A Survey of Organic Pollutants in the South African Sewage Sludges

By

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ABSTRACT

A comprehensive literature survey looking at different aspects of organic contaminants in sewage sludge is incorporated in the thesis. 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 polychlorinated dibenzo-p-dioxins and –furans (PCDD/Fs), polychlorinated biphenyls (PCBs) or polynuclear aromatic hydrocarbons (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 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.

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 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, Aldehydes, 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 pollutants are concerned. The reasons for this are most likely due to the fact that most of the pesticides listed are banned or their use is severely restricted.

The results for the quantification of *p*-cresol and nonylphenol, when comparing the liquid and the solid extracts of the liquid sludge, show that 99% of p-cresol is concentrated in the liquid phase. The opposite is true when looking at 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 concentrations of both *p*-cresol and nonylphenol when compared to the solid sludge.

DECLARATION

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

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

Signed:

....

M. M. Mamabolo (BSc., BSc. Hons.)

I hereby certify that the above statement is true.

Signed:

....

Prof. D. Jaganyi, MSc, PhD
Supervisor

Pietermaritzburg

February 2006

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All praises, honour and glory belong to GOD of the first, second, third…. chances for without Him I will not be the woman I am today. For I have learned that I need to do all the good I can, in all the ways I can, in all the places I can, at all times possible to all the people I can as long I can because I might be the only bible some people might ever read.
AMEN!!!!

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Abbreviations

α	Selectivity
ABS	Alkylbenzene Sulfonates
AOX	sum of Adsorbable Organic Halogen Compounds
As	Peak Asymmetry factor
ATSDR	Agency for Toxic Substances and Disease Registry
BaP	Benzo [a] pyrene
γ-BHC	Benzene Hexachloride
CB	Chlorobenzene
CHs	Chlorinated Hydrocarbons
CI	Chemical ionization
DAF	Dissolved Air Floatation
DBP	Dibutylphthalate
DDT	Dichlorodiphenyltrichloroethane
DEHP	Di- 2-(ethylhexyl)phthalate
DEP	Diethylphthalate
$\mathbf{d_f}$	film thickness.
DNBP	Di-n-butylphthalate
dw	dry weight
ECD	Electron Capture Detector
ECF	Elemental Chlorine Free
EDTA	Ethylene diaminetetraacetic acid
EI	Electron Ionization
EPA	Environmental Protection Agency
EU	European Union
FAO	Food and Agricultural Organisation
FID	Flame Ionization Detector

GC	Gas chromatogram
GC-ECD	Gas Chromatography Electron Capture Detector
GC-FID	Gas Chromatography Flame Ionization Detector
GC-MS	Gas Chromatography Mass Spectrometer
GLC	Gas-Liquid Chromatogram
GSC	Gas-Solid Chromatogram
H	Plate Height
HCB	Hexachlorobenzene
HCH	Hexachlorocyclohexane
HETP	Height Equivalent to Theoretical Plate
ID	Internal Diameter
K-D	Kuderna Danish
K_d -	distribution constant
L	column length
LABs	Linear alkylbenzenes
LC	Lethal Concentration
LSP	Liquid Stationary Phases
N	Number of theoretical separation steps
MS	Mass Spectrometer
NDMA	N-Nitroso dimethylamine
Neff	Effective plate number
NIOSH	National Institute for Occupational Safety and Health
NP	Nonylphenol
NPE	Nonylphenol(+ethoxylate)
(NPnEO)	4-Nonylphenolpolyethoxylates
PAHs	Polynuclear Aromatic Hydrocarbons
PBBs	Polybrominated Biphenyls
PBDE	Polybrominated Diphenyl Ether (flame retardants)
PSTs	Primary Settling Tanks
PCA	Chlorinated Paraffins
PCBs	Polychlorinated Biphenyls

PCDD/Fs	Polychlorinated Dibenzo-p-Dioxins and -Furans
PCP	Pentachlorophenol
PVC	Polyvinyl Chloride
r	radius of the column
RBC	Rotating Biological Contactors
Rs	Resolution factor
SA	South Africa
SIM	Single Ion Monitoring
SST	Secondary Settling Tank
STP	Sewage Treatment Plants
TBA	Tetrabutylammonium
TBT	Tributyltin
TBTO	Bis-tributyltin oxide
TCE	Trichloroethylene
TEF	Toxicity Equivalency Factor
THM	Trihalomethanes
TOC	Total Organic Carbon
t_M	gas hold-up time
t'_R	retention time for a peak of a non-retained component
t_W	peak width at the base of the peak
$t_{W1/2}$	width at half the peak height
$\bar{u}$	average linear velocity of the mobile phase.
USEPA	United States Environmental Protection Agency
VOCs	Volatile Organic Chemicals
$W_{0.6065h}$	peak-width at the point of inflection
$W_{0.5h}$	peak-width at half peak-height
W_B	peak-width at the peak base
WRC	Water Research Commission
WWTPs	Waste Water Treatment Plants
WWWs	Wastewater Works

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CHAPTER 1

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1. Literature Review

1.1 Introduction

The natural growth of population and the increase in standard of living has resulted in a constant increase in the quantities of solid waste generated in residential areas. Sewage sludge is mainly a by-product of the wastewater treatment plants' (WWTPs) cleaning process, which takes place after primary and secondary treatment processes. There are various sources that are responsible for the organic pollutants found in wastewater, catchments *viz.* human excretion products, household disposal and fossil fuel spillages. Sewage sludge is made up of highly hazardous components including pathogens (i.e. viruses, bacteria, protozoa, eggs of parasitic worms), toxic organic substances and heavy metals (Ross *et.al.*, 1992).

Modern wastewater treatment plants employ numerous processes, which are capable of reducing the content of organic pollutants, namely: volatilisation, sorption onto the surfaces of sewage sludge particles and/or association with fats and oils, biological as well as chemical breakdown (Galil & Yaacov, 2001). The stages of collection, transportation, treatment and removal of solid waste have resulted in a growing demand for resources, space, energy, labour as well as money.

The ultimate disposal of sewage sludge includes application on agricultural land, 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). Over the long term, continuing 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 spreading of sewage sludge on agricultural land is more valuable to the soil because the sludge contains a significant amount of organic matter and plant nutrients (Galil & Yaacov, 2001). Although sewage sludge has been employed as soil conditioner since the 1980's, this approach is inexpensive but environmentally doubtful since sludges do contain high amount of potentially hazardous compounds (*i.e.* organic and inorganic pollutants). Many western countries dispose sludge mainly by spreading it on the agricultural land. Most of European Union (EU) countries apply more than 30% of the total sludge produced on agricultural land (Galil & Yaaacov, 2001).

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. Due to the presence of toxic organic substances and heavy metals, the long-term benefits of application of sewage sludge to land are limited.

The terminology used in this thesis is based on 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 the health and environmental hazards when it is used on land.

Wastewater Treatment: Plants	A facility that treats sewage from the a community; usually primary and secondary treatment are included (Lemley *et al.*, 1992).

1.2 Production and Treatment of Sewage Sludge

The aim of sewage treatment is to produce a final effluent suitable for discharge to the selected receiving water and thickened sludge with reduced hazardous microbial organisms, nuisance from odour (Bruce & Davis, 1989). The volume of sludge generated is reduced by removing water resulting in the formation of thickened sludge, which reduce sludge transportation costs from wastewater treatment plants (WWTPs) to disposal areas. The extent of sludge treatment usually depends on the final use/disposal option selected such as agricultural land, landfills and land reclamation.

The wastewater treatment process involves preliminary screening, which remove larger floating and suspended materials such as rags and litter. This process is followed by primary sedimentation where approximately 55% of the suspended solids settle out and are concentrated into primary sludge. Primary settlement produces the majority (60-75%) of the final sewage sludge produced at a treatment works. The wastewater may then undergo secondary (biological) treatment, usually consisting of a percolating filter or activated sludge treatment with further settling of sludge, from which secondary sewage sludge is produced. In some cases, a further tertiary treatment is required to treat the effluent prior to final discharge.

As more stricter water quality legislation is being enforced on water and sewage treatment across Europe, more energy intensive processes are increasingly being used (Zakkhour, *et al.*, 2000). These processes are capable of eliminating large quantities of contaminants, resulting in the production of enormous sludge quantities, which require treatment and disposal, thereby further increasing the energy consumption. Due to these conditions, it is estimated that the amount of sewage sludge generated will rise by 36% from 2000-2005 to approximately 1.5 million tonnes per year in England (DETR, 1998). At the same time the enforcement of stricter standards on the quality of biosolids applied to agricultural land is expected to further increase power consumption in these operations (ADAS, 2001). The term "biosolids" has been used to designate sludge that meets the United States Environmental Protection Agency (USEPA's) standards for land application (Lue-Hing *et al.*, 1992).

1.2.1 A typical South African Wastewater Treatment Plant

This study investigated sludges from all types of wastewater treatment plants (WWTPs) in South Africa. Umgeni Water is one of South Africa's largest wastewater plant, which operates three wastewater works (WWWs) and twelve portable water treatment plants. The principal objective of these WWWs is to clean the domestic and industrial wastewater with the intention of returning the cleaned water safely to the rivers. Darvil wastewater treatment plant is one of Umgeni's works treating mainly domestic sewage and to a certain extent industrial waste from the city of Pietermaritzburg in KwaZulu-Natal province. A pictorial description of Darvil wastewater treatment plant is shown in Figure 1-1.

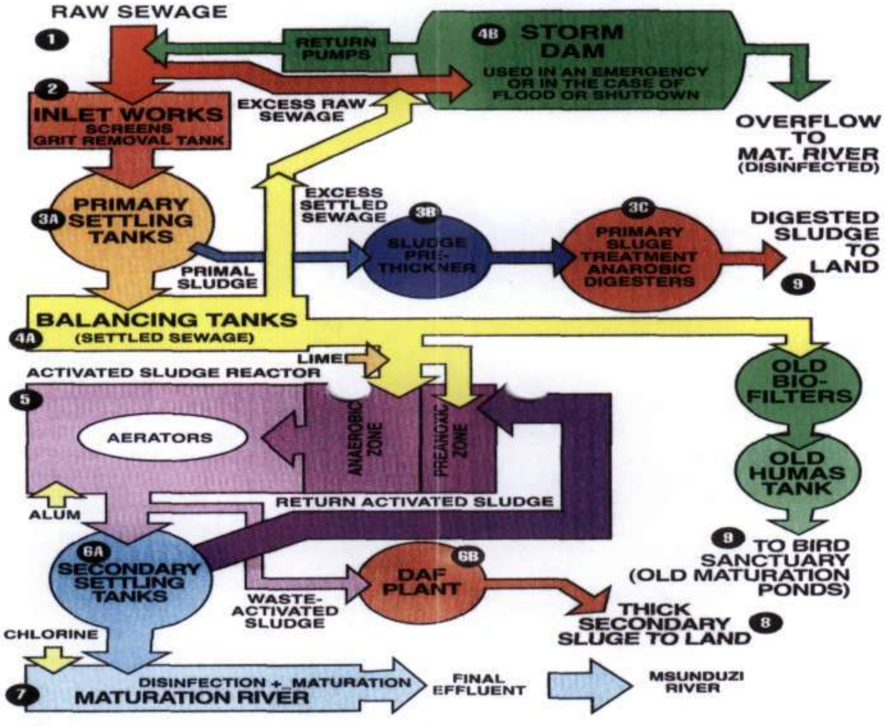


Figure 1-1 A diagram representing Darvil wastewater treatment process.

It is estimated that on average each individual in Pietermaritzburg generates wastewater ranging from 80-250 litres daily, which is introduced into the plant through the sewer outfall **(1)** (Umgeni Water). The sewer is capable of holding approximately 330 million litres of wastewater each day and has 1.2 m diameter. The wastewater treatment process starts at the inlet works **(2)**, whereby materials over 13 mm diameter are eliminated as the raw sewage flows through channels fitted with mechanically, raked screens. It is at this stage that the majority of non-biodegradable coarse solids are removed, permitting rough suspended particles to settle (Carlsson, 2003). Thereafter, heavier sand and grit particles that have settled at the bottom centre of the tanks are pumped out and removed in mechanical degritters.

Following the removal of sand and grit, the raw sewage is introduced into a distribution box then transferred into primary settling tanks (PSTs) **(3A)**, where sludge particles settle at the bottom. The settled raw or primary sludge is then removed from the bottom of PSTs and directed to the pre-thickener **(3B)**. The raw sludge is estimated to contain 30% of the total organic weight (Umgeni Water). At the same time the overflow from the PSTs is drawn into the balancing tank **(4A)**. Thereafter the effluent is transported to the anaerobic digesters for further treatment.

In the pre-thickener, the raw sludge is hardened and fermented by a natural process. This process involves the use of a group of microorganisms that live in clusters and these microorganisms act as sweeping filters. The removal of water content in sludge material significantly reduces the volume and thickens the sludge. This process discharges fatty acids into the supernatant, which is removed from the sludge in the pre-thickener and then returned to the settled sewage since it aids in the elimination of phosphates. At regular intervals the thickened sludge is fed to primary sludge treatment anaerobic digesters **(3C)** heated to a temperature of approximately 36 °C. The sludge is left in these digesters for 30 to 40 days, where the organic waste is transformed into methane gas, carbon dioxide and water by means of natural biodegradation. The anaerobic conditions take place in the absence of air or oxygen and it is capable of reducing the amount of volatile solids by more that 38% (Lue-Hing *et al.*, 1992). The purpose of heating sludge directly or indirectly with hot gases at a temperature of about 36 °C is to dry the sludge such that the moisture is decreased by 10 % or less.

The main purpose of the balancing tank (**4A**) is to trap the inflow of sewage, which occurs roughly from 08h00 to 14h00 daily. It is also used to store the settled sewage and pump it out in a regulated pattern to the activated process. In cases of emergencies (*i.e.* heavy rains, floods and shutdowns) sewage sludge is pumped into the stormwater attenuation dam (**4B**). This dam protects the river from pollution by redirecting the raw sewage from the inlet works and also stores and captures the overflow from the balancing tank. The contents of the dam are pumped back to the works for treatment once the normal flow conditions have been restored.

The settled sewage is transferred from the balancing tank to the activated sludge reactor (**5**) via pumps, where a natural process destroys most of the fine particles and organic contaminants. As a result of this process a clear effluent is generated and sometimes chemicals like lime and alum are added to help in the flocculation. Alum and lime are flocculating agents, which aid in the sedimentation of colloidal and finer suspended particles (Carlsson, 2003). In addition, lime is used to stabilise the effluent such that the corrosion and scaling of the distribution appliances is kept to a minimum. Phosphate and nitrogen are eliminated with the aid of supernatant as the sewage pass through anaerobic zone.

The pH of sludge is kept at 12 or more by the addition of lime in order to kill or inactivate pathogens, provided that sufficient contact time is allowed (Lue-Hing *et al.*, 1992). Generally there is no or insignificant deposition taking place and irritating smell associated with the release of gases as a result of biological activities is absent from sludge that has been appropriately stabilized. The stabilized sludge contains calcium, nitrogen and valuable organic matter, hence it is beneficial to agricultural land. In addition lime stabilization is user-friendly, safer and inexpensive as it restricts the movement of certain metallic ions in sludge, virtually making them unavailable for intake by plants (Lue-Hing *et al.*, 1992).

The lime stabilization is most suitable and practical to small wastewater treatment plants, which are allowed to dispose sludge on an agricultural land or landfill (Carlsson, 2003). Nevertheless, this process results in the increase in the weight of solid particles, relative to digestion processes, due to the precipitation of calcium carbonate, thereby making the disposal and transportation of sludge expensive as a result of the increased sludge load.

As the living organisms within the sludge increase the volume of the activated sludge, the unwanted sludge is removed as waste-activated sludge. The sludge left in the reactors is recycled and used as substrate for micro-organisms for about eight days. It takes ten hours for the treated effluent to pass through the aerators. The treated effluent is transported to the secondary settling tank (SST) **(6A)** where it is removed from the activated sludge. Subsequently the treated effluent flows into the maturation river **(7)** and large quantities of activated sludge are pumped from the bottom of the tanks to the activated sludge reactor. The waste-activated sludge is thickened by combining it with water saturated with air generated under pressure in the dissolved air flotation (DAF) **(6B)** plant, after its passage through fine screens. At this treatment step, approximately 10% of the original water content is left in the thickened sludge. Then thickened sludge together with the primary sludge from the anaerobic digesters is pumped onto the land **(8)** for disposal.

The final process before pumping treated water into rivers is chemical disinfection with disinfection agents such as chlorine (Carlsson, 2003). Chlorination averts any potential discharge of pathogenic bacteria and viruses into the river by destroying them. These organisms can trigger different types of waterborne gastro-intestinal diseases such as diarrhoea, cholera and typhoid fever.

1.3 The Sludge Types

The sludge meeting South African standards for land disposal is categorized as Class C and D (WRC, 1997). Basically Class C sludge has been treated such that the pathogen content is reduced. On the other hand pathogens content in Class D sludge has been significantly reduced relative to those in Class C and this sludge can be applied on land without restrictions. In addition, Class D sludge can be employed with or without the addition of plant nutrients or other materials and must be registered in terms of Act 36 of 1947 in case it is used for agricultural purposes. The Class A and B sludges are considered environmentally undesirable because they tend to cause uncomfortable smell and high rate of fly breeding. In addition they are capable of transferring pathogens to humans and the environment (Snyman *et al.* 2000). The classification of South African sewage sludges is represented in Table 1-1.

Table 1-1 **The classification of sewage sludge as shown in the South African Water Research Commission report (WRC, 1997).**

Type of Sewage Sludge	Treatment	Characteristics
A	-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.
B	-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.
C	-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.
D	-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. -User must be informed about the moisture and nitrogen (N), Phosphorus (P) and potassium (K) content. -User must be warned that not more than 8t/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.

1.4 Organic Contaminants and their Sources in Sewage Sludge

A literature review consisting of 900 papers published between 1977 to 1992 revealed that German sewage sludges did consist of 332 organic compounds (Drescher-Kaden *et al.*, 1992). Some of these compounds are known or suspected to have toxic effects, 42 of them 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 from urban origin where the highest and the lowest values were found. But in general the residues in rural plants were found to be slightly lower, 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.

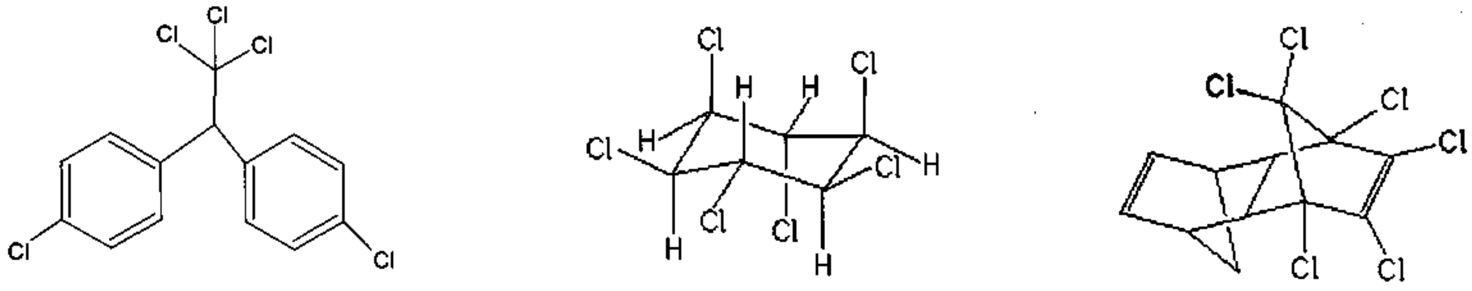
1.4.1 Organochlorine Pesticides

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). The effectiveness of particular organochlorine insecticides as pesticides was noticed during 1939-1945 war (Hassal, 1982). Initially DDT [1,1,1-trichloro-2, 2-bis (*p*-chlorophenyl) ethane] and γ-BHC (benzene hexachloride) were admired as virtually ideal insecticides (Hassal, 1982). This was because they were inexpensive to manufacture and thought to be harmless to humans and other warm-blooded animals.

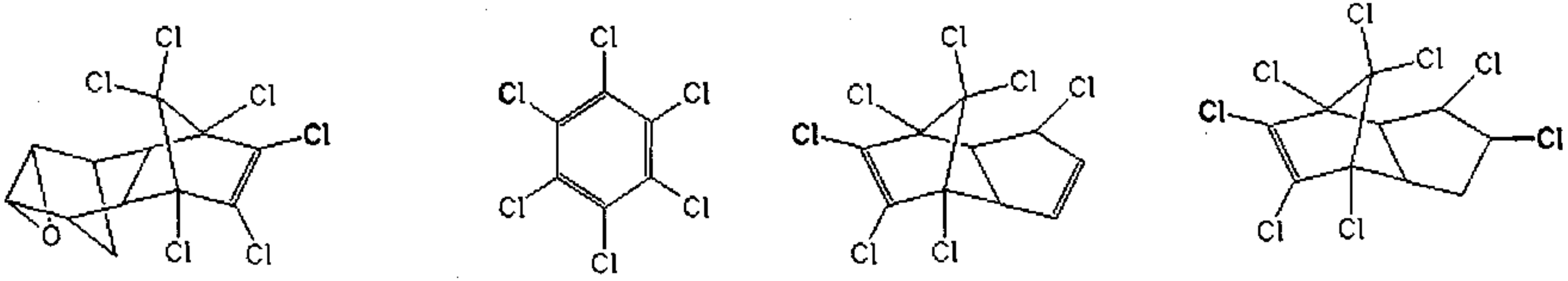
It has been suggested that a number of these chemicals are a potential hazard to plants and possibly humans as well as animals since they are known to be extremely persistent in the environment. In addition, the continuous utilization of these pesticides has resulted in more insects becoming resistant to them and killing both the 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 used in 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 of sewage sludge (WRC, 1997). Moreover, they form part of the priority pollutants identified by USEPA and UK organization. A brief description and structures of the SA target pesticides are included below. ***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 application 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 (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 World Health Organisation (WHO) (WFPHA, 2000). The 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 are estrogenic properties and anti-adrogenic sexual development feminization of males (*i.e.* alligators and Florida panthers) as well as eggshell thinning of offspring (WFPHA, 2000).



Dichloro-diphenyl-trichloroethane (DDT) ***Lindane*** ***Aldrin***



Dieldrin ***Hexachlorobenzene*** ***Heptachlor*** ***Chlordane***

<u>Figure 1-2</u> **The structural representation of the 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 as well as seed treatment when used in conjunction with fungicides (EXTOXNET, http://extoxnet.orst.edu/pips/lindane.htm). Currently lindane is added into lotions, creams and shampoos in order to regulate lice and mites in people. In addition, it is more preferable relative 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). Acute exposure as a result of the inhalation of lindane can cause nasal discomfort and results in some skin deformation or anemia. Oral exposure in humans can result in nervous system disorders causing seizures and vomiting (ATSDR, 1997, http://www.atsdr.cdc.gov/toxprofiles/tp19.html). On the other hand chronic exposure can result in the destruction of the liver and kidney according to the studies performed on animals (ATSDR, 1997, http://www.atsdr.cdc.gov/toxprofiles/tp19.html)

Aldrin is more similar to lindane since it has moderate high vapour pressure (2.31×10^{-5} mm Hg at 20 C.) hence is more desirable in cases where fumigant action in the soil is required (Hassal, 1982; Ritter *et al.,* 1995). The 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 in 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 (*i.e.* animals, humans) 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 chemicals in humans can result in neurological symptoms such as severe convulsions (WFPHA, 2000). These effects can last for several weeks. The prolonged exposure can result in headache, dizziness, nausea and vomiting, anorexia, muscle twitching, physiological illness and Parkinson's disease.

Pure ***chlordane*** consists of two geometric isomers containing eight chlorine atoms in their molecules when found in its technical form (Hassal, 1982). It is more efficient in regulating aphids, Colorado beetle larvae as well as grasshoppers compared to DDT. The other functions for chlordane include regulation of ants, earthworms, earwigs, household insects, moth larvae, termites and wireworms. Its use in the US has been suspended 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 placenta and during breastfeeding (UNEP, 2000, http://pops.gpa.unep.org/13chlo.htm). Chlordane is considered fairly toxic and hazardous. Generally people who are exposed to different concentrations of 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, 1997, http://www.atsdr.cdc.gov/tfacts90.html). It was also used in the chemical industries to make fireworks, ammunition, and synthetic rubber. Practically, HCB is no longer manufactured but it is still produced as a by-product during the production of several chlorinated chemicals. It has been found in the flue gas and the fly ash of municipal incinerators and other thermal processes (UNEP, 2000 http://pops.gpa.unep.org/16hexac.htm). Short-term exposure to 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 have given birth to babies with enlarged thyroid glands, and arthritis. On the other hand animals exposed to high HCB content exhibit acute neurological toxicity with symptoms like tremors, paralysis, in 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 causes liver damage and changes 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 the sales (Naidoo and Buckley, 2002). The agricultural sector include the emerging farmers, small-scale subsistence farmers, large scale commercial farmers and co-operatives (i.e. food plots or farm groups). There are others 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 the 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 the pesticide wastes from homes and businesses is more likely to end up in sewage works (Naidoo and Buckley, 2002). Other potential organic pollutants that are likely to be found in the sludge are discussed in the following sections.

1.4.2 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, http://home.att.net/~WFM/Trichloroethylene.htm; McNeill, 1979). The main route through which TCE can be introduced in 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, http://home.att.net/~WFM/Trichloroethylene.htm):

(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 1-3.

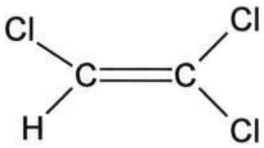


Figure 1-3 **Trichloroethylene chemical structure.**

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, http://home.att.net/~WFM/Trichloroethylene.htm; ATSDR, 1997, http://www.atsdr.cdc.gov/toxprofiles/tp19.html). Studies have also shown that inhaling higher amounts than is recommended (The four-hour inhalation LC_{50} in rats is 12500ppm) may damage liver and kidney resulting in tumours of the liver, kidney, lung and male sex organs and leukaemia (Siegel J., 1971).

1.4.3 Polynuclear Aromatic Hydrocarbons (PAHs)

PAHs are generally introduced into the environment through incomplete combustion of matter such as coal but their primary origin is the burning of fossil fuels (Langenkamp & Pärt, 2001). The PAHs are released during the burning of coals used to heat buildings, but the replacement of coals 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). This group of compounds can be found everywhere in the environment and there is a possibility that they can be generated by natural processes (*e.g.* forest fires).

The most extensively studied PAH is benzo(a)pyrene and is included in SA regulation on utilization and disposal of sewage sludge. The structural representation of benzo(a)pyrene is given the Figure 1-4.

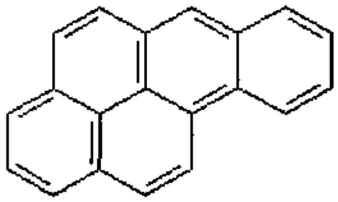


Figure 1-4 **Benzo(a)pyrene chemical structure.**

The oral toxicity of PAHs on a short-term basis seems to be from low to moderate (oral toxicity in rats varies from 50 to 1000s mg/kg body weight in rats) while chronic exposure in experimental animals resulted in detrimental haematological effects (Eisler, 1987b). Immunosuppressive, irritation of skin, 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, experimental animals and epidemiological studies have shown that inhalation and dermal exposure of PAHs 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 the specific PAH. For these reasons the 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 their application on land decreases with time. The higher molecular weight PAHs are more persistent relative to the ones with lower molecular weights. The LD_{50} and LC_{50} of some of the known PAHs apart from benzo(a)pyrene are recorded in Table 1-2. LD_{50} (lethal dose 50) is defined as single dose of a material that, on the basis of laboratory tests, is expected to kill 50 % of a population group of test animals. The lethal concentration 50 (LC_{50}) is the concentration of a material in air that, on the basis of laboratory tests, is expected to kill 50 % of a group of test animals when administered as a single exposure (usually 1- or 4 hours) (Analytical Chemistry Resources, http://delloyd.50megs.com/hazard/LD50.htm)

Table 1-2 **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 (University of Oxford, Department of Chemistry, 1995-2005)	
Anthracene	18000 in rat (IPEN Body Burden Community Monitoring Handbook)	
Benzo(a)anthracene	10 in mice (IPEN Body Burden Community Monitoring Handbook, 2003)	
Benzo(a)pyrene		*Daphnia pulex* 0.005 (IPEN Body Burden Community Monitoring Handbook, 2003)
Fluoranthene	2000 (Smyth, 1962)	
Naphthalene	490 in rat (IPEN Body Burden Community Monitoring Handbook, 2003)	*Daphnia pulex* 1.00 (IPEN Body Burden Community Monitoring Handbook, 2003)
Phenanthrene		*Daphnia pulex* 0.10 (IPEN Body Burden Community Monitoring Handbook, 2003)
Pyrene	2700 (University of Oxford, Department of Chemistry, 1995-2005)	
1,2,3,4-tetrahydronaphthalene	2860 (University of Oxford, Department of Chemistry, 1995-2005)	

1.4.4 Dimethyl Nitrosamines

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

(Verscheunsen, 1983). These reactions have been reported to lead to the contamination of treated drinking water with NDMA (Verscheunsen, 1983).

The most likely source for the contamination of water supply was thought to be through bacterial action or chemical reactions (Ayanaba *et al.*, 1973; Calmels *et al.*, 1988). 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 1-5.

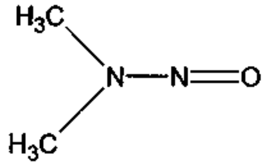


Figure 1-5 **The chemical structure of N-Nitroso dimethylamine.**

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

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

A group of polychlorinated dibenzo-p-dioxins (PCDDs) and dibenzofurans is 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 like municipal waste combustion, cigarette smoking and combustion of wood. Moreover these 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 PCDD and PCDF varies and there are 75 and 135 congeners of PCDD and PCDF respectively (Langenkamp and Pärt, 2001). Household wastewater is considered as the main source of PCDD/Fs due to significant generation of PCDDs from laundry wastewater (Horstmann & McLachlan, 1994.). The other PCDD/Fs source is sewage sludge during the treatment of municipal sewage sludge, whereby ^{13}C-PCP (pentachlorophenol) is biologically converted to ^{13}C-PCDDs. Pentachlorophenol (PCP) is used as a fungicide on cotton textile (McLachlan *et al.,* 1996; Horstmann & McLachlan, 1994). It is suggested that another source of PCDDs and PCDFs is the chlorine treatment of sludge (Nestrick and Lamparski, 1983.). This recommendation is based on the data found from the sample collected prior to the introduction of pentachlorophenol and other organochlorine pesticides in the industries (Rappe *et al*., 1989). The general molecular structures of PCDD and PCDF are provided in the Figure 1-6.

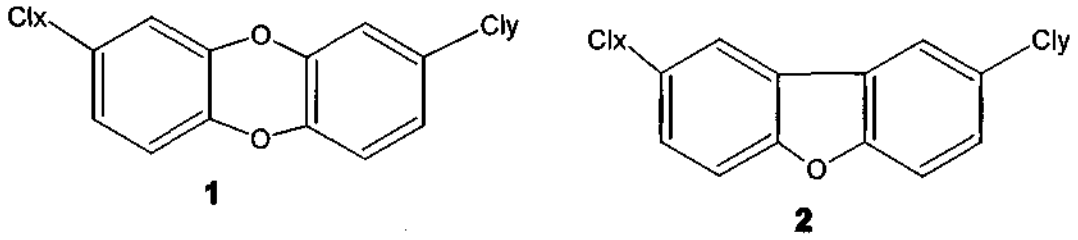


Figure 1-6 **Typical molecular structures of PCDD (1) and PCDF (2) respectively.**

A representative PCDD/PCDF compound is 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD) as it is the most poisonous and most well-investigated dioxin (Langenkamp and Pärt, 2001). There are various adverse effects associated with the exposure to 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 results in reproductive and fetotoxicity (Schneider and Kalberlah, 1999; Schrenk & Fürst, 1999; EPA, 2000). It has been shown that the oral and dermal exposure of rats and mice to TCDD 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) content in the environment is high and fairly 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.

1.4.6 Polychlorinated Biphenyls (PCBs)

PCBs were first introduced in the market in 1929 and because of their chemical and physical features have broadened their applications in heavy-duty transformers and capacitors (Jones, 1989). These special characteristics of PCBs included its electrical resistance, high chemical stability, low volatility, and poor tendency to combustion and resistance to degradation at elevated temperatures. 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, plasticiser, adhesives and lubricating additives. 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 biphenyl chlorination (Rogers *et al.*, 1989). The PCB general molecular structure is shown in Figure 1-7.

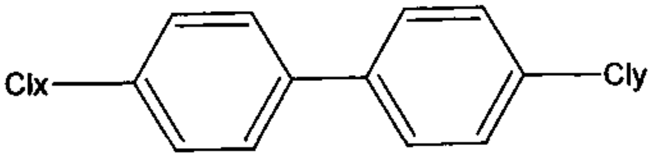


Figure 1-7 General molecular structure of polychlorinated biphenyl.

Exposure to PCB can cause discomfort to the skin and eyes, which results in chloracne, neurotoxicity, hepatotoxicity and high blood pressure as well as reproductive effects in both animals and humans. It has been seen in the 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 rats and mice to PCB can result in liver tumors. There is no 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 on 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 and their place of work. These chemicals can be deposited in all 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 indicating that they are capable of passing through the placenta (Jensen, 1987; Ando *et al.*, 1985; Rogan, 1983). However, environmental exposure is much lower relative to the former two routes. The LD_{50} and LC_{50} of various biphenyls are provided in Table 1-3.

Table 1-3 **Biphenyls' LD_{50} and LC_{50}.**

PCBs	**LD_{50} (mg/kg) (ORL-Rat)**	**LC_{50}**
1,1'-Biphenyl	3280 (University of Oxford, 1995-2005)	4.7 and 2.1 mg/L (per 48 hr) (Gersich 1989)
PCBs	1315 mg/kg (for Aroclor 1260) (Sax, 1984)	2.0 to 283 µg/L (Dillon & Burton)

1.4.7 Phenols

Phenols can be generated through normal human metabolism from tyrosine and applied pharmaceuticals by means of areneoxides. Phenols are useful substance in the natural defence mechanism for biological systems, hence is used as a disinfectant. However, the use of phenol as a disinfectant has declined as a result of its toxicity. Nevertheless, the use of phenol in cosmetics is still permitted when the relevant restrictions are observed (Gomez *et al.*, 1985). Two of the most common phenols in sewage sludges are nonylphenol (+ ethoxylates) and nonlyphenol, which are considered to be toxic organic compounds formed as a result of the degradation of alkylphenol polyethoxylate (Jones & Northcott, 2000). These degradation products have short chain lengths, formed under aerobic and anaerobic conditions and tend to adsorb to 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. Nonylphenol (+ Ethoxylates) (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). The most commonly encountered phenols in sewage sludges are cresols (i.e. para-cresol) and nonylphenol, whose structures are illustrated in the figure below.

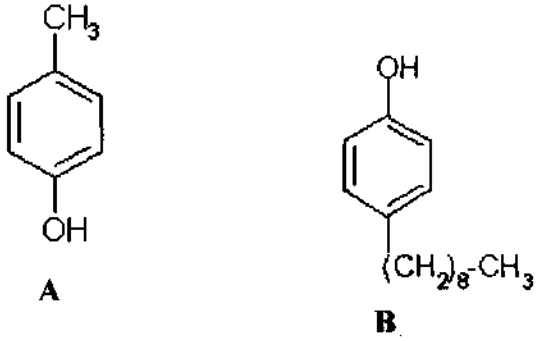


Figure 1-8 **The structural representation of para-cresol (A) and nonylphenol (B).**

Environmental problems caused by phenolic compounds are attributed to their long-term, large-scale uncontrolled release, as well as their persistence and above all, their toxicity (Lue-Hing *et al.*, 1992). The toxicities of individual phenols varies depending on the type, number and position of substituents. In human exposure studies, phenol itself is 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 (nonylphenol)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, borne out by NP's illustrated affinity for binding to the oestrogen and progesterone receptors (Laws *et al.*, 2000).

The toxicity of p-cresol in humans is similar to the phenols but with 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 health effects relating to consumption of p-cresol are abdominal pain, headaches, dizziness, muscular weakness, irregular breathing, weak heartbeat, coma, burning pain in mouth and throat as well as lung, pancreas, kidney and liver damage. In addition, there is 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 numbness on in the skin and result in severe pain in the eyes as well as long-term damage to the eye. Long-term exposure can results in liver damage as well as the symptoms described in short-term exposure (MSDS, 1999). In addition, the LC_{50} and/or LD_{50} of some of the phenolic compounds expected to be present in most sewage sludge and considered to be capable of causing severe animal health effects are provided in table 1-4.

Table 1-4 **The LD_{50} and LC_{50} of some selected phenols.**

Phenols	LD50(mg/kg) (ORL-Rat)	LC50(mg/L)
2-Methyl-phenol/ o-cresol	121 (Papa 1995)	5.00 in *Daphnia* (Parkhurst *et al.*, 1979)
3-Methyl-phenol/ m-cresol	207 (Papa 1995)	1.60 in *Daphnia* (Bringmann, 1977)
4-Methyl-phenol/ p-cresol	242 (Papa 1995)	1.40 in *Daphnia* (Parkhurst., 1979)
Nonylphenol	1300 (University of Oxford, 1995-2000)	0.13-1.4 (per 96 hr) Fish (University of Oxford, 1995-2000)
Phenol/Izal		3.90 (Bringmann *et al.* 1977)
4-(1,1,3,3-Tetramethylbutyl)-phenol	4600 (University of Oxford, 1995-2000)	5.15 in fathead minnow (Geiger, 1985, 1986 & 1988)

1.4.8 Di-2-(Ethyl-Hexyl)-Phthalate (DEHP)

Phthalates are mainly used in plastics as plasticisers. However, there are several uses of these compounds, which include additive roles in paints, lacquers, glues and inks (Langenkamp and Pärt, 2001). The most commonly encountered phthalate ester is di-2-(ethyl-hexyl)-phthalate. 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 mimic properties (Madsen *et al.*, 1997). In addition, there is the possibility that plants can absorb these phthalates once sewage sludge has been applied to land.

The LD_{50} of DEHP is fairly low (*i.e.* greater than 25000 mg/kg) in rats after short-term exposure (Langenkamp and Pärt, 2001). Laboratory animals develop hepatoxic 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 latest study has shown that long-term exposure of DEHP in mice resulted in various changes including change in kidney, liver and testes weights in male mice (David *et al.*, 2000). In addition, the LD_{50} and LC_{50} of the other common phthalates (*i.e.* diethylphthalates & diisooctyl-phthalates) as provided by various sources are recorded in Table 1-5.

Table 1-5 **The LD_{50} and LC_{50} of diethylphthalates & diisooctyl-phthalates.**

Phthlates	**LD50(mg/kg) (ORL-Rat)**	**LC50(mg/L)**
Diethylphthalates	9000 (University of Oxford, 1995-2000)	>100 mg/L for fish (University of Oxford, 1995-2000)
Diisooctyl-phthalates	27 000 (Keep & Sons, 1998)	>0.24mg/ in fathead minnow (Keep & Sons, 1998)

Figure 1-9 shows the chemical structure of di-2- (ethyl-hexyl)-phthalate .

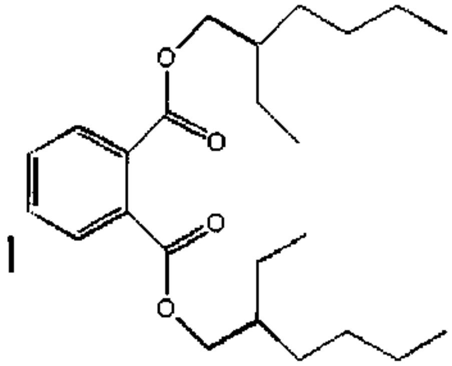
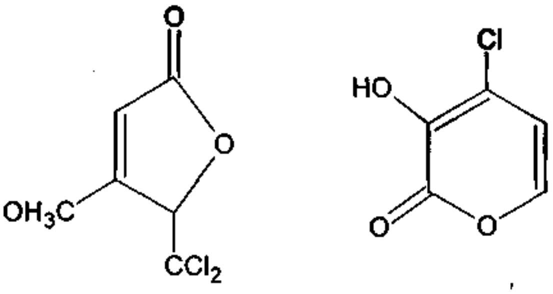


Figure 1-9 **The structural representation of di-2- (ethyl-hexyl)-phthalate.**

1.4.9 Adsorbable Halogenated Organic Compounds (AOX)

Adsorbable Halogenated Organic compounds (AOX) do not signify particular organic compounds but are an analytically determined parameter, which is the sum of all halogen-containing (*i.e.* chlorine, bromine, iodine) chemicals (Langenkamp and Pärt, 2001). The main source of AOX in municipal wastewater are the household, hospital and self-service restaurant cleaning agents and disinfectants (Schulz and Hahn, 1998). These chemicals are capable of giving off activated chlorine, as they usually possess inorganic compounds. 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 compositions of some of the chlorinated hydrocarbons that have been detected from bleaching effluent from elemental free chlorine (EFC) are shown in Figure 1-10 (McKague and Grey, 1996; Smith *et al.*, 1994).



1 **2**

Figure 1-10 **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 of organic compounds in wastewater and activated chlorine. Studies have shown that the addition of hypochlorite with 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 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.

The toxicity is not quantified by AOX. Other crucial sources of the AOX are the paper and 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 vinnyl chloride, which is a known human carcinogen can be formed as a result of the transformation of organic halogens (Salkinoja-Salonen *et al*, 1995). Since AOX is a parameter that represents various halogenated organic compounds with different chemical structures and toxicological profiles it cannot be used to indicate the toxicity of various compounds (Langenkamp and Pärt, 2001).

1.4.10 Linear Alkyl Benzene Sulfonates (LAS)

LAS is manufactured from alkybenzene sulfonates (ABS). It is considered to be the world's number one surfactant due its effectiveness, versatility, low-cost and biodegradability (Fact Sheets, http://www.cler.com/facts/sludge.html). It has several applications, which include its use as detergent, emulsifying, dispersing, wetting and foaming agent. LAS are mainly used in laundry and dishwashing detergent formulations 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 degradation. In addition, a foam-related environmental problem was observed in surface waters, groundwater, and drinking water as well as in wastewater treatment plants. Hence this lead to the discovery of easily biodegradable and environmentally friendly detergent (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 1-11.

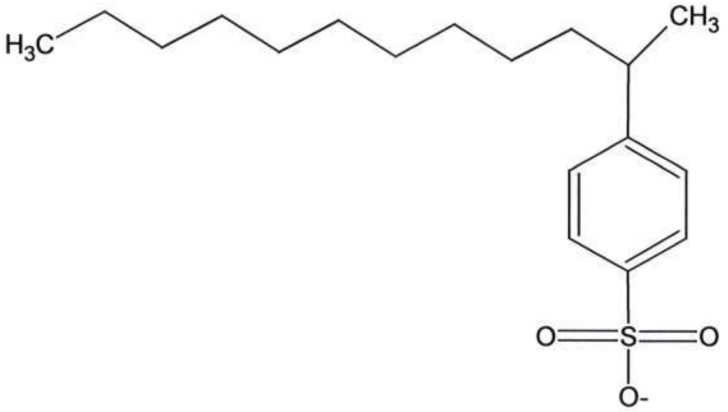


Figure 1-11 A general structural formula of linear alkylbenzene sulfonate.

