THE CONCENTRATIONS, DISTRIBUTION AND HEALTH RISK ASSESSMENT OF SUSPECTED ENDOCRINE DISRUPTING CHEMICALS (PHENOLS, PHTHALATES AND HEAVY METALS) IN FRESHWATER SYSTEMS OF CAPE TOWN, SOUTH AFRICA

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The concentrations, distribution and health risk assessment of suspected endocrine disrupting chemicals (phenols, phthalates and heavy metals) in freshwater systems of CapeTown, South Africa

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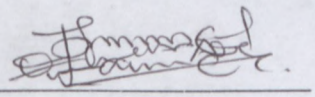
DECLARATION

I, Olanrewaju Olusoji Olujimi, hereby declare that the contents of this thesis represent my own unaided work, and that it has not previously been submitted for academic examination towards any qualification. Further, it represents my own opinions and not necessary those of the Cape Peninsula University of Technology



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ABSTRACT

Environmental pollution with persistent organic chemicals and inorganic trace metals is an increasingly important issue. Recently, a variety of chemicals are introduced in a very large scale on the surface water network. The main pathway of these pollutants into the environment was identified as wastewater treatment plants (WWTPs). The extended use of chemicals in many product formulations and insufficient WWTPs has lead to an increase in the levels of the detected micro-pollutants wastewater effluents. The majority of these compounds are characterized by a rather poor biodegradability. A large spectrum of pollutants present in waste as traces has been reported to exert adverse effects on human and wildlife. Even though compounds are found in wastewater in a very small amount, they may have the undesirable capability of initiating health effect on various high forms of life.

This survey constitutes the first study in the City of Cape Town to report data for a variety of priority substances (phenols and phthalate esters) in WWTP effluents and receiving rivers. These results are of critical importance since the data generated are used to generate potential health risk associated with both the organic and inorganic compounds analyzed. A gas chromatography-mass spectrometric (GC-MS) method was successfully developed to simultaneously analyze 17 environmental Endocrine Disrupting Chemicals (EDCs) after initial derivitization of the phenolic congeners. Heavy metals (Cd, Hg, Pb and Zn) and metalloid (As) were analyzed using ICP-MS.

Chemical analysis by GC-MS revealed the presence of DEP, POH, PCP, DEHP, DBP, BBP, 2,4-DMP and 2-NP as the most abundant of the phthalate esters and phenolic congeners. In respect to the organic congeners, Zandvliet WWTP is the most polluted, followed by Stellenbosch WWTP as they received as wastes from the largest informal settlement and leachate from landfill site, respectively. Generally, concentration ranged from below limit of detection (LOD) for most of the congeners to 34.520 mgl^{-1} for DBP at Zandvliet WWTP. Also, statistical analysis showed that there is correlation between levels of congeners in effluent and downstream water samples, an indication of point source pollution from the WWTP.

The level of congeners in the river systems were generally higher than values reported in the effluents water from the WWTPs, an indication of non-point sources of water pollution. From the monitoring exercise, data obtained for most compounds analyzed showed that they are effectively removed (approximately 80 to 100%) with the exception of 2-nitro phenol that was poorly removed. The production of 2,4-DMP is also noteworthy in the final effluent of investigated treatment plants.

The influent metal concentrations ranged from 3.95 ± 0.31 to 43.76 ± 5.06 μgl^{-1}; 1.07 ± 0.17 to 17.99 ± 0.55 μgl^{-1}; 18.3 ± 2.00 to 282.59 ± 21.60 μgl^{-1}; 0.60 ± 0.03 to 14.5 ±5.10 μgl^{-1}; 380.20 ± 14.80 to 5128.30 ± 10.20 μgl^{-1} for arsenic, cadmium, lead, mercury and zinc, respectively, while it ranged from 1.12 ± 0.06 to 5.69 ± 0.47 μgl^{-1}; 0.52 ± 0.23 to 2.50 ± 0.59 μgl^{-1}; 7.5 ± 0.6 to 40.8 ± 18.20 μgl^{-1}; 0.1 ± 0.01 to 3.9 ± 0.31 μgl^{-1} and 133.7 ± 13.4 to 909.4 ± 23.1 μgl^{-1} in the effluent for the metals in corresponding order for influent.

The sewage sludge from the wastewater treatment plants acted as sink for the influent metal concentration. The concentrations of metals in the sludge samples are generally within the limits set by South Africa, United State of America and the European Union, however, lead and arsenic exceeded the limits and could pose health risk if used as agricultural fertilizer.

Metal concentrations in the river systems showed that arsenic and cadmium are within the South Africa target water quality guideline for human consumption and livestock watering for most of the sampling period, nevertheless, all the metals and arsenic in most cases exceeded the sustainable aquatic life protection guidelines of the republic of South Africa and Canadian Council of Ministers for the Environment (CCME) standards. In the sediment samples, arsenic, mercury and zinc exceeded the interim sediment quality guidelines by CCME, while cadmium and lead are within the probable interventions limits.

The organic congeners responsible for the risks include DEHP and to a lesser extent, DBP. DEHP was found to be the major contributor of risk of developing cancer in this screening health risk assessment. The highest potential risks were observed at Kirstenbosch botanical garden. The potential risk through the use of this water is if it were used to irrigate vegetables. Toxic risks could be anticipated resulting from exposure to both DEHP and DBP with individual exposure concentrations predicted at up to 14 times that considered to be safe for a lifetime exposure. The doses calculated for possible exposure to arsenic and cadmium showed that it may be twice that considered safe for arsenic, whereas cadmium was measured at concentrations considered to be safe. The reference dose for arsenic is much more certain than that for the phthalates.

Keywords: Phthalates; phenols; heavy metals; arsenic; wastewater treatment plants; HPLC; GC-MS, health risk assessment; Cape Town.

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DEDICATION

I would be glad and honoured to dedicate this work of hard labour to **ALMIGHTY GOD**; my blessed redeemer, my hope, my yesterday, my today and my future, for His love, protection, guidance and provision without Whom I am nothing but through Whom I am more than conqueror. Also, I will to dedicate this work to my love, my wife **Olufunmilola Victoria Olujimi, my daughter Oluwafadekemi Olaide Favour Olujimi, Taiwo James Oluwanifemi and Kehinde John Temiloluwa Olujimi.**

BIOGRAPHICAL SKETCH

Olanrewaju Olusoji Olujimi was born in Mushin, Lagos State, Nigeria, on the 2nd March 1978. He attended Owu Methodist Primary School, Abeokuta and African Church Grammar School for his secondary school in Abeokuta, Ogun State where he graduated in May, 1996. He enrolled at the University of Agriculture, Abeokuta in 1998 and obtained a B.Sc. degree in Environmental Management and Toxicology in 2003. Mr. Olujimi was granted University Scholarship for his undergraduate study at the University of Agriculture, Abeokuta. With the support of Ogun State Human Capital Development Programme and University of Nottingham Development Solution Scholarship, Olanrewaju enrolled at the University of Nottingham, United Kingdom in 2005 and obtained his M.Sc. degree in Environmental Sciences in 2006. Mr. Olujimi has enjoyed National Research Foundation Scholarship and A.G. Leventis International Scholarship, Switzerland during the course of his doctoral study. Mr. Olujimi currently works as a lecturer at the University of Agriculture, Abeokuta, Ogun State in Nigeria. Following this research outputs, Mr. Olujimi had secured an International Foundation for Science (IFS) grant to evaluate the impact of wastewater treatment plants effluents on the concentration levels of some selected endocrine disrupting chemicals in South-Western, Nigeria.

List of publication/ submitted manuscript from this study/conference presentation

Olujimi, O.O. Fatoki, O.S. and Odendaal, J.P. 2012. Chemical monitoring and temporal variation in levels of endocrine disrupting chemicals (phenols and phthalate esters) from selected wastewater treatment plant and freshwater systems in the Republic of South Africa. ***Microchemical Journal*** 101: 11-23.

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Olujimi, O. O., Fatoki, O.S Odendaal, J.P., and Okonwko, O.J. 2011. Solid-phase extraction method for the analysis of eleven phenolic pollutants in water samples. ***Asian Journal of Chemistry*** 23 (2): 657-662.

Olujimi, O. O., Fatoki, O.S., Odendaal, J.P. and Okonwko, J.O. 2010. A review of endocrine disrupting chemicals (Phenol and Phthalates) in the South African environment: A need for more monitoring. ***Water SA*** 36(5): 671-682.

Fatoki, O.S., **Olujimi, O. O.,** Odendaal, J.P. and Daso, A.P. Preliminary investigation into occurrence and removal of heavy metals (As, Cd, Hg and Zn) in wastewater treatment plants in Cape Town and Stellenbosch. ***Polish Journal of Environmental Studies*** (Submitted manuscript).

Fatoki, O.S., **Olujimi, O.O**., Odendaal, J.P. and Daso, A.P. Seasonal variation in levels and removal efficiency of endocrine disrupting metals and trace metals from wastewater treatment plant effluents in Cape Town and Stellenbosch, South Africa. ***Environmental Monitoring Assessment*** (submitted manuscript).

Manuscripts to be submitted

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Olujimi, O.O. Fatoki, O.S. Odendaal, J.P. Seasonal variability in the concentrations of heavy metals in water and sediment of river receiving wastewater treatment plants effluents in Cape Town, South Africa.

Olujimi, O.O. Fatoki, O.S. Odendaal, J.P. Health risk assessment of heavy metals in final effluents and river water receiving wastewater effluent in Cape Town, South Africa.

Book Chapter

Fatoki, O.S., **Olujimi, O.O**., Odendaal, J.P. and Genthe, B. Health risks assessment of phthalate esters in freshwater systems (Chapter submitted-under review).

Conference presentation

Olujimi, O. O, Fatoki, O.S. Odendaal, J.P., Genthe, B. and Daso, A.P. Seasonal variation and potential health risks assessment of endocrine disrupting metals in wastewater effluents and river water receiving wastewater effluent. Poster to be presented at the 32nd Annual Conference of Society for Environmental Toxicology and Contamination, 13-17 November, 2011, Boston, Massachussets, USA

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Olujimi, O. O, Fatoki, O.S. and Odendaal, J.P. Occurrence and removal of heavy metals (As, Cd, Hg, and Zn) in wastewater treatment plants from Cape Town and Stellenbosch, South Africa. Oral presentation at the 1st Joint Conference between Cape Peninsula University of Technology and Bondo University College, February 19-24, 2011, Kisumu, Kenya.

Olujimi, O. O, Fatoki, O.S. and Odendaal, J.P. Analysis of Phthalate and Priority Phenols from wastewater treatment plants in Cape Town, South Africa: Method and Results. Oral presentation at the 1st Chemical and Electrical Engineering Conference, Nov. 26 -28, 2010, Kuala Lumpur, Malaysia

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CLARIFICATION OF BASIC TERMS AND CONCEPTS

2,4-DCP	2,4-Dichlorophenol
2,4-DNP	2,4-Dinitrophenol
2CP	2-Chlorophenol
2M,4,6-DNP	2-Methyl, 4,6-Dinitrophenol
2NP	2-Nitrophenol
ANOVA	Analysis of variance
APEOs	Alkylphenols-ethoxylates
BBP	Butylbenzyl phthalate
CVAAS	Cold Vapour Atomic Absorption Spectrometry
DBP	Di-n-butyl phthalate
DCM	Dichloromethane
DCP	Dioctyl phthalate
DEHP	Di-(2-ethylhexyl) phthalate
DEP	Diethyl phthalate
DMP	Dimethyl phthalate
EDCs	Endocrine Disrupting Chemicals
EDMs	Endocrine disruptive metals
GC-FID	Gas Chromatography/Flame Ionization Detector
GFAAS	Graphite furnace atomic absorption spectrometry
HPLC	High Pressure Liquid Chromatography
ICP-MS	Inductive Coupled Plasma-Mass Spectrometry
ICP-OES	Inductive Coupled Plasma-Optical Emission Spectrometry
LLE	Liquid-Liquid Extraction
MeOH	Methanol
MTBE	Methyl tert-butyl ether
NO(A)EL	No observed adverse effect level
PCBs	Polychlorinated biphenyls
PCP	Pentachlorophenol
PCP	Polychlorinated Phenols
PEC	Predicted environmental contamination
PEs	Phthalates Esters
P-OH	Phenol
PTFE	Polytetrafluoroethylene
SPE	Solid Phase Extraction
SPME	Solid Phase Microphase Extraction
SVOCs	Semi Volatile Organic Compounds

TWQR	Target Water Quality Range
US EPA	United State Environmental Protection Agency
WHO	World Health Organization
WWTPs	Wastewater treatment plants

CHAPTER ONE: INTRODUCTION

1.1 Background

The endocrine system is also known as the hormonal system. It is found in all mammals, birds, fish, and many other types of living organisms (Ying *et al.*, 2004). It is one of the body's main systems for communicating, controlling and coordinating the body's activities. It works with the nervous system to regulate essential body functions ranging from body energy level, reproduction, growth and development, internal balance of the body systems, stress and injury, metabolism, puberty, a woman's menstrual cycle, bone growth among others (Vogel, 2004; Ying *et al.*, 2004; Burger and Moolman, 2006; Bornman *et al.*, 2007; Dowshen, 2007).

Endocrine system disorder happens when one or more of the functional units in a living organism is not functioning very well and consequently leading to diseases like diabetes, growth hormone deficiency, osteoporosis, birth defects, altered or reduced sexual behaviour, infertility and several underdevelopments (Vogel, 2004; Ying *et al.*, 2004). Environmental pollution by bioactive chemicals such as pesticides, persistent pollutants and pharmaceutical residues are suspected to display endocrine disrupting effects in animals and humans (Scrippo *et al.*, 2004; Moder *et al.*, 2007). Endocrine disrupting chemicals have become an issue of concern because they are not readily or are slowly degraded and due to their effects on human, animals and environment (Mohamed *et al.*, 2008). Examples include derivatives of persistent organohalogens and herbicides (Vogel, 2004; Campbell *et al.*, 2006).

Acording to World Health Organization (2002), "Endocrine Disrupting Chemicals (EDCs) are defined as exogenous substances or mixtures that can alter function(s) of the endocrine system and may cause health effects in an intact organism, or it progeny." EDCs have a high residence period and may cause serious problems when they are bio-accumulated. Industrial, agricultural, domestic and municipal wastes most often contain EDCs at high concentration which when exposed to environmental organisms can result in biological effect (Fattahi *et al.*, 2007). These compounds sometimes are able to pass through wastewater treatment plant system into receiving water system.

Research had shown in the USA and some part of Europe that male fish held in wastewater or rivers below wastewater treatment plants gave signs of prononuced increase of estrogen-dependent plasma vitellogin concentration (Folmar *et al.*, 1996; McArdle *et al.*, 2000; Lavado *et al.*, 2004; Diniz *et al.*, 2005). EDCs have been reported to have a multitude of deleterious effects on wildlife and humans, that include, dermal toxicity, immunotoxicity, carcinotoxicity, reproductive and teratogenic effects, as well as neuro-behavioural and endocrine

malfunctioning (Kim *et al.*, 2000; Scrippo *et al.*, 2004; Vogel, 2004; Segner, 2005; Hjelmborg *et al.*, 2006; Gelbke *et al.*, 2007).

Because EDCs are part of complex effluents, they exist as mixtures. Each chemical within the mixture vary in the estrogenic potency and may interact with each other in an unpredictable manner. Determing the concentrations of EDCs present in water or solid phases typically involves extraction and analysis steps. It is important to develop effective methods that can extract wide range of EDCs simultaneously from water samples. Solid-phase extraction (SPE) is commonly used extraction method for trapping targeted analytes in water samples. In situation where analytes concentration may vary with time, it is often advisable to extend the sampling time and increase the number of samples within the time frame.

1.2 Statement of research problem

Heavy metal contamination of aquatic ecosystems have been recognized and accepted as a pollution problem in the City of Cape Town (Odendaal and Reinecke, 2004; Jackson *et al.*, 2007; Shuping *et al.*, 2008; Ayeni *et al.*, 2010). In addition to metal contamination, there has been evident cases of endocrine disrupting chemicals in South African environments, for example, p-Nonyl phenols (p-NP) has been reported in water and sediment (Burger and Moolman, 2006), leaching of p-Nonyl phenols (p-NP) from plastic wraps into food (De Jagel *et al.*, 1998), polychlorinated biphenyl (PCBs)4, 1,1,1-trichloro-2,2-bis (p-chlorophenyl) ethane (DDT) and its metabolites have also been reported in rivers and sediment samples (Barnhoorn *et al.*, 2003; Fatoki and Awofulo, 2003; Burger and Moolman, 2006).

Despite the evident cases of EDCs and heavy metals in some quarters of the South African environment, currently, there are no studies that address the removal efficacies of EDCs (phenol, phthalates and heavy metals) in different technologies of wastewater treatment plants in Cape Town in particular and South Africa in general. Within this context, this present research, present analytical approaches using HPLC and GC-MS for organic compounds and ICP-MS for heavy metals and metalloid analysis to address the levels of analytes in selected wastewater treatment plants (WWTPs) and receiving river sytems in Cape Town. Furthermore, health risk assessment of EDCs (phthalate and phenols) and heavy metals (cadmium, lead, arsenic and mercury) in water samples have not been previously investigated in the City of Cape Town.

1.3 Research questions

1. Are suspected endocrine disrupting chemicals (phenols, phthalate esters and EDMs) present in wastewater and freshwater systems of the City of Cape Town?
2. If yes, at what concentrations are they present in wastewater and freshwater systems?
3. Are their availability and distribution in river systems associated with wastewater treatment plants?
4. Are there any seasonal and spatial differences in organic compounds and heavy metal concentrations in wastewater treatment plants and river systems?
5. Are EDCs (organic, metals and metalloid) and concentrations significant enough to pose a human health risk?

1.4 Research objectives

1.4.1 Broad objective

The broad objective of this study was to assess the concentrations and potential human health risk that phenols, phthalate esters and heavy metals in wastewater and receiving river systems could pose in the City of Cape Town.

1.4.2 Specific objectives

1. The first objective was to develop a robust technique for the extraction and simultaneous analysis of the endocrine disrupting chemicals (phenols and phthalates) in wastewater and freshwater with good recovery.
2. To apply the optimal conditions of extraction and analysis for the identification and quantification of selected phenols and phthalates from river water and wastewater effluents.
3. To assess the seasonal variation in the concentration and distribution of heavy metals and organic compounds in wastewater treatment plants and receiving river systems.
4. To determine the efficiency of selected wastewater treatment plants at removing phenols, phthalates and heavy metals from the wastewater stream.
5. To assess the health risk posed by prevalent phenols, phthalates and EDMs in the selected WWTPs and the river systems in the City of Cape Town.

1.5 Delineation of the research

Wastewater and water samples were collected from six treatment plants (Athlone, Bellville, Kraaifontein, Potsdam, Stellenbosch and Zandvliet) and receiving rivers, namely: Kuils River, Vygekraal River, Mosselbank River, Veldwachters River and Diep River. These rivers were chosen to reflect the possible impact of wastewater treatment plant effluent on the concentration of phenols, phthalates and heavy metals.

CHAPTER TWO: LITERATURE REVIEW

2.1 The endocrine system

The endocrine system is one of the body's main systems for communicating, controlling and coordinating the body's activities in mammals, also called the hormonal systems (Ying *et al.*, 2004). It works with the nervous system to regulate essential body functions. These body functions include energy metabolism, reproduction, growth and development, osmoregulation and homeostasis. The endocrine system also regulates reproductive processes and skeletal development (Vogel, 2004; Ying *et al.*, 2004; Burger and Moolman, 2006; Bornman *et al.*, 2007).

Endocrine disrupting chemicals (EDCs) consist of many natural and synthetic organic compounds, mostly man made products such as alkylphenols, alkylphenols-ethonylates, polychlorinated biphenyls (PCBs). Others include polychlorinated dibenzo-p-dioxins, polychlorinated dibenzofurans, organochlor pesticides, dichlorodiphenyl, dichloroethylene, nonylphenols, steroid hormones and phthalates (Hjelmborg *et al.*, 2006; Mauricio *et al.*, 2006; Arditsoglou and Voutsa, 2008). EDCs are able to cause abnormalities in invertebrates, fish, birds, reptiles and mammals (Hjelmborg *et al.*, 2006; Mauricio *et al.*, 2006; Peng *et al.*, 2006; Moder *et al.*, 2007; Ferraz *et al.*, 2007; Arditsoglou and Voutsa, 2008).

There has been scientific debate for and against the occurrence of EDCs in humans, which has been politically in some quarters. However, there are increased incidences of abnormalities in human sexual and cognitive development in some societies with speculation that it is caused by EDCs exposure (Matthiessen, 2000; Solomon and Schettler, 2000; Campbell *et al.*, 2006; Falconer *et al.*, 2006; Suliman *et al.*, 2006). These abnormalities include low sperm count and decrease in sperm quality (Van Wyk *et al.*, 2003), immunological and neurological effects (Patandin *et al.*, 1999).

Over the last two decades, there has been increasing concern about the likely impacts of exposure to chemical compounds with endocrine disrupting activity in the environment (Segner, 2005; Sumpter, 2005; Game *et al.*, 2006; Mauricio *et al.*, 2006; Xue and Xu, 2006; Moder *et al.*, 2007; Shin *et al.*, 2007; Hecker and Giesy, 2008). Endocrine disrupting effects of chemicals were first documented in the 1930s but research was only accelerated in the late 1970s and early 1980s along two initially isolated pathways, i.e. human health effects and wildlife biology (Matthiesen, 2000; Vogel, 2004; Trenholm *et al.*, 2006; Moder *et al.*, 2007). The endocrine system's glands, hormones and their respective functions are listed in Table 2.1, while Table 2.2 shows some EDCs with their common utilization, target hormones and animals affected.

Considering that many of these compounds can elicit estrogenic response at very low concentrations (parts per billion to parts per trillion), there is need for concern as many of the these compounds (phthalates, phenols and heavy metals) have been found at measurable concentrations in wastewater effluents, sludge, surface waters, sediments, groundwater and even in drinking water in many countries (Cai *et al.*, 2003; Cortazar *et al.*, 2005; Sha *et al.*, 2007; Huang *et al.*, 2008).

Table 2.1: Endocrine system's glands, hormones and their function

Gland	Hormones	Functions
Hypothalamus	Releasing hormones	Stimulate pituitary activity,
Pituitary	Trophic (stimulating) hormones	Stimulate thyroid, adrenal, gonadal and pancreatic activity
Thyroid	Thyroid hormones	Regulate metabolism, growth and development, behaviour and puberty
Adrenal	Corticosteroid hormones Catecholamines	Regulate metabolism and behaviour
Pancreas	Insulin and glucagons	Regulate blood sugar levels
Gonads	Sex steroid hormones (estrogens and androgens)	Regulate development and growth, reproduction, immunity, onset of puberty and behaviour.

Adapted from Bornman *et al.*, 2007

2.2 Mechanisms of endocrine disruption

Endocrine disruptors initiate their disruption activities using one or more of the following mechanisms:

a) By binding to receptors and mimicking or antagonizing the effects of the endocrine hormones (Barcelo and Kettrup 2004; Vogel, 2004; Sumpter, 2005; Burger and Moolman, 2006; Jiao and Cheng, 2008).

b) By affecting the concentration of hormones through the altering of the synthesis or metabolism of natural hormones (Bradlow *et al.*, 1995; Toppari *et al.*, 1996; Rice *et al.*, 2003; Ying *et al.*, 2004; Sumpter, 2005).

c) By interfering with the signal between the different components of the hypothalamus-pituitary-endocrine gland axes (Dawson, 2000; Clotfelter *et al.*, 2004; Kitano *et al.*, 2006).

d) By modifying the number of hormone receptors in cells (Welch *et al.*, 1969; Soto *et al.*, 1995; Lascombe *et al.*, 2000; Rajapakse *et al.*, 2001).

Table 2.2: Endocrine disrupting chemicals, their uses, associated target hormone and animals affected

Compound	Common usage	Target hormone	Animals affected
Industrial chemicals			
-Bisphenol A[b],	Plasticizer	Thyroid, Cortisol	Mammals, Birds, Fish
-PCBs,	flame retardants	Estrogens	Reptiles, Amphibians
-PCP, PCDFs	unintended		
-Dioxins,	by-products during incineration		
Phthalates[a]			
-BBP, DEHP	Plasticizer	Estrogens	Mammals, Birds, Fish
D-n-BP			Reptiles, Amphibians
Alkylphenols[b]			
-p-Nonylphenol	Plasticizer	Estrogens	Mammals, Birds, Fish Reptiles, Amphibians
Other phenols[c]			
Phenols,	Wood preservation,		Fish, rats
Chlorophenols	production of pesticides		
Nitrophenols	intermediates, herbicides		
Organochlorine Pesticides[b]			
-DDT, DDE, Chlordane	Insecticides	Estrogens	Mammals, Birds, Fish
-Deldrin, Heptachlor, Lindane, Endosulfan Oxychlordane etc.		& Androgens	Reptiles, Amphibians
Heavy metals[b]			
Cadmium, Mercury Lead	Batteries, paints	Adrenaline, Estrogens	Mammals, Birds, Fish

[a] Hill *et al.*, 2001
[b] Zala and Penn, 2004
[c] Renberg *et al.*, 1983

2.3 Routes of exposure of EDCs to humans and animals

Human beings can be exposed to endocrine disrupting chemicals via water, air, soil or food through ingestion (i.e. oral), inhalation and dermal absorption (US EPA, 1992; Rice *et al.*, 2003; WHO, 2003). The major route of exposure of EDCs to young infants and children is via the oral route by direct ingestion of the chemicals, breast milk, infant formula, cow's milk, contaminated media like water, food, surface and carpet dust, toys and medical devices (Rice *et al.*, 2003; Huang *et al.*, 2008; Sathyanarayana, 2008).

Animals are also exposed to EDCs in the air, water and in their food (Clotfelter *et al.*, 2004; McKinlay *et al.*, 2008). EDCs enter animal bodies through the skin, gills and even via the mother in *utero* or in *ovo*. Because EDCs are lipid-soluble, they tend to accumulate in animal body fat tissues. This problem is further aggravated by the process of biomagnification, in which chemical concentrations increase at higher trophic levels (Huang *et al.*, 2008; McKinlay *et al.*, 2008). In aquatic birds, contaminant concentrations are often 100 times greater in body tissue

than in the surrounding water. In the case of marine animals, significant bioaccumulation has been observed in several species (Alatriste-Mondrageon *et al.*, 2003). Top predators are essential for maintaining the integrity of food webs, thus, biomagnification of EDCs can affect entire ecosystems by harming species at the highest trophic levels (Clotfelter *et al.*, 2004). The most common routes of human and animal exposure to EDCs are given in Figure 2.1.

Some of the chemicals used as pesticides remain as residues in fresh and processed food (Vogel, 2004; Bornman, *et al.*, 2007). The effects of EDCs on the human body differ substantially: poisoning or toxic exposure which could cause cancer, physiological birth defects, gene mutation, cell damage or acute health effects (Sharpe and Skakkabaek, 1993; Vogel, 2004; Campbell *et al.*, 2006). The health effects of EDCs may be pervasive throughout the planet due to fast and universal transport of chemicals through the world's atmosphere and oceans. Endocrine disruption may take effect over long time spans, or selectively during certain stages of development, or only in later generations for the effects to manifest (Vogel 2004; Falconer *et al.*, 2006; Juvancy *et al.*, 2008).

2.4 Routes of exposure of EDCs to the aquatic environment

There is growing concern regarding water quality, consequently industries around the world are faced with the challenge of ensuring a sustained and safe supply of drinking water from various sources. However, population growth, urbanization, industrial development and associated changes in agricultural and land-use practices, have contributed significantly to reducing water quality through naturally occurring and anthropogenic contamination (Falconer *et al.*, 2006; Suliman *et al.*, 2006).

