate. The organic layer was then transferred to a Kuderna-Danish (K-D) apparatus for concentration (section 3.6). The beaker used was then washed with 120 ml of dichloromethane and the rinsate transferred into the K-D apparatus to complete quantitative transfer.

The solid sewage sludge extracts were dried by passing the extracts through a drying column containing 10 cm anhydrous sodium sulfate. The dried extracts were collected in a 250 ml Erlenmeyer flask. Thereafter the round-bottom flask used during the Soxhlet extraction was rinsed with the mixture of hexane and dichloromethane (120 ml, 1:1 v/v) and the rinsate was transferred into the drying column to complete the quantitative transfer. When the drying process was completed (*i.e.* no solution was dripping from the column) the extract was transferred into the K-D apparatus for concentration.

3.3 EXTRACT CONCENTRATION

The dried extracts from both the aqueous and solid sewage sludge were in a K-D concentrator containing three boiling chips. The flask used to collect the dried extract was rinsed with the extraction solvent (30 ml) and the rinsate was transferred into the evaporation flask attached to a concentrator tube. The K-D apparatus was placed on a steam bath with boiling water to effect the evaporation of the solvent. The extract was concentrated to a volume of approximately 2 ml.

Thereafter the evaporation flask was sealed with a glass stopper and allowed to cool to room temperature (*i.e.* 23°C). If there was a sulfur precipitate at the bottom of the extract, a sulfur clean-up was performed (section 3.7.1) (USEPA, 2003). However, if there were no crystals observed the cooled extract was transferred into a storage glass bottle. The K-D apparatus was washed with 1 ml of the extraction solvent and the rinsate transferred into the bottle. The volume of the concentrated extract was adjusted to 3.0 ml by blowing nitrogen over the extract. The extract was thereafter transferred to a 3 ml storage glass vial with a Teflon® screw top and stored at approximately 4°C. A 1 ml sample was then transferred into a 1.8 ml autosampler vial ready for GC or GC-MS analysis.

3.4 PURIFICATION OR CLEANUP TECHNIQUES

It is recommended that sludge extracts need to be cleaned prior to analysis due to the presence of a large number of contaminants, which tends to damage the GC column. In addition, the cleanup process minimizes interferences during analysis. There are several clean-up techniques that have been suggested by the USEPA that are specific in removing certain impurities from the extracts. Brief descriptions of several clean up techniques recommended by the EPA are listed in Table 3-3.

A list of the different EPA methods is shown below.
- Method 3660B   Sulfur Cleanup
- Method 3610B   Alumina cleanup
- Method 3620B   Florisil Cleanup
- Method 3630C   Silica Gel Cleanup
- Method 3640A   Gel-Permeation Cleanup
- Method 3650B   Acid-Base Partition Cleanup
- Method 3665A   Sulfuric Acid/Permanganate Cleanup

The advantages and disadvantages of each cleanup method are shown in Table 3-3.

Table 3-3: The different types of Purification methods that can be used to clean the samples prior analysis

Method (EPA)	Analytes	Advantages	Disadvantages
Sulfur Clean-up **(Method 3660B)**	Non-volatile and semi-volatile organic compounds.	Useful for the elimination of sulfur from sample extract, which may cause chromatographic interferences with the analytes of interest.	
Alumina Clean-up **(Method 3610B)**	- *Basic alumina* (pH of 9-10) is used to separate basic and neutral compounds that are stable to alkali, alcohols, hydrocarbons, steroids, alkaloids and natural pigments. - *Neutral alumina* (pH of 6-8), used to separate aldehydes, ketones, quinines, esters, lactones and glycosides. - *Acidic alumina* (pH 4-5), separates acidic pigments (natural and synthetic) and strong acids (that otherwise chemisorb to neutral and basic alumina).	It is used to separate analytes from interfering compounds of a different polarity.	- Basic alumina is capable of causing polymerization, condensation and dehydration reactions. In addition acetone or ethyl acetate cannot be used as eluates. - Neutral alumina is considerably less active than the basic form.
Florisil Clean-up **(Method 3620B)**	-Pesticide residues and other chlorinated hydrocarbons, phthalate esters, nitrosamines, aniline and aniline derivatives, chlorinated hydrocarbons, organochlorine pesticides and PCBs. - It is also used for the separation of aromatic compounds from aliphatic-aromatic mixtures.	It is used to separate analytes from interfering compounds prior to sample analysis by GC.	It cannot be used for samples with high boiling materials.
Silica Gel Clean-up **(Method 3630C)**	PAHs, derivatised phenolic compounds, organochlorine pesticides and PCBs such as Aroclors.	It provides the best separation of PCBs from most single component organochlorine pesticides.	It cannot be used for samples with high boiling materials.
Gel-Permeation Clean-up **(Method 3640A)**	Separation of a broad range of semi-volatile organics and pesticides as well as separating high molecular-weight, high boiling material from sample analytes.	- It is most efficient for removing high boiling materials that condense in the injection port area of GC or the front of GC column.	Cannot separate interfering materials from target compounds, if they have same molecular size.
Acid-Base Partition Clean-up **(Method 3650B)**	Separate acid analytes (i.e. organic acids and phenols) from base/neutral analytes (i.e. amines, aromatic hydrocarbons and halogenated organic compounds) using pH adjustment.	It is very useful for separating the neutral PAHs from acidic phenols when analyzing a site contaminated with creosote pentachlorophenol.	
Sulfuric Acid /Permanganate Clean-up **(Method 3665A)**	-Particularly for PCBs. Should be used when elevated baselines or complex chromatograms prevent accurate quantitation of PCBs. - It can also be used for the separation of chlorinated benzenes, chlorinated naphthalenes and chlorinated pesticides from PCBs.	Is suitable for rigorous clean-up of sample extracts prior to PCBs analysis.	Will destroy most other organics including the pesticides: aldrin, dieldrin, endosulfan and endosulfan sulfate.

Among these purification techniques, the sulfur clean-up process was applied because sulfur crystals were observed in most of the concentrated extracts, particularly extracts from solid sludge samples. The procedure for the sulfur cleanup is described in section 3.4.1.

3.4.1 Sulfur Cleanup (EPA Method 3660B)

There are two methods that can be employed for the removal of sulfur from the sludge extracts, namely: the use of copper powder or tetrabutylammonium sulfite. The latter method was selected, due to the fact that it results in an insignificant damage to a wide range of pesticides and organic compounds when compared to copper. The metal is capable of damaging organophosphorus and some organochlorine pesticides (*i.e.* some of the target compounds) (USEPA, 2003).

The procedure for the cleanup of an extract using tetrabutylammonium sulfite (TBA sulfite) is briefly described. A concentrated extract (3.0 ml) was transferred into a 50 ml transparent glass bottle having a ground glass stopper sealed with Teflon® tape. TBA sulfite solution (1.0 ml) and 2-propanol (2.0 ml) were added to the bottle, the cap was replaced and the contents vigorously shaken for 3 minutes until clear crystals were observed. If no crystals were observed, sodium sulfite was added and the contents shaken until crystals were observed. Ultrapure water (5.0 ml) was added to the saturated solution and the contents were shaken until all the solid residue was dissolved. The solution was left to stand for 10 minutes to allow the organic layer to separate from the aqueous layer. The organic layer was transferred into a storage glass bottle with the help of a glass Pasteur pipette. The final volume of the extract was adjusted to 3.0 ml by blowing nitrogen over the extract. Thereafter the extract was stored in a 3 ml glass vial having Teflon® lined cap and stored at approximately 4°C prior to analysis. The summary of this cleanup procedure is shown diagrammatically in Figure 3-7.

Start

Transfer extract to the bottle

Add TBA sulfite and 2-propanol

Is the sample colourless or colour unchanged and are crystals of sodium sulfite present?

Yes **No**

Add ultra-pure water, shake, and allow settling. Transfer hexane layer to concentrator.

Add additional crystalline sodium sulfite until residue remains after shaking.
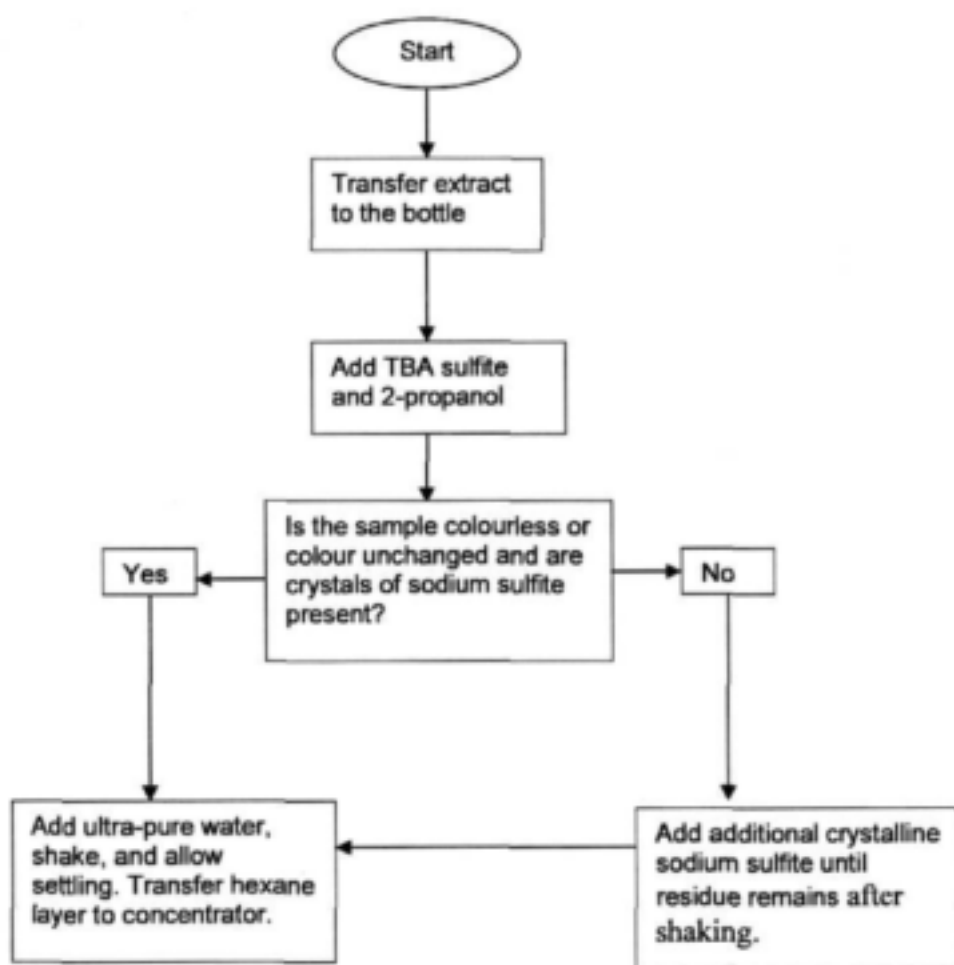
Figure 3-7:   Schematic representation of the sulfur cleanup (Method 3660B)

3.5   ANALYTICAL TECHNIQUES

The following determinative methods shown in Table 3.4 are recommended by USEPA for the analysis of the different organic compounds[31].

Table 3-4:   Determinative EPA methods for organic analytes

Analyte Type	GC-MS Method	Specific GC Method	HPLC Method
Acid Extractables	8270		
Acrolein, Acrylonitrile, Acetonitrile	8260	8031 8033[1]	8315[2] 8316
Acrylamide	8260	8032	8316
Aniline and Selected Derivatives	8270	8131	
Aromatic Volatiles	8260	8021	
Base/Neutral Extractables	8270		8325[4]
Carbamates			8318, 8321
Chlorinated Herbicides	8270[3]	8151	8321
Chlorinated Hydrocarbons	8270	8121	
Dyes			8321
Explosives			8330, 8331, 8332
Formaldehyde			8315
Haloethers	8270	8111	
Halogenated Volatiles	8260	8011, 8021	
Nitroaromatics and Cyclic Ketones	8270	8091	8330[5]
Nitrosamines	8270	8070	
Non-halogenated Volatiles	8260	8015	8315
Organochlorine Pesticides	8270[3]	8081	
Organophosphorus Pesticides	8270[3]	8141	8321
Phenols	8270	8041	
Petroleum Hydrocarbons		8015	
Phthalate Esters	8270	8061	
Polychlorinated Biphenyls	8270[3]	8082	
PCDDs and PCDFs	8280, 8290		
Polynuclear Aromatic Hydrocarbons	8270	8100	8310
Volatile Organics	8260	8011, 8015, 8121, 8031, 8032, 8033	8315 8316

[1] Of these analytes, Method 8033 is for acetonitrile only.
[2] Of these analytes, Method 8315 is for acrolein only.
[3] This method is an alternative confirmation, not the method of choice.
[4] Benzidines and related compounds.
[5] Nitroaromatics.