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

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

In summary it can be stated that 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 concentrations 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 onto the outer cell wall.

1.5 Priority Organic Pollutants

There are thousands of organic chemicals that are currently manufactured for industrial and domestic use. These compounds are more likely to be encountered in the wastewater and sewage sludges. Various so-called 'priority pollutant' lists have been produced by international organizations aimed at identifying those compounds which may require regulation. All these lists are not specific to wastewater and sludge contaminants but are illustrative of the range of types of organic contaminants. 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), United Kingdom (UK) agencies as well as the South African Government.

A summary of the priority lists for these countries is shown in Table 1-6. A detailed list set according to UMK-AG 2000 is presented in Appendix A (Table A-13). The lists produced by these different organizations differ according to the purpose and reasons for which these lists were produced.

In 1976 the USEPA initiated a scheme for establishing drinking water quality. The priority lists included those substances:

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

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

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

(d) which have been identified frequently in waste or potable water and which are produced in considerable quantities by industry and are available as analytical standards.

The lists compiled by USEPA, UK and EU is made up of 129 priority pollutants, of which 114 are organic compounds and the rest comprise 13 metals and metalloids, cyanides and asbestos. More recently the USEPA has proposed a priority list of pollutants in sewage sludge, known as the USEPA 503 list. This has highlighted 30 substances of which 15 are organic compounds.

Table 1-6 Priority pollutants regulated by USEPA, European Union, UK organizations and South African government.

Priority Pollutants		
USEPA, EU and UK Organisations (UMK-AG 2000)		**South Africa (WRC, 1997)**
Monocyclic aromatics: Benzene	**Polycyclic aromatic hydrocarbons** Naphthalene	**Polycyclic aromatic hydrocarbons**
Ethylbenzene	Acenaphthene	
Toluene	Phenanthrene	
Chlorobenzene	Fluorene	
Dichlorobenzenes	Fluoranthene	
Trichlorobenzenes (specially 1,1,4- TCB)	Pyrene	
Hexachlorobenzene	Benzo (b+j+k) fluoranthene	
Pentachlorophenol	Benzo(a)pyrene	Benzo(a)pyrene
Phthalates	Benzo(ghi)perylene	
Di-2-(Ethyl-Hexyl)-Phthalate (DEHP)	Indeno (1,2,3-c,d)pyrene	
Linear Alkyl Sulfonates (LAS)	**Organochlorines:** PCBs	**Organochlorines:** PCBs
Halogenated aliphatics	PCDD/Fs	Heptachlor
Carbon tetrachloride	Aldrin	Aldrin
Chloroform	Dieldrin	Dieldrin
1,2-Dichloroethane	Endrin	
Hexachloro-1, 3-butadiene	DDT (and isomers)	DDT
Tetrachloroethene	α-and-β-endosulfan	Chlordane
Trichloroethene	γ-HCH (lindane)	Lindane
Absorbable Halogenated Organic Compounds	**Phthalates:** Di-2-(Ethyl-Hexyl)-Phthalate	**Volatile Organic Compounds:** Dimethyl nitrosamine
Phenols:	Linear Alkyl Sulfonates	Trichloroethylene
Nonylphenol		
Nonylphenol Ethoxylates		

1.6 Use and Disposal of Sewage Sludge

By 1990 sewage sludge production in South Africa was estimated to be 318 million tonnes per year (Herselman, 2001). Smith and Vasiloudis (1991) approximated the production per person to be 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 (Ekama, 1993). Almost half (47%) of the sludge produced in South Africa is disposed to land in a non-beneficial way (du Preez *et al.*, 1999). Beneficial uses, which include agricultural application, soil reclamation and application in gardens, form only 28%. This is in contrast to the situation in Europe and the United States where application of sludge to agricultural land is practiced extensively and accounts for more than 40% of the sludge produced (Agg *et al.*, 1992; Anderson, 1992; DoE, 1993; Matthews, 1992; WPCF, 1989 and Sieger & Hermann, 1993).

1.6.1 Fate of Organic Contaminants in Sludge-Amended Soils

There are several factors that will determine the fate of the organic pollutants in the environment. These factors include different chemical processes (*i.e.* oxidation, reduction, hydrolysis, hydration and photolysis), physicochemical processes (*i.e.* adsorption, volatilisation) and biological processes (*i.e.* biodegration, biotransformation, bioaccumulation and biopolymerization) (Deanna and Shieh, 1986). Thus the actions of these processes reduce the concentration of persistent organic pollutants potentially available for plant uptake (O'Connor, 1996). The accumulation in soils exists, but the persistence of these pollutants varies between different groups and specific compounds within each group. However, there are certain aspects that need to be taken into consideration. For instance, the application rate of sludge on land should not surpass the degradation rate of sewage sludge organic contaminants even though they are subject to these different processes (O'Connor, 1996).

Soil sorption is widely recognized to affect microbial degradation of many compounds. Strongly adsorbed chemicals 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 chemicals 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 persistence of organic contaminants in soils (O'Connor, 1996). Microbial degradation is the most important loss mechanism for many organic chemicals in soils. The rate of degradation of a particular chemical is influenced by many environmental factors such as temperature, water content and soil pH. Biodegradation of organic chemicals can generally be described by the first order rate constant. Half-lives of many organic chemicals have been published and reported values show enormous variations between soil types and with experimental conditions (O'Connor, 1996).

Due to spiking of organic compounds to soil, 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 (O'Connor, 1996). 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 chemicals may also differ significantly between laboratory and field experiments due to the different environmental conditions (Wild and Jones, 1992). Compounds such as LAS, DEHPs and NPs are less likely to absorb to humus and are more easily degraded than are PCBs or PCDD/Fs.

The PAHs are potentially biodegradable compounds, especially by soil microorganisms. Hence the soil offers excellent conditions for the biodegradation of PAHs relative to water environments (Radding, 1976.). The rate of the biodegradability of the polychlorinated biphenyls (PCBs) differs extensively.

from the soil in a period ranging from one to twelve weeks (Rippen, 2001).

Chemical breakdown and biotic degradation are the two processes mainly liable for the removal of PAHs from soil. The rate at which PAHs are removed from the soil depends on their molecular weights, whereby; those with smaller weight are quickly removed relative to the high molecular weight compounds (Wild & Jones, 1992). In addition, it has been seen that naphthalene is among the most volatile PAHs, but compounds that strongly adhere to the soil particles decrease their volatility (Wild & Jones, 1992).

Generally DEHP is readily degraded in soils (Duarte-Davidson & Jones 1996, Grüttner *et al.*, 1997). One of the many studies performed has shown that half of the DEHP content is removed.

PCDD/Fs are the common pollutants in sewage sludges and are known to accumulate in soils treated with sludge, especially the heavily chlorinated compounds (Hembrock-Heger, 1992; Jones, 1989). The PCDD/Fs content in soils can be significantly increased by repeated application of sludge to agricultural land; hence the application of sludge contaminated with these chemicals is considered an important source of soil contamination (McLachlan & Reissinger, 1990; Eljarrat *et al.*, 1997; McLachlan *et al.*, 1996). Since the biodegradation of these chemicals is very slow they tend to bioaccumuate and biomagnify in the food chain. It has been recorded that the half-lives of 2,3,7,8 substituted PCDFs are between two to ten years in humans (McLachlan & Reissinger, 1990; Eljarrat *et al.*, 1997; McLachlan *et al.*, 1996).

Generally PCBs are quite stable in sewage sludge especially those that are heavily chlorinated. Studies have shown that approximately 20 % PCBs in the sludge applied in surface soil fifteen years ago were still present (Amundsen *et al.*, 1997). It has been recommended that volatilisation is a crucial mechanism for the removal of PCBs from soil following sludge application although studies showed the process to be too slow during the 32-day experiment (Cousins *et al.*, 1997). Aerobic biodegradation of chlorinated PCBs is regarded as the main mechanism responsible for the removal of

PCBs from an aerobic environment. On the other hand heavily chlorinated PCBs are anaerobically degraded in the existing anaerobic micro-environments in the soil (Gan & Berthouex, 1994). The half-lives of the majority of slightly chlorinated PCBs congeners (*i.e.* 2-, 3- and 4-chlorines) range from 4-58 months (Gan & Berthouex, 1994).

The PCBs containing five or more chlorine atoms per molecule are more likely to be adsorbed on the suspended matter and sediments. These conditions result in the bioaccumulation of the PCBs due to their low solubility and their resistance to biodegradation (Baxter, 1975; Clark 1979; Tucker, 1975; Tulp, 1978 and Wong & Kaiser, 1976).

The movement of nonylphenol towards groundwater is insignificant as has been shown in a loam soil study (McGrath, 2000). There is no evidence that repeated application of sewage sludge on the same land results in the accumulation of nonylphenol (Günther & Pestemer, 1992).

According to the studies carried out in the United States of America the removal efficiency of LAS is greater than 99 % in the majority of sewage treatment plants (STP), which use sludge activated units. On the other hand the LAS removal efficiency ranged from 96-99 % in rotating biological contactors (RBCs) and oxidation ditches (McAvoy *et al.*, 1993). The high removal rate of LAS during sewage treatment process is because of quick and complete biological breakdown (McAvoy *et al.*, 1993; Rapaport *et al.*, 1992; Trehy *et al.*, 1996). In addition, several studies of sewage treatment in Europe have shown that LAS easily breaks down and are considerably eliminated during biological treatment (McAvoy *et al.*, 1993; Sáchez Leal *et al.*, 1994; Berna *et al.*, 1989; Berna, 1993; Prats, 1993; Di Corcia A., 1994; Schöberl P., 1994; Waters and Feijtel, 1995)

In addition, a comprehensive study has been conducted in several countries (USA, Europe, Japan) around the world to determine the behaviour of LAS during the sewage treatment process. The breakdown of LAS has been observed in the raw sewage prior to its introduction into the sewage works and the biodegradation rate increases radically once the sewage enters the plant. It has been reported that in advanced treatment plant over 99 % of LAS initially present in the raw sewage can be removed (McAvoy *et al.*, 1993; Cavalli *et al.*, 1993; Sáchez Leal *et al.*, 1994; Waters and Feijtel, 1995).

The rate at which LAS is biologically broken down is the same in the river water and river sediments (Larson *et al.*, 1993). It takes five to thirty days for half the concentration (i.e. half-life) of LAS to completely break down in sludge-amended soil. (Knaebel *et al.*, 1990). Regardless of the high usage of LAS and huge amounts entering the sewage works there is still a low LAS content in the environment: an indication that LAS does not accumulate in the environment (McAvoy *et al.*, 1993; Rapaport & Eckhoff, 1990).

The transfer of chemicals such as PAHs, PCBs and PCDD/Fs by plants via their roots is insignificant relative to the transfer of these chemicals to parts of the plants located above the soils by means of atmospheric deposition, apart from *Cucurbitacea* (Hülster, 1994; Rudling *et al.*, 1997). However, studies done on numerous organic compounds mainly chlorobenzenes, PAHs, PCBs, PCDD/Fs and some organochlorine pesticides (*i.e.* pentachloronitrobenzene, DDT, heptachlor epoxide and delta HCH) have shown that if absorbed by the plant roots they remain in the root surface and root crops, and are not transferred to other parts of the plant (Duarte-Davidson and Jones 1996; Jones & Sewart, 1997).

1.6.2 Exposure Pathways

The most likely route through which persistent lipophilic organic compounds enter the human body is through the application of fluid sludges, which stick to forage/pasture crops and are afterwards ingested by livestock that is used for human consumption (Chaney *et al.*, 1998; Smith, 2000). Besides this there is the direct ingestion of sludge by children. It is documented (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 animals 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.*, 1985). The principal pathways for transfer of substances to man from sludge amended agricultural land are listed below (Dean & Suess 1985; Jacobs *et al.*, 1985; Wang & Jones, 1994):

1) direct ingestion of sludge contaminated soil by children, a behaviour attribute known as "pica" (Eikamann *et al.*, 2000).
2) direct application to edible parts of plants as sludge, dust or mud when sludge is mixed with soil - consumption by humans. (Duarte-Davidson and Jones, 1996).
3) uptake via plants used as feed or fodder for animals, transfer to animal food products - consumption by humans. (Jones and Alcock 1997; Chaney *et al.*, 1998; Fries, 1996; McLachlan *et al.*, 1994 & 1996 and Stark & Hall, 1992).
4) uptake by plant roots in sludge treated soil - transfer to edible parts of plants - consumption by humans. (Smith, 2000; O'Connor, 1996; Wild & Jones 1992 and Topp *et al.*, 1986).
5) direct atmospheric deposition to edible parts of plants - consumption by humans (Hembrock-Heger 1992; McLachlan *et al.*, 1994).
6) direct intake of airborne dust (soil or sludge).
7) direct ingestion of soil or sludge by grazing animals and transfer to animal food products-consumption by humans
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).

1.7 Legislative Measures

As a guide to assist and give direction a National Guideline was developed in 1991 to promote safe handling, disposal and utilisation of sewage sludge. The South African Sludge National Guidelines of 1991 was revised in 1997 (WRC, 1997) stipulating the maximum annual loading limits for some organic chemicals. The limits as presented in Table 1-7 were based on lethal concentration (LC_{50}) or dose (LD_{50}) calculations.

The LD_{50} is determined by measuring the number of milligrams of active ingredients per kilogram of body weight needed to kill 50 % of a test sample of animals (*e.g.* rats) (FAO, 2000). The lethal dose for LD_{50} is expressed in mg/kg mass of the test animal. The higher the LD_{50} the less toxic is the substance.

Table 1-8 shows the 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" (EU, 2000). Table 1-9 gives the French guide values for concentration of PAHs and for the maximum accumulated input over a period of ten years. The tables show the difference in type(s) of organic compounds that are controlled by different countries.

Table 1-7 **Maximum limits for organic pollutants in South African Sewage Sludge (WRC, 1997).**

Pollutants	**Dry sludge concentration** (mg/kg)	**Group**	**State of the pollutant** (Naidoo & Buckley, 2002)
Aldrin	0.2020	Pesticide	Withdrawn in 1992
Chlordane	3.500	Pesticide	Restricted to stem treatment of citrus and vineyards as from 1993
DDT	0.3500	Pesticide	Banned in 1983 except for the control of malaria by government
Dieldrin	0.3030	Pesticide	Banned in 1983
Heptachlor	0.3500	Pesticide	Registration withdrawn in **1976**
Hexachlorobenzene (HCB)	16.20	CB-Chlorobenzene	Banned in 1983 (DEAT)
Lindane	1.360	Pesticide	Registration withdrawn in 1971. But is used in some shampoos.
Benzo (a) pyrene	2.530	PAH	
Dimethyl nitrosamine	2.900	VOC	
Trichloroethylene	2020.0	VOC	
PCB	1.000	PCB	Still used in transformers (DEAT)

Table 1-8 Concentration limits for organic contaminants in sewage sludge in different countries of the EU (EU, 2000).

Country	Organic Contaminants				
	DEHP 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)	100	20	6[1]	0.8[2]	100
Denmark[a]	50	10	3[1]	-	-
Sweden[b]	-	50	3[3]	0.4[4]	-
Lower Austria[c]	-	-	-	0.2[5]	100
Germany[d]	-	-	-	0.2[5]	100

*Dry mass

[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

[a] (Danish Ministerial Order No. 823)

[b] Langenkamp and Pärt, 2001

[c] NÖ, 1994 cit. FÜRHACKER & LENCE 1997

[d] Sauerbeck & Leschber 1992

Table 1-9 French guidelines 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)fluoranthene	4	60
benzo(k)fluoranthene	4	60
benzo(ghi)perylene	4	60
benzo(a)pyrene	1.5	20
indeno(1, 2, 3-c,d)pyrene	4	60

Literature information regarding legislative measures involving organic compounds is mainly available for European countries and the USA. Some of these are summarized below. In Denmark, the Ministry of Environment and Energy identified organic chemical residues, for which limit values should be elaborated (Madsen *et al.*, 1997). Until 1997, the use of sludge in Denmark was regulated with respect to the maximum content of selected heavy metals, maximum quantities of phosphorus, nitrogen and dry matter of waste to be applied per hectare and 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 *et al.*, 1997).

In Germany the fertilizer effects of sludge have to been 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 regulations comprise limits for AOX, PCB and PCDD/F. The German Ministry of the Environment set these limit values as purely precautionary; they were not based on scientific evidence of imminent toxicological implications. Instead the limit values were based on the existing concentrations of the respective compounds in German sewage sludges (Sauerbeck and Leschber, 1992). Since concentrations of AOX in sludges do not really give information about the absence or presence of hazardous substances, the limit were to protect the soil by preventing 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 were 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. However, there is an informal agreement between the Swedish EPA, the Farmers Union and the Water and Wastewater Associations. These agreements are based more on practical experience than on scientific data. In addition, Sweden used to have a recommended limit value for toluene, but this has been omitted (EU, 2000).

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 (Smith 2000, USEPA, 1995). Concentrations of several organic contaminants determined by some European researches are recorded in Appendix A (A-1 to A-12).

1.8 Aims and Objectives

The pollutants in sewage sludges originate from a wide variety of organic compounds used in households and industries. These compounds are usually detected in sewage sludge unchanged or metabolised after wastewater treatment processes. 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. 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 need to identify and quantify the organic pollutants in sewage sludge.

Currently the behaviour and fate of the organic pollutants throughout the sewage sludge treatment processes has continued to invoke interest in various countries (Rogers *et al.*, 1989). Moreover, there is insignificant information available with regard to the types and content of synthetic organic chemicals relative to that of heavy metals present in sewage sludge. Thus the degradation and removal efficiency of the organic pollutants during the treatment process as well as their general contents in sewage sludge and treated effluent is practically unknown (Smith *et al.*, 2001).

On agricultural side, the three factors that hinder the detailed study on the effect of organic pollutants present in sewage sludge when this is applied to agricultural land (Smith *et al.*, 2001; O'Connor, 1996; Duarte-Davidson and Jones, 1996 and Wild & Jones, 1992) are:

(i) lack of comprehensive information on the content, fate and behaviour of organic contaminants in sewage sludge and the sludge amendment of soils associated with the risk assessment process.

(ii) expensive nature of regulating organic contaminant limits

(iii) inadequate consensus on whether limits are essential or useful.

In addition, the characteristics of sewage sludge are specific to a particular country. It is therefore important that each country develop its national guidelines for the disposal of sewage sludge. These guidelines should be based on the knowledge about the nature and content of metal and organic pollutants in their sewage sludge. In addition 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 disposed on land should be taken into consideration. The South African Sludge Guidelines (WRC, 1997) stipulates limits for organic pollutants. The maximum concentration limits, as stipulated in the document are based the on calculated lethal concentration (i.e. LC_{50}) and not on researched values.

Hence the purpose of this study is to provide the much-needed statistical information on the types of organic pollutants that can be found in South African sewage sludge. The data from this study is to validate current stipulated limits for organic pollutants in the South African Sludge Guidelines (WRC, 1997). In addition the outcome is to 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. Thus the aims and objectives of this study were to:

(a) screen sewage sludge samples to determine the existence of the most persistent organic pollutants.

(b) test the extraction method for efficiency and reproducibility.

(c) quantify the selected organic contaminants and

(d) compare the values obtained in this work to the current Sludge Guidelines and make recommendations.

1.9 References

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CHAPTER 2

CHAPTER 2

2 Instrumentation

The main purpose of this chapter is to describe in detail the analytical techniques employed in the analysis of the extracts of sewage sludge samples. A brief history and the detailed developments as well as applications of these techniques in relation to their employment in this project will be discussed. Gas Chromatography (GC) [with the following detectors: mass spectrometer (MS), flame ionization detector (FID) and electron capture detector (ECD)] was the main analysis technique employed throughout the course of this project.

2.1 Gas Chromatography

Chromatography describes the separation method whereby components of a mixture are separated, based on their partition or distribution between the two phases in a dynamic system (*i.e.* mobile and stationary phases) (Fowlis, 1998). There are different types of chromatographic techniques available on the market such as gas chromatography (GC), high-performance liquid chromatography (HPLC), thin layer chromatography (TLC) and supercritical fluid chromatography (SFC).

Martin and James are the two individuals responsible for the first publication describing GC operation in 1952 (James & Martin, 1952). Early in the history of gas chromatography, it was recognized by Golay that open tubular or capillary columns would be more efficient and give better separations than packed columns (Lee *et al.*, 1984). However, the first capillary columns were made of glass and very difficult to work with. The introduction of fused silica column technology lead to the use of open tubular (or capillary) columns in gas chromatography on a permanent basis since it overcame the fragility and inconsistent performance of glass columns (Fowlis, 1998).

There are two forms of gas chromatography: gas-solid chromatography (GSC) and gas-liquid chromatography (GLC). However, the most common gas chromatography in all of the science fields is GLC and is generally known as gas chromatography (GC) (Skoog *et al.*, 1996). The mobile and the stationary phases in GSC are gas and solid respectively. In addition, the compounds of interest are separated based on their physical adsorption to the stationary phase. In GLC gas and liquid (retained on the surface of an inert solid) are the mobile and the stationary phases respectively and the separation is due to the adsorption or chemical bonding to the stationary phase (Skoog *et al.*, 1996).

2.1.1 Gas Chromatography Components

A normal gas chromatograph is composed of five components, namely carrier gas supply and control, sample injector system, chromatographic column and oven, detector and amplifier and signal processing as well as control electronics (Braithwaite & Smith, 1985). A schematic representation is shown in figure 2-1.

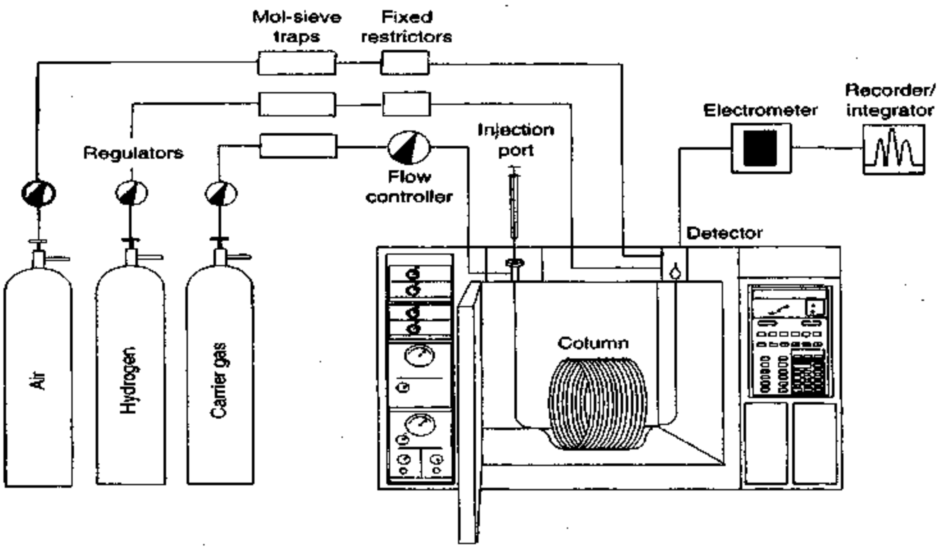

Figure 2-1 **A schematic representation of gas a chromatograph based upon the Hewlett-Packard model (Settle, 1997).**

2.1.2 Carrier Gas

The choice of carrier gas that is used as the mobile phase depends on its inertness, dryness, absence of oxygen, safety, cost and availability (Fowlis, 1998). The main purpose of the carrier gas is to carry the sample through the gas chromatography system (Settle, 1997). The particular application and detector that is employed will determine the type of the carrier gas that is used in gas chromatography. Helium is by far the most common carrier gas; the other gases that are usually employed in GC include hydrogen and nitrogen.

Helium and hydrogen are taken as the ideal gases for GC because the ratio of viscosity to diffusion coefficient is kept at a minimum resulting in rapid analysis. The effect of the carrier gas molecular weight on the chromatographic column efficiency is shown by the van Deemter equation (equation 2.1). At the optimum linear gas velocity, which is at the minimum of the curve, the efficiency of the chromatographic column is at its maximum (Figure 2-2). The efficiency of most chromatographic columns is represented by equation 2.1 (Skoog *et al.*, 1996).

$$H = A + \frac{B}{u} + Cu \qquad (2.1)$$

Where:	H	Plate Height
	A	Eddy diffusion term
	B	Longitudinal diffusion coefficient
	C	Mass transfer term
	u	mobile phase linear velocity

The A term (equation *2.1*)relates to the packing in the GC columns, therefore the A term for an open tubular column is zero because there is no packing in the column (Fowlis, 1998). The B term (equation *2.1*) relates to linear diffusion, i.e. the movement of particles, along the column, from a highly concentrated area to a less concentrated region (Skoog *et al.,* 1996). This term is inversely proportional to the mobile phase velocity, hence when the gas is moving through the column at a high speed there is less time for diffusion hence the band broadening is small since the analysis time is shorter. The C term provides an explanation for band broadening due to the lack of equilibrium in the partitioning of the solute between the two phases (stationary and mobile phases) in the chromatographic column.

This term is directly proportional to the mobile phase velocity; at low velocity there is more time for mass transfer between the stationary and mobile phases, equilibrium is more closely approached and band broadening is less. Since the B term requires high mobile phase velocity for small band broadening whereas the C term requires the opposite, it is clear that there will be an optimum mobile phase velocity at which overall band broadening will be a minimum.

The optimum linear gas velocity (*u*) of each of the commonly used carrier gases (hydrogen, helium & nitrogen) is shown in the Figure 2-2. It can be seen that the nitrogen optimum linear velocity (at the bottom of the curve) is low relative to helium and hydrogen. This is because hydrogen and helium have low molecular weights and hence low viscosities and large diffusion coefficients (Fowlis, 1998). This means that the C term is smaller for hydrogen and helium and so the van Deemter curves for hydrogen and helium do not go up as steeply as that for nitrogen, at the flow rates above the optimum. Therefore, with helium or hydrogen the chromatographic efficiency is still good at flow rates above optimum and, hence, separations can be performed more quickly with helium or hydrogen than with nitrogen.

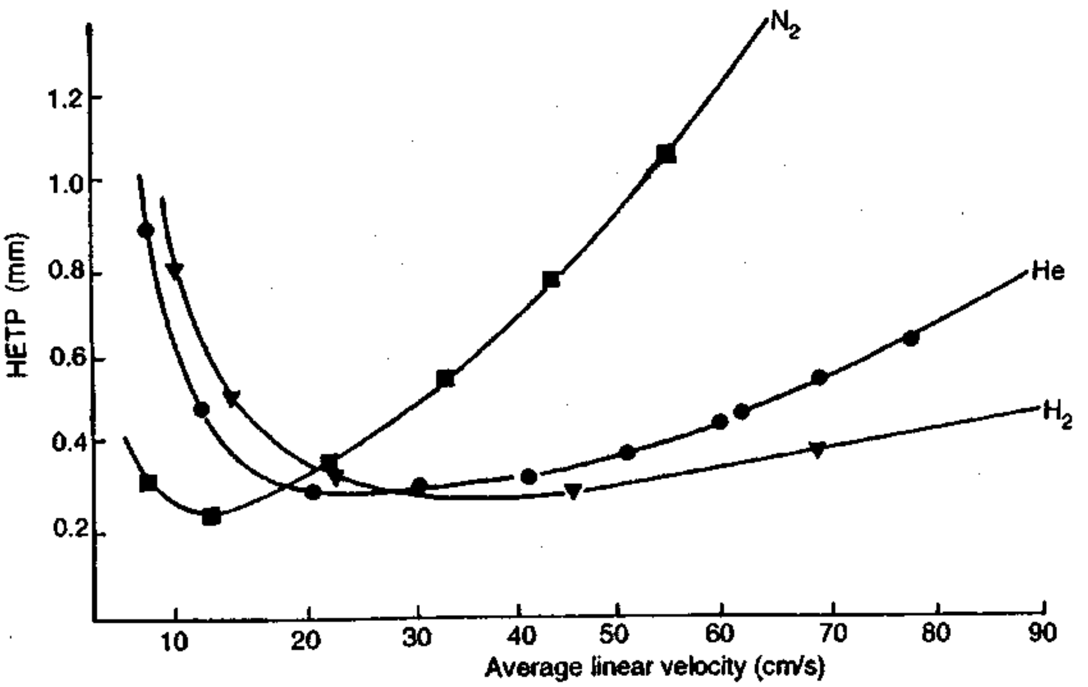

Figure 2-2 **HETP plots comparing the performance of N_2, He and H_2, run through non-polar column, which is 25 m long and has an ID of 0.25 mm (Fowlis, 1998).**

The plate height can be found from the experimentally determined plate number (N). Equation 2.2 illustrates how N can be determined from a chromatogram by measuring the retention time (t'_R) and the width of the peak at its base (W) in units of time:

$$N = 16\left(\frac{t_R}{W}\right)^2 \qquad (2.2)$$

Equation 2.3 illustrates the relationship between N, H and L, column length. This equation indicates that the column efficiency increases as the number of plates (N) becomes greater and the plate height (H) smaller (Skoog *et al.*, 1996).

$$N = \frac{L}{H} \qquad (2.3)$$

There are several different approaches to using the peak profile for measuring column efficiency (see figure 2-3 and equations 2.4 & 2.5).

(1) $$N = 4\left({t_R}/{W_{0.6065h}} \right)^2 \qquad (2.4)$$

(2) $$\mathrm{N} = 5.54\left({t_R}/{W_{0.5h}} \right)^2 \qquad (2.5)$$

Where:		
	t_R	uncorrected retention time
	$W_{0.606h}$	peak-width at the point of inflection
	$W_{0.5h}$	peak-width at half peak-height

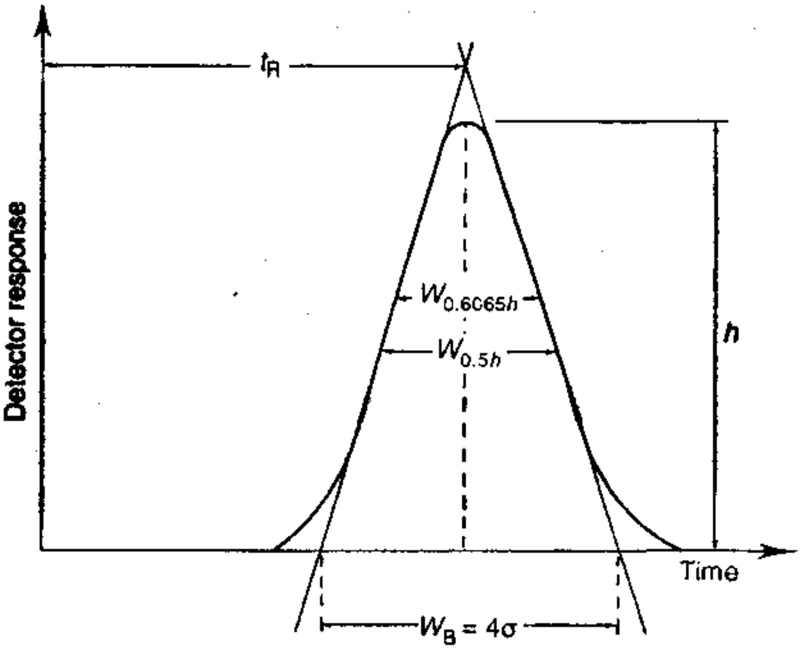

Figure 2-3 **A peak diagram illustrating how number of theoretical plates (N) can be measured (Fowlis, 1998).**

Plate height is generally used by chromatographers to measure the column performance (Skoog *et al.*, 1996). Thus the breadth of chromatographic peaks, the variance per unit length of the column, indicates the efficiency of the column. The plate height is also referred to as the height equivalent of a theoretical plate (HETP).

2.1.3 Injection Systems

For use with open tubular columns, there are two types of injectors: split/splitless and direct on-column. The split/splitless injector can be operated in either split or splitless mode. The type of analysis that is performed will determine the mode of injection *i.e.* split or splitless. The sample is introduced onto the column by means of a standard microlitre syringe through a septum into the vaporizing chamber. A general representation of the split/splitless injector is illustrated in Figure 2-4.

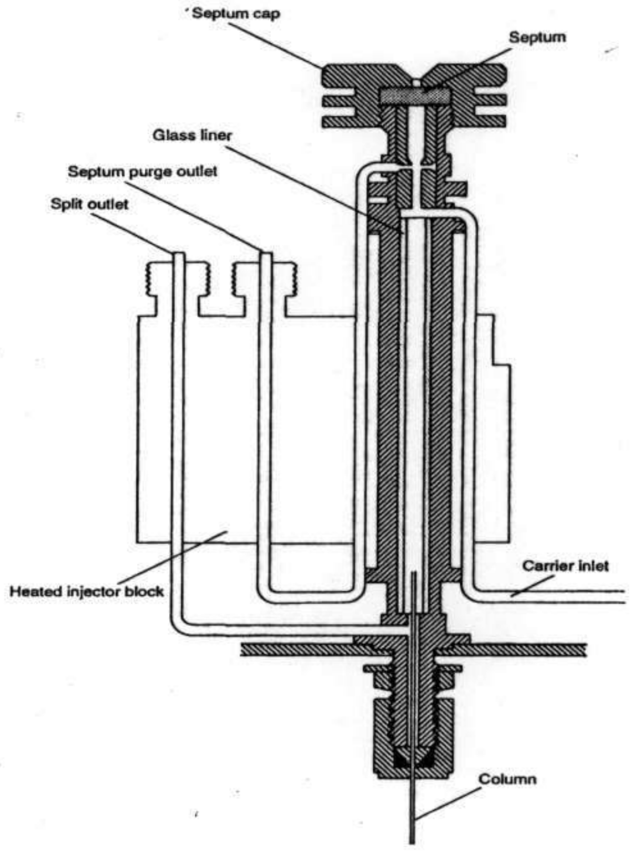

Figure 2-4 **The schematic representation of a split-splitless vaporizing injector for capillary columns (Fowlis, 1998).**

The injector contains a heated chamber with a glass liner. The heating of the chamber is carried out separately from the chromatographic oven, whereby the temperature is generally adjusted to be slightly above the final column temperature (Fowlis, 1998). Under these temperature conditions the sample evaporates rapidly.

In the split mode only a small fraction of the vapour actually enters the column while the larger amount exists through the split outlet (Fowlis, 1998). The split mode is useful when analyte concentrations are high since it prevents overloading of the column. In the splitless mode, the split vent is closed when the sample is injected.

This means that the entire sample goes into the column. After a short time (e.g. 1 minute) the split vent is opened whereby significant quantities of the solvent vapour are then vented away from the column. However, the less volatile solutes (*i.e.* analytes) are retained on the column and eluted to the detector. The splitless mode of operation is preferred when analyte concentrations are low since it eliminates most of the solvent but leaves most of the analytes to go through the column and be detected.

In the case of direct on-column injectors, the sample is directly injected into the bore of the column, which in most cases is more inert than the glass injection liner (SRI Instruments, 1998-2003). The likelihood of the boiling point discrimination of analyte within the sample is eliminated with the on-column injectors since the whole sample is injected into the column. As a result sharper peaks are produced due to the gradual volatilization of the sample initially in the liquid phase.

2.1.4 Chromatographic column

The most crucial component of the GC is the column since it is where the separation of the components of the sample takes place. There are two main categories of GC columns, namely packed and capillary (or open tubular) column systems. The latter type of chromatographic column was employed in this project; therefore it will be discussed in detail. The first capillary columns were generally made from copper, stainless steel or glass (Braithwaite & Smith, 1985). Nowadays, flexible inert chromatographic columns, which are manufactured from silica, are preferred (Braithwaite & Smith, 1985).

The GC columns are coated on the inside with a thin film of liquid stationary phase. The effectiveness of a liquid stationary phase is dependent on it being non-volatile as well as chemically and thermally stable. Liquid stationary phases are categorized according to their polarity (*i.e.* non-polar, intermediate, moderately polar or very polar).

Generally the stationary phases are relatively high molecular weight polymeric materials (*i.e.* saturated hydrocarbons, silicones, ethers, esters and amides – silicones being the most common) (Fowlis, 1998). It is essential that the analytes of interest are soluble in the stationary phase. The type of stationary phase that is employed is selected with the intention to influence the selectivity (α), such that the target compounds are more likely to be resolved (Fowlis, 1998). Selectivity indicates how well a stationary phase differentiates between components in a mixture and is defined as:

$$\alpha = {}^{K_a}\!/_{K_b} \qquad (2.6)$$

K_a and K_b are the distribution constants for the distribution of substance A and B respectively between the mobile and stationary phases. Substances with the same distribution constant (*i.e.* K_a=K_b) will coelute when run through the GC column. Components that have the same polarity as the stationary phase will be attracted more by the stationary phase, and hence retained in the column for a longer period. If the substances are not retained by the stationary phase, they cannot be separated. So, generally polar stationary phases are used for the separation of polar compounds whilst non-polar stationary phases are used for non-polar compounds.

Generally, liquid stationary phases (LSPs) are more commonly employed than the solid stationary phases because they offer several benefits (Fowlis, 1998). For instance there are a wide variety of LSPs available on the market thereby enabling users worldwide to select the stationary phase that is most appropriate to the specific application. Another advantage is that reproducible retention times are more likely to be obtained because the LSPs are available in a well defined purity. Lastly the amount of the stationary phase can be adjusted such that it is suitable for either analytical or preparative separations. Some typical LSPs are: Squalane, Apiezon L, Silicone oils and gums (eg polymethyl siloxanes, polymethylphenyl siloxanes, polyfluoropropyl siloxanes, polycyanopropyl siloxanes, polycyanopropylmethylphenylmethyl siloxanes), dinonyl phthalate (DNP), polyethylene glycols (eg carbowax 20 M), polyethylene glycol succinate and polydiethylene glycol succinate. The main disadvantage of LSPs is that they are volatile if used above the maximum allowed temperature which can result in reasonable quantities of the liquid phase bleeding into the detector causing a baseline drift, loss of sensitivity and change in the nature of the column.

The solid stationary phase is less commonly used compared with the liquid stationary phase since it results in long retention times, badly tailed peaks and poor reproducibility (Fowlis, 1998). In addition, solid stationary phases are readily contaminated and the separation is more likely to be irreproducible. Nevertheless, solid stationary phases have been found to be much more selective that the liquid stationary phases (Fowlis, 1998). GSC has a place in the separation of mixtures of gases and/or very volatile compounds. There are several solid stationary phases that are commonly used in gas chromatography column, which include alumina, carbon black, zeolites, silica gel and porous polymers.

There are generally two classes of open tubular columns namely wall coated open tubular (WCOT) and support coated open tubular (SCOT) columns as well as related porous layer open tubular (PLOT) columns (Fowlis, 1998). The most commonly used column is the WCOT column and the tube can be made from glass, silica or steel with the internal diameter ranging from 0.1-0.75 mm. The first WCOT columns were made from glass and required extensive cleaning in order to remove impurities (*i.e.* metal ions) from the surface of the glass. If these impurities are not removed they result in adsorption problems and poor chromatographic performance (*i.e.* broadened peaks).

However, with the fused silica columns, there are no impurity problems because a core of very high purity silica is employed (Fowlis, 1998). In order to overcome this problem the column is protected by coating it with a polyimide film, which maintains the flexibility of the fused silica and ensures trouble-free column fitting and handling. There is are considerable amount of hydroxyl groups on the silica tubing providing an area where an appropriate silane can be joined. Figure 2-5 shows a portion of the stationary phase molecule.

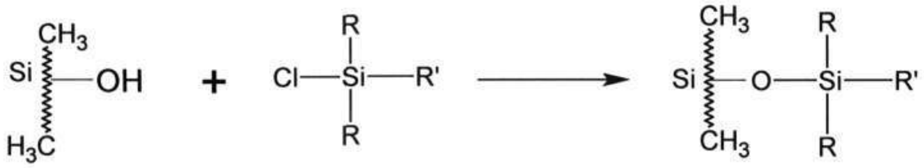

Figure 2-5 **The structural composition of silica with silanol groups (Fowlis, 1998).**

Where: R and R′ are different alkyl groups.

The efficiency of wide bore columns (≥ 0.50 mm internal diameter, ID) is less than that of narrow bore columns (≤ 0.25 mm ID) but the wide bore columns can be used with direct injection techniques unlike the narrow bore columns. Generally the film thickness of WCOT columns can be between 0.1-1.0 µm and its length usually between 15-30 m but columns up to 60 m long are commercially available.

The main purpose of producing PLOT or SCOT columns was to eliminate the problems arising from use of thick film columns, such as broadened peaks, while injecting large volumes of sample into the column at high flow rates (Fowlis, 1998). However, this goal was never achieved because the resolution achieved with these columns was very poor compared to that obtained with typical wall coated capillaries. The PLOT columns are produced in situ by chemically etching the internal glass surface before the usual coating process. The SCOT columns are considered substitute columns for PLOT columns and are prepared in a volatile dense solvent by packing the capillary with a stable suspension of 0.01 mm diameter support particles in a solution of the stationary phase. The solvent is removed by passing a small zone furnace along the length of the capillary leaving the support particles and stationary phase on the wall of the column.

In addition, the narrow bore WCOT can have the efficiency or separating power as high as 6 000 plates m^{-1}, hence its resolution is higher relative to the wide bore WCOT columns (Fowlis, 1998). The number of theoretical plates, *N*, is largely used to measure the column performance (Skoog *et el.*, 1996). The bigger the plate number, the better will be the separation of different components of a mixture (Fowlis, 1998). On the other hand the advantage of wide bore WCOT columns is that their elution times are about twice as short as those for narrow bore columns provided that stationary phase film thickness in both cases is the same.

2.1.5 Detectors

Detectors are measuring tools in the chromatographic system and are employed for the monitoring of analytes in the gas stream as it leaves the column (Fowlis, 1998). These measuring devices are located in an isolated temperature-controlled zone in the instrument. The efficiency of the detection system and its ability to achieve the intended task determines the performance of the gas chromatograph to a great extent. The most widely used detector is the flame ionization detector (FID) because of its sensitivity, wide dynamic range, robust nature and it is relatively non-problematic during routine analysis (Fowlis, 1998). A very selective and sensitive detector for halogenated compounds in gas chromatography is the electron capture detector (ECD). Another detector that is extensively employed in GC is the mass spectrometer (MS). The combination of GC and MS gives a very powerful analytical tool as it is combining the separation power of GC with the ability of MS to give structural information.

The flame ionization detector is considered an almost ideal GC detector and is employed in routine and general-purpose analysis. The excellent characteristics of the FID are (Braithwaite & Smith, 1985):

a) Its sensitivity is high to almost all organic compounds.
b) It has insignificant response to water, carbon dioxide, and the common carrier gas impurities and therefore results in zero signals when the sample is absent.

c) It results in a stable baseline because it is not affected by the fluctuations in temperature or carrier gas flow rate and pressure to a greater extent.

d) It has high-quality linearity over a wide sample content range (Skoog *et al.*, 1996).