Surface water contaminants include metals, carcinogens, synthetic chemicals, pharmaceuticals, veterinary and illicit drugs. Others are ingredients in cosmetics, personal care products, food supplements together with their respective metabolites and transformed products (Brasher and Wolff, 2004; Cortarzar *et al.*, 2005; Falconer *et al.*, 2006). Some of these compounds and their metabolites are endocrine disrupting chemicals and get into water through direct discharge of pharmaceuticals, chemicals, households, agricultural and industrial wastes. EDCs also get into water through accidental spills and indirect sources such as storm water runoff (Falconer *et al.*, 2006; Huang *et al.*, 2008).

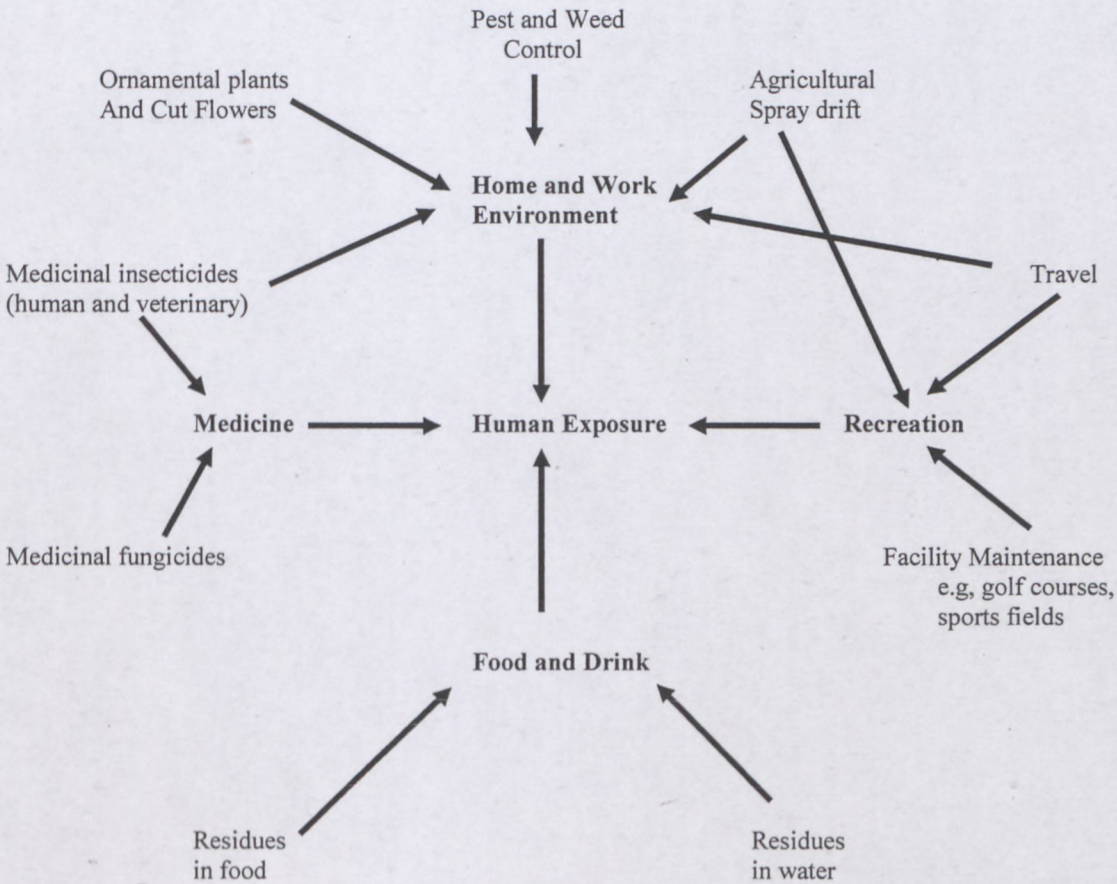


Figure 2.1: Exposure routes of EDC's to humans (Adapted from: McKinlay *et al.*, 2008)

Drinking water sources can be contaminated due to flow of water through agricultural areas where agrochemicals are extensively used to improve crop yield (Falconer *et al.*, 2006). EDCs are not only concentrated in the environment through biogeochemical processes but are also scavenged from water through sorption onto suspended materials and deposited to be part of the bottom substrate. Aquatic wildlife appears to be particularly at risk since the aquatic environment is usually a sink for many hormonally active chemicals including, industrial chemicals, pesticides, organochlorides, pharmaceuticals, natural and synthetic estrogens or phytoestrogens (Luks-Betlej *et al.*, 2001; Yuan *et al.*, 2002; Alatriste-Mondragon *et al.*, 2003; Segner, 2005; Li *et al.*, 2006; Suliman *et al.*, 2006; Xue and Xu, 2006).

Many aquatic ecosystems are faced with spatially or temporally alarming levels of persistent complex mixtures of EDCs as a result from pollution with industrial chemicals (Schmidt *et al.*, 2005). The aquatic environment is susceptible to pollution partly because there is

very considerable intentional release of chemicals into rivers, lakes and the sea, also partly because it receives a lot of accidental releases of chemicals through spills, runoff, waste effluent from wastewater treatment plants and atmospheric deposition (Luks-Betlej *et al.*, 2001; Sumpter, 2005; Sanchez-Avila *et al.*, 2009).

The main sources of endocrine disrupting chemicals in rivers and lakes of Europe and North America are sewage effluents and agricultural chemicals runoff. In the developing countries, like Africa and Asia, uncontrolled domestic and industrial discharge to waterways contribute tremendously to high levels of EDCs in aquatic environments (Falconer *et al.*, 2006; Peng *et al.*, 2006). The pressure of waste dumping or accidental spills has recently been on the increase with growing population. The increasing use of water by people has contributed to the spatial and temporally alarming levels and complex mixtures of these chemicals (Schmidt *et al.*, 2005; Sumpter, 2005; Falconer *et al.*, 2006).

EDCs are introduced into the environment as by-products of various technological processes. In the aquatic environment, the mobility of EDCs is increased when associated with fulvic or humic acids and particulates, which are often deposited in sediments, which often determines their rates of transformation (Sun *et al.*, 2006; Huang *et al.*, 2008). They are transported through the food chain via benthic algae and invertebrates, which thereafter, can be eaten by fish or birds. They may also undergo a series of processes such as biodegradation, dilution and photolysis once in waterways; activities that contribute to their elimination from the environmental water (Czaplicka, 2001; Petrovic *et al.*, 2001; Brasher and Wolff, 2004; Cortazar *et al.*, 2005). However, this creates potential routes of exposure of endocrine disrupting chemicals to terrestrial and aquatic wildlife.

Phthalates, heavy metals and phenol and its derivatives have been included in the list of priority pollutants by United State Environmental Protection Agency (USEPA) and European Union due to their health effects on aquatic and terrestrial life (Llompart *et al.*, 2002).

2.5 Selected endocrine disrupting chemicals (Phthalate esters and phenols)

2.5.1 Phthalates

2.5.1.1 Background information on phthalate esters

Phthalates esters (PEs) are diakyl or alkyl esters of 1,2 benzene carboxylic acid (Luks-Betlej *et al.*, 2001; Alatriste-Mondragon *et al.*, 2003; Adeniyi *et al.*, 2008). They are formed when methanol, ethanol or other alcohols react with the carboxyl groups on the benzene ring of phthalic acids. The corresponding esters are formed with different alkyl chains, e.g. dimethyl phthalate (DMP), dibutyl phthalate (DBP) and di(2-ethylhexyl) phthalate (DEHP). PEs are hydrophilic in

nature and vary in structure (Figure 2) and in composition. Generally, the molecular weight of phthalates range between 194 and 396 with a low melting point ranging between -4.6 °C to 5.5 °C (Table 2.4).

Globally, several millions of phthalate esters are produced and used annually as primary additives to polyvinyl chloride (PVC) based plastics (Alatriste-Mondragon *et al.*, 2003; Ling *et al.*, 2007; Adeniyi *et al.*, 2008; Yuan *et al.*, 2008; Rudel and Perovich, 2009). PEs migrate into environmental components during production and distribution processes, usage and disposal. Ways of entering environment are aqueous leaching from plastics and waste, incineration of plastic waste, volatilization from resin matrices and wet deposition from the atmosphere (Muszkat *et al.*, 1997; Luks-Betlej *et al.*, 2001; Polo *et al.*, 2005; Ling *et al.*, 2007; Rudel and Perovich, 2009).

Phthalates have been detected in water (Fatoki and Venon, 1990; Fatoki and Noma, 2002; Fatoki *et al.*, 2010). They have also been found in foods, especially fatty food, as they migrate from food packing materials (Gartner *et al.*, 2009). Some phthalates are suspected of disrupting the endocrine system especially by mimicking estrogens (Harris *et al.*, 1997).

2.5.1.2 Application of phthalates Esters

PEs have been widely used as plasticizers in the production of polyvinyl chloride (PVC) base plastics, which include rubber, cellulose film, styrene, adhesives, coatings, pulp and paper manufacturing (Yuan *et al.*, 2002; Cortazar *et al.*, 2005; Huang *et al.*, 2008; Rudel and Perovich, 2009). Other important usages of PEs are plumbing, pesticides formulation, non-ionic surfactants, construction materials, vinyl upholstery, table cloths, shower curtains to improve mechanical properties of the plastic resin, particularly its flexibility and softness (Luks-Betlej *et al.*, 2001; Yuan *et al.*, 2002; Alatriste-Mondragon *et al.*, 2003; Cortazar *et al.*, 2005; Kayali *et al.*, 2006; Ling *et al.*, 2007; Huang *et al.*, 2008; Yuan *et al.*, 2008; Rudel and Perovich, 2009).

This component makes up 10 to 60 % of plastic products to provide flexibility; the phthalate plasticizers are not chemically bonded to resin and therefore are easily released or leached during the life cycle of plastic products (Adeniyi *et al.*, 2008; Yuan *et al.*, 2008). Phthalates occur as components of plastics that are used for major domestic and industrial purposes. Such include teething rings, pacifiers, soft squeeze toys, plastic bottles, food containers and medical equipment. They are also parts of laboratory products (tubes, caps, gas chromatography septa, vinyl gloves), cosmetics and industrial solvents that are made from plastics (De Jager *et al.*, 1998; Alatriste-Mondragon *et al.*, 2003; Kayali *et al.*, 2006; Adeniyi *et al.*, 2008; Huang *et al.*, 2008).

2.5.1.3 Phthalates as EDCs

Since PEs are ubiquitous in our environment, the major sources of their exposure to man are shown in Table 2.3. Studies have revealed detectable levels of phthalate esters in samples of foodstuff, human mother's milk, dust, environmental samples (water, soil, sediment) and textiles with di (2-ethylhexyl) phthalate (DEHP) and di-n-butyl phthalate (DBP) as the most abundant. Generally, phthalates are of low acute toxicity with short biologic half lives of approximately 6-12 hours (Duty *et al.*, 2005). They are metabolized and eliminated within 48 hours of exposure to vertebrates and are therefore not highly bioaccumulative in the system (Van den Berg *et al.*, 2003). However, the frequent use of phthalates-containing personal care and consumers products along with the frequent detection of metabolites in random population samples suggests that phthalate exposure is continuous and ubiquitous.

Consequently, endocrine disrupting nature of some phthalates is potentially responsible for adverse effects on human reproduction and development. Based on previous human and animal studies, phthalates have been classidied according to their impact strength. DEHP has been included in class B2 and has been shown to be embryotoxic and teratogenic (Altriste-Mondragon *et al.*, 2003; Kayali *et al.*, 2006; Latini *et al.*, 2009), while butyl-benzyl phthalate (BBP) is in class C (possible human carcinogen) and di-n-butyl phthalate (DBP), di-ethyl phthalate (DEP) and dimethyl phthalate (DMP) were included in class D (not yet classified as human carcinogens (Altriste-Mondragon *et al.*, 2003).

Table 2.3: Sources of exposure for phthalate parent compounds

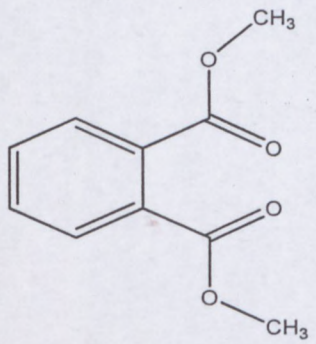
Phthalate parent compound	Potential sources of exposure
Di-2-ethylhexyl phthalate (DEHP)	PVC containing medical tubing, blood storage bags, medical devices, food contamination, food packaging, indoor air, plastic toys, wall coverings, tablecloths, floor tiles, furniture upholstery, shower curtains, garden hoses, swimming pool liners, rainwear, baby pants, dolls, some toys, shoes, automobile upholstery and tops, packaging film and sheets, and sheathing for wire and cable.
Diethyl phthalate (DEP)	Cosmetics, nail polish, deodorant, perfumes/cologne, lotions, aftershave, pharmaceuticals/herbal coating, insecticide.
Di-butyl phthalate (DBP)	Nail polish, make-up, aftershave, perfumes, pharmaceuticals or herbal coating, chemiluminescent glow sticks.
Di-*n*-octyl phthalate (DnOP)	Children's toys
Butyl benzyl phthalate (BBzP)	Vinyl flooring, adhesives, sealants, food packaging, furniture upholstery, vinyl tile, carpet tiles, and artificial leather and is also used in certain adhesives
Di-methyl phthalate (DMP)	Insecticides, indoor air, adhesives, hairstyling products, shampoo, aftershave.

Adapted from Swan, 2008

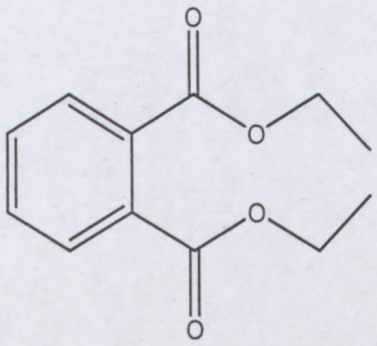
Table 2.4: Physical properties of selected PAEs

	Dimethyl Phthalate	Diethyl Phthalate	Dibutyl Phthalate	Butylbenzyl Phthalate	Di-n-octyl Phthalate	Di-(2-ethylhexyl) Phthalate
Abbreviation	DMP	DEP	DBP	BBP	DNOP[a]	DEHP
CAS RN	131-11-3	84-66-2[a]	84-74-2	85-68-7[a]	117-84-0[a]	117-81-7
Molecular weight	194.1886	222.24[a]	278.3[d]	312.36[a]	390.6[b]	390.5618
Molecular formula	$C_{10}H_{10}O_4$[c]	$C_{12}H_{14}O_4$[c]	$C_{16}H_{22}O_4$[c]	$C_{19}H_{20}O_4$[c]	$C_{24}H_{38}O_4$[c]	$C_{24}H_{38}O_4$[c]
Density	1.19	1.12[a]	1.043	1.1[a]		0.9732
Melting Point	5.5°C[c]	-40.5°C[c]	-35 °C	61.3 °C[a]	-46 °C[c]	-50 °C
Boiling Point	283.7 °C	295 °C[a]	340 °C	92.5 °C[a]	390[c]	386.9 °C
Water Solubility	4200 mgl^{-1} at 20°C	1100 mgl-1 at 25°C	11.2 mgl^{-1}[b]	2.7 mgl^{-1}[b]	0.0005 mgl^{-1}[b]	0.003 mgl^{-1}[b]
Log Kow	1.48[d]	2.51[d]	4.63[d]	4.77[d]	8.3[d]	7.54[d]
Physical State	Colourless, oily liquid with a slight ester odor	Colourless, oily liquid	Colourless, oily liquid with a very weak aromatic odor			Colourless, oily liquid with almost no odor

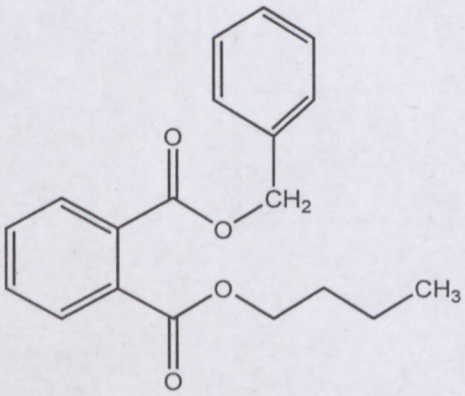
[a] http://en.wikipedia.org/wiki/Phthalate
[b] Luks-Betlej *et al*., 2001
[c] Huang *et al*., 2008
[d] Parketon and Konkel, 2000



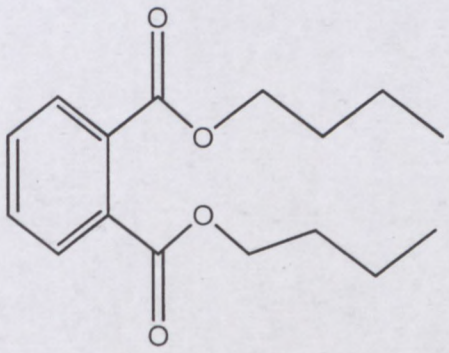
Dimethyl phthalate (DMP)



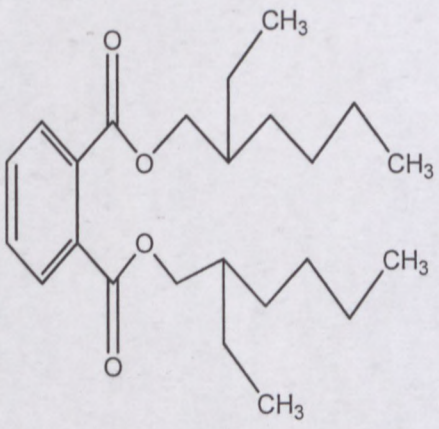
Diethyl phthalate (DEP)



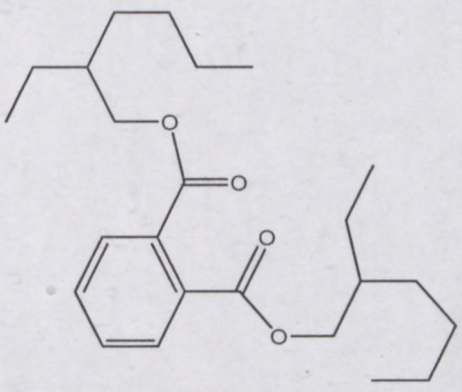
Butyl benzyl phthalate (BBzP)



Dibutyl phthalate



Di-(2-ethylhexyl) phthalate (DEHP)



Dioctyl phthalate

Figure 2.2: Chemical structures of phthalates

2.5.1.4 Levels of phthalate esters in environmental samples

A simple solid-phase microextraction (SPME) coupled with gas chromatography flame ionization detection (GC-FID) method was developed by Li *et al.* (2006) to determine phthalate ester in water samples. Polyaniline (PANI) used as coating materials for the SPME fiber was developed through the process of polymerization of aniline because of its conductivity and thermal stability. The PANI-SPME fiber was optimized by investigating parameters such as ionic strength, pH, extraction and desorption times and temperature for spiked water samples. This was compared with commercially available polyacrylate (PA) fiber. The detection limit of PANI-SPME was lower than 0.24 μgl^{-1}. The method demonstrated the feasibility of using PANI-SPME-GC for monitoring phthalates in water samples. When compared to PA, PANI fiber exhibits a wider range and lower detection limit than PA when used for raw water samples.

Yuan *et al.* (2002) determined the concentrations and microbial degradation of eight phthalates in 14 surface water and six sediment samples from Taiwan. Samples were extracted with Soxhlet extraction method and analyzed using GC/MS. The recovery percentage ranged between 85.5 % and 99.5 %, while detection limit was in the range of 0.6 to 1.0 μgl^{-1}. For degradation determination, sediments were extracted with hexane on rotating shaker followed by analysis using GC-ECD with DB-5 capillary column. The percent recovery range from 89.1 % to 98.1 %, while the detection limit ranges between 50 and 100 μgl^{-1}.

In another study Cai *et al.* (2003) developed solid-phase extraction for five phthalate ester from water samples using polytetrafluoroethylene turning packed column as SPE adsorbent material. The analytes were sorbed on polytetrafluoroethylene turning initially pre-conditioned with 5 ml acetonitrile and 10ml of Milli-Q purifies water, from which they were eluted with 5ml of Milli-Q and 10ml acetonitrile and analyzed by HPLC-UV. Effects of desorption volume of eluent, flow rate of sample solution and volume of sample solution were investigated. Detection limit was in the range of 3.1 – 5.8 μgl^{-1} and percent recovery was in the range of 92.1 -127.5 % for the phthalates ester spiked samples.

Fatoki and Noma (2002) used solid phase extraction method coupled to capillary gas chromatography – flame ionization detection for the determination of four phthalate esters in freshwater and harbour water samples. The eluent (methanol and dichloromethane) volume was optimized by varying the percentage of each of the component of the mixture and phthalate esters extracted using Envi C18 SPE cartridge pre-conditioned with deionized water followed by 2 ml methanol. The limit of detection ranged between 27.2 ngl^{-1} and 60.6 ngl^{-1} while percentage recovery ranged from 83 ± 0.09 % to 94 ± 0.4 % for phthalate esters in spiked deionized water. Analysis of real water samples revealed the presence of phthalate esters in the range of 0.03 to 2309 ± 0.9 μgl^{-1}.

Luks-Betlej and co-workers (2001) used six different solid phase microextraction (SPME) fibers to extract phthalate esters from water samples for analysis by gas chromatography-mass spectrometry single ion monitoring (SIM) mode. The extraction efficiency and repeatability of the fibers were determined using spiked water. Extraction was carried out at 22°C by intensive agitation of the liquid (1000 rpm) with magnetic stirrer. Limit of detection was in the range of 0.015 to 0.06 $\mu g ml^{-1}$and reproducibility was below 8.5 %. The efficiency of fibers ranged between 2.5 and 60 % and phthalate esters were best extracted with DVB-Carboxen-PDMS fiber. The fiber was then used for water sample analysis from Poland and Germany.

Trace levels of diethylhexylphthalate in water sample was studied by Kayali *et al.* (2006) using SPME/HPLC. PDMS/DVB 60 μm fiber was used along with seven other fibers. Conditioning of the fiber, extraction time, extraction temperature, agitation method, sample volume desorption time and the nature of the desorption solvent was investigated and optimized. The fiber was thermally conditioned for 12hr at 200 °C and 0.2 bars under nitrogen stream and introduced into 1000 ml vessel containing 500mL of water sample. The sample was stirred magnetically while rotating the fiber from the other side. The optimized condition was used to analyze for phthalate esters in four different drinking water, MilliQ-water and water sample packed in plastic bag. The MilliQ-water and water sample packed in plastic bag were discovered to contain 22 and 9 $\mu g l^{-1}$ while phthalate was not detected in other water sample. This was attributed to the detection limit of the instrument.

In a recent study by Ling *et al.* (2007) cloud point extraction coupled with HPLC-UV was used for the quantification of phthalate esters in environmental water samples. Extraction efficiency parameters such as concentration of Triton X-114 and Na_2SO_4, equilibration temperature, equilibration time and centrifugation time was investigated and optimized. The cloud point extraction was achieved by adding 0.25 % Triton X-114 and 0.4 mol/L Na_2SO_4 to 10ml of the sample in thermostatic bath at 45 °C for 60 min followed by centrifugation for 5 min at 3500 rpm. Back aqueous phase was removed and 20 μl of the surfactant injected into the HPLC for analysis. The detection limit ranged between 1.0 to 3.8 $ng ml^{-1}$ while percent recovery ranged between 85.8 ± 4.5 % and 103.2 ± 10.3 % for spiked water samples. The method was adopted for real water sample from waste water treatment plant but no phthalate ester was detected.

Huang *et al.* (2008) investigated the occurrence of phthalate compounds in sediments and fishes of 17 Taiwan's river using accelerated solvent extraction with GC/MS- SIM (selected ion monitoring mode). Sediment and fish samples were extracted by spiking with 10 μl dibenzyl phthalate as surrogate standard and placed in incubator at 100 °C. Sample was purged with 6 ml of ethyl acetate at initial flow rate of 9 $ml\ min^{-1}$ for 10 min and changed to 2 for 50 min. 6 ml of ethyl acetate was collected and concentrated with N_2 and 5 μl of benzyl benzoate spiked into the extraction

and volume was adjusted to 1ml using hexane. Recoveries for sediment and fish samples ranged from 77.1 % to 102.5 % and 79.1 % to 109.1 %, respectively. DEHP was found to be higher in both sediment and fish samples investigated.

PEs in suspended particles, sediment and water from main river and tributaries of yellow river, China was analyzed by Sha *et al.* (2007) using a cleanup column (prepared by inserting silicon alkylation glass wool at the bottom with about 1 cm of anhydrous sodium sulfate above it and 10 g activated dry silica gel with small amount of distilled water 3ml/100g) with GC-FID. PAEs in sediment and particulate were extracted by adding 80 ml of carbon bisulfide (CS_2) and shaken vigorously on mechanical shaker for 30 minutes (200 rpm). The clean-up of the extract was achieved by pre-conditioning the column with 20 ml hexane and 2 ml of the extract added and rinsed with 40 ml hexane at a flow rate of 2 ml min^{-1}. The eluate was discarded and PAEs extracted with 80 ml of hexane/ether (volumetric proportion 7:3). Eluate was concentrated by rotary evaporator to 2 ml and analyzed by GC-FID. PAEs in water, sediment and particulate samples ranged from 3.99 x 10^{-3} to 45.45 x 10^{-3} $mgkg^{-1}$, 40.56 to 94.22 $mgkg^{-1}$, and 30.52 ± 0.83 to 63.96 ± 4.65 $mgkg^{-1}$, respectively.

Levels of phthalate ester and heavy metals were assessed at Muledane open dump site, Thohoyandou, Limpopo province, South Africa by Adeniyi *et al.* (2008). Soil samples were extracted using Soxhlet extractor with 120 ml dichloromethane (DCM) for 10 hr. The extracts was left to dry on standing at ambient temperature, reconstituted with 2 ml of DCM and cleaned-up with silica gel column using 20 ml of benzene/ethyl acetate mixture (95:5). The extract was allowed to dry at room temperature and reconstituted with 0.5 ml butyl benzoate (internal standard) from which 1 ml was injected into GC-FID for analysis. Levels of PAEs and percentage recoveries from spiked samples were reported to be in the range of 0.031 ± 0.01 to 0.31 ± 0.12 $mgkg^{-1}$ and 88.72 ± 0.5 to 89.95 ± 0.34 percent, respectively.

Microwave-assisted extraction for the determination of nonphenols and phthalate ester in sediment sample was compared with pressurized solvent extraction by Cortazar *et al.* (2005). The clean-up step was optimized using C-18, 60 and 200mg oasis and LiChrolut cartridges. The four cartridges were conditioned with 4 ml of MeOH at a flow rate of 4 ml min^{-1}. MeOH was spiked with 17 μgml^{-1} of standard stock solution of the nonphenol and phthalate and 1 ml of spiked MeOH was then passed through each of the cartridges, rinsed with 1 ml H_2O:MeOH (3:1) and cartridge C-18 rinsed with 5 ml of MeOH, Oasis cartridges rinsed with 5 ml of MTBE:MeOH (9:1) and LiChrolut cartridge rinsed with 5 ml of ethyl acetate. All the cartridges were then rinsed with 5 ml DCM. All eluates were blown to dryness with N_2, re-constituted in 1 ml MeOH after addition of the internal standard and analyzed with GC-MS. Extraction of sediments MAE was optimized by varying the composition of extraction solvent mixture (n-hexane, MeOH and acetone), pressure and time of

extraction. The extract was filtered with PTFE filter (13 mm, 0.45 μm), blown to dryness, re-dissolved to 0.5 ml and cleaned-up using the optimal clean-up step. For PSE, sediments were extracted for 5 min at 100°C and 10,000 KPa with MeOH. The extracted analytes were purged for 90s with pressurize N_2, the extracts were blown to dryness, re-constituted to 0.5 ml in MeOH and clean-up with optimal clean-up method. The extract from MAE and PSE were subjected to GC-MS-SIM and HPLC-DAD-UV-FLD. The optimized procedures was used for analysis of sediment, it was reported that there was no significant difference between MAE-GC-MS and MAE-HPLC-DAD-UV-FLD, however, result obtained with PSE-GC-MS were comparable with MAE-GC-MS but not for all the compounds.