The method of analysis chosen for screening the samples was EPA Method 8270 GC-MS. In the case of quantification, a mixture of appropriate methods involving GC-MS, and GC was used. (e.g. Organochlorine Pesticides method of choice is EPA Method 8081)

3.5.1 Qualitative Analysis

For the screening (*i.e.* identification of organic compounds) of the 78 samples from 69 wastewater treatment plants an HP6890-Series gas chromatograph-mass spectrometer (GC-MS) was used. The samples were made up of 9 liquids and 69 solids. An autosampler fitted with a 10-µl syringe was used to inject 1 µl aliquots of each extract into the GC-MS.

The chromatographic separation was achieved using DB-5 MS capillary column. The GC-MS was operated in splitless mode with the gas saver on and helium as the carrier gas. Before each injection, the syringe was flushed six times with the sample to be injected. After the injection, the syringe was washed six times each with acetone and methanol. The acquisition mode was used for scanning. The instrument conditions and parameters as used are summarized in Table 3-4. The identification of the organic compounds was performed using Wiley 275.L Library. A typical mass spectrum for one of the organic compounds that was identified using this library in shown in Figure 3-8. The organic compounds that could be identified with a confidence of at least 80% were recorded.
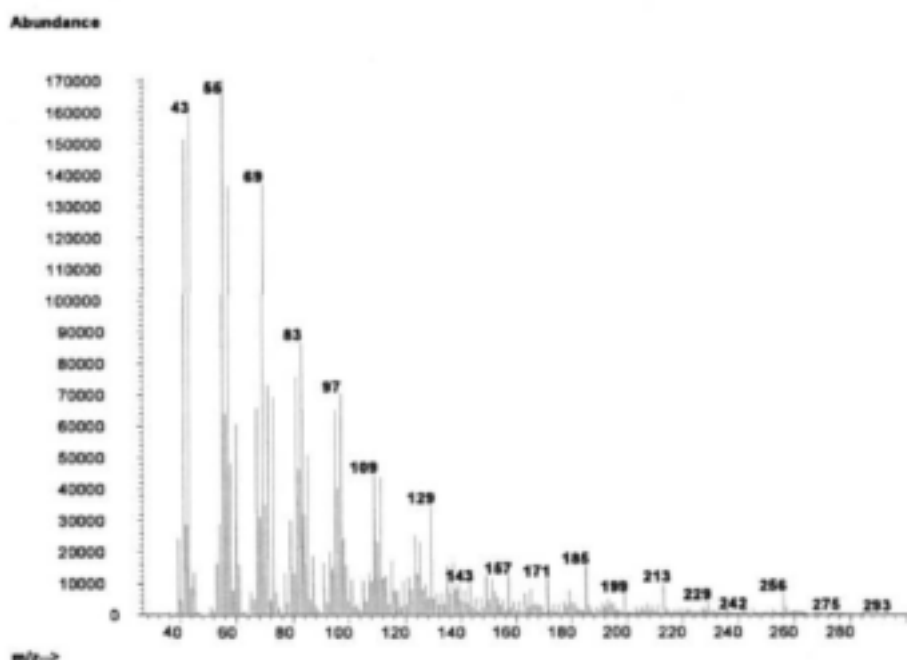
Figure 3-8: Mass spectrum of one of the components from one sludge sample identified using Wiley 275.L Library.

Table 3-5: HP6890-Series GC-MS operating conditions

Parameter	Value	Parameter	Value
Oven Temperature Programme:		**Front Inlet**	
Initial Temp	40°C	Initial temperature	250°C
Initial Time	4.0 minutes	Pressure	48.6 kPa
Final Temp	350°C	Purge flow	50.0 ml/min
Equilibration time	0.50 min	Purge time	1.0 min
Ramp:		Total flow	53.8 ml/min
Rate	10°C/min	Saver flow:	20.0 ml/min
Initial temperature	270°C	Saver time:	2.0 min
Final time	15.0 min	Gas type:	Helium
MS detector information:		Gas saver	On
Solvent delay	5.0 min	**Column 1**	
EM absolute	False	Maximum temperature	325°C
EM offset:	494	Initial flow	1.0 ml/min
Resulting EM voltage	2658.8	Nominal initial pressure	48.7kPa
Low mass scan parameters	35 m/z	Average velocity	36 cm/sec
High mass scan parameters	500 m/z	**Post run**	
Thermal AUX		Post time	0.0 min
Initial time	0.0 min	**7673 Injector (front injector)**	
Initial temperature	280°C	Sample wash	6
Viscosity delay	**0.0 sec**	Sample pump	6
Plunger speed	**Fast**	**Post Injection**	
Pre-injection & post-injection dwell	**0.0 min**	Solvent A washes	6
		Solvent B washes	6

3.5.2 Quantitative Analysis

The samples that were subjected to quantitative analysis were those classified as the worst and the best South African sewage sludge samples, based on the quantification of metal ions (WRC, project K5/1283). The organic contaminants that were quantified were those known to be toxic to soil, plants and humans once introduced into the environment.

The results obtained from the screening of samples from 78 sewage sludge samples revealed that polynuclear aromatic hydrocarbons (PAHs), nonylphenols and p-cresol were among the most common organics and prevalent across the country. In addition, these compounds appear in the recent USEPA 503 list of priority organic pollutants and the EU 2000 (Appendix A, Table A-2; UMK-AG, 2000; EU, 2000).

The other organic compounds that were quantified were pesticides, since these are listed in the South African guidelines of 1997: Permissible Utilization and Disposal of Sewage Sludge (WRC, 1997; Table 1-3 in section 1.7). This was done so as to confirm the screening results. The quantification was done using GC-MS in the selected ion detection mode where sensitivity is 5 000 times that at the scanning mode as used in the scanning process. Samples were also subjected to GC analysis using a flame ionisation detector (FID) and an electron capture detector (ECD).

Since some target compounds (*e.g.* pesticides) were not detected in the preliminary results that involved the screening of sludge samples for organic compounds, the efficiency and effectiveness of the extraction as well as the analysis method were investigated. This was achieved by generating a reference sludge from one of the sludge samples (Heidelberg, sample 10) collected in 2002. This was then spiked with a mixture of six organochlorine pesticides at half the regulatory limit concentration. The spiked reference sludge was extracted at different time intervals in order to determine whether ageing had any effect on the extractability of the organics. The details are discussed in sections 3.5.4 and 3.5.5.

3.5.3   Calibration Standard for Pesticides and Phenols

Pure samples of hexachlorobenzene, 4,4'-DDT, dieldrin, heptachlor, lindane and aldrin were accurately weighed (0.0100 g) and dissolved in approximately 3.0 ml of hexane. This was transferred into a 10-ml volumetric flask and made up to the mark with hexane. The stock solution concentration was thus 1 000 mg/L. Composite stock standard solutions of phenols (*i.e.* p-cresol and nonylphenol) with concentrations of 1000 mg/L were prepared by weighing 0.0100g of the pure compounds and making up in a 10 ml volumetric flask with hexane. The composite calibration standard solutions of both the pesticides and phenols were prepared from their respective stock solutions by dilution with hexane. The pesticide calibration standard concentrations were 0.0625, 0.125, 0.250, 0.500 and 1.00 mg/L. The phenol composite calibration standard solutions were 5, 25, 50, 100 and 200 mg/L.

The calibration standards of pesticides and phenols were run on the GC-ECD and GC-FID respectively for the purpose of plotting the calibration graphs. The individual pesticide peaks were identified by running one standard solution on the GC-MS. The two chromatograms of the composite pesticides from the GC-MS and GC-ECD are shown in Figures 3-9 and 3-10. The retention times are not the same with each instrument as the operating conditions are different. However, the order of elution of the pesticides is the same in both chromatograms since columns with a similar stationary phase were used. In case of the phenols it was found that the peaks of p-cresol and nonyphenol were very distinct and the confirmation of their identity by the GC-MS was not necessary. All the peaks were also confirmed by spiking the composite standard solution with pure pesticide solution of the six target pesticides.

Figure 3-9:   GC-MS chromatogram of the composite pesticide standard solution.
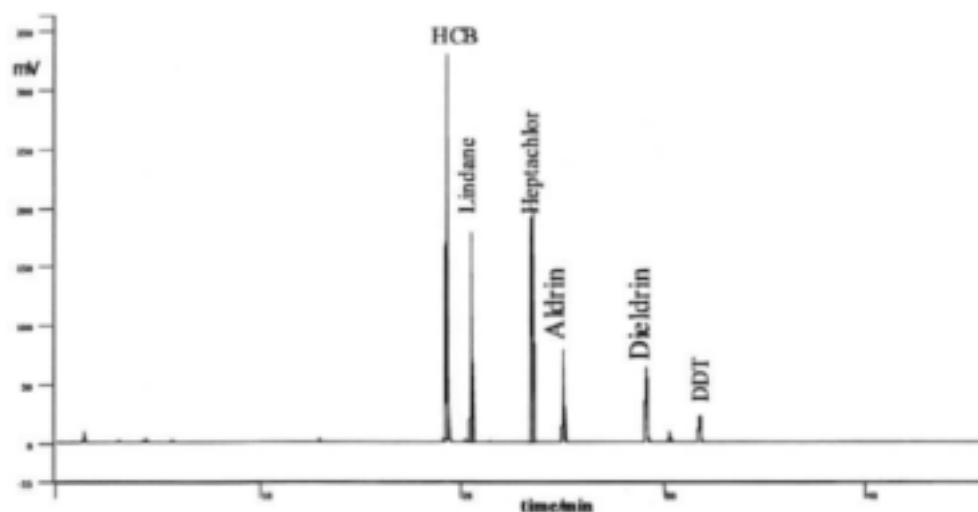
Figure 3-10:   GC-ECD chromatogram of the pesticide composite standard solution.

The pesticide calibration equations in the form of $y = mx + c$ were generated, where y = peak area x = concentration, m = slope and c = intercept. The calibration equations of the phenol standard solutions took the form of $y = mx$. The graphs were constructed with the help of Origin 5.0, a data analysis and technical graphical software.

3.5.4   Preparation of Reference Sludge

The sewage sludge sample from Heidelberg was arbitrarily chosen for the preparation of a reference sludge. This was achieved by taking five fractions of the sample (~25 g) and extracting each one five times by means of Soxhlet extraction as a cleanup process. The mixing of the anhydrous sodium sulfate with the sludge sample before extraction was omitted. This was to ensure that no foreign material was introduced into the organic matrix. The first and fifth extracts were subjected to the usual process drying, cleaning and concentrating. The effectiveness of removing the organic compounds from the sludge was monitored by analysing the first and the fifth extracts using GC-MS. Representative chromatograms for the first and last are shown in Figure 3-11.
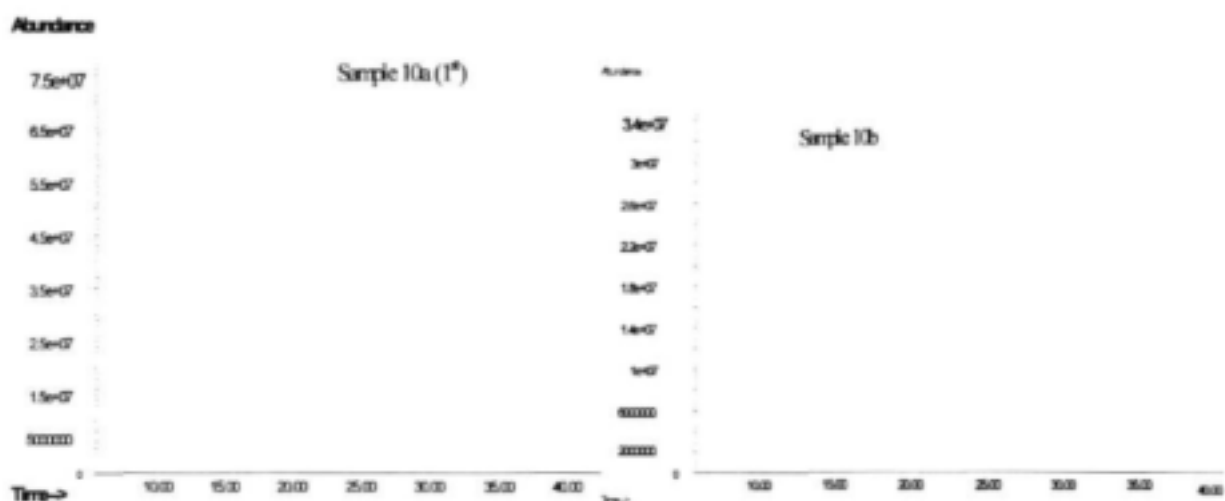
Figure 3-11: The GC-MS chromatograms of first and fifth chromatograms of reference sludge 10a.