The conventional FID is generally made up of a base in which the column eluent is mixed with hydrogen, a polarized jet and a cylindrical electrode arranged concentrically with the flame (Fowlis, 1998). The air that is transferred to the detector supports the combustion. The assembly is enclosed in a stainless steel or aluminum body to which the flame ignition coil, electrical connections as well as polarizing voltage to the detector jet are fitted. The hydrogen gas in the FID is introduced into the column eluent where it completely mixes with carrier gas prior to its appearance at the jet and subsequent entrance into the air stream. Organic compounds separated in the column are ionized as a result of the burning process that occurs.

Thus a high voltage (few hundred volts) is applied between the jet and the electrode resulting in the formation of electron/ion pairs at the jet and cylindrical electrode as the carbon containing analyte is burnt (Scott, 2002-2003). The electrons/ions generated from this process cause the current to flow, which is proportional to the amount of the analyte entering the flame. Thereafter the current is increased and fed to a recorder or to the analogue to digital (A/D) converter of a computer data acquisition system. The schematic representation of a FID is illustrated in Figure 2-6.

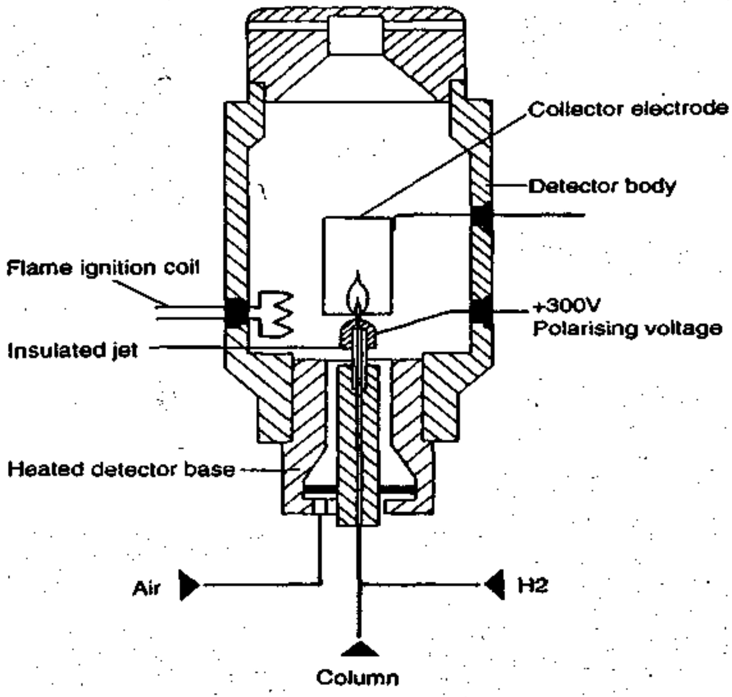

Figure 2-6 **A typical diagram of flame ionization detector (Fowlis, 1998).**

The electron capture detector (ECD) is commonly employed for the analysis of environmental samples with chlorinated pesticides and herbicides since it has a high sensitivity for the halogenated compounds (Braithwaite & Smith, 1985). The internal chamber of the detector is lined with a radioactive β-emitter held in a sealed foil and is maintained as small as necessary (Fowlis, 1998). Usually, either nickel (^{63}Ni) or hydrogen (^{3}H) can be used as the source. The inlet tube and cylindrical body are employed as electrode cells whereby they are insulated from one another. A general diagram of an ECD is shown in Figure 2-7 below.

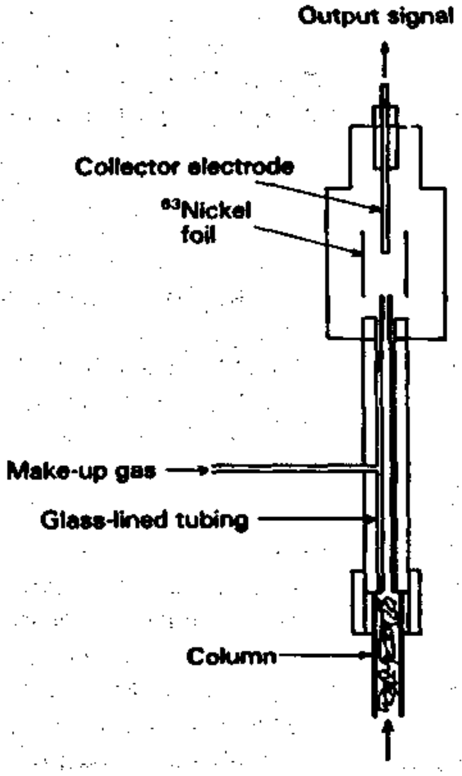

Figure 2-7. **A diagram illustrating an electron capture detector (Braithwaite & Smith, 1985).**

The β-radiation is used to ionize the carrier gas in the detector resulting in the formation of free electrons. A high molecular weight carrier gas is required for effective operation of the ECD, thus nitrogen is commonly used. These free electrons, before they recombine with the nitrogen cations to form neutral nitrogen molecules, rapidly move to the anode under the impact of the potential gradient (Fowlis, 1998), hence an ion current is produced. Below is the ionization equation of nitrogen.

$$N_2 \xrightarrow{\beta} N_2^+ + e^- \qquad (2.7)$$

In the presence of electron accepting components the electrons may be captured before reaching the anode, resulting in the decrease in total ion current and the appearance of a chromatographic peak.

The mass spectrometer is a detector that can be used for both the identification and quantification of volatile and semi-volatile organic compounds. The current mass spectrometer is considered the most sensitive, specific and multipurpose of all analytical devices. In general it is utilized for the identification of organic compounds by virtue of a fragmentation pattern (Settle, 1997). Other MS uses include its employment for the identification of structural features in an unknown sample; determination of incorporation of stable isotopes as well as the determination of the concentrations of organic compounds present in trace amounts.

The mass spectrometer positively identifies the peaks of separated components of a mixture from GC using their mass spectrum (West Coast Analytical Services, www.wcas.com/tech/gcms.htm). These mass spectra are usually referred to as the fingerprints of the individual compounds. An analyzer (usually either a quadrupole mass filter or ion trap) is used to separate the ions produced based upon their mass/charge ratio. The ionization processes are responsible for the conversion of an analyte into a charged species. The ion source in each mass spectrometer will determine the conditions suitable for a specific ionization process. There are two routes through which the mass spectra are usually generated namely: electron and chemical ionization. It is essential that in both these ionization processes the compound of interest be in the gaseous state in order to interact efficiently with 70-eV electrons in electron ionization (EI) or with proton-rich reagent ions in chemical ionization (CI) (Settle, 1997).

Electron impact (EI) ionization is the more commonly used mode and it uses electrons to ionize analytes separated in the GC. In the EI mode molecular ions are generated as a result of their collision with the electron beam (West Coast Analytical Services, www.wcas.com/tech/gcms.htm). Individual fragments are separated on the basis of their mass-to-charge-ratio, which is normally equal to the molecular weights of small molecules as a significant amount of the ions produced are singly charged. EI generates a considerable amount of structural information and this can be observed from the EI spectrum.

Electron impact (EI) is a perfect ionization technique for analyzing samples containing unknown constituents because the spectra are reproducible from one instrument to the next. As a result libraries of spectra are assembled such that the spectra of unknown peaks can be searched against these libraries to assist in the identification.

In chemical ionization (CI) reagent gases such as methane and isobutene are usually employed whereby they enter the MS at a pressure of approximately 1 torr (Watson, 1985). This process moderates the energy transfer and as a result fewer fragmentations are stimulated. This ionization technique is suitable for the determination of molecular weights rather than structural identification of compounds (West Coast Analytical Services, www.wcas.com/tech/gcms.htm). Therefore it can be concluded that the two different ionization processes compliment each other. This is because, in the CI mass spectrum, the molecular weight (m) of the analyte is clearly shown by an intense m+1 peak, which represents the protonated parent molecule. On the other hand, significant fragmentation is observed in the EI mass spectrum (Fowlis, 1998). Figure 2-8 represents a mass analyzer with a chemical ionization source.

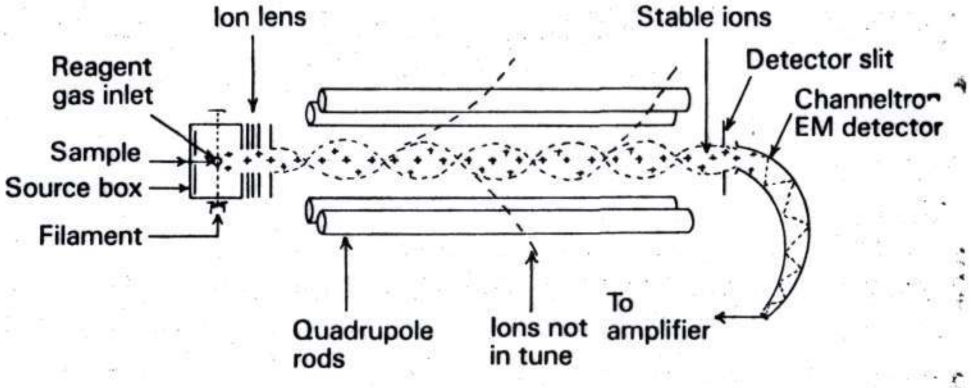

Figure 2-8 **A schematic representation of a quadrupole mass analyzer with a chemical ionization source (Braithwaite & Smith, 1985).**

To emphasize the differences in the mass spectra from electron impact and chemical ionization methods, two spectra of 3-nitrobenzyl-alcohol are provided in Figures 2-9 and 2-10 respectively.

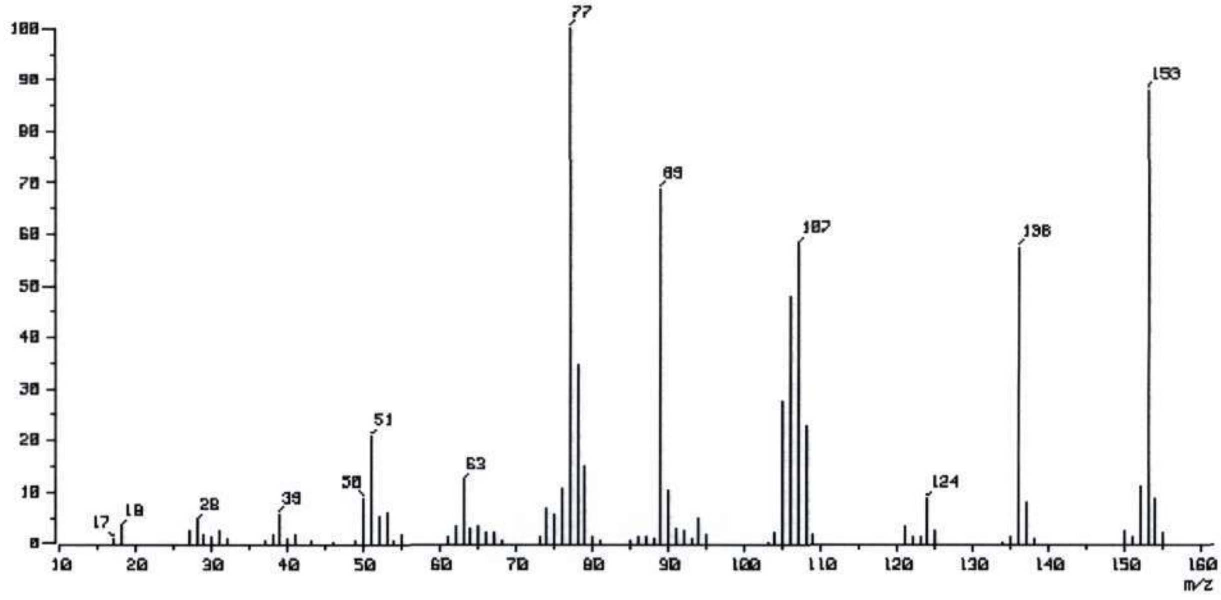

Figure 2-9 **Electron impact ionization mass spectrum of 3-nitrobenzyl-alcohol (Mass Spectrometry Facility http://www.nd.edu/~massspec/ions.html).**

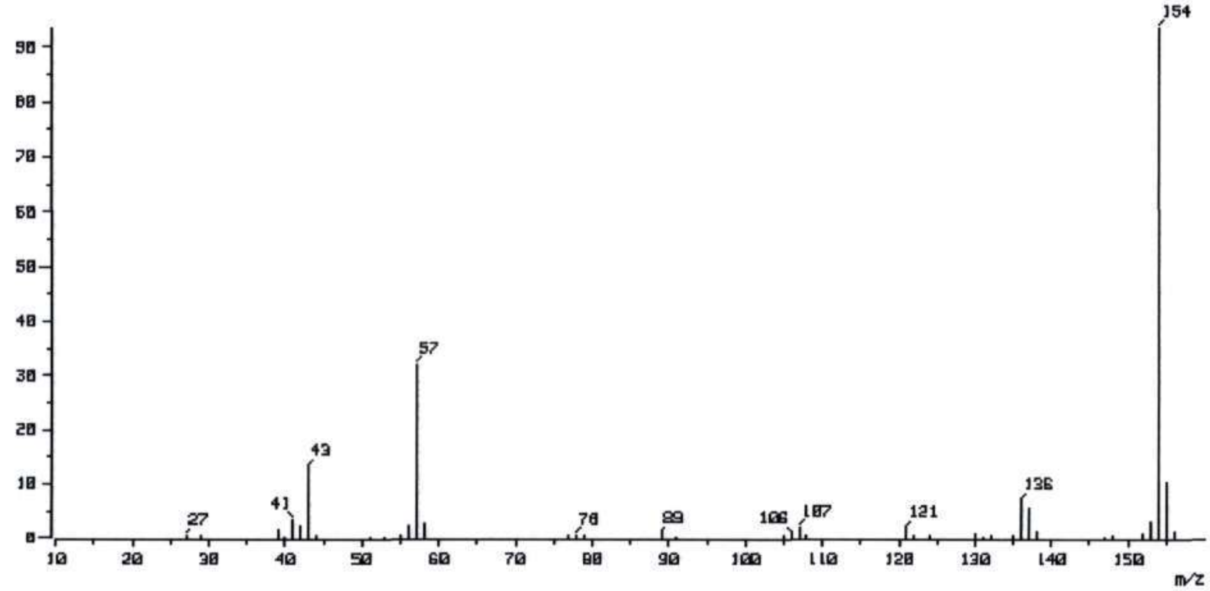

Figure 2-10 **Chemical ionization mass spectrum of 3-nitrobenzyl-alcohol (University of Notre Dame 2004).**

2.2 Analysis by Gas Chromatography

Gas chromatography with an appropriate detector can be employed to determine the amount or the identity of analytes present in the sample. Thus detectors such as ECD and FID linked to GC are usually used to determine the concentrations of compounds of interest in samples. When mass spectrometry is attached to the gas chromatography, retention times can be employed to determine both the amount and the identity of the analytes in samples. The approach whereby the amount and identity of analytes is determined by gas chromatography is known as quantitative and qualitative analysis respectively and these approaches will be described.

2.2.1 Qualitative Analysis

There are two approaches that are used for the identification of organic components in a mixture, namely mass spectrometry and retention times. The retention time is the time taken for a compound to elute from a GC column following the injection of sample (Douglas, http://www.scientific.org/tutorials/articles/gcms.html). The retention times were initially used to identify the target compound, whereby the retention time for the peak of the target compound was matched against the retention time of the genuine compound (Fowlis, 1998). The approach was straightforward and results obtained were considered reasonable, provided the analysis conditions were held constant. In order to allow for changes in conditions, relative retention times can be used where an internal standard is used and retention times are measured relative to the retention time of this standard. For the use of retention time to be effective it is essential that the target compounds are known and that standard solutions are available for retention time comparison (Fowlis, 1998).

In addition, the identity of the analytes in complex mixtures can be determined by comparing their mass spectra with reference spectra stored in a MS library (Settle, 1997). Thus the generated fragmentation by either electron impact or chemical ionization can be used to determine the structural composition of the components in the sample.

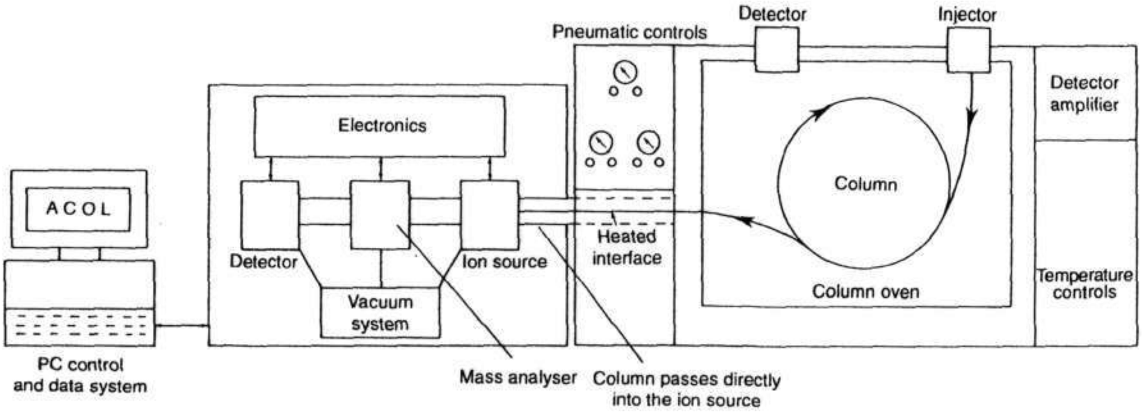

Figure 2-11 **A schematic diagram of a gas chromatography mass spectrometer (Fowlis, 1998).**

2.2.2 Quantitative Analysis

The United States Environmental Protection Agency (USEPA) techniques have proved that GC-MS can be used for the quantification of organic pollutants in drinking and wastewater (Settle, 1997; USEPA, 2003). Thus it is capable of determining the content of several analytes in sample extracts. This process is achieved by measuring the peak areas from mass chromatograms or from selected ion monitoring. In the selected ion monitoring approach not all the masses of the mass spectrometer are scanned but the device only scans selected masses.

This technique is beneficial since there is improvement in signal-to-noise ratio at the selected mass and the average sensitivity of the experiment increases by a factor of 100 to 1000 as the mass spectrometer spends a significant amount of time on those few selected masses (Settle, 1997).

There is a considerable distinction between mass chromatograms and selected ion monitoring (SIM). In the SIM technique responses are recorded from only a few masses (*i.e.* target compounds) that are selected prior to the quantification of analytes. On the other hand all masses in the mass chromatograms are scanned, as there is no need for preselection. These conditions compromise the sensitivity of the experiment. Selected ion monitoring is practically fully software driven because it is highly flexible as it is easy to assemble different sets of masses, time windows and integration times (Settle, 1997). However, it is essential that the mass spectrum of the analyte is known, which can be obtained from the library of reference spectra.

In order to convert the peak areas from mass chromatogram or selected ion monitoring to mass of the analyte, the peak areas need to be calibrated using external or internal standards (Settle, 1997). When external standards are used, the analyte with a known concentration is injected into the GC-MS, in a different experiment, and a calibration curve of peak area *vs* concentration is obtained. This type of calibration can achieve the detection limits of a few nanograms.

The use of internal standards is considered the best calibration technique as it can provide the most accurate quantitative results. This is because a known quantity of the internal standard is added into the sample prior to the start of the analyte extraction from the sample. Then the relative response between the analyte and the internal standard is measured after the extraction and cleanup of the sample is completed. The concentration of the analyte injected into the GC-MS is calculated by multiplying the ratio of the analyte and internal standard by the concentration of the internal standard. The surrogate is considered an ideal internal standard as it is chemically similar to the analytes, hence the behaviour of the surrogate during the sample preparation (*i.e.* extraction, cleanup & analysis) will resemble the likely behaviour of the target compound, allowing adjustments whenever it is necessary (Settle, 1997).

The actual concentrations of the analytes in samples is largely calculated by using calibration standards. Thus a set of calibration standard solutions with different concentrations (i.e. minimum of five standards) is run through the column to calibrate the column and plot a straight calibration graph. From this graph an equation will be obtained which will be used to determine the concentration of compounds in samples that are similar to the compounds used for plotting the calibration graph. The common equation that is usually used in the quantitation of samples takes the form: $y = mx + c$, where (1) y is the peak intensity, (2) m is a slope, (3) x is the concentration and (4) c is the intercept on the y-axis. In the calibration equation the only unknown is x while m and c are given from of the equation and peak intensity will be measured from the GC chromatogram of the analyte in the sample extracts.

2.3 References

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CHAPTER 3

CHAPTER 3

3 Experimental

3.1 Reagents

The following HPLC-grade solvents were used in the extraction and drying processes, dichloromethane (BDH), 2-propanol (BDH) and hexane (BDH). Analytical-grade anhydrous granular sodium sulfate (SMM Chemicals) was purified by heating at 400 °C for four hours in a shallow tray in order to remove impurities. Thereafter it was cooled in a dessicator for 24 hours prior to its use in the drying of sewage sludge extracts. Sodium hydroxide solution (NaOH, 10 N) was prepared by dissolving 40.00 g of NaOH pellets (Merck Chemicals) in 100-mL of ultra-pure water using a volumetric flask.

Sulfuric acid solution, (H_2SO_4, 1:1 v/v) was prepared by slowly adding 50.00 mL of H_2SO_4 (Riedel-de Haën) to 50.00 mL of ultra-pure water. Tetrabutylammonium (TBA) sulfite was prepared by, initially, dissolving tetrabutylammonium hydrogen sulfate in ultra pure water (100.0 mL). This was followed by the removal of impurities by extracting the aqueous solution with three 20-mL portions of fresh hexane, followed by dissolving 25.00 g of sodium sulfite in the purified TBA aqueous solution.

The composite stock standard solution of organochlorine pesticides was prepared from: pure hexachlorobenzene (HCB), 4,4'-DDT, dieldrin, heptachlor, lindane and aldrin (all were brought from Supelco except HCB and lindane which were supplied by Fluka and Aldrich respectively). A composite standard solution of phenols was also prepared from pure p-cresol (Fluka) and nonylphenol (Riedel-de Haën). These stock and calibration composite standard solutions were stored in 50.00 mL glass bottles with a Teflon®-lined glass stopper and stored at ± 4 °C in the dark in order to prevent degradation of the organic components. Pesticide composite calibration standards were prepared from the pesticide stock standard solutions.

The calibration standard concentrations were 0.0625, 0.125, 0.250, 0.500 and 1.00 mg/L. The phenol composite calibration standard solutions were prepared from the stock standard solution in the concentration range of 5, 25, 50, 100 and 200 mg/L.

3.2 Apparatus

The following equipment was used for the extraction of solid and aqueous sewage sludge.

- *For solid sewage sludge:*
  Soxhlet extractor (40.00 mm internal diameter, ID), a round bottom flask (500.0 mL), boiling chips, cellulose extraction thimbles (28.00 mm ID, 80.00 mm external length) from Whatman®, heating mantle (rheostat controlled) and condenser.

- *Aqueous sewage sludge:*
  Separation funnel (2.00 litre) with a ground glass stopper, pH indicator paper (range 0-14), Erlenmeyer flask (250.0 mL) and a 1.00 L graduated glass cylinder.

The drying and the concentration of both the solid and aqueous sewage sludge extracts were done using the following equipment:

- 20.00 mm ID Pyrex chromatographic drying columns, boiling chips, glass vials (3.00 mL & 1.00 mL), disposable glass Pasteur pipettes, bulbs and Kuderna Danish (K-D) apparatus. The K-D apparatus consists of concentrating tube (10-mL), evaporation flask (500.0 mL) and Snyder column (three-ball macro).

In the case of qualitative and quantitative analysis of the sewage sludge extracts the following apparatus were used

- The instrument used for qualitative analysis and qualification of pesticides was a Hewlett Packard (HP) 6890 series gas chromatograph interfaced to an HP 5973 Mass Selective Detector (MSD) and controlled by HP Chemstation software (version b.02.05, 1989-1997). The chromatographic separation was achieved using a DB-5 MS capillary column (30.0 m x 250 μm x 0.25 μm). The column stationary phase comprised 5% Diphenylpolysiloxane and 95% Dimethylpolysiloxane.

- A Varian CP-3800 Gas Chromatograph with Varian CP-8400 autosampler was employed for the quantification of phenols and organochlorine pesticides. The Varian CP-8736 capillary column used for the analysis of phenols was 30 m (L)×0.53 mm (ID) wall coated open tubular (WCOT) fused silica with CP-Sil 8 CB stationary phase with film thickness of 1.50 μm. The Varian Factor Four CP 8946 capillary column was employed for the quantification of organochlorine pesticides. This was 30 m (L)×0.25 mm (ID) WCOT fused silica with stationary phase: VF (Varian Four) 5 ms and 1.00-μm film thickness. The GC isotope that was used in the ECD (Electron Capture Detector) was ^{63}Ni with the amount of 15 mCi. The identity of both the phenol and pesticide analysed by GC-ECD were confirmed by GC-MS from Umgeni PLC Laboratory.

3.3 Sampling

The selection of sampling sites (Appendix B) was based on the work done by the Water Research Commission (WRC) (Synman *et al.*, 2004, 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 in 1.00 litre glass bottles having polytetraflouroethylene (PTFE) lined screw caps. 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 Cape (EC), 4 in Northern Cape (NC) and 2 in Mpumalanga. The objective in sampling is to extract small portions from the source such that it is representative of that source. At each of the WWTPs, a series of smaller samples were taken randomly from different spots into a 2.00 litre glass container having PTFE lined screw caps. The collected samples were mixed within the container to make the sample uniform in composition.

Sampling for the second phase of the study, which served as the reproducibility check on the first set of results, was reduced to 13 sites (7 worst case and 5 best cases – class D sludge) (Synman *et al.,* 2004). One extra site (Flip Human sample no. 22) was added to the list because it was found to contain a large variety of organic pollutants, particularly hazardous contaminants, when first screened. The names of the selected sites for the second round of sampling are shown in Table 3-1.

Table 3-1 **Names of the selected sites for second round of sampling: The five best and 7 worst sites according to Snyman *et al.*, 2004.**

Best Sites	Worst Sites
Sample 41 (KZN) Hammarsdale	Sample 1 &2 (GP) Vlakplaats
Sample 75 (KZN) Klipfontein	Sample 4 (GP) Dekama
Sample 54 (NW) Boitekong	Sample 6 (GP) Rondebult
Sample 37 (WC) Oudtshoorn	Sample 15 (GP) Zeekoegat
Sample 28 (WC) Borchards W\Quarry	Sample 21 (GP) Percy Steward
	Sample 55 (NW) Brits
	Sample 30 (WC) Athlone
Sample 22 (Gauteng) Flip Human based on organic analysis	

KZN	KwaZulu Natal province	NW	North-West province
WC	Western Cape province	GP	Gauteng province

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 packs 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 reduce any possibility of photodegradation and stored in a chest freezer that had been set to maintain a temperature of between 2.5 and 3.5°C. The best sludge samples were all solid (sample nos. 28, 37, 41, 54 & 75) while of the worst sludges, three were aqueous (sample nos. 21, 22 & 30) and six were solids (sample nos. 1,2,4,6,15 & 55).

3.4 Extraction

The USEPA recommends a number of different methods for the extraction of organic compounds from liquid or solid matrices. A list and brief description of each method, including their advantages and disadvantages with respect to the type of analytes has been recorded in table 3-2.

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

Extraction Method	**Analytes**	**Advantages**	**Disadvantages**
AQUEOUS SAMPLES			
Solid-Phase Extraction **(EPA 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 thus reducing the extraction efficiency. -It requires specialized equipment.
Continuous Liquid-Liquid Extraction (**EPA 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 prove difficult to extract.	-Requires expensive glassware, uses fairly large volumes of solvent and extraction times are lengthy (18-24 hours).

Table 3-2 cont.

Extraction Method	Analytes	Advantages	Disadvantages
AQUEOUS SAMPLES			
Supercritical Fluid Extraction of PCBs and Organochlorine Pesticides **(EPA Method 3562).**	PCBs and Organochlorine Pesticides	-It is applicable without any liquid treatment needed to stabilize the liquid prior to extraction.	
Purge-and-Trap for Aqueous Samples **(EPA Method 5030 B).**	Volatile Organic Compounds (VOCs) that have boiling points below 200 °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 (approximately) 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 **(EPA Method 5031).**	(VOCs)	An alternative to Method 5030 A/B	Clean-up is required if significant interferences are likely to occur.
Separatory Funnel Liquid-Liquid Extraction **(EPA Method 3510C).**	Water-insoluble and slightly water-soluble organic compounds	Uses relatively inexpensive glassware and is fairly rapid (2-3 minutes) extractions.	It is labour intensive, uses a large volume of solvent and is subject to emulsion problems.
VOCs by Vacuum Distillation **(EPA Method 5032).**	VOCs with boiling point less than 180 °C and insoluble or slightly soluble in water.	It is applicable to almost all types of matrices regardless of water, soil, sediments, oil and sludge	

Table 3-2 cont.

Extraction Method	Analytes	Advantages	Disadvantages
SOLID SAMPLES			
Soxhlet Extraction **(EPA 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. -It uses relatively inexpensive glassware.	Extraction time is very long (18-24 hours).
Automated Soxhlet **(EPA Method 3541)**.	Semi-volatile and non-volatile water insoluble and slightly water-soluble organics.	-Guarantees intimate contact of sample with the extraction solvent, providing efficient extraction. - Extraction complete in 2 hours.	Costly devices are required.
Microwave Extraction **(EPA Method 3546).**	Semi-volatile organics such as 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 equipment.
Pressurized Fluid Extraction **(EPA 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 extraction but uses less solvent and it is much faster.	Requires the use of expensive apparatus.
Ultrasonic Extraction **(EPA Method 3550C)**.	Non-volatile and semi-volatile organic compounds.	-Fast and extraction takes about 2-3 minutes. -There is intimate contact between sample matrix and extracting solvent.	-Extraction method not very rigorous; hence choice of extraction solvent is very critical. -Clean up is highly recommended prior to analysis. -Not validated for organophosphorus compounds.

Table 3-2 cont.

Extraction Method	Analytes	Advantages	Disadvantages
SOLID SAMPLES			
Supercritical Fluid Extraction of Total Recoverable Petroleum Hydrocarbons **(EPA Method 3560).**	Total recoverable petroleum hydrocarbons.	No organic solvents required for extraction.	-Expensive machinery. -Not suitable for the extraction of liquid samples.
Waste Dilution **(EPA Method 3580A).**	Non-volatile and semi-volatile organic compounds.	For wastes with organics greater than 20 000 mg/kg and soluble in dilution system.	
Supercritical Fluid Extraction of Polynuclear Aromatic Hydrocarbons (PAHs) **(EPA Method 3561)**	Polynuclear Aromatic Hydrocarbons (PAHs)	No organic solvents required for extraction.	-Expensive tools. -Clean up is required prior to analysis. -Not suitable for liquid samples.
Closed-System--Purge-And-Trap **(EPA Method 5035)**	(VOCs)	Sample is never exposed to atmosphere hence the loss of the analytes is negligible.	Cannot be used for samples with organics greater than 200μg/kg.

The techniques that were selected for the extraction of both the aqueous and solid sewage sludge samples were Methods 3510 C and 3540 C respectively. These two methods were chosen because they were inexpensive, simple and effective. The 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 as described in sections 3.4.1 and 3.4.2

3.4.1 Separatory Liquid-Liquid Extraction (Method 3510C)

All the aqueous sludge samples were extracted at neutral, acidic and basic pHs as recommended by the EPA, since GC-MS was to be used for the screening of the extracts.

This is because some of the organic compounds of interest such as organochlorine pesticides may chlorinate, phthalate esters may exchange and phenols may react to produce tannates (USAEPA, 2003). The reactivity of these compounds is more likely at high pH (*i.e.* under basic extraction).

The extraction procedure involved measuring 1.00 litre of sample and transferring the contents in the glass bottle into a 2.00 litre graduated glass measuring cylinder. The samples were first extracted at neutral pH, which was the pH of all the aqueous samples. The sample was quantitatively transferred from the measuring cylinder into a separating funnel.

The extraction and drying solvent recommended by EPA method for aqueous samples was dichloromethane. The cylinder was rinsed with dichloromethane (60.00 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 of the solvent (*i.e.* 60.00 mL) and all the three extracts were collected into one Erlenmeyer flask. This was then transferred into a glass beaker (1.00 litre) ready for drying (section 3.5). The flask was rinsed with dichloromethane (60.00 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 1.0 by addition of sulfuric acid. The acidic sample was extracted three times with fresh portions of dichloromethane (60.00 mL). The three extracts were combined then transferred into a 1.00 litre glass beaker ready for drying (section 3.5). Thereafter, the acidic aqueous layer was adjusted to pH 13 using NaOH (10 N) and the sample was extracted three times like in the previous cases. These pH changes were measured using a wide-range pH paper. The combined extracts were transferred into glass beaker for drying. The summary of this extraction method is represented in Figure 3-1.

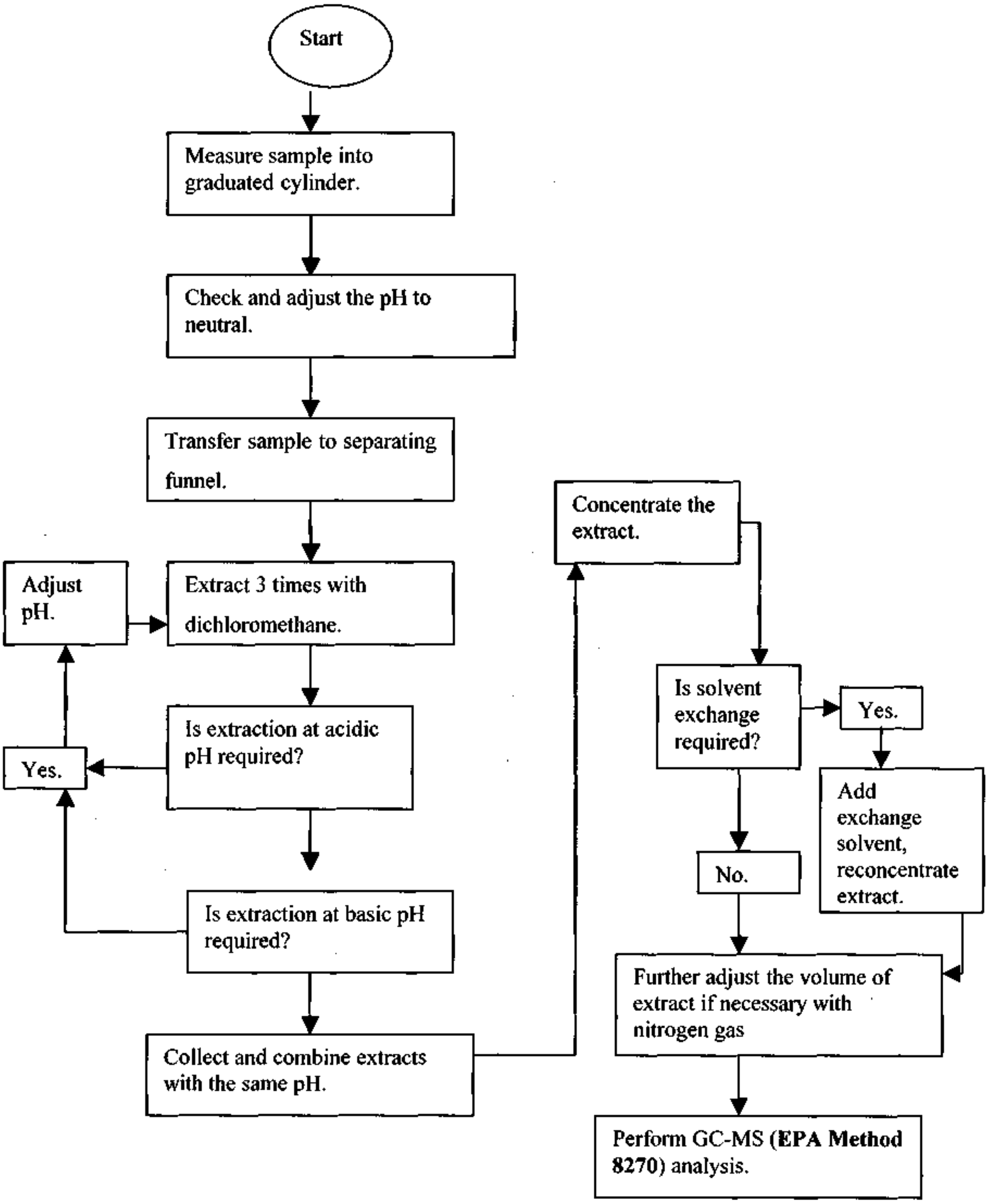

Figure 3-1 **The diagram indicating sample preparation using the separatory liquid –liquid extraction.**

3.4.2 Soxhlet Extraction (Method 3540C)

In cases where the solid sludge was still very wet it was allowed to dry under cover in the laboratory 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 a mortar and pestle or/and grinding machine (Glen Creson grinder). The purpose of grinding was to increase the extraction efficiency by increasing the surface area. Since the results were to be expressed on a dry weight basis, two portions of sludge were weighed. Thus one portion was used for the determination of moisture content while the second was extracted with the Soxhlet extractor. A 10 g sludge sample was dried in an oven set at 106 °C for 24 hours. The samples were cooled in a dessicator 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 portion of the sample (10 g) was thoroughly mixed with an equal amount of dried anhydrous sodium sulfate. This was done such that any remaining moisture in sludge is absorbed by sodium sulfate and sludge particles are 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 (300.0 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 3-2.

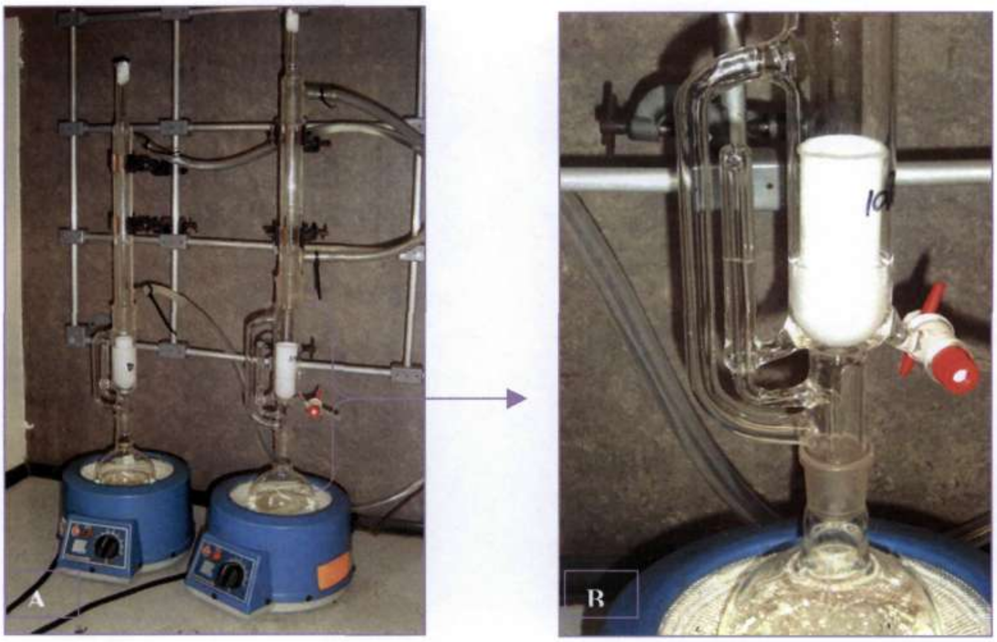

Figure 3-2 **The Soxhlet extractor placed in heating mantle (A) and enlarged view of cellulose extraction thimble (B).**

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 3.5). The Soxhlet extraction procedure is summarized in the flow diagram in Figure 3-3.

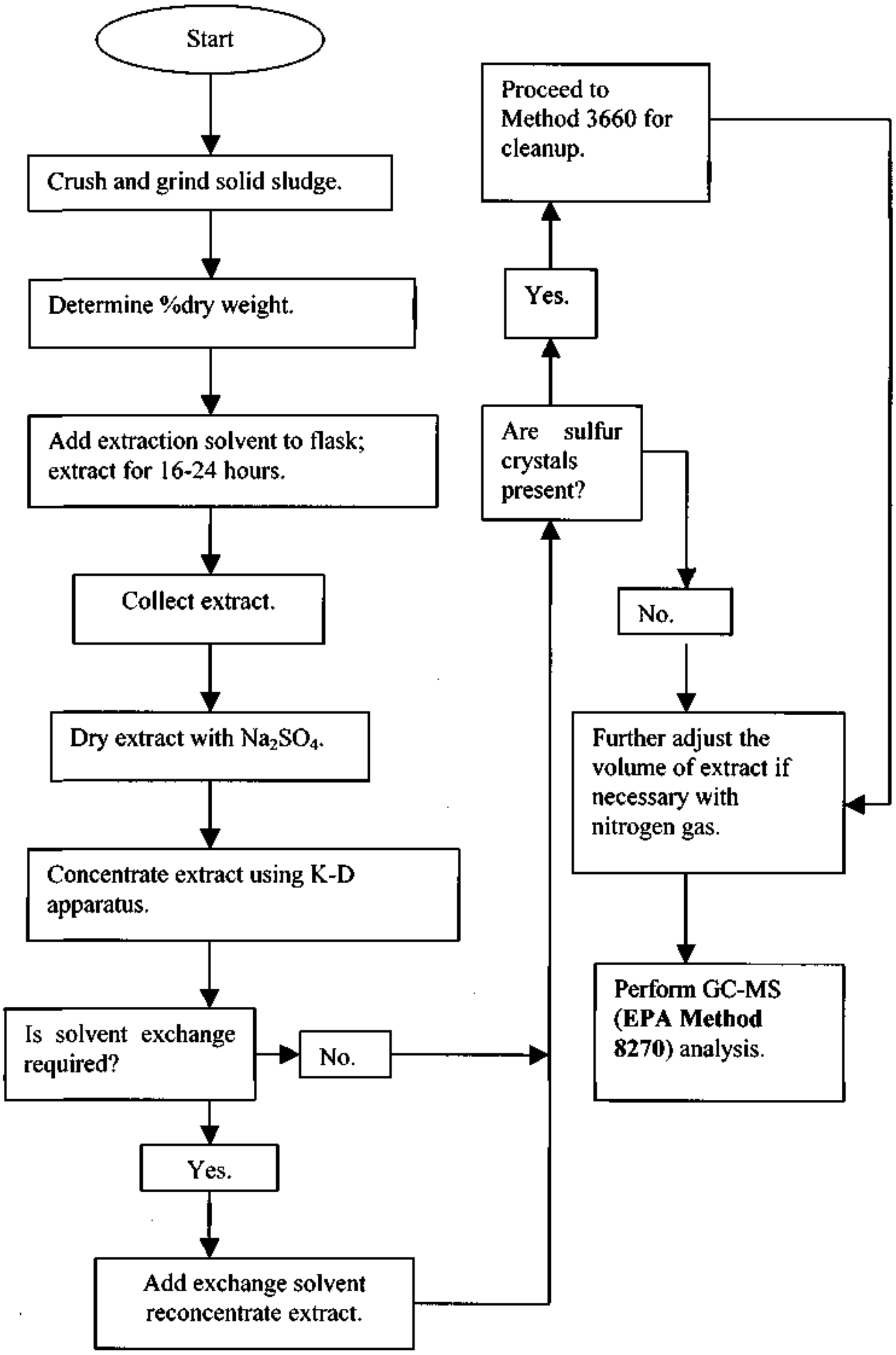

Figure 3-3 The schematic representation of the Soxhlet extraction procedure (USEPA, 2003).