Levels and risk assessment of DEHP in surface water and sediment of Thailand was reported by Sirivithaya and Thuyviang (2010). Water and sediment samples from river receiving effluent from industrial estate were analysed using solid-phase micro extraction techniques (SPME). DEHP was analysed using GC-MS equip with capillary column. The detection limits were 1.1 μgl^{-1} and 8.4 ugg^{-1} for water and sediment respectively. DEHP ranged from below detection to 8.64 μgl^{-1} in water while it was not detected in sediment as concentration was below detection limit.

2.5.2 Phenols

2.5.2.1 Background information on phenols

Phenol and its derivatives are aromatic molecules containing hydroxyl (OH^-), methyl (CH_3), amide (NH_2) or sulphonic groups (McNeely *et al.*, 1979) attached to the benzene ring structure (Huang *et al.*, 2007; Toniolo *et al.*, 2007). Phenols are widely present in the environment and occur in nature as building blocks for plant (Baltussen *et al.*, 1999; Santana *et al.*, 2005; Santana *et al.*, 2009). They are formed naturally from decomposition of leaves and wood as well as through human activity like water purification processes (Schmidt-Baumler *et al.*, 1999; Santana *et al.*, 2005; Santana *et al.*, 2009).

Phenol and its methyl derivatives show a stronger tendency to adsorb onto solid matrices and some have been found to be toxic to fish and other aquatic life,. The compounds at very low concentration have adverse effects on taste and odour of water and fish (Baldwin and Debowski, 1988; Schmidt-Baumler *et al.*, 1999; Czaplicka, 2001). The compounds are introduced into rivers, ground waters and soil directly through industrial effluents or indirectly through natural or synthetic chemicals (Ribeiro *et al.*, 2002; Bagheri *et al.*, 2004; Suliman *et al.*, 2006). They are considered major environmental risks, with speculations of being suspected endocrine disruptors or carcinogens (Bagheri *et al.*, 2004; Suliman *et al.*, 2006).

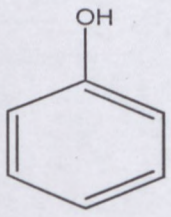
2.5.2.2 Application of phenols

Industrially, phenol and their derivatives are used in several useful products. They are used to manufacture chemicals such as pesticides, explosives, dyes, pulp bleaching with chlorine, wood preservatives, insecticides, herbicides, antioxidants, adhesives, plastics and synthetic intermediates (Baldwin and Debowski, 1988; Czaplicka, 2001; Ribeiro *et al.*, 2002; Ozkaya, 2005; Santana *et al.*, 2005; Cledera-Castro *et al.*, 2006; Suliman *et al.*, 2006; Hartung *et al.*, 2007; Santana *et al.*, 2009).

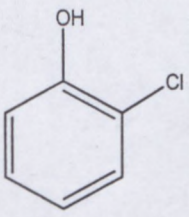
Globally, the production of phenolic compounds is over 300,000 tons per annum. They have been widely used in the last 40 years as components of detergents, emulsifiers, dispersants and anti-foamers (Schmidt-Baumler *et al.*, 1999; Petrovic *et al.*, 2002; Gabriel *et al.*, 2007). Phenol is also used in the pharmaceutical industry for the production of aspirin (Suliman *et al.*, 2006). Sixty percent of phenolic compounds that are introduced into sewage are released into the environment with 85% being in the form of potentially estrogenic degradation products (Petrovic *et al.*, 2002). Phenolic derivatives are among the most important pollutants that are widely present in the environment. These compounds are used in several industrial processes. The major routes of phenolic compounds into the environment are presented in Table 2.5.

Table 2.5: Routes of phenolic compounds to the environment

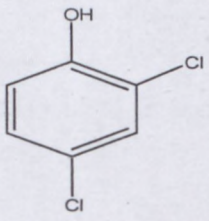
Compounds	sources	references
Phenol	Car exhaust gases	Grynkiewicz *et al.*, 2002
Methylphenols	Wood impregnation	Sirvent *et al.*, 2004
Nitrophenols	Combustion processes of motor vehicles	Luttke *et al.*, 1997
	Hydrolysis/photolysis of nitrite/nitrate	Minero *et al.*, 2007
	Production of dyes, pigments etc	Sirvent *et al.*, 2004
		Galceran and Jauregui, 1995
		Santana *et al.*, 2005
Chlorophenols	Wood distillation, disinfection of drinking	Renberg *et al.*, 1983
	water, wood pulp bleaching, paper production	Schummer *et al.*, 2006
		Santana *et al.*, 2005
		Vidal *et al.*, 2004



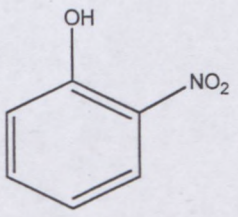
Phenol (PH)



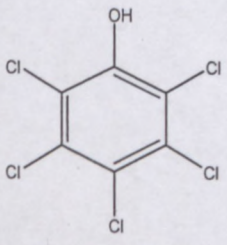
2-Chlorophenol (2-CP)



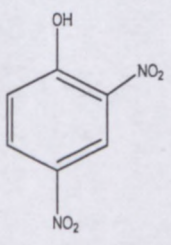
2,4-Dichlorophenol



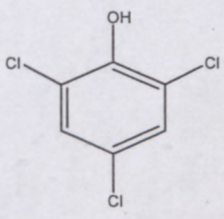
2-Nitrophenol (2NP)



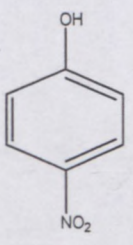
Pentachlorophenol (PCP)



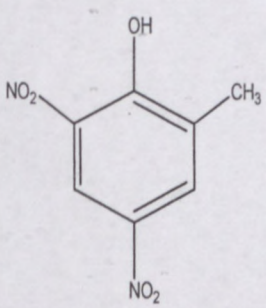
2,4-Dinitrophenol (2,4-DNP)



2,4,6-Trichlorophenol (TCP)

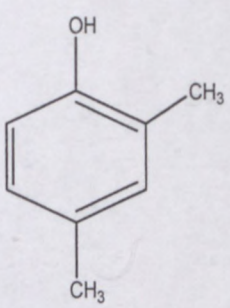


4-Nitrophenol (4NP)



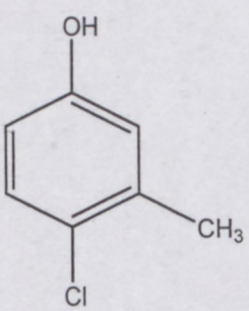
4,6-Dinitroorthocresol

(4,6-DNOC)



2,4-Dmethylphenol

(2,4-DMP)



4-Chloro-3 methyl phenol

(4-C 3MP)

Figure 2.3: Chemical structures of the investigated phenolic congeners

Table 2.6: *Physical properties of selected phenolic compounds*

	Molecular formula	Molecular weight	Boiling point °C	Melting Point °C	pKa	Log Kow (octanol/water)	Water Solubility gL^{-1} at 20°C
Phenol	C_6H_5OH[b]	94.11[a]	181.7[c]	40.5[c]	10.0[b]	1.46[a]	83[b]
2-Methyl 4,6-Dinitrophenol	$C_8H_{10}O$ [d]	122.17[i]	211[c]	22-23	10.58[d]	2.30[a]	0.05[c]
4-Chloro-3-mehtyl phenol	C_7H_7ClO [a]	142.58[b]	235[b]	63-65[c]	9.6[c]	3.10[c]	4[e]
2-Chlorophenol	C_6H_5ClO	128.6[e]	175[e]	9.3[e]	8.56[c]	2.15[a]	28.5[e]
2,4-Dichlorophenol	$C_6H_4Cl_2O$	163[e]	210[e]	45[e]	7.85[b]	3.06[a]	4.5[b]
2-Nitrophenol	$C_6H_5NO_3$	139.1[c]	216[c]	45 - 46[d]	7.23[b]	1.89[c]	2.5[b]
4-Nitrophenol	$C_6H_5NO_3$	139.11[d]	279[d]	113–114[e]	7.08[c]	2.04[c]	11.6[e]
2,4-Dinitrophenol	$C_6H_4N_2O_5$	184.106	113[d]	108	3.94[c]	1.67[c]	5.45
2,4,6-TCP	$C_6H_3Cl_3O$[e]	197.45[c]	246[c]	69[c]	6.15[c]	3.69[a]	
Pentachlorophenol (PCP)	C_6HCl_5O[b]	266.34[b]	309-310[b]	190-191[e]	4.7[b]	5.12[a]	0.01[a]

[a] Montero *et al.*, 2005
[b] Fiamegos *et al.*, 2003
[c] Castillo *et al.*, 1997
[d] Cledera-Castro *et al.*, 2005
[e] Krijgsheid and Van der Gen, 1986

2.5.2.3 Levels of phenols in environmental samples

Suliman *et al.* (2006) used simple, sensitive and rapid reversed-phase high-performance liquid chromatography (RP-HPLC) method for the analysis of phenols in water with Coumarin-6-sulphonyl chloride (C6SCl) as a fluorescence-labeling reagent. The compound was reacted with 0.5 ml of phenol standard solution within 20 min under mild conditions (ambient temperature, pH 9.0) to give sulphonates that was separated by RP-HPLC employing fluorescence detection (DAD). The optimum conditions for fluorescence, derivatization and chromatographic separation was established and detection limits in the range 0.1–0.9 $\mu g\ l^{-1}$ were obtained for the studied compounds.

In another study by Bagheri *et al.* (2007), solvent-minimized sample pretreatment was developed for pre-concentration of phenols from aqueous sample. A micro aliquot of butyl acetate (internal standard) was introduced into the sample solution for a preset time by immersing the syringe. The drop was retracted into syringe, syringe cleaned with tissue and injected into GC-MS for analysis. Various parameters affecting the SME like type of solvent, stirring rate, extraction time, temperature of sample solution and ionic strength were optimized. The optimized method was adopted for analysis of some phenols in water samples. The detection limit was in the range of 5 to 22 ngl^{-1}.

Hartung and co-workers (2007) studied the reductive degradation of polychlorinated phenols in water using palladium on charcoal as catalyst and sodium formate as reducing agent. The method optimized by first using 4-chlorophenol and 2,4,6-trichlorophenol by adding sodium formate to the reaction mixture at a definite time interval to maintain the production of H_2 and CO_2. GC-MS (SIM) mode was used for the analysis. Result showed that >99.9 % of the chlorophenols were converted to phenols and subsequently, the method was applied to more chlorinated phenols and result compared with 11 other methods. Result of comparison with other methods showed that the developed method is acceptable.

The isocratic HPLC method for the determination of phenol and nitrophenols was developed and validated by Cledera-Castro *et al.* (2006) by suing 2-chlorophenol as internal standard and monolithic column in tap water samples. The method was optimized for by using methanol and acetonitrile as organic modifier, pH and flow rate using chromolith RP-18e column and extraction solvent volume. The recoveries of test samples were in the range of 90-112 %. The method was applied to waste water sample and several industrial samples.

Bestamin (2005) investigated chlorophenols in leachate from landfill and aerobic composting plants. Toxic derivatives of chlorophenols were identified using polyacrylate (PA) 0.85 μm fiber coupled with GC-flame ionization detector. Phenols were detected in the range of 0.01 to 40 μgl^{-1} in the landfill leachate but not in the aerobic composting leachate.

Phenol and chlorophenols in bottom sediment were studied by Czaplicka (2001) using ultrasonic extraction with GC-MS. Bottom sediment samples were extracted with methylene chloride in an ultrasonic field for 15 min (3 times). 0.1 M of sodium hydroxide was added to the extract to raise the pH > 11 and derivatized with by adding 3 ml of 0.1 M K_2CO_3 and 2 ml of n-hexane containing 100 μl of acetic anhydride. The extract was dried, concentrated and analyzed with GC-MS. Percentage recovery of phenol varied from 81.1 % to 95.0 %, while chlorophenol varied from 89.9 % to 96.0 %. Analysis of estuary samples showed that phenols vary from 4.0 to 21.7 μgKg^{-1}, while 3-methylphenol content varies from 25.0 to 76.5 μgKg^{-1}.

In another study, SPME-GC-MS analysis of 13 chlorophenols and phenol in leachate was investigated by Ribeiro *et al.* (2002). Experimental conditions were optimized (extraction time and temperature, pH, salt addition, extraction mode and desorption time in the GC). Polyacrylate (PA) fiber used for the extraction was conditioned prior to analysis in GC injector for 1hr at 250 °C. Optimized experimental condition obtained were immersion sampling at 40 °C for 60 min, 85 μm PA fiber, saturated salt condition and sample pH < 2. The optimal conditions were applied to environmental samples and percentage recovery was >80 % and detection limits ranged between 0.005 to 2.4 μgl^{-1}.

Simultaneous determination of endocrine-disrupting phenols and steroid estrogens in sediment by gas chromatography–mass spectrometry was investigated by Peng *et al.* (2006). Pre-extracted sediments were spiked and extracted using ultra-sonication, mechanical shaking and soxhlet extraction. The extract was cleaned-up with activated silica gel and derivatized with pentafluropropionic anhydride, and gas chromatography–mass spectrometry (GC–MS) in selected ion monitoring mode (SIM). Satisfactory recoveries were obtained for phenolic, xenoestrogens and steroid estrogens. The method applied for the determination of targets compounds in sediments collected from river estuary. Nonylphenol and bisphenol-A (BPA) were detected in the range from 204.2 to 664.5 ngg^{-1} and 0.6 to 4.0 ngg^{-1}, respectively. None of the estrogens were found in the sediment samples.

Arditsoglou and Voutsa (2008) reported the determination of phenolic and steroid endocrine disrupting chemicals in environmental matrices. Water samples was extracted using Oasis SPE catridges while marine sediment samples were ultrasonically extracted, cleaned up and extract derivatized with BSTFA at 70 °C for 60 minutes. The silylated derivatives were analysed

by GC-MS. The method detection limits ranged from 1.91 to 13.9 ngl^{-1} and 4.2 to 13.3 ngg^{-1} for water and sediment, respectively. The limit of quantification ranged from 6.1 to 24.3 ngl^{-1} and 13.5 to 42 ngg^{-1} for water and sediment, respectively.

Four phenolic compounds were investigated in surface water and industrial wastewater from Beijing, China by Ge *et al.* (2010). C-18 SPE cartridge was conditioned with 2 ml each of acetonitrile and methanol prior to extraction of 1,000 ml of water sample after fortification with twenty gram of sodium chloride. Sample was eluted with 2 ml of Isopronal and n-hexane, eluent was blown to dryness, reconstituted with 1 ml of acetonitrile and subjected to HPLC analysis. Out of the 102 samples collected for analysis, phenols were detected in 19 samples at different levels ranging from 0.8 to 26.1 μgl^{-1}.

In another study in west Ukraine, Sprynskyy *et al.* (2007) investigated the occurrence of phenolic compounds in surface water of the Dniester River basin. Phenolic compound concentrations in water was determined using spetrophotometric method. Phenol was extracted using octanol or nonanol after re-extraction to akali with fraction of potassium phenolate. The extract was measured at 235 nm using Perkin-Elmer-402.

Barrico *et al.* (2006) investigated sources of phenolic compounds in two catchments of southern Portugal. Using SPE cartridges initially conditioned using 2 x 3 ml of tetrahydrofuran. 500 ml of water was aspirated through the SPE column, eluted with 3 ml of tetrahydrofuran. The eluent was concentrated and analysed using HPLC. 2,4-DNP was the most prominent of all the phenolic compounds in water and leachate sample analysed with concentration range of 0.6 to 3.49 mgl^{-1}.

Kovacs *et al.* (2008) reported method developed for the simultaneous determination of phenols and chlorophenol as trimethylsilyl derivatives using gas chromatograph-mass spectrometry. Six phenols and 19 chlorophenols were simultaneously determined after initial derivatization with trimethyl-N, N-dimethyl carbamate (TMSDMC). Derivatization was carried out at room temperature. Percentage recovery of spiked samples was higher than 75 % while analytes were detected in the range of 0.1 to 10 ngl^{-1} for phenols and 10 to 75 ngl^{-1} for chlorophenols.

2.6 Methods for the detection and monitoring of EDCs

Established analytical methods are available for many of the compounds designated as EDCs. Most developed countries like the USA and the European countries have established regulatory authorities and requirements for chemical and biological analytical procedures for testing pesticides, metals, industrial chemicals and PCBs in food and environmental matrices. Despite the institutional frameworks for the analysis of the designated compounds (hormones, drugs and personal care products) suitable instrumental techniques or standard methods of analysis are lacking. Different methods used to assess the occurrence, distribution and characterization of phthalates and phenolic compounds in the environment matrices and human samples in different countries around the world are summarised in Table 2.6.

2.6.1 Extraction of EDCs in liquid samples

Extraction of EDCs from liquid samples are based on liquid-liquid extraction (LLE) which is often followed by column chromatography cleanup and gas chromatography (GC) or high performance liquid chromatography (HPLC) determination using array of detectors (Cai *et al.*, 2003; Zhou *et al.*, 2005; Ling *et al.*, 2007). LLE is a well developed, efficient and precise method, it requires time and consumption of large volume of organic solvent (Santana *et al.*, 2005; Zhou *et al.*, 2005; Santana *et al.*, 2009). EDCs often vary in concentration with different ecological risks in different environmental compartments. LLE has remained the preferred extraction methods for liquid samples because it is cheap compared to other method like SPE, SPME and MAE (Piug and Barcelo, 1996; Polo *et al.*, 2005; Santana *et al.*, 2005). However, use of large amounts of generally toxic and inflammable organic solvents, formation of emulsions and losses during cleanup are still curtailing the use of LLE.

The procedure is thus becoming less popular with the introduction of the solid phase extraction (SPE) technique. SPE is currently used in sample preparation for determination of trace EDCs in environmental, drugs and biological samples. It offers a faster and easier manipulation, higher concentration factors and requires smaller amounts of organic solvents (Zhou *et al.*, 2005; Eberlin and Cesar de Silva, 2008). Disposable cartridges for SPE have been in used for more than 20 years.

The desire to decrease the use of organic solvent especially dichloromethane which is suspected to be carcinogenic has encouraged the requirement of solvent-free procedures. This has greatly contributed to the rapid growth in the demand for this method at the expense of LLE. Selection of SPE cartridges with particular sorbent materials also plays a key role in the achievement of high and reproducible recovery of analytes in environmental samples. Most

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sorbent used in SPE are porous silica particles-bounded with C-18 or other hydrophobic alkyl group such as strene-divinylbenzene. Recovery of organic compounds by SPE is highly dependent on the polarity of the eluent (Patrolecco *et al.*, 2004).

2.6.2 Gas Chromatography – Mass Spectrometry (GC-MS) method

Phenols and phthalate esters have been determined in environmental matrices through the use of different analytical techniques, e.g. high-performance liquid chromatography (HPLC) with ultraviolet, fluorescence, electrochemical, or mass spectrometric (MS) detection, as well as gas chromatography (GC) coupled with sensitive and specific detection systems (Liu *et al.*, 2004; Huang *et al.*, 2008; Zeng *et al.*, 2009). GC-MS has been widely used in the determination, analysis and monitoring of phthalates and phenolic compounds (Rompa *et al.*, 2003; Liu *et al.*, 2004; Psillakis *et al.*, 2004; Zhao *et al.*, 2009). EDCs with hydroxyl group are usually derivatized for GC analysis.

It is well known that oxygen atom possessed by hydroxyl has a weak nuclephilicity owing to its low electron density. Therefore, the derivatization procedures for hydroxyl compounds need either high temperature or long reaction period, which makes the derivatized compounds convenient to be analyzed on GC with ECD or MS. The high polarity of phenols affects their chromatographic resolution and usually results in broad and tailed peak heights (Heberer and Stan, 1997; Rompa *et al.*, 2003; Santana *et al.*, 2009; Schummer *et al.*, 2009; Zhao *et al.*, 2009). These problems are often overcome by derivatising free phenols to less polar compounds, more volatile and thermally stable, and to giver larger and more selective analytical response through the use of derivatising reagents (Helaleh *et al.*, 2001; Rompa *et al.*, 2003; Santana *et al.*, 2009; Schummer *et al.*, 2009; Zhao *et al.*, 2009).

Phenol and other phenolic compounds are usually derivatized either before or after extraction, or with an on column reagent in the GC-injector (Rompa *et al*, 2003; Helaleh *et al.*, 2001). Derivatization reactions used in GC analysis of phenolic compounds are in four categories, i.e. acylation, alkylation, esterification, and silylation (Helaleh *et al.*, 2001; Rompa *et al*, 2003; Moghadam *et al.*, 2008). In derivatization reactions, methylation by diazomethane is slow and carcinogenic while esterification by acetic hydride does not sufficiently improve the separation and derivatization of mono-nitro compounds (Heberer and Stan, 1997). Silylation of all the derivatization has shown to improve chromatographic parameters such as accuracy, reproducibility, sensitivity and resolution by suppressing tailing, rugged and enhancing thermal stability (Li and Park, 2001; Saraji and Bakhshi, 2005).

Different methods of extraction and analysis of levels of phthalates and phenols have been reported in different countries of the world. Analyzing different environmental matrices, researchers had reported pollutants at alarming concentration that could trigger health complications. To mention a few, Table 2.7 gives an insight into levels of phenols and phthalate esters found in different biological, environmental matrices (water, sediment and soil) and countries.

2.7 Heavy metals and metalloid (Arsenic)

Metals are elements that may occur naturally in rocks, soils and water (Khairiah *et al.*, 2002; Bornman *et al.*, 2007; Horng *et al.*, 2009). Some metals at low doses are essential for growth and development of some plants (e.g. Cu, Zn, Cr, Ni) but at high doses may cause metabolic disorders and growth inhibition for plant species (Goyer, 1997; Chojnacki *et al.* 2005; Bornman *et al.*, 2007). Metal pollution of the environment can result from direct atmospheric deposition, geological weathering, coal combustion, discharge of agricultural, municipal, residential or industrial wastes (Fatoki *et al.*, 2004; Demirak *et al.*, 2006; Oymak *et al.*, 2009). Pollution of the aquatic environment by metals and their accumulation in fish and other aquatic life has posed so much environmental concern in recent years (Krishnamurti and Naidu, 2000; Guo *et al.*, 2006; Dural *et al.*, 2007). Build up of metals in sediment has significant implication for local communities as well as river quality (Awofolu *et al.*, 2005; Demirak *et al.*, 2006). Elevated levels of metals have been reported in different environmental and biological samples (Ikem *et al.*, 2003; Demirak *et al.*, 2006; Dural *et al.*, 2007; Horng *et al.*, 2009).

High concentrations of these metals in sediments, sludge, soils, water, groundwater, plants and biomagnification in the food web through trophic transfer may have a negative effect on animal and human health as they are considered non-essential but rather toxic to body growth and development (Horng *et al.*, 2009; Kazi *et al.*, 2009; Oymak *et al.*, 2009). Consumption of heavy metals through soil-crop-food chain have been proposed as the major source of human exposure to potentially toxic metals (Horng *et al.*, 2009; Jing *et al.*, 2009, Kazi *et al.*, 2009). The endocrine disruptive properties of these metals have been reported in different experimental works (Lafuente *et al.*, 2000; Choe *et al.*, 2003; Handy, 2003).

Table 2.7: Matrix, methods and concentration of endocrine disrupting chemicals (phenols and phthalate esters)

Country	Environmental matrix	Method	Concentration/ Detection range	Compound	Reference
China	water	GC-FID	0.05 – 3.91 μgl^{-1}	Phthalate esters	Li *et al.*, 2006
Taiwan	water	GC-MS/ GC-ECD	50 – 100 μgl^{-1}	phthalate esters	Yuan *et al.*, 2002
China	water	HPLC-UV	3.1 – 5.8 μgl^{-1}	phthalate esters	Cai *et al.*, 2003
South Africa 2002	water	GC-FID	0.03 – 2309 μgl^{-1}	phthalate esters	Fatoki and Noma,
Poland and Germany 2001	water	GC-MS	0.015 – 0.06 μgml^{-1}	phthalate esters	Luk-Betlej *et al.*,
Spain	water	SPME/HPLC	9 – 22 μgl^{-1}	phthalate esters	Kayali *et al.*, 2006
China	water	HPLC-UV	1.0 – 3.8 μgl^{-1}	phthalate esters	Ling *et al.*, 2007
Spain	water	DSPME/HS-SPME/GC-MS	< LOD to 6172 $pgml^{-1}$	phthalate esters	Polo *et al.*, 2005
China	water	GC-FID	3.99 x 10^{-3} – 45.45 x 10^{-3} $mgkg^{-1}$	phthalate esters	Sha *et al.*, 2007
	Sediment	GC-FID	40.56 – 94.22 $mgkg^{-1}$	phthalate esters	Sha *et al.*, 2007
	Particulate matter	GC-FID	30.52-63.96 $mgkg^{-1}$	phthalate esters	Sha *et al.*, 2007
	Fish	GC-FID	1.4-253 $mgkg^{-1}$	phthalate esters	Huang *et al.*, 2008
Spain 2006	water	HPLC		phenol	Cledra-Castro *et al.*,
	sediment	GC-MS	3 – 76 μgl^{-1}	phenol	Czaplicka, 2001
Italy	leachate	SPME/GC-MS	0.005 -2.4 μgl^{-1}	phenol	Ribeiro *et al.*, 2002
China	sediment	GC-MS	0.6 – 664.5 ngg^{-1}	phenol	Peng *et al.*, 2006
China	wastewater	GC-FID	0.47 - 9.01 μgl^{-1}	phenol	Zhou *et al.*, 2005
South Africa	soil	GC-FID	3.8 – 48.89 $ngkg^{-1}$	phthalate esters	Adeniyi *et al.*, 2008
Italy	breast milk	LC/LC – MS/MS	8.4 – 18.8 μgl^{-1}	phthalate esters	Latini *et al.*, 2009
Taiwan	sediment	GC-MS	0.05 – 46.5 $mgkg^{-1}$	phthalate	Huang *et al.*, 2008
China	water	GC-NCI-MS	17 – 685 ngl^{-1}	phenol	Zhao *et al.*, 2009
Japan	soil	GC-MS	1.0 ngl^{-1}	phenol	Helaleh *et al.*, 2001
China	sediment	SPE/GC-FID	0.02 – 0.701 μgl^{-1}	phenol	Wang *et al.*, 2006
Germany	Urine	HPLC/MS/MS	0.1 -13.6 $ngkg^{-1}$ b.w	phthalate esters	Seckin *et al.*, 2009
Sweden	breast milk	GC-MS	0.06 – 305 $ngmL^{-1}$	phthalate esters	Hogberg *et al.*, 2008
	blood	GC-MS	0.050 -129 $ngml^{-1}$	phthalate esters	Hogberg *et al.*, 2008
	urine	GC-MS	0.50 - 761 $ngml^{-1}$	phthalate esters	Hogberg *et al.*, 2008

Table 7: Continued

China	soil	GC-MS	ND – 293 μgl^{-1}	phthalate esters	Zeng *et al.*, 2009
South Africa	water	GC-MS	ND – 119 μgL^{-1}	phthalate esters/p-NP	Mahomed *et al.*, 2008
Oman	water	RP-HPLC	0.1 – 0.9 μgl^{-1}	phenols	Suliman *et al.*, 2006
	water	GC-MS	5 – 22 ngl^{-1}	phenol	Bagheri *et al.*, 2007

Key: GC-FID = Gas Chromatography Flame Ionization Detector; GC-MS = Gas Chromatography Mass Spectrometer; GC-ECD = Gas Chromatography Electron Capture Detector; HPLC = High Performance Liquid Chromatography

2.7.1 Arsenic (As)

Arsenic (As) is a naturally occurring element widely distributed in the earth crusts (Duker *et al.*, 2005; Bornman *et al.*, 2007) and is one of the toxic metalloids of global environmental concern (Bauer *et al.*, 2008; Reyes *et al.*, 2009; Wang *et al.*, 2009). It has an atomic weight of 74.92 with several oxidation states including elemental (0), trivalent (-3, +3) and pentavalent (+5) (Rodriguez *et al.*, 2003; Duker *et al.*, 2005; Wang *et al.*, 2006). The natural sources of arsenic are: As sulphide or realgar (As_2S_2), As tri-sulphide or orpiment (As_2S_3) and arsenopyrite or mispickel or ferrous As sulphide ($FeAsA_2$) (Hossain, 2006; Wang and Mulligan, 2006), enargite, arsenopyrite, tennantite, smaltite, domeykite, safflorite, rammelsbergite, cobaltite, niccolite and loellingnite (Mandal and Suzuki, 2002).