The purpose of extracting the sludge five times was to ensure that most of the organic compounds in the sludge were significantly reduced in concentration. The different portions of the reference sludge were then mixed together to form a representative sample. A control sewage sludge and nine spiked sewage sludges were prepared from this sample.

3.5.5 Spiking of Reference Sludge with Pesticides

A representative reference sludge sample (120 g) was obtained according to the procedure in Section 3.6.2. Before the mixture was spiked, 10 g was set apart to be used as a control sludge. The main purpose of the control sludge was to monitor the performance of the system by acting as the background correction to the spiked sludge. This was used to check whether the organic compounds identified in the spiked sludge were those from the spiked or from the control reference sludge. A control GC-MS chromatogram was obtained by extracting 10 g of the reference sludge and subjecting the extract to the normal processes of analysis.

The remaining reference sludge sample (110 g) was spiked with a mixture of six organochlorine pesticides *(i.e.* aldrin, DDT, dieldrin, heptachlor, hexachlorobenzene

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and lindane) at a concentration that was half the regulatory limit. A summary of the pesticides with their respective masses that were weighed using a 5 decimal place weighing balance is tabulated in Table 3-6. The weighed pesticides were mixed and dissolved into 200-ml of hexane. This was poured over the reference sludge, which was later thoroughly mixed before allowing the hexane to evaporate at room temperature.

Table 3-6:   The concentration and mass of the target compounds added to the reference sewage sludge.

Pollutant	Half the regulatory limit in dry sludge (mg/kg) (WRC, 1997)	Mass (mg) weighed for 110 g of dry sludge
Aldrin	0.101	0.0111
4,4'-DDT	0.175	0.193
Dieldrin	0.152	0.167
Heptachlor	0.175	0.194
Lindane	0.680	0.0748
Hexachlorobenzene	8.10	0.891

The sample was left for a specified time period prior to taking 10 g for extraction. The time intervals were 2, 6 and 9 days.

The organochlorine pesticides that were extracted from the reference sludge were diluted in order to fit within the range of the calibration graphs. In addition, the hexane used in the preparation of calibration standards was also spiked with the same organochlorine pesticides. But in this case the concentration of the pesticides spiked in the solvent were $\frac{1}{16}$, $\frac{1}{8}$, $\frac{1}{4}$ and $\frac{1}{2}$th of regulatory limit. This was used to test the sensitivity of the instruments towards the pesticides of choice. The concentrations used were achieved through a dilution process. The extracts were then analysed using the GC-ECD and GC-MS.

3.5.6   Gas Chromatography Analysis

A Varian CP-3800 Gas Chromatograph with a Varian CP-8400 autosampler was used for the analysis of both the pesticide and phenol extracts. The analysis of the extract for phenols and organochlorine pesticides was carried out using FID (Flame Ionization Detector) and ECD (Electron Capture Detector) respectively. A 10.00 µL

syringe was used for injecting the sample into the instrument. This was cleaned three times with hexane prior and after sample injection. The HP6890 series GC-MS was used to quantify and confirm the identity of the compounds detected using GC-FID and GC-ECD. The GC operating conditions for the analysis of both the phenols and pesticides are provided in Tables 3-7 and 3-8 respectively.

Table 3-7: **GC-ECD operating conditions employed for the determination of pesticides.**

Instrument	Varian 3800 GC			
Column Specifications				
Stationary phase	VF-5ms (5% phenyl, 95% methyl polysiloxane)			
Length	30 m			
Inside diameter	0.25 mm			
Outside diameter	0.39 mm			
Film thickness	1.0 μm			
Oven temperature program:	Temperature (°C)	Rate (°C/min)	Hold (min)	Total (min)
	100	0.0	2.00	
	160	15.0	3.00	
	270	5.0	15.00	46.00
Column flow	3.0 ml/min			
Carrier gas	Nitrogen			
Detector	Electron Capture detector (ECD)			
Temperature	300 °C			
Injection system	8400 Auto sampler			
Injection mode	Standard split/splitless			
Injector type	1177 Split/splitless			
Operating temperature	225 °C			
Mode	Split			
Split ratio	10			

Table 3-8: The operating conditions for the determination of phenols using GC-FID.

Instrument	Varian 3800 GC			
Column Specifications				
Length	30 m			
Stationary phase	CPSil 8 CB			
	(5% phenyl, 95% methyl polysiloxane)			
Inside diameter	0.53 mm			
Film thickness	1.5 μm			
Oven temperature program:	Temperature (°C)	Rate (°C/min)	Hold (min)	Total (min)
	80	0.0	1.50	
	230	6.0	0.00	
	275	10.0	4.50	35.50
Column flow	6.0 ml/min			
Carrier gas	Nitrogen			
Detector	Flame Ionization Detector (FID)			
Temperature	300 °C			
Injection system	8400 Auto sampler			
Injection mode	Direct on-column			
Injector type	1044			
Operating temperature	200 °C			

Figure 3-12 shows the GC chromatogram of the spiked solvent (hexane) at ½ the regulatory concentration of chlorinated pesticides. Represented in Figure 3-13 is the variation in peak size for one of the pesticides (dieldrin) as the concentration changed from ⅟₁₆ to ½ of the regulatory limit.
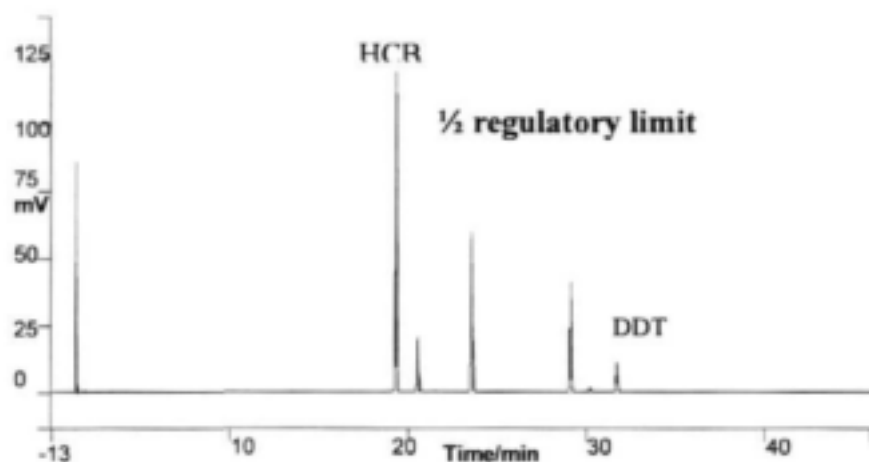
Figure 3-12: GC-ECD chromatogram of spiked solvent at concentrations equivalent to half the regulatory limit.
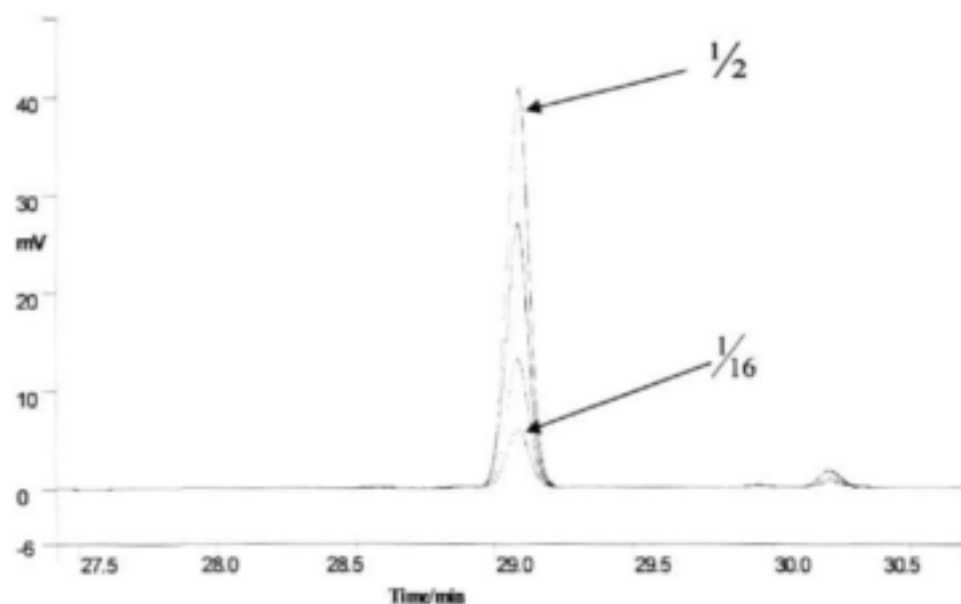
Figure 3-13: GC-ECD chromatogram of dieldrin showing differences in peak height for concentrations ranging from ⅟₁₆ to ½ of the regulatory limit.

3.5.7   Setbacks Encountered During the Quantification of Phenols

It was discovered during the analysis of phenol calibration standards that sometime after every run the p-cresol and nonylphenol peaks were decreasing in size and becoming broader and their elution times increased. Thus it seem as if the compounds were affecting the column. Every effort to clean or regenerate the column was not successful. The quantification problem associated with this problem was solved by introducing a standard solution after every five samples that were being analysed. All the samples were analysed non-stop using an autosampler. This is because it was also found that the column deteriorated faster if it was let to stand after use. The concentrations were then corrected with respect to the standard.

3.5.8   The GC conditions for the analysis of PAHs (USEPA Method 8100)

The column used in the analysis of PAHs was VF-5ms (Chrompak, Middelburg, Netherlands). The GC-FID optimum conditions that gave the best separation and resolution are given in Table 3-9.

Prior to use, 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 clean and condition the column.

Environmental samples are known to contaminate GC columns 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 were cut from the injector end to remove contamination, 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.

Table 3-9:   GC conditions 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 (5% phenyl, 95% methyl polysiloxane)		
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		
Carrier gas	Nitrogen		
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		
Mode	Splitless		
Delay time	1 min		
Split ratio	100		

3.5.9   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)fluoranthene, benzo(k)fluoranthene, dibenzo(a,h)anthracene, benzo(g,h,i)perylene, benzo(a)pyrene, and indeno(1,2,3-cd)pyrene.. These compounds were present in different concentrations in the mixed standard as indicated in Table 3-10. Included is the sequence of these compounds in terms of retention times.

Table 3-10: Concentration of each PAH in the composite standard.

Compound Name	Concentration in the stock (pm).	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 1 ml 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 (mg/l) used are shown in Table 3-11.

Table 3-11: Concentrations (mg/l) 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				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
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	

A composite standard was run on GC-MS in an instrument with a column having a stationary phase similar to the one that was used on the GC-FID. From the GC-MS results a sequence of peak appearances was established. This sequence was in agreement with data reported in literature on PAH analysis. The instrument type and the conditions for GC-MS are summarized in Table 3-12.