3.5 Drying of the Extract

The extracts from the aqueous and solid sludge samples were dried using two different processes. 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 hence enhancing the drying process. A drying column was not used in this case because the extract contained some emulsion and 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 the K-D apparatus for concentration (section 3.6). The beaker used was then washed with 120.0 mL of the dichloromethane and the rinsate transferred into the K-D apparatus to complete quantitative transfer.

The solid sewage sludge extract was dried by passing the extracts through a drying column containing 10 cm anhydrous sodium sulfate. The dried extract was collected in a 250.0 mL Erlenmeyer flask. Thereafter the round-bottom flask used during the Soxhlet extraction was rinsed with the mixture of hexane and dichloromethane (120.0 mL, 1:1 v/v) and the rinsate 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.

3.6 Extract Concentration

The dried extracts from both the aqueous and solid sewage sludge were concentrated by transferring them into 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 2.00 mL.

Thereafter the evaporation flask was sealed with a glass stopper and allowed to cool to room temperature (*i.e.* 23 °C). If there were sulfur precipitates at the bottom of the extract, 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 1.00 mL of the extraction solvent and the rinsate transferred into the bottle. The volume of the concentrated extract was adjusted to 3.00 mL by blowing nitrogen through the extract. The extract was thereafter transferred to a 3.00 mL storage glass vial with a Teflon® screw top and stored at ± 4 °C. A 1.00 mL sample was then transferred into a 1.00 mL vial ready for GC or GC-MS analysis.

3.7 Purification Technique

It is recommended that sludge extracts 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.

Among these purification techniques, the sulfur clean-up process was applied because sulfur precipitate was observed in most of the concentrated extracts, particularly extracts from solid sludge samples. The procedure for the sulfur cleanup is described in section 3.7.1.

3.7.1 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 extract using tetrabutylammonium sulfite is briefly described.

The concentrated extract (3.00 ml) was transferred into a 50.00 ml transparent glass bottle having a ground glass stopper sealed with Teflon® tape. TBA sulfite solution (1.00 ml) and 2-propanol (2.00 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, more of crystalline sodium sulfite was added and the contents shaken until crystals were observed. Ultrapure water (5.00 ml) was added to the saturated solution and the contents were shaken until the entire solid residues were 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 a glass Pasteur pipette. The final volume of the extract was adjusted to 3.00 ml by blowing nitrogen through the extract. Thereafter the extract was stored in a 3.00 ml glass vial having a Teflon® lined cap and stored at ± 4 °C prior to analysis. The summary of this cleanup procedure is shown diagrammatically in Figure 3-4.

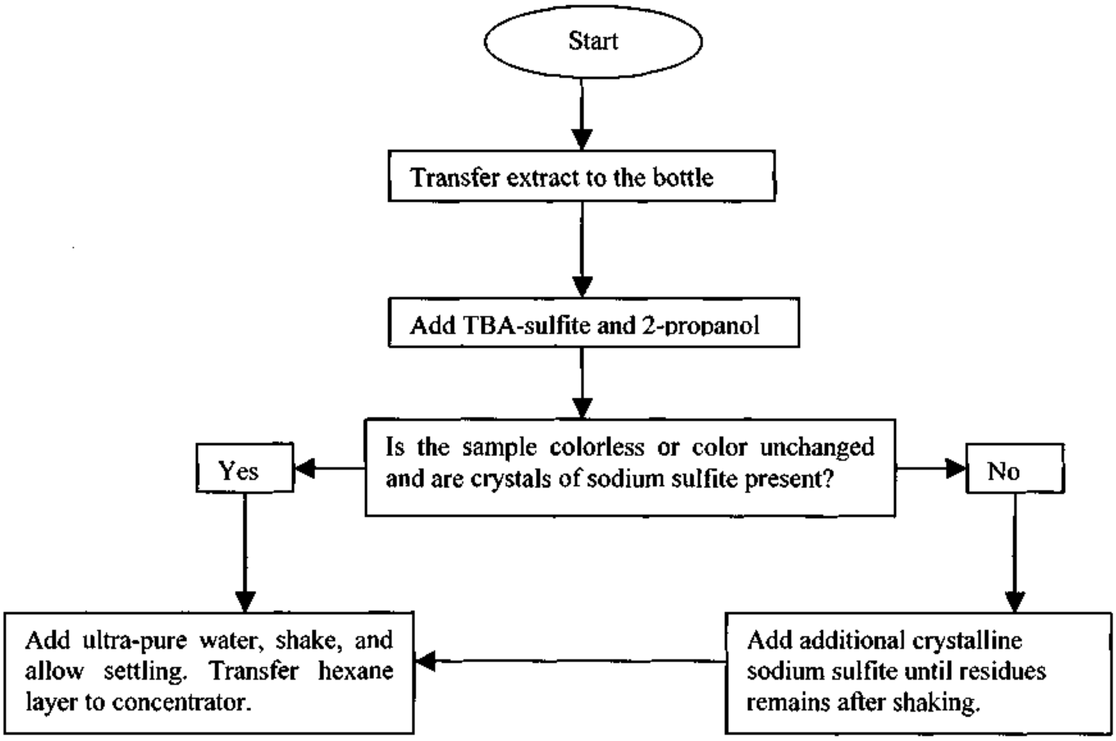

Figure 3-4 **The diagrammatical representation of the sulfur cleanup method.**

3.8 Qualitative Analysis

The screening of 109 samples was carried using Environmental Protection Agency (EPA) methods, namely Separatory Liquid-Liquid extraction (section 3.4.1) and Soxhlet extraction (section 3.4.2) for liquid and solid samples respectively. The extraction was followed by clean-up using USEPA approved method (section 3.7.1). The clean extracts were then scanned for all possible organic compounds using GC-MS. All the screening (*i.e.* identification of organic compounds) of 78 samples from 69 wastewater treatment plants was done at Umgeni Water PLC Laboratory using an HP6890-Series gas chromatography mass spectrometer. The samples were made up of 9 liquids and 69 solids. One microlitre of each of the concentrated and several cleaned extracts were injected into the GC-MS using a 10-μl syringe.

The chromatographic separation was achieved using a DB-5 MS capillary column. The GC-MS was operated in splitless mode with the gas saver on and helium as the carrier gas. The sample injector and sample pumps were washed six times prior to the injection of the sample and after the injection with acetone and methanol. The acquisition mode was used for scanning. The identification of the organic compounds was performed using the Wiley 275.L Library. A typical GC-MS spectrum for one of the organic compounds that was identified using this library in shown in Figure 3-5.

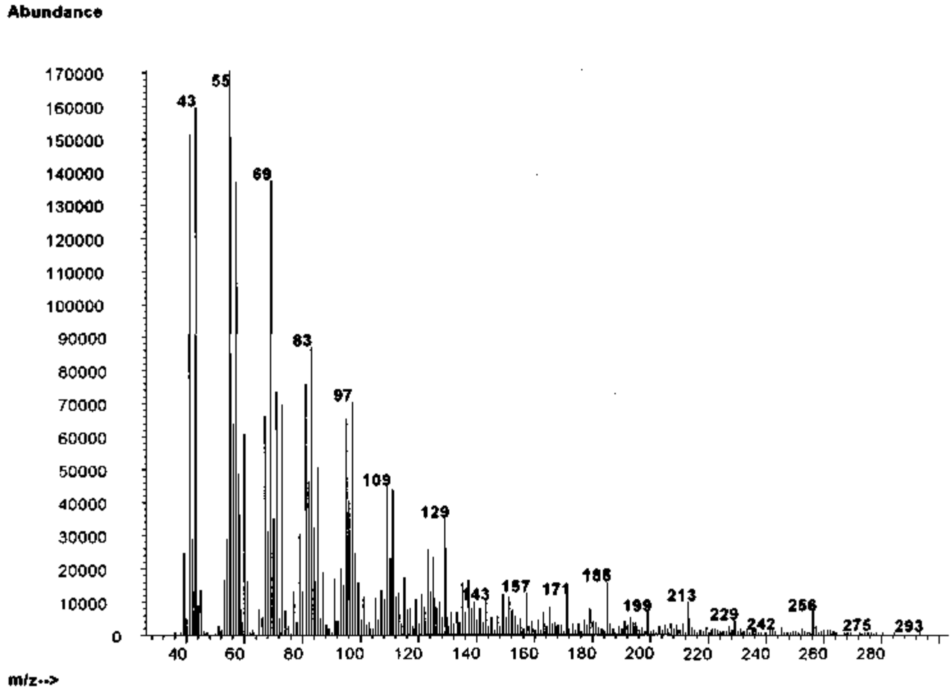

Figure 3-5 **GC-MS spectrum of one sludge sample obtained using Wiley 275.L Library.**

The organic compounds that the GC-MS could identify with a confidence limit of 80 % and above were recorded. The instrument conditions and parameters as used are summarized in Table 3-3.

Table 3-3 **HP6890-Series GC-MS operating conditions.**

Parameters	Values	Parameters	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

3.9 Quantitative Analysis

The samples that were subjected to quantification process are those classified as worst and best South African sewage sludge samples based on the quantification of metal ions (Synman *et al.*, 2004). The organic contaminants that were quantified were those known to be toxic to soil, plants and humans once introduced into the environment. In addition, these compounds appear in the recent USEPA 503 list of priority organic pollutants and the EU 2000 working paper of sludge (A-2 in Appendix A, UMK-AG, 2000; EU, 2000).

A total of 13 wastewater plants were selected for the quantification of p-cresol and nonylphenol (7 worst cases and 5 best cases – class D sludge based on mineral elements in Syman *et al.*, 2004, as well as one plant chosen on the basis of the organic content of its sludge). These two compounds as well as PAHs were widespread 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 pollutants. The names of the selected sites are listed in Table 3-1. 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.

The other organic compounds that were quantified were pesticides 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 to confirm the screening results by doing the quantification using GC-MS at the ion detection level where sensitivity is 5 000 times that at the scanning mode, as used in the scanning process. Samples were also subjected to GC-analysis.

Since target compounds (*i.e.* 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 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 time had an effect on the extractability of the organics. The details are included in sections 3.9.1 and 3.92.

3.9.1 Preparation of the Calibration Standard Solutions

Pure compounds of hexachlorobenzene, 4,4'-DDT, dieldrin, heptachlor, lindane and aldrin were weighed (0.0100 g) and dissolved in small amount of hexane. Thereafter the volume was made to the mark with hexane in a 10.00 mL volumetric flask, making the stock solution of 1 000 mg/L. Composite stock standard solutions of phenols (*i.e.* p-cresol & nonylphenol) with concentrations of 1000 mg/L were prepared by weighing 0.0100g of pure compounds. The volume was made to the mark (10.00 mL) with hexane. The composite calibration standard solutions of both the pesticides and phenols were prepared from their respective stock solutions by dilution. 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 pesticides peaks were identified by running one standard solution on the GC-MS in order to identify each organochlorine pesticide.

3.9.2 Preparation of Reference Sludge

The sewage sludge sample from Heidelberg (sample number 10) was arbitrarily chosen for the preparation of 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 purpose of extracting the sludge five times was to ensure that most of the organic compounds in the sludge were significantly reduced. The different portions of the reference sludge were mixed together to form a representative sample. A control sewage sludge and nine spiked sewage sludge samples were prepared.

3.9.3 Spiking of Reference Sludge with Pesticides

A representative reference sludge sample (120 g) was obtained by mixing the individual reference sludge samples together. Before the mixture was spiked, 10 g were 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 the organochlorine pesticides (*i.e.* aldrin, DDT, dieldrin, heptachlor, hexachlorobenzene 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 3-4. The weighed pesticides were mixed and dissolved in 200.0 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 3-4 **The concentrations and masses of the target compounds added to 110g reference sewage sludge.**

Pollutants	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 at which each sample, given numbers 10 i to 10 iii were extracted is recorded in Table 3-5.

Table 3-5 **The time interval at which the spiked reference sludge was extracted.**

Sludge number	Extraction time after spiking/days
10i	2
10ii	6
10iii	9

The organochlorine pesticides that were extracted from the reference sludge were diluted in order to fit within 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 achieved through the dilution process. The extracts were analysed using the GC and GC-MS.

3.9.4 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 to and after sample injection. The HP6890 series GC-MS was used to confirm the identity of the compounds detected using GC-FID and GC-ECD. The operating conditions for the analysis of both the phenols and pesticides are provided in Table 3-6 and 3-7 respectively.

Table 3-6 **The operating conditions for the single analysis of the phenols using GC-FID.**

Parameters	**Values**	**Parameters**	**Values**
Ramp 1		***Ramp 3***	
Initial temperature	80 °C	Final temperature	275 °C
Holding time	1.50 minutes	Rate	10 °C/min
Total time	1.50 minutes	Hold time	4.50 minutes
Ramp 2		Total time	35.50 minutes
Temperature	230 °C	Injector temperature	200 °C
Rate	6.0 °C/min	***FID***	
Total time	26.50 minutes	Temperature	50 °C
		Range	10

Table 3-7 **GC-ECD operating conditions employed for the analysis of pesticides compounds.**

Parameters	**Values**	**Parameters**	**Values**
Ramp 1		***Ramp 3***	
Initial temperature	100 °C	Final temperature	270°C
Hold time	2.00 minutes	Rate	5.0 °C/min
Total time	2.00 minutes	Hold time	15 minutes
Ramp 2		Total time	46.0 minutes
Temperature	160 °C	Pressure	540 kPa
Rate	15 °C/min	Injector temperature	225 °C
Hold time	3.00 minutes	***ECD***	
Total time	9.0 minutes	Temperature	300 °C
		Range	10

3.9.5 Setbacks Encountered During the Quantification of Phenols

It was discovered during the analysis of phenol calibration standards that after every run the p-cresol and nonylphenol peaks were decreasing in size and becoming broader and their elution time increased. Thus it appeared as if the column was becoming more contaminated with phenolic compounds that were retained during analysis. The broadened and smaller phenol peaks with varying retention times of the calibration standards will make the analysis of phenols in samples difficult as phenols in sludge extracts could not be identified and quantified with certainty. Every effort to clean or regenerate the column was not successful.

3.10 References

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CHAPTER 4

CHAPTER 4

4 Results and Discussion

4.1 The organic compounds in the South African Sewage Sludge

In general a total of 712 organic compounds were detected in the South African sewage sludge. The qualitative results in section 4.1.1 focus on results obtained from all the wastewater treatment plants (WWTPs) in the nine provinces. In section 4.1.2 an overview of the different types of organic compounds that are likely to be found in South African WWTPs is provided using the results from sampled plants. A detailed discussion of provincial and national results are given the sections (section 4.11 & 4.1.2) below.

4.1.1 Provincial Results

The results obtained from the individual wastewater treatment plants (WWTPs) have been summarized in terms of provinces and the individual results are compiled in Appendix C. Table 4-1 gives an indication of the type of organic compounds that were identified in various sewage sludges. The numbers in the Table 4-1 represent the number of times the compound was detected in the different sewage plants within the province. The compounds have been grouped within a major functional group or properties. "Identification" is based on the results of gas chromatography coupled with mass spectrometric detection (GC-MS) (section 3.8) 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 Appendix C was further compressed to give Table 4-1. 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.

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

Organic Compounds	Province/Frequency									
	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
Biphenyls	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.*

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

The results provided above (Table 4-1) are discussed below according to their functional group.

- **Phenols**

A total of fifteen different phenols were detected countrywide and it was found that 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. Phenols have also been reported in several European countries even though the individual contaminants are not the same (Langenkamp & Pärt, 2001; EU, 2000). Gauteng province (GP) samples were the most contaminated with phenolic compounds as they appeared 38 times in WWTPs, followed by the Western Cape with a frequency of 18. These two provinces were followed by the North-West and Eastern Cape each with a frequency of five, lastly Limpopo, Free State, KwaZulu-Natal 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. Para-cresol (p-cresol) was detected in all provinces except in Mpumalanga, North-West and Free State provinces. The province with the highest frequency of p-cresol was Gauteng (14) followed by Western Cape (6), Limpopo (3) and KZN as well as Eastern Cape each with a frequency of one. The other phenols were detected in few sewage sludges and at a lower frequency of occurrence.

A high level of phenols in sewage sludges could be hazardous to humans, animals, surface and groundwater and soil living organisms depending on the phenol concentration once introduced into the environment (ICON, 2001). It has been reported in literature that over 50 % of 4-nonylphenolpolyethoxylates gets converted into nonylphenol (NP) (ICON, 2001). The screening of the South African sewage sludge, especially the solid samples, has shown that these samples contain NP (Appendix C). The source of these compounds can be assumed to be the NpnEO (nonylphenolpolyethoxylates).

- **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 (WFPHA, 2000). 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 legislation 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** (Naidoo and Buckley, 2003)
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 frequency in all provinces except in Mpumalanga. Unlike phenols there was no specific PAH that was common to all or most provinces at a high frequency of occurrence. There were many different PAHs identified in most sludge samples with Gauteng having the highest frequency (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 twice in KZN as well as the Western Cape province. 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 a frequency of two or three.

The similarity between the SA and French (Table 1-5) results is that both recorded the presence of fluoranthene in their sludge samples. In addition according to the studies done on digested sludge from 14 UK wastewater treatment plants, it was found that several PAHs occurred more frequently than others. These were 2,6-dimethyl naphthalene, 2,3,6-trimethyl naphthalene, fluorene and phenanthrene (Stevens *et al.*, 2003). All these compounds were also detected in some of the SA sludge samples. It is reported in literature that PAHs undergo biodegradation by soil microorganisms especially under aerobic conditions. (Radding, *et al.*, 1976). Hence it can be said that the application of sewage sludge contaminated with PAHs will not increase the PAH content in the environment depending on the half-life of PAH and whether the soil is turned frequently.

- **Phthalates**

Studies carried out 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 frequency 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 frequency in Gauteng (4) and it appeared in four provinces. Diethyl phthalate was detected twice in some of 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).

- **Biphenyls**

Three types of biphenyls that were identified by the GC-MS namely 1,1'-biphenyl, phenylmethyl-1,1'-biphenyl and 2,2',3,3',4,4'5,5'-biphenyl. All three biphenyls appeared in Gauteng and only one (*i.e.* 1,1'-biphenyl) in KZN province. Biphenyl is mainly employed in the production of dye carriers, heat-transfer fluids and alkylated biphenyls (Gersich *et al.*, 1989). In addition, it is used as the starting material for the generation of polychlorinated biphenyls (PCBs) (Rogers *et al.*, 1989). Thus the chlorination of biphenyl results in the formation of PCBs since biphenyls have 10 sites available for chlorination.

The scanned results indicate that 1,1'-biphenyl was detected four times while the other two appeared once. It can be said that in South Africa, especially in Gauteng there are some industries that use biphenyls during the production of dyes, heat-transfer fluids and alkylation of biphenyls. The presence of chlorinated biphenyl (PCB) indicates that some industries still use them as coolants and lubricants in transformers, capacitors, and other electrical equipment since PCBs are not banned in South Africa (DEAT; Hardy, ATSDR). Moreover, international studies by some European Union countries have shown that PCBs have been detected in sewage sludges (Appendix A, Table A-7, A-8 & A-13) and regulatory limits have been set in several European countries (Table 1-8, section 1.7) as well as in South Africa (Table 1-8, section 1.7).

- **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 in KZN and NCP. 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 be 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 other 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 frequency (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 in 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 frequency (6) as tributylamine but appeared only once in the other two provinces (LP and KZN). The other amide that was detected more than once was n-tetradecanoic acid amide, 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 wastewater treatment plants around the country. In each province there were sample(s) that were contaminated with these compounds and Gauteng recorded the highest frequency (36) of occurrence. The number of times that the aldehydes were detected in other provinces are:

Western Cape (9), KZN (6), Limpopo (4) while the frequency 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).

- **Carbonyl compounds**

A significant number (more than the above compounds) of different carbonyl compounds were detected in eight provinces where a total of seventy-two esters were identified. Gauteng (frequency of 83) had the greatest number of carbonyl compounds in its sludge samples followed by the Western Cape with a frequency of twenty-five. The frequency 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 carbonyl compounds relative to the other provinces.

Ketol (indole) appeared in five provinces and was detected at greatest frequency 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).

- **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, a frequency of 235 being recorded. The province that recorded the highest frequency 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 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 frequency (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. 1,4-Dichlorobenzene (DCBs) have been categorized by organizations such as the United States Environmental Protection Agency (USEPA) as priority pollutants (Liu, 2002) – of these, only dichlorobenzene was detected and that only in two samples.

- **Alcohols**

A total of 48 different alcohols were identified. Samples with the most alcohols were those from Gauteng where a frequency of 54 was recorded, followed by the Western Cape with forty. The frequencies from other provinces were as follows: 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 alcohols can be found in solvents such as car shampoos and degreasing products, household cleaners as 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 frequency 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 all 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 frequency was observed in samples collected in Gauteng with a frequency of 180 followed by the Western Cape with a frequency 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.

There were two other 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 (ICON, 2001). Nonetheless siloxanes do not display considerable environmental toxicity nor do they bioaccumulate (ICON, 2001).

- **Summary**

Volatile organic compounds are mostly 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 show insignificant or no degradation during the treatment process such as PCBs and most organochlorine pesticides (*i.e.* aldrin, chlordane, DDT, endrin and heptachlor) (Carson, 1963; Baxter, 1975; Clark, 1979; Tucker 1975; Tulp, 1978 and Wong & Kaiser, 1976).

From this screening study it can be said that the SA sewage sludges do not contain the target pesticides listed in the legislation. 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	**Province/Number of different compounds**									
	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)**	**Total no. of different compounds**
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**
Biphenyls	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**

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

In general the samples from Gauteng contained the highest number of 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 2-15 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. Consider Limpopo and North-West provinces, the same number of samples (7) were collected from these areas but the number of compounds in each group were different in most cases. In addition, a similar trend can also be observed in the Eastern and Northern Cape results where the same number of samples was taken. Percentage comparisons indicating the number of treatment plants that were sampled in each province.

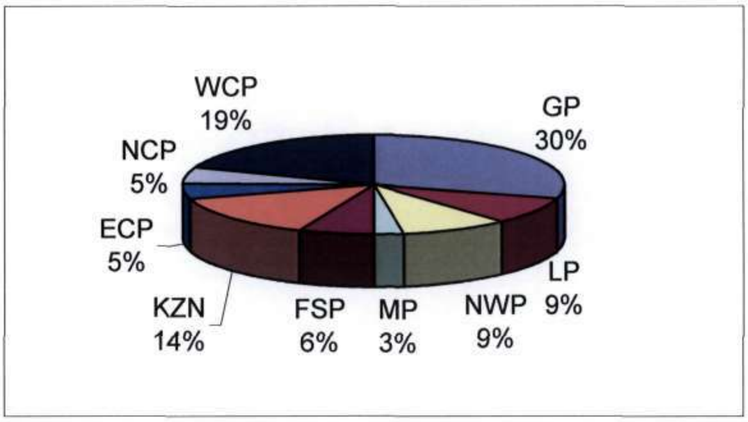

Figure 4-1 **A percentage comparison of WWTPs sampled in SA nine provinces.**

Furthermore, all the nine provinces recorded a reasonably high number of acids, hydrocarbons and others (relative to number of phenols, pesticides, phthalates, biphenyls, furans) with Gauteng and Western Cape recording the highest numbers. There was a relatively low number of the different types of organic compounds considered as the 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 ones.

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 was tested. For this reason standard reference sludge was prepared as described in section 3.9.2 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 (Figure 4-2 & Table 4-4). The results as indicated by the GC-MS chromatograms in Figure 4-2 show that the cleaning process was successful, having removed a considerable amount of the organic compounds in the sludge matrix. The result in Table 4-4 is a summary of five extracts from one samples. These are recorded in terms of frequency of occurrence of organic compounds (*i.e.* how many times a group of compound was detected to exist with the 80 % or above confidence limit).

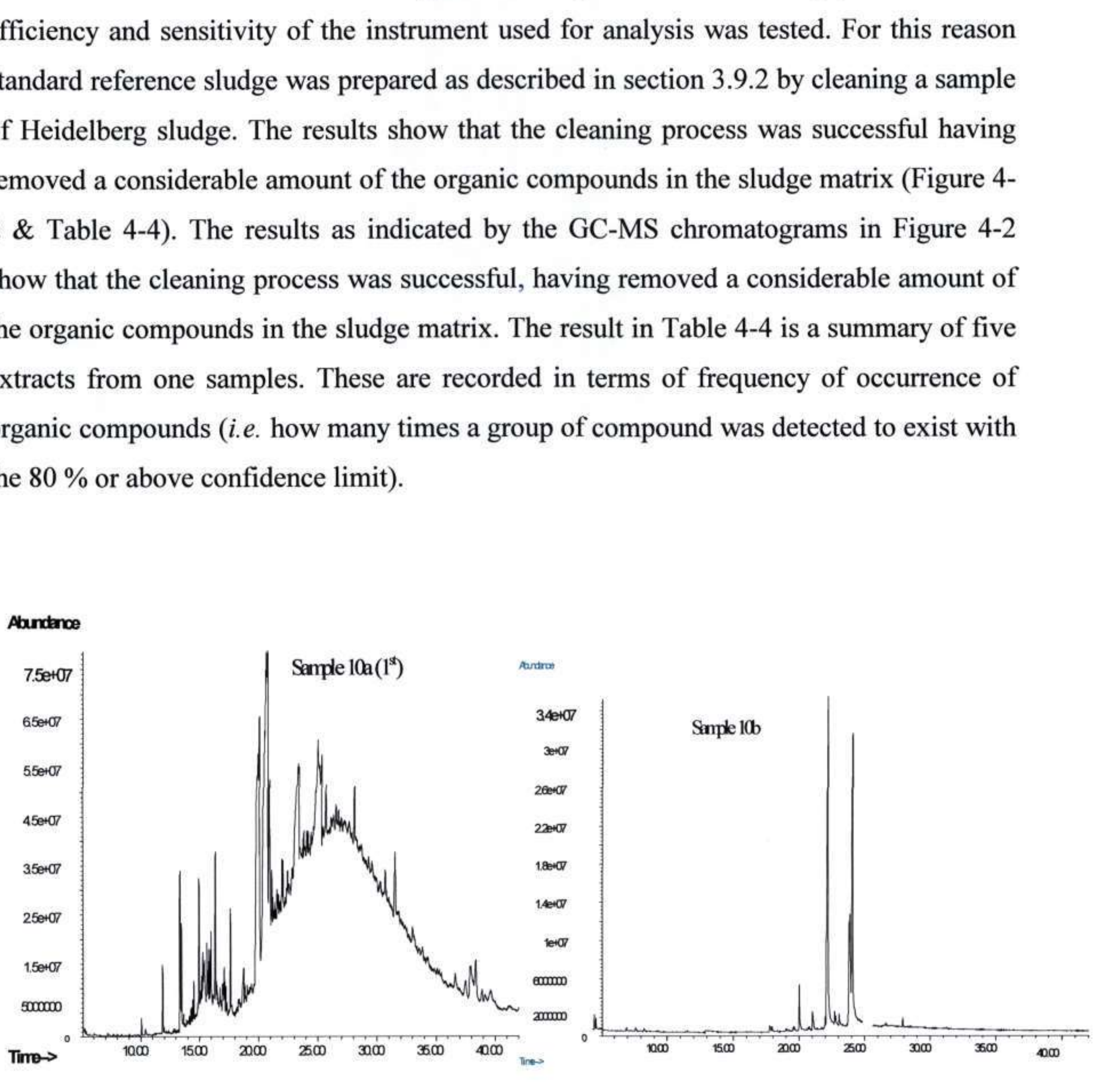

Figure 4-2 The GC-MS chromatograms of first [sample 10 a (1st)] and fifth [sample 10 b] extracts of reference sludge.

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

Organic Compounds	First Extract	Fifth Extract
Phenols	1	-
Amines	1	-
Esters		-
Acids	7	6
Chlorinated Hydrocarbons	2	-
Alcohols	1	-
Hydrocarbons	22	-
Others	8	-

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 devoid 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 screened results indicated 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 legislation. 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 two chromatograms of the composite pesticides from the GC-MS and GC-ECD are shown in the Figure 4-3 and 4-4 although the retention times are not the same due to the difference in operating conditions and columns. However, the order of elution of the pesticides is the same in both chromatograms.

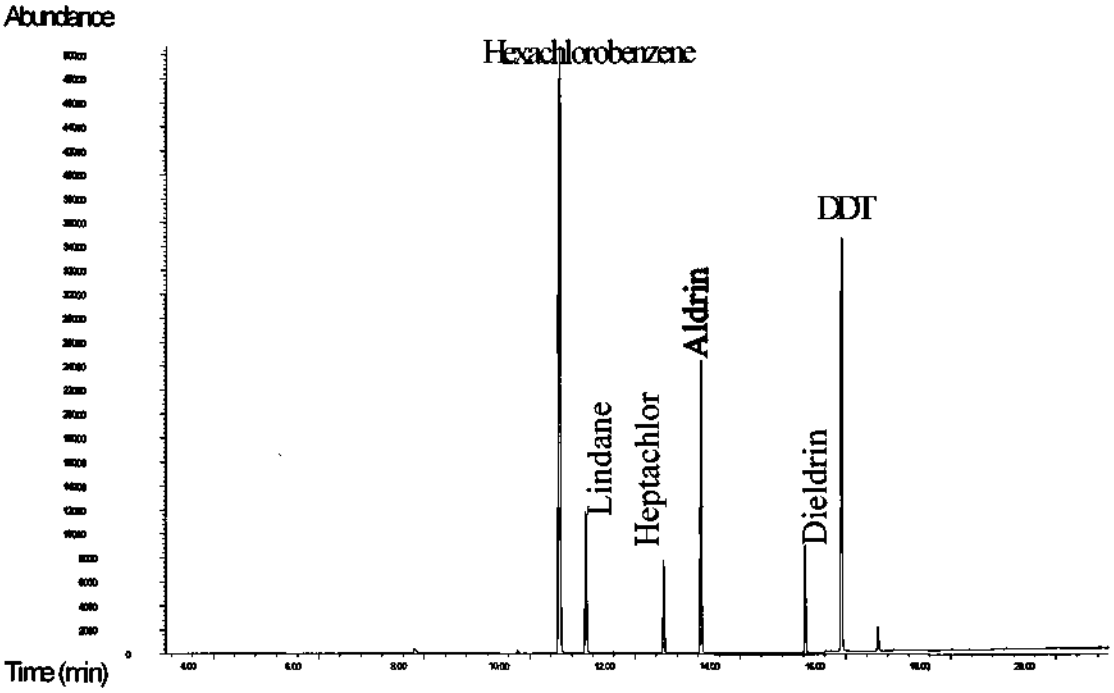

Figure 4-3 GC-MS chromatogram of the six pesticides in the standard solution.

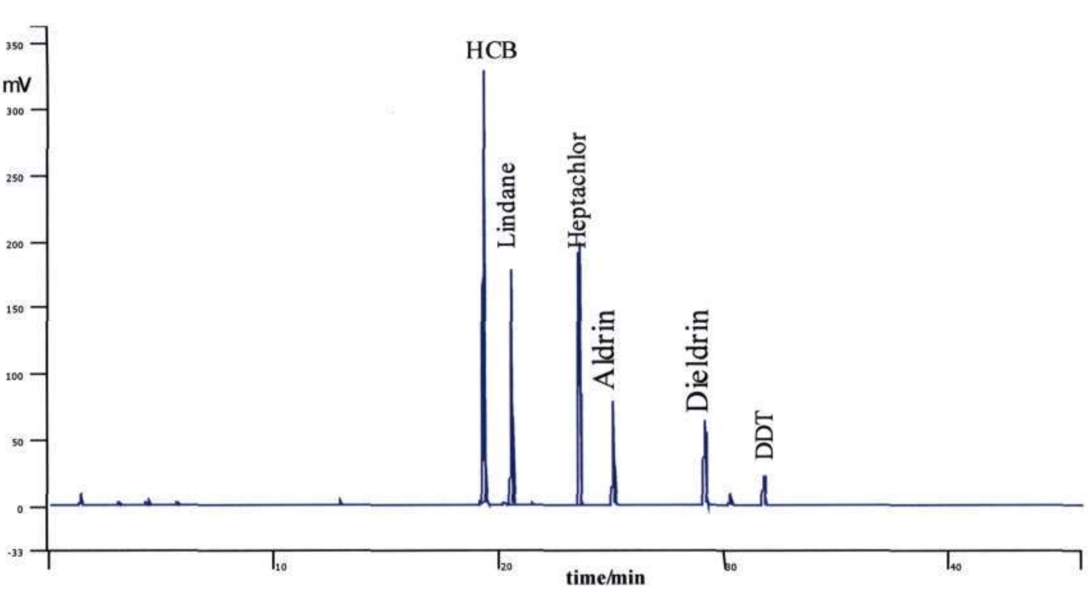

Figure 4-4 **GC-ECD chromatogram of the six pesticides in a composite standard solution.**

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. Thus p-cresol exists, as pure compound while nonylphenol is a mixture of compounds, hence the peaks of the quantified phenols using GC-FID are shown in Figure 4-6. All the peaks were also confirmed by spiking the samples with standard solutions.

The pesticide calibration equations in the form of $y = mx + c$ are shown in Figure 4-5, where y= area count, x= concentration, m= slope and c= intercept. While the calibration equations for phenol standard solutions took the form of $y = mx$ as indicated in Figure 4-7 and the variables are the same as those in the pesticide graphs. These graphs were constructed with the help of Origin 5.0, a data analysis and technical graphical software.

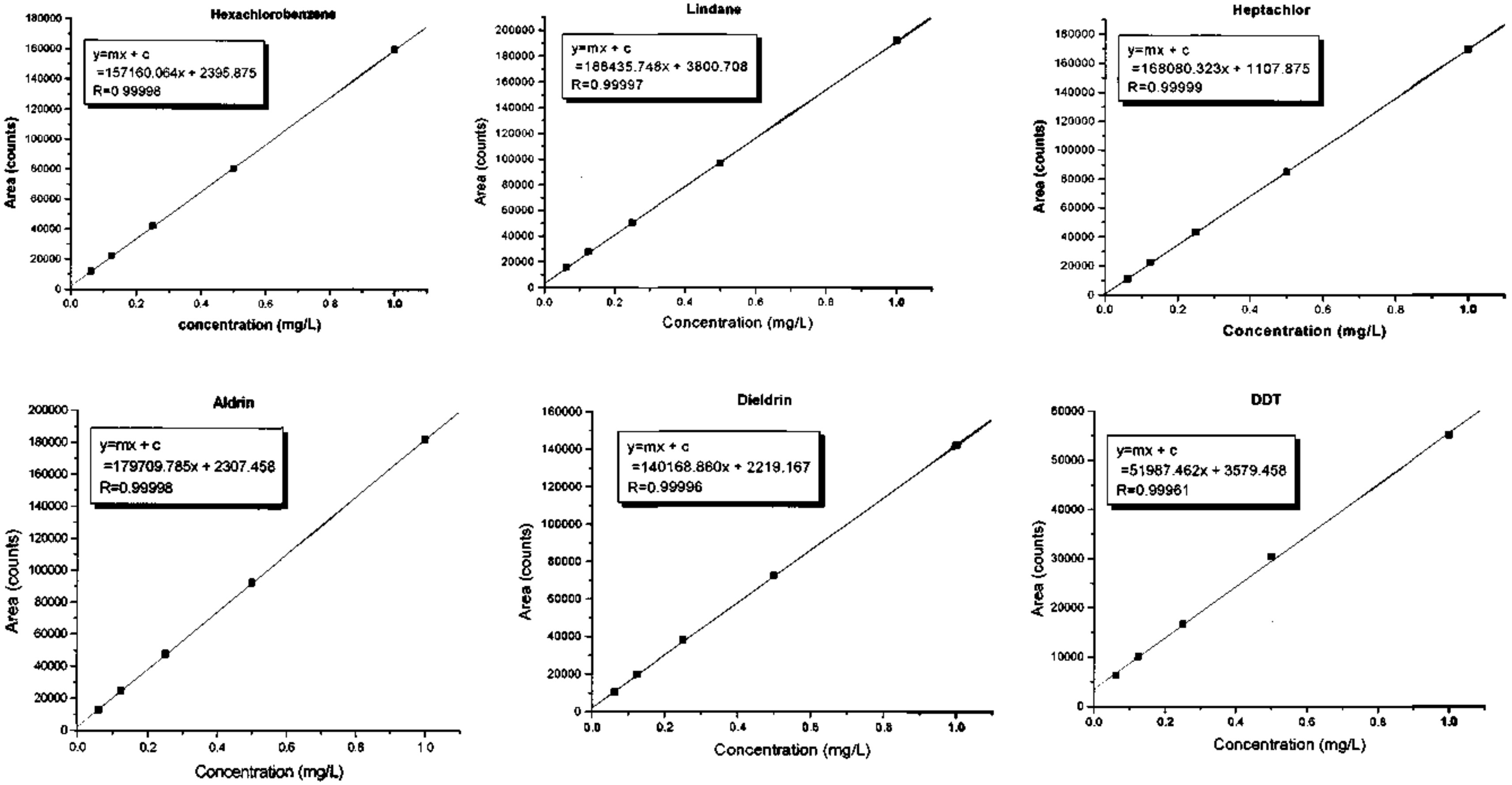

Figure 4-5 The calibration graphs for hexachlorobenzene, lindane, heptachlor, aldrin, dieldrin and DDT.

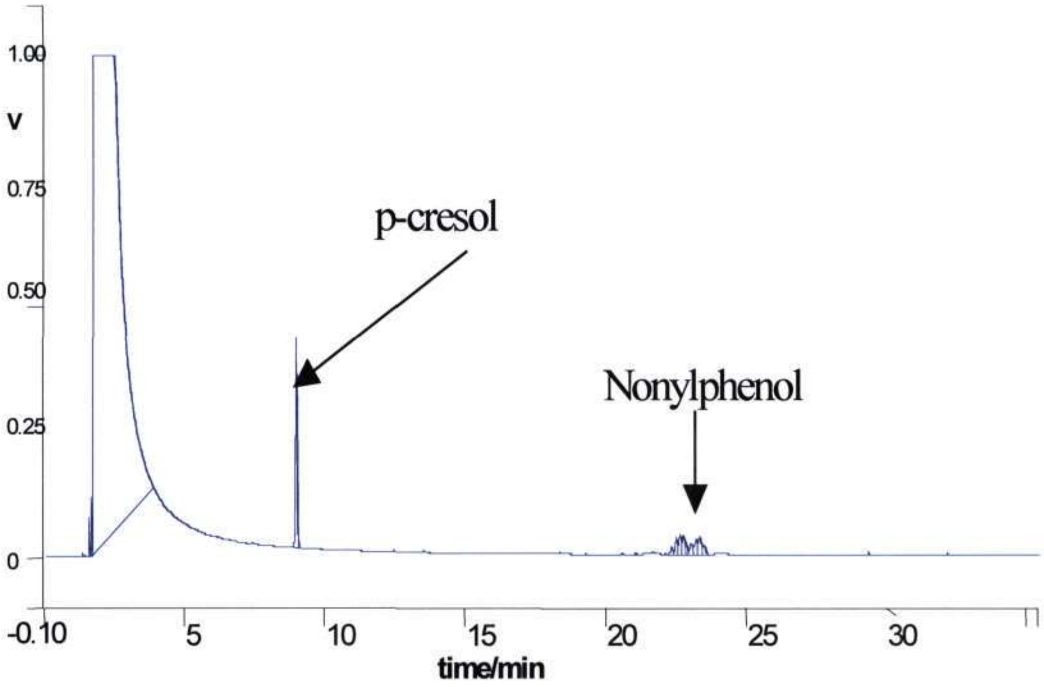

Figure 4-6 **GC-FID chromatogram of the phenols in the standard solution.**

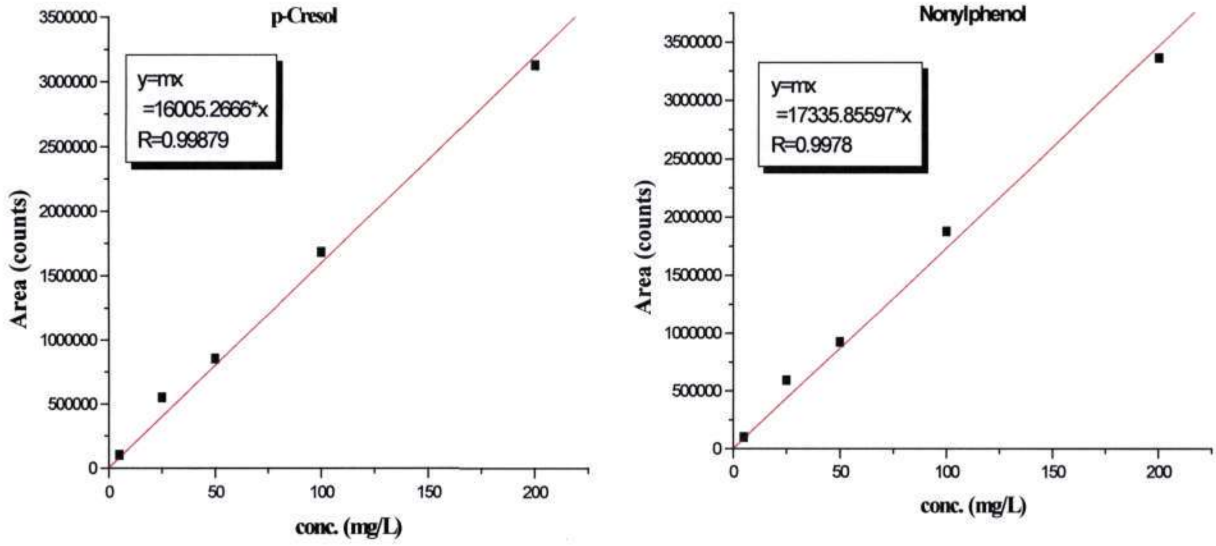

Figure 4-7 **The calibration graphs for p-cresol and nonylphenol.**

The spiked sewage sludge extracts were analysed by GC-MS using the selected ion-monitoring (SIM) mode, while the GC was attached to electron capture detector (ECD). A chromatogram obtained using GC-ECD is shown in Figure 4-8.