Inorganic arsenic is often found in two oxidation states, namely arsenate [As(V)] and arsenite [As(III)] in soil, groundwater and aquatic environments (Duker *et al.*, 2005; Baskan and Pala, 2009; Liao *et al.*, 2009; Reyes *et al.*, 2009; Wang and Zhao, 2009). However, As species may be methylated into monomehtylarsonous acid [MMA(III)], monomehtylarsonic acid [MMA(V)], dimehtylarsinous acid [DMA(III)], dimehtylarsinic acid [DMA(V)] and trimethylarsine oxide (TMAO) by microorganisms, humans and animals (Mandal and Suzuki, 2002; Rodriguez *et al.*, 2003; Duker *et al.*, 2005; Wang and Mulligan, 2006; Liao *et al.*, 2009), a pathway for its detoxification mechanism which may however triggered its activation (Rodriguez *et al.*, 2003).

Natural sources of arsenic to the environment includes: volcanic rocks, marine sedimentary rocks, hydrothermal ore deposits and associated geothermal waters and fossil fuel (Wang and Mulligan, 2006). The environmental prevalence is triggered by human activities such as the application of pesticide primers on cotton plants, rodenticides and fungicides (Matschullat, 2000; Duker *et al.*, 2005; Bornman *et al.*, 2007), wood preservatives, mining and smelting operations, coal combustion, burning of sawdust, domestic and industrial wastes and fossil fuel processing (Wang and Mulligan, 2006; Bornman *et al.*, 2007; Wang and Zhao, 2009; Cuypers *et al.*, 2009). Other includes growth promoter and bacteria and parasitic diseases suppressor (Duker *et al.*, 2005; Yao *et al.*, 2009) hardening of alloys to produce glass, semiconductors and pigments (Matschullat, 2000; Duker *et al.*, 2005), depilatories, cosmetics and poisons (Rodriguez *et al.*, 2003).

Inorganic arsenic species As(III) and As(V) have been classified as human carcinogens (Pandey *et al.*, 2002; Bhattacharya *et al.*, 2007; Reyes *et al.*, 2009) and the methylated forms, e.g. monomehtylarsonic acid (MMA) and dimehtylarsinic acid (DMA) have been labeled as cancer

promoters (Reyes *et al.*, 2009). The chronic effect of Arsenic is mainly observed from exposure to drinking water with ppb levels of inorganic arsenic (Liao *et al.*, 2009). High concentrations of arsenic in drinking water have been reported all over the world with India and Bangladesh being the most threatened countries (Baskan and Pala, 2009). Oral exposure to arsenic occurs through the consumption of contaminated seafood, e.g. fish and shellfish (containing arsenobetaine and arsenocholine) (Rodriguez *et al.*, 2003; Reyes *et al.*, 2009).

Arsenic is known to be completely stable and does not break down, thus leading to its accumulative levels in soil, sediments in lakes and rivers often affect living organisms over a period of time (Rodriguez *et al.*, 2003; Bornman *et al.*, 2007;). Epidemiological studies have shown that oral ingestion of inorganic arsenic is associated with a range of health effects which include lung, bladder, liver, prostate and kidney cancers, dermatitis, hyperkeratosis, melanosis and vascular diseases (blackfoot disease (BFD) and hypertension), cardiovascular, neurological, heamatological, renal and respiratory diseases (Pandey *et al.*, 2002; Duker *et al.*, 2005; Halim *et al.*, 2009; Liao *et al.*, 2009).

The permissible concentration set by USEPA and WHO standards for arsenic in drinking water is 10 μgl^{-1} (Mandal and Suzuki, 2002; Liao *et al.*, 2009). Levels of arsenic have not been well reported in the South African environment, especially in rivers in Cape Town. Various concentrations of Arsenic in different environmental compartment reported in different countries around the world are presented in Table 2.8.

Table 2.8: Arsenic contents in soil of various countries

Country	Types of soil/sediment	Number of samples	Range ($mgkg^{-1}$)	Mean ($mgkg^{-1}$)
India	Sediments	2235	10-196	
Bangladesh	Sediment	10	9.0-28	22.1
Argentina	All types	20	0.8-22	5
China	All types	4095	0.01-626	11.2
France	All types	-	0.1-5	2
Germany	Berlin type	2	2.5-4.6	3.5
Italy	All types	20	1.8-60	20
Japan	All types	358	0.4-70	11
	Paddy	97	1.2-38.2	9
Mexico	All types	18	2-40	14
South Africa		2	3.2-3.7	3
Switzerland		2	2-2.4	2.2
United States	Various states	52	1.0-20	7.5
	Tiller	1215	1.6-72	7.5

Adapted from Mandal and Suzuki, 2002.

2.7.2 Cadmium (Cd)

Cadmium is a non-essential, widely distributed metal that is extremely toxic to living organisms even at relatively low concentration (Jones *et al.*, 1987; Das *et al.*, 1997; Brzoska and Moniuszko-Jakoniuk, 2001; Limei *et al.*, 2008). Cd has an atomic number weight of 112.4 $gmol^{-1}$ is a silver-white malleable metal, soft with a oxidation state of +2 and chemically similar to zinc (DWAF, 1996; Hays *et al.*, 2008). The naturally occurring isotopes are 106, 108, 110, 111, 112, 113, 114 and 116 (Hays *et al.*, 2008). Cd is a transitional metal belonging to the group IIB of the periodic table which is present at concentration ranging from 0.06 to 0.5 $mgkg^{-1}$ in the earth crust (Das *et al.*, 1997; Safarzadeh *et al.*, 2007; Hays *et al.*, 2008; Lalor, 2008; Joseph, 2009; Szollosi *et al.*, 2009). It is ranked 67^{th} in abundance among the 90 naturally occurring elements on earth (Joseph, 2009).

Cd is introduced into the environment both by natural and anthropogenic sources with the later accounting for 3 – 10 times more than the former. Natural sources are volcanic activity, fossil fuel combustion, forest fires and transportation of contaminated particles by wind (Joseph, 2009). It has several industrial applications with the world production at 20,000 metric tons in 2005 (Joseph, 2009). The increase in Cd concentrations in agricultural soil are from human activities, e.g. application of phosphate fertilizer, sewage sludge, wastewater and pesticides, mining and smelting of metalliferous ores with high Cd content as well as atmospheric deposition (Cabrera *et al.*, 1994; Limei *et al.*, 2008; Yang *et al.*, 2009; Wang *et al.*, 2009).

Cadmium occurs mostly in association with zinc ores where it substitutes for Zn in the structure of sphalerite or wurtzite (Safarzadeh *et al.*, 2007) and is also found as the mineral Greenockite (cadmium sulphide). The ratio of Cd to Zn varies considerably and in most minerals and soil ranges from 1:100 to 1:1000 (Safarzadeh et al., 2007). It is widely used in electronic, electroplating, pigments, paints (as a stabilizer), welding, Ni-Cd batteries, solar battery, metallurgical and photographic products, synthetic chemicals, ceramics, metal coating and some metal alloys (Safarzadeh *et al.*, 2007; Hays *et al.*, 2008; Joseph, 2009; Kumar *et al.*, 2009;). Cd compounds consist of acetate, sulfide (yellow pigment), sulfoselenide, selenium sulfide (red pigment), stearate, oxide, carbonate, sulfate and chloride (Hays *et al.*, 2008).

Cadmium is generally classified as a 'soft' metal that is more likely to form covalent linkages with electron-donating ligands where Zn is classified as intermediate in softness (Brzoska and Moniuszko-Jakoniuk, 2001). Cadmium has a low solubility under conditions of neutral or alkaline pH and is highly soluble under acidic conditions, where toxic concentrations can easily arise from the dissolution of cadmium from cadmium-plated materials (Hays *et al.*,

2008; DWAF, 1996). Many organic Cd compounds are soluble in water, e.g. Cd acetate, chloride and sulfate Cd and its compounds are highly toxic and carcinogenic in nature (Kumar *et al.*, 2009). The basis of cadmium toxicity is its negative influence on the enzymatic systems of cells by substituting other metals ion e.g. Zn^{2+}, Cu^{2+}, Ca^{2+} in metalloenzymes (Brzska and Moniuszko-Jakoniuk, 2001).

Cd is one of the most readily absorbed and accumulated elements in plants grown on contaminated soil (Yang *et al.*, 2009; Zang *et al.*, 2009). Cadmium chloride and cadmium carbonate usually occurs in freshwater systems and the Cd^{2+} is readily taken up by aquatic organisms (DWAF, 1996). Cadmium binds strongly to sulphydryl groups, hence, the pronounced tendency of cadmium to bioaccumulate in the food chain (Jones *et al.*, 1987). Cadmium is strongly adsorbed by soil clay minerals and coprecipitated with iron and manganese oxides and oxy-hydroxides (Wang *et al.*, 2009). Soil pH, temperature, ionic strength plays a major role on the reactivity, mobility, bioavailability and toxicity of cadmium in the soil solution and solubility decreases with increasing pH (DWAF, 1996). Contaminated drinking water thus may expose people and have adverse effects on human health (DWAF, 1996).

Cadmium has a long biological half-time that makes it to bioaccumulate as toxin in living organism (Waalkes, 2000; Bi *et al.*, 2009). Population exposures to Cd are principally from food and tobacco smoking, ingestion of high doses of Cd can result in stomach irritation (Hays *et al.*, 2008). The organs that store Cd include liver, kidney, testis, spleen, heart, lungs, thymus, salivary glands, epididyms and prostate (Waalkes, 2000; Joseph, 2009; Yadav and Khandelwal, 2009). The most severe form of chronic poisoning is known as Itai-itai disease (Limei *et al.*, 2008).

Cadmium has been designated as a probable human carcinogen (B1), mutagens and teratogens based on limited evidence of carcinogenicity in humans but sufficient evidence of carcinogenicity in animals (Waalkes, 2000; Fatoki *et al.*, 2002). Cadmium has been linked with many clinical conditions including: anosmia, cardiac failure, cancers, cerebrovascular infarction emphysema, osteoporosis, proteinuria, glucosuria, and cataract formation in the eyes (Lalor, 2008; Edwards and Prozialeck, 2009). The deleterious effect of cadmium on plants include: oxidative stress, chlorosis, biomass reduction, root elongation reduction, inhibition of DNA repair enzymes (Jones *et al.*, 1987; Das *et al.*, 1997; Yadav and Khandelwal, 2009; Zang *et al.*, 2009).

2.7.4 Lead (Pb)

The primary industrial sources of Pb contamination include metal smelting and processing, secondary metals production, lead battery manufacturing, pigment and chemical manufacturing, and lead-contaminated wastes. Widespread contamination due to the former use of lead in petrol is also of concern. Lead released to groundwater, surface water and land is usually in the form of elemental lead, lead oxides and hydroxides, and lead metal oxyanion complexes (Smith *et al.*, 1995). Lead occurs most commonly with an oxidation state of 0 or +II. Pb(II) is the more common and reactive form of lead and forms mononuclear and polynuclear oxides and hydroxides. Under most conditions Pb^{2+} and lead-hydroxy complexes are the most stable forms of lead. In water bodies, a significant fraction of lead is undissolved and occurs as precipitates ($PbCO_3$, Pb_2O, $Pb(OH)_2$, $PbSO_4$), sorbed ions or surface coatings on minerals, or as suspended organic matter. Lead carbonate solids form above pH 6 and PbS is the most stable solid when high sulfide concentrations are present under reducing conditions. The primary processes influencing the fate of lead in soil include adsorption, ion exchange, precipitation, and complexation with sorbed organic matter. These processes limit the amount of lead that can be transported into the surface water or groundwater (Evanko and Dzombak, 1997).

Lead is a "probable carcinogen" based on animal studies. Toxic effects of lead can cause neurological impairment in foetuses and young children causing behavioural changes and impaired mental performance. ATSDR, RIVM and U.S.EPA have evaluated the noncancer oral toxicity data for inorganic lead. ATSDR did not derive any minimal risk levels (MRLs) for lead because a clear threshold for some of the more sensitive effects in humans has not been identified. Subtle neurobehavioral effects in children may occur at very low blood lead levels.

2.7.5 Mercury (Hg)

Mercury is a naturally occurring element in environment with a fixed amount on earth (Moore, 2000; Zahir *et al.*, 2005), which can be mobilized through both natural and anthropogenic processes (Wong *et al.*, 2006). Mercury is a heavy, silvery-white liquid with three oxidation states that pose different health impact (Moore, 2000; Bornman *et al.*, 2007) with no beneficial biological function (Oehmen *et al.*, 2009). It is a global pollutant that is present in all environmental compartments. It is circulated through complex biogeochemical cycles and can be found in the atmosphere, water, soil, sediments, plants, animals and other biota. (Zahir *et al.*, 2005; Kuban *et al.*, 2007). Important forms of mercury are elemental mercury (Hg0), with high vapour pressure and relatively low solubility in water at room temperature (Bornman *et al.*, 2007;

Kuban *et al.*, 2007), mercurous (Hg_2^{2+}) and mercuric (Hg^{2+}) in organic cation with better solubility and affinity for inorganic and organic ligands (Kuabn *et al.*, 2007). Also, mercury binds with organometallic compounds with one or two alkyl or aryl substituents to form alkylated or arylated mercury species (Kuban *et al.*, 2007).

The major ore of mercury is cinnabar (HgS) and from by-products from other metals (Wong *et al.*, 2006). Natural sources of mercury emissions include: outgassing of earth's crust, evasion from surficial soils, water bodies, vegetation surfaces, wild fires, volcanic activities and geothermal processes while anthropogenic sources are: combustion of fossil fuel, non-ferrous metal production, pig iron and steel production, cement production and waste disposal primarily from incineration (Wong *et al.*, 2006). It is hazardous environmental contaminant and thus listed as a priority pollutant by international agencies (Mirlean *et al.*, 2003; Wang *et al.*, 2004). Mercury has found extensive application in industry (Arabab-Zavar *et al.*, 2003; Oehmen *et al.*, 2009). The major applications of mercury despite the ban on its usage can be found in electrolytic production of chlorine and caustic soda in chlor-alkali plants, amalgamation in gold production and production of electrical and electronic devices (Wong *et al.*, 2006).

Exposure to elemental, inorganic and organic forms can lead to long-term and severe environmental and health effects e.g. erethism, tremor, psellism, respiratory, and renal failures, cardiac arrest and cerebral oedema, behavioural and cognitive dysfunctions, neurological disorder and teratogenic effects causing poisoning of fetus with severe consequences such as development delays, mental retardation, coordination disturbance, limb deformation (Wong *et al.*, 2006), interferes with many cell metabolic processes e.g. respiration, photosynthesis, lipid biosynthesis and enzymes inhibitions (Jones *et al.*, 1987). The most toxic form of mercury is methyl mercury (MeHg), which is mainly produced by microscopic organisms in water and soil and it builds up in the tissues of fish. Mercury enters water and soil from natural deposits, disposal of wastes and volcanic activity.

2.7.6 Zinc (Zn)

Zinc is a metallic element. The stable oxidation states of zinc are the metal (0) and the +II, oxidation state, which is the form found in nature. The carbonate, hydroxide and oxide forms of zinc are relatively resistant to corrosion and therefore zinc has many industrial applications which include coating and corrosion protection components (DWAF, 1996; Heijerick *et al.*, 2002). Environmental levels of zinc are currently increasing due to increased industrial emission and association with automobiles materials (Flinn *et al.*, 2005). The presence of zinc in domestic

water arises mainly from the leaching of galvanized plumbing and fittings. Zinc is an essential nutritional trace element for plants and animals. The adult human body contains about 2 – 4g of Zn (Maret and Sandstead, 2006; Jansen *et al.*, 2009). Humans have a high tolerance level to elevated zinc concentrations, while fish are highly susceptible to poisoning. Zinc is the fourth most abundant trace essential metal critical for the function of over 300 enzymes (Salgueiro *et al.*, 2002; Flinn *et al.*, 2005; Haase *et al.*, 2008; Jansen *et al.*, 2009).

Zinc has diverse functions that include biological functions, enzymatic catalysis, redox regulation, cellular signal transduction, immune systems, nervous systems, milk production during lactation, bone formation (Haase *et al.*, 2008; Salgueiro *et al.*, 2002), while zinc deficiency consists of the following: retardation of growth and development in children, retarded genital development, dermatitis, weakened resistance to infectious and early death, hypogonadism, cirrhosis (Salgueiro *et al.*, 2000; Maret and Sandstead, 2006; Haase *et al.*, 2008; Jansen *et al.*, 2009). The most common mineral form of zinc is the sulphide (sphalerite). Zinc is also found as a carbonate, oxide or silicate and may occur in association with many other metal ores such as copper and arsenic. The chloride, sulphate and nitrate salts of zinc are highly soluble in water, but at neutral and alkaline pH they hydrolyse to form relatively insoluble hydroxides which tend to be associated with sediments (DWAF, 1996).

Zinc and zinc salts are used in many industrial processes. Zinc itself is extensively used in galvanising processes and in alloys. Zinc salts are used in paint pigments, in cosmetics and in the manufacture of pharmaceuticals, dyes and insecticides. Zinc strongly interacts with cadmium, to which it is chemically very similar (Synergistic interaction). Zinc is an essential nutritional micro-element of relatively low toxicity, whereas cadmium, which is not essential, is highly toxic to all higher organisms. Metabolically, zinc interacts with copper. As is the case with all metals, the pH of the water determines the concentration of soluble zinc.

2.7.10 Levels of EDMs in environmental and biological samples

Dural *et al.* (2007) investigated the concentrations of metals (Cd, Pb, Cu, Pb, Zn and Fe) in muscle, gill, liver and gonad of three fish species over two seasons. Fish samples were digested with concentrated nitric acid and perchloric acid (2:1 v/v) at 60 °C for 3 days and samples diluted with distilled water. Fe and Zn were determined in air-acetylene flame while Cd, Cu and Pb were analyzed in a graphite furnace. Highest level of Zn (99.8 μgg^{-1} dw) was found in the liver in winter and Cd (1.59 μgg^{-1} dw) and Pb (6.75μgg^{-1} dw) was detected in the gill in spring. Highest

Cu (12.03 μgg^{-1} dw) and Fe (383.7μgg^{-1} dw) was found in the liver in autum and winter, respectively.

Effects of sediment-bound Cd, Pb and Ni on growth, feeding and survival of *Capitella* sp. I was studied by Horng *et al.* (2009). *Capitella* sp. I was exposed to different concentrations of metals in sediment prepared from $CdCl_2$, $NiCl_2$ and $PbCl_2$ stock solution. Growth rate, ingestion rate, and percent survival were estimated in three separated experiments. Sediment metal concentration was determined by digesting 3-g of the sediment with 21 ml concentrated HCl and 7 ml concentrated HNO_3, incubated for 16h, heated on hot plate until dried. The dried sample was washed with 0.5 M diluted HNO_3, filtered and analyzed with GFAAS. The growth and feeding of the worms were sensitive to even the lowest concentrations of each metal added to the sediments. The lowest observable adverse effect levels for Cd, Ni, and Pb were 0.03, 1.59, and 0.41$\mu mol\ g^{-1}$ sediment, respectively. Growth rates decreased drastically with elevated metal contamination. *Capitella* sp. I was most sensitive to Cd, followed by Ni and Pb, which had similar effects. Sediment productivity remained unchanged at different contamination levels of Ni and Pb, but was drastically reduced at 4.75 $\mu molg^{-1}$ Cd in the sediment.

The concentrations of trace elements in water, sediment and fish (*Micropterus salmoides*) samples were investigated by Ikem *et al.* (2003). Water sample was analyzed by adding 15 ml concentrated nitric acid to 45 ml of the water sample and digested with microwave. Sediment samples was analyzed using ICP-OES after sequential extraction while fish sample (muscle, vertebral column, gills and liver) was digested with 15 ml of nitric and subjected to microwave. Level of metals in sediments ranged from 0.2 ± 0.1 to 37 ± 28.3 with lead having the highest concentration. Concentration in fish ranged from not detectable to 244.57 ± 95.61. The potential risks to human health for heavy metals in fish were all below the recommended value.

Levels of heavy metals (Cd, Co, Cu, Fe, Mn, Ni, Pb, Zn) were measured in muscle, gill and liver samples of two fish species (*Leuciscus cephalus and Lepomis gibbosus*) by Yilmaz *et al.* (2007). Tissue samples were digested with concentrated nitric acid on hot plate by varying the time and temperature of digestion. After digestion, 10 ml of 1 N HNO_3 was added to the solution, filtered through 0.45 μm filter and analyzed with ICP/OES. The mean concentrations (μgg^{-1} wet weight) of heavy metals in tissues of *Leucis cephalus* were 0.010 and 172 for Cd and Fe, respectively, while concentrations in *Lepomis gibbosus* were 0.008 and 125.00 for Cd and Fe, respectively. Ni was not determined in all organs studied. The results show similarities in metal accumulation in tissues of the both *Leuciscus cephalus* and *Lepomis gibbosus* concentrations are below the limits for fish as proposed by FAO.

Usero *et al.* (2003) investigated the level of heavy metals in the muscle and livers of three species of fish (*Solea vulgaris, Anguilla anguilla and Liza aurata*), water and sediment in Odei reservoir and bay of Cadiz. Fish samples were digested with HNO_3 and H_2O_2, while sediment samples were digested with HNO_3 and $HClO_4$ using AMDS. Water samples was filtered with 0.45 μm membrane, acidified with 2 ml of concentrated HNO_3, stored at room temperature until analysis. All samples were analyzed for heavy metals with AAS except for Hg and arsenic were analyzed by GFAAS. Heavy metals ($mgKg^{-1}$) in sediment ranged from 0.7 ± 0.1 for Hg to 55,500 ± 4700 for Fe at Odei reservoir, while it ranged from 0.3 ± 0.1 for Cd to 7600 ± 290 for Fe at Cadiz bay. In water, concentration of metal ranged between 0.1 for Hg and 60 ± 3 for As at Odei reservoir and 0.1 for Hg and 2.6 ± 0.2 for Ni at Cadiz bay. The concentrations of metals were generally high in the livers than in the muscles.

2.8 Wastewater treatment plants as sources of EDCs

Increased living standards, rising population level, agricultural and industrial development have put pressure on the existing scare water resources in many countries. Consequent upon the upsurge, there is urgent need to treat, recycle and reuse available water resources. To complement scare water resources, there has been increase in the number of wastewater facilities in many countries. This is to forestall the outbreak of environmental pollution and spread of diseases, remove conventional pollutants (such as ammonia and phosphate), and to maintain and restore the biologic integrity of surface waters (Wang *et al.*, 2005; Sun *et al.*, 2008). Domestic and industrial wastewaters are significant sources of EDCs to the receiving surface, coastal waters and regional environments (Ahel *et al.*, 1994; Ahel *et al.*, 1996; Ying *et al.*, 2002; Vethaak *et al.*, 2005; Voutsa *et al.*, 2006; Zuccato *et al.* 2006).

A number of investigations suggested that final effluents of wastewater treatment plants (WWTPs) were mainly responsible for the increasing estrogenic activity in many aquatic environments (Sprynskyy *et al.*, 2007). Removing microconstituents in a wastewater treatment plant can be important in many ways. The effluents from WWTPs are usually discharged into surface waters, such as rivers. Contaminants from the treated wastewater have been shown to adversely affect surrounding wildlife and the aquatic environment. Processes such as transformation and biodegradation may remove a large fraction of EDCs in WWTPs, physical processes like coagulation, sedimentation, filtration and membrane separation might result in EDCs accumulation in sludge that might require further treatment (Fiali-Meknassi *et al.*, 2004).

Removal rate of EDCs from the effluent of WWTPs vary greatly due to plant location and physico-chemical parameters of the contaminants (Lazier and Mackay, 1993; Leusch *et al.*, 2006). Generally, fate of organic compounds and heavy metals in a water cycle is greatly dependent on their ability to interact with particulates. These can include clay, sediments, colloid coated with organic material and microorganisms. The fate is often not well understood, however, is dependent on particulate contaminant interactions (Filali-Meknassi et al., 2004).

2.9 Evidence and monitoring of EDCs (phenols and phthalate esters) in the South African environment

South Africa has experienced rapid industrial and urban growth, especially increase in the number of small scale industries (Mahomed *et al.*, 2008). South Africa is known to have used and abused most chemicals listed by developed and developing countries as endocrine disrupting chemicals (Burger and Nel, 2008). The presence of EDCs has been reported in the South African environment, therefore exposing human and wildlife to possible health problems (Fatoki and Noma, 2002; Burger and Moolman, 2006; Mahomed *et al.*, 2008; Aneck-Hahn *et al.*, 2009). Many water bodies in the country receive significant inputs of natural and synthetic chemicals (from both point and diffuse source) which often act as EDCs, thus constituting a threat to reproductive health of aquatic organisms (Burger and Moolman, 2006; Govender *et al.*, 2007).

South Africa as an emerging world economy depending largely on agriculture, chemical industries and mining still faces challenges in the area of proper waste disposal from a number of industrial and agricultural sources (Fatoki *et al.*, 2004; Bornman *et al.*, 2007; Mahomed *et al.*, 2008; Aneck-Hahn *et al.*, 2009). An audit of wastewater in Pretoria (Mahomed *et al.*, 2008) and water, sediment and serum samples (Bornman *et al.*, 2007) confirmed the presence of EDCs in water, sediment and serum samples analyzed. This weight of evidences gathered on EDCs in the South African environment has posed a huge challenge to water resources management. South Africa is faced with the problems of limited water resources with most rural and urbanized settlements depending on the available resources for their consumption, industrial and agricultural usage (Fatoki et al., 2001).

In addition, most research in South Africa on EDCs is centered on estrogenic compounds such as 17-β estradiol, p-Nonyl phenol, PCBs, estrone, estriol, organochlorine pesticides and heavy metals (Van Wyk *et al.*, 2003; Barnhoorn *et al.*, 2004; Mahomed *et al.*, 2008; Aneck-Hahn *et al.*, 2009). It is evident from various studies that EDCs are capable of initiating various health disorders in aquatic organisms. Van Wyk *et al.* (2008) reported the testicular effects of some

EDC compounds and metals on *Clarias gariepinus*. The impact of 17-α estradiol to stimulate vitellogenin (VTG) on *Xenopus laevis* has also been reported (Barnhoorn *et al.*, 2004).

Though significant concentration of phthalates have been reported in some environmental samples in the country (Fatoki and Noma, 2002; Adeniyi *et al.*, 2008; Fatoki *et al.*, 2010), there has been paucity in research on phenols on the priority list not until recently (Abboo and Pletschke, 2010). Concentrations of some of the compounds have been reported in drinking water, lakes and swimming pools, as well as their inhibitory effects on β-D-galactosidase and β-D-glucuronidase (Abboo and Pletschke, 2010). Assessing the potential ecological and health impacts of EDCs (phenol and phthalate esters) in the country's environment requires investigation of level and distribution in both aquatic and terrestrial systems.