Table 3-12: GC-MS conditions used in the analysis of PAHs

Instrument Parameters	ThermoFinnigan, Model K07300000000080, S. No. 200031445, Milan.
Injector	
Splitless 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, 95% 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
Ionisation mode	EI
Scan mode	Full Scan
Mass range (amu)	50.0-600.0

Representative chromatograms for the 16 PAHs are shown in Figure 3-14. The expanded portions of the chromatogram, showing increase in peak height with increasing standard concentrations for the individual PAHs, are shown in Figures 3-15 and 3-16.
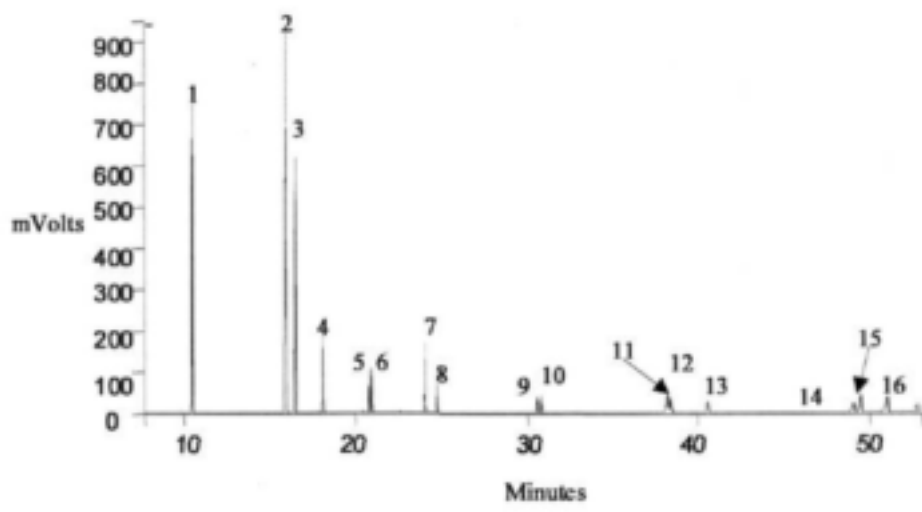
Figure 3-14: GC chromatograms for PAH mixed standard
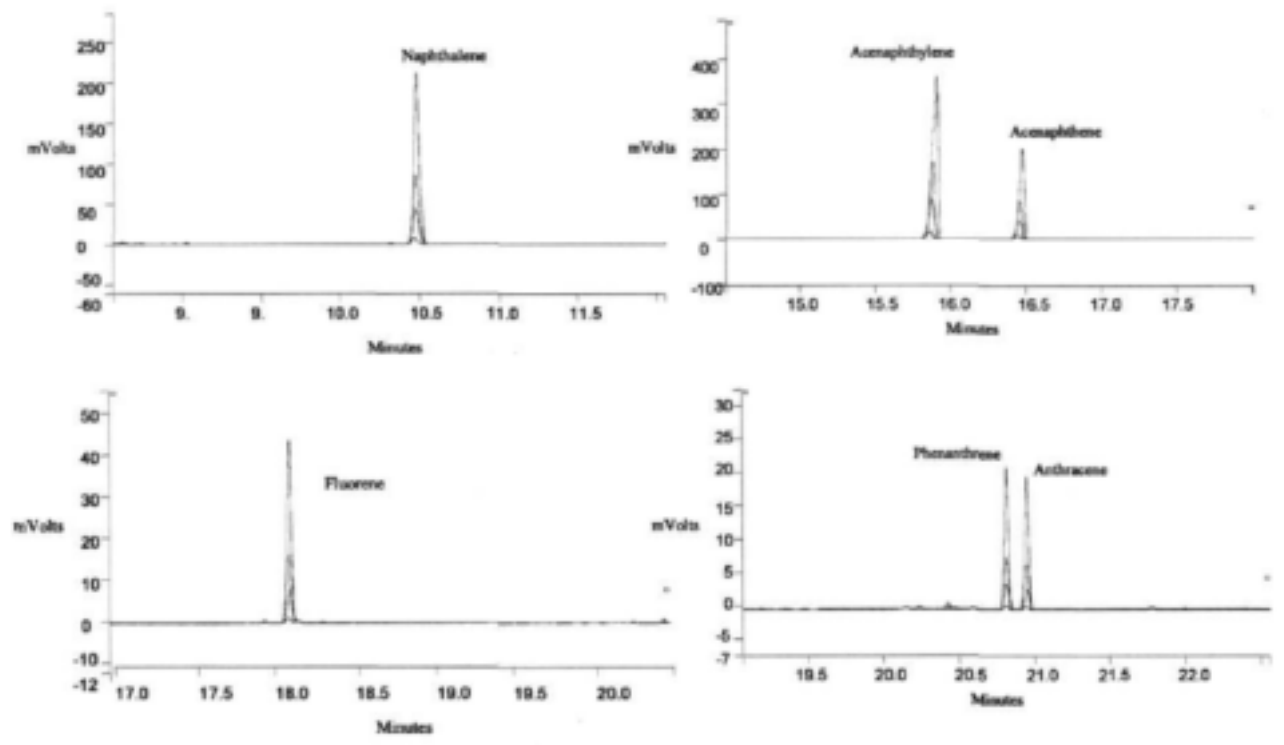
Figure 3-15: A zoomed view of standard peaks as observed in the GC.
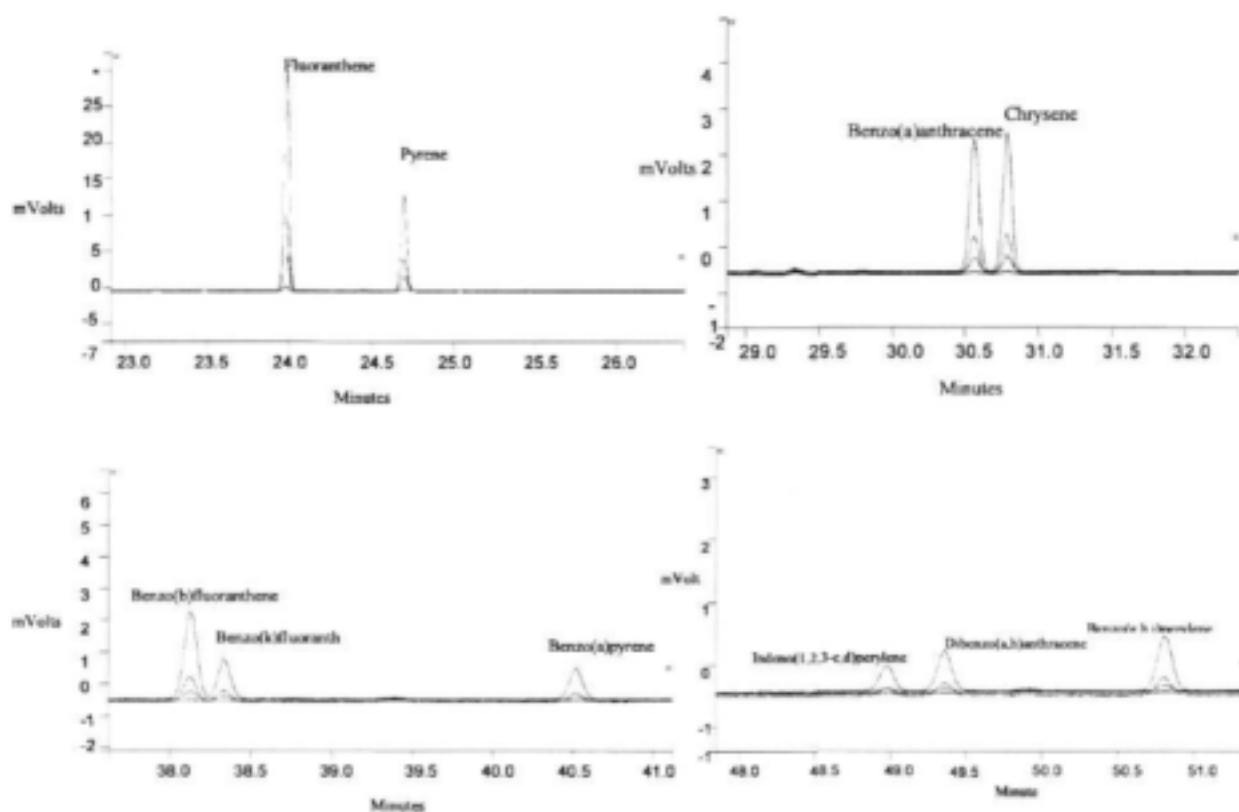
Figure 3-16:   A zoomed view of standard peaks as they appeared in the GC.

The peak areas corresponding to each PAH were plotted against concentrations to generate calibration curves. These parameters were used to quantify the respective PAHs in the sludge extracts.

3.5.10 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 six concentrations (2, 6, 10, 15, 20 and 30 mg/l) in total. These concentrations were prepared from a stock standard solution of 100 mg/l by dilution process. The linear plots that were obtained by using Origin 5.0 software were used to calculate the amount of surrogate standards recovered in the extracted samples.

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 the quantification of PAHs the concentration of the surrogate used was 10 mg/l. A total of 34 samples were spiked with 3 ml of surrogate standard solutions of 10 mg/l. The spiked samples were left to age before subjecting them to the Soxhlet extraction process

4   RESULTS AND DISCUSSION

4.1   QUALITATIVE RESULTS FOR ORGANIC COMPOUNDS IN SOUTH AFRICAN SLUDGE

The screening of 109 samples was carried out using United States Environmental Protection Agency (USEPA) extraction methods, namely Separatory Funnel Liquid-Liquid Extraction (section 3.2.2) and Soxhlet Extraction (section 3.2.1) for liquid and solid samples respectively. The extraction was followed by clean-up using USEPA approved methods (section 3.4) and analysis of the extracts using USEPA-based gas chromatography methods (section 3.5). This section reports the summary of the finds, while the raw data is compiled in the appendix.

4.1.1   Provincial Results

The results obtained from the individual wastewater treatment plants (WWTPs) have been summarized by province and the individual results are compiled in Volume 2 of this document. Volume 2 gives an indication on the type of organic compounds that were identified in various sewage sludges. The numbers in the table represent the number of times the compound was detected in the different sewage plants within a province. The compounds have been grouped according to major functional group or properties. "Identification" is based on the results of gas chromatography coupled with mass spectrometric detection (GC-MS) (section 3.5.1) and a compound was "identified" if the experimentally determined mass spectrum matched the library mass spectrum with a quality match of 80% or above.

To simplify the picture, the information in Volume 2 was further compressed to give Table 4-1 (below). Included in the final column is the number of different organic compounds within the group that were detected. This table summarises the number of times the organic compounds within that group were detected in all the WWTPs within the nine provinces of South Africa.

It should be noted that Mpumalanga province has no entries in the table since none of the organic compounds detected in the two samples were detected at a quality match of 80% or above.

Table 4-1: Summary of the organic compounds detected in the nine South African provinces.

Organic Compounds	Number of Occurrences by Province									
	GP (23 WWTPs)	LP (7 WWTPs)	NWP (7 WWTPs)	MP* (2 WWTPs)	FSP (5 WWTPs)	KZNP (11 WWTPs)	ECP (4 WWTPs)	NCP (4 WWTPs)	WCP (15 WWTPs)	No. of different compounds
Phenols	38	4	5		4	4	6	4	18	15
Pesticides	1				1					2
PAHs	55	8	1		1	14	8	1	12	48
Phthalates	7	7			1				5	3
PCBs	5					1				3
Furans	7	1	1			1		2		9
Amines	24	6	4		2	13	3	4	11	17
Aldehydes	36	4	2			6	2	2	9	12
Esters	83	20	11		3	21	3	8	25	36
Acids	235	66	41		11	58	18	27	164	105
Chlorinated Hydrocarbons	10	4	2		4	8		4	6	16
Alcohols	54	9	12		1	13	6	1	40	58
Hydrocarbons	526	82	97		15	181	41	49	200	249
Others	180	57	19		13	32	8	14	64	139

* *Organic compounds identified in two Mpumalanga sewage works were below the 80% confidence limit, hence are not shown.*

WTTPs	Wastewater Treatment Plants
GP	Gauteng Province
LP	Limpopo Province
NWP	North-West Province
MP	Mpumalanga Province
FSP	Free State Province
KZNP	KwaZulu-Natal Province
ECP	Eastern Cape Province
NCP	Northern Cape Province
WCP	Western Cape Province

The number of occurrence indicated in Table 4.1 indicates the different compounds per functional group that were detected in each province. Since these results were generated for the purpose of the screening exercise in order to guide the selection of compounds worth quantifying, detail information with respect to the individual compounds have not been included in Table 4.1. To identify the specific compounds in each functional group the reader should look at the raw data in the appendix. In order to discuss the results obtained, these will be considered according to functional group or function.

- **Phenols**

A total of fifteen different phenols were detected countrywide, while only two pesticides were identified. The number of PAHs that were scattered across the country was 48 in total. Of these compounds the most common phenols (*i.e.* compounds found in more than five provinces) were 2,6-bis(1,1-dimethylethyl)-4-methyl-phenol, p-cresol and nonylphenol. In general the groups of compounds found are similar to those that have been reported in European countries even though the individual contaminants were not the same (Langenkamp & Pärt, 2001; EU, 2000; CSHPF, 1997).

Gauteng province (GP) samples were the most contaminated with phenolic compounds as they appeared 38 times in sewage works, followed by the Western Cape with an occurrence of 18. These two provinces were followed by the North-West and Eastern Cape each with a frequency of five, lastly Limpopo, Free State and Northern Cape where phenols appeared four times in each province. Only one sample from the Eastern Cape was contaminated with a chlorinated phenol, triclosalan-5-chloro-2-(2,4-dichlorophenoxy)-phenol.