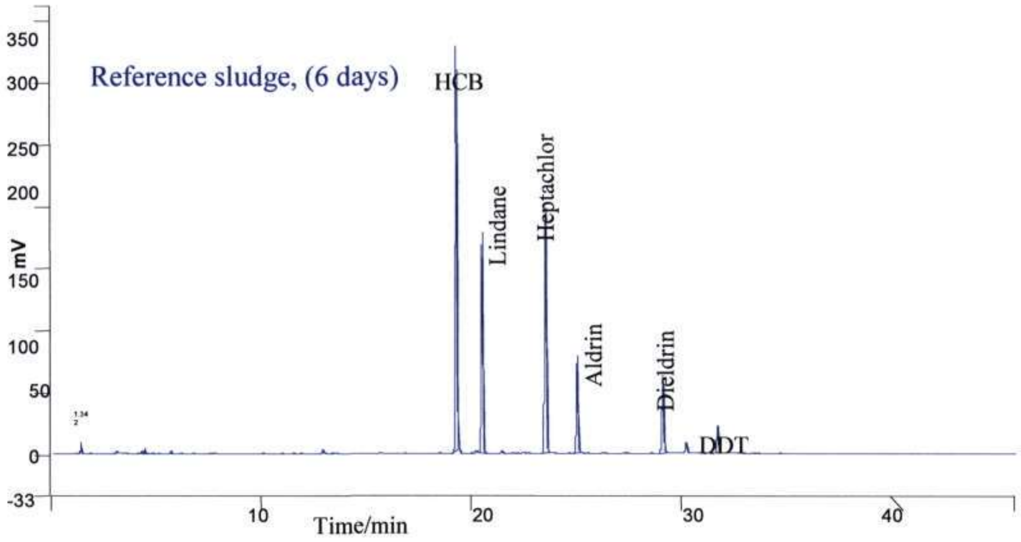

Figure 4-8 GC chromatogram of spiked reference sludge extracted six days after spiking (extracted samples were concentrated to 3 mL).

Using the GC calibration graph (section 3.9.1) the concentration of each of the six pesticides was determined and the results are recorded in Table 4-5. Included in the table are the masses of the target pesticides spiked to 110 g of reference sludge.

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

Pesticide	**Mass added (mg)**	**Concentration added (mg/kg)**	**Recovered conc. (mg/kg)**			**% Efficiency**		
			6 days	**9 days**	**16 days**	**6 days**	**9 days**	**16 days**
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 shows 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 pesticides from the solid particles. The extraction efficiency ranged from as low as 39 % six days after spiking to 99 % after 16 days. The increase in efficiency can be related to the amount of the moisture in the sample.

After 16 days the loosely covered sample having been left in a room whose temperature during the day was approximately 23 °C and having had free movement of air, will most likely have a moisture content less than that of a sample extracted after two days. This explains 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 used 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 the boiling point of water. This means 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, hexane was spiked with various concentrations (¼, ½, ⅛, and 1/16 of the regulatory limit) of six target pesticides. All the peaks were observed except for dieldrin. A GC chromatogram showing the peaks is shown in Figure 4-9. Figure 4-10 is that of lindane showing how the intensity increased with increasing concentration.

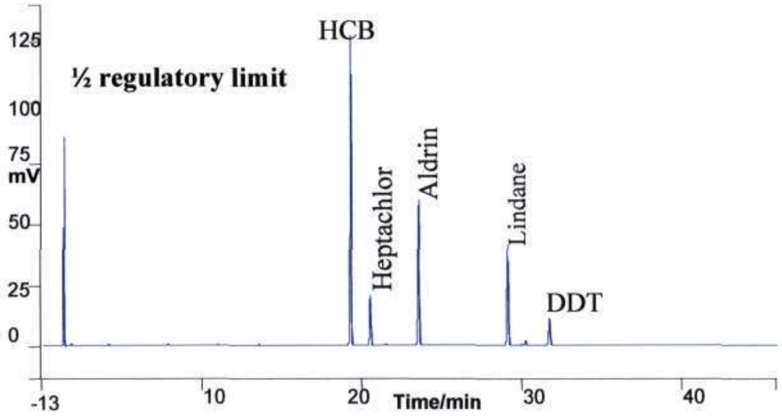

Figure 4-9 **GC chromatogram of hexane spiked with the six target pesticides at half the regulatory limit**

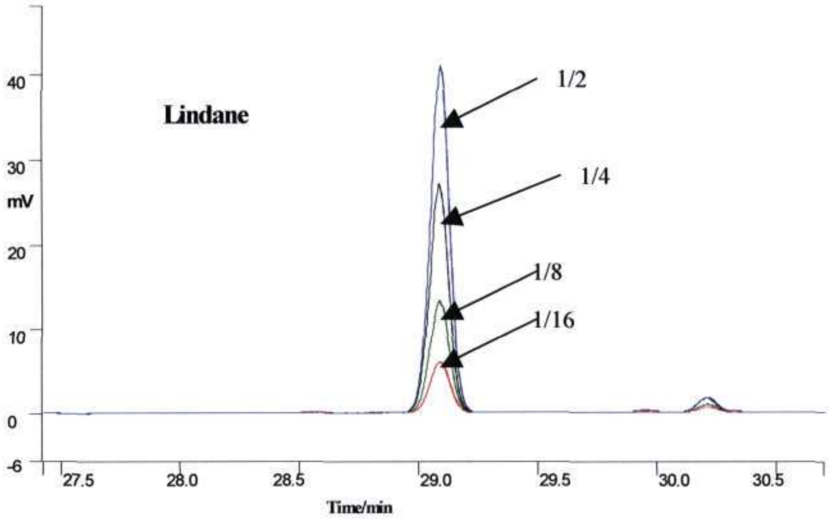

Figure 4-10 **The GC-ECD chromatogram showing the difference in the peak of solvents spiked with different concentrations of lindane.**

In addition to testing the extraction efficiency and sensitivity of GC-ECD, it was important to re-analyse all the samples using GC-MS in SIM mode. The instrument was calibrated using the calibration standards and the samples re-analysed. The results 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, organophosphates, carbamate/thiocarbamate, aniline/acetanilide and organochlorine (DDT – only for the control of malaria by government) (Naidoo and Buckley, 2003).

4.3 Quantification of p-Cresol and Nonylphenols

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

The samples, both best and worst sludges were subjected to the quantification of these compounds. The GC-MS and GC-FID chromatograms of one of the worst samples

(Sample 30) that were quantified for the phenols and the identity confirmed by the GC-MS, are shown in Figures 4-11 and 4-12.

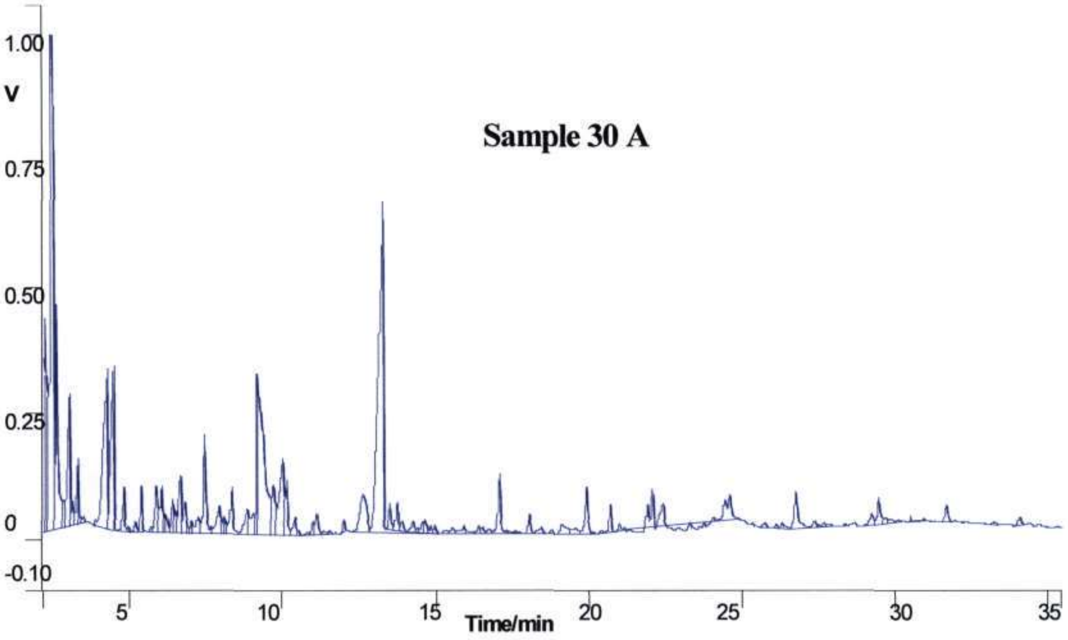

Figure 4-11 The GC-FID chromatogram used for the quantification of phenols.

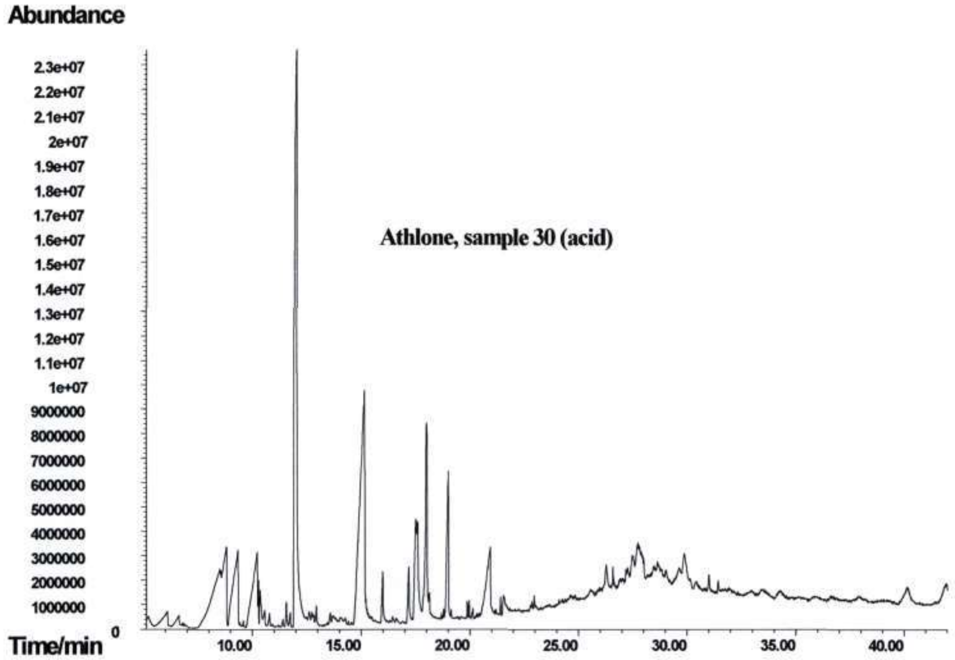

Figure 4-12 GC-MS chromatogram used to confirm the presence of phenols in Sample 30 A.

The extracts were analysed using GC-FID and the concentrations were determined using the standard calibration graph method (section 3.9.1). The average of three sets of concentrations of p-cresol and nonylphenol that were obtained is recorded in Table 4-6.

Table 4-6 **The concentration of phenols identified in the least- and most-contaminated sewage sludge samples.**

Sample no.	Sampling point	Treatment Process	p-Cresol conc. mg/kg)	Nonylphenol conc. (mg/kg)
Top best:				
Sample 28 (WC) Borcherds Quarry	Return Flow	Waste Activated Sludge	2.32	14.1
Sample 37 (WC) Oudshoorn	Compost heap	Compost	-	-
Sample 41 (KZN) Hammansdale	Centrifuge	Waste Activated Sludge	1.82	12.2
Sample 54 (NW) Boitekong	Return Flow		1.67	2.36
Sample 75 (KZN) Klipfontein	Heaps	Heated & Digested	-	-
Top worst:				
Sample 1 (Gauteng) Vlakplaats (wet sludge)	Wet Sludge	Anaerobic Digested	5.73	350
Sample 2 (Gauteng) Vlakplaats (compost)	Compost	Anaerobic Digested	0.35	203
Sample 4 (Gauteng) Dekema	Peddies	Anaerobic Digested	-	0.30
Sample 6 (Gauteng) Rondebult	Peddies	Anaerobic Digested	-	0.45
Sample 15 (Gauteng) Zeekoegat	Wet Sludge	Anaerobic Digested	-	0.15
Sample 21 (Gauteng) Percy Steward	Wet Sludge	Anaerobic Digested	0.50 **252**	114 **16.1**
Sample 22 (Gauteng) Flip Human	Wet Sludge	Anaerobic Digested	1.70 **192**	2079 **220**
Sample 30 (WC) Athlone	Drying Lagoon	Waste Activated Sludge	2.57 **464**	821 **65**
Sample 55 (NW) Brits	Drying Beds	Anaerobic Digested	-	-

- *The values in boldface are from the aqueous sludge samples*

There is no indication from the results in Table 4-7 that the sludge with the highest level of inorganic contamination according to Synman *et al.*, 2004, also has the highest level of phenol contamination.

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. This observation can be explained in terms of the high solubility of p-cresol in water, which is reported to be 1.9 g/100 ml (IPCS & CEC, 2001). 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 having a range of 0.15-2079 mg/kg with the values in Table 4-7 it can be concluded that the range of values found in SA sludges is not very different to the reported data from other countries.

Table 4-7 **Overview of concentrations of Nonylphenols (+ethoxylates) in Scandavian sewage sludges**

Investigations	**Number of samples**	**Range** mg/kg ds	**Median** mg/kg ds	**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

Higher NP concentrations (*i.e.* 330-640 mg/kg ds-dry solid) have also been recorded in the United Kingdom (UK) sewage sludges. These quantities are significantly higher than the EU limit of 20 mg/kg ds (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 (EU, 2000).

A 1996-1997 survey of Norwegian sewage sludge from eight plants has shown that m-/p-cresol concentrations ranged from 0 - 470 mg/kg ds (Paulsrud *et al,* 2000), while the range in the current study is between 0.35 – 5.73 mg/kg ds. 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 deduced that a lot of the p-cresol remains in the wastewater effluent 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 attributes this 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 in soil treated with NP-contaminated sludge. Hence those sewage sludges that are highly contaminated with nonylphenols pose a potential environmental hazard. However, there is no proof that continuous application of sewage sludge on the same land results in the accumulation of nonyphenol although they are known to be persistent (Günther & Pestemer, 1992).

The high content of NP in sewage sludge can be managed by composting, which is a recommended sludge treatment process for highly contaminated industrial waste (ICON, 2001). In this process the sludge is exposed to aerobic conditions whereby dewatered sludge is normally mixed with bulking agent (*i.e.* straw or wood chips). This promotes the activity of the microorganisms by increasing the porosity of sludge hence providing a suitable environment for rapid degradation of phenols (ICON, 2001). This means that the danger posed by these NPs to the environment or its transfer to the human food chain can significantly be reduced.

4.4 Conclusion

The results from the screening and the quantification of analytes in samples have shown that organochlorine pesticides listed in South African legislation do not necessarily need to be monitored on a regular basis as they were absent in selected sludge samples. It has been shown by the qualitative and quantitative results that p-cresol, nonylphenol and PAHs are the most common pollutants in the majority of South African sewage sludges. In addition, the results have 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 p-cresols more than when solid sludge is used.

4.5 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 legislation.

- PAHs, p-cresol, and nonylphenol are the three compounds that require regular monitoring (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.

- 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 instance regulating the use of NPE in detergents and paints.
- PCBs should be quantified and periodically checked especially where they have been identified in the current study (*e.g.* Gauteng). This is because of their potential harm to the environment and to man. Moreover, internationally these compounds have very low limits (Appendix A-7 & A-8). 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 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).

4.6 References

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APPENDIX

APPENDIX

APPENDIX A Different organic compounds identified in various countries worldwide

A summary of experimentally determined data as reported in the current literature is presented, in A-1 to A-13. These tables document the typical concentrations of different groups of organic pollutants found in sewage sludge.

A-1 **AOX content in sewage sludges from Germany (UMG-AG, 2000).**

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

A-2 **Concentration of LAS in sewage sludge from Norway and Denmark.**

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

A-3 **Concentration of LAS in sewage sludge from selected countries (Jones, 2000).**

Country	No. of WWTP	Sludge description	Range mg./kg dm
Denmark	19	Various	11-16100
Germany	8	Anaerobically Digested	1600-11800
Germany	10	Aerobically Digested	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

A-7 Concentrations of PCBs in sewage sludge of various countries.

Investigations	No. of samples	No. of congeners	Range mg/kg dm	Median 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 congeners	<0.2	-	UMK-AG, 2000

A-8 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
1992	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

A-9 Comparison of investigation of PCDD/Fs 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	-	0.02-1.15	9-192
Average NgTEq/kg dm	14.5	21	20-40	64	20	

A-10 **Concentrations of PCBs in sewage sludge of various European countries.**

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

A-11 **Concentrations of PAHs in sewage sludges of various countries.**

Investigations	No. of samples	Range mg/kg dm	Median mg/kg dm
Danish (1995) (Sum of 18 compounds) (Törslöv *et al.*, 1997)	20	<0.01-1.85	-
Danish (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) (UMK-UG, 2000)	124	0.4-12.83	-
Parts of Germany (sum of 16 compounds) (UMK-UG, 2000)	88	0.25-16.28	-

A-12 Typical concentrations of organic pollutants in sewage sludge and priorities with respect to the sludge-soil pathway

[UKWIR (United Kingdom Water Industry Research) 1995, Identification of priority organic contaminants in sewage sludge, vol. **2**, Report Ref. No. 96/SL/03/1; UMK-AG, 2000].

Compounds	Typical conc. in sludge (mg/kg dm)	Country	Reference
AOX	<400		
Brominated Flame retardants	-	-	
PBB Polybrominated Biphenyls	-	-	
PBDE Polybrominated diphenyl ether	-	-	
Decabromodiphenylether	-		
Pentabromodiphenylether	-		
Octabromodiphenylether	-		
TBBPA Tetrabromobisphenol	-	-	
CB Chlorobenzenes	-	-	
1,4-Dichlorobenzene	561-2320	UK	Wang & Jones, 1994
1,2,4-Trichlorobenzene	14.7-1070	UK	Wang & Jones, 1994
HCB Hexachlorobenzene	0.013-0.118	Switzerland	Frost et al, 1993 industrial
Chloroorganic Phosphate	-		
Bromophosethyl	-		
Tris-(chloroethyl)-phosphate	-		
Chlorophenols			
2,4-Dichlorophenol	0.35-2.6	UK	Wild et al., 1993
2,4,6-Trichlorophenol	0.008-0.254	UK	Wild et al., 1993
PCP Pentachlorophenol (1986)	<0.03-8500	USA & Germany	Drescher-Kaden et al., 1992
Chloro acetic acids	-	-	
Monochloroacetic acid	-	-	
TCA Trichloroacetic acid	-	-	
Lipid-lowering substances	-	-	
Clofibrine acid	-		

A-12 cont.

Compounds	Typical conc. in sludge (mg/kg dm)	Country	Reference
EDs Endocrine disruptors	-	-	
Ethynyl estradiol			
Ethanolamine	-	-	
EDTA Ethylenediaminetetraacetic acid	-		
Musk xylenes and ketones		-	
Musk xylene			
Musk ketone		-	
Pesticides	-	-	
Aldrin (1979)	-	-	
Chlordane (1971)	-	-	
DDT + metabolites (1977)	-		
DDE	-		
DDD	-		
Dieldrin	-	-	
Endosulfan (1991)	-	-	
Endrin	-	-	
Hexachlorocyclohexane (HCH)	-	-	
Alpha-HCH	0.00001-0.003	UK	Welsh Water, unpublished
Beta-HCH	0.00004-0.343	UK	Welsh Water, unpublished
Gamma-HCH (Lindane)	-		
Heptachlor (1981)	-	-	
Nitrofen (1980)	-	-	
Quintozen (1987)	-	-	
Precipitation chemicals	-	-	
Polyacrylamide (cationic)	-		

A-12 cont.

Compounds	Typical conc. in sludge (mg/kg dm)	Country	Reference
Phenols	-		
Alkylphenol	-	-	
Methylphenol	-	-	
NP Nonylphenol	-		
NPE Nonylphenol (+ethoxylate)	1-1000	-	
Nitrophenol	-	-	
DNOC 2-Methyl-4,6-dinitrophenol	-		
2,4-Dimethylphenol	-		
Phthalates	-	-	
DEHP Di-(2-ethylhexyl) phthalate	200-3000		
DBP Dibutylphthalate	50-1000	-	
DEP Diethylphthalate	-	-	
DNBP Di-n-butylphthalate			
PAHs	0.1-30	-	
Naphthalene (2-ring)	0.5-14.9	UK	Sweetman et al., 1991
Acenaphthene (3-ring)	<0.3-6.3	UK	Sweetman et al., 1991
Fluorene (3-ring)	3.4-15.8	UK	Sweetman et al., 1991
Pyrene (4-ring)	0.01-0.7	Sweden	Paxeus et al., 1991
Benz(a)anthracene (4-ring)	0.3-1.1	UK	Sweetman et al., 1991
Benzo(a)pyrene (5-ring)	0.1-15	Germany	Drescher-Kaden et al., 1992
Dibenz(a,h)anthracene (5-ring)	13-13	USA	Naylor & Loehr, 1982
PCA Chlorinated paraffins	-		
C10-C13	-	-	
C14-C17	-	-	
C20-C30	-	-	
Polycarboxylates (anionic)	-	-	
Polyacrylic acid-Na-salt	-		
Silicones	-	-	
Silicone oil	-		
Surfactants	-	-	
Fluorotensides	-		
LAS	10-10 000		

A-12 cont.

Compounds	Typical conc. in sludge (mg/kg dm)	Country	Reference
PCBs	0.001-0.1		
Coplanar PCBs	-		
Trichlorobiphenyls (PCB 28)	-	-	
Tetrachlorobiphenyls (PCB 52)	-	-	
Pentachlorobiphenyls (PCB 101)	-	-	
Hexachlorobiphenyls (PCB 138, 153)	-	-	
Heptachlorobiphenyls (PCB 180)	-	-	
PCDD/F	-		
2,3,7,8-TCDD	-	-	
1,2,3,7,8-PeCDD	-	-	
1,2,3,4,7,8-HxCDD	-	-	
1,2,3,4,6,7,8-HpCDD	-	-	
OCDD	-	-	
2,3,7,8-TCDF	-	-	
OCDF	-	-	
Organo-tin compounds			
TBTO Tributyltin oxide		-	
TBT Tributyltin			
Ugelic (60% Tetrach.benzyltol.)	-		
VOCs	-	-	
BTX-Aromatics	-	-	
Toluene	-		
Trichloroethylene	-		
Tetrachloroethylene	-		

APPENDIX B Detailed description of WWTPs collected from various provinces in South Africa.

Sample no.	WWTP name	Sample Description	Town	Sampling point
GAUTENG				
WRC 1339 01/01	Vlakplaats	Anaerobic digested	Alberton	Wet sludge
WRC 1339 02/01	Vlakplaats	Anaerobic digested	Alberton	Compost
WRC 1339 03/01	Vlakplaats	Anaerobic digested	Alberton	Paper, pulp compost
WRC 1339 04/01	Dekema	Anaerobic digested	Germiston	Peddies
WRC 1339 05/01	Waterval	Anaerobic digested	Germiston	Peddies
WRC 1339 06/01	Rondebult	Anaerobic digested	Alberton	Peddies
WRC 1339 07/01	CF Grundlingh	WAS	Nigel	Return flow
WRC 1339 08/01	Herbert Bickley	Anaerobic digested	Nigel	Digesters
WRC 1339 09/01	Tsakane WWTP	WAS	Brakpan	WAS
WRC 1339 10/01	Heidelberg	WAS	Heidelberg	Pit
WRC 1339 11/01	Heidelberg	Anaerobic digested	Heidelberg	Digesters
WRC 1339 12/01	Baviaanspoort WCW	Aerobic digested	Pretoria	Wet sludge
WRC 1339 13/01	Rooiwal Northern	Anaerobic digested	Pretoria	Wet sludge
WRC 1339 14/01	Rooiwal West/East	Aerobic digested	Pretoria	Wet sludge
WRC 1339 15/01	Zeekoegat WCW	Aerobic digested	Pretoria	Wet sludge
WRC 1339 16/01	Centurion WCW	Anaerobic digested	Verwoedburg	Belt press
WRC 1339 17/01	Daspoort WCW	Anaerobic digested	Pretoria	Drying beds
WRC 1339 18/01	Olifantsvlei	Compost	JHB	Compost heap
WRC 1339 19/01	JHB Northern Works	WAS	JHB	Belt press
WRC 1339 20/01	JHB Northern Works	Compost	JHB	Compost heap
WRC 1339 21/01	Percy Steward	Anaerobic digested	Krugersdorp	Wet sludge
WRC 1339 22/01	Flip Human	Anaerobic digested	Krugersdorp	Wet sludge
WRC 1339 77/01	Rietspruit	Digested	Van der Bijl	Drying beds
LIMPOPO				
WRC 1339 47/01	Pietersburg WTP	Aerobic digested	Pietersburg	Plough fields
WRC 1339 48/01	Seshego	Anaerobic digested	Pietersburg	Drying beds
WRC 1339 49/01	Phalaborwa	WAS	Phalaborwa	Drying beds
WRC 1339 50/01	Tzaneen	Anaerobic digested	Tzaneen	Drying beds
WRC 1339 51/01	Mankweng	Anaerobic digested	Pietersburg	Drying beds
WRC 1339 52/01	Mankweng	Anaerobic digested	Pietersburg	Compost (UNIN)
NORTH-WEST				
WRC 1339 53/01	Rustenburg	Anaerobic digested	Rustenburg	Drying beds
WRC 1339 54/01	Boitekong	Waste Activated	Rustenburg	Return flow
WRC 1339 55/01	Brits	Anaerobic digested	Brits	Drying beds
WRC 1339 69/01	Orkney	WAS & Digested	Orkney	Stock pile
WRC 1339 70/01	Klerksdorp	WAS & Digested	Klersdorp	Drying beds
WRC 1339 71/01	Wolmaranstad	Compost	Wolmaranstad	Pit
WRC 1339 73/01	Vryburg	WAS	Vryburg	Drying beds
WRC 1339 23/01	Kingstonvale	Digested sludge	Nelspruit	Drying beds
WRC 1339 24/01	Lydenburg	Digested sludge	Lydenburg	Drying beds

APPENDIX B cont.

Sample no.	WWTP name	Sample Description	Town	Sampling point
FREE STATE				
WRC 1339 25/01	Thabong	WAS	Welkom	Return flow
WRC 1339 26/01	Witpan	Digested sludge	Welkom	Drying beds
WRC 1339 27/01	Theronia	Digested sludge	Welkom	Drying beds
WRC 1339 38/01	Harrismith	Digested	Harrismith	Drying beds
WRC 1339 39/01	Phuthadithjaba	Digested sludge	Qwaqwa	Drying beds
KWAZULU-NATAL				
WRC 1339 40/01	Escort	Digested sludge	Escourt	Drying beds
WRC 1339 41/01	Hammansdale WCW	WAS	Pietermaritzburg	Centrifuge
WRC 1339 42/01	Darvil WCW	Digested + WAS	Pietermaritzburg	Return flow
WRC 1339 44/01	Isipingo	Digested sludge	Durban	Drying beds
WRC 1339 45/01	Kwa-Mashu	Digested sludge / DAF	Durban	Belt press
WRC 1339 56/01	Kwa-Mashu	Pellets	Durban	Bins
WRC 1339 57/01	Phoenix	Waste Activated	Pietermaritzburg	Belt press
WRC 1339 58/01	Durban Northern	WAS / Digested	Durban	Belt press
WRC 1339 59/01	Durban Northern	Pellets	Durban	Bins
WRC 1339 75/01	Klipfontein	Heated & digested	Vryheid	Heaps
WRC 1339 76/01	New Castle	Petro	New Castle	Drying beds
EASTERN CAPE				
WRC 1339 61/01	East London	Petro-process	East London	Drying beds
WRC 1339 78/01	Potsdam	Digested	East London	Drying beds
WRC 1339 79/01	Fishwater Flats	Heated , Centrifuged	Port Elizabeth	Centrifuge
WRC 1339 80/01	Cape Receife	WAS	Port Elizabeth	Drying beds
NORTHERN CAPE				
WRC 1339 67/01	Kameelmond	WAS	Upington	Drying beds
WRC 1339 68/01	Kameelmond	Digested sludge	Upington	Drying beds
WRC 1339 72/01	Kimberley	WAS & Digested	Kimberley	Drying beds
WRC 1339 74/01	Kuruman	WAS	Kuruman	Drying beds
WESTERN CAPE				
WRC 1339 28/01	Borcherds Quarry	WAS	Cape Town	Return flow
WRC 1339 29/01	Bellville	WAS	Cape Town	Belt press
WRC 1339 30/01	Athlone	WAS	Cape Town	Drying lagoons
WRC 1339 31/01	Cape Flats	Pellets	Cape Town	Old stock bags
WRC 1339 32/01	Mitchell's plain	Digested sludge	Cape Town	Centrifuge cake
WRC 1339 33/01	Wesfleur	WAS	Cape Town	Industrial drying beds
WRC 1339 34/01	Wesfleur	WAS	Cape Town	Domestic drying beds
WRC 1339 35/01	Gwain	Petro Sludge	George	Drying beds
WRC 1339 36/01	Mosselbay	WAS	Mosselbay	Drying beds
WRC 1339 37/01	Oudshoorn	Compost	Oudshoorn	Compost heap
WRC 1339 60/01	Beaufort West	WAS	Beaufort West	Drying beds
WRC 1339 62/01	Vredenburg WCW	WAS	Vredenburg	Fenced DLD area
WRC 1339 63/01	Saldana	WAS	Saldanah bay	Drying beds
WRC 1339 64/01	Clanwilliam	WAS	Clanwilliam	Drying beds
WRC 1339 65/01	Vredendal WCW	WAS	Vredendal	Stockpile

APPENDIX C The organic compounds identified in individual sewage sludge samples across the country using the GC-MS at confidence limit equal or greater than 80 %.

C-1A GAUTENG

	Sample Number/%																						
Organic compounds	1S	1N	1A	1B	2	3	4	5	6	7	8	9N	9A	9B	10	11S	11N	11A	11B	12S	12N	12A	12B
Phenols																							
2,6-bis (1,1-dimethylethyl)-4-methyl-phenol	91	95																					
3,5-Dimethyl-phenol		95																					
4-(1-methylethyl)-phenol							93																
4,4'-(1-Methylethylidene)bis-phenol/ p,p'-Isopropylidenebisphenol																	89						
2-Methyl-phenol/o-Cresol		97	97																				
3-Methyl-phenol/m-Cresol																		96				96	
4-Methyl-phenol/p-Cresol	95	97	96	96					94		94		94	94			97						
Nonylphenol						80					90												
Nonylphenol isomer					90																		
Phenol/Izal													94	94			95						
4-(1,1,3,3-Tetramethylbutyl)-phenol	81																						
PAHs																							
6-Acetyl-7-hydroxy-2,2-dimethylbenzopyran												83											
(-)-.alpha.-Amorphene																							
Benz[a]anthracene						93																	
Decahydro-2-methyl-naphthalene													94										
.delta.Cadinene																							98
7,12-Dihydro-7,12-dimethyl-benz[a]anthracene															94								
1,3-Dimethylnaphthalene						95																	
1,5-Dimethylnaphthalene	96																						
1,8-Dimethyl-naphthalene						93																	
1,7-Dimethyl-naphthalene									98														

C-1A cont.

	Sample Number/%																						
Organic Compounds	1S	1N	1A	1B	2	3	4	5	6	7	8	9N	9A	9B	10	11S	11N	11A	11B	12S	12N	12A	12B
PAHs																							
2,6-Dimethyl-naphthalene									98														
2,7-Dimethyl-naphthalene						96																	
Epizonaren												87											
Fluoranthene						96																	
Fluorene	93														81								
1,2,3,7,8,9-hexahydro-Perylene												83											
1H-Indene/Indonaphthene																	94						
Methoxy-3-methylcholanthrene											83												
1,6-Methanofluorene						80																	
1-Methyl-naphthalene	90																						
2-Methyl-naphthalene						94			93														
Naphthalene/White tar						95			91														
4a,4b,8,8,2-pentamethyl-1-butyperhydrophenanthrene					81																		
Phenanthrene	86					96																	
Pyrene						93																	
Perylene						94																	
1,2,3,4-Tetrahydro1,1,6-trimethylnaphthalene	97										89												
1,2,3,4-Tetrahydro-6-methyl-naphthalene									89														
1,3,6-Trimethyl-naphthalene							80																
Phthalates																							
Di-(2-ethylhexyl)-phthalates			91								83												
Diethyl phthalate														97								94	
Biphenyls																							
1,1`-Biphenyl									81						95								
(Phenylmethyl)-1,1'-biphenyl						95																	
2,2',3,3'4,4'5,5'-octachloro-1,1'-Biphenyl															91								

C-1A cont.

	Sample Number/%																						
Organic Compounds	1S	1N	1A	1B	2	3	4	5	6	7	8	9N	9A	9B	10	11S	11N	11A	11B	12S	12N	12A	12B
Furans																							
5-Acetyl-4,7-dimethoxy-6-hydrobenzofuran									83														
5-Acetyl-4,7-dimethoxy-6-hydrobenzofuran									83														
1,2,3,4,6,7,8-Heptachlorodibenzofuran							90																
4-Methyl-dibenzofuran	93																						
2-Pentyl-furan											91												
Amines																							
4-Chloro-benzanamine	95																						
N,N-Dibutyl-1-butanamine	95						91				81	90											
N,N-Dimethyl-1-octadecanamine	80																						
N,N-Dimethylpalmitamide																		94					
Hexadecanamide			81																				
(Z)-9-Octadecenamide			91	91								86	93										
N-(2-phenylethyl)-acetamide																							
n-Tetradecanoic acid amide			91	90																			
Aldehydes																							
Decanal											91												
Friedenlan-y-al															80								
Heptanal											83				90								
Hexadecanal/Palmitic aldehyde			91															87				97	
n-Hexanal							90		90		90												
4-Hydroxy benzaldehyde			89																				
Ios-.alpha.-cedren-15-al															81								
n-Nonanal											91				91								
Nonylaldehyde																							

C-1A cont.

	Sample Number/%																						
Organic Compounds	1S	1N	1A	1B	2	3	4	5	6	7	8	9N	9A	9B	10	11S	11N	11A	11B	12S	12N	12A	12B
Aldehydes																							
9-Octadecenal													91										
Octanal											87				90								
Pentadecanal	94		95																				
Tetradecanal/Myristaldehyde	91		91															95					
Tridecanal					86																		
Esters																							
5.alpha.-Cholestan-3-one	93								87														
1-(2-Aminophenyl)-ethanone		94												93									
5-(3-Aminopropyl)-5,10-dihydro-11H-dibenzo[b,e][1,4]diazepin-11-one											91												
5-(3-Aminopropyl)-1,5-diazacycloheptadecan-6-one															83								
14.beta.-3-Methoxy-6-oxaestra-1,3,5(10),8,15-pentaen-7,17-dione			83																				
6-(Bromomethyl)-5-[(ethoxycarbonyl)-(phenylthio)-methyl]-4-methoxy-2H-pyran-2-one												90											
Cholest-4-en-3-one													99										
Cholestan-3-one								83	95		93												
Cholestan-4-one		93																					
Coprostan-3-one	93																						
.delta.-Decalactone/ Tetrahydro-6-pentyl-H-pyran-2-one																		80					
7,8-dihydrobenzo[g] chrysen-5(6H)-one																							83
1,3-dihydro-2H-Indol-2-one														93									
2,3-Dihydro-4-methyl-1H-indole																		94				95	96
6,10-Dimethyl-5,9-undecadien-2-one							93																
(1R+,6S+,7R+)-10,10-Dimethyl-7-vinyl-tricyclo (4.3.2.0)undec-2-en-one																86							

C-1A cont.

	Sample Number/%																						
Organic Compounds	1S	1N	1A	1B	2	3	4	5	6	7	8	9N	9A	9B	10	11S	11N	11A	11B	12S	12N	12A	12B
Esters																							
Diphenyl-methanone															95								
3-Ethenyl-4-isopropylcyclohexanone							93																
Geranyl acetone																							
2-Heptadecanone																							
Hexahydro-2H-azepin-2-one																							
2-Hydroxy-cyclopentadecanone							95																
1H-Indole/Ketol									91						97			94					
1,3-Isobenzofurandione							95	91	94														
5-Methyldibenz(6,F)azapine-10-one																							
6-Methyl-5-hepten-2-one																							
Methyl 6(r,s)-8-hydroxy-7-oxo-8,9-secolabdan-15-oate					87																		
3-Methyl-1H-indole		91									94				91			91					
5-Methyl-1H-indole																							
7-Methylindole									93														
3-Methylindole-2(3H)-one		87	87														90						
Methyl 9,10-methylene Octadecanoate											83												
Muskalactone															87								
Oxacyclotetradecane-2,11-dione																							
2-Pentadecanone																							
2-Piperidinone																							
2-Tridecanone																							
2-Undeconone																							
Acids																							
Benzeneacetic acid			91						87				91					91				91	
Benzenebutanoic acid/ 4-Phenylbutyric acid																		90				91	
Benzenepropanoic acid																	94	94				94	
Benzoic acid/Retardex																		96					
Bis(2-ethylhexyl) ester of 1,2-Benzenedicarboxylic acid																							83

C-1A cont.

	Sample Number/%																						
Organic Compounds	1S	1N	1A	1B	2	3	4	5	6	7	8	9N	9A	9B	10	11S	11N	11A	11B	12S	12N	12A	12B
Acids																							
Bis(2-methoxyethyl) ester of 1,2-Benzenedicarboxylic acid																							80
Butanoic acid/n-Butyric acid									83				91					91				91	
Butyl cyclohexyl ester of 1,2-benzenedicarboxylic acid																						86	
Cyclohexanecarboxylic acid			92																				
Cyclohexanepropanoic acid			91																				
Decanoic acid/Capric acid																	89						
Dibutyl ester 1,2-Benzenedicarboxylic acid		91				95							89	96			91	83					
Diethyl ester of 1,2-Benzenedicarboxylic acid													92										96
Diethyl-carbamodithioic acid														81									
Diethyl-4-nitrophenyl Ester of phosphoric acid															90								
Diisodecyl ester of 1,2-benzenedicarboxylic acid													91										
Docosanoic acid	91																						
Dodecanoic acid/Lauric acid											97				95								
2-Ethyl-hexanoic acid								83	91									94					
2-Ethylhexyl diphenyl of ester Phosphoric acid													86										
Hepatadecanoic acid/ Margaric acid	95								96								99	97					
Heptanoic acid																		91					
Heptadecene-(8)-carbonic acid(1)		95																					
Hexadecanoic acid/ Palmitic acid			99				93		98								99	99					
9-Hexadecenyl ester of palmitic acid	93	99									97												
Hexadecyl ester of hexadecanoic acid												91											99

C-1A cont.

	Sample Number/%																						
Organic Compounds	1S	1N	1A	1B	2	3	4	5	6	7	8	9N	9A	9B	10	11S	11N	11A	11B	12S	12N	12A	12B
Acids																							
Hexadecyl ester of dodecanoic acid																							
Hexadecyl ester of hexadecanoic acid													98										
n-Hexanoic acid																		90				90	
2-Hydroxy-methyl ester of docosanoic acid															90								
5-Isobutylidene-N,N-dimethylbarbituric acid															83								
Linoleic acid											93												
2-Methyl butanoic acid/ 2-Methybutyric acid																		90				83	
3-Methyl-butanoic acid/ Isovaleric acid																							
3-Methyl decanoic acid		92	95																				
Methyl ester hexadecanoic acid	94										91												
2-Methyl-hexanoic acid																		80				83	
5-Methyl-hexanoic acid																		91				91	
Methyl ester of 9,12-octadecadienoic acid																							
Methyl ester of (Z)-9-octadecenoic acid																							81
2-Methyl-pentanoic acid																		90				90	
2-Methyl-propanoic acid													80					90				90	
2-Methylvaleric acid																							
2-Methyl pentanoic acid																							
2-Methylpropyl ester of 1,2-benzenedicarboxylic acid				86																			
Moronic acid											86												
3-Nitro-1,2-benzenedicarboxylic acid																						91	
Nonanoic acid	87							80															

C-1A cont.

	Sample Number/%																						
Organic Compounds	1S	1N	1A	1B	2	3	4	5	6	7	8	9N	9A	9B	10	11S	11N	11A	11B	12S	12N	12A	12B
Acids																							
Octadecanoic acid/Stearic acid		99							96		93						99	99					
(Z)-9-Octadecenoic acid									99		95						98						
Octanoic acid/Caprylic acid																		95					
Oleic acid																							
(Z)-9-Octadecenoic acid																	98						
9-Octadecenyl ester of (Z)-Octadecanoic acid																							90
Octadecyl-(Z)-9-octadecenoic acid																		95					
Pentadecanoic acid	86	99	95						91								96	98					
14-Pentadecenoic acid																							
Pentanoic acid/Valeric acid			91															83				90	
3-Phenylbutyric acid			97																				
(R)-2-Phenylpropionic acid																		87					
1,2,3-Propanetricarboxylic acid			91				90	98	98														
Propanoic acid																		94					
Tetradecanoic acid/ Myristic acid	98	83	81								98							93					
Tetradecyl ester of hexadecanoic acid																							
Tridecanoic acid																							
Tributyl ester 2-hydroxy-1,2,3-propanetricorbixylic acid				80																			
Undecanoic acid																							

C-1A cont.

	Sample Number/%																						
Organic Compounds	1S	1N	1A	1B	2	3	4	5	6	7	8	9N	9A	9B	10	11S	11N	11A	11B	12S	12N	12A	12B
Chlorinated hydrocarbons																							
1-Chloro-2-isocyanato-benzene							96																
Chloromethyl-benzene																							
1-Chloro-octadecane						99									83								
5,7-Dichloro-1-methyl-1,4-benzodiazepin-2-one																		83					
1,2-Dichloro-benzene									86								83						
2,4-Dichlorophenyl isocyanate							94																
3-p-Chlorophenyl-1-methyldioxindol								90															
Trichlorododecyl-silane													83										
Trichloroeicosyl-silane								91															
Alcohols																							
Benzenemethenethiol	81										91												
2H-1-Benzopyran-6-ol/Vitamin E											81												
3.beta.-Cholest-5-en-3-ol																	96						
3.beta.-lup-20(29)-en-3ol									90														
7,8-dihydrobenzo[g] chrysen-5(6H)-one																							83
Dihydrocholesterol/ 5.alpha.-Cholestan-3.beta.-ol	86	93	86														93						
1-Dodecanethiol																							
1,16-Hexadecanediol																							
1-Hexanethiol											91												
2-Ethyl-1-hexanol		86																					
Farnesol												89											
D:A-Friedooleanane-1,24-diol											80												
Isoheptadecanol																							
20.xi.-Lanosta-7,9(11)-diene-3.beta.,18,20-triol											92												

C-1A cont.