Areas of significant importance that have been neglected in the monitoring of EDCs in the South African environment are treated wastewater from municipal wastewater treatment plants and landfill sites. Though wastewater from household and industries are usually treated before they are released into the river systems or used for irrigation purposes, studies have shown that they often contain EDCs. Also, leachates from landfill sites are always treated before onsite application, a process that can result in contamination of the water table by EDCs and heavy metals.

2.10.1 The risk assessment framework

In recent decades, the interest about environmental issues has increased very quickly. Not only scientists, but also other active members of the society (politicians, industrialists and the general public), have paid much attention in all aspects related to the environment, in general, and environment protection, in particular. In this context, environmental pollution has been one of the fields where more efforts have been aimed to control. Because of the lack of environmental consciousness and technical capacity, many industries released toxic substances into the air, water and soil, for a number of years. As a first consequence, levels of pollution in areas surrounding industrial sites became much higher than background (unpolluted) zones. Recently, implementation of legislative measures carried out by public administrations has obliged to companies to improve their production processes in order to reduce the pollutant emissions.

However, even though these measures are sometimes quantitatively quite restrictive, they are only focused on reducing the impact of an individual source of contamination, rather than aimed to control the integral state of the environment. It must be taken into account that industrial companies are rarely located isolately. Usually, they are in industrial sites together with many

other facilities. Thus, these industrial complexes may include a large variety of potential sources of pollution which altogether can mean a significant entrance pathway of pollutants into the environment. On the other hand, in developed countries industries tend to be located close to city suburbs, so pollution may pose a potential risk for the population living near these facilities.

The concern resulting from the potential exposure to contaminants was the starting point to develop methodologies in order to evaluate the consequences that those might have over both the environment and human health. Among these methods, risk assessment has been one of the most widely used. Risk assessment is a formalized process for estimating the magnitude, likelihood, and uncertainty of environmentally induced health effects (Sexton *et al.*, 1995). In 1983, the US National Research Council (NRC), in the so-called "Red Book", defined a series of principles to be considered for human health risk assessment, and defined it as a process in which information is analyzed to determine if an environmental hazard might cause harm to exposed persons and ecosystems (NRC, 1983).

In addition to definition, NRC proposed a framework for human health risk assessment, which involved 4 basic steps (NRC, 1993). The four steps of the process are:

1) Hazard identification
2) Dose-response assessment
3) Exposure assessment and
4) Risk characterization.

2.10.2 Hazard identification

This step can be defined as the qualitative determination of whether or not a particular hazardous agent is associated with health effects of sufficient importance to warrant further scientific investigations. Different kinds of tools (QSAR, short-term toxicity test, etc.) are used in order to estimate the chemical damage of a single substance. When establishing the hazard from industrial sources, the chemicals are also identified according to measurements of amount and typology of emissions.

2.10.3 Dose-response assessment

This component is focused on examining quantitative relationships between the magnitude of the exposure (or dose) and the probability of occurrence of adverse effects in the population. Usually, dose-response assessment is based on extrapolations from data about laboratory animals, to which have been given high-doses of toxicant.

2.10.4 Exposure assessment

Exposure assessment may be defined as the quantitative determination of the extent of exposure of the population to the hazardous agent in question. Since they provide a real knowledge of the state of pollution of an area, data obtained in the environmental monitoring are commonly used as a starting point. Factors that need to be considered include frequency and duration of exposure, rates of uptake or contact, and rate of absorption (NRC, 1993). Other factors in assessing exposure include release patterns, cumulative versus non-cumulative exposure, persistence, failure of exposure controls, quality of data and quality of models.

2.10.5 Risk characterization

This fourth component can be defined as the description of the nature and magnitude of the risk, expressed in terms which are comprehensible to decision makers and the public. Information acquired in the previous 3 steps is integrated in order to communicate the overall meaning of, and confidence in, the hazard, exposure, and risk conclusions. Risk is expressed as a probability of suffering a particular kind of harm from a hazard to a specified group of population (Bennion *et al.*, 2005). Moreover, qualitative and quantitative uncertainty related to risk must be also supplied.

As it has been seen, environmental monitoring is basic in order to carry out a correct evaluation of the exposure. Its aim is to quantitatively determine the concentration of pollutants in different media as a way to assess the impact of potential sources of contamination. Two approaches can be distinguished: biological and environmental monitoring. On one hand, human biomonitors, such as human milk, hair, adipose tissue, plasma and urine, may be used in surveillance programs. Although these may provide in a very realistic and direct way how population is exposed to pollution, they are very variable and highly dependent on personal characteristics, such as dietary habits, smoking and weight rather than on low-level environmental exposures (Paustenbach *et al.*, 1997).

In contrast, the chemical analysis of the pollutant concentrations in different environmental compartments (i.e., air, soil, vegetation, sediment) may be an interesting indirect methodology for human health risk assessment. Human exposure may be considered to occur through 2 routes: direct and indirect. Direct exposure is the sum of exposure to pollutants by direct pathways, such as air inhalation, dermal absorption or soil ingestion (US EPA, 1989a). In turn, pollutants can ultimately reach humans after crossing one or several paths, and they have

been released by at least one intermediate (Rikken and Lijzen, 2004). For instance, contaminants can deposit in vegetation and, following the food chain, be ingested by animals. Finally, they can reach humans as a final step, through dietary intake, which should be considered consequently an indirect pathway of exposure. In fact, different studies have reported that food intake is the main exposure route to several pollutants for non-occupationally exposed populations (Capdevila *et al.*, 2003; Hellstrom *et al.*, 2004).

As it has been noted, it is imperative to adequately characterize variability and uncertainty in all the steps of risk assessment process. In fact, this qualitative and quantitative characterization becomes critical in the fourth paradigm. Uncertainty and variability are related to heterogeneity inherit in the population and lack of total knowledge of the same, respectively (US EPA, 2001). Consequently, risk assessment must be performed since a probabilistic point of view, rather than by considering deterministic aspects. Monte-Carlo analysis has been increasingly used to adapt the necessity of including these aspects. This method has the advantage of allowing the analyst to account for relationships between input variables and of providing the flexibility to investigate the effects of different modeling assumptions (US EPA, 1997).

Risk assessment has been marked really as a procedure to link scientific information about potentially hazardous substances to the decision-making process, through which human exposures to these substances are regulated. A clear differentiation between the role of scientists (risk assessors) and decision makers (risk managers) in the evaluation process must be carried out (Williams, 2004). Risk assessment is just a part of risk analysis, which comprises 2 further steps: risk communication and risk management. Risk management is the subsequent stage where social, cultural, economic, and political issues are taken into account, and integrated to the evaluation process of risk. Finally, risk communication is the interactive exchange of information and opinions among individuals, groups and institutions.

CHAPTER THREE: MATERIALS AND METHODS

To prevent the introduction and contamination by congeners of interest from the materials used especially during phthalate esters determination, materials used were thoroughly cleaned in accordance with laid down experimental protocols and contact with plastics for organic sample collection, samples processing and analysis were avoided.

3.1 Cleaning of glassware

All glassware were washed with soapy water, cleaned with tap water and subsequently soaked in 10 % nitric acid. They were then soaked in acetone for at least 30min, then rinsed with hexane, and dried at 200 °C for at least 4 hours in an oven before rising with triple distilled pesticide-grade acetone just before use. This is to prevent phthalate contamination. The caps or lids of all sample bottles, jars and vials were lined with PTFE.

3.2 Study areas

Six wastewater treatment plants namely; Athlone, Bellville (which consist of the Old and New plants), Kraaifontein, Potsdam, Stellenbosch and Zandvliet) were investigated for the occurrence of heavy metals and seventeen organic compounds (eleven priority phenols and six phthalate esters) and for the effectiveness of the wastewater treatment plants in removing them from waste stream. Five of these WWTPs were located in the City of Cape Town, while one is located in Stellenbosch. Rivers associated with each treatment plant are: Athlone - Vygekraal River; Bellville - Kuils River; Kraaifontein -Mosselbank River; Potsdam - Diep River; Zandvliet - Kuils River and Stellenbosch -Veldwachters River. The plants and rivers investigated are presented in Figure 3.1. For heavy metal analysis, six points were sampled at each wastewater treatment plant (Fig 3.2): raw water (RW), primary settling tank water (PST), secondary settling tank water (SST), primary sludge (PS), secondary sludge (SS) and final effluents (FE), while samples for organic compounds were only collected from raw and final effluents of the investigated plants. All the sampled WWTPs receive wastewater from both domestic and industrial effluents, except kraaifontein that receives mainly (about 90 %) domestic wastewater. In addition to samples from water treatment plants, water and sediment samples were collected from rivers that receive the final effluent from the WWTPs. Samples were taken at the point of

discharge, as well as upstream and downstream from point of discharge (about 1-2km) to evaluate the possible impact of effluent on heavy metals and organic compounds load on the aquatic

Figure 3.1: Map showing five of the six wastewater treatment plants (Department of Water Affairs).

environment. The geographical location, population equivalent and treatment processes of the investigated treatment plants are presented in Table 3.1. The plant configuration and operational parameters is described in Section 3.2.1 through to 3.2.6

3.2.1 Athlone WWTP

3.2.1.1 Plant configuration and operating parameters

Athlone WWTP is a nitrification-denitrification biological excess phosphorous removal (NDBEPR) plant with a design capacity to treat approximately 120 ML effluent per day. The plant houses six identical bioreactors named from A to F, which operate in a University of Cape Town (UCT) configuration with diffuse aeration. The raw influent consists of approximately 70 % industrial effluent and 30 % domestic effluent. Influent to the primary settling tank (PST) consists of raw influent as well as the liquid component from the digesters and thickeners. The plant operates at dissolved oxygen (DO) concentration of 2.5 to 3 mgl^{-1}, anaerobic mass fraction of 15 %, anoxic mass fraction of 29 % and aerobic mass fraction of 56 %.

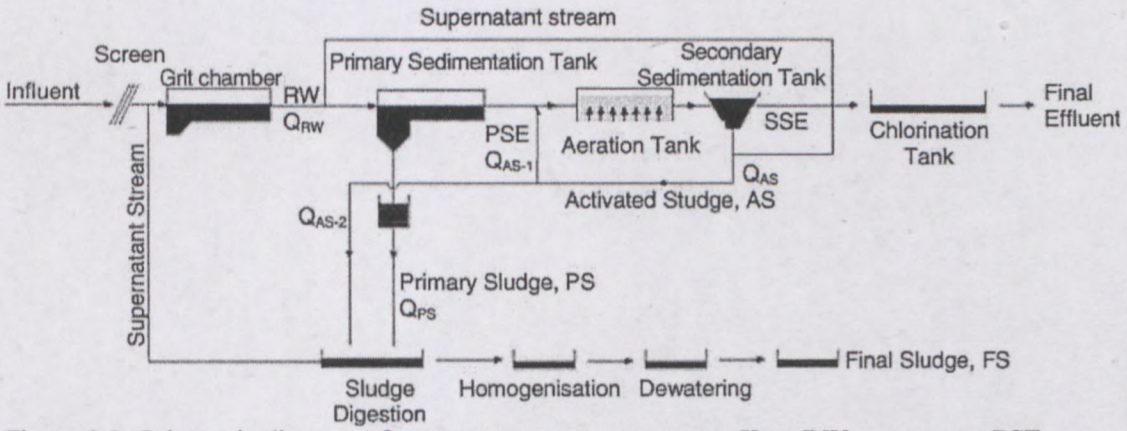

Figure 3.2: Schematic diagram of wastewater treatment system. Key: RW- raw water, PSE-primary sedimentation effluent, SSE-secondary sedimentation effluent, PS-primary sludge, AS-Activated secondary sludge

3.2.2 Bellville WWTP

3.2.2.1 Plant configuration and operating parameters

The three industrial bioreactors (named North, Center and South), at Bellville have the capacity to treat approximately 60 ML effluent per day. The configuration is the Modified Ludzack-Ettinger (MLE) and the method of aeration is diffuse. The influent consists of raw, unsettled influent of industrial origin that is supplemented by the primary sludge from the PST of

the nearby domestic WWTP. The plant operates at a dissolve oxygen of 1-2 mgl^{-1}, an anoxic mass fraction of 20 % and an aerobic mass fraction of 80 %.

3.2.3 Kraaifontein WWTP

3.2.3.1 Plant configuration and operating parameters

Kraaifontein is a relatively small NDEBPR WWTP for the treatment of domestic wastewater. The configuration of the plant is classic UCT and surface aeration is employed. There is only one bioreactor and the aerobic, anoxic and anaerobic mass fractions are 59 %, 30 % and 11 %, respectively and the average dissolved oxygen concentration is 2.8 mgl^{-1}. Influent is first settled in PST's before entering the bioreactor.

3.2.4 Potsdam WWTP

3.2.4.1 Plant configuration and operating parameters

Potsdam WWTP uses both activated sludge bioreactors and fixed medium (stone) trickling filter systems to treat the influent. This influent consists of primarily domestic waste with an industrial component. The trickling filter system is ageing and function is poor. The plant is presently being upgraded to increase both capacity and efficiency. Approximately half of the influent is treated in the two identical bioreactors after undergoing primary settling. The plant operates in the UCT configuration with surface aeration. Potsdam WWTP experiences intermittent scum problems, mainly in winter and during periods of overloading.

3.2.5 Stellenbosch WWTP

3.2.5.1 Plant Configuration and operating parameters

Stellenbosch WWTP uses both activated sludge bioreactors and fixed medium (stone) trickling filter systems to treat the influent. This influent consists of primarily domestic waste with a huge industrial component. The trickling filter system is ageing and function is also poor. The plant is presently being upgraded to increase both capacity and efficiency. Approximately half of the influent is treated in the two identical bioreactors after undergoing primary settling. The plant operates in the UCT configuration with surface aeration. Potsdam WWTP experiences intermittent scum problems, mainly in winter and during periods of overloading.

3.2.6 Zandvliet WWTP

3.2.6.1 Plant Configuration and operating parameters

Zandvliet WWTP uses extended aeration activated sludge with gas chlorination of effluent. There is no maturation pond, so impact of process upset is immediate. Several standby generators on site can supply entire works except for sludge dewatering. Secondary sludge is mechanically dewatered and removed off-site for application to agricultural land. Design capacity of 59 Mld^{-1} at 700 mgl^{-1} Chemical Oxygen Demand equivalent to 338 000 population equivalents. Presently treating – 56 Mld^{-1} (95 %) equivalent to 400 000 population equivalents (93 %).

3.2.7 Kirstenbosch Botanical Garden (Control site)

Kirstenbosch was established in 1913 to promote, conserve and display the extraordinarily rich and diverse flora of southern Africa (http://www.sanbi.org). The geographical co-ordinates is E 18°26'06.48" 33°59'15.76" S Long 18.43209 Lat -33.99039. The Garden covers 36 hectares in a 528 hectare estate that contains protected mountainside supporting natural forest and fynbos along with a variety of animals and birds. Kirstenbosch lies in the heart of the Cape Floristic Region, also known as the Cape Floral Kingdom. The site was chosen as the control site on the assumption that the site will be less contaminated compared to WWTP and the freshwater systems investigated.

3.3 Method development on HPLC

This method was developed only for eleven priority phenol. This is to allow for their determination in drinking water prior to the combined method development for phenols and phthalate esters on GC-MS.

3.3.1 Chemicals

Phenols were obtained from the following sources: phenol (99 %), 2-nitrophenol (99 %), 4-chloro-3-methylphenol (98 %), 2-chlorophenol (98 %), 2,4-dinitrophwnol (99%), pentachlorophenol 2,4-dimethylphenol (99 %), 2,4,6-trichlorophenol (99 %), 2,4-dichlorphenol (99 %), 2-methyl,4,6-dinitrophenol (99 %), from Sigma Aldrich (South Africa); 4-nitrophenol (99 %), 2,4,6-tribromophenol (99 %) from Separations (South Africa), phosphoric acid 85 % Sigma Aldrich, 2,4,6-tribromophenol (99 %) from Dr. Ehrenstorfer (Germany). Methanol and

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Table 3.1: Description of the six wastewater treatment plants investigated

WWTP ID	Geographical Location of plant	People equivalent	Source	Treament Process	River
A	S33.5709° E18.3048°	900,000	Domestic Industrial	S + G + Sed + AS (BNR) + Sed + Chl + AD + Dew	Vygekraal River
B	S33.5923° E18.4332°	591,000	Domestic Industrial	S + G + EAAS (N) + Sed + UVdis + Dew	Kuils River 1
C	S33.82539° E18.70442°	133,000	Domestic	S + G + Sed + AS (N) + Sed + Chl + AD + Dew	Mosselbank River
D	S33.5070° E18.3108°	385,000	Domestic Industrial	S + G + Sed + AS (BNR) + Sed + Chl + AD + Dew	Diep River
E	S33.94345° E18.82492°	N/K	Domestic Industrial	S + G + Sed + FB + AS (BNR) + Sed + Chl + AD + Dew	Veldwatchers River
F	S34.0312° E18.4259°	400,000	Domestic Industrial	S + G + EAAS (N) + Sed + UVdis + Dew	Kuils River 2

Abbreviations: S = Screening; G = Grit removal; Sed = Sedimentation; AS = Activated Sludge; EAAS = Extended Aeration Activated Sludge; N = Nitrogen; BNR = Biological nutrient removal; Chl = Chlorination; UVdis = UV disinfection; AD = Anaerobic digestion; FB = Filter bed; N/K = Not known; WWTP ID = Wastewater treatment plant identification.

acetonitrile gradient-grade were purchased from Sigma Aldrich and Merck (Germany), respectively and were futher purified through distillation. Standard solutions of phenols, (1000 mgl^{-1}) were prepared in methanol; aliquots of the standard solution were further diluted with methanol to prepare the working solutions.

3.3.2 Columns and cartridges

C18-E cartridges (strata) containing 500 mg/ 6 ml of adsorbent (Separations, South Africa) and a newly launched kinetex C18-100A column (150 mm×4.6 mm i.d., 5 μm particle size) from Phenomenex (Torrance, CA, USA) were used.

3.3.3. Instrumentation

Instrumentation and software analyses were performed using a Agilent 1100 series high-performance liquid chromatography equipped with a quaternary pump, a vacuum membrane degasser, an automatic autosampler, an automatic injector and connected "on-line" to a Agilent photodiode array detector (DAD). A gradient mobile phase of 0.1 % phosphoric acid in acetonitrile/water was used for the chromatographic separation flow-rate of 1.0 $mlmin^{-1}$. The optimized gradient programme is shown in Table 3.2. A Supelco Visiprep SPE vacuum manifold (South Africa) was used for the elution of SPE columns. Detection was conducted at 280 nm for all the target analytes.

3.3.4. Water samples/extraction optimization studies

Mili-Q water was used as the matrix for all the recovery experiments. Blank experiments showed that phenols were undetectable in this water. The water pH was adjusted to 2 using sulphuric acid. All solvents and solutions prepared for LC were filtered through 0.22 μm cellulose acetate disk filters (Millipore) before use. All water samples were collected in glass bottles and stored in a refrigerator at 4 ^{o}C prior to extraction. Water samples were filtered using a vacuum system through 0.45 μm and 0.22 μm to remove particulate matter. The phenolic compounds were concentrated on SPE as described below.

3.3.5 Chromatographic conditions

Mobile phases were water (0.1 % phosphoric acid) and acetonitrile (0.1 % phosphoric acid). All solvent and mobile phases were firstly filtered under vacuum through 0.45 μm nylon filters and degassed using a vacuum degasser. The chromatographic system was conditioned by passing the solvents through until a stable baseline signal was obtained. Once the chromatographic system was conditioned with mobile phases, the chromatograms were obtained by injecting 20 μl of appropriate mixture of phenols. For optimization purposes, mobile phase methanol/water (1% acetic acid) and acetonitrile/water (0.1% phosphoric acid) was used. The flow rate was in the range of 0.6 $mlmin^{-1}$ to

1.2 $mlmin^{-1}$ while the temperature was maintained at 25°C. The eluent condition varied from 70% water (5 min isocratic) to 100% of organic modifier (gradient) in 15 min at 1 $mlmin^{-1}$. The UV was set at 280 nm. After use, 50:50 (v/v) water-acetonitrile mixtures (0.75 $mlmin^{-1}$) for 30 min (Table 3.2) washed the column.

Table 3.2: Chromatographic parameters used for the analysis of phenols on HPLC

Chromatograph	Agilent Technologies 1100 series
Detector	DAD
Column (length x internal diameter x particles)	Kinetex 100 C-18 100A (150 mm x 4.6 mm x 2.6 µm)
Injection volume	20 µl
Mobile phase	A: water with 0,1% H_3PO_4 B: Acetonitrile with 0,1% H_3PO_4
Flow rate	1 ml/min
Gradient elution	Time % A % B 0 min. 70 30 5 min. 60 40 10 min. 30 70 15 min. 0 100
Temperature	Ambient (25°C)
Data collection	Chemstation D-7000 HPLC System Manager (HSM) Software (Version 3.0)

3.3.6 Extraction procedures

3.3.6.1 Strata C18 SPE cartridge

Prior to extraction, cartridges were washed with 2 ml of acetonitrile to remove impurities. They were then conditioned with two 5 ml portions of methanol and left to soak for 1 min before methanol was drawn off; excess of methanol was subsequently displaced with 2 ml of MilliQ water at pH 2. Air contact with the column was avoided until sample extraction had been completed. The water sample was pumped through the column by a vacuum pump, connected by PTFE tubing, with the vacuum adjusted to give a flow-rate of 7-8 $mlmin^{-1}$. After passage of the water sample, the cartridge was dried by vacuum suction for 1 min. The analytes were eluted from the cartridge with 1.5 ml of acetonitrile and concentrated to 0.5 ml under gentle flow of dry nitrogen and 20 µl was injected for LC analysis.

3.3.7 Real water analysis on HPLC

Potable water samples were either purchased or collected from taps, while freshwater were collected from dam, pond and swimming pool from the Bellville campus of Cape Peninsula University of Technology (CPUT). Purchased bottle water were classified as Brand water 1 (BD1), Brand water 2 (BD2) and Brand water 3 (BD3), while tap water were

collected from Postgraduate Residence and Food Technology Laboratory from CPUT and from selected informal settlements namely; Khayelitsha, Langa and Guguletu in Cape Town. Water samples were collected in triplicates on monthly basis over a three month period. Water samples were stored on ice from the point of purchase or collection and kept at 4°C in the fridge until analysis. The samples were extracted, treated and analyzed as outlined in section 3.3.6.

3.3.8 Quality assurance and quality control (QA/QC)

Spiked procedural blanks with the surrogate standards, solvent blanks and control samples were included in each batch of analyses. Blanks and controls were treated in the same manner as the samples were always analyzed after every sample injection. A calibration standard solution of 2.5 $ng\mu l^{-1}$ was injected in duplicate to monitor the instrumental sensitivity and reproducibility every time before sample analyses.

3.4 Method development on GC-MS

Seventeen organic compounds (phenols and phthalate esters) were determined in wastewaster and fresh water samples on GC-MS collected on seasonal basis from six wastewater treatment plants and five Rivers after initial instrument optimization.

3.4.1 Chemicals and reagents

Analytical grade phenol (PH) 99.9 %, 2-nitrophenol (2-NP) 99 %, 4-nitrophenol (4-NP) 99 %, 2,4-dinitrophenol (2,4-DNP) 99.7 %, 4,6-dinitro-2-methylphenol (DNMP) 98 %, 2,4-dimethylphenol (2,4-DMP) 98 %, 2-chlorophenol (2-CP) 99.8 %, 4-chlorophenol (4-CP) 99 %, 2,4-dichlorophenol (2,4-DCP) 100 %, 4-chloro-3-methylphenol (4-C-3MP) 99 %, pentachlorophenol (PCP) 99.6 %, dimethyl phthalate (DMP), diethyl phthalate (DEP) 99 %, benzybutyl phthalate (BBP) 98 %, dioctyl phthalate (DOP) 99 %, diethylhexylphthalate (DEHP) 99 %, dibutyl phthalate (DBP) 99 % were purchased from Superlco (Bellefonte, PA USA). Helium (99.999 %) is supplied by Afrox gas, South Africa, Potassium Carbonate, acetic anhydride were supplied by Separations (South Africa). The solvents (methanol, n-hexane, acetone and acetonitrile) were of analytical grade from Sigma Aldrich and were further purified by distillation. Separate stock solutions (1000 mgl^{-1}) of individual congeners were prepared in methanol A working mixture containing each compound at 10 mgl^{-1} was also prepared and stored at 4°C in the dark. Milli-Q water used was from apparatus Millipore (Bedford, MA, USA).

3.4.2 Instrumentation

An Agilent 6890N gas chromatograph/5975 mass selective detector system operating at 70 eV with ion source temperature set at 230 °C was used for this study. The gas chromatograph was equipped with a DB-5MS fused silica column (phenyl methyl siloxane) (30 m x 0.25 mm i.d.; 0.25 μm film thickness). The injector temperature and GC–MS interface temperature were maintained at 260 and 280 °C, respectively. The sample was introduced into the gas chromatograph in splitless mode and the helium carrier gas flow rate was set at 1.0 ml/min. The oven temperature of the GC was set at 80 °C for 1 min, increased to 150 °C at 5 °C/min and finally increased to 280°C at 12 °C/min and held for 7 min. The post run temperature was set at 300 °C for 2 min to clean up the column before the next injection. The ramped oven temperature programmes optimized for GC-MS is presented in Table 3.3, while the best instrumental conditions of GC and MS used for sample analysis are tabulated in Table 3.4.

Table 3.3: Ramped oven temperature programmes optimize for GC-MS

Oven Temperature programme	Injector temp (^{0}C)	Carrier gas flow rate (ml/min)	Analysis time (min)
100°C (1 min) to 150°C @ 10°C (7min), to 280°C, @ 15 °C (20min)	260	1	35.67
100°C (1 min) to 150°C @ 30°C (1min), to 205°C, @ 3°C, to 260°C @10°C (7min)	250	1	34.50
100°C (1 min) to 150°C @ 30°C (1min), to 205°C, @ 3°C, to 260°C @10°C (7min)	260	1	35.00
80°C (1 min) to150°C @5°C (1 min), to 280°C @ 12°C (7 min)	**260**	**1**	**33.83**

Table 3.4: Gas Chromatography and Mass Spectrometer Parameters

Gas chromatography		Mass spectrometer	
GC-MS	Agilent 6890N	5975	
Capillary Column	DB-5MS, 30 m x 0.25 mm i.d. (0.25 μm film thickness)	Ion source	Electron impact ionization, 70 ev
Carrier gas	Helium, purity: 99.999%	Ion source temperature	230°C
Injector parameters	1 μL splitless, injection temperature 260°C	Inlet temperature	260°C
Oven temperature	80°C (1 min) -5°C min^{-1} 150°C held for 1 min, then to 280°C at 12°C (7 min), carrier gas flow rate: 1.0 mL min^{-1} Post run temperature: 300°C (2 min)	Transfer line	280°C
		Scan mode (m/Z)	50-450

3.4.3 Derivatization procedure

Some EDCs such as phenols with hydroxyl group within the molecule have to be derivatized with N-Methyl-N- (Tert-Butyldimethylsilyl) trifluoroacetamide (MTBSTFA), which results in the formation of tert-butyltrimethylsilyl (TBMS) derivatives. The high polarity of the phenolic compounds gives rise to poor chromatographic performance and as a consequence derivatization was carried. The phenol-silylate tends to be more volatile and affords a better detection limits when using GC. The detection limits observed after derivatization on GC-MS was better than when phenols were determined using HPLC.

3.4.3.1 Acetylation procedure

For acetic anhydride derivatization, 1 ml of standard mixture was added to 3 ml of 0.1 M K_2CO_3 followed by the addition of 2 ml of n-hexane containing 100 uL of acetic anhydride. The mixture was vigorously shaken in a 6 ml glass vial and allowed to stand for 30 mins. The organic phase was pipette using Pasteur pipette and dry using Na_2SO_4, this was concentrated to about 400 ul under gentle flow of nitrogen gas and injected into GC-MS.