In addition, the results show that a significant number of sewage treatment plants generate sludge polluted with p-cresol, followed by nonylphenol and 2,6-bis(1,1-dimethylethyl)-4-methyl-phenol respectively. Para-cresol (p-cresol) was detected in all provinces except in Mpumalanga, North-West and Free State provinces. The province with the highest occurrence was Gauteng (14) followed by Western Cape (6), Limpopo (3) and KZN as well as Eastern Cape each with an occurrence of one. The other phenols were detected in few sewage sludges and at a lower number of occurrence.

- **Pesticides**

Two types of pesticide, namely epoxyheptachlor and 2,4,6-trimethlylindane were detected in Free State and Gauteng provinces respectively. The epoxyheptachlor or heptachlor epoxide, is a metabolic product of heptachlor while trimethyllindane is a derivative of Lindane. These were found in one sludge sample in each of the two provinces. The GC-MS confidence limit for these pesticides was 91 and 80%

respectively. The target pesticides that are listed in the guideline were not found. The reason for their absence is explained in Table 4-2. Most of these compounds are banned or their use is severely restricted.

Table 4-2: **The Pesticides and the year in which they were restricted and/or banned in South Africa (WRC, 1997).**

Pesticides	State of the Pollutant (WRC Project No. K5/1128)
Aldrin	Banned in 1992
Chlordane	Restricted to stem treatment of citrus and vineyards as from 1993
DDT	Banned in 1983 except for the control of malaria by government
Dieldrin	Banned in 1983
Heptachlor	Registration withdrawn in 1976
Hexachlorobenzene	Banned in 1983 (DEAT)
Gamma-BHC (lindane)	Registration withdrawn in 1971. But is used in some shampoos.

- **PAHs**

PAHs were detected in high occurrence in all provinces except in Mpumalanga. Unlike phenols there was no specific PAH that was common to all or most provinces at a high number of occurrence. There were many different PAHs identified in most sludge samples with Gauteng having the highest occurrence (55) followed by KZN (14), Western Cape (12), Limpopo (8), Eastern Cape (8), North-West (1), Free State (1) and Northern Cape (1).

There were forty-eight different PAHs that were identified by the GC-MS instrument. Fluorene was the most common among all the detected PAHs as it appeared five times in Gauteng and was twice in KZN and the Western Cape provinces. Other PAHs that were common in several provinces were anthracene and fluoranthene as they appeared in four provinces while decahydro-2-methylnaphthalene, 2,6-dimethylnaphthalene, 1-methyl-2-(2-methyl-3-butenyl)naphthalene and phenanthrene appeared in three provinces. The rest of the PAHs appeared once or twice in all the nine provinces. A significant number of PAHs appeared once in most provinces and a handful had an occurrence of two or three.

- **Phthalates**

Studies carried in some European countries have shown that phthalates (*i.e.* di-(2-ethylhexyl)phthalates) (table 1-4, EU, 2000) were common in most sewage sludges.

The same was also observed in some of the South African sewage sludge samples as di-(2-ethylhexyl)-phthalates (DEHP) was among the phthalates detected. Gauteng and Limpopo province both have the same number of occurrence (7) followed by the Western Cape (5) and Free State (1). There were no phthalates in the other provinces.

There were two different phthalate compounds that were identified, namely: di-(2-ethylhexyl)phthalate (DEHP) and diethyl phthalate. The most commonly detected of these compounds was di-(2-ethylhexyl)phthalate as it has the highest occurrence in Gauteng (4) and it appeared in four provinces. Diethyl phthalate was detected twice in some the sludge samples collected in the Gauteng area. DEHP has been classified as a potentially toxic compound and the maximum content that is allowed in sewage ranges from 50-100 mg/kg dry weight (dw) (EU, 2000). The presence of phthalates in these sewage sludges could be as a result of their employment as plasticisers, and their use in paints, lacquers, glues and inks (Langenkamp and Pärt, 2001).

- **PCBs**

Three types of PCBs that were identified by the GC-MS appeared in Gauteng and only one in KZN province. The scarcity of PCBs, especially heavily chlorinated PCBs, might be because the use of PCBs in South Africa is relatively low. However, there is no restriction on the application of PCBs in SA since they are still used in transformers by the industries even though they have been identified as persistent organic pollutants POPs (DEAT).

- **Furans**

Several furans were observed in some of the sewage sludge samples. All nine furans appeared only once except 2-methyl-dibenzofuran which was detected twice. The only polychlorinated dibenzofuran (PCDF), namely 1,2,3,4,6,7,8-heptachlorodibenzofuran, was found in only one sample (from Gauteng). In the case of the sewage sludge significantly contaminated with 1,2,3,4,6,7,8-heptachlorodibenzofuran it would advisable not to apply the sewage sludge on land, especially that used for agricultural purposes. This is because the PCDFs are known to accumulate in soils treated with sludge and it takes several years (2-10 years) for half the concentration to be degraded in soil (McLachlan & Reissinger, 1990;

McLachlan et al., 1996; Eljarrat et al., 1997). From the results obtained in this study, it can be said that the more toxic form of furans and dioxins (*i.e.* PCDDs and PCDFs) are virtually absent from the South African sewage sludges.

- **Amines and amides**

Amines, aldehydes and esters are the third group of organic compounds that were identified in South African sewage sludges. Each province, except Mpumalanga, had some sludge samples contaminated with amines and a total of seventeen different amines were identified. Gauteng recorded the highest occurrence (24) followed by KZN (13), Western Cape (11), Limpopo (6), North-West (4), Northern Cape (4), Eastern Cape (3) and Free State (2). N,N-dibutyl-1-butanamine (tributylamine) was the only amine that was detected all eight provinces appearing seven times in KZN and the Western Cape provinces. In the other provinces the recorded frequencies were Gauteng (6), North-West (4), Eastern Cape (3), Northern Cape (3), Limpopo (1) and Free State (1).

Within the Gauteng WWTPs (Z)-9-octadecenamide was detected at the same number of occurrence (6) as tributylamine but appeared only once in the other two provinces. The other amide that was detected more than once was n-tetradecanamide which appeared three times and twice in Gauteng and Limpopo respectively. The remaining amides appeared only once or were absent in the eight provinces.

The amines in sludge might have originated from dyes, which are capable of generating amines. The amines are present in dyes as contaminants or as degradation products in cases where the dyes are stored in light or high temperature environment (Textile Working Group, http://www.emcentre.com/textile/HealthSafety.htm).

- **Aldehydes**

There were several different types of aldehydes (12) that were detected in the numerous wastewater treatment plants around the country. In each province there were sample(s) that were contaminated with these compounds and Gauteng recorded the highest number (36) of occurrence. The number of times that the aldehydes were detected in other provinces is: Western Cape (9), KZN (6), Limpopo (4) while the

number of occurrence in North-West, Eastern Cape and Northern Cape was two in each Province. There was no record of aldehydes in the Free State and Mpumalanga provinces. Stearaldehyde (n-octadecanal) was the most common aldehyde within the provinces, as it appeared in six provinces followed by tetradecanal, which was observed in five provinces.

The source of aldehydes in sewage sludge can be as a result of the reaction of some of the products of incomplete combustion (*i.e.* paraffins, olefins, aromatics and acetylene) with other compounds (Lue-Hing et al., 1992). Aldehydes are also produced during the biodegradation of linear alkyl benzenesulfonates (LAS) which are widely used as detergents (ICON, 2001)

- **Esters**

A significant number of different esters were detected in eight provinces where a total of seventy-two esters were identified. Again Gauteng (occurrence of 83) had the greatest number of esters identified in its sludge samples followed by the Western Cape with occurrence of twenty-five. The number of occurrence recorded in each of the other provinces is as follows: KZN (21), Limpopo (20), North-West (11), Northern Cape (8), Free State (3) and Eastern Cape (3). The sludge samples in the Free State and Eastern Cape were the least contaminated with esters relative to the other provinces.

- **Acids**

Acidic compounds were among the group of organic contaminants that were common in almost all the sewage sludge samples and a total of 105 different acids were identified. The results have shown that Gauteng samples contained most of the acids, an occurrence of 235 being recorded. The province that recorded the highest occurrence after Gauteng was the Western Cape (164) followed by Limpopo (66), KZN (58), North-West (41), Northern Cape (27), Eastern Cape (18) and Free State (11). There were 56 different kinds of the acidic compounds that were identified in general. There were several acids that appeared in all the provinces except Mpumalanga, namely dodecanoic, pentadecanoic, hexadecanoic, heptadecanoic, and octadecanoic acids.

The presence of significant quantities of acids, mainly fatty acids, could be as a result of inefficient removal of oily and greasy materials during the sewage sludge treatment process. Since the purpose of adding lime during the sewage sludge treatment process is to neutralize the acids, it might be that insufficient lime was added such that large quantities of acids were still present in sludge after the treatment process has been completed (Showalter, 2001). The potential sources of these highly hydrophobic long chain fatty acids and esters are faeces, soaps and food oils (ICON, 2001). Due to their hydrophobic nature these compounds tend to adsorb on the sewage sludge matrix rather than dissolve in the wastewater effluent. Hence it is not surprising that various and significant quantities of long chain esters and acids were observed in the solid product of WWTPs.

- **Chlorinated Hydrocarbons**

There were 16 chlorinated hydrocarbons (CHs) found in the collected sludge samples. As usual Gauteng had the highest occurrence (10) followed by KZN (8), Western Cape (6), Limpopo (4), Free State (4), Northern Cape (4) and North-West (4). 1-Chlorooctadecane is considered the most common CH because it was detected in four provinces at relatively higher frequencies of occurrence compared to other CHs. Dichlorobenzene (DCBs), 1,2,4-trichlorobenzene (1,2,4-TCB) and hexachlorobenzene (HCB) have been categorized by organizations such as the United States Environmental Protection Agency (USEPA) and the European Commission (EC) as priority pollutants – of these, only dichlorobenzene was detected and that only in two samples.

- **Alcohols**

A total of 48 different alcoholic compounds were identified. Samples with the most alcoholic compounds were those from Gauteng where an occurrence of 54 was recorded, followed by the Western Cape with forty. The occurrence from other provinces was as follow: KZN (13), North-West (12), Limpopo (9), Eastern Cape (6), Free State (1) and Northern Cape (1). The two most common alcohols were dihydrocholesterol and 2-methyl-1-hexadecanol, which appeared in five provinces. A

considerable number of alcohols appeared once or twice in each province while a handful was detected more than twice.

The majority of alcoholic compounds can be found in solvents such as car shampoos and degreasing products, household cleaners a well as degreasing agents from vehicle maintenance and production (ICON, 2001).

- **Hydrocarbons**

Generally hydrocarbons were the most frequently detected organic compounds in the eight provinces as a total of 249 different kinds of hydrocarbons were identified.

Gauteng province recorded the highest occurrence of 526 followed by the Western Cape (200), KZN (181), North-West (97), Limpopo (82), Northern Cape (49), Eastern Cape (41) and Free State (15). Docosane was the only hydrocarbon that appeared in the eight provinces. However, there were several compounds that appeared in seven provinces namely (1-butylheptyl)benzene, 2-methyldecane, 1-nonadecene, n-octadecane, (1-pentyloctyl)benzene, (1-propylnonyl)benzene, 2,6,10,14-tetranethylhexadecane, n-tridecane and n-undecane.

It has been reported that urban rainfall runoff contains several hydrocarbons especially those derived from petrol, fuel oils and lubricants (ICON, 2001). Generally, large proportions (*i.e.* 70-75 %) of these compounds tend to be strongly adsorbed to suspended solid particles (Luker & Montague, 1994). Probably because of the hydrophobic nature of the hydrocarbons a considerable proportion of various hydrocarbons were detected in most of the sewage sludge samples. Ultimately large amounts of hydrocarbons in the environment are eliminated slowly by a mixture of microbial and oxidative processes (ICON, 2001).

- **Others**

There were 139 different compounds identified in the sludges that are classified as "others". The highest occurrence was observed in samples collected in Gauteng which was 180 followed by the Western Cape with an occurrence of 64. These compounds also appeared in the other six provinces, for instance Limpopo (57), KZN (32), North

West (19), Northern Cape (14), Free State (13) and Eastern Cape (8). Galaxolide 1 and 2 were the most common compounds in this group since they appeared in eight provinces.

Galaxolides, also known as synthetic musks, are found in industrial detergents (ICON, 2001). The results indicate that these compounds are commonly used in industrial detergents around the country.