	Sample Number/%																						
Organic Compounds	1S	1N	1A	1B	2	3	4	5	6	7	8	9N	9A	9B	10	11S	11N	11A	11B	12S	12N	12A	12B
Alcohols																							
(22E,24S)-24-Methyl-5.alpha.-cholesta-8,22-dien-3.beta.-ol																							
p-Menth-3-en-1-ol		86																					
2-Methyl-1-hexadecanol																							
(R)-(-)-(Z)-14-Methyl-8-hexadecen-1-ol			86																				
(E)-13-Methyl-11-tetradecen-1-ol	80																						
1-Octadecanethiol																							97
(Z)-9-Octadecen-1-ol																						83	
1-Octanethiol							91				97												
1-Pentadecanethiol																							90
1,15-Pentadecanethiol																							
Terpinene-1-ol																		86					
(E)-2-Tridecen-1-ol	90																						
2-(Tetradecyloxy)-ethanol																							
Hydrocarbons																							
.alpha.-Humulene																							
.alpha-Pinene												94											
.alpha.-phellandrene												95											
5-(3-Aminopropyl)-1,5-diazacycloheptadecan-6-one															83								
.beta.-Caryophyllene	99																						
7H-Benzocycloheptene						90																	
.beta.-Caryophyllene															99								
1,1-Bis(p-tolyl)ethane						91																	
11-Butyl-docosane	94																						
(1-Butylheptyl)-benzene					94		91		95			90											
(1-Butylhexyl)-benzene					95				95														
(1-Butyloctyl)-benzene	96								96														
(1-Butylnonyl)-benzene									87						91								
Butylated hydroxy toluene																							
11-Butyl-docosane	94																						

C-1A cont.

	Sample Number/%																						
Organic Compounds	1S	1N	1A	1B	2	3	4	5	6	7	8	9N	9A	9B	10	11S	11N	11A	11B	12S	12N	12A	12B
Hydrocarbons																							
cis-Caryophyllene	97					97																	
Cyclodecane																	89						
Cyclodecene																							
Cyclododecane																	91						
Cycloeicosane																							81
Cyclohexadecane																							87
Cyclooctane															92								
Cyclopentadecane																							
Cyclotetradecane	95																						
Cyclotridecane																							
n-Decane	95	94				94	91	95			91			94	95								
11-Decyl-docosane															91								
10-Demethylsqualene																							
1,2-Diethyl-benzene									86														
1,5-Diethyl-3-methyl-2-methylene-[1.alpha.,3.alpha.,5.alpha.]cyclohexane																							
1,2-Dimethyl-benzene	97					93		97	97		97												
1,3-Dimethyl-benzene															97								
1,4-Dimethyl-benzene							97					81											
1,2-Dimethyl-cyclooctane	86																						
1,3-Dimethyl-2(2,4,6-trimethylphenyl)-1,3-cyclopentadiene						83																	
3,6-Dimethyl-decane																							
3,8-Dimethyl-decane									81														
4,6-Dimethyl-dodecane															91								
1,3-Dimethyl-2(2,4,6-trimethylphenyl)-1,3 cyclopentadiene																	83						
2,10-Dimethyl-undecane															90								
n-Docosane			93				93		91		94		92										
1-Docosene																							
n-Dodecane	87					93	95	90			91				97		94	93					
1-Dodecene/Adecene							93																

C-1A cont.

	Sample Number/%																						
Organic Compounds	1S	1N	1A	1B	2	3	4	5	6	7	8	99N	9A	9B	10	11S	11N	11A	11B	12S	12N	12A	12B
Hydrocarbons																							
(E)-9-Eicosene																							83
4R*,5R*,6S*,8S*)-4,5-Epoxy-8-isopropenyl-2,2,6-trimethyl-7-oxabicyclo[4.3.0]non-9-ene						83																	
1,1'-[1,2-Ethanediylbis(oxy)]bis-benzene/1,2-Diphenoxyethane																	83						
(1-Ethenyloxy)-hexadecane																							93
5-(Ethyldecyl)-benzene									93														
4-Ethyl-1,2-diethyl-benzene									94														
2-Ethyl-1,3-dimethyl-benzene									87														
4-Ethyl-1,2-dimethyl-benzene																				94			
1-Ethyl-2-methyl-benzene									95														
3-Ethyltoluene																				86			
4-Ethyltoluene																				95			
3-Ethyl-tridecane																							
Hentriacontane															90								
n-Heptacosane																				80			
6(Z),9(E)-Heptadecadiene	89																						
n-Heptadecane	95	96	97		87		95	93	90		93				95		93	95					
1-Heptadecene/Hexahydroap																							
8-Heptadecene																							
2,2,4,4,6,8,8-Heptamethyl-nonane						90									95								
n-Hexacosane	95	91		86			86	92							95								
9-Hexacosene																							
n-Hexadecane	97		94		93	94		95	97			90											
1-Hexadecene/Cetene	94				93																		
2,6,10,15,19,23-Hexamethyl-2,6,10,14,18,22-tetracosahexaene	93	91	98	91			96	98	93					95	96			94				83	
7-Hexyl-docosane																							
(1-Hexyloctyl)-benzene									92														
1-Iodo-tetradecane		93						93															
Isoterpinolene																	90						

C-1A cont.

	Sample Number/%																						
Organic Compounds	1S	1N	1A	1B	2	3	4	5	6	7	8	9N	9A	9B	10	11S	11N	11A	11B	12S	12N	12A	12B
Hydrocarbons																							
2-Methoxy-3,8-dioxocephalotax-1-ene					90																		
(2-Methyl-1-butenyl)-benzene	91																						
2-Methyl-decane	83							86															
3-Methyl-decane	94																						
4-Methyl-decane	89																						
5-Methyl-decane	90																						
4-Methyl-dodecane															97								
6-Methyl-dodecane															93								
10-Methyl-eicosane	83																						
1,1'Methylenebis(4-methyl)-benzene															91								
1-Methylethyl-benzene									94														
1-Methyl-2-(methylethyl)-benzene	95																						
1-Methyl-2-[(3-methylphenyl) methyl]-benzene						90																	
9-Methyl-nonadecane																							
2-Methyl-pentadecane															91								
3-Methyl-pentadecane									89														
1-Methyl-2-propyl-benzene									90														
2-Methyl-6-propyl-dodecane											83												
2-Methyl-tetradecane							83																
2-Methyl-tridecane																95							
3-Methyl-tridecane																81		86					
4-Methyl-tridecane																91							
2-Methyl-undecane																87							
(1-Methylundecyl)-benzene									87														
Neopentyliindenecyclohexane																							
n-Nonacosane	95										86												
1-Nonadecene																89							
n-Nonane/Shells						91		97					93			93							

C-1A cont.

	Sample Number/%																						
Organic Compounds	1S	1N	1A	1B	2	3	4	5	6	7	8	9N	9A	9B	10	11S	11N	11A	11B	12S	12N	12A	12B
Hydrocarbons																							
n-Octacosane	91	91					92	96			95												
n-Octadecane	92	93	98			93							93				95	98					89
1-Octadecene	94																						96
9-Octyl-heptadecane							96				95												
Octyl-heptadecane								91															
1,1'-Oxybis-decane									94														
Pentacosane	91		90						93		93				87		91						
n-Pentadecane	98		97	86		95	89	98	96		97				98		97	97					
1-Pentadecene		94	90								95												
Pentyl-benzene											81												
(1-Pentyheptyl)-benzene	93				83				94			90											
(1-Pentylhexyl)-benzene	94				95				94														
(1-Pentyl-2-propyl)-benzene					90																		
(1-Pentyloctyl)-benzene	96				80	95	97																
(1-Propylnonyl)-benzene	94				80		97																
(1-Propyloctyl)-benzene	93				90	95	93					83											
Spiro[4.5]decane																							
n-Tetracosane	90	96						96	87				83		90								
1,13-Tetradecadiene																							
n-Tetradecane	97				95	98		96	96		97		98				98						
(Z)-3-Tetradecene																							
2,6,10,14-Tetramethyl-hexadecane	95						93	95							97								
2,6,10,14-Tetramethyl-pentadecane									91														
trans.-Caryophyllene											80				87								
n-Triacontane						90		98	91														
Tricosane	91							86			97						97						
(Z)-11-Tricosene																							84
n-Tridecane	98					96	95	94							98								

C-1A cont.

	Sample Number/%																						
Organic Compounds	1S	1N	1A	1B	2	3	4	5	6	7	8	9N	9A	9B	10	11S	11N	11A	11B	12S	12N	12A	12B
Hydrocarbons																							
1,2,3-Trimethyl-benzene								94									87						
1,2,4-Trimethyl-benzene						97	95																
1,3,5-Trimethyl-benzene																	95						
1,7,11-Trimethyl-cyclotetradecane							94																
2,6,11-Trimethyl-dodecane									86						91								
2,7,10-Trimethyl-dodecane	80																						
Tritetracontane					91																		
Tritriacontane															91								
n-Undecane	96					97		95	95		95				96		97						
Others																							
Alloaromadendrene					95																		
5.alpha.,14.beta.)-Cholestane								86						90									
(5-alpha)-Cholest-3-ene																							96
(5-alpha)-Cholest-7-ene														93									
.alpha.-Copaene	95																						
.alpha.Cubebene	98																						
.alpha.(p-chlorobenzoyl)-p-chloro															91								
.alpha.-(dimethylphenylsilyl)styre															83								
.alpha.-Gurjunene												94											
5.alpha.-Pregnane						91			95														
Aromadendrene												99											
Bacchotricuneatin									95						90								
(Benzene)ethylene e(trimethylphosphine)ruthenium(0)											83												
Benzo[b]phenanthro[2,1-d]thiophene											83												
.beta.-Bisabolene	92																						
14.beta.-H-Pregna												86		86									

C-1A cont.

	Sample Number/%																						
Organic Compounds	1S	1N	1A	1B	2	3	4	5	6	7	8	9N	9A	9B	10	11S	11N	11A	11B	12S	12N	12A	12B
Others																							
2,5-Bisdimethylamino-3,9-dimethyl-3H-1,3,4,6-tetrazacyclopent(E)azulene	83																						
(+)-Calarene	95																						
3-(1-Camphenyl)-2-chlorpansuare	83																						
1,8-Cineole									89														
cis-Caryophyllene	97					97																	
(+-)-cis-3,4,6,9-tetrahydro-10-hyd7								83															
5-Cyano-3,6-dimethyl-3,4-dihydropyrrolo(1,2,3-de)-2H-1,4-benzoxazine																83							
Decamethyl-cyclopentasiloxane					90																		
(c-4a,c-7a)-.delta.6-Dodecahydro-3,3-dimethyl-r-2,c-4,c-8-metheno-3a,7c-diazapentaleno[6,1,2-bcd]-as-indacene						83									90		83						
10-Demethylsqualene	87															90							
2,3-dicyano-7,7-dimethyl-5,6-benzonorbornadiene						83	83																
1a,9b-dihydro-1a-(methylsulfinyl)							86																
3,7-Dihydroxy-5-methoxy-4,6-diphenyldibenzophosphole 5-oxide			83			90							90										
3',4'-Dihydro-2'-(morpholin-4-yl)-5',7'-nitrospiro[cyclopentane-1,3'-quinazoline]	80																						
3,12-Dimethylphenyl-isocynate																							
3-(2,2-Dimethylpropylindene)(bicyclo [3.3.1]nonane-2,4-dione			83																				

C-1A cont.

	Sample Number/%																						
Organic Compounds	1S	1N	1A	1B	2	3	4	5	6	7	8	9N	9A	9B	10	11S	11N	11A	11B	12S	12N	12A	12B
Others																							
Dimethyl tetrasulphide											87												
Dimethyl-Trisulfide									95														
7,9-di-tert-butyl-1-oxaspiro[4.5]d												91											
Docosanolide																							
Dodecamethyl-cyclohexasiloxane					90	91						86											
1-Ethyldibenzothiophene						83						83	80		83					83	83		
2-Ethyldibenzothiophene					83			83															
3-Ethyldibenzothiophene			83			83		83	83														
Galoxide 1 and 2					87	93						98									91		
.gamma.-Gurjunene																							
Geranyl linalool isomer																							
(+-)-15-Hexadecanolide		87																					
Hexamethyl-cyclotrisiloxane					91	90	91	90	91		91	91											
8-Hydroxyquinoline		96	94	96																			
Isomaturnin						90																	
Junipene	99											93											
Koiganal II		83																					
Koiganal I			90																				
Lycopersen											90												
3-methoxy-(3.beta.22E)-Stigmasta-5,22-diene							90																

C-1A cont.

	Sample Number/%																							
Organic Compounds	1S	1N	1A	1B	2	3	4	5	6	7	8	9N	9A	9B	10	11S	11N	11B	11A	11B	12S	12N	12A	12B
Others																								
7-Methylbenz[c]acridine																								
Methyl-d3-hydrazine sulfate	81	93			83						93		97										90	
5-Methyl-19-norcholest-8(11)-ene						90																		
3-(1-Methyl-2-pyrrolidinyl)-pyridine/Nicotine																	95							
(E,Z,Z)-and-(Z,E,Z)-14-Methyl-16							90																	
Muscopyridine											90													
28-Nor-17-.alpha(h)-hopane	83														83									
28-Nor-17-.beta(h)-hopane							83								83									
Octamethyl-cyclotetrasiloxane					91	90	90					91												
1,1,4,5,6-Pentamethyl-2,3-dihydroindene	87																							
1-Phellandrene					95																			
4-Phenyl-bicyclohexyl															81									
3-Phenyl-5-t-butylpyridine					90	90						83			83		83	83						
2-(Phenylthiomethyl)-pyridine																								
5.alpha.-Pregnane						91																		
N-propyl-3-aza-5.alpha.-cholestane																								
Pyrrolo(3,2,1-b)carbazole																								

C-1A cont.

	Sample Number/%																						
Organic Compounds	1S	1N	1A	1B	2	3	4	5	6	7	8	9N	9A	9B	10	11S	11N	11A	11B	12S	12N	12A	12B
Others																							
Sabinene												81											
Terbuthylazine/Gardoprim		98																					
1-[1(tert-butyldimethylsilyl)ox															83								
Trendione						87							96										
Tricorbonyl(n-phenyl-2-pyridine)iron																	86						
Triethylammonio-N-diphenylphosphin																							
4,8,8-trimethyl-3-oxatricyclo [5.4.0.0(1,4)]undec-11-yl) isopropyl ether													89										
Vitamin E acetate							83								89								

C-1B GAUTENG

	Sample Number/%																			
Organic Compounds	13	14	15				16	17	18	19	20	21S	21N	21A	21B	22S	22N	22A	22B	77
Phenols																				
2,6-Bis(1,1-dimethylethyl)-4-methyl-phenol							93								97					
3-Methyl-phenol/m-Cresol																		96		
4-Methyl-phenol/p-Cresol	95	97					95		95		95									
Octyl-phenol isomer			83																	
Nonylphenol							87			83						80				
4-(1,1,3,3-Tetramethylbutyl)-phenol/ p-tert-Octylphenol																91				
Pesticides																				
2,4,6-Trimethylindane																80				
PAHs																				
Acenaphthene																90				
Anthracene/Anthracin																96				
(-)-.alpha.-Amorphene		86																		
.dalta.Cadinene		98																		
7,12-Dihydro-7,12-dimethyl-benz[a]anthracene,											83									
9,9-Dimethyl-1,4-dihydro-1,4-methanonaphthalene								87												
1,5-Dimethyl-naphthalene																86				
1,7-Dimethyl-naphthalene																97				
2,6-Dimethyl-naphthalene								97								95				
2-Ethyl-naphthalene								86								95				
Fluorene								95			95					97				
1,3,4,5,6,7-Hexahydro-1,1,5,5-tetramethyl-(2S)-2H-2,4a-methanonaphthalene/ Isolongifolene							99													
6-Methoxy-1-acetonaphthone										83										
1-Methyl-naphthalene							94									94				
2-Methyl-naphthalene																94				
Naphthalene/White tar																91				
Phenanthrene																94				
1,2,3,4-tetrahydro-phenanthrene								83												
1,2,3,4-Tetrahydro-1-1,6-trimethylnaphthalene		94								97						93				

C-1B cont.

	Sample Number/%																
Organic Compounds	13	14	15	16	17	18	19	20	21S	21N	21A	21B	22S	22N	22A	22B	77
Phthalates																	
Di-(2-ethylhexyl)-phthalates						91									91		
Diisooctyl-phthalate												86					
Biphenyls																	
1,1`-Biphenyl													93				
Furans																	
Dibenzofuran													90				
4-Methyldibenzofuran/4-Methyldiphenylene oxide													90				
2-Octylfuran					83												
Amines																	
4-Chloro-benzanamine					94												
6-Chloro-N,N'-diethyl1,3,5-triazine-2,4-diamine								86									
N,N-Dibutyl-1-butanamine		92			83												
Dodecanamide															90		
1-Methyl-acetamide					86												
N-(2-phenyl)-acetamide		86															
(Z)-9-Octadecenamide							86								90		
n-Tetradecanoic acid amide															91		
Aldehydes																	
2,2-Dideutero-octadecanal					86												
Friedelan-y-al					90		94										
Hexanal					90												
4-Hydroxy-benzaldehyde															97		
Nonanal					90												
Nonylaldehyde			91														
Octadecanal		98	90		91												
Pentadecanal															93		
Tetradecanal/Myristaldehyde		97													95		
Esters																	
5.alpha.-Cholestan-3-one		80			95								96				
5-alpha,17.xi.-21-Norcholest-24-en-20-one							95										
1-(2-Aminophenyl)-ethanone				97													
5-(3-Aminopropyl)-1,5-diazacycloheptadecan-6-one													90				
Cholestan-3-one					90								91				
Cholestan-4-one						81		86							93		

C-1B cont.

	Sample Number/%																
Organic Compounds	13	14	15	16	17	18	19	20	21S	21N	21A	21B	22S	22N	22A	22B	77
Esters																	
1,3-Dihydro-2-H-indol-2-one		94															
2,3-Dihydro-4-methyl-1H-indole								94									
Geranyl acetone			94														
2-Heptadecanone	93																
Hexahydro-2H-azepin-2-one		87															
2-Hydroxy-cyclopentadecane		81															
2-Hydroxy-1,2,3-propanetricarboxylic acid tributyl ester / Citric acid tri-n-butyl ester															91		
1H-Indole/Ketol	95		91	91		97		97									
5-Methoxy-2,2-dimethyllindan-1-one							83										
5-Methyldibenzo(6,F)azapine-10-one		90															
6-Methyl-5-hepten-2-one			87														
3-Methylindole-2(3H)-one				87													
3-Methyl-1H-indole	91																
5-Methyl-1H-indole		91															
7-Methyl-1H-indole				94				94									
3-Methylindole-2(3H)-one	86							87									
Methyl tetradecanoate							91										
Muskalactone																	
Neryl acetone					81												
Oxacyclotetradecane-2,11-dione			91														
2-Pentadecanone			91												86		
2-Piperidinone	80																
4,4a,5,9-Tetrahydro-4a,8-dimethyl-5,9-dioxoazuleno(6,5-b)furan-3-carboxylic acid-methyl ester							83										
2-Tridecanone			93				83										
Acids																	
Benzeneacetic acid	91														91		
Benzenebutanoic acid															94		
Benzenepropanoic acid	94			80													
Benzoic acid/Retardex															94		
Bis(2-ethylhexyl) ester of 1,2-Benzenedicarboxylic acid				90													

C-1B cont.

	Sample Number/%																
Organic Compounds	13	14	15	16	17	18	19	20	21S	21N	21A	21B	22S	22N	22A	22B	77
Acids																	
Butanoic acid/n-Butyric acid	91	95				91											
Dibutyl ester of 1,2-benzenedicarboxylic acid			90		81		87										
Diisodecyl ester of 1,2-benzenedicarboxylic acid			86														
Docosanoic acid																	
Dodecanoic acid/Lauric acid		97	99	99	86								98				
Eicosanoic acid/Arachidic acid																	
Ethyl ester of cis and trans-4-(1,1-dimethylethyl)-1-ethenylcyclohexanacetic acid					86												
2-Ethyl-hexanoic acid			83	80													
Hepatadecanoic acid/Margaric acid		95	94	96									99				
Heptadecene-(8)-carbonic acid																	
Heptanoic acid		90															
Hexadecanoic acid/Palmitic acid	98	99	93	99	95	99		99					96		99		
Hexadecyl ester of dodecanoic acid			97	95													
Hexadecyl ester of octanoic acid								91									
Hexadecyl ester of tetradecanoic acid								84									
n-Hexanoic acid	90	90				83		90									
Linoleic acid			90					83									
3-Methyl-benzoic acid															90		
2-Methyl butanoic acid	86			86		86									86		
3-Methyl butanoic acid		83															
3-Methyl-2-butenoic acid						80											
Methyl ester hexadecanoic acid				91		95		97									
Methyl ester of 9,12-octadecadienoic acid			90					87									
2-Methyl-hexanoic acid	86																
14-Methyl-methyl ester Heptadecanoic acid								91									
2-Methyl pentanoic acid		90		80		90		90							93		
4-Methyl pentanoic acid	90							83									
2-Methyl-propanoic acid	91					90		91									
2-Methylvaleric acid		80															
Nonadecanoic acid				80													
Nonanoic acid		96	95														
Octadecanoic acid/Stearic acid				96	93	96		93					96				

C-1B cont.

	Sample Number/%																
Organic Compounds	13	14	15	16	17	18	19	20	21S	21N	21A	21B	22S	22N	22A	22B	77
Acids																	
(Z)-9-Octadecenoic acid	98			99	93								98				
Octanoic acid		86	93														
Oleic acid	94																
Pentadecanoic acid		96	91	91	93								96		84		
Pentanoic acid/Valeric acid	90	90		80				83									
Tetradecanoic acid/Myristic acid	83	98	98	98		98		95					98				
Tetradecyl ester of dodecanoic acid				91													
Tetradecyl ester of hexadecanoic acid		92															
Tridecanoic acid			98	87													
Undecanoic acid		87	86														
Chlorinated hydrocarbons																	
7-Chloro-7-heptadecene															83		
1,4-Dichloro-benzene					93												
Alcohols																	
Benzene methenethiol					91												
2H-1-Benzopyran-6-ol/Vitamin E				93													
3.beta.-Cholest-5-ene-3-ol			83														
(2Z,Z)-Dehydrocholesterol								90									
Dihydrocholesterol/Cholestan-3-ol													95				
1-Dodecanethiol		94															
.gamma.-Tocopherol					83												
Geranyl acetone																	
1-Heptacosanol					83												
1,16-Hexadecanediol		86															
1-Hexadecen-1-ol/Cetal				83									87				
20.xi.-Linosta-7,9(11)-diene-3.beta.18,20-triol					81												
(22E,24S)-24-Methyl-5.alpha.-cholesta-8,22-diene-3.beta.-ol		87															
2-Methyl-1-hexadecanol			91														
1-Octadecanethiol		91															
1-Octadecanol/Stenol				91													
1,15-Pentadecanethiol			86														
2-(Tetradecyloxy)-ethanol																	
(E)-2-Tridecen-1-ol															90		

C-1B cont.

	Sample Number/%																
Organic Compounds	13	14	15	16	17	18	19	20	21S	21N	21A	21B	22S	22N	22A	22B	77
Hydrocarbons																	
.alpha.-Caryophyllene													94				
.alpha.-Copaene				90		99	99										
.alpha.-Curcumen													86				
.alpha.-phellandrene							95										
.alpha.-Humulene		99	95	91													
Azulene/Cyclopentacycloheptene															81		
7H-Benzocycloheptene					86												
.beta.-Caryophyllene		99			99	99		99					94				
.beta.-Bisabolene													94				
Butylated hydroxy toluene		90															
11-Butyl-docosane				90													
(1-Butylheptyl)-benzene			95	94	94			96					94				
(1-Butylhexyl)-benzene			93	91	87												
(1-Butyloctyl)-benzene		94	95	91			95	94					86				
(1-Butylnonyl)-benzene			91		87			87									
cis-Caryphyllene			97		96												
Cyclohexadecane			95														
Cyclopentadecane			91														
Cyclotetradecane		81	94					87					94				
Decahydro-4H-cyclopentacyclooctene								90									
n-Decane				95	97	95		95					95		93		
10-Demethylsqualene			90														
5,14-Dibutyl-octadecane				93													
1,5-Diethyl-3-methyl-2-methylene-[1.alpha.,3.alpha.,5.alpha.]cyclohexane		89															
1,3-Dimethyl-benzene			97		97								97				
1,4-Dimethyl-benzene/p-Xylene				95													
3,6-Dimethyl-decane			83														
4,11-dimethyl-tetradecane					83												
3,4-Dimethyl-undecane													90				
n-Docosane			94	98	95			93					91		97		
n-Dodecane				96	87	96		90					97		87		
1-Dodecene/Adecene				93													

C-1B cont.

	Sample Number/%																
Organic Compounds	13	14	15	16	17	18	19	20	21 S	21 N	21 A	21 B	22 S	22 N	22 A	22 B	77
Hydrocarbons																	
Eicosane				96													
2-Ethenyl-1,3,5-trimethyl-benzene													87				
1-(Ethyldecyl)-benzene						92											
5-(Ethyldecyl)-benzene								93									
3-Ethyl-tridecane													87				
Heneicosane				96													
1-Heneicosene												86					
Heptacosane	95	96															
6(E),8(E)-Heptadecadiene			91					91									
n-Heptadecane				97	94	97		96					97				
1-Heptadecene/Hexahydroap		91	91			96		91									
8-Heptadecene	95					93		93									
n-Hexacosane					98	93							97				
9-Hexacosene		94			83												
n-Hexadecane		93		97	95	97		95					97		97		
1-Hexadecene/Cetene		91				86		83									
7-Hexadecyne						94											
2,6,10,15,19,23-hexamethyl-2,6,10,14,18,22-Tetracosahexaene	93	96	94	94	86	96	95						95		96		
2,6,10,15,19,23-Hexamethyl-tetracosane/ Squalane						80											
7-Hexyl-docosane	91																
7-Hexyl-eicosane													90				
1-Isopropentyl-2-methyl-benzene					91												
3-Methyl-decane				90													
5-Methyl-decane				90													
2-Methyl-decane					80								86				
7-Methyl-(Z)-decene													95				
4-Methyl-dodecane													97				
6-Methyl-dodecane													81				
2-Methyl-eicosane													94				
10-Methyl-eicosane					90			86									
1-Methyl-3-(methylethyl)-benzene				80									90				

C-1B cont.

	Sample Number/%																
Organic Compounds	13	14	15	16	17	18	19	20	21 S	21 N	21 A	21 B	22 S	22 N	22 A	22 B	77
Hydrocarbons																	
1-Methyl-4-(1-methylethyl)-benzene				93	95												
1-Methyl-4-(1-methylethenyl)-cyclohexene				93													
9-Methyl-nonadecane			90		93												
10-Methyl-nonadecane						81											
2-Methyl-nonane				87													
4-Methyl-nonane				80													
3-Methylpentacosane							83										
3-Methyl-pentadecane				86													
1-Methyl-3-propyl-benzene				93													
3-Methyl-tetradecane					93												
2-Methyl-tridecane													93				
4-Methyl-tridecane													80				
2-Methyl-undecane													80				
5-Methyl-undecane													91				
n-Nonacosane													89				
n-Nonadecane				90													
1-Nonadecene					99		95										
n-Octacosane		98		93	98								93		91		
n-Octadecane	92	90	91	95	95	97		93					95		98		
1-Octadecene	86					80	94	83									
9a-octahydro-3,5,5-trimethyl-9-methylene(4aS-cis)-1H-banzocycloheptene							94										
Octyl-cyclohexane					95			97									
9-Octyl-heptadecane			93					91									
Pentacosane		93													95		
n-Pentadecane	96	98	97	98	96	97		97					98		97		
1-Pentadecene		94				99		98									
Pentyl-benzene													90				
(1-Pentylheptyl)-benzene		95	86			94							80				
(1-Pentylhexyl)-benzene		95	94	90		81							81				
(1-Pentyloctyl)-benzene			96	91		96											
(1-Propylheptyl-benzene				81			94	93									
(1-Pentylhexyl)-benzene					96			96									

C-1B cont.

	Sample Number/%																
Organic Compounds	13	14	15	16	17	18	19	20	21 S	21 N	21A	21 B	22 S	22 N	22 A	22 B	77
Hydrocarbons																	
(1-Propylnonyl)-benzene		95	95	94	96		95	94					97				
(1-Propyloctyl)-benzene		95															
Spiro[4.5]decane		94															
n-Tetracosane						94							97		95		
1,13-Tetradecadiene			95	91		91									81		
n-Tetradecane				98	97	97		97					97		91		
(Z)-3-Tetradecene			91														
(Z)-3-Tetradecen-5-yne							86										
1,2,3,4-Tetramethyl-benzene				93													
2,6,10,15-Tetramethyl-heptadecane				91													
4,8,12,16-Tetramethyl-heptadecane-4					80												
2,6,10,14-Tetramethyl- hexadecane					98		94						99		91		
trans.-Caryophyllene	99		99										99				
trans-2-Nonadecene				91													
n-Triacontane		97			96												
Tricosane		91	98	95	96	95							95				
n-Tridecane		94		96	95	96		96					97				
2,7,10-Trimethyl-dodecane													90				
2,6,10-Trimethyl-pentadecane					83								80				
2,3',4-Trimethylphenyl methane					95			96									
Undecane				96	95	93		96					97		94		
Others																	
Alloaromadendrene							97										
5-alpha,14-beta,17-beta-cholestane							86										
(5.alpha.,14.beta.)-Cholestane							83										
.alpha.(p-Chlorobenzoyl)-p-chloro																	
.alpha.-Copaene		98	99														
.alpha.Cubebene			99	97			93										
.alpha.-Pinene							97										
.alpha.-Ylangene							91										
5-amino-2-(p-methoxyphenyl)-2-methyl-2H -[1,2,4]triazolo[1,5-a][1,3,5]triazine								83									
Aromadendrene							99										

C-1B cont.

	Sample Number/%																
Organic Compounds	13	14	15	16	17	18	19	20	21S	21N	21A	21B	22S	22N	22	22 B	77
Others																	
Bacchotricuneatin					94												
(+)-.beta.-Funebrene							84										
.beta.-Himachalene							95										
14.beta.-H-Pregna					83	81											
Bicyclogermacrene							93										
(+)-Calarene							90										
9-Carbomethoxy-6,-11-dimethoxy-5-oxoxantho[3,2-g]tetralin		83															
Cholest-3,5-diene															90		
Cholest-4-ene													95				
cis-Calamenene													83				
Citroflex A												91					
(+)-Cycloisosativene					98												
Decamethyl-cyclopentasiloxane			90	90	90	90		90					83				
(2Z,Z)-Dehydrocholesterol								90									
2,3-dicyano-7,7-dimethyl-5,6-benzonorbornadiene		83															
1a,11c-Dihydrochryseno[5,6-b]azirine/ 1a,11c-Dihydro-1H-chryseno[5,6-b]azirine													86				
2,3-Dihydro-1,2-dimethyl-1H-Indene					91												
3',4'-dihydro-2'-(morpholin-4-yl)-5',7'-dinitrospiro[cyclopentane-1,3'-quinazoline]				83													
3,12-Dimethylphenyl-isocynate								86							86		
3-(2,2-Dimethylpropylindene) bicyclo[3.3.1]nonane-2,4-dione			90														
n-Docosyl-formate/1-Docosanol formate													80				
Dodecamethyl-cyclohexasiloxane		90	81	80			87										
3,4-Epoxy-4a-ethyl-2,3,4,4a,5,6-hexahydro-1H-pyrido[3,2-C]carbazole				93			83										
1-Ethyldibenzothiophene	83																
2-Ethyldibenzothiophene						83	83	83									
3-Ethyldibenzothiophene						83											

C-1B cont.

	Sample Number/%																
Organic Compounds	13	14	15	16	17	18	19	20	21 S	21 N	21A	21 B	22 S	22 N	22 A	22 B	77
Others																	
Galoxide 1 and 2					90	94	94										
gamma.-Gurjunene			94														
.gamma.-Terpinene					93												
Garvin A					90												
Garvin B													83				
Geranyl linalool isomer		87															
Hahnfett												93					
Hexadecyl-oxirane							90										
Hexamethyl-cyclosiloxane							86										
8-Hydroxyquinoline															94		
Junipene		99	99		93		99						99				
7-Methylbenz[c]acridine		83															
3-Methylbenzo[2,3]phenanthro [4,5-bcd]thiophene					83												
Methyl-d3-hydrazine sulfate		93		90													
1-(3-Methylphenyl)4-methyl-3-pente					89												
10-Methylsqualene					89												
28-Nor-17-.alpha(h)-hopane	86			81													
28-Nor-17-beta(H)-hopane					89												
n-Propyl-3-aza-5.alpha.-cholestane	83																
Octamethyl-cyclotetrasiloxane	91						90										
Sabinene							91										
Tricarbonyl[N-(phenyl-2-pyridinylmethylene) benzenamine-N,N']-iron													90				

C-2 LIMPOPO

	Sample Number/%						
Organic Compounds	46	47	48	49	50	51	52
Phenols							
2,6-Bis(1,1-dimethylethyl)-4-methyl-phenol							89
4-Methyl-phenol/p-Cresol			97			94	97
PAHs							
.delta.-Cadinene						87	
2,6-Dimethyl-naphthalene	95						
3,7-Dimethyl-naphthalene	98						
1-Ethyl-naphthalene	87						
6-methoxy-1-acetonaphthone		83					
8-methoxy-1-acetonaphthone		83					
1,2,3,4-Tetrahydro-1,1,6-trimethyl-naphthalene				96		91	
Phthalates							
Di-(2-ethylhexyl)-phthalates			86				
Furans							
2-Octyl-furan			83				
Amines							
4-Chloro-benzanamine							93
N,N-Dibutyl-1-butanamine							96
(Z)-9-Octadecenamide		91					
N-(2-Phenylethyl)-acetamide						86	
n-Tetradecanoic acid amide		91		91			
Aldehydes							
Hexadecanal/Palmitic aldehyde						87	
Octadecanal/Stearaldehyde				94			
Tetradecanal/Myristaldehyde						91	90
Esters							
5.alpha.-Cholestan-3-one							93
5.alpha.-Cholestan-4-one			90				
(5.alpha.,17.xi.)-21-Norcholest-24-en-20-one				96			
.beta.-Ionone							87
3-(2,2-dimethylpropylidene)bicyclo [3.3.1]nonane-2,4-dione				83			
(+-)-cis-3,4,6,9-tetrahydro-10-hydroxy-1,3,,8-trimethyl-1H-naphtho[2,3-c]pyran6,9-dione		83					

C-2 cont.

	Sample Number/%						
Organic Compounds	46	47	48	49	50	51	52
Esters							
Geranyl acetone				89			
Hex-2-one						86	
2-Hydroxy-cyclopentadecanone				86			
1H-Indole/Ketol			94			97	91
5-Methyl-1H-indole			91				91
7-Methylindole						91	
5-Methyl-4-phenyl-trans-2-oxazolidinone			83				
Muskolactone/Oxacyclohexadecan-2-one				93			
Oxacycloheptade-2-one				91			
2-Pentadecanone				94			
2-Tridecanone				91			
Acids							
S-(2-Aminoethyl) ester thiosulfuric acid						86	
Benzenepropanoic acid			87				
Bis(2-ethylhexyl) ester 1,2-Benzenedicarboxylic acid				90			91
Butanoic acid/n-Butyric acid			94				
Butyl ester of linoleic acid							93
Butyl ester of octadecanoic acid							93
Decanoic acid/Capric acid				91		96	
Dibutyl ester of 1,2-benzenedicarboxylic acid		83					95
Dodecanoic acid/Lauric acid			98	99		99	
Hepatadecanoic acid/Margaric acid			99	99		99	86
6-Heptadecatri-8(Z),11(Z),14(Z)-enyl-2-hydroxybenzoic acid			86				
Heptadecene-(8)-carbonic acid				86			
Hexadecanoic acid/Palmitic acid		99	98	95		98	99
Hexadecyl ester of tetradecanoic acid			91	87			
n-Hexanoic acid						87	
Linoleic acid				92			
2-Methyl butanoic acid			83				
2-Methylhexanoic acid			83				
Methyl ester of hexadecanoic acid			95			97	97

C-2 cont.

	Sample Number/%						
Organic Compounds	46	47	48	49	50	51	52
Acids							
Methyl ester of 7,10-octadecadienoic acid						90	
Methyl ester of octadecanoic acid							95
Methyl ester of 8-octadecenoic acid							99
Methyl ester of tetradecanoic acid							96
2-Methyl pentanoic acid			83				
3-Nitro-1,2-benzenedicarboxylic acid						86	
Nonadecanoic acid				89			
Nonanoic acid				81		90	
(Z,Z)-9,12-octadecadienoic acid		83		95			
Octadecanoic acid/Stearic acid		97	99	96		99	95
(Z)-9-Octadecenoic acid			99			93	
Octanoic acid/Caprylic acid			98	87		95	
2-Octenoic acid						86	
Pentadecanoic acid			98	97		98	98
Pentanoic acid/Valeric acid			90				
Tetradecanoic acid/Myristic acid			99	97		99	96
Tetradecyl ester of hexadecanoic acid				93			
Tridecanoic acid				97		97	
Undecanoic acid				96			
Chlorinated hydrocarbons							
17-Chloro-7-heptadecene						89	
1-Chloro hexadecane							98
1-Chloro-2-isocyanato-benzene		90					
1-Chloro-octadecane							99
Alcohols							
Cyclododecanol				90			
1-Dodecanol				81		91	
Epifriedelinol		89					
2-Methyl-1-hexadecanol				93			
1-Octadecanol/Stenol						91	
1,15-Pentadecanethiol						91	
1-Phenyl-6-oxanonan-1-ol			80				
Totarol		93					

C-2 cont.

	Sample Number/%						
Organic Compounds	46	47	48	49	50	51	52
Hydrocarbons							
.alpha.-Humulene/.alpha.-Caryophyllene				98			86
.beta.-Caryophyllene			99	99		99	99
(1-Butylheptyl)-benzene						93	91
(1-Butylhexyl)-benzene			91	87			
(1-Butyloctyl)-benzene		96	97	92		89	95
cis-Caryophyllene						94	
Cyclopentadecane				91			
Cyclotetracosane		90					
Cyclotetradecane				91			
n-Decane			95				
1,3-Dimethyl-benzene						97	
1,4-Dimethyl-benzene				97			87
n-Docosane				80			
n-Dodecane			81				
1-Dodecene/Adecene							86
n-Eicosane			96			91	
(E)-9-Eicosene		96					
1-Heneicosene		83					
n-Heptadecane			97			97	95
1-Heptadecene/Hexahydroap			95				
8-Heptadecene			98				
n-Hexacosane			81				
n-Hexadecane			89				93
1-Hexadecene/Cetene				94			99
2,6,10,15,19,23-hexamethyl-2,6,10,14,18,22-Tetracosahexaene			98	96		95	
(1-Hexylheptyl)-benzene				91			
2-Methyl-decane				93			
2-Methyl-1,1-diphenyl-1-propene						83	
2-(Methylthio)-benzothiazole						98	
7-Methyl-3, 4-octadiene						89	
n-Nonadecane			94			93	90
1-Nonadecene			81				

C-2 cont.

	Sample Number/%						
Organic Compounds	46	47	48	49	50	51	52
Hydrocarbons							
n-Octacosane				99			
n-Octadecane			93			93	
1-Octadecene				90			93
(E)-9-Octadecene				91			
Octyl-heptadecane						93	
9-Octyl-heptadecane							93
Pentacosane			89			96	93
n-Pentadecane			98	94		96	96
1-Pentadecene			95			98	
Pentylbenzene						81	
(1-Pentyheptyll)-benzene		94	91	94		94	94
(1-Pentylhexyl)-benzene			91				
(1-Pentylnonyl)-benzene			97				
(1-Pentyloctyl)-benzene			94				
(1-Propylnonyl)-benzene		87					
n-Tetradecane			94			93	91
1-Tetradecene			80			90	93
2,6,10,14-Tetramethyl-hexadecane		93					
trans.-Caryophyllene				91			
Tricosane				90			
n-Tridecane			91			91	
Undecane			95				
Others							
7-Ac-6-et-1144-me4-tetralin		90					
(5.alpha.)-cholest-3-ene		93				89	95
.alpha.-Copaene							92
.alpha.Cubebene			89	97		94	92
.alpha.-Elemene		86					
.alpha.-Phellandrene		94					
.alpha.-Pinene		90					
5-amino-2-(p-methoxyphenyl)-2-methyl-2H-[1,2,4]triazolo[1,5-a][1,3,5]triazine			83				

C-2 cont.

	Sample Number/%						
Organic Compounds	46	47	48	49	50	51	52
Aromadendrene		87					
(+)-Aromadendrene		98					
.beta.-Himachalene		87					
Caryophyllene oxide				83			
Cystathionine-DTMS				90			
Decamethyl-cyclopentasiloxane		90	91	91		87	91
.delta.3-Carene		86					
10-Demethylsqualene							94
Digitoxigenin		91					
2,3-Dihydro-1,1-dipropyl 1H-1-silaindene							86
2,3-Dimethyl-trisulfide						96	
Dodecamethyl-cyclohexasiloxane		90	86	87		87	91
1-Ethyldibenzothiophene		83	90				83
Galoxide 1 and 2	93	93	94				90
.gamma.-Terpinene							91
Heneicosane			91	93		94	
(+-)-Hexadecanolide			90				
Hexamethyl-cyclotrisiloxane		91				91	80
Junipene						95	90
(+)-Longifolene		94					
Methyl-d3-hydrazine sulfate			83			91	94
5-Methyl-19-norcholest-8(11)-ene			87				
Muscopyridine		90					
Octamethyl-cyclotetrasiloxane		91					86
2,6,10,14,18-Pentamethyl-eicosane							91
3-Phenyl-5-t-butylpyridazine							90
Sabinene		91					
(-)-Sinularene				95			
Valencene		91					

C-3 NORTH-WEST

	Sample Number/%						
Organic Compounds	53	54	55	69	70	71	73
Phenols							
2,6-Bis(1,1-dimethylethyl)-4-methyl-phenol		96					
Nonylphenol	93			91			
4-Nonylphenol/p-Nonylphenol						83	
Nonylphenol isomer				90			
PAHs							
6-*Methoxy-7(2h)-benz[a]anthracenon				83			
Furans							
1,3-Isobenzofurandione					87		
Amines							
N,N-Dibutyl-1-butanamine				95	97	97	94
Aldehydes							
Hexadecanal/Palmitic aldehyde							94
Octadecanal/Stearaldehyde							95
Esters							
(24S)-5.alpha.-Ergostan-3-one					93		
.beta.-Ionone					93		
14.beta.-3-Methoxy-6-oxaestra-1,3,5(10),8,15-pentaen-7,17-dione		80					
Butyl tetradecanoate/Myristate							86
Cholestan-4-en-3-one	99						
Coprostan-3-one							96
Hex-2-one	93						
D-Homoestra-1,3,5(10)-triene-17a-one	95						
Stigmast-4-ene-3-one	83						
2-Tridecanone					87		
Acids							
Bis(2-ethylhexyl) ester 1,2-Benzenedicarboxylic acid	91				83		83
Dodecanoic acid/Lauric acid				99		97	98
Exo-methyl-cholan-24-oic acid				86			
Hepatadecanoic acid/Margaric acid				99			
Hexadecanoic acid/Palmitic acid	99	98					

C-3 cont.