3.4.3.2 Silylation procedure

For silylation derivatization, the silylating reagent used is N-Methyl-N- (Tert-Butyldimethylsilyl) trifluoroacetamide (MTBSTFA). Two derivatization method were tried, derivatization using heating block as proposed by Heberer and Stan (1997) and the developed method in our laboratory using GC-oven. For the heating block method, 50 µl of phenolic standards were measure and 50 µl of derivatization reagent added. The mixture was heated at varying temperature and subjected to GC-MS analysis. For the new method, 1 ml of the standard mixture was measured into sample vial and blown to dryness under gentle flow of nitrogen gas. The dried standard mixture was reconstituted with 50 µgl acetonitrile and 50 µgl of the derivatization reagent (MTBSTFA). The mixture was vortex mix for 90s. This was derivatized at 90°C for 20 min in GC oven. The sample was cool down to room temperature and 1µl was injected into GC-MS for analysis. The stepwise derivatization procedure is shown in Figure 3.2.

3.4.5 Determination of limits of detection and quantification on HPLC and GC-MS

The best optimized conditions were obtained from a series of experiment (Tables 3.2 and 3.4) were used for LC and GC analysis. From the stock standard solution, lower standards were prepared through serial dilution of individual standard of phenols and phthalate esters as well as the mixture standards. 20 µl and 1 µl of each of the standard was injected into LC and GC, respectively to determine the lowest concentration. Different procedures for the determination of limits of detections (LODs) and limit of quantifications (LOQs) are reported in the literature. These limits can be

experimentally estimated from the injection of serially diluted standard solutions or extracts of fortified water samples until the signal-to-noise ratio (s/n) ratio reaches a value of three. LOD could also be estimated as three times the noise level of the baseline in the chromatogram, while the limit of quantification (LOQ) is set at three times the LOD. For this study, LOD and LOQ were calculated using the equations below:

$$LOD = 3.3 \times Sb/a \quad \ldots\ldots (1)$$

and

$$LOQ = 10 \times Sb/a \quad \ldots\ldots (2)$$

where a is the slope and Sb is the standard deviation of the y-intercept (De Sousa *et al.,* 2003).

3.4.6 Solid phase extraction for water samples

C18-E cartridges (strata) containing 500 mg/ 6 ml from separations were used for the extraction of phenols and phthalates from water samples based on recoveries obtained for phenols in section 3.2.4. Prior to sample processing, the cartridges were fitted onto a vacuum manifold (Supelco) connected to pump and the cartridges were conditioned with 5 ml of n-hexane:acetone (50:50, v/v), followed sequentially by 5 ml of methanol and 10 ml of Milli-Q purified water (purified by Milli-Q System, Millipore, Bedfore, MA, USA). Prior to extraction of each 500 ml, water samples were filtered on vacuum using a 0.22 μm to remove suspended particulate matter that might block the SPE cartridges. Hydrochloric acid (37 %) was used to adjust the pH of the water sample to pH ≤ 3 before passing it through the conditioned cartridge. Then, 5 ml of Milli-Q was passed through and left on the vacuum manifold for 30 min to dry (-70Kpa). The retained analytes of interest were eluted with 3.5mL of methanol followed by 3.5 ml of n-hexane:acetone (50:50, v/v) into 10 ml glass vial . This was blown to dryness on hot plate at 70 °C under gentle flow of nitrogen followed by derivatization.

3.4.7 Quality assurance and quality control (QA/QC) for GC-MS

Spiked procedural blanks, solvent blanks and control samples were included in each batch of analyses. Blanks and controls were treated similarly as the samples and analyzed after every sample injection. A calibration standard solution of 50 μgl^{-1} was injected in duplicate to monitor the instrumental sensitivity and reproducibility every time before sample analyses.

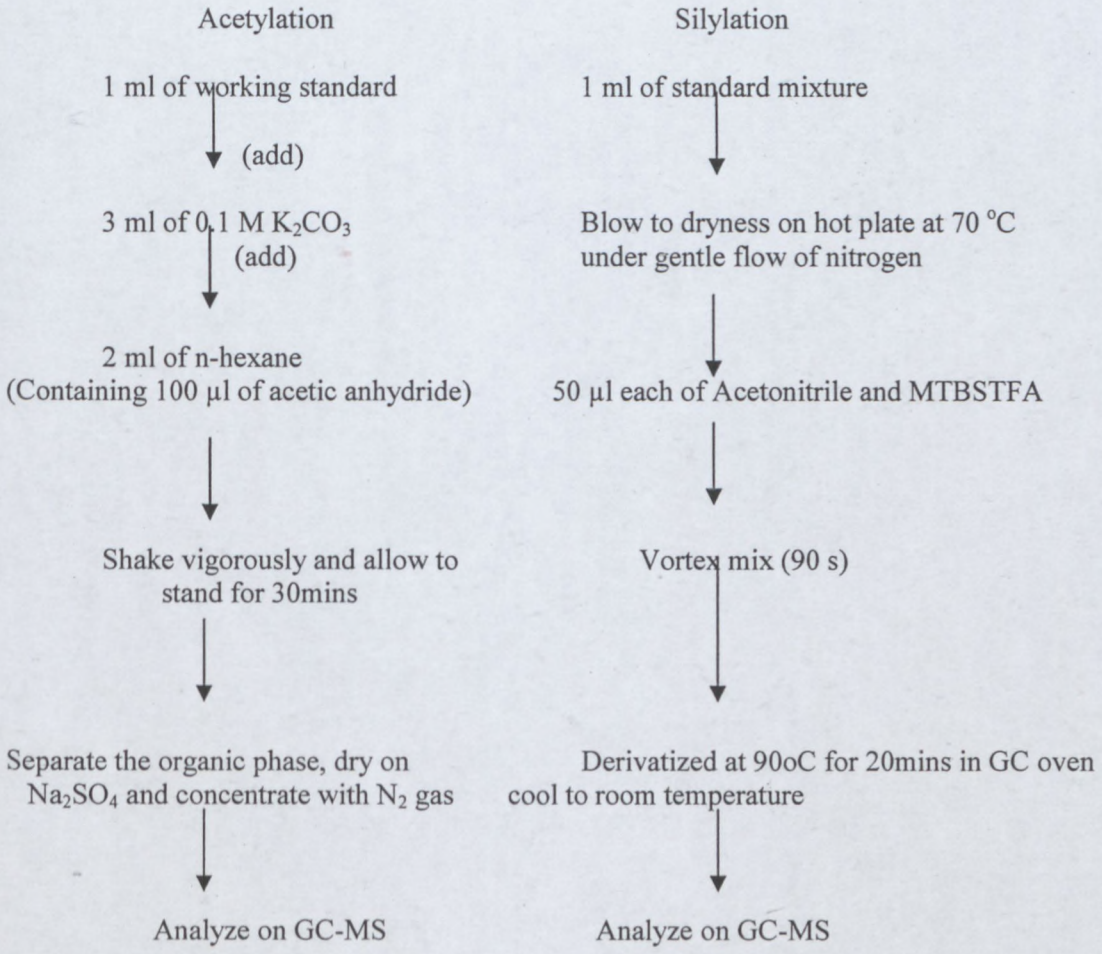


Figure 3.3: Derivatization procedure for acetylation and silylation

3.5 Method development for metal analysis using ICP-MS

3.5.1 Methods

All the determinations were carried out by Inductively Coupled Plasma Mass Spectrometry (ICP-MS) located at the geology Department, University of Stellenbosch. The Agilent 7700 instrument was used with a Meinhardt nebulizer and silica cyclonic spray chamber with continuous nebulization. The operation parameters are: Plasma RF power: 1550 W; Sample depth: 8.0 mm; Carrier gas: 1.08 L/min; Nebulizer pump: 0.10 rps; Helium gas: 5.3 $mlmin^{-1}$ for ICPMS. The isotopes of the elements determined were: ^{111}Cd, ^{75}As, ^{208}Pb, ^{202}Hg, ^{66}Zn.

3.5.2 Reagents: Water (resistivity 18.2 MΩ cm) was de-ionized by use of a Milli-Q system (Millipore, Bedford, MA, USA). Certified standard of all the metals (As, Cd, Pb, Hg and Zn) to cheek for instrument performances and $AuCl_3$ were obtained from Merck, South Germany. Ultrapure nitric acid (65 %) and 32 % hydrogen peroxide were obtained from Fluka Kamika, Switzerland. 1000 mgl^{-1} of metal stock standard solution (As, Cd, Pb, Hg and Zn) was supplied by Sigma-Aldrich.

3.5.3 Measurement of physico-chemical parameters for water and sediment samples

The pH, conductivity and temperature of the river and wastewater were determined on-site with a dual pH and conductivity meter supplied by Merck NT Laboratory Pty Ltd and a thermometer.

3.5.4 Wastewater and river water digestion

Water samples for the heavy metals analysis were collected in 1litre plastic container which were initially washed with detergent and rinsed with distilled water. The containers were finally soaked in 10 % Nitric acid. The containers were then rinsed at least three times with MilliQ water. At the sampling sites, containers were rinsed three times with the water samples before being filled with the samples. The samples were preserved by adding conc. HNO_3 to each sample bottle and the pH adjusted to 2.0 by the use of pH meter. The samples were stored in a refrigerator at about 4 °C, before subsequent analysis. As samples may contain particulate or organic materials, pretreatment in the form of digestion is required before analysis. Nitric acid digestion was employed in accordance with Akan *et al.* (2008). A few drops of $AuCl_3$ were added to 100 ml of unfilteres wastewater and river water samples to keep Hg ion in solution prior to digestion.

3.5.5 Sediment and sludge digestion

Sediment and sludge samples were collected into a well-labeled zip-block bags. The sludge and sediment samples were dried in an oven at 60 °C for 24 hr, grounded using pestle and mortar. The samples were passed through a 1 mm sieve discarding the fraction > 1 mm and eliminating stones, roots and fragments of plastic and metal. The sieved samples were kept in well labeled pre-cleaned dried plastic containers. For the analysis, 1 g of both sediment and sludge were weighed using a fine analytical balance (RADWAG) into a test-tube and 10 ml of 1:1 HNO_3/water was added. The slurry was covered with wash glass and digested at 95 °C ± 5 °C after the addition of few drops of $AuCl_3$ to stabilize Hg ion that may be present using a Grant dry-block heater for 30 min (USEPA 3050B). The sample was allowed to cool down and 5 ml of HNO_3 was added and watch glass replaced. The samples were returned to the block heater and further heated for 2 hours. The samples were cooled down and 2 ml of water and 3 ml of hydrogen peroxide was added and the cover immediately replaced to prevent volatilization of mercury and samples heated for another 2 hours. A blank (control) of reagents without the samples were treated the same way as for samples. The

samples were cooled to room temperature, filtered with using 0.45 μm cellulose nitrate ultra-filtration membrane filters (Whatman) into 100 mℓ volumetric flasks, made up to a volume with MilliQ water. The digested samples (water, sediment and sludge) were analyzed using ICP-MS using the parameters stated in section 3.5.1

To obtain the soil and sediment concentrations, the ICP values were converted using the formula:

$$SMC = \left(\frac{ICP_{Reading} - C_{reading}}{WSS} \right) * DF \quad \text{..... (3)}$$

Where: SMC = soil or sludge concentration ($\mu g g^{-1}$); ICP = Inductively Coupled Plasma values; C = blank; DF = dilution factor; WSS = weight of soil or sludge sample (g).

3.4.6 Quality assurance for instrumentation and analytical method

The spiking method (standard addition method) was used for water, sediment and sludge samples due to non-availability of reference materials. For water samples, 100 ml of wastewater, freshwater and MilliQ water were measured into 250 ml conical flask and spiked with known concentration of the metal standard and digested as described above. 1 g of pre-digested sediment and sludge samples was also spiked and recovery determined following digestion outlined above. Triplicate analysis of each of the metals was carried out with water, sediment and sludge samples along with blank samples.

3.6 Removal efficiency

Unfortunately, none of the WWTPs were monitored for both influent and effluent flow rates. The removal efficiency (ε) of each metal and organic compound was calculated based on influent and effluent concentrations, and on the assumption of steady-state conditions and that precipitation or evapotranspiration had minimal impact on the water storage as compared to inflow and outflow:

$$\varepsilon(\%) = \left(\frac{EDCi/Mi - EDCe/Me}{Mi} \right) \times 100\% = \frac{QiCi - QeCe}{QiCi} \times 100\% = \frac{Ci - Ce}{Ci} \times 100\% \quad \text{..... (4)}$$

With *EDCi/e or Mi/e* = the organic or metal flux in influent/effluent (mgd^{-1});

Ci/e = the metal concentration in influent/effluent (mgl^{-1});

Qi/e = the mean flow rate of influent/effluent ($l\ d^{-1}$).

3.7 Seasonal sampling protocol

Grab water samples for heavy metals analysis were collected from all the sections of the wastewater treatment plants as described in section 3.2 in triplicates on monthly basis but the samples were pooled together for each quarter and analyzed in triplicates (section 3.5.5). This is to allow for the possible seasonal variation in the concentration of the metals in the WWTPs and the receiving water bodies. For the organic congeners monitored, grab samples were collected from the influent and effluent points and from the upstream and downstream sections (about 1 to 2 Km) from the discharge point of the effluent to the receiving water bodies. The organic analysis was carried as stated in section 3.4 and mean values for the congeners were computed as the average of the number of samples collected per quarter. Sampling for heavy metals analysis commenced in January 2010 and ended in December 2010, while sampling for organic compounds started in April 2010 and ended in March 2011.

3.8 Statistical analysis

Statistical analysis was performed using Statistical Package for the Social Sciences (SPSS) 19.0. Normality of the distribution was tested by means of the Kolmogorov-Smirnov test of normality ($\alpha = 0.05$). As metal concentration in the water were not normarlly distributed, significance of difference between raw wastewater, settling tank and effluents were assessed by means of non-parametric Wilcoxon tests ($\alpha = 0.05$). Seasonal effects were analysed by means of the non-parametric Kruskal-Wallis rank test ($\alpha = 0.05$).

3.9 Health risk assessment

A human health risk assessment was conducted to provide an indication of whether the organic compounds, heavy metals or metalloid (arsenic) detected in the water samples tested may cause adverse health effects to humans. The methodology used to assess this potential human health risk was that described by US-EPA (1988, 1996) and the WHO (2002). The exposures considered in the assessment include:

a) Ingestion through drinking of final effluents or river water,
b) Dermal absorption due to daily washing/bathing in the river water,
c) Irrigating farm lands with final effluent or river water,
d) If fish from these areas is consumed.

Human exposure to toxic effects are expressed in terms of average daily dose (ADD) which is the amount of substance taken into the body on daily basis during the exposure period calculated.

$ADD = (C_{medium} \times IR \times ED \times F_c) / BW \times AT$ (mg/kg·d) ..... (5)

where:

ADD is the average daily dose

C_{medium} is the concentration in the contaminated water

IR is the daily intake rate

ED is the exposure duration

F_c, the fraction contaminated

BW is the body weight

AT is the lifetime averaging time

For risk of carcinogens for exposures that last less than lifetime, the dose is adjusted using the formula:

$LADD = ADD \times (ED/Lft)$ ..... . (6)

where:

Lft is lifetime

3.9.1 Non-Cancer toxic effects (Hazard Quotient)

For agents that cause non-cancer effects, a Hazard Quatient (H.Q) was calculated, comparing the expected exposure to the agent to an exposure that is assumed not to be associated with toxic effects. For oral or dermal exposures, the Average Daily Dose (ADD) was compare to a Reference Dose (RfD):

H. Q. = Average Daily Dose / Reference Dose .... (7)

Any Hazard Quotient less than 1 is considered to be safe for a lifetime exposure.

3.9.2 Cancer risks

For chemicals that may cause cancer if ingested, risk is calculated as a function of Oral Slope Factor and was calculated by using the formula:

Risk = Oral Slope Factor * Lifetime Average Daily Dose .....8)

3.9.3 Cross-Media transfer equations used to generate exposure estimates

The formulae used to generate the exposure concentration based on water concentrations was by using the method described by the US-EPA (1990) for water to fish; vegetables; dairy and meat concentrations. Consumption of recreationally caught fish and shellfish-water to edible tissue is presented in equations below:

$$C(f) = BCF * (\frac{fat}{3}) * C(w) \quad \text{..... (9)}$$

$$BCF = [0.79 * \log (Kow)] - 0.40 \quad \text{..... (10)}$$

Where:

C (*f*) = concentration in fish

C (w) = concentration in water

C(sd) = Concentration in Sediment

DN = Sediment Density (Relative to Water Density of 1.0 kg/l) (1.90)

OC = Organic Carbon Fraction of Sediment (4.00%)

Koc = Octanol-Carbon Partition Coefficient of the Compound

Kow = Octanol - Water coefficient of the compound

BCF = Bioconcentration factor

3.9.4 Homegrown fruit and/or vegetables - Water to root (root uptake)

Limitations:not applicable to polar species, where RCF(w) = 0.82

$$C(r) = RCF\ (w) * C(w) \quad \text{..... (11)}$$

$$\log(RCF(w) - 0.82) = (0.77 * \log(Kow)) - 1.52 \quad \text{..... (12)}$$

Where:

C(r) Concentration in root	Calculated
C(w) Concentration in water	Chemical Specific
Proportion in root	100.00%

RCF = Root concentration factor

Kow = Octanol-water partition coefficient of the compound Chemical Specific

3.9.5 Homegrown fruit and/or vegetables - Water to transpiration stream (root uptake)

$$C(st) = TSCF(w) * C(w) \quad \text{.....(13)}$$

$$TSCF(w) = 0.784 \exp -((\text{Log}(Kow) - 1.78) ** 2)/2.44) \quad \text{..... (14)}$$

Where:

C(st) Concentration in Stem	Calculated
C(w) Concentration in Water	Chemical Specific
Proportion in Stem:	100.00%

TSCF = Transpiration Stream Concentration Factor

Kow = Octanol-water partition coefficient of the compound Chemical Specific

3.9.6 Homegrown meat or dairy - Water to edible tissue

Limitations: If either of these conditions occur, BCF = 0, Log Kow < 3.5, Log S > 4 where S is the water solubility of the compound.

$$C(t) = BCF(f) * F * C(w) \quad \text{.....(15)}$$

$$\log(BCF(f)) = -3.457 + 0.5(\log(Kow)) \quad \text{.....(16)}$$

Where:

C(t) = Concentration in edible tissue	calculated
C(w) = Concentration in water	chemical Specific
F = Fat content in tissue (dairy) 4.00%	
F = Fat content in tissue (Meat) 14.00%	
BCF = Bioconcentration factor for tissue fat	chemical specific
Kow = Octanol-water partition coefficient of the compound	chemical Specific

3.9.7 Exposure parameters used to calculate exposure estimates

The dose estimates in this assessment, as well as the risk estimates derived from them, refers only to the specific exposures that have been described in Table 3.5. The average daily dose was calculated taking into account the concentration of the chemicals in water, sediment, for a 70 Kg adult, assuming an intake of 0.054 kg fish on a daily basis (equivalent to 378 g per week). A range of risks is presented making use of average and 95th percentile concentrations of chemicals detected in water, calculated to represent concentrations expected in fish. The 95th percentile represents the "reasonable maximum" risk.

Table 3.5: Exposure parameters used to generate exposure estimates

Exposure parameter	Amount
Events per year	350
Kg fish per day	0.054
Kg dairy	0.4
Kg meat per day	0.1
L water per day	2
Body weight	70 kg
Exposure duration	30 years

CHAPTER FOUR: RESULTS AND DISCUSSION

4.1 Physicochemical parameter assessment

4.1.1 pH

A variety of human activities e.g. agricultural activities, urban and industrial development, mining and recreation, significantly alter the quality of natural waters, and changes the water use potential (Spinks *et al.,* 2006; Madungwe and Sakuringwa, 2007). Water quality may be referred to as a combination of many parameters (e.g. pH, temperature, conductivity etc.) (Fatoki *et al.,* 2001; Fatoki *et al.,* 2003). Water quality degradation world-wide is mainly due to anthropogenic activities which are known to release environmental contaminants into the river and marine ecosystems thereby resulting in adverse effects upon the aquatic ecosystems.

Geology and atmospheric influences determines the pH of natural waters and thus most freshwater within the South Africa are relatively well buffered with ranges between 6 and 8 (Morrison *et al.,* 2001; Igbinosa and Okoh, 2009). pH affects the aquatic ecosystems by determining the chemical species and the potential toxicity and availability in which numerous elements (trace metals, non-metallic elements and essential elements) are found in water (DWAF, 1996). A change in pH from around neutral will result in changes to the water quality and subsequently increase the stresses upon aquatic organisms.

The pH regimes for all the sampling sites in this study is presented in Table 4.1. The pH vary significantly ($P < 0.05$) for some of the sampling sites over the study period and ranged from 6.5 to 7.83 during summer; 6.63 to 8.93 during autum; 6.5 to 7.83 during winter and 6.5 to 7.93 during spring. The pH of the treated effluent ranged from 6.5 (Sites 12 and 24) to 8.03 (Site 16). Generally speaking, the obtained pH values fall within the World Health Organization standard of 7.0 and 8.5 and water quality guideline ranges of 6.5 to 8.5 for drinking water and water meant for full contact for recreation, respectively (DWAF, 1996; WHO, 1984). However, the pH range value of 8.93 obtained at site 10 during autumn exceeded the water quality guidelines but falls within the European Union limit of 6.0 to 9.0 for fisheries and aquatic life (Chapman, 1996). The trend in pH for all the sampling sites indicated that the wastewater treatment plants effluent acted as a dilution factor to lower the river water pH value. The pH values in this study is similar to results reported elsewhere (Morrison *et al.,* 2001; Jaji *et al.,* 2007; Igbinosa and Okoh, 2009).

Table 4.1: Seasonal pH values of water samples

	Summer	Autumn	Winter	Spring
Site 1	7.1	6.9	7.4	7.1
Site 2	N/A	7.16 ± 0.06	7.37 ± 0.1	7
Site 3	7.1	7.3 ± 0.1	7.01 ± 0.6	7.3
Site 4	7.23 ± 0.2	6.63 ± 0.06	6.73 ± 0.07	6.8
Site 5	7.5 ± 0.1	6.77 ± 0.1	7.1 ± 0.1	7.6
Site 6	7.7	7.7	7.5	7.3
Site 7	7.23 ± 0.06	7.93 ± 0.08	7.65 ± 0.16	7.32 ± 0.35
Site 8	7.4	7.4	7.4	6.83 ± 0.06
Site 9	7.6	7.8	7.6	7.2
Site 10	6.83 ± 0.06	**8.93 ± 0.1**	7.7	7.93 ±0.1
Site 11	7.67 ± 0.1	7.63 ± 0.1	7.67 ± 0.1	6.77 ± 0.1
Site 12	6.5	7.17 ± 0.21	6.5	6.87 ± 0.24
Site 13	7.17 ± 0.1	6.8	7	6.67 ± 0.06
Site 14	7.2	7.23 ± 0.08	7.19 ± 0.26	7.13 ± 0.5
Site 15	7.67 ± 0.1	7.6 ± 0.25	7.23 ± 0.1	7.3
Site 16	8.03 ± 0.21	7.5	7.5	7.1
Site 17	7.43 ± 0.25	7.37 ± 0.18	7.07 ± 0.06	7
Site 18	6.9	6.8	6.6	6.9
Site 19	7.6	7.6	7.63 ± 0.33	7.3
Site 20	7	7.2	7.2	6.8
Site 21	7.2	7.17 ± 0.36	7	6.76 ± 0.2
Site 22	7.17 ± 0.2	7.1 ± 0.1	7.23 ± 0.31	6.83 ± 0.21
Site 23	7.2	7.9	7.83 ± 0.14	7.67 ± 0.57
Site 24	7.2	7.19 ± 0.33	7	6.5
Site 25	7.2	7.2	7.43 ± 0.14	7.16 ± 0.49

Mean (±SD); Site 1: Kirstenbosch botanical garden; Site 2: Athlone upstream; Site 3: Athlone influent; Site 4: Athlone effluent; Site 5: Athlone downstream; Site 6: Bellville upstream; Site 7: Bellville influent; Site 8: Bellville effluent; Site 9: Bellville downstream; Site 10: Kraaifontein upstream; Site 11: Kraaifontein influent; Site 12: Kraaifontein effluent; Site 13:Kraaifontein downstream; Site 14: Potsdam upstream; Site 15: Potsdam influent; Site 16: Potsdam effluent; Site 17: Potsdam downstream; Site 18: Stellenbosch upstream; Site 19: Stellenbosch influent; Site 20: Stellenbosch effluent; Site 21: Stellenbosch downstream; Site 22: Zandvliet upstream; Site 23: Zandvliet influent; Site 24: Zandvliet effluent; Site 25: Zandvliet downstream; N/A: Not analyzed.

4.1.2 Electrical conductivity

Conductivity is the ability of a water sample to conduct electrical current and measures the total quantity of total dissolved salts. Electrical conductivity (EC) has been reported to range from as low as 9 μScm^{-1} to as high as 97600 μScm^{-1} in South Africa waterbodies (Dalla and Day, 2004). The electrical conductivity of water samples in this study is presented in Table 4.2. The electrical conductivities profile of the water samples are significantly different ($P < 0.05$) from site to site, especially from upstream to downstream sampling sites. The EC of waterbodies ranged from 410 μScm^{-1} (Site 1, KBG) to 1312.67 ± 11.6 μScm^{-1} (Site 22, Zandvliet upstream) during summer; 436.67 ± 41.63 μScm^{-1} (Site 25, Zandvliet downstream) to 1327 ± 23.22 μScm^{-1} (Site 5, Athlone downstream) during autumn; 390 μScm^{-1} (Site 1, KBG) to 2050.23 ± 45.54 μScm^{-1} (Site 14, Potsdam upstream) during winter and 430 μScm^{-1} (Site 1, KBG) to 2980 ± 45 μScm^{-1} (Site 14, Potsdam upstream) during spring.

The EC profiling showed that the obtained values at the upstream and downstream sites are generally higher than the values obtained at the discharge point i.e. the effluent. The high EC levels at site 14 may be attributed to stormwater, domestic and industrial effluents around the City of Cape Town. According to the Government Gazette (1984), the permissible concentration of EC in effluent that could be released into the receiving waterbodies is 250 μScm^{-1}. On this basis, the effluent quality from all the WWTPs investigated failed to comply with this regulation. The South Africa water quality guideline for conductivity in domestic water supply is 70 µScm-1(DWAF, 1996). This limit was exceeded in the receiving waterbodies and in the effluent samples. The obtained EC values for all the sites gives concern about the domestic suitability of the water. The reported concentrations were significantly higher than values reported elsewhere in the country (Fatoki *et al.*, 2003; Igbinnosa and Oboh, 2009).

4.1.3 Temperature

Temperature plays a significant role in affecting the quality and ecological processes of a river system. It affects not only the physical nature of water bodies by changing the water viscosity, density and surface tension but also affects the rates and types of chemical processes that occur within the systems. Thus, temperature can be used as a first step in predicting the effects of anthropogenic activities on the aquatic ecosystems (Rivers-Moore *et al.*, 2004). Temperature changes can also affect the timing of life cycles, the development of different life stages, predator-prey interactions, genetic selection and the abundance of aquatic algae and plants (king *et al.*, 2003). Generally, increased temperature will reduce the period of fish and other aquatic organisms' survival in a polluted river.