Ketol (indole) appeared in five provinces and was detected at greatest occurrence in Gauteng (8) and the Western Cape (6). 3-Methyl-1H-indole (skatole) also appeared in five provinces but at lower frequencies relative to ketol and coprostan-3-one. Oxacycloheptadec-8-en-2-one appeared in four provinces. None of these compounds is harmful and their presence in domestic sewage sludge is not surprising – indole and skatole are foul-smelling compounds found in faeces and coprostan-3-one (which is derived from cholesterol) is a faecal steroid that has been used as a biomarker for sewage contamination (Kawakami & Montone, 2002).

There were another two compounds that appeared in seven provinces namely dodecamethyl-cyclosiloxane and hexamethylcyclotrisiloxane. The presence of siloxanes show that these non-volatile silicone polymers might be employed as lubricants, electrical insulators and antifoams in industrial and consumer products (ICON, 2001). Due to their hydrophobic nature they tend to be adsorbed onto the sludge particles and are fairly persistent in the soil as the degradation process ranges from months to years. Nonetheless siloxanes do not display considerable environmental toxicity nor do they bioaccumulate.

- **Summary**

Volatile organic compounds are not expected to be found in sewage sludge since they are eliminated from the wastewater during the aeration process (Lue-Hing et al., 1992). While organic compounds with higher molecular weight are generally removed by sedimentation and adsorption processes. There are certain organics that have shown insignificant or no degradation during the treatment process such as PCBs and most organochlorine pesticides (*i.e.* aldrin, chlordane, DDT, endrin and

heptachlor). From this screening study it can be said that the SA sewage sludges do not contain the target pesticides recommended in the guideline.

In addition, it can be said that biodegradable compounds are more likely to be broken down by soil bacteria once the sewage sludge is applied on land, disposed or left to dry in drying beds.

4.1.2   National Results

The different types of organic compounds detected across the country were counted and the results are recorded according to functional group in Table 4-3. The purpose of this was to determine which province recorded the highest number of various organics especially those that are of environmental concern (*i.e.* phenols, pesticides, PAHs).

Table 4-3:   Different types of organic compounds identified in nine South African provinces.

Organic Compounds	Number of Different Organics by Province									
	GP	LP	NWP	FSP	KZNP	ECP	NCP	WCP	MP	Total*
Phenols	11	2	3	3	2	5	3	7		15
Pesticides	1			1						2
PAHs	35	7	1	1	10	8	1	9		48
Phthalates	3	1		1				1		3
PCBs	3				1					3
Furans	4	1	1		1		2			9
Amines	11	5	1	2	7	1	2	5		17
Aldehydes	10	1	1		1	1	1	1		12
Esters	25	10	4	1	6	3	5	9		36
Acids	77	37	20	10	25	14	18	47		105
Chlorinated Hydrocarbons	9	4	2	4	4		2	6		16
Alcohols	33	8	11	1	11	6	1	22		58
Hydrocarbons	173	51	67	36	75	37	32	72		249
Others	85	33	14	13	25	7	11	34		139

*The total column represents the total number of organic compounds within the group that were find to be present in the South African sludge through the screening process.

In general, the samples from Gauteng contained the highest number of different organic compounds in each group. Nevertheless it should be noted that more samples were taken from Gauteng as compared to the other provinces since 23 treatment plants were sampled while in the other provinces a range of 15-2 plants were used in this study. Despite the high number of samples collected from Gauteng individual samples (Appendix C) have shown that most of the contaminated samples, especially with potentially toxic compounds were from this province.

Thus, the actual number of samples does not necessarily determine the number of organic compounds that will be detected in sewage sludge samples. For example, from Limpopo and North-West provinces the same number of samples (7) was collected but the number of compounds in each group are different in most cases except in few cases. In addition, the similar trend can also be observed in the Eastern and Northern Cape results where the same number of samples was taken. Hence it can be said that the source of pollution and the type of sewage treatment technique that is employed in the generation of sludge are the two factors that are likely to determine the type of organic compounds that can be detected in sludges.

Furthermore, the eight provinces recorded a reasonably high number of acids, hydrocarbons and others with Gauteng and Western Cape recording the highest number. There was a relatively low number of different types of organic compounds considered as being potentially toxic (e.g. phenols, pesticides, phthalates, PCBs, furans, chlorinated hydrocarbons) that were identified but a high number of PAHs (35) were detected. On the other hand, organic compounds that are considered less harmful to the environment (*i.e.* hydrocarbons, fatty acids, etc) are abundant. Hence it can be said that the sewage sludges generated in South Africa are more likely to contain the less harmful compounds than the more harmful.

4.2 QUANTIFICATION OF ORGANOCHLORINE PESTICIDES

4.2.1 Reference Sludge

In order to confirm the absence of organochlorine pesticides from sludge, the extraction efficiency and sensitivity of the instrument used for analysis had to be tested. For this reason standard reference sludge was prepared as described in section 3.5.4 by cleaning a sample of Heidelberg sludge. The results show that the cleaning process was successful having removed a considerable amount of the organic compounds in the sludge matrix.

Table 4-4: The number of organic compounds detected in the first and fifth extracts of the Heidelberg sludge sample.

Organic Compounds	First Extract	Fifth Extract
Phenols	1	Not detected
Amines	1	Not detected
Esters	Not detected	Not detected
Acids	7	6
Chlorinated Hydrocarbons	2	Not detected
Alcohols	1	Not detected
Hydrocarbons	22	Not detected
Others	8	Not detected

The results in Table 4-4 show that not all the acidic compounds were removed, as their frequencies in the first and last extracts were seven and six respectively. The remaining organic compounds, which include phenols, amines, esters, aldehydes, chlorinated hydrocarbons, alcohols, hydrocarbons and others, were practically completely removed. It can therefore be concluded that the reference sludge that was prepared for spiking purposes was clean of most organic compounds except the acids. The other deduction from this exercise is that Soxhlet extraction is not very effective in removing these organic acids from sewage sludge.

4.2.2 Extraction efficiency and GC sensitivity

The screening results indicate that the pesticides listed in the South African sludge guidelines (WRC, 1997) were not present in the sludge samples. It was therefore decided to test the sensitivity and the conditions that were selected for GC-MS

analysis. This was done by spiking the reference sludge with six pesticides, namely DDT, lindane, hexahlorobenzene, heptachlor, dieldrin and aldrin at half the concentration recommended in the guideline. The GC-MS was able to identify and quantify all pesticides. The GC was mainly used for the quantification of the target organochlorine pesticides while the GC-MS was employed to confirm the GC results and to quantify the amount of pesticides in the sludge.

The spiked sewage sludge extracts were analysed using GC-MS using the selected ion monitoring (SIM) mode, while the GC was attached to electron capture detector (ECD). Chromatograms obtained using GC-ECD and GC-MS using the SIM mode are shown in Figures 4-1 and 4-2 respectively.
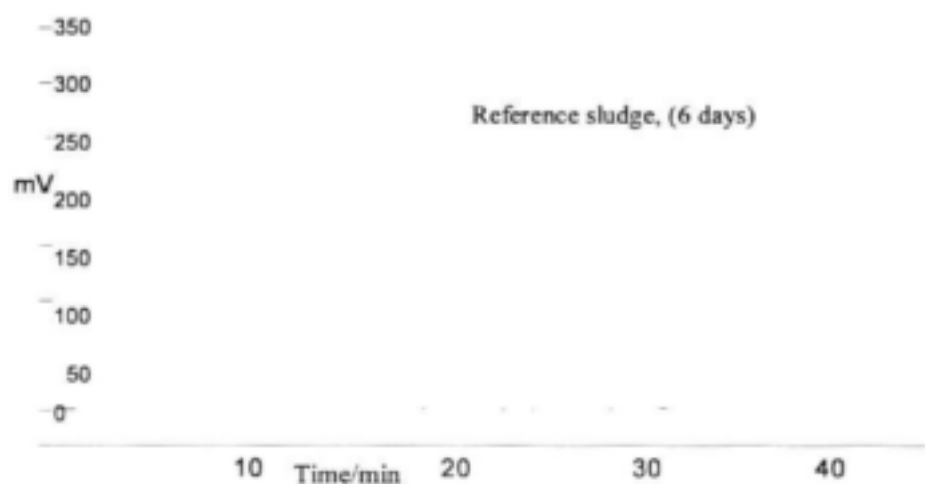
Figure 4-1: GC chromatogram of spiked reference sludge extracted six days after spiking.
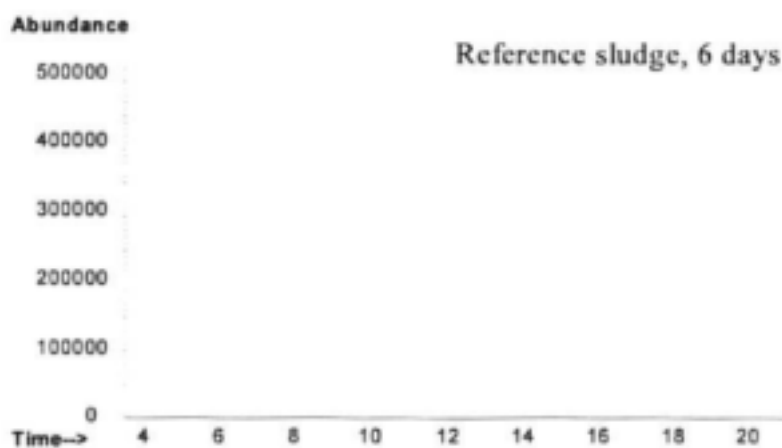
Figure 4-2: GC-MS SIM mode chromatogram of spiked reference sludge extracted six days after spiking.

Using the calibration graph (section 3.5.3) the concentration of each of the six pesticides was determined and the results are recorded in Table 4-5.

Table 4-5:   The amount of pesticides extracted from spiked sludge and the corresponding extraction efficiency.

Pesticide	Mass added (mg)	Concentration added (mg/kg)	Recovered conc. (mg/kg)			% Efficiency		
			6 d	9 d	16 d	6 d	9 d	16 d
HCB	1.89	17.18	7.583	8.816	15.15	44	51	81
Lindane	0.43	3.909	3.101	3.429	3.649	79	88	93
Heptachlor	1.11	10.09	4.499	4.973	8.925	45	49	82
Aldrin	0.29	2.636	1.184	1.442	2.578	45	55	98
Dieldrin	0.41	3.727	1.471	1.668	3.607	39	45	99
DDT	0.43	3.909	1.941	2.205	3.747	50	56	96

The results in table 4-5 show that the recovered concentration and the corresponding extraction efficiency increased with the increase in curing time (i.e. the time delay between spiking of the reference sludge and extraction). The longer the curing period the easier it was to extract the pesticides from the solid particles. The extraction efficiency ranged from as low as 39% six days after spiking to 98% after 16 days. The increase in efficiency can be related to the amount of the moisture in the sample. After 16 days the sample having been left in a closed environment at approximately 23°C, the moisture content is likely to be less than that one after two days. This is the reason why sodium sulfate (Na_2SO_4) is used to dry the sample before extraction is carried out. It is clear that the amount of Na_2SO_4 that was insufficient to extract all the moisture from the sample. The amount of moisture in the sample creates a partition of the target compounds between the aqueous and the organic phase. Since the refluxing temperature is that of organic solvent, it is much lower than that of water. This means that whatever is trapped in the aqueous phase is likely to remain in the sludge accounting for the variation in the extraction efficiency.

To test the sensitivity of the GC-ECD, the hexane was spiked with various concentrations (¼, ½, ⅛, and ⅟₁₆ of the regulatory limit) of six target pesticides. All the peaks were observed except for aldrin.

In addition to testing the extraction efficiency and sensitivity of GC-ECD, it was important to re-analyse the extracted sludge samples using GC-MS in SIM mode. The instrument was calibrated using the calibration standards and the samples re-analysed. The results that were obtained showed that none of the six pesticides were present in the sludge extracts.

It can therefore be deduced that the extraction procedure used has an extraction efficiency of over 80% which means that it is very effective. This is true if the sample is dry or when enough Na_2SO_4 is used to dry the sample. The method is not recommended for very wet samples. The GC-ECD combination is capable of detecting samples having pesticides at levels as low as 0.16 mg/kg (e.g. aldrin).

From this part of the investigation it can be concluded that the non-detection of organochlorine pesticides from sludge samples is due to their absence in the samples and not because the extraction method was inefficient or the GC-ECD was not sensitive enough. Table 4-2 shows that most of these pesticides are either banned or under restricted use (DEAT). This is why it is not strange not to find them in the sludge. The classes of pesticides that have been recorded to be in current use in South Africa are triazines, organometallic compounds, carbamate/thiocarbamate, organophosphates, aniline/acetanilide and organochlorine (DDT – only for the control of malaria by government) (WRC Project No. K6/1128).