	Sample Number/%						
Organic Compounds	53	54	55	69	70	71	73
Acids							
Methyl ester of hexadecanoic acid						96	
Methyl ester of 9-hexadecenoic acid					99		
12-Methyl ester of tetradecanoic acid					96		
3-Nitro-1,2-benzenedicarboxylic acid		91		86		96	
Nonadecanoic acid					99		
Nonanoic acid						98	
(Z,Z)-9,12-octadecadienoic acid	95						80
Octadecanoic acid/Stearic acid	99			93	70		91
(Z)-9-Octadecenoic acid	99	93		99	89	99	97
Octanoic acid/Caprylic acid					86		
Oleic acid	94					89	
2-Oxo-methyl-cholan-24-oic acid							80
Pentadecanoic acid						99	99
14-Pentadecenoic acid					89	99	97
Tetradecanoic acid/Myristic acid				99			98
Chlorinated hydrocarbons							
1-Chloro-hexane	90						
1-Chloro-octane	86						
Alcohols							
Benzene methenethiol	87						
3.beta.-Cholest-5-ene-3-ol	97						
Dihydrocholesterol	90					99	
1-Dodecanethiol					87		
Geranyl acetone					89		
1-Hexadecanol/Cetal							94
(Z)-11-Hexadecen-1-ol					87		
Isoheptadecanol				87			
2-Methyl-1-hexadecanol							93
1,15-Pentadecanethiol	86						
Podocarpan-14-.beta.-ol							90

C-3 cont.

	Sample Number/%						
Organic Compounds	53	54	55	69	70	71	73
Hydrocarbons							
11-Butyl-docosane		91					
(1-Butylheptyl)-benzene	86				93		
(1-Butylhexyl)-benzene					93		
(1-Butyloctyl)-benzene							96
(1-Butylnonyl)-benzene	93						
2-Butyl-1,1,3-trimethyl-cyclohexane					96		
Cyclopentadecane		87				95	
Cyclotetradecane						95	
n-Decane						95	
(2-Decydodecyl)-cyclohexane	81						
11-Decyl-heneicosane	96						
2,5-Dimethyl-nonane						90	
3,6-Dimethyl-undecane						83	
n-Docosane	95	96			95	84	
n-Dodecane	87						
(E,E,E)-1,4,8-Dodecatriene						89	
Dotriacontane					83		
n-Eicosane	95	92				97	
Heneicosane	94	99		97			
1-Heneicosene					86		
n-Heptacosane	94						
n-Heptadecane		89					86
8-Heptadecene						99	
n-Hexacosane	92				83		
n-Hexadecane						96	95
1,E-8,Z-10-Hexadecatriene						93	
1-Hexadecene/Cetene	89				83	83	
2,6,10,15,19,23-hexamethyl- 2,6,10,14,18,22-Tetracosahexaene	94	96			98		98
1-Iodo-decane					86		
Isocaryophyllene					90		
9-Methyl-acridine						86	
2-Methyl-decane	94						
3-Methyl-decane						87	

C-3 cont.

	Sample Number/%						
Organic Compounds	53	54	55	69	70	71	73
Hydrocarbons							
2-Methyl-heptadecane						91	
(R)-(-)-(Z)-14-Methyl-8-hexadecene	86						
2-Methyl-octadecane	84						
2-Methyl-tetradecane						94	
4-Methyl-tetradecane						93	
5-Methyl-tetradecane						87	
2-Methyl-tridecane						93	
3-Methyl-tridecane						90	
2-Methyl-undecane						83	
Neopentyliindenecyclohexane					86		
n-Nonadecane						97	
1-Nonadecene				86			
n-Octacosane	94	93					
n-Octadecane				94		98	97
1-Octadecene	96						
Octyl-eicosane	89						
n-Pentadecane					96	98	
Pentatriacontane	91						
(1-Pentyheptyll)-benzene					83		
(1-Pentyloctyl)-benzene	86				81		93
5-Propyl-decane						91	
(1-Propylnonyl)-benzene					90		97
(1-Propyloctyl)-benzene					81		94
6-Propyl-tridecane						81	
1,13-Tetradecadiene					83		
n-Tetradecane					93	98	
Tetratetracontane						81	
n-Triacontane		93					
2,6,10,14-Tetramethyl-hexadecane						99	
Tricosane	97	93				95	93
n-Tridecane	81			90			
n-Tridec-1-ene					99		
1,2,4-Triethyl-benzene					86		

C-3 cont.

	Sample Number/%						
Organic Compounds	53	54	55	69	70	71	73
Hydrocarbons							
1,7,11-Trimethyl-cyclotetradecane						83	
2,6,11-Trimethyl-dodecane						86	
2,610-Trimethyl-pentadecane						94	
Undecane	90					97	
Others							
.alpha.-Copaene						99	
.alpha.Cubebene						86	
3-(1-Amphenyl)-2-chlorpropsaure	90						
(+-)-Cularicine	90						
Decamethyl-cyclopentasiloxane		91			91	91	91
Epi-isopodophyllotoxin				90			
3,4-Epoxy-4a-ethyl-2,3,4,4a,5,6-he	91						
5-Ethyl-3,4-bis(trifluoromethyl)-2	86						
2-Ethyldibenzothiophene						90	
3-Ethyldibenzothiophene							90
Galoxide 1 and 2	93			94		87	
(+-)-15-Hexadecanolide							83
Hexamethyl-cyclotrisiloxane	90						
Hexatriacontane							93
(14a)-Homo-27-nor-14.beta.-gammac				84			
Junipene					96		
Methyl-arachidonate						89	
28-Nor-17-.alpha(h)-hopane				86			

C-4 FREE STATE

	Sample Number/%						
Organic Compounds	25N	25A	25B	26	27	38	39
Phenols							
2,6-Bis(1,1-dimethylethyl)-4-methyl-phenol							81
Nonylphenol						91	90
Nonylphenol isomer						98	
Pesticides							
Epoxyheptachlor							91
PAHs							
7-Ac-6-et-1144-me4-tetralin/ 1,1,4,4-tetramethyl-6-ethyl-7-acetyl-1,2,3,4-tetrahydronaphthalene							91
Phthalates							
Di-(2-ethylhexyl)-phthalates							83
Amines							
N,N-Dibutyl-1-butanamine							96
N,N-Dimethyl-tetradecanamine						80	
Esters							
(+-)-cis-3,4,6,9-tetrahydro-10-hydroxy-1,3,8-trimethyl-1H-naphtho[2,3-c]pyran-6,9-dione							83
Coprostan-3-one							89
6,10,14-Trimethyl-2-pentadecanone							94
Acids							
Bis(2-ethylhexyl) ester of 1,2-Benzenedicarboxylic acid							81
Butyl ester of octadecanoic acid						87	
Dodecanoic acid/Lauric acid						96	
Ethyl ester of (Z)-9-octadecenoic acid						99	
Hepatadecanoic acid/Margar						99	
Hexadecanoic acid/Palmitic acid						99	98
Hexadecyl ester of tetradecanoic acid						99	
Octadecanoic acid/Stearic acid						99	
Pentadecanoic acid						97	
Tridecanoic acid						96	
Chlorinated hydrocarbons							
1-Chloro-octadecane							93
1-Chloro-2-isocyanato-benzene							94
1,4-Dichloro-benzene							93

C-4 cont.

	Sample Numbers/%						
Organic Compounds	25N	25A	25B	26	27	38	39
Chlorinated hydrocarbons							
1,4-Dichloro-2-isocyanato-benzene							98
Alcohols							
Hexadecanol/Cetal						91	
Hydrocarbons							
(1-Butylhexyl)-benzene							87
N,N-Dimethyl-cycloundecane						96	
n-Docosane						95	
(E,E,E)-1,4,8-Dodecatriene							
n-Eicosane	93					93	
1-Heptadecene/Hexahydroap				94			
n-Hexadecane				93		95	
2,6,10,15,19,23-hexamethyl-2,6,10,14,18,22-Tetracosahexaene						95	
2-Methyl-decane						93	
1-Nonadecene						99	
n-Octadecane						96	
n-Pentadecane						95	81
n-Tetracosane						90	
Tetratetracontane						87	
trans.-Caryophyllene							99
Others							
5.alpha-Cholest-3-ene							81
.alpha.-Guaiene							80
.beta.-Bisabolene						99	
Chromolaenim							90
Dodecamethyl-cyclohexasiloxane							90
(Z)-3-(2-Ethoxyethenyl)pyridine							80
1-Ethyldibenzothiophene							83
Galoxide 1 and 2							
Hexadecyl-oxirane							
Hexamethyl-cyclotrisiloxane							
Methyl-d3-hydrazine sulfate							91
Octahydro-1,9,9-trimethyl-4-methylene-(1.alpha.,3a.alpha.,7.alpha.,8a.beta.)-1H-3a,7-Methanoazulene							87
Octamethyl-cyclotetrasiloxane							91

C-5 KWAZULU-NATAL

Organic Compounds	Sample number/%													
	40	41	42S	42N	42A	42B	44	45	56	57	58	59	75	76
Phenols														
4-Methyl-phenol/p-Cresol												97		
Nonylphenol											83	93		83
PAHs														
4-Allyl-1,2-dimethyl-naphthalene											83			
Anthracene/Anthracin									83					86
Chrysene/Benzo[a]phenanthrene									95					
2,3-Dimethyl-naphthalene								97						
Fluoranthene									93					
Fluorene								95			94			
4-Methoxy-acenaphthene									86					
1-Methyl-naphthalene								89			91			
2-Methyl-naphthalene								90			92			
Phenanthrene									96					
Biphenyl														
1,1'-Biphenyl											81			
Furans														
Dibenzofuran								93						
Amines														
N,N-Bis(2-hydroxyethyl)dodecamide												92		
N,N-Dibutyl-1-butanamine							95	97	97		95	97	86	97
2,5-Dichloro-benzanamine												95		
3,4-Dichloro-benzanamine									96					
3,5-Dichloro-benzanamine								80						
(Z)-9-Octadecenamide						93								
Aldehydes														
n-Dodecanal												90	91	
(E,E)-2,6-Nonadienal														
Octadecanal/Stearaldehyde	90												91	
Tetradecanal/Myristaldehyde										98		91		

C-5 cont.

	Sample Number/%													
Organic Compounds	40	41	42S	42N	42A	42B	44	45	56	57	58	59	75	76
Esters														
(24S)-5.alpha.-Ergostan-3-one									93					
5.alpha.-Stigmast-3-one									83					
(24R)-5.alpha.-Stigmastan-3-one									80					
14.beta.-3-Methoxy-6-oxaestra-1,3,5(10),8,15-pentaen-7,17-dione											90		90	
Butyl octadecanoate														91
Cholestan-5-en-3-one							94							
2-Chloroethyl-linoleate							91							
Coprostan-3-one									81			83	83	90
.delta.-4-Cholestene3-one			96							96				
2,3-Dihydro-4-methyl-1H-indole					95							95		
5-Methylindole												94		
3-Methylindole-2(3H)-one												83		
Oxacycloheptade-8-en-2-one													83	
3-Phenyl-4-hydroxyacetophenone							83							
2-Tridecanone												90		
6,10,14-Trimethyl-2-pentadecanone													91	
Acids														
Benzeneacetic acid									81					
Benzenepropanoic acid									94			94		
Butyl ester of octadecanoic acid	95													
Decanoic acid/Capric acid	89							95	83	83	91	97		
Dibutyl ester of 1,2-benzenedicarboxylic acid									96					
Diethyl ester of 1,2-Benzenedicarboxylic acid									90					
Diiso-1,2-benzenedicarboxylic acid														
[1-(1,1-Dimethylethyl)-4,4-dimethyl-1,2-pentadienyl-phosphonic acid									91					
Dodecanoic acid/Lauric acid									93					
Hepatadecanoic acid/Margar	93								98					
Heptadecene-(8)-carbonic acid	90													
Hexadecanoic acid/Palmitic acid	99	99					99	99	93		99	99	99	99
Hexadecyl ester of hexadecanoic acid		93												

C-5 cont.

	Sample Number/%													
Organic Compounds	40	41	42S	42N	42A	42B	44	45	56	57	58	59	75	76
Acids														
Methyl ester of hexadecanoic acid									98			97		
Methyl ester of octadecanoic acid	95													86
3-Nitro-1,2-benzenedicarboxylic acid	91													
Nonahexacontanoic acid										92				
Octadecanoic acid/Stearic acid	97	91						93			90			
(Z)-9-Octadecenoic acid	99							99				99		97
Octadecyl ester of tetradecanoic acid												87		
2-Octenoic acid														
Oleic acid	94	87						86					80	
2-Oxo-methyl-cholan-24-oic acid												86		
Pentadecanoic acid	91							96				99		
Pentanoic acid/Valeric acid												99		
Tetradecanoic acid/Myristic acid	98							96					98	
Tetradecanoic acid amide						93								
Chlorinated hydrocarbons														
1-Chloro-7-heptadecene												92		
1-Chloro-hexadecane	96													97
1-Chloro-octadecane	93										86	96		93
1-Chloro-pentadecane												87		
Alcohols														
Benzene methenethiol	94													
2H-1-Benzoypyran-6-ol/Vitamin E														91
6,10,14-Hexadecatrien-1-ol	86													87
(E)-13-Methyl-11-tetradecen-1-ol													80	
1-Nonadecanol/Nonadecyl alcohol													80	
(Z)-9-Octadecen-1-ol													90	
Peucelenediol														
n-Tridecanol												86		

C-5 cont.

	Sample Number/%													
Organic Compounds	40	41	42S	42N	42A	42B	44	45	56	57	58	59	75	76
Hydrocarbons														
(1-Butylheptyl)-benzene								94	96		94			96
2-Butyl-1,1,3-trimethyl-cyclohexane	90													
Cyclodecene	94													
Cyclotetradecane									93				95	
n-Decane	95							94			95			
1,5,9-Decatriene							80							
1,2-Diethyl-benzene											91			
1,4-Dimethyl-benzene													90	
N,N-Dimethyl-cycloundecane	96													80
3,8-Dimethyl-decane												90		
4,6-Dimethyl-dodecane								90			86			
3,6-Dimethyl-octane											93			
2,6-Dimethyl-undecane	95							95						
n-Docosane											87	87		
n-Dodecane	95							95	90	87		97		
1-Dodecene/Adecene													81	
n-Eicosane	90	91				96		97	91		98	96		
5-(Ethyldecyl)-benzene											90			
2-Ethyl-1,3-dimethyl-benzene											95			
3-Ethyl-tridecane												87		
Heneicosane	96	94							91					95
n-Heptadecane	96	95								93	97		96	
n-Heptadecyl-cyclohexane											81			
n-Hexacosane		86							94			94		
n-Hexadecane								98	93		95	97		94
1-Hexadecene/Cetene	90													
2,6,10,15,19,23-hexamethyl-2,6,10,14,18,22-Tetracosahexaene								87	87		98	87		
(1-Heptylhexyl)-benzene								81						

C-5 cont.

	Sample Number/%													
Organic Compounds	40	41	42S	42N	42A	42 B	44	45	56	57	58	59	75	76
Hydrocarbons														
2-Methyl-decane		90							90					
3-Methyl-decane								94			91			
4-Methyl-decane	90							90						
5-Methyl-decane								91			91			
4-Methyl-dodecane	90										93			
6-Methyl-dodecane											81			
3-Methyl-hexadecane								83						
1-Methyl-2-(methylethyl)-benzene											80			
1-Methyl-3-(methylethyl)-benzene											80			
1-Methyl-4-(1-methylethyl)-benzene											90			
9-Methyl-nonadecane											87			
3-Methyl-nonane											87			
2-Methyl-octadecane								81						
3-Methyl-pentadecane								97			81	93		91
1-Methyl-2-propyl-benzene											80			
3-Methyl-3-propyl-nonane								91						
3-Methyl-tetradecane								87						
4-Methyl-tetradecane											91			
5-Methyl-tetradecane								80						
2-Methyl-tridecane	86							93			80			
3-Methyl-tridecane								90						
4-Methyl-tridecane	86													
2-Methyl-undecane								87						
4-Methyl-undecane	90							90			91			
n-Nonadecane										94			94	
1-Nonadecene	83													
2-Nonadecene										86				
n-Nonane/Shells								94			96			

C-5 cont.

	Sample Number/%													
Organic Compounds	40	41	42 S	42N	42 A	42 B	44	45	56	57	58	59	75	76
Hydrocarbons														
n-Octacosane		87									83			
n-Octadecane	95							96	95	90	97	95		
1-Octadecene												94		
(E)-5-Octadecene									91					
Oxacyclotetradecane-2,11-diene									86					
n-Pentadecane	96					97			96	93	97	96		
1-Pentadecene									83				90	91
Pentyl-cyclohexane								89						
(1-Heptylpentyl)-benzene	96	94					96				94			97
(1-Pentyloctyl)-benzene							83				89	92		91
(1-Propyldecyl)-benzene														86
(1-Propylnonyl)-benzene											91			
(1-Propyloctyl)-benzene														94
n-Tetracosane	86							98	86		83	95		
n-Tetradecane	94					98		98	95	81	98	96		93
1,2,3,4-Tetramethyl-benzene								95				80		
4,8,12,16-Tetramethyl-heptadecane-4									83					93
2,6,10,14-Tetramethyl-hexadecane	90										98	91		98
2,6,10,14-Tetramethyl-pentadecane														93
Tetratetracontane	83													
trans.-Caryophyllene											99			
n-Triacontane											83	83		
Tricosane		93					90	98			93			90
n-Tridecane	90					96		94	93		96			
1,2,4-Triethyl-benzene											95			
1,2,3-Trimethyl-benzene								97						
2,6,11-Trimethyl-dodecane								90						
2,6,14-Trimethyl-dodecane	86							90			90			
2,610-Trimethyl-pentadecane											80			
Tritetracontane		86												
n-Undecane	96							94			96			

C-5 cont.

	Sample Number/%													
Organic Compounds	40	41	42 S	42N	42A	42 B	44	45	56	57	58	59	75	76
Others														
5.alpha-Cholest-3-ene										93				
5-amino-2-(p-methoxyphenyl)-2-methyl-2H-[1,2,4]triazolo[1,5-a][1,3,5]triazine												83		
Bacchotricuneatin	83													
14.beta.-H-Pregna							81				92			
Cholest-3,5-diene									95					
Citroflex A						91								
Cystathionine-DTMS												90		
Decamethyl-cyclopentasiloxane									90		90			
Dibenz(b,f)azepine														86
4,6-Dibromo-1(N)-methyl-2-methylsu							86							
Dihydrocholesterol								91						95
(+)-Dihydroreciferolide														90
Docosanolide									80					
Dodecamethyl-cyclohexasiloxane											86			
Dotriacontane	86	86												
1,1-Dodecanediol diacetate												91		
5-Ethyl-3,4-bis(trifluoromethyl)-											90			
1-Ethyldibenzothiophene								90				83		
2-Ethyldibenzothiophene	90										83			
Galoxide 1 and 2	91							89			93			93
.gamma.-Terpinene														97
Garvin B											83			
Hexamethyl-cyclotrisiloxane	87													
8-Hydroquinoline						95								
Junipene												98		
20.*1-Lacosta-7,9(11)-diene									90					
2-Naphthalene-carbonitrile									95					
Octahydro-1,9,9-trimethyl-4-methylene-(1.alpha.,3a.alpha.,7.alpha.,8a.beta.)-1H-3a,7-Methanoazulene														
Octamethyl-cyclotetrasiloxane									90					
Tetratetracontane	83													
trans.Anethole								93						

C-6 EASTERN CAPE

	Sample Number/%			
Organic Compounds	61	78	79	80
Phenols				
3,5-Di-tert-butyl-2,6-dinitrophenol			83	
2-Methoxy-4-(1-propenyl)-phenol			93	
4-Methyl-phenol/p-Cresol	97			
Nonylphenol		91	87	
Chlorinated Phenols				
Triclosanal-5-chloro-2-(2,4-dichlorophenoxy)-phenol	90			
PAHs				
Anthracene/Anthracin		92		
Cadinene	89			
1,4-Dimethoxy-phenanthrene	90			
Fluoranthene		93		
6-Methyl-7(12h)-benz[a]anthracenon		98		
1,2,3,4,4a,5,6,8a-Octylnaphthalene	96			
Pyrene		95		
.beta.-Selinene	96			
Amines				
N,N-Dibutyl-1-butanamine	91	95	80	
Aldehydes				
2,2-Dideutero-octadecanal			86	
Tetradecanal/Myristaldehyde			94	
Esters				
1H-Indole/Ketol	91			
2-Pentadecanone			86	
2-Undeconone			87	
Acids				
Benzenepropanoic acid	93			
Butyl ester octadecanoic acid			91	
Decanoic acid/Capric acid			90	
Dipropyl-1,2-benzenedicarboxylic acid		80		
Dodecanoic acid/Lauric acid			99	
Hepatadecanoic acid/Margaric acid			98	
Hexadecanoic acid/Palmitic acid	99		99	
Linoleic acid			97	

C-6 cont.

	Sample Number/%			
Organic Compounds	61	78	79	80
Acids				
3-Nitro-1,2-benzenedicarboxylic acid	91			
Octadecanoic acid/Stearic acid	95	99	94	
(Z)-9-Octadecenoic acid		83	99	
Pentadecanoic acid			99	
Tetradecanoic acid/Myristic acid			98	
Undecanoic acid			90	
Alcohols				
7.beta.-Trichlorohec-9-en-4-.beta.-ol	86			
1-Docosanal/Behenic alcohol	80			
1-Hentetracontanol	86			
2-Methyl-1-hexadecanol		89		
1-Octadecanol/Stenol			91	
Hydrocarbons				
.alpha.-Humulene	96			
(1-Butylheptyl)-benzene	93			
Cyclotetradecane	92			
n-Decane			95	
3,6-Dimethyl-decane			83	
2,5-Dimethyl-nonane			81	
n-Docosane	90		97	
n-Dodecane	91			
1-Ethyl-2,3-dimethyl-benzene			80	
n-Heneicosane	97		89	
n-Heptadecane	95			
Hexatriacontane				83
(Z)-3-Hexadecene			83	
Isocaryophyllene	99			
2-Methyl-decane			96	
3-Methyl-decane			94	
4-Methyl-dodecane			96	
(1-Methyldodecyl)-benzene			87	
1-Methyl-2-(methylethyl)-benzene			95	
3-Methyl-nonane			91	

C-6 cont.

	Sample Number/%			
Organic Compounds	61	78	79	80
Hydrocarbons				
4-Methyl-nonane			86	
3-Methyl-tridecane			83	
2-Methyl-undecane			87	
3-Methyl-undecane			87	
5-Methyl-undecane			96	
9-Methyl-(E)-2-undecane	87			
n-Octadecane	91		94	
n-Pentadecane			94	
1-Pentadecene			97	
(1-Pentyloctyl)-benzene	93			
(1-Propylnonyl)-benzene	95			
n-Tetracosane	95		91	
n-Tetradecane	93			97
2,6,10,14-Tetramethyl-hexadecane			96	
Tetratetracontane			83	
n-Triacontane			91	
3-Thio-8-p-methadien-7			98	
Tricosane	97			
n-Tridecane		94		
1,2,3-Trimethyl-benzene				
2,3,6-Trimethyl-decane				
2,3',4-Trimethylphenyl methane				
Undecane			96	
Others				
5-Bromo-(3.beta.)-cholest-5-ene		93		
10-Demethylsqualene			86	
Dihydrocholesterol			89	
Dodecamethyl-cyclohexasiloxane	91			
Galoxide 1 and 2	90	93		
.gamma.-Terpinene	97			
Hahnfett	80			
28-Nor-17-.alpha(h)-hopane	86			
2(10)Pinene	91			

C-7 NORTHERN CAPE

	Sample Number/%			
Organic Compounds	67	68	72	74
Phenols				
2,6-Bis(1,1-dimethylethyl)-4-methyl-phenol	86			
4-Methyl-phenol/p-Cresol		93		97
Nonylphenol mix of isomers		81		
PAHs				
4-Methoxybenzo[c]phenanthrene			90	
Furans				
2(4H)-Benzofuranone	95			
Dibenzofuran			80	
Amines				
N,N-Dibutyl-1-butanamine	97		95	97
N,N-Dimethyl-1-dodecanamine	80			
Aldehydes				
2-Methyl-undecanal		80		
Octadecanal/Stearaldehyde				90
Esters				
.beta.-Isomethyl-ionone	91			
Butyl tetradecanoate/Myristate	87			
Cholestan-4-en-3-one		92		
Friedelan-y-al	98			
1H-Indole/Ketol				97
Methyl ester 9-octadecanoate				95
5-Methyl-1H-indole				94
Muskolactone/Oxacyclohexadecan-2-one				89
2-Nonadecanone	81			
2-Pentadecanone				83
Acids				
(E)-2-Butenoic acid	93			
Butyl ester of linoleic acid				86
Butyl ester of octadecanoic acid				93
Acids				
Decanoic acid/Capric acid				91
Diiso-1,2-benzenedicarboxylic acid	93			
Dodecanoic acid/Lauric acid	97			91
Eicosanoic acid/Arachidic acid				

C-7 cont.

	Sample Number/%			
Organic Compounds	67	68	72	74
Acids				
Ethyl ester of (Z)-9-octadecenoic acid	93			
Hepatadecanoic acid/Margaric acid	98			91
Hexadecanoic acid/Palmitic acid	99	99		90
Methyl ester of hexadecanoic acid	97			
Methyl ester of 9,12-octadecadienoic acid				91
Methyl ester of octadecanoic acid	94			93
Methyl ester of tetradecanoic acid	90			
Nonahexacontanoic acid		83		
Octadecanoic acid/Stearic acid		96		
(Z)-9-Octadecenoic acid	90	96		87
Pentadecanoic acid	93			99
Tetradecanoic acid/Myristic acid	94			98
Chlorinated hydrocarbons				
1-Chloro hexadecane			90	
1-Chloro-octadecane	93		98	80
Alcohols				
4,4-Dimethyl-cholestan-3-ol	92			
Hydrocarbons				
.beta.-Caryophyllene			90	91
(1-Butylheptyl)-benzene	93	93		
(1-Butylhexyl)-benzene	97			
(1-Butylnonyl)-benzene				94
2,6-Dimethyl-hepatadecane		94		
n-Docosane	93	93	96	97
n-Heneicosane			96	98
n-Heptadecane				96
n-Heneicosane	94	90		
n-Heptadecane	96	95		
1-Heptadecene/Hexahydroap	93			
n-Hexacosane		96		
Hexatriacontane	91	91		
(Z)-7-Hexadecene	90			
1-Hexadecene/Cetene	95			

C-7 cont.

	Sample Number/%			
Organic Compounds	67	68	72	74
Hydrocarbons				
2-Methyl-decane		87		
Methyl eicosa-5,8,11,14,17-pentaen				86
6-Methyl-dodecane		81		
3-Methyl-nonane		86		
3-Methyl-5-propyl-nonane		80		
1-Nonadecene	91			
1-Nonene	93			
n-Octacosane	90		94	
n-Octadecane	98			
n-Pentadecane				96
(1-Pentyheptyll)-benzene	80	94	96	96
(1-Pentyloctyl)-benzene			91	
(1-Propylnonyl)-benzene	90	89		
n-Tetracosane				98
n-Tetradecane		95		
(Z)-3-Tetradecene		83		
2,6,10,14-Tetramethyl-hexadecane	89	98		
trans.-Caryophyllene		99		
n-Tridecane		90		
2,3,6-Trimethyl-decane		80		
Undecane	96			
Others				
.alpha.Cubebene		93		
Decamethyl-cyclopentasiloxane	90	90		
Dodecamethyl-cyclohexasiloxane	90			
Galoxide 1 and 2	91	93	93	
Germacrane B		80		
Hexamethyl-cyclotrisiloxane	91			
Methyl-arachidonate				94
Methyl-dihydromalvate		91		
Methyl-3D.5,9,13-tetramethyl-5-vin	81			
Octamethyl-cyclotetrasiloxane	90			
Pyrrolo(3,2,1-b)carbazole			83	
3,3'-Trimethylene-2,2'-biquinoline		83		

C-8 WESTERN CAPE

	Sample Number/%																	
Organic Compounds	28	29	30S	30N	30A	30B	31	32	33	34	35	36	37	60	62	63	64	65
Phenols																		
2,6-Bis(1,1-dimethylethyl)-4-methyl-phenol			92			93			92					91				
2-Methyl-phenol/o-Cresol				97	97													
3-Methyl-phenol/m-Cresol						94												
4-Methyl-phenol/p-Cresol		97	97	97	96		97		93									
Nonylphenol							90				86			95				
Phenol/Izal					95													
Octyl-phenol isomer															80			
PAHs																		
Anthracene/Anthracin												96						
.beta.-Selinene			98						98									
2,6-Dimethyl-naphthalene									89									
2,3-Dimethyl-naphthalene														86				
Fluoranthene												94						
Fluorene									94					90				
1-Methyl-naphthalene														95				
2-Methyl-naphthalene									83									
Phenanthrene														95				
.beta.-Selinene/Naphthalene,de			98						98					97				
Phthalates																		
Di-(2-ethylhexyl)-phthalates		90						83						83	83		83	
Amines																		
4-Chloro-benzanamine									93									
N,N-Dibutyl-1-butanamine									96	96			95	97		96	97	95
2,5-Dichloro-benzanamine										96								
3,5-Dichloro-benzanamine									92									
N,N-Dimethyl-1-dodecanamine							80											
(Z)-9-Octadecenamide					89													
Aldehydes																		
Hexadecanal/Palmitic aldehyde					91											91		
Octadecanal/Stearaldehyde														95				
Tetradecanal/Myristaldehyde					91			94		91		83			87			90

C-8 cont.

	Sample Number/%																	
Organic Compounds	28	29	30S	30N	30A	30B	31	32	33	34	35	36	37	60	62	63	64	65
Esters																		
5.alpha.-Cholestan-3-one										90								
Butyl octadecanoate										83								
Cholestan-1,1-dien-3-one					94	94												
2-Chloroethyl-linoleate				90														
Coprostan-3-one											91					89	92	86
Ethyl linoleate		90						87				86			87			
2-Heptadecanone								90										
1H-Indole/Ketol	94		95						92	95		94		94				
3(2H)-Isoquinolinone					93													
Methyl-hexadecanoate							97			97								
3-Methylindole		91					91							95				
5-Methylindole									94	94								
7-Methylindole									94	94								
5-Methyl-1H-indole					90													
15-Methyl-oxacyclopentadecan-2-one												91						
Oxacycloheptade-8-en-2-one												91						
Acids																		
Benzenepropanoic acid	91				91										93			
Benzoic acid/Retardex					96													
Butanoic acid/n-Butyric acid	91													60				
(E)-2-Butenoic acid				97														
Butyl ester of linoleic acid														91				
Butyl ester of octadecanoic acid		93	95				93	93			93	93						
2-Chloro-benzeneacetic acid					91													
Decanoic acid/Capric acid			83				95		95	95				96				
Dioctadecyl ester of phosphonic acid										86								
Docosanoic acid														90				
Dodecanoic acid/Lauric acid	99	98	98					98	98	98	97			98		98		

C-8 cont.

	Sample Number/%																	
Organic Compounds	28	29	30S	30N	30A	30B	31	32	33	34	35	36	37	60	62	63	64	65
Acids																		
Ethyl ester of (Z)-9-octadecenoic acid	99			81												81		
2-Ethyl-hexanoic acid																99		93
Hepatadecanoic acid/Margar	99	99	99				96	98			99	99		99				
Heptadecene-(8)-carbonic acid																		87
Hexadecanoic acid/Palmitic acid	93			99	99			94		99	99	94	95	96	99	99	99	99
9-Hexadecenoic acid		91	91					93										
9-Hexadecenyl ester of palmitic acid												92						
9-Hexadecenyl ester of stearic acid									94									
Hexadecyl ester of hexadecanoic acid		99				99	99		98		99	99				98		
Hexadecyl ester of tetradecanoic acid			99				90		99	99								
n-Hexanoic acid	90				90													
2-Methyl butanoic acid					83													
Methyl ester of hexadecanoic acid									97					98		97		
Methyl ester of 9,12-octadecadienoic acid			90				95											
Methyl ester of octadecanoic acid							97	97	95	97								
Methyl ester of 3-octadecenoic		93												94				
Methyl ester of 8-octadecenoic acid		95																
Methyl ester of 15-octadecenoic acid			87															
Methyl ester of tetracosanoic acid							87											
Methyl ester of tetradecanoic acid										95				94				
2-Methyl pentanoic acid				83														
2-Methyl-propanoic acid					91													
3-Nitro-1,2-benzenedicarboxylic acid												86	91					
(Z,Z)-9,12-octadecadienoic acid			89														96	
Octadecanoic acid/Stearic acid	99	96	94				98	93	94	97	94	99	99	98	95	96	95	99
(Z)-9-Octadecenoic acid	86	99						99		98	99	99	99	95	86	90	93	99
Octadecyl ester of tetradecanoic acid										94								
Oleic acid		93														93		
2-Oxo-methyl-cholan-24-oic acid															90			
Pentadecanoic acid	99	97	97					99	94	98	99	99		99		97		95
14-Pentadecenoic acid	90		99															
Pentanoic acid/Valeric acid	83				90													
2-Pentenoic acid				83										86				

C-8 cont.

	Sample Number/%																	
Organic Compounds	28	29	30S	30N	30 A	30 B	31	32	33	34	35	36	37	60	62	63	64	65
Acids																		
Tetradecanoic acid/Myristic acid	98	99	99				99	99	98	98	98	99		98		98		98
Tetradecyl ester of hexadecanoic acid		81										91						
Tridecanoic acid		98	98						89	97								
Chlorinated hydrocarbons																		
1-Chloro-hexane															99			
1-Chloro-hexadecane				89														
1-Chloro-octadecane				94														
1-Chloro-octane															98			
1,2-Dichloro-benzene														97				
Dichlorotoluene									93									
Alcohols																		
2H-1-Benzoypyran-6-ol/Vitamin E								90		90				89		91		
3.beta.-Cholest-5-ene-3-ol		99	97				91		90	91						91		
Cycloheptadecanol										89								
(2Z,Z)-Dehydrocholesterol						81												
Dihydrocholesterol		99								94		86				99		
1,3-Dimethyl-cyclopentanol										80								
2-(Dodecyloxy)-ethanol																	89	
.gamma.-Tocopherol			90															
Hexadecanol/Cetal			94	80												94		
6,10,14-Hexadecatrien-1-ol														90				
2-(Hexadecyloxy)ethanol							87											
2-Methyl-1-hexadecanol										87								
(E)-13-Methyl-11-tetradecen-1-ol																87		
9,12-Octadecadien-1-ol									94	95								
2-(9,12-Octadecadienyloxy)-ethanol														83				
1-Octadecanethiol					93	94					92							
1-Octadecanol/Stenol				83														
(Z)-9-Octadecen-1-ol										90								
2(9-Octadecenyloxy)-(Z)-ethanol												83						
1,15-Pentadecanethiol																91		
8-Quinolinol				90		93												
1-Tetradecanol			98							99								

C-8 cont.

	Sample Number/%																	
Organic Compounds	28	29	30S	30N	30A	30 B	31	32	33	34	35	36	37	60	62	63	64	65
Hydrocarbons																		
.beta.-Caryophyllene			99															
11-Butyl-docosane														95				
(1-Butylheptyl)-benzene								96	96	91				90	94			95
(1-Butylhexyl)-benzene																		
(1-Butyloctyl)-benzene									83	86								92
2-Butyl-1,1,3-trimethyl-cyclohexane			91															90
cis-1,4-Dimethyl-cyclooctane								86										
cis-2-Methyl-7-octadecene		83																
Cyclohexadecane						90	98											
Cyclohexane									81									
Cyclopentadecane		95					95											
Cyclotetradecane			95				89		94									95
n-Decane			94						94					93				
Dec-1-ene									96									
1,5-Diethyl-3-methyl-cyclohexane										86								
1,3-Dimethyl-benzene														93				
1,5-Dimethyl-cyclooctane										93								
N,N-Dimethyl-cycloundecane	91	95	95	97			95	96			96	96						
1,1-Dimethyl-2,3-diphenylindene					80													
2,6-Dimethyl-undecane															80			
n-Docosane			98					98	97			99		89	96	97		
1-Docosene												90		89				
n-Dodecane			87	91					87	90				91				
1-Dodecene/Adecene																		86
(E,E,E)-1,4,8-Dodecatriene										92								
n-Eicosane	93					96	98	91	83						93			
(1-Ethenyloxy)-hexadecane												89		97	93			
Heneicosane	97		96				93	97		95					95			
n-Heptacosane									95						95			
1-Heptadecene/Hexahydroap									86	94						84		

C-8 cont.

	Sample Number/%																	
Organic Compounds	28	29	30S	30N	30 A	30 B	31	32	33	34	35	36	37	60	62	63	64	65
Hydrocarbons																		
n-Hexacosane							93		98	97								
1,E-8,Z-10-Hexadecatriene										89								
1-Hexadecene/Cetene			86									98				93		
2,6,10,15,19,23-hexamethyl-2,6,10,14,18,22-Tetracosahexaene	96	95	98	98				95	96	98		98	98	98	97	98	97	
1-Iodo-decane															83			
1-Iodo-2-methyl-undecane			91															
Isocaryophyllene													99				98	
1-Isocyanato-2-methyl-benzene			93															
Methyl-cycloheptane																84		
7-Methyl-(Z)-decene											92							
1-Methyl-4-(1-methylethyl)-benzene									97					94				
7-Methyl-tridecane									86									
1-Nonadecene								94						93			96	
n-Nonane/Shells														96				
n-Octacosane	97		80			91						95						89
1-Octadecene		90				95			98				91			96		
(E)-9-Octadecene														83				
Pentacosane										96								
n-Pentadecane	97	97	98				96	96	97	91						98	95	94
1-Pentadecene		83	92															
(1-Heptylpentyl)-benzene			95	94				93		91		93			80	90		94
9-Hexyl-heptadecane							93											
(1-Hexylpentyl)-benzene							87											
(1-Pentyloctyl)-benzene															90	90	90	
3-Phenyl-1,4-(E)-dodecadiene					86													
(1-Propylnonyl)-benzene															80			

C-8 cont.

	Sample Number/%																	
Organic Compounds	28	29	30S	30N	30 A	30 B	31	32	33	34	35	36	37	60	62	63	64	65
Hydrocarbons																		
n-Tetracosane	94		86					93				95						
1,13-Tetradecadiene				81			93		95									
1-Tetradecene									95			91						
(Z)-3-Tetradecene		83																
2,6,10,14-Tetramethyl-hexadecane	94																	
2,6,10,14-Tetramethyl-pentadecane										98	94							
trans.-Caryophyllene	99	99						99	99	99		99	99	99	99			
Tricosane			83					94						91	92			
(Z)-9-Tricosene										86								
n-Tridecane	96	95	97				96		94	95		86		97				
n-Tridec-1-ene								89										
1,2,4-Triethyl-benzene																89		
1,2,3-Trimethyl-benzene														97				
Tritriacontane												95						
n-Undecane			97						96					96				
Others																		
.alpha.-Copaene			98					99										95
.alpha.(p-chlorobenzoyl)-p-chloro						92												
.alpha.Humulene									99									
.alpha.-Pinene									97					96				
.alpha.Terpipene									98									
(-)-.alpha.-Terpineol														83				
5-amino-2-(p-methoxyphenyl)-2-methyl-2H-[1,2,4]triazolo[1,5-a][1,3,5]triazine																	83	83
.beta.-Pinene									97									
14.beta.-H-Pregna						81		92									83	
Cadina-1,4-diene									89	93								
Carotol													95					
Caryophyllene oxide													98					
Chromolaenim		90																

C-8 cont.

Organic Compounds	28	29	30S	30N	30 A	30 B	31	32	33	34	35	36	37	60	62	63	64	65
	Sample Number/%																	
Others																		
Decamethyl-cyclopentasiloxane		91						90	91	91		91				91		91
Dihydrocholesterol		99								94		86				99		
.gamma.-Tocopherol			90															
Docosanolide							87			90								
Dodecamethyl-cyclohexasiloxane			91						90	87								90
Epi-isopodophyllotoxin														90				
2-Ethyldibenzothiophene		83						86								83		
Farnesol isomer B					91													
Galoxide 1 and 2								93			93	93			93		94	94
.gamma.-Terpinene									95									
Hahnfett																91		
(+-)-Hexadecanolide	93	97	93									89						
Hexadecyl-oxirane												86						
Hexamethyl-cyclotrisiloxane				91														
18-Hydroxy- ($1S^{*}$, $1R^{*}$)-dolabella			83															
Isocaryophyllene													99				98	
Koiganal												86						
Limonene									98					98				
Methyl-arachidonate											89							
28-Nor-17-.alpha(h)-hopane																		95
Octamethyl-cyclotetrasiloxane				87														
3-Phenyl-5-t-butylpyridazine		83										83			83			86
2-(Phenylthiomethyl)-pyridine						80												
Terpinolene									98									
Tetradecamethy-hexasiloxane										91								
trans.beta.-Farnesene													97					
trans.Farnesol									90									
Tricorbonyl(n-phenyl-2-pyridine)iron														90				

C-9 Summary of the organic compounds detected in the nine South African provinces.

	Province/Frequency								
Organic Compounds	**GP**	**LP**	**NWP**	**MP***	**FSP**	**KZNP**	**ECP**	**NCP**	**WCP**
Phenols									
2,6-Bis (1,1-dimethylethyl)-4-methyl-phenol	4	1	1		1			1	4
3,5-Dimethyl-phenol	1								
3,5-Di-tert-butyl-2,6-dinitrophenol							1		
2-Methoxy-4-(1-propenyl)-phenol							1		
4-(1-Methylethyl)-phenol	1								
4,4'-(1-Methylethylidene) bis-phenol	1								
2-Methyl-phenol/o-Cresol	2								2
3-Methyl-phenol/m-Cresol	3								1
4-Methyl-phenol/p-Cresol	14	3				1	1	2	6
Nonylphenol	6		3		2	3	2		3
Nonylphenol mix of isomers	1		1		1			1	
Octyl-phenol isomer									1
Phenol/Izal	3								1
4-(1,1,3,3-Tetramethylbutyl)-phenol/ p-tert-Octylphenol	2								
Chlorinated Phenols									
Triclosanal-5-chloro-2-(2,4-dichlorophenoxy)-phenol							1		
Pesticides									
Epoxyheptachlor					1				
2,4,6-Trimethyllindane	1								

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

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

C-9 cont.