Table 4.2: Seasonal electrical conductivity (μScm^{-1}) values of water samples

	Summer	Autumn	Winter	Spring
Site 1	410	450	390	430
Site 2	N/A	993 ± 14.33	733.33 ± 5.79	1616 ± 11.55
Site 3	1323 ± 5.79	1256.67 ± 9.67	1175.23 ± 16.23	1706.67 ± 32.11
Site 4	1114 ± 34.22	1033 ± 21.33	863.33 ± 5.87	666.67 ± 6.96
Site 5	1290 ± 113.58	1327 ± 23.22	740 ± 20	650 ± 15.49
Site 6	850.76 ± 14.33	820.67 ± 16.77	770 ±	1050 ±
Site 7	795 ± 155.40	953.33 ± 73.12	765 ± 82.16	1293.33 ± 95.01
Site 8	720	760 ± 15.67	720 ± 45.22	1076.67 ± 11.55
Site 9	910	980	820	1130
Site 10	1936.7 ± 73.7	1030 ± 33.33	1140	1266.67 ± 20.81
Site 11	1253.33 ± 5.78	1396.67 ± 5.77	1110	1080
Site 12	1030 ± 5.7	860	790	1140 ± 43.47
Site 13	1290 ± 40	1040	1070	1140 ± 28.42
Site 14	590 ± 20	1230	2050	2980 ± 45
Site 15	1253.33 ± 5.8	923.33 ± 15.27	1150	1400
Site 16	1030 ± 20.82	1030	910	1030
Site 17	1160	1120	1340	2940
Site 18	500	650	750	560
Site 19	803.33 ± 5.85	1110	810	873.33 ± 5.78
Site 20	1030	800 ± 17.32	610	830
Site 21	580	753.33 ± 5.94	630	810
Site 22	1312.67 ± 1.2	1243.33 ± 20.82	1143.33 ± 81.45	1936.67 ± 73.71
Site 23	1041.33 ± 6.7	1060	910	1253.33 ± 5.83
Site 24	1096	686.67 ± 4.97	680	696.67 ± 5.77
Site 25	1110.67 ± 1.2	436.67 ± 41.63	970	1290

Mean (±SD); Site 1: Kirstenbosch botanical garden; Site 2: Athlone upstream; Site 3: Athlone influent; Site 4: Athlone effluent; Site 5: Athlone downstream; Site 6: Bellville upstream; Site 7: Bellville influent; Site 8: Bellville effluent; Site 9: Bellville downstream; Site 10: Kraaifontein upstream; Site 11: Kraaifontein influent; Site 12: Kraaifontein effluent; Site 13:Kraaifontein downstream; Site 14: Potsdam upstream; Site 15: Potsdam influent; Site 16: Potsdam effluent; Site 17: Potsdam downstream; Site 18: Stellenbosch upstream; Site 19: Stellenbosch influent; Site 20: Stellenbosch effluent; Site 21: Stellenbosch downstream; Site 22: Zandvliet upstream; Site 23: Zandvliet influent; Site 24: Zandvliet effluent; Site 25: Zandvliet downstream; N/A: Not analyzed.

The seasonal profile for all the sampling sites is presented in Table 4.3. The water temperature ranged from 19 to 31 °C during summer; 14 to 25 °C during autumn; 9-18 °C during winter and 12-21 °C during the spring. The water temperature was generally lower as againt other seasons, while temperature reached the highest during the summer. Except for the summer, the water temperature was generally below 25 °C, which is the acceptable limit for no risk according to the South African water quality guidelines for domestic use (DWAF, 1995). Aside for sites 4, 8, 20 and 24 during the summer sampling season, the effluent from the WWTPs does not appear to pose any threat to the homeostatic balance of the receiving water bodies. The trend in water temperature reported in this study is similar to findings in a rual community in South Africa and in Nigeria (Jaji *et al.*, 2007; Igbinosa and Okoh, 2009).

4.1.4 Total dissolved solid (TDS)

One of the major descriptions of water quality is the total amount of substances dissolved in it. The natural weathering of rocks by erosion often results in the majority of dissolved particles in most natural water, whilst anthropogenic activities such as domestic and industrial effluent may contribute to the increase level usually observed in freshwater systems. TDS is a general indicator of overall water quality. It is a measure of inorganic and organic materials dissolved in water. High levels of TDS in surface water may be due to several factors, including: sedimentation, mining, or storm water runoff. Increased TDS may impart a bad odor or taste to drinking water, as well as cause scaling of pipes and corrosion. The total dissolved solid (TDS) in this study is presented in Table 4.4. Statistically, the level of total dissolved solid in treated effluent and the receiving waterbodies are significantly different ($P < 0.05$). Also, there was significant difference in the level of TDS between influent and effluent concentration due to the WWTPs treatment processes.

Total dissolved solid in the waterbodies ranged from 200 ± 10 [Site 1, Kirstenbosch Botanical Garden (KBG)] to 973.33 ± 35.12 mgl^{-1} (Kraaifontein upstream) during summer; 200 ± 10 mgl^{-1} (Site 1, KBG) to 623 ± 15.16 mgl^{-1} (Site 5, Athlone downstream) during autumn; 230 ± 15 mgl^{-1} (Site 1) to 1010 mgl^{-1} (Site 14, Potsdam upstream) during winter and 190 ± 25 mgl^{-1} (Site 1, KBG) to 1480 mgl^{-1} (Site 14, Potsdam upstream) during spring. The study showed further that the influent wastewater into the WWTP contains in most cases higher concentration of total dissolved solids than upstreams and downstreams samples. However, effluent from all the WWTPs investigated helped to further dilute the upstream water samples as this is reflected in the concentration of total dissolved solid found downstreams of the WWTPs.

Table 4.3: Seasonal temperature (°C) values of water samples

	Summer	Autumn	Winter	Spring
Site 1	21	17	14	19
Site 2	N/A	24	15	17
Site 3	27	24.5 ± 2.5	18	22
Site 4	27	25	19	20
Site 5	26.67 ± 0.6	22	19	19
Site 6	31 ± 1.41	16	10	18
Site 7	27 ± 1.09	20	18	18 ± 1.09
Site 8	27.33 ± 1.6	17	15	17
Site 9	30	17	9	20
Site 10	23	16	10	21
Site 11	21	18	16	19
Site 12	19	17	17	20
Site 13	24	14	12	19
Site 14	26	15	13	17
Site 15	20	19	16	21
Site 16	25	18	18	19
Site 17	25	18	16	19
Site 18	27	21	15	16
Site 19	27	22	22	19
Site 20	28	21	21	18
Site 21	30	20	20	16
Site 22	27	18	10	15
Site 23	26.67 ± 0.1	20	16	16
Site 24	29	19	16	17
Site 25	27.33 ± 0.6	18	13	12

Mean (±SD); Site 1: Kirstenbosch botanical garden; Site 2: Athlone upstream; Site 3: Athlone influent; Site 4: Athlone effluent; Site 5: Athlone downstream; Site 6: Bellville upstream; Site 7: Bellville influent; Site 8: Bellville effluent; Site 9: Bellville downstream; Site 10: Kraaifontein upstream; Site 11: Kraaifontein influent; Site 12: Kraaifontein effluent; Site 13:Kraaifontein downstream; Site 14: Potsdam upstream; Site 15: Potsdam influent; Site 16: Potsdam effluent; Site 17: Potsdam downstream; Site 18: Stellenbosch upstream; Site 19: Stellenbosch influent; Site 20: Stellenbosch effluent; Site 21: Stellenbosch downstream; Site 22: Zandvliet upstream; Site 23: Zandvliet influent; Site 24: Zandvliet effluent; Site 25: Zandvliet downstream; N/A: Not analyzed.

Table 4.4: Seasonal concentration of total dissolved solids (mgl^{-1}) in water samples

	Summer	Autumn	Winter	Spring
Site 1	200 ± 20	200 ± 10	230 ± 15	190 ± 25
Site 2	N/A	470 ± 20	360	800
Site 3	533.33 ± 37.86	633.33 ± 58.59	863.33 ± 57.7	843.33 ± 16.35
Site 4	**343.33 ± 5.77**	**386.67 ± 5.8**	**560**	**666.67 ± 58.7**
Site 5	623.33 ± 11.78	623.69 ± 15.16	363.43 ± 57.7	650
Site 6	393.33 ± 28.28	403.33 ± 3.37	380 ± 7.07	530
Site 7	435 ± 95.66	470 ± 32.86	583.33 ± 200.17	641.67 ± 45.79
Site 8	**323.33 ± 58.59**	**370**	**533.33 ± 5.8**	**530**
Site 9	400 ± 45.83	480	403.33 ± 57.87	550
Site 10	973.33 ± 35.12	506.67 ± 15.28	560	620
Site 11	663.33 ± 58.59	663.33 ± 58.59	543.33 ± 11.55	530
Site 12	**343.33 ± 5.9**	**393.33 ± 47.26**	**390**	**560**
Site 13	623.33 ± 5.8	446.67 ± 66.58	530	560
Site 14	283.33 ± 5.78	616.67 ± 30.55	1010	1480
Site 15	663.33 ± 58.59	466.67 ± 40.42	570	690
Site 16	**400 ± 26.46**	**383.33 ± 40.42**	**460**	**510**
Site 17	600 ± 24.46	563.33 ± 73.71	660	1450
Site 18	250 ± 30	320	370	270
Site 19	353.33 ± 32.15	550	400	430
Site 20	**273.33 ± 15.28**	**386.67 ± 11.55**	**300**	**410**
Site 21	623.33 ± 58.79	370	310	400
Site 22	683.33 ± 30.55	513.33 ± 25.17	563.33 ± 37.86	973.33 ± 35.12
Site 23	493.32 ± 15.36	456.67 ± 15.34	450	663.33 ±57.8
Site 24	**383.3 ± 30.55**	**360 ±20**	**330**	**343.33 ± 5.86**
Site 25	593.33 ± 35.12	436.67 ± 41.63	480	623.33 ± 51.35

Mean (±SD); Site 1: Kirstenbosch botanical garden; Site 2: Athlone upstream; Site 3: Athlone influent; Site 4: Athlone effluent; Site 5: Athlone downstream; Site 6: Bellville upstream; Site 7: Bellville influent; Site 8: Bellville effluent; Site 9: Bellville downstream; Site 10: Kraaifontein upstream; Site 11: Kraaifontein influent; Site 12: Kraaifontein effluent; Site 13:Kraaifontein downstream; Site 14: Potsdam upstream; Site 15: Potsdam influent; Site 16: Potsdam effluent; Site 17: Potsdam downstream; Site 18: Stellenbosch upstream; Site 19: Stellenbosch influent; Site 20: Stellenbosch effluent; Site 21: Stellenbosch downstream; Site 22: Zandvliet upstream; Site 23: Zandvliet influent; Site 24: Zandvliet effluent; Site 25: Zandvliet downstream; N/A: Not analyzed.

Water samples from the control site (Site 1, KBG) and all the effluent samples from the WWTPs fell within the allowed limits of 0 to 450 mgl^{-1} (DWAF, 1996d). For the river water samples (i.e. upstream and downstream), all the sites except Site 2 (winter), Site 6 (summer, and winter), Site 9 (summer), Site 13 (autumn), Site 14 (summer) Site 18 (all seasons) and Site 19 (summer, winter and spring) exceeded the DWAF (1996d) allowed limit. High concentration of TDS observed upstream of Potsdam WWTP may be due to grey and domestic wastewater from an informal settlement close the river. The trend reported in this study is higher than reported values in literature for a river receiving effluent from a wastewater treatment plant in South Africa and for Ogun river in Nigeria (Jaji *et al.*, 2007; Igbinosa and Okoh, 2009).

4.2 Results of heavy metals in wastewater treatment plants

4.2.1 Occurrence, distribution and removal pattern of heavy metals in wastewater treatment plants

To date, no study had reported on the concentrations of heavy metals and metalloid that are capable of initiating endocrine disruptions in human beings and wildlife (cadmium, arsenic, lead and mercury) in the influent and effluent wastewater from wastewater treatment plants in Western Cape Province. Previous studies have largely concentrated on the water, sediment and plant samples from Diep and Berg rivers (Jackson *et al.*, 2007; Shuping, 2008; Jackson *et al.*, 2009; Ayeni *et al.*, 2010). Despite the fact that the province is one of the provinces with largest number of WWTPs in South Africa, no study have reported on total metals concentration and distribution pattern in wastewater treatment plants. Though a nationwide survey was carried in 1989 and 2002 to assess the levels of heavy metals in sewage sludge from 77 wastewater treatment plants, the country's population had increased and there has been rural-urban migration, thus, pressure on the available WWTPs facilities have increased over the last decade (Jaganyi *et al.*, 2005). Paucity of information on available endocrine disrupting metals, other trace metals and public outcry on poor performance of WWTPs facilities necessitates the need for this study to establish; 1) The occurrence and distribution pattern of endocrine disrupting metals and 2) to access the impact of seasonal changes on EDMs concentration and removal from wastewater effluents.

4.2.1.1 Arsenic

Seasonal variation of arsenic in the Athlone WWTP is shown in Table 4.5, while Figure 4.1 (a) presents the annual distribution pattern in the WWTPs. The percentage removal of arsenic in the treatment plant ranged from 22.14 to 68.44 %. The annual mean removal efficiency of the plant for arsenic was 43.78 % (Figure 4.2). Statistical analysis showed no significant difference ($P>0.05$) in the level of arsenic received at the plant during the studied period. However, it is noteworthy that the plant was not functioning optimally during the second and fourth sampling season. For the studied period, the removal efficiency of the plant could be adjudged ineffective as less than 50 % of the total

arsenic concentration was removed from the waste stream. The annual distribution trend showed that about 20 % of arsenic was removed at the primary settling tank, while secondary settling tank accounted for about 60 % (Figure 4.1). The ineffective removal of arsenic from the Athlone WWTP could be attributed to the plant overload and frequent breakdown of the treatment plant.

The arsenic concentrations in the old and new Bellville plants ranged from 4.62 to 9.2 μgl^{-1} and 6.01 to 43.76 μgl^{-1}, respectively. Effluent concentration ranged from 2.57 to 4.69 μgl^{-1} and 1.12 to 5.10 μgl^{-1} in new and old plants, respectively (Table 4.5). For the two plants, there was significant difference ($P < 0.05$) in seasonal arsenic concentrations. Also, there was significant differences in arsenic concentrations within the plant during summer and autum sampling seasons due to plant treatment processes for old and new plants. The annual distribution pattern of arsenic in the WWTPs is presented in Figures 4.1(b) and (c). The seasonal removal efficiency of the plants ranged from 39.08 to 75.95 % (old plant) and 40.31 to 94.12 % (new plant) (Table 4.5). In the old plant, primary settling tank accounted for about one-quarter percent removal of arsenic on an annual basis while the secondary settling tank removed about 40% of the total arsenic concentration.

The new Bellville plant uses the UCT system with returned activated sludge, raw effluent were pumped straight into the bioreactor with no primary settling tank. Secondary settling tank removed about 75 % of the total concentration of arsenic. The annual mean removal efficiency of these treatment plants (old and new combined) was about 62 % and thus, could be rated above average in performance (Figure 4.2).

Arsenic concentrations at the Kraaifontein WWTP ranged from 4.27 to 8.8 μgl^{-1} in the influent sample and 1.78 to 3.71 μgl^{-1} in the final effluent (Table 4.5). The removal efficiency of the plant increased by 22 % over the sampling seasons (Table 4.1). The annual mean distribution pattern revealed that 25 % of arsenic was removed at the primary settling tank, while 36.8 % was removed at the secondary settling tank (Figure 4.1 (d)). The annual mean removal efficiency of the plant was 55.92 % (Figure 4.2). There was significant difference ($P < 0.05$) in the concentration over season due to the plant treatment process.

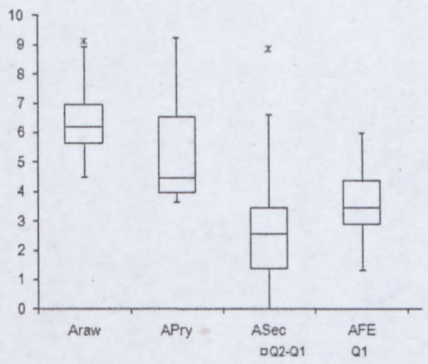
The Potsdam WWTP arsenic concentrations varied between 4.23 to 7.38 μgl^{-1} in raw wastewater and 1.21 to 3.10 μgl^{-1} in the final effluent (Table 4.5). The annual mean with distribution pattern of arsenic is presented in Figure 4.1(e). There was a significant difference ($P < 0.05$) in arsenic levels from one season to the other. The distribution and removal pattern showed that about 28 % of arsenic in the wastewater was removed at the primary settling tank, while about 50 % was removed at secondary settling tank. The annual mean removal efficiency of the plant was 61.07 % (Figure 4.2). This showed that the treatment plant was more effective at arsenic removal compared to the Athlone and Bellville treatment plants.

The Stellenbosch WWTP received a concentration range of 5.07 to 28.20 μgl^{-1} for fourth and first quarter respectively in the influent wastewater, while the final effluent had a concentration range of 2.56 to 2.98 μgl^{-1} (Table 4.5). The seasonal removal efficiency of the plants varied between 45.37

Table 4.5: Mean concentration (±SD) of As in the influent, primary, secondary and final effluent of WWTPs during the different seasons (µgl^{-1}) with removal efficiency.

WWTP	Season	Concentration (µg l^{-1})				$\alpha_{concentration}$	Removal efficiency
		Influent	Primary Effluent	Secondary Effluent	Final Effluent		
Athlone	Summer '10	6.21 ± 0.53	4.07 ± 0.42	2.02 ± 0.38	1.91 ± 1.03	**	68.44
	Autum '10	8.24 ± 0.83	7.99 ± 1.21	6.09 ± 2.42	5.69 ± 0.47		30.93
	Winter '10	6.14 ± 0.33	5.72 ± 1.17	2.83 ± 0.29	2.86 ± 0.29		53.42
	Spring '10	3.95 ± 0.31	3.95 ± 0.31	N/A	3.89 ± 0.19	**	22.14
	α_{season}	*					
Old Bellville	Summer '10	4.62 ± 0.19	4.12 ± 0.48	3.71 ± 0.10	1.12 ± 0.06	**	75.67
	Autum '10	9.35 ± 0.54	3.62 ± 0.02	2.71 ± 0.81	2.25 ± 0.22	**	75.97
	Winter '10	8.38 ± 0.22	8.00 ± 0.34	6.04 ± 0.41	5.10 ± 0.48		39.08
	Spring '10	6.16 ± 1.28	5.97 ± 0.60	4.62 ± 0.79	2.63 ± 0.17		57.35
	α_{season}	*					
New Bellville	Summer '10	6.77 ± 2.36	NPST	4.60 ± 0.77	3.14 ± 1.13		53.67
	Autum '10	43.76 ± 5.06	NPST	3.52 ± 0.20	2.57 ± 0.14	**	94.12
	Winter '10	7.86 ± 0.74	NPST	5.91 ± 0.81	4.69 ±0.90		40.31
	Spring '10	6.01 ± 0.27	NPST	2.19 ± 0.45	2.63 ±0.17		56.33
	α_{season}	*					
Kraaifontein	Summer '10	4.27 ± 0.27	3.32 ± 0.16	2.38 ± 0.16	2.38 ± 0.15	**	44.28
	Autum '10	5.27 ± 0.15	3.93 ± 0.22	2.98 ± 0.65	2.38 ± 0.10		54.87
	Winter '10	8.88 ± 1.10	6.03 ± 0.47	5.16 ± 1.11	3.71 ± 0.31		58.27
	Spring '10	5.27 ± 0.09	4.48 ± 0.47	4.44 ± 0.57	1.78 ± 0.21		66.27
	α_{season}						
Potsdam	Summer '10	4.23 ± 0.16	3.11 ± 0.15	2.23 ± 0.21	1.20 ± 0.12	**	71.52
	Autum '10	7.38 ± 0.10	5.53 ± 0.49	4.24 ±1.08	2.09 ± 0.31	**	71.64
	Winter '10	6.59 ± 0.31	5.08 ± 0.54	3.27 ± 0.23	2.64 ± 0.07		59.96
	Spring '10	5.28 ± 0.21	3.25 ± 0.31	2.00 ± 0.08	3.10 ± 0.09		41.18
	α_{season}	*		*			
Stellenbosch	Summer '10	28.20 ± 3.43	4.20 ± 0.44	2.03 ± 0.07	2.75 ± 0.20	**	90.25
	Autum '10	5.33 ± 2.17	3.26 ± 0.26	3.04 ± 0.21	2.91 ± 0.49		45.37
	Winter '10	6.71 ± 0.47	6.49 ± 0.47	2.34 ± 0.12	2.98 ± 0.05		55.54
	Spring '10	5.07 ± 0.47	2.60 ± 0.55	2.01 ± 0.29	2.56 ± 0.16		49.48
	α_{season}	*					
Zandvliet	Summer '10	4.04 ± 0.38	NPST	3.3 ± 0.1	2.75 ± 0.20	**	42.63
	Autum '10	4.07 ± 0.45	NPST	2.8 ± 0.1	2.6 ± 0.1		35.54
	Winter '10	4.53 ± 0.24	NPST	2.3 ± 0.3	1.6 ± 0.8		62.77
	Spring '10	7.36 ± 0.49	NPST	5.8 ± 1.0	2.56 ± 0.16		66.58
	α_{season}						

NA = Not analysed; NPST = no primary settling tank; $\alpha_{concentration}$ denotes the significance of difference between the stages of WWTP, **: difference is significant at $\alpha = 0.05$; α_{season} denotes the significance of difference of seasonal differences, *: difference is significant at $\alpha = 0.05$.



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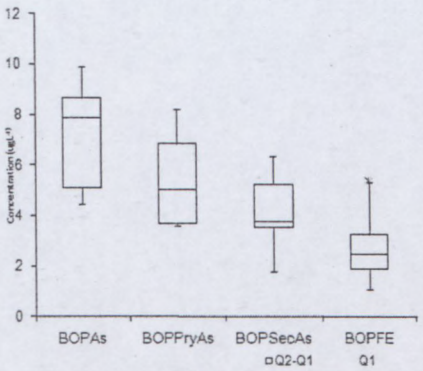

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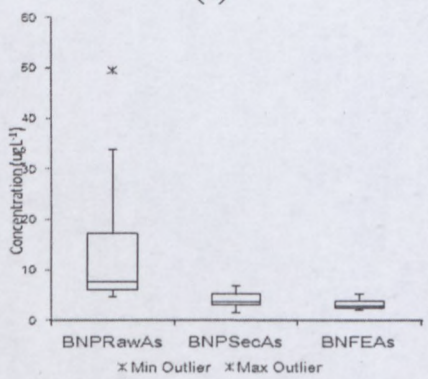

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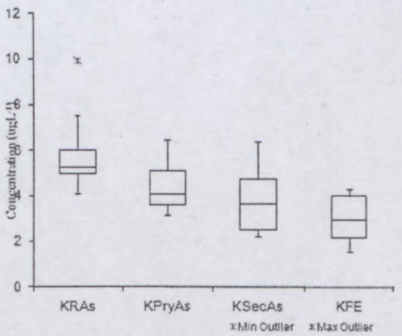

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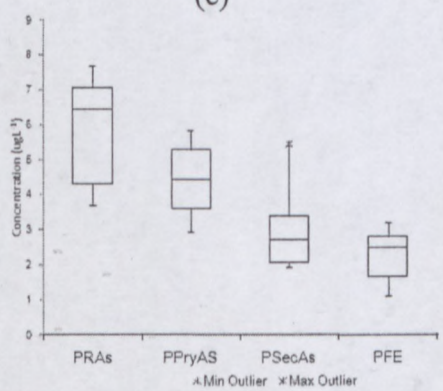

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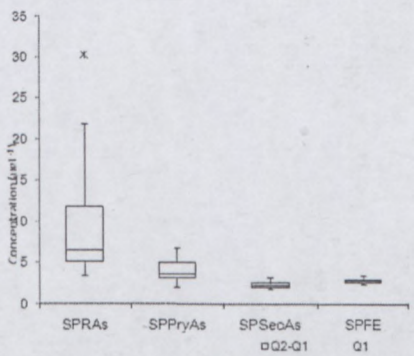

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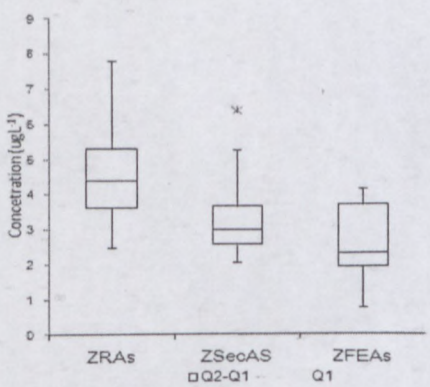


(g)

Figure 4.1
Box and whisker plot for annual spread of arsenic concentrations in WWTP: (a) Athlone WWTP, (b) Old Bellville WWTP, (c) New Bellville WWTP, (d) Kraaifontein WWTP, (e) Potsdam WWTP, (f) Stellenbosch WWTP and (g) Zandvliet WWTP.

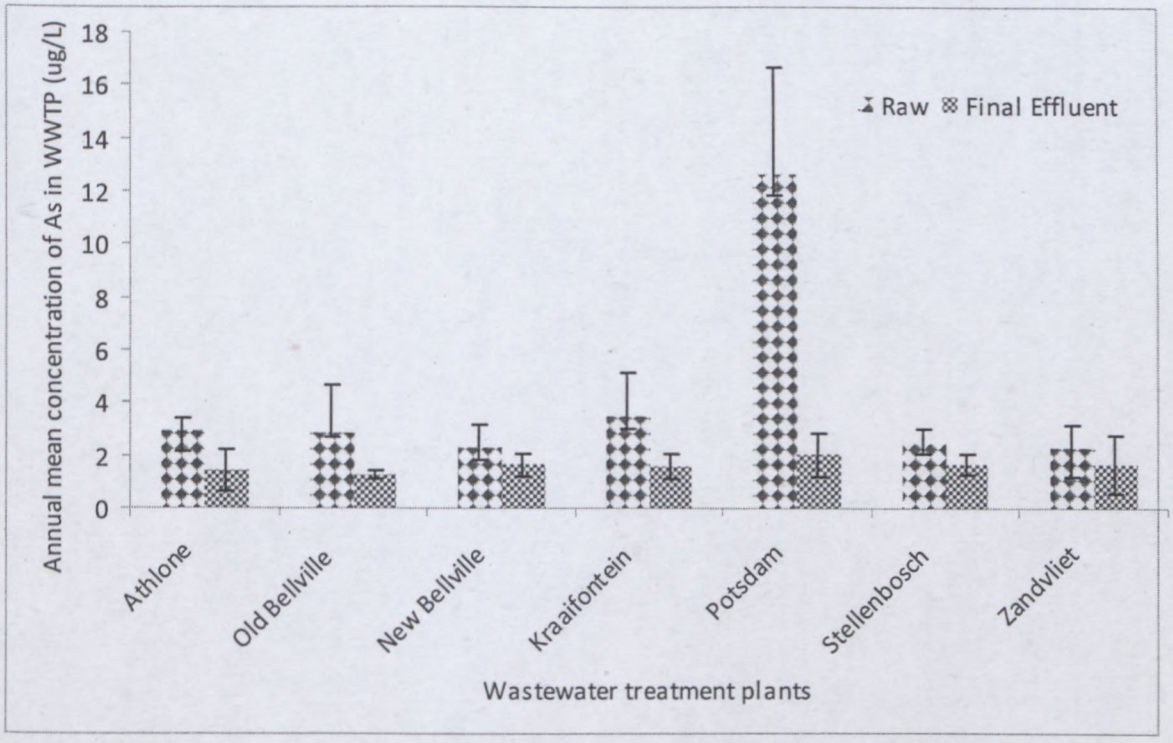


Figure 4.2: Annual mean (±SD) of influent and effluent concentrations of arsenic in WWTPs

to 90.25 % with an annual mean removal efficiency of 60.16 %. There was a significant different in the arsenic concentration into the plant over the study period.

An increase in concentration of arsenic at the Zandvliet WWTP was also observed from 4.04 to 7.36 μgl^{-1} in the influent wastewater, while the final effluent concentration ranged from 1.69 to 2.62 μgl^{-1}. The plant operational pattern is similar to the new Bellville plant. The plant seasonal removal efficiency varied between 35.54 to 66.58 % (Table 4.5). About 30 % of arsenic concentration was removed at the secondary settling tank while the remaining can be accounted for in the wastewater sludge. The annual distribution pattern is presented in Figure 4.1(g). Though over 35 % of arsenic concentration into the plant was removed in the influent wastewater, there was no significant difference ($P > 0.05$) due to plant treatment processes except for the summer season.