4.3   QUANTIFICATION OF p-CRESOL AND NONYLPHENOLS

A total of 13 wastewater plants were selected for the quantification of p-cresol and nonylphenol (5 low (Group B) and 7 high (Group A) metal content sites as reported in WRC Project K5/1283 plus one plant chosen on the basis of the organic content of is sludge). These two organic compounds as well as PAHs were chosen because they were found to be widely spread throughout the different wastewater plants according to the screening results. One extra site was added to the list because it was found to contain a large number of organic contaminants. The selected sites are listed in Table 4-6. The two techniques that were employed for the analysis are GC-FID for

quantification and GC-MS to confirm the identity of compounds detected by the GC-FID.

Table 4-6: List of the WWTPs selected for the quantification of phenols (WWTPs selected from WRC Project K5/1283 based on the lowest (Group A) and highest (Group B) metal content as found by WRC Project K5/1283).

*Group A sites	*Group B sites
KwaZulu Natal Province (KZN/41)	Gauteng Province (Gauteng/1/2)
KwaZulu Natal Province (KZN/75)	Gauteng Province (Gauteng/4)
North West Province (NW54)	Gauteng Province (Gauteng/6)
Western Cape Province (WC/28)	Gauteng Province (Gauteng/15)
Western Cape Province (WC/37)	Gauteng Province(Gauteng/21)
	North West Province (NW/55)
	Western Cape Province (WC/30)
Gauteng Province (Gauteng/22) based on the preliminary organic analysis	

*Names of the WWTP are not given for confidentiality reasons

4.3.1 Quantitative Determination of p-cresol and nonylphenols

The compounds selected for quantification in this study were phenols namely p-cresol and nonylphenols. These were selected based on the outcome of the screening process. Apart from just having been detected in the majority of the sludge samples, these pollutants are known to have detrimental effects on marine and human life (Langenkamp & Pärt, 2001; Lue-Hing et al., 1992).

The samples from both groups were subjected to the quantification of these compounds. The extracts were analysed using GC-FID and the concentrations were determined using the standard calibration graph method. The concentrations of p-cresol and nonylphenols determined are recorded in Table 4-7.

The least contaminated South African sewage sludge samples have relatively low concentrations of p-cresol and nonylphenol, which ranged from 1.67-2.32 mg/kg and 2.36-14.1 mg/kg respectively.

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There is no clear indication from the results that the sludges with the highest level of inorganic pollutants according to WRC project K5/1283 also have the highest level of phenols. The level of pollution is scattered without a definite trend.

Table 4-7: The concentration of phenols as identified in Group A and Group B sewage sludge samples. (Group A & B refers to the lowest and highest metal content as found by WRC Project K5/1283 respectively).

Sample no.	p-Cresol Conc. (mg/kg)	Nonylphenol Conc. (mg/kg)
Group A:		
Sample 28 (WC)	2.32	14.1
Sample 37 (WC)	-	-
Sample 41 (KZN)	1.82	12.2
Sample 54 (NW)	1.67	2.36
Sample 75 (KZN)	-	-
Group B:		
Sample 1 (Gauteng)	5.73	350
Sample 2 (Gauteng)	0.35	203
Sample 4 (Gauteng)	-	0.30
Sample 6 (Gauteng)	-	0.45
Sample 15 (Gauteng)	-	0.15
Sample 21 (Gauteng)	0.50	114
	252	**16.1**
Sample 22 (Gauteng)	1.70	2079
	192	**220**
Sample 30 (WC)	2.57	821
	464	**65**
Sample 55 (NW)		

- The values in boldface are from liquid sludge samples.

Table 4-8: Overview of concentrations of Nonylphenols (+ethoxylates) in Scandavian sewage sludges

Investigations	Number of samples	Range mg/kg dm	Median mg/kg dm	References
Norwegian (1989)	19	25-2298	189	Vigerust, 1989
Swedish (1993)	23	23-171	82	National Swedish Environmental Protection Board, 1995 cit in Paulsrud et al., 2000
Swedish (1989-91)	27	44-7214	825	National Swedish Environmental Protection Board, 1992 cit in Paulsrud et al., 2000
Danish (1995)	20	0.3-67	8	Törslöv et al., 1997
Danish (1993-91)	9	55-537	-	Törslöv et al., 1997

When analysing liquid sludges, the solid and liquid phases were separated using a centrifuge. The results show that 99% of the p-cresol is concentrated in the liquid phase, whereas 90% of the nonylphenols (NP) are trapped in the solid matrix leaving 10% in the liquid phase. It is also noted that liquid sludge contains high concentrations of the two phenols when compared to solid sludge. This finding means that the drying process is very important when looking for these two pollutants. Comparing the concentrations of NP obtained in the current study with the values in Table 4-8 it can be concluded that the range of values found in SA sludges is not very different to the reported data from other countries.

Higher NP concentrations (*i.e.* 330-640 mg/kg dm) have also been recorded in United Kingdom (UK) sewage sludges. These quantities are significantly higher than the EU limit of 20 mg/kg (ICON, 2001). The values found in South African sewage sludges are comparable with those reported for other countries, with most of the solid sludge meeting the EU limit.

A 1996-1997 survey of Norwegian sewage sludge from eight plants has shown that m-/p-cresol concentrations ranged from 0 - 470 mg/kg dm (Paulsrud et al., 2000), while the range in the current study is between 0 and 464 mg/kg dm. Since p-cresol decomposes readily when exposed to aerobic conditions, significant quantities can be removed from heavily contaminated sludge. It is clear from this study that the state of the sludge, whether solid or liquid, will partly determine the concentration of p-cresol and nonylphenols. It can be assumed that a lot of the p-cresol is kept in the wastewater during the sewage sludge treatment process while nonylphenols tend to be adsorbed onto the sludge particles. In general it can be concluded that the highest concentrations of p-cresol and nonylphenols in sludge will be in the liquid and solid phases respectively.

The results show a high concentration of nonylphenols in the anaerobically digested sewage sludges. This is in agreement with the literature information which explains this to be due to their slow degradation during the anaerobic treatment process (Langenkamp & Pärt, 2001). Moreover, it has been found that NPs tend to build-up in

the digested sludge and consequently also in soil treated with NP-contaminated sludge. Hence those sewage sludges that are highly contaminated with nonylphenols pose a potential environmental hazard.

4.4 CONCENTRATIONS OF PAH IN THE INDIVIDUAL SEWAGE WORKS

Polynuclear aromatic hydrocarbons in the sewage sludges were identified using GC-MS and their concentrations were determined using GC analysis as explained in section 3.5.9. The different PAHs that were determined were naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, dibenzo(a,h)anthracene, benzo(g,h,i)perylene, benzo(a)pyrene, and indeno(1,2,3-cd)pyrene. All concentrations are expressed in mg kg^{-1} on a dry mass basis and are tabulated in Table 4-9. 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 (Eliot, 2003) the sum of concentrations for the nine PAHs should not exceed 6 mg kg^{-1}. The nine 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 4-9 it can be seen that out of the 32 samples analysed for PAHs only twelve had 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 large number of industries found within the province and the associated use of coal and other fossil fuels as energy source, thus high contents of PAHs are likely to be present in this province.

The table also includes the sum of the 16 PAHs that were analyzed.

A resent study of 14 sewage works in the UK showed PAH concentrations above the recommended EU limit of 6 mg kg^{-1} (Stevens, 2003). In fact, the concentration in these sewage sludges ranged between 18 and 50 mg kg^{-1}. The most abundant compounds were the lighter PAHs such as fluorene and phenanthrene. However, in

the current study the lower molecular weight PAHs are not the most abundant, the likely reason for this is that the samples taken for this study might have degraded and the PAHs volatilized due to the climate difference between UK and RSA.

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. Table 4-9 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 Guideline (WRC, 1997) 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, which has a concentration of 3.45 mg kg^{-1}.

Table 4-9: Concentrations of PAHs in South African sewage sludge in mg kg^{-1} 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)anthracene, 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 4-9 (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)anthracene, 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.

4.4.1 A summary of PAH content classified according to provinces

The means and standard deviations calculated from the values in Table 4-9 are compiled in Table 4-10. These values are used to compare the level of PAH pollution between the provinces.

Table 4-10: Mean±standard deviation of concentrations of PAHs in mg kg^{-1} by province.

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)anthracene	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	-	-	-

- = compound not detected.

The row in bold refers to the PAH recommended for monitoring by SA Guideline (WRC, 1997).

There is no clear 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 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 4-3, 4-4 and 4-5 respectively.

Note: the dotted line represents the recommended EU limit - see text for details.
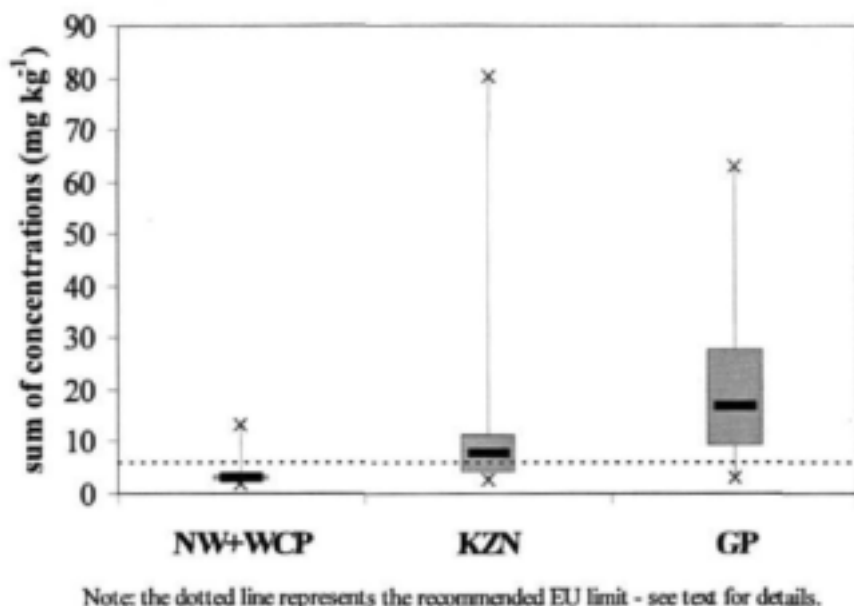
Figure 4-3: **Box and Whisker plot for the sum of 9 priority PAHs by province.**
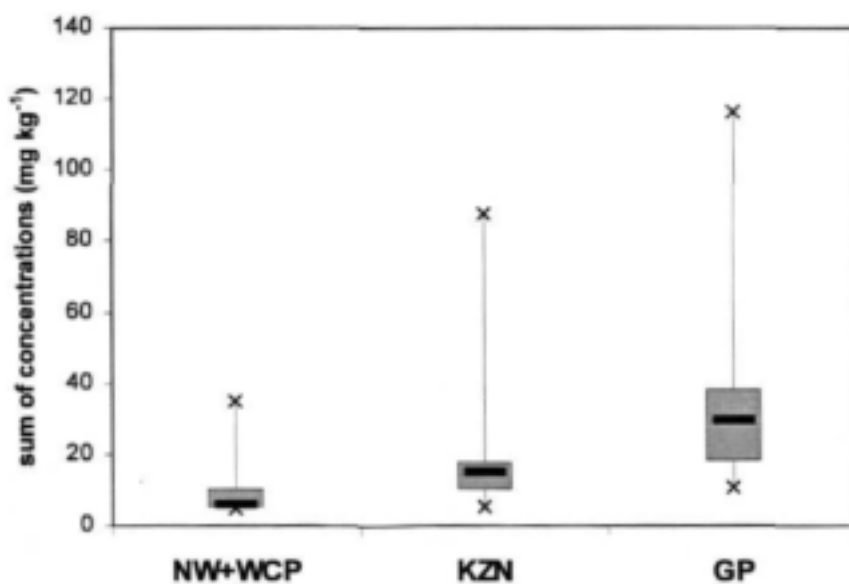
Figure 4-4: **Box and Whisker plot for the sum of 16 PAHs by province.**

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

Figure 4-5: *Box and Whisker plot for benzo(a)pyrene by province.*

The general conclusion from these results is that, overall, the total PAH content 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.

It should be noted that the EU recommended limits are the only limit that could be found in literature. There was also no clear indication as to how these limits were arrived at. It can therefore be assumed that the value is based on a precautionary approach and not scientific bases.

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.