	Province/Frequency								
Organic Compounds	**GP**	**LP**	**NWP**	**MP**	**FSP**	**KZNP**	**ECP**	**NCP**	**WCP**
PAHs									
Acenaphthene	1								
6-Acetyl-7-hydroxy-2,2-dimethylbenzopyran	1								
7-Ac-6-et-1144-me4-tetralin/1,1,4,4-tetramethyl-6-ethyl-7-acetyl-1,2,3,4-tetrahydronaphthalene		1			1				
4-Allyl-1,2-dimethyl-naphthalene						1			
(-)-.alpha.-Amorphene	1								
Anthracene/Anthracin	1					2	1		1
Benz[a]anthracene	1								
.beta.-Selinene							1		3
Chrysene/Benzo[a]phenanthrene						1			
.delta.-Cadinene		1					1		
Decahydro-2-methylnaphthalene	3					2			1
7,12-Dihydro-7,12-dimethyl-benz[a]anthracene	2								
1,4-Dimethoxy-phenanthrene							1		
9,9-Dimethyl-1,4-dihydro-1,4-methanonaphthalene	1								
1,3-Dimethylnaphthalene	1								
1,5-Dimethylnaphthalene	2								
1,8-Dimethyl-naphthalene	1								
1,7-Dimethyl-naphthalene	2								
2,3-Dimethyl-naphthalene						1			1
2,6-Dimethyl-naphthalene	3	1							1
2,7-Dimethyl-naphthalene	1								
3,7-Dimethyl-naphthalene		1							
Epizonaren	1								
1-Ethyl-naphthalene		1							
2-Ethyl-naphthalene	2								
Fluoranthene	1					1	1		1
Fluorene	5					2			2
1,2,3,7,8,9-Hexahydro-perylene	1								
1,3,4,5,6,7-Hexahydro-1,1,5,5-tetramethyl-2H-2,4a-methanonaphthalene	1								
1H-Indene/Indonaphthene	1								
1,6-Methanofluorene	1								
4- Methoxy-1-acetonaphthone						1			
6-Methoxy-1-acetonaphthone	1	1							
8-Methoxy-1-acetonaphthone	1								
6-Methyl-7(12h)-benz[a]anthracenone			1				1		
4-Methoxybenzo[c]phenanthrene								1	
Methoxy-3-methylcholanthrene	1								
1-Methyl-2-(2-methyl-3-butenyl)-naphthalene	3					2			1
Naphthalene/White tar	3								
1,2,3,4,4a,5,6,8a-Octylnaphthalene							1		
Phenanthrene	3					1			1
Pyrene	1						1		
Perylene/Dibenz[de,kl]anthracene	1								
1,2,3,4-Tetrahydro-1,4-epoxyphenanthrene	1								
1,2,3,4-Tetrahydrol,1,6-trimethylnaphthalene	2								
1,2,3,4-Tetrahydro-6-methyl-naphthalene	1								
1,2,3,4-Tetrahydro-1-1,6-trimethylnaphthalene	2	2							
1,3,6-Trimethyl-naphthalene	1								

C-9 cont.

	Province/Frequency								
Organic Compounds	**GP**	**LP**	**NWP**	**MP**	**FSP**	**KZNP**	**ECP**	**NCP**	**WCP**
Phthalates									
Di-(2-ethylhexyl)-phthalate	4	1			1				5
Diethyl phthalate	2								
Diisooctyl-phthalate	1								
Biphenyls									
1,1`-Biphenyl	3					1			
(Phenylmethyl)-1,1'-biphenyl	1								
2,2',3,3'4,4'5,5'-octachloro-1,1'-Biphenyl	1								
Furans									
5-Acetyl-4,7-dimethoxy-6-hydrobenzofuran	1								
5-Acetyl-4,7-dimethoxy-6-hydrobenzofuran	1								
2(4H)-Benzofuranone								1	
Dibenzofuran						1		1	
1,2,3,4,6,7,8-Heptachlorodibenzofuran	1								
1,3-Isobenzofurandione			1						
4-Methyl-dibenzofuran	2								
2-Octylfuran	1	1							
2-Pentyl-furan	1								
Amines									
N,N-Bis(2-hydroxyethyl)dodecamide						1			
4-Chloro-benzanamine	2	1							1
6-Chloro-N,N'-diethyl1,3,5-triazine-2,4-diamine	1								
N,N-Dibutyl-1-butanamine	6	1	4		1	7	3	3	7
2,5-Dichloro-benzanamine						1			1
3,4-Dichloro-benzanamine						1			
3,5-Dichloro-benzanamine						1			1
N,N-Dimethyl-1-dodecanamine								1	1
N,N-Dimethyl-1-octadecanamine	1								
N,N-Dimethyl-tetradecanamine					1				
N,N-Dimethylpalmitamide	1								
Dodecanamide	1								
Hexadecanamide	1								
1-Methyl-acetamide	1								
(Z)-9-Octadecenamide	6	1				1			
N-(2-phenylethyl)-acetamide	1	1							
n-Tetradecanoic acid amide	3	2				1			
Aldehydes									
Decanal	1								
2,2-Dideutero-octadecanal	1						1		
n-Dodecanal						2			
Friedenlan-y-al	3								
Heptanal	2								
Hexadecanal/Palmitic aldehyde	3	1	1						2
n-Hexanal	4								
p-Hydroxy-m-methoxybenzaldehyde	2								
Ios-.alpha.-Cedren-15-al	1								
2-Methyl-undecanal								1	
n-Nonanal	3								
Nonylaldehyde	1								

C-9 cont.

	Province/Frequency								
Organic Compounds	**GP**	**LP**	**NWP**	**MP**	**FSP**	**KZNP**	**ECP**	**NCP**	**WCP**
Aldehyes									
Octadecanal/Stearaldehyde	3	1	1			2		1	1
9-Octadecenal	1								
Octanal	2								
Pentadecanal	3								
Tetradecanal/Myristaldehyde	5	2				2	1		6
Tridecanal	1								
Esters									
6-Acetyl-7-hydroxy-2,2-dimethylbenzopyran	1								
5.alpha.-Cholestan-3-one	5	1							1
5.alpha.-Cholestan-4-one		1							
(24S)-5.alpha.-Ergostan-3-one			1						
5-alpha,17.xi.-21-Norcholest-24-en-20-one	1	1							
5.alpha.-Stigmast-3-one						1			
(24R)-5.alpha.-Stigmastan-3-one						1			
1-(2-Aminophenyl)-ethanone	3								
5-(3-Aminopropyl)-5,10-dihydro-11H-dibenzo[b,e][1,4]diazepin-11-one	1								
5-(3-Aminopropyl)-1,5-diazacycloheptadecan-6-one	3								
.beta.-Ionone		1	1						
.beta.-Isomethyl-ionone								1	
14.beta.-3-Methoxy-6-oxaestra-1,3,5(10),8,15-pentaen-7,17-dione	1		1			2			
6-(Bromomethyl)-5-[(ethoxycarbonyl)-(phenylthio)-methyl]-4-methoxy-2H-pyran-2-one	1								
Butyl octadecanoate						1			
Butyl tetradecanoate/Myristate			1					1	
Cholestan-1,1-dien-3-one									
Cholest-4-en-3-one	1		1					1	
Cholest-5-en-3-one						1			
Cholestan-3-one	5		1						
Cholestan-4-one	4								
2-Chloroethyl-linoleate						1			
(+-)-cis-3,4,6,9-Tetrahydro-10-hydroxy-1,3,,8-trimethyl- 1H-naphtho[2,3-c]pyran6,9-dione		1			1				
Coprostan-3-one	1		1		1	4			
.delta.-4-Cholestene3-one						2			
.delta.-Decalactone/ Tetrahydro-6-pentyl-H-pyran-2-one	1								
7,8-Dihydrobenzo[g]chrysen-5(6H)-one	1								
1,3-Dihydro-2H-Indol-2-one	3								
2,3-Dihydro-4-methyl-1H-indole	4					2			
3-(2,2-Dimethylpropylidene)bicyclo [3.3.1]nonane-2,4-dione		1							
6,10-Dimethyl-5,9-undecadien-2-one	1								
(1R+,6S+,7R+)-10,10-Dimethyl-7-vinyl-tricyclo (4.3.2.0)undec-2-en-one	1								
Diphenyl-methanone	1								
3-Ethenyl-4-isopropylcyclohexanone	1								
Ethyl linoleate									4
Geranyl acetone	1	1							

C-9 cont.

	Province/Frequency								
Organic Compounds	**GP**	**LP**	**NWP**	**MP**	**FS**	**KZN**	**EC**	**NC**	**WC**
Esters									
2-Heptadecanone	1								1
Hexahydro-2H-azepin-2-one	1								
Hex-2-one		1	1						
D-Homoestra-1,3,5(10)-triene-17a-one			1						
2-Hydroxy-cyclopentadecanone	2	1							
2-Hydroxy-1,2,3-propanetricarboxylic acid tributyl ester / Citric acid tri-n-butyl ester	1								
1H-Indole/Ketol	8	3					1	1	6
1,3-Isobenzofurandione	3								
3(2H)-Isoquinolinone									1
5-Methoxy-2,2-dimethyllindan-1-one	1								
5-Methyldibenz(6,F)azapine-10-one	1								
6-Methyl-5-hepten-2-one	1								
Methyl-hexadecanoate									2
Methyl 6(r,s)-8-hydroxy-7-oxo-8,9-secolabdan-15-oate	1								
3-Methyl-1H-indole	5								3
5-Methyl-1H-indole	1	2				1		1	3
7-Methylindole	2	1							2
3-Methylindole-2(3H)-one	1					1			
Methyl 9,10-methylene octadecanoate	1								
15-Methyl-oxacyclopentadecan-2-one									1
5-Methyl-4-phenyl-trans-2-oxazolidinone		1							
Methyl tetradecanoate	1								
Muskolactone/Oxacyclohexadecan-2-one	1	1						1	
Neryl acetone	1								
2-Nonadecanone								1	
Oxacycloheptade-8-en-2-one	1	1				1			1
13-Methyl-oxacyclotetradecane-2,11-dione	1								
2-Pentadecanone	2	1					1	1	
3-Phenyl-4-hydroxyacetophenone						1			
2-Piperidinone	1								
Stigmast-4-ene-3-one			1						
2-Tridecanone	1	1	1						
4,4a,5,9-Tetrahydro-4a,8-dimethyl-5,9-dioxoazuleno(6,5-b)furan-3-carboxylic acid-methyl ester	1								
6,10,14-Trimethyl-2-pentadecanone					1	1			
2-Tridecanone	2					1			
2-Undeconone							1		
Acids									
S-(2-Aminoethyl) ester thiosulfuric acid		1							
Benzeneacetic acid	7					1			
Benzenebutanoic acid/4-Phenylbutyric acid	3								
Benzenepropanoic acid	5	1				2	1		3
Benzoic acid/Retardex	2								1
Bis(2-ethylhexyl) ester of 1,2-Benzenedicarboxylic acid	3	2	3		1				
Bis(2-methoxyethyl) ester of 1,2-Benzenedicarboxylic acid	1								
Butanoic acid/n-Butyric acid	7	1							1
(E)-2-Butenoic acid								1	1

C-9 cont.

	Province/Frequency								
Organic Compounds	**GP**	**LP**	**NWP**	**MP**	**FSP**	**KZNP**	**ECP**	**NCP**	**WCP**
Acids									
Butyl cyclohexyl ester of 1,2-benzenedicarboxylic acid	1								
Butyl ester of linoleic acid		1						1	1
Butyl ester of octadecanoic acid		1			1	1	1	1	6
2-Chloro-benzeneacetic acid									1
Cyclohexanecarboxylic acid	1								
Cyclohexanepropanoic acid	1								
Decanoic acid/Capric acid	2	2				6	1	1	5
Dibutyl ester 1,2-Benzenedicarboxylic acid	4	2				1			
Diethyl ester of 1,2-Benzenedicarboxylic acid	2					1			
Diethyl-carbamodithioic acid	1								
Diethyl-4-nitrophenyl ester of phosphoric acid	1								
Diisodecyl ester of 1,2-benzenedicarboxylic acid	2							1	
[1-(1,1-Dimethylethyl)-4,4-dimethyl-1,2-pentadienyl-phosphonic acid						1			
Dinonyl ester of 1,2-Benzenedicarboxylic acid	1								
Dioctadecyl ester of phosphonic acid									1
Dipropyl-1,2-benzenedicarboxylic acid							1		
Docosanoic acid	1								1
Dodecanoic acid/Lauric acid	8	3	3		1	1	1	2	9
Eicosanoic acid	1								
2-Ethyl-hexanoic acid	4								2
Ethyl ester of cis and trans-4-(1,1-dimethylethyl)-1-ethenylcyclohexanacetic acid	1								
Ethyl ester of (Z)-9-octadecenoic acid					1			1	3
2-Ethyl-hexanoic acid	1								
2-Ethylhexyl diphenyl of ester Phosphoric acid	2								
Exo-methyl-cholan-24-oic acid			1						
Heptadecanoic acid/Margaric acid	8	4	1		1	2	1	2	8
Heptanoic acid	2								
6-Heptadecatri-8(Z),11(Z),14(Z)-enyl-2-hydroxybenzoic acid		1							
Heptadecene-(8)-carbonic acid(1)	1	1				1			1
Hexadecanoic acid/Palmitic acid	15	5	2		2	9	2	3	13
9-Hexadecenoic acid	1								3
9-Hexadecenyl ester of palmitic acid	4								1
Hexadecyl ester of dodecanoic acid	2								
9-Hexadecenyl ester of stearic acid									1
Hexadecyl ester of hexadecanoic acid	3					1			7
Hexadecyl ester of octanoic acid	1								
Hexadecyl ester of tetradecanoic acid	1	2			1				4
n-Hexanoic acid	7	1							2
2-Hydroxy-methyl ester of docosanoic acid	1								
5-Isobutylidene-N,N-dimethylbarbituric acid	1								
Linoleic acid	3	1					1		
2-Methyl-benzoic acid	1								
2-Methyl butanoic acid/2-Methybutyric acid	6	1							1
3-Methyl-butanoic acid/Isovaleric acid	1								
3-Methyl-2-butenoic acid	1								
3-Methyl decanoic acid	2								
Methyl ester of hexadecanoic acid	1		1			2		1	3

C-9 cont.

	Province/Frequency								
Organic Compounds	**GP**	**LP**	**NWP**	**MP**	**FSP**	**KZNP**	**ECP**	**NCP**	**WCP**
Acids									
Methyl ester of 9-hexadecenoic acid			1						
Methyl ester of 7,10-octadecadienoic acid		1							
Methyl ester of 9,12-octadecadienoic acid	2							1	2
Methyl ester of octadecanoic acid		1				2		2	4
Methyl ester of 3-octadecenoic									2
Methyl ester of 8-octadecenoic acid		1							1
Methyl ester of(Z)-9-octadecenoic acid	2								
Methyl ester of 15-octadecenoic acid									1
Methyl ester of tetracosanoic acid									1
Methyl ester of tetradecanoic acid		1	1					1	2
2-Methyl-hexanoic acid	3	1							
5-Methyl-hexanoic acid	2								
14-Methyl methyl ester heptadecanoic acid	1								
2-Methyl-pentanoic acid	7	1							1
4-Methyl-pentanoic acid	1								
2-Methyl-propanoic acid	6								1
2-Methylvaleric acid	1								
2-Methylpropyl ester of 1,2-benzenedicarboxylic acid	1								
Moronic acid	1								
3-Nitro-1,2-benzenedicarboxylic acid	1	1	3			1	1		2
Nonadecanoic acid	1	1	1						
Nonahexacontanoic acid						1		1	
Nonanoic acid	5	2	1						
(Z,Z)-9,12-Octadecadienoic acid		2	2						2
Octadecanoic acid/Stearic acid	11	5	4		1	5	3	1	15
(Z)-9-Octadecenoic acid	8	2	6			4	2	3	12
Octadecyl ester of tetradecanoic acid						1			
Octanoic acid/Caprylic acid	4	3	1						
2-Octenoic acid		1				1			
Oleic acid	1		2			4			2
9-Octadecenyl ester of (Z)-octadecanoic acid	1								
Octadecyl ester of tetradecanoic acid									1
Octadecyl-(Z)-9-octadecenoic acid	1								
2-Oxo-methyl-cholan-24-oic acid			1			1			1
Pentadecanoic acid	13	4	2		1	4	1	2	11
14-Pentadecenoic acid			3						2
Pentanoic acid/Valeric acid	8	1				1			2
2-Pentenoic acid									2
3-Phenylbutyric acid	1								
(R)-2-Phenylpropionic acid	1								
1,2,3-Propanetricarboxylic acid	4								
Propanoic acid	1								
Tetradecanoic acid/Myristic acid	13	4	2			4	1	2	12
Tetradecyl ester of dodecanoic acid	1								
Tetradecyl ester of hexadecanoic acid	2	1							2
Tridecanoic acid	2	2			1				4
Tributyl ester 2-hydroxy-1,2,3-propanetricorbixylic acid	1								
Triphenyl ester phosphoric acid	1								
Undecanoic acid	3	1					1		

C-9 cont.

	Province/Frequency								
Organic Compounds	**GP**	**LP**	**NWP**	**MP**	**FSP**	**KZNP**	**ECP**	**NCP**	**WCP**
Chlorinated hydrocarbons									
7-Chloro-7-heptadecene	1	1				1			
1-Chloro hexadecane		1				2		1	1
1-Chloro-hexane			1						1
1-Chloro-2-isocyanato-benzene	1	1			1				
1-Chloro-octadecane	2	1			1	4		3	1
1-Chloro-octane			1						1
1-Chloro-pentadecane						1			
3-p-Chlorophenyl-1-methyldioxindol	1								
1,2-Dichloro-benzene									1
1,4-Dichlorobenzene	1				1				
1,4-Dichloro-2-isocyanato-benzene					1				
5,7-Dichloro-1-methyl-1,4-benzodiazepin-2-one	1								
2,4-Dichlorophenyl isocyanate	1								
Dichlorotoluene									1
Trichlorododecyl-silane	1								
Trichloroeicosyl-silane	1								
Alcohols									
Benzenemethenethiol	3		1			1			
2H-1-Benzopyran-6-ol/Vitamin E	2					1			4
3.beta.-Cholest-5-en-3-ol	2		1						6
3.beta.-lup-20(29)-en-3ol	1								
7.beta.-Trichlorohec-9-en-4-.beta.-ol							1		
Cyclododecanol		1							
Cycloheptadecanol									1
1-Docosanal/Behenic alcohol							1		
1-Dodecanol		2							
7,8-Dihydrobenzo[g]chrysen-5(6H)-one	1								
(2Z,Z)-Dehydrocholesterol	1								1
Dihydrocholesterol/ 5.alpha.-Cholestan-3.beta.-ol	5		2			2	1		4
4,4-Dimethyl-cholestan-3-ol								1	
1,3-Dimethyl-cyclopentanol									1
1-Dodecanethiol	1		1						
2-(Dodecyloxy)-ethanol									1
Epifriedelinol		1							
2-Ethyl-hexanol	1								
Farnesol	1								
D:A-Friedooleanane-1,24-diol	1								
.gamma.-Tocopherol	1								1
Geranyl acetone			1						
1-Hentetracontanol							1		
1-Heptacosanol	2								
1,16-Hexadecanediol	2								
6,10,14-Hexadecatrien-1-ol						2			1
1-Hexadecen-1-ol/Cetal	2		1		1				3
(Z)-11-Hexadecen-1-ol			1						
2-(Hexadecyloxy)ethanol									1
Hexanethiol	2								
8-Hydroxyquinoline	4					1			
Isoheptadecanol			1						
20.xi.-Linosta-7,9(11)-diene-3.beta.18,20-triol	2					1			

C-9 cont.

	Province/Frequency								
Organic Compounds	**GP**	**LP**	**NWP**	**MP**	**FSP**	**KZNP**	**ECP**	**NCP**	**WCP**
Alcohols									
(22E,24S)-24-Methyl-5.alpha.-cholesta-8,22-dien-3.beta.-ol	1								
p-Menth-3-en-1-ol	1								
2-Methyl-1-hexadecanol	2	1	1				1		1
(R)-(-)-(Z)-14-Methyl-8-hexadecen-1-ol	1								
(E)-13-Methyl-11-tetradecen-1-ol	1					1			1
1-Nonadecanol/Nonadecyl alcohol						1			
9,12-Octadecadien-1-ol									2
2-(9,12-Octadecadienyloxy)-ethanol									1
1-Octadecanethiol	2								3
1-Octadecanol/Stenol	1	1					1		1
(Z)-9-Octadecen-1-ol	1					1			1
2(9-Octadecenyloxy)-(Z)-ethanol									1
1-Octanethiol	2								
1-Pentadecanethiol	1								
1,15-Pentadecanethiol	1	1	1						1
Peucelenediol						1			
1-Phenyl-6-oxanonan-1-ol		1							
Podocarpan-14-.beta.-ol			1						
8-Quinolinol									2
Totarol		1							
Terpinene-1-ol	1								
n-Tridecanol						1			2
(E)-2-Tridecen-1-ol	1								
2-(Tetradecyloxy)-ethanol	1								
(E)-2-Tridecen-1-ol	1								
Hydrocarbons									
.alpha.-Caryophyllene/.alpha.-Humulene	4	2					1		
.alpha.-Copaene	3								
.alpha.-Curcumen	1								
.alpha.-Phellandrene	1								
.alpha-Pinene	1								2
Azulene/Cyclopentacycloheptane	1								
.beta.-Caryophyllene	6	4						2	1
.beta.-Bisabolene	1								
1,1-Bis(p-tolyl)ethane	1								
11-Butyl-docosane	2		1						1
(1-Butylheptyl)-benzene	10	2	2			4	1	2	6
(1-Butylhexyl)-benzene	6	2	1		1			1	
(1-Butyloctyl)-benzene	9	5	1						3
(1-Butylnonyl)-benzene	5		1					1	
Butylated hydroxy toluene	1								
11-Butyl-docosane	1								
2-Butyl-1,1,3-trimethyl-cyclohexane			1			1			2
cis-Caryophyllene	4	1							
cis-1,4-Dimethyl-cyclooctane									1
cis-2-Methyl-7-octadecene									1
Cyclodecane	1								
Cyclodecene						1			
Cyclododecane	1								
Cycloeicosane	1								
Cyclohexadecane	2								2

C-9 cont.

	Province/Frequency								
Organic Compounds	**GP**	**LP**	**NWP**	**MP**	**FSP**	**KZNP**	**ECP**	**NCP**	**WCP**
Hydrocarbons									
Cyclohexane									1
Cyclooctane	1								
Cyclopentadecane	2	1	2				1		2
Cyclotetracosane		1							
Cyclotetradecane	5	1	1			2			3
Decahydro-4H-cyclopentacyclooctene	1								
n-Decane	14	1	1			3	1		3
Dec-1-ene									1
1,5,9-Decatriene						1			
(2-Decyldodecyl)-cyclohexane			1						
11-Decyl-docosane	1								
11-Decyl-heneicosane			1						
10-Demethylsqualene	3	1					1		
5,14-Dibutyl-octadecane	1								
1,2-Diethyl-benzene	1					1			
1,5-Diethyl-3-methyl-cyclohexane									1
1,5-Diethyl-3-methyl-2-methylene-[1.alpha.,3.alpha.,.5.alpha.]cyclohexane	1								
1,2-Dimethyl-benzene	5								
1,3-Dimethyl-benzene	4	1							1
1,4-Dimethyl-benzene/p-Xylene	4	2				1			
1,2-Dimethyl-cyclooctane	1								
N,N-Dimethyl-cycloundecane					1	2			8
1,2-Dimethyl-cyclooctane	1								
N,N-Dimethyl-cycloundecane					1	2			8
3,6-Dimethyl-decane	1						1		
3,8-Dimethyl-decane	1					1			
1,1-Dimethyl-2,3-diphenylindene									1
4,6-Dimethyl-dodecane	1					2			
2,6-Dimethyl-hepatadecane								1	
2,5-Dimethyl-nonane			1				1		
3,6-Dimethyl-octane						1			
2,6-Dimethyl-undecane						2			1
2,10-Dimethyl-undecane	1								
3,4-Dimethyl-undecane	1								
3,6-Dimethyl-undecane			1						
4,11-Dimethyl-tetradecane	1								
1,3-Dimethyl-2(2,4,6-trimethylphenyl)-1,3-cyclopentadiene	1								
n-Docosane	12	1	4		1	2	2	4	7
1-Docosene									2
n-Dodecane	14	1	1			5	1		5
(E,E,E)-1,4,8-Dodecatriene			1						1
1-Dodecene/Adecene	2	1				1			1
Dotriacontane			1						
Eicosane	2	2	3		2	7			6
(E)-9-Eicosene	1	1							
4R*,5R*,6S*,8S*)-4,5-Epoxy-8-isopropenyl -2,2,6-trimethyl-7-oxabicyclo[4.3.0]non-9-ene	1								
1,1'-[1,2-Ethanediylbis(oxy)]bis-benzene/1,2-Diphenoxyethane	1								

C-9 cont.

Organic Compounds	Province/Frequency								
	GP	LP	NWP	MP	FSP	KZNP	ECP	NCP	WCP
Hydrocarbons									
(1-Ethenyloxy)-hexadecane	1								3
2-Ethenyl-1,3,5-trimethyl-benzene	1								
1-(Ethyldecyl)-benzene	1								
5-(Ethyldecyl)-benzene	2					1			
4-Ethyl-1,2-diethyl-benzene	1								
2-Ethyl-1,3-dimethyl-benzene	1					1			
4-Ethyl-1,2-dimethyl-benzene	1								
1-Ethyl-2,3-dimethyl-benzene							1		
1-Ethyl-2-methyl-benzene	1								
4-Ethyl-tetradecane	1								
3-Ethyltoluene	1								
4-Ethyltoluene	1								
3-Ethyl-tridecane	1					1			
Heneicosane	2		3			4	2	4	6
1-Heneicosene	1	1	1						
Hentriacontane	1								
n-Heptacosane	3		1						2
6(Z),8(E)-Heptadecadiene	1								
6(Z),9(E)-Heptadecadiene	2								
n-Heptadecane	16	3	2			5	1	3	
1-Heptadecene/Hexahydroap	5	1			1			1	3
8-Heptadecene	3	1	1						
n-Heptadecyl-cyclohexane						1			
2,2,4,4,6,8,8-Heptamethyl-nonane	2								
n-Hexacosane	9	1	2			3		1	3
9-Hexacosene	2								
n-Hexadecane	14	2	2		2	5			
1,E-8,Z-10-Hexadecatriene			1						1
1-Hexadecene/Cetene	6	2	3			1		1	3
(Z)-3-Hexadecene							1		
(Z)-7-Hexadecene								1	
7-Hexadecyne	1								
2,6,10,15,19,23-Hexamethyl-2,6,10,14,18,22-tetracosahexane	21	3	4		1	4			13
2,6,10,15,19,23-Hexamethyl-tetracosane/Squalane	1								
Hexatriacontane			1					2	
7-Hexyl-eicosane	1								
9-Hexyl-heptadecane									1
(1-Hexylheptyl)-benzene		1				1			
(1-Hexyloctyl)-benzene	1								
1-Iodo-decane			1						1
1-Iodo-2-methyl-undecane									1
1-Iodo-tetradecane	2								
Isocaryophyllene			1				1		2
1-Isocyanato-2-methyl-benzene									1
1-Isopropentyl-2-methyl-benzene	1								
Isoterpinolene	1								
2-Methoxy-3,8-dioxocephalotax-1-ene	1								
9-Methyl-acridine			1						
(2-Methyl-1-butenyl)-benzene	1								
Methyl-cycloheptane									1
2-Methyl-decane	4	1	1		1	2	1	1	
3-Methyl-decane	2		1			2	1		

C-9 cont.

	Province/Frequency								
Organic Compounds	**GP**	**LP**	**NWP**	**MP**	**FSP**	**KZNP**	**ECP**	**NCP**	**WCP**
Hydrocarbons									
4-Methyl-decane	1					2			
5-Methyl-decane	2					2			
7-Methyl-(Z)-decene	1								1
2-Methyl-1,1-diphenyl-1-propene		1							
4-Methyl-dodecane	2					2	1		
6-Methyl-dodecane	2					1		1	
(1-Methyldodecyl)-benzene							1		
2-Methyl-eicosane	1								
10-Methyl-eicosane	3								
1,1'Methylenebis(4-methyl)-benzene	1								2
1-Methylethyl-benzene	1								
2-Methyl-heptadecane			1						
3-Methyl-hexadecane						1			
(R)-(-)-(Z)-14-Methyl-8-hexadecene			1						
1-Methyl-2-(methylethyl)-benzene	1					1	1		
1-Methyl-3-(methylethyl)-benzene	2					1			
1-Methyl-4-(1-methylethyl)-benzene	2					1			
1-Methyl-4-(1-methylethenyl)-cyclohexene	1								
9-Methyl-nonadecane	2					1			
10-Methyl-nonadecane	1								
2-Methyl-nonane	1								
3-Methyl-nonane						1	1	1	
4-Methyl-nonane	1						1		
2-Methyl-octadecane			1			1			
7-Methyl-3, 4-octadiene		1							
3-Methylpentacosane	1								
2-Methyl-pentadecane	1								
3-Methyl-pentadecane	2					4			
1-Methyl-2-propyl-benzene	1					1			
1-Methyl-3-propyl-benzene	1								
2-Methyl-6-propyl-dodecane	1								
3-Methyl-3-propyl-nonane						1			
3-Methyl-5-propyl-nonane								1	
2-Methyl-tetradecane	1		1						
3-Methyl-tetradecane	1					1			
4-Methyl-tetradecane			1			1			
5-Methyl-tetradecane			1			1			
2-(Methylthio)-benzothiazole		1							
2-Methyl-tridecane	2		1			3			
3-Methyl-tridecane	2		1			1	1		
4-Methyl-tridecane	2					1			
7-Methyl-tridecane									1
2-Methyl-undecane	2		1			1	1		
3-Methyl-undecane							1		
4-Methyl-undecane						3			
5-Methyl-undecane	1						1		
9-Methyl-(E)-2-undecane							1		
(1-Methylundecyl)-benzene	1								
Neopentyliindenecyclohexane			1						
Neophytadiene	1								
n-Nonacosane	3								
n-Nonadecane	1	3	1			2			

C-9 cont.

	Province/Frequency								
Organic Compounds	**GP**	**LP**	**NWP**	**MP**	**FS**	**KZNP**	**ECP**	**NCP**	**WCP**
Hydrocarbons									
1-Nonadecene	4	1	1		1	1		1	3
2-Nonadecene						1			
n-Nonane/Shells	4					2			1
1-Nonene								1	
Nonyl-cyclopropane	1								
n-Octacosane	10	1	2			2		2	5
n-Octadecane	18	2	3		1	6	2	1	
1-Octadecene	6	2	1			1			5
(E)-5-Octadecene						1			
(E)-9-Octadecene		1							1
Octyl-cyclohexane	2								
Octyl-eicosane			1						
9-Octyl-heptadecane	5	2							
Oxacyclotetradecane-2,11-diene						1			
1,1'-Oxybis-decane	1								
9a-Octahydro-3,5,5-trimethyl-9-methylene(4aS-cis)-1H-banzocycloheptene	1								
Octyl-cyclohexane	2								
Octyl-eicosane			1						
9-Octyl-heptadecane	5	2							
Oxacyclotetradecane-2,11-diene						1			
1,1'-Oxybis-decane	1								
Pentacosane									1
n-Pentadecane	1								10
1-Pentadecene	1								2
Pentyl-benzene	2	1							
Pentyl-cyclohexane						1			
(1-Pentylheptyl)-benzene	9	5	1			5		4	8
(1-Pentylhexyl)-benzene	3	1							1
(1-Pentylnonyl)-benzene		1							
(1-Pentyloctyl)-benzene	7	1	3			4	1	1	3
(1-Pentyl-2-propyl)-benzene	1								
3-Phenyl-1,4-(E)-dodecadiene									1
5-Propyl-decane			1						
(1-Propyldecyl)-benzene						1			
(1-Propylheptyl)-benzene	3								
(1-Propylnonyl)-benzene	10	1	2			1	1	2	1
(1-Propyloctyl)-benzene	6		2			1			3
6-Propyl-tridecane			1						
Spiro[4.5]decane	1								
n-Tetracosane	9				1	5	2	1	4
1,13-Tetradecadiene	4		1						3
n-Tetradecane	15	3	2			8	1	1	
1-Tetradecene									2
(Z)-3-Tetradecene								1	1
1,2,3,4-Tetramethyl-benzene	1					2			
2,6,10,15-Tetramethyl-heptadecane	1								
4,8,12,16-Tetramethyl-heptadecane-4	1					2			
2,6,10,14-Tetramethyl-hexadecane	9	1	1			4	1	2	1
2,6,10,14-Tetramethyl-pentadecane	1					1			2
Tetratetracontane			1			1	1		

C-9 cont.

	Province/Frequency								
Organic Compounds	**GP**	**LP**	**NWP**	**MP**	**FSP**	**KZNP**	**ECP**	**NCP**	**WCP**
Hydrocarbons									
trans.-Caryophyllene	6	1			1	1		1	9
trans-2-Nonadecene	1								
n-Triacontane	5	1	4			2	1		
Tricosane	10					5	1		4
(Z)-11-Tricosene	1								1
n-Tridecane	11	2	2			5	1	1	8
Tridec-1-ene			1						1
1,2,4-Triethyl-benzene						1			1
1,2,3-Trimethyl-benzene	2					1			1
1,2,4-Trimethyl-benzene	2								
1,3,5-Trimethyl-benzene	1								
1,7,11-Trimethyl-cyclotetradecane	1								
2,3,6-Trimethyl-decane								1	
2,6,11-Trimethyl-dodecane	3					1			
2,6,14-Trimethyl-dodecane						3			
2,7,10-Trimethyl-dodecane	2								
2,6,10-Trimethyl-pentadecane	2		1			1			
2,3',4-Trimethylphenyl methane	2								
2,6,10-Trimethyl-pentadecane	2		1			1			
2,3',4-Trimethylphenyl methane	2								
Tritetracontane	1					1			1
Tritriacontane	1								
n-Undecane	13	1	2			3	1	1	3
Others									
Alloaromadendrene	2								
5-alpha,14-beta,17-beta-cholestane	3								
(5-alpha)-Cholest-3-ene	1	3			1	1			
(5-alpha)-Cholest-7-ene	1								
.alpha.-Copaene	4	1	1						3
.alpha.Cubebene	5	4	1					1	
.alpha.-Elemene		1							
.alpha.-Guaiene					1				
.alpha.-Gurjunene	1								
.alpha.-Pinene	1	1							
(-)-.alpha.-Terpineol									1
.alpha.Terpipene									1
5.alpha.-Pregnane	2								
5-Amino-2-(p-methoxyphenyl)-2-methyl-2H-[1,2,4]triazolo[1,5-a][1,3,5]triazine	1	1				1			2
3-(1-Amphenyl)-2-chlorpropsaure			1						
Aromadendrene	2	1							
Bacchotricuneatin	3					1			
(Benzene)ethylene(trimethylphosphine)ruthenium(0)	1								
Benzo[b]phenanthro[2,1-d]thiophene	1								
.beta.-Bisabolene	1				1				
(+)-.beta.-Funebrene	1								
.beta.-Himachalene	1	1							
.beta.-Pinene									1
14.beta.-H-Pregna	4					2			3

C-9 cont.

	Province/Frequency								
Organic Compounds	**GP**	**LP**	**NWP**	**MP**	**FSP**	**KZNP**	**ECP**	**NCP**	**WCP**
Others									
Bicyclogermacrene	1								
N,N,N',N'-Bis(cyclopentamethylene)urea	1					1			
2,5-Bisdimethylamino-3,9-dimethyl-3H-1,3,4,6-tetrazacyclopent(E)azulene	1								
5-Bromo-(3.beta.)-cholest-5-ene							1		
Cadina-1,4-diene									2
(+)-Calarene	2								
3-(1-Camphenyl)-2-chlorpansuare	1								
9-Carbomethoxy-6,11-dimethoxy-5-oxoxantho[3,2-g]tetralin	1								
Carotol									1
Caryophyllene oxide		1							1
Cholest-3,5-diene						1			
Chromolaenim					1				1
1,8-Cineole	1								
Cis.-Calamenene	1								
Citroflex A	1					1			
(+-)-Cularicine			1						
5-Cyano-3,6-dimethyl-3,4-dihydropyrrolo(1,2,3-de)-2H-1,4-benzoxazine	1								
(+)-Cycloisosativene	1								
Cystathionine-DTMS		1				1			
Decamethyl-cyclopentasiloxane	8	5	4			2		2	7
.delta.3-Carene		1							
(c-4a,c-7a)-.delta.6-Dodecahydro-3,3-dimethyl-r-2,c-4,c-8-metheno-3a,7c-diazapentaleno[6,1,2-bcd]-as-indacene	3								
Dibenz(b,f)azepine						1			
2,3-Dicyano-7,7-dimethyl-5,6-benzonorbornadiene	3								
Digitoxigenin		1							
1a,11c-Dihydrochryseno[5,6-b]azirine/	1								
2,3-Dihydro-1,2-dimethyl-1H-Indene	1								
2,3-Dihydro-1,1-dipropyl 1H-1-silaindene		1							
3,7-Dihydroxy-5-methoxy-4,6-diphenyldibenzophosphole 5-oxide	3								
3',4'-Dihydro-2'-(morpholin-4-yl)-5',7'-nitrospiro[cyclopentane-1,3'-quinazoline]	2								
(+)-Dihydroreciferolide						1			
3,12-Dimethylphenyl-isocynate	2								
3-(2,2-Dimethylpropylindene)(bicyclo[3.3.1] nonane-2,4-dione	2								
2,3-Dimethyl-trisulfide		1							
Docosanolide						1			2
n-Docosyl-formate/1-Docosanol formate	1								
Dodecamethyl-cyclohexasiloxane	3	5			1	1	1	1	4
1,1-Dodecanediol diacetate						1			
Epi-isopodophyllotoxin	1		1						1
3,4-Epoxy-4a-ethyl-2,3,4,4a,5,6-hexahydro-1H-pyrido[3,2-C]carbazole	2								

C-9 cont.

	Province/Frequency								
Organic Compounds	**GP**	**LP**	**NWP**	**MP**	**FSP**	**KZNP**	**ECP**	**NCP**	**WCP**
Others									
(Z)-3-(2-Ethoxyethenyl)pyridine					1				
1-Ethyldibenzothiophene	5	3			1	2			
2-Ethyldibenzothiophene	5		1			2			3
3-Ethyldibenzothiophene	6		1						
Farnesol isomer B									1
Friedelan-y-al								1	
Galoxide 1 and 2	6	4	3		1	4	2	3	6
.gamma.-Gurjunene	1								
.gamma.-Terpinene	1	1				1	1		1
Garvin A	1								
Garvin B	1					1			
Geranyl linalool isomer	1								
Germacrane B								1	
Hahnfett	1						1		1
(+-)-15-Hexadecanolide	1	1	1						4
Hexadecyl-oxirane	1				1				1
Hexamethyl-cyclosiloxane	1								
Hexamethyl-cyclotrisiloxane	8	3	1		1	1		1	1
18-Hydroxy- (1S*, 1R*)-dolabella									1
Isomaturnin	1								
Junipene	7	2	1			1			
Koiganal II	1								1
Koiganal I	1								
Limonene									2
(+)-Longifolene		1							
Lycopersen	1								
3-Methoxy-(3.beta.22E)-Stigmasta-5,22-diene	1								
Methyl-arachidonate			1					1	1
7-Methylbenz[c]acridine	1								
3-Methylbenzo[2,3]phenanthro[4,5-bcd]thiophene	1								
Methyl-d3-hydrazine sulfate	9	3			1	1			
5-Methyl-19-norcholest-8(11)-ene	1	1							
3-(1-Methyl-2-pyrrolidinyl)-pyridine/Nicotine	1								
10-Methylsqualene	1								
Muscopyridine	1	1							
28-Nor-17-.alpha(h)-hopane	4		1				1		1
28-Nor-17-.beta(h)-hopane	3								
Octahydro-1,9,9-trimethyl-4-methylene-(1.alpha.,3a.alpha.,7.alpha.,8a.beta.)-1H-3a,7-Methanoazulene					1				
Octamethyl-cyclotetrasiloxane	6	2			1	1		1	1
1,1,4,5,6-Pentamethyl-2,3-dihydroindene	1								
2,6,10,14,18-Pentamethyl-eicosane		1							
1-Phellandrene	1	1							
3-Phenyl-5-t-butylpyridine	6	1							4
2-(Phenylthiomethyl)-pyridine									1
2(10)Pinene							1		
N-Propyl-3-aza-5.alpha.-cholestane	1								
Pyrrolo(3,2,1-b)carbazole								1	

C-9 cont.

	Province/Frequency								
Organic Compounds	**GP**	**LP**	**NWP**	**MP**	**FSP**	**KZNP**	**ECP**	**NCP**	**WCP**
Others									
Sabinene	1	1							
(-)-Sinularene		1							
Terbuthylazine/Gardoprim	1								
Terpinolene									1
trans.Anethole						1			
Trendione	2								
Terbuthylazine/Gardoprim	1								
Tetradecamethy-hexasiloxane									
trans.Anethole						1			
trans.beta.-Farnesene									1
trans.Farnesol									1
Trendione	2								
Tricarbonyl[N-(phenyl-2-pyridinylmethylene) benzenamine-N,N']-iron	2								1
Triethylammonio-N-diphenylphosphin	1								
3,3'-Trimethylene-2,2'-biquinoline								1	
4,8,8-Trimethyl-3-oxatricyclo[5.4.0.0(1,4)]undec-11-yl) isopropyl ether	1								
Valencene		1							
Vitamin E acetate	2								

APPENDIX D GC-FID areas of p-cresol and nonylphenol used to calculate the phenol concentration in top best and worst sludge samples.

Sample no.	p-Cresol Area/Counts	Nonylphenol Area/Counts
Top best:		
Sample 28 (WC) Borcherds Quarry	753065	134062
Sample 37 (WC) Oudshoorn	-	-
Sample 41 (KZN) Hammansdale	649718	105266
Sample 54 (NW) Boitekong	89342	136523
Sample 75 (KZN) Klipfontein	-	-
Top worst:		
Sample 1 (Gauteng) Vlakplaats (wet sludge)	306388	20207433
Sample 2 (Gauteng) Vlakplaats (compost)	18642	11727224
Sample 4 (Gauteng) Dekema	-	17136
Sample 6 (Gauteng) Rondebult	-	25854
Sample 15 (Gauteng) Zeekoegat	-	8541
Sample 21 (Gauteng) Percy Steward	26894 **13456788**	6564051 **1036072**
Sample 22 (Gauteng) Flip Human	90944 **12694810**	120162200 **10223449**
Sample 30 (WC) Athlone	137274 **25210353**	47453632 **3227920**
Sample 55 (NW/Brits)	-	-

- The bolded numbers are from the liquid extracts.