4.4.2   PAHs in South African Sewage sludge

To have a general picture of the sewage sludge within the country, the data in Table 4-10 were combined and average values are shown in Table 4-11. What is noted 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 levels of these pollutants differ a great deal from one sewage works 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 4-11:   National mean ± standard deviation concentrations (mg kg^{-1} dm) for PAHs in South Africa.

Compound	Mean	Median	Range	No. of samples that were below the detection limit
Benzo(b)anthracene	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)anthracene 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 of the PAHs was as follows:

benzo(b)anthracene ~ 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 number 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)anthracene > 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

The trend above is based on median concentrations of those sewage works in which the compounds were detected. Hence 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 the number of appearance. Table 4-12 compares the rankings by occurrence and by concentration for the 16 target PAHs.

Table 4-12: Ranking of PAHs according to the number of occurrence and concentration.

Compound	Rank by occurrence	Rank by National median concentration
Benzo(b)anthracene	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

Table 4-12 shows that there is no significant correlation between median concentrations and number of occurrence trends. The analysis that is relevant is the number 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 pasture-land where PAHs might transfer to and bio-accumulate in grazing animals since these animals can ingest surface soil as they feed (Jones et al., 1979; Wilson et al., 1997; Fries, 1982; Flemming, 1986). 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 (Simonich & Hites, 1992; Wild & Jones, 1992; Wegman et al., 1987; Killian et al., 2001).

4.4.3 Influence of the source and the method of treatment of sewage sludge

To control the pollution that ends up in the wastewater plants it is important to try to ascertain the source of the pollutants. It is for this reason that the data in Table 4-9 were re-analysed 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 number of occurrence as in Table 4.-12 are shown in Table 4-13.

Statistical analysis of the two groups of data using 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 for indeno(1,2,3-cd)pyrene which was only detected in samples from sewage works that received at least 10% of industrial effluent.

Table 4-13: Mean±standard deviation of PAH concentrations (mg kg^{-1} dm) according to the sewage origin, arranged in the order of number of occurrence of appearance.

Compounds	≥ 10% Industrial	≥ 90% Domestic
Benzo(b)anthracene	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	-	-

Note: The compounds shown in boldface are the 9 considered in EU regulations.

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 4-9 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 4-14.

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)anthracene 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 4-14. 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)anthracene, but in this case the digested sludge also has a high concentration. 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 4-14: 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)anthracene	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.

4.4.4 Comparison of the results from the current study with the SA guidelines and guidelines from other countries

The SA guidelines on permissible utilisation and disposal of sewage sludge for organic compounds (WRC, 1997) 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 bar one of the samples that were analysed, the concentration for this compound was below the threshold value. The sludges from 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 guideline 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 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 4-14. 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 the 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 assess our status in comparison to the international community.

Table 4-15: Limit value (mg kg^{-1} dm) for PAHs in various countries

Country	EU 2000 (Eliot, 2003)	Denmark (Leschber, 1997)	Sweden (Langenkamp & Pärt, 2001)	South Africa (WRC, 1997)
Limits*	6	3	3	2.53
Basis	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		Sum of 6 compounds	Benzo(a)pyrene

* These are recommended guideline values.

Making reference to Table 4-9 and using the EU limits in Table 4-15, 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 4-16 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 4-16: Concentrations of PAH in sewage sludge from various countries

Investigation	No. of samples	Range mg/kg dm	Median mg/kg dm
Denmark (1995) (Sum of 18 compounds) (Törslöv et al., 1997)	20	<0.01-1.85	-
Denmark (1993-94) (sum of 18 compounds) (Törslöv et al., 1997)	9	0.42-2.4	-
Norway (Paulsrud et al., 2000)	36	0.7-30	3.9
Sweden (Sum of 6 compounds) (Tideström, 1997)	-	-	1.6
Parts of Germany (sum of 6 compounds) (Sultan & Rahman, 2001)	124	0.4-12.83	-
Part of Germany (Sum of 16 compounds) (Sultan & Rahman, 2001)	88	0.25-16.28	-
South Africa 2004 (sum of 16 compounds) (this study)	34 (32)*	4.72-116.3 (4.72-50.19)	18.31 (17.72)
South Africa 2004 (sum of 9 compounds) (this study)	34 (32)*	1.96-80.8 (1.96-31.7)	10.55 (10.1)

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 show that the sewage sludge produced by South African wastewater treatment plants is highly contaminated with PAHs – judging from the international limits. It is therefore recommended that SA guidelines be reviewed to include more PAHs in its limits, taking into account the most common PAHs.

5   DISCUSSION AND CONCLUSIONS

A comprehensive literature survey looking at different aspects of organic contaminants in sewage sludge is incorporated in this report. It is clear from the data available that plants do not take up most of the organic pollutants. However, a risk of contamination of the food chain exists when sludge is spread directly onto crops that are to be consumed raw or semi-cooked. The major source of human exposure to sludge-borne organic pollutants is through the consumption of animal products such as meat and milk through the bioaccumulation of compounds such as PCDD/Fs, PCBs or PAHs. This is due to the ingestion of soil and sludge by livestock due to the spreading of sludge on the land used for grazing. Currently little is known about the plant uptake of phthalates and nonylphenols, which are present in relatively high levels in sludge.

Included in the literature survey is a list of the most common methods normally used for extraction of organic compounds and the possible methods of analysis. What is noted is that there is no universally accepted and validated analytical method for analysing most of the organic compounds. In addition, data concerning levels of organic pollutants is scarce worldwide. Based on the literature available, the only other country that has carried out a detail analysis of organic pollutants to the level done in this study is USA.

The methods selected for this project were EPA Methods 3510C (Liquid-liquid extraction) and 3540C (Soxhlet extraction) for the aqueous and solid sewage sludge respectively. These two methods were chosen because they are simple, inexpensive and effective. The chosen purification method was the sulfur clean-up process (EPA Method 3660B). This is because sulfur precipitates were observed in most of the concentrated extracts, especially from the solid samples.

The screening for organic pollutants involved a total of 109 samples from 78 sewage works. These samples were extracted using Soxhlet extraction for solids and liquid-liquid extraction for liquid samples. All the extracts were analysed using GC-MS. The identification of the organic compounds was made possible by the use of GC-MS Wiley library. A total of 712 organic compounds were identified in the South African

sewage sludge. These included Phenols, Pesticides, PAHs, Phthalates, PCBs, Furans, Amines, Aldehyde, Esters, Acids, Chlorinated Hydrocarbons, Alcohols, Hydrocarbons and others (all sorts of organic compounds that did not belong to the named categories).

The extraction efficiency and reproducibility using a "clean" sludge matrix was carried out. The results showed that the method chosen for extraction *i.e.* Soxhlet method had an efficiency of over 80% and the results were reproducible

A total of 14 samples were selected for the quantification of p-cresol, nonylphenol and pesticides listed in the current legislation. The results showed negative results for pesticides, confirming that the pesticides listed in the legislation are not the compounds that need to be regulated as far as organic pollutant is concerned. The reasons for the absence of these compounds in the sludge is most likely due to the fact that most of the pesticides listed are banned or their use is severely restricted.

The quantification of p-cresol and nonylphenol, when comparing the liquid and the solid extracts of the liquid sludge, showed that 99% of p-cresol is concentrated in the liquid phase. The opposite is true when looking at the nonylphenol where 90% of it is trapped in the solid matrix leaving 10% in the liquid phase. It is also noted that liquid sludge contains high values for the two organic compounds when compared to the solid sludge.

The analysis for PAHs was based on the number of occurrence in 32 sewage samples collected from KwaZulu-Natal, Gauteng, North West and Western Cape provinces. A total of 16 PAHs were monitored namely: naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, dibenzo(a,h)anthracene, benzo(g,h,i)perylene, benzo(a)pyrene, and indeno(1,2,3-cd)pyrene.

The following conclusions are drawn from the analysis of the work done:

A total of 712 organic compounds were detected in the South African sewage sludge. These were sampled from 78 wastewater treatment plants existing in all nine the provinces.

The scanning and quantification of samples have shown that the organochlorine pesticides as listed in the South African Guideline as the organic compounds that need monitoring were absent from the sludges analysed.

The qualitative and quantitative results have shown that p-cresol, nonylphenol and PAHs are the most common organic pollutants.

The results have also indicated that nonylphenol and p-cresol are more concentrated in solid and aqueous sludge respectively. This means that the spraying of liquid sludge on agricultural land is likely to increase the levels of nonylphenols more than when solid sludge is used.

The PAH analysis has revealed that SA sewage sludge contains a number of PAH compounds at a significant concentration. Using the concentration of the indicator PAH (*i.e.* benzo(a)pyrene), as stipulated in the South African Guideline, is misleading. Using the EU limit, the current results show that most of the sludge being produced in this country exceeds the set limit. In general South Africa sludge fares badly in terms of PAH levels found internationally.

The only province where PCBs were found was Gauteng.

It can also be concluded that no correlation exists between the inorganic and organic contaminants in the sewage sludge. A sludge sample having high level of metal content will not necessarily have a high amount of organic pollutants.

6 RECOMMENDATIONS

- The recommended methods of extraction are EPA Methods 3510C (Separatory Funnel Liquid-Liquid Extraction) for liquid sludge, 3540C (Soxhlet extraction) for solid sludge and EPA Method 3660B for sulfur clean-up.

- There is clear evidence that organochlorine pesticides are not the group of organic pollutants that need to be monitored because of their low level of occurrence. These should therefore be removed from the guideline or their frequency of monitoring be reduced to a minimum.

- The three compounds that require regular monitoring are p-cresol, nonylphenol and PAHs (group of 9 as in the EU 2000 draft).

- The water that is discharged from wastewater plants after separation from the solid material should be analysed for both p-cresol and nonylphenols. There should be a requirement that wastewater plants should hold the water for a minimum of 24 hours to allow the p-cresol to degrade. This is because of the potential danger that they are likely to cause in the water system.

- WWTPs that produce liquid sludge need to monitor the levels of both p-cresol and nonylphenol. Plants producing only solid sludge should determine the concentration of only nonylphenol.

- In order to control levels of nonylphenol, legislation is needed that will end or control the use of nonylphenol ethoxylates (NPE) as well as the discharge and emission of alkylphenolic compounds into the water resources; for example by regulating the use of NPE in detergents and paints.

- The use of benzo(a)pyrene as the indicator PAH should be replaced with the use of the 9 PAHs recommended by the EU.

Therefore, the recommended organic pollutants that should be monitored together with the relevant limits are:

Pollutant	Recommended values / (mg/kg)	
Nonylphenol	20	Based on EU limit
PAH	6*	Based on EU limit

*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.

It must be emphasised that there is a strong argument that each country should develop their own guidelines based on their research findings. Our recommendation of using EU limits is for precautionary purposes until such a time that enough research looking at the rate of degradation of the recommended organic pollutants under South African conditions is done. It is important to note that the types of the pollutants found in the South African sludge are similar to those reported by EU countries.

Further research:

- There is a need for carrying out a five year screening process. This will keep the legislator abreast with the dynamic changes of the restricted compounds and will also bring into light new compounds that may need to be introduced into the restriction category (e.g. LAS or AOX).

- PCBs should be quantified and regularly checked especially where it they have been identified in the current study (*e.g.* Gauteng). This is because of their potential harm to the environment and to man. Also, internationally these compounds have very low limits. The presence of the other listed compounds namely PCDD/F, DEHP, LAS and AOX should be quantified in only a few areas to gauge their level of pollution. There is no need to do regular checks on LAS and AOX compounds because, based on EU limits, their toxicity levels are not so critical.

- In order for South Africa to modify the EU limits that have been recommended, it is important that an investigation into the rate of degradation of the recommended organic pollutants is carried out. This will provide the much needed knowledge of how long these compounds are likely to persist in the soil if sludge is used as a bio-fertilizer.

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Other related WRC reports available:

A metal content survey of South African sewage sludge and an evaluation of analytical methods for their determination in sludge

Snyman HG; Herselman JE; Kasselman G

Current sludge disposal guidelines indicate that even sludges from predominantly domestic wastewater catchments do not meet the heavy metals criteria proposed for unrestricted beneficial reuse (Class D). It is, however, difficult to be categorical about this, firstly because analytical techniques for determining metal concentrations in sludges and soils are not standardised and are expensive, and secondly because the mobilities of metals as they affect groundwater quality and absorption into the food chain are not well understood. This project addresses the first concern, by evaluating different analytical methods for metals in sludges and receiving soils, and by sampling and analysing sludges from 50 wastewater plants in 5 categories (industrial, domestic, waste activated, digested and Class D sludges)..

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