4.2.1.2 Cadmium

Cadmium concentrations ranged from 2.21 to 3.38 μgl^{-1} and 0.52 to 2.31 μgl^{-1} in the influent and effluent wastewater of Athlone plant, respectively (Table 4.6). Generally, 65 % of heavy metals in raw waste are believed to be removed at the primary settling tank. This assumption could not hold for cadmium in this plant as overall annual mean removal efficiency for the plant revealed that 25 % of the total Cd influx was removed at the primary settling tank, while about 35 % was taken off the waste stream at the secondary tank. The annual distribution pattern of cadmium in the treatment plant and the annual removal efficiency are presented in Figure 4.3 (a) and Figure 4.4. Based removal

efficiency, the plant could be rated average at cadmium removal. There was no significant difference in the influent cadmium concentration in the plant over the study period.

The influent concentration of cadmium at the old Bellville plant varied between 1.53 and 5.52 μgl^{-1}, while the new plant concentration varied between 1.64 and 3.55 μgl^{-1}. The final effluent concentration ranged from 1.42 to 2.24 μgl^{-1} and 1.07 to 1.36 μgl^{-1} for new and old plant, respectively (Table 4.6). The annual distribution pattern of cadmium in the two plants presented in Figures 4.3 (b) and (c) indicated that 18.8% of cadmium concentration was removed at the old Bellville plant primary settling tank, while 28.9 % and 25.22 % were removed at the secondary settling tanks of old and new plants, respectively. The annual mean percentage removal was 44.88 % and 24.61 % for old and new plants (Figure 4.4). For new plant, with the exception of the summer season, no significant difference ($P > 0.05$) in cadmium concentration occurred over the study period or between the influent and effluent concentration.

The Kraaifontein plant received an influent concentrations range of 1.85 to 8.88 μgl^{-1} and released effluent concentration range of 1.25 to 2.29 μgl^{-1} (Table 4.6). The removal efficiency of the treatment plant varied between 7.68 to 74.97 % with an annual mean of 45.22 % (Figure 4.4). The annual distribution pattern presented in Figure 4.3(d) revealed that 36.2 and 30.1 % of total cadmium concentration were removed at primary and secondary settling tanks respectively. The annual mean removal efficiency showed that the plant was below average for removing cadmium.

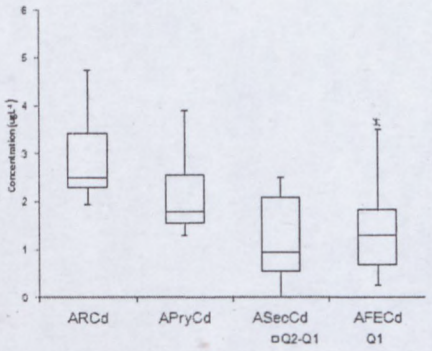
Cadmium concentration into Potsdam plant varied between 8.67 and 17.39 μgl^{-1} with an annual mean of 12.62 μgl^{-1}, while the effluent concentration varied between 1.33 to 2.85 with annual mean of 2.02 μgl^{-1} (Table 4.6). The distribution of cadmium in the plant (Figure 4.3 (e)) showed that 45.2 % and 36.02 % was removed from waste stream at the primary and secondary settling tanks, respectively. The annual mean removal efficiency was 82.58 % (Figure 4.4). The high concentration of cadmium in the waste could be due to high industrial effluent received at the plant. There was significant difference in cadmium concentration over the sampling seasons and in the concentration due to treatment processes during summer.

The Stellenbosch plant received a concentration range of 1.68 to 2.96 μgl^{-1} with annual mean concentration of 2.45 μgl^{-1}, while cadmium concentration in the final effluent ranged from 1.29 to 2.23 μgl^{-1} with annual mean of 1.65 μgl^{-1} (Table 4.6). The annual distribution pattern in the Stellenbosch plant presented in Figure 4.3 (f) showed that about 25 % was removed at the primary settling tank, while 4.9% was removed at the secondary settling tank. The annual mean removal efficiency was 29.17 % (Figure 4.4). There was no significant difference ($P > 0.05$) due to seasonal change; however, there was significant difference ($P < 0.05$) due to treatment plant processes during the summer.

Table 4.6: Mean concentration (±SD) of Cd in the influent, primary, secondary and final effluent of WWTPs during the different seasons ($\mu g l^{-1}$) with removal efficiency.

WWTP	Season	Concentration ($\mu g\ l^{-1}$)				$\alpha_{concentration}$	Removal efficiency
		Influent	Primary Effluent	Seconfary Effluent	Final Effluent		
Athlone	Summer '10	2.94 ± 0.31	1.35 ± 0.04	0.86 ± 0.15	1.01 ± 0.51		65.61
	Autum '10	3.09 ± 0.69	2.64 ± 1.01	2.06 ± 0.5	1.80 ± 0.13		32.43
	Winter '10	2.21 ± 1.10	1.86 ± 0.42	1.71 ± 0.76	0.52 ± 0.23		74.97
	Spring '10	3.38 ± 0.1	2.91 ± 1.16	N/A	2.31 ± 1.27		7.68
	α_{season}						
Old Bellville	Summer '10	2.40 ± 0.26	1.74 ± 0.04	1.07 ± 0.15	1.07 ± 0.5		55.44
	Autum '10	5.52 ± 0.69	4.10 ± 1.01	2.45 ± 0.49	1.36 ± 0.13		41.86
	Winter '10	1.53 ± 0.24	1.50 ± 0.43	0.69 ± 0.76	1.25 ± 0.24		18.08
	Spring '10	2.05 ± 0.54	1.97 ± 0.51	1.91 ± 0.38	1.42 ± 0.37		30.59
	α_{season}						
New Bellville	Summer '10	1.64 ± 0.05	NPST	1.33 ± 0.25	1.18 ± 0.17	**	28.16
	Autum '10	3.55 ± 0.87	NPST	3.36 ± 1.69	2.24 ± 0.23		36.81
	Winter '10	1.68 ± 0.33	NPST	0.74 ± 0.24	1.64 ± 0.96		2.38
	Spring '10	2.23 ± 0.98	NPST	1.31 ± 0.18	1.42 ± 0.38		36.11
	α_{season}			*			
Kraaifontein	Summer '10	4.57 ± 0.31	2.69 ± 0.19	N/A	1.56 ± 0.9	**	65.78
	Autum '10	1.85 ± 0.05	1.54 ± 0.23	1.27 ± 0.24	1.25 ± 0.10		32.43
	Winter '10	8.88 ± 1.10	6.03 ± 0.47	1.71 ± 0.46	1.28 ± 0.72		74.97
	Spring '10	2.48 ± 0.1	2.43 ± 0.41	1.65 ± 0.25	2.29 ± 0.49		7.68
	α_{season}	*	*				
Potsdam	Summer '10	17.39± 0.55	4.49 ± 0.24	1.64 ± 0.91	1.33 ± 0.9	**	92.33
	Autum '10	14.53± 5.10	12.14 ± 0.37	3.08 ± 1.19	2.57 ± 0.59		82.29
	Winter '10	8.67± 1.62	4.91 ± 0.12	1.97 ± 0.62	1.35 ± 0.18		84.47
	Spring '10	9.89± 1.35	6.15 ± 1.50	2.44 ± 0.15	2.85 ± 0.53		71.24
	α_{season}	*					
Stellenbosch	Summer '10	2.96 ± 0.46	1.31 ± 0.29	0.96 ± 0.11	1.29 ± 0.36	**	56.33
	Autum '10	2.54 ± 0.57	1.57 ± 0.26	2.46 ± 0.62	2.23 ± 1.16		12.34
	Winter '10	1.68 ± 0.52	2.33 ± 1.35	1.61 ± 0.31	1.61 ± 1.16		4.17
	Spring '10	2.62 ± 1.33	2.42 ± 0.58	2.13 ± 0.58	1.47 ± 0.51		43.86
	α_{season}						
Zandvliet	Summer '10	2.32 ± 0.23	NPST	0.84 ± 0.20	1.17 ± 0.15		49.62
	Autum '10	3.10 ± 0.54	NPST	2.17 ± 0.59	2.53 ± 0.43		18.39
	Winter '10	1.07 ± 0.17	NPST	1.05 ± 0.45	0.53 ± 0.08		50.78
	Spring '10	3.22 ± 0.38	NPST	1.96 ± 0.45	1.95 ± 0.65		39.62
	α_{season}						

NA = Not analysed; NPST = no primary settling tank; $\alpha_{concentration}$ denotes the significance of difference between the stages of WWTP, **: difference is significant at $\alpha = 0.05$; α_{season} denotes the significance of difference of seasonal differences, *: difference is significant at $\alpha = 0.05$.



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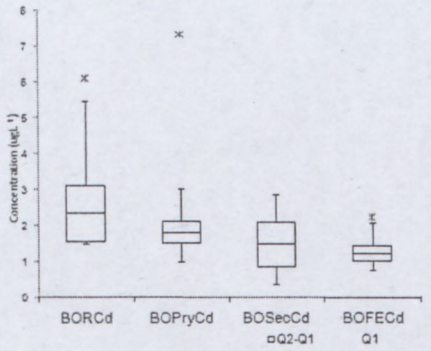

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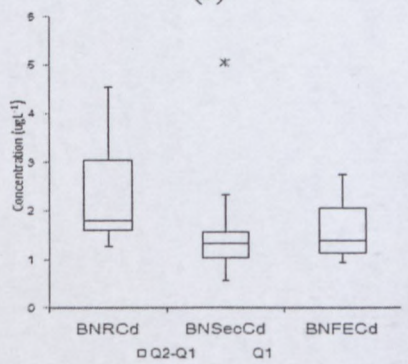

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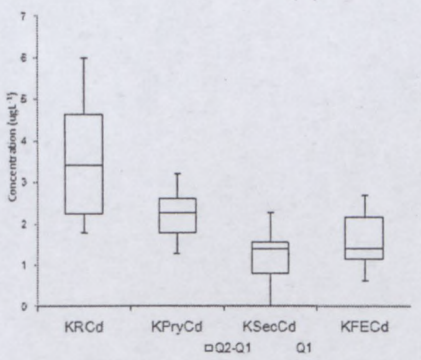

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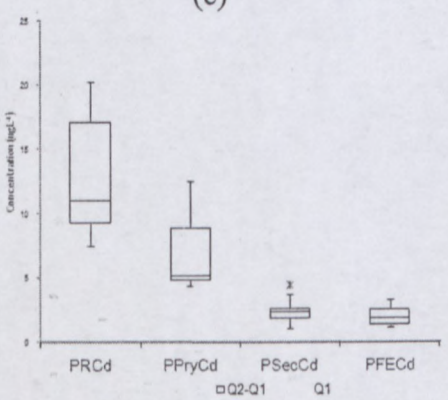

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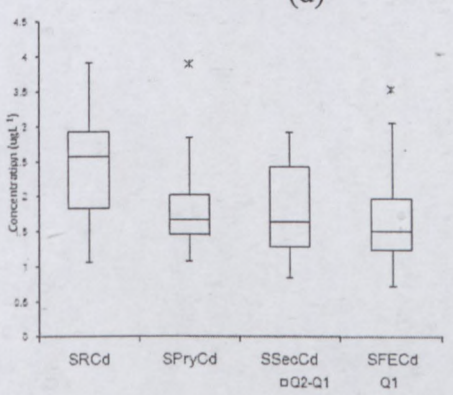

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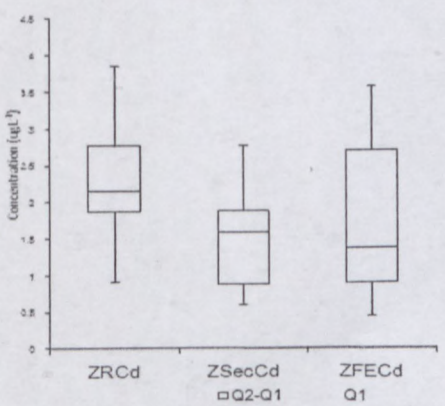


(g)

Figure 4.3

Box and whisker plot for annual spread of Cd concentrations in WWTP: (a) Athlone WWTP, (b) Old Bellville WWTP, (c) New Bellville WWTP, (d) Kraaifontein WWTP, (e) Potsdam WWTP, (f) Stellenbosch WWTP and (g) Zandvliet WWTP.

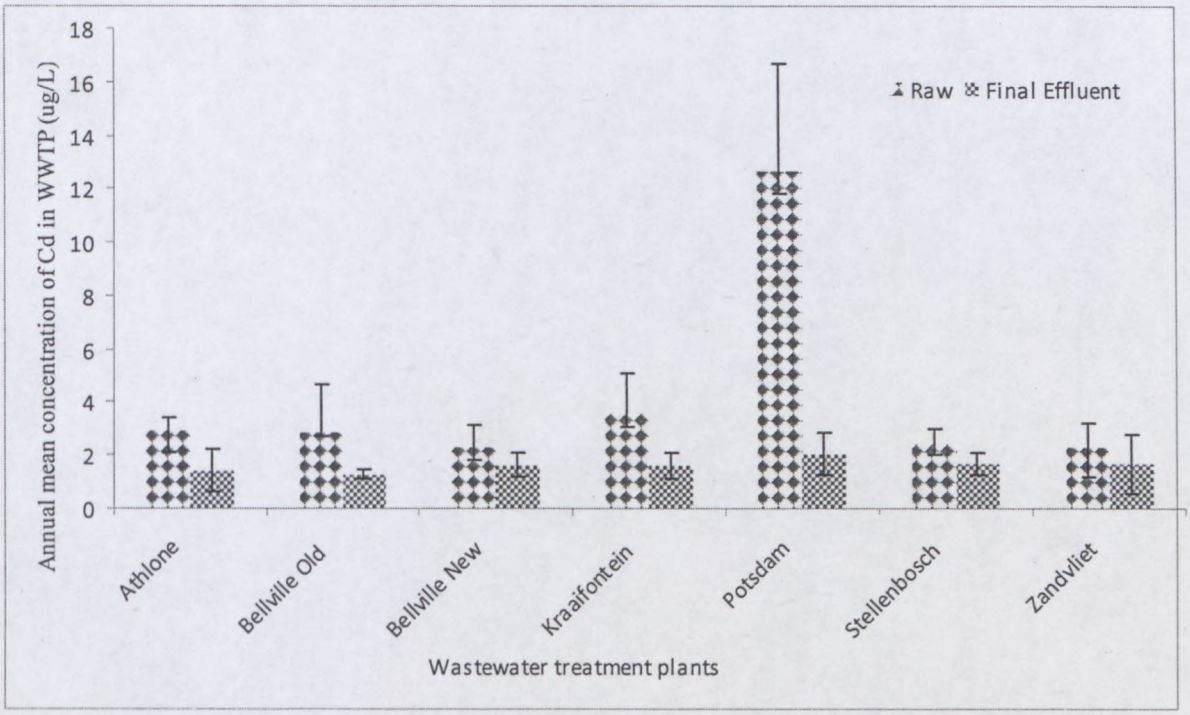


Figure 4.4: Annual mean (±SD) of influent and effluent concentrations of cadmium in WWTPs

Zandvliet concentration was in the range of 1.07 to 3.10 μgl^{-1} with annual mean influent of 2.43 μgl^{-1}. The final effluent concentration ranged from 0.53 to 2.53 μgl^{-1} (Table 4.6). The annual distribution pattern for cadmium in the treatment plant revealed that 34% and 7 % of cadmium in the wastewater was removed into primary and secondary sludge's, respectively (Figure 4.3 (g)). The annual mean percentage efficiency for plant shows that less than 40 % of total cadmium concentration was removed from the waste stream (Figure 4.4).

4.2.1.3 Lead

The Athlone WWTP Pb influent concentrations ranged from 49.61 to 81.89 μgl^{-1} and 20.40 to 30.31 μgl^{-1} in the final effleunt (Table 4.7). Pb removal in the influent waste was above average for all the seasons except for the spring. Influent annual mean was 64.46 % while annual mean in final effleunt was 26.57 μgl^{-1}. The annual distribution pattern of Pb in the plant is presented in Figure 4.5 (a). 47.07 % of total Pb conecntration was removed at the primary settling tank into the primary sludge while about 22 % was trapped into the secondary sludge through the secondary sedimentation tank. The annual mean removal efficiency of the plant was 57.19 % (Figure 4.6). There was no significant difference due influent concentration over the study period, but, there was significant difference during the summer sampling season due to plant treatment process between the influent and effluent concentration.

The concentration into the old Bellville plant ranged between 29.88 and 138.35 μgl^{-1} with an annual mean of 86.32 μgl^{-1}, while the effluent concentration varied from 15.03 to 37.29 μgl^{-1} with an annual mean of 22.84 μgl^{-1} (Table 4.7). The seasonal removal efficiency ranged from 36.45 to

84.23 %. The annual spread of the Pb revealed that 58 % of total annual concentration was removed at the primary settling tank and about 20 % was removed at the secondary sedimentation tank (Figure 4.5). The annual removal efficiency of the plant was 67.30 % (Figure 4.6).

For the new plant, influent concentrations ranged from 23.66 to 282.59 μgl^{-1} with annual mean of 102.20 μgl^{-1} (Table 4.7). The final effluent cocnentrations ranged between 18.99 and 20.94 μgl^{-1}, while about 77.29% of total influx trapped into the secondary sludge (Figure 4.11). The annual mean removal efficiency of the plant was 57 % (Figure 4.6). There was seasonal significant difference due to influent concentration into the two plants. However, significant difference was only observed during summer for old plant and during summer and winter for the new plant due to the plants treatment processes.

Concentration of Pb into Kraaifontein ranged from 31.5 to 78.6 μgl^{-1} with final effluent concentration range of 9.49 to 38.66 (Table 4.7). The annual distribution pattern of Pb in the plant is presented in Figure 4.5 (d). 42.69 % of Pb was removed through the primary sludge while 23.45 % was eliminated in the waste stream through sludge re-circulation. The annual plant removal efficiency was 55 % (Figure 4.6). There was significant difference during the summer due to plant treatment process. There was no significant difference in the influent concentration but there was significant difference between the influent and effluent concentration due to plant treatment processes.

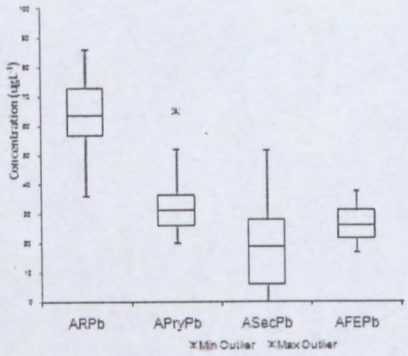
Potsdam received Pb concentration range of 36.5 to 77.2 μgl^{-1} and released a concentration range of 7.5 to 27.4 μgl^{-1} (Table 4.7). The annual mean of influent concentration was 60.58 μgl^{-1}, while the annual mean final effluent concentration was 19.27 μgl^{-1}. The annual distribution in the plant shows that 42.69 and 23.13 % of total annual influx was removed at the primary and secondary settling tanks, respectively (Figure 4.5 (e)). There was no significant difference in the influent concentration but there was significant difference between the influent and effluent concentration due to plant treatment processes.

The annual mean concentration into the Stellenbosch and Zandvliet plants was 64.88 μgl^{-1} and 34.93 μgl^{-1}. The annual spread pattern for Stellenbosch (Figure 4.5 (f)) and Zandvliet (Figure 4.5 (g)) showed that 34.28 and 22.30 % of Pb was removed at the primary and secondary tanks of Stellenbosch while 25.02 % was trapped into secondary sludge and the un-trapped was retuned in the re-circulated sludge. The annual percentage removals of Pb at the plants were 57.03 and 47 % for Stellenbosch and Zandvliet plant (Figure 4.6). There was significant difference in the

Table 4.7: Mean concentration (±SD) of Pb in the influent, primary, secondary and final effluent of WWTPs during the different seasons ($\mu g l^{-1}$) with removal efficiency.

WWTP	Season	Concentration ($\mu g\ l^{-1}$)				$\alpha_{concentration}$	Removal efficiency
		Influent	PrimaryEffluent	Secondary Effluent	Final Effluent		
Athlone	Summer '10	81.89 ± 4.2	22.7 ± 3.7	10.3 ± 4.0	28.9 ± 5.9	**	64.75
	Autum '10	61.5 ± 8.8	28.9 ± 4.8	23.9 ± 1.1	26.7 ± 9.2		56.58
	Winter '10	64.8 ± 5.4	52.2 ± 15.0	43.2 ± 7.6	20.4 ± 1.4		68.52
	Spring '10	49.6 ± 11.6	32.6 ± 5.9	N/A	30.3 ± 7.2		38.89
	α_{season}						
Bellville old	Summer '10	138.35 ± 5.8	30.0 ± 1.6	14.9 ± 6.7	37.29 ± 2.4	**	73.1
	Autum '10	81.8 ± 23.4	57.9 ± 16.4	21.3 ± 5.1	20.0 ± 1.9		75.5
	Winter '10	95.3 ± 2.2	26.1 ± 5.1	19.2 ± 8.9	15.03 ± 5.0		84.2
	Spring '10	29.88 ± 4.3	27.9 ± 4.3	23.5 ± 7.4	18.9 ± 1.4		36.5
	α_{season}	*					
Bellville new	Summer '10	65.9 ± 12.7	NPST	48.1 ± 13.2	20.7 ± 4.7	**	68.7
	Autum '10	282.59 ± 21.6	NPST	21.4 ± 7.8	20.9 ± 0.2	**	92.6
	Winter '10	36.7 ± 3.2	NPST	12.6 ± 4.6	20.2 ± 0.4		44.9
	Spring '10	23.66 ± 2.7	NPST	18.9 ± 2.3	18.9 ±1.4		19.7
	α_{season}	*					
Kraaifontein	Summer '10	31.5 ± 15.2	12.0 ± 2.6	N/A	9.49 ± 2.5	**	69.8
	Autum '10	78.6 ± 59.0	73.4 ± 15.0	51.1 ± 17.9	38.66 ± 2.9		50.8
	Winter '10	52.8 ± 4.6	36.3 ± 12.3	35.1 ± 3.4	29.2 ± 5.3		44.7
	Spring '10	44.5 ± 3.8	32.8 ± 4.3	25.9 ± 9.3	19.6 ± 2.9		55.9
	α_{season}						
Potsdam	Summer '10	62.9 ± 1.7	28.8 ± 0.5	17.7 ± 1.6	7.5 ± 0.6	**	88.1
	Autum '10	77.2 ± 1.8	46.2 ± 4.3	24.4 ± 0.4	27.4 ± 2.2		64.5
	Winter '10	65.6 ± 2.6	37.8 ± 7.7	21.5 ± 3.9	17.2 ± 2.7		73.8
	Spring '10	36.5 ± 1.2	26.1 ± 0.8	19.2 ± 1.4	24.9 ± 1.5		31.8
	α_{season}						
Stellenbosch	Summer '10	72.5 ± 8.9	13.7 ± 1.7	14.6 ± 0.4	14.3 ± 0.1	**	80.3
	Autum '10	102.9 ± 8.2	83.4 ± 4.5	49.5 ± 32.4	40.8 ± 18.2		60.4
	Winter '10	56.8 ± 15.6	51.5 ± 12.8	29.9 ± 4.8	25.5 ± 4.7		55.2
	Spring '10	27.2 ± 4.8	21.9 ± 5.4	18.7 ± 2.6	18.5 ± 3.6		32.2
	α_{season}	*					
Zandvliet	Summer '10	45.7 ± 2.3	NPST	33.9 ± 6.2	15.4 ± 3.0	**	66.4
	Autum '10	42.7 ± 1.6	NPST	31.3 ± 19.1	25.7 ± 4.9		39.9
	Winter '10	18.3 ± 2.0	NPST	13.9 ± 1.3	11.5 ± 3.9		37.1
	Spring '10	32.9 ± 16.9	NPST	11.5 ± 3.9	17.9 ± 3.3		45.5
	α_{season}						

NA = Not analysed; NPST = no primary settling tank; $\alpha_{concentration}$ denotes the significance of difference between the stages of WWTP, **: difference is significant at $\alpha = 0.05$; α_{season} denotes the significance of difference of seasonal differences, *: difference is significant at $\alpha = 0.05$.



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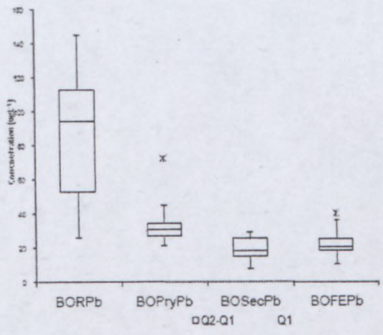

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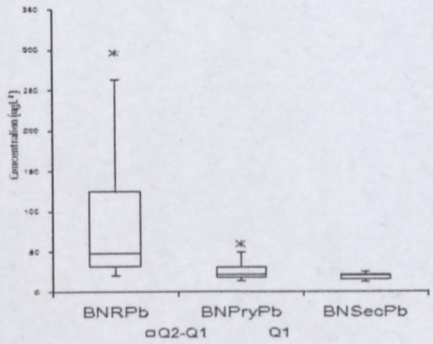

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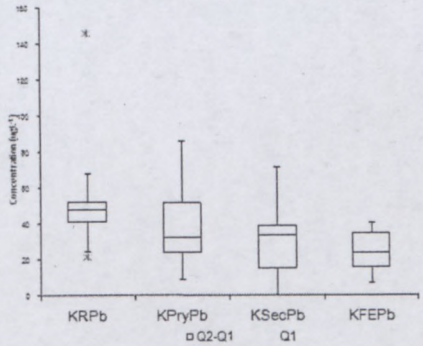

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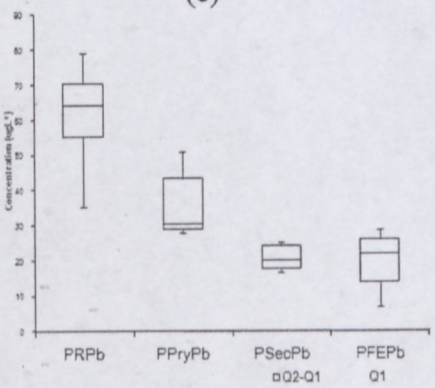

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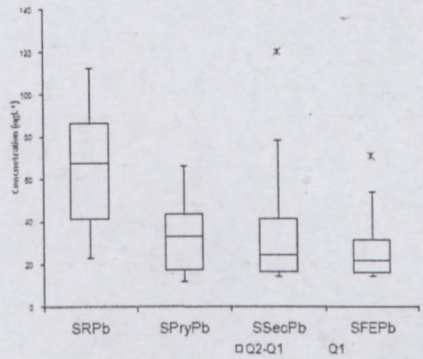

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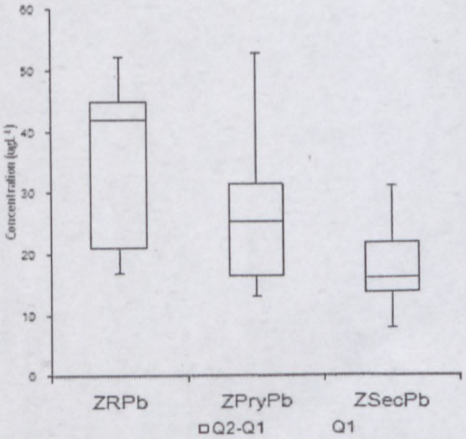


(g)

Figure 4.5

Box and whisker plot for the annual spread of lead concentrations in WWTP: (a) Athlone, (b) Old Bellville WWTP, (c) New Bellville WWTP, (d) Kraaifontein WWTP, (e) Potsdam WWTP, (f) Stellenbosch WWTP and (g) Zandvliet WWTP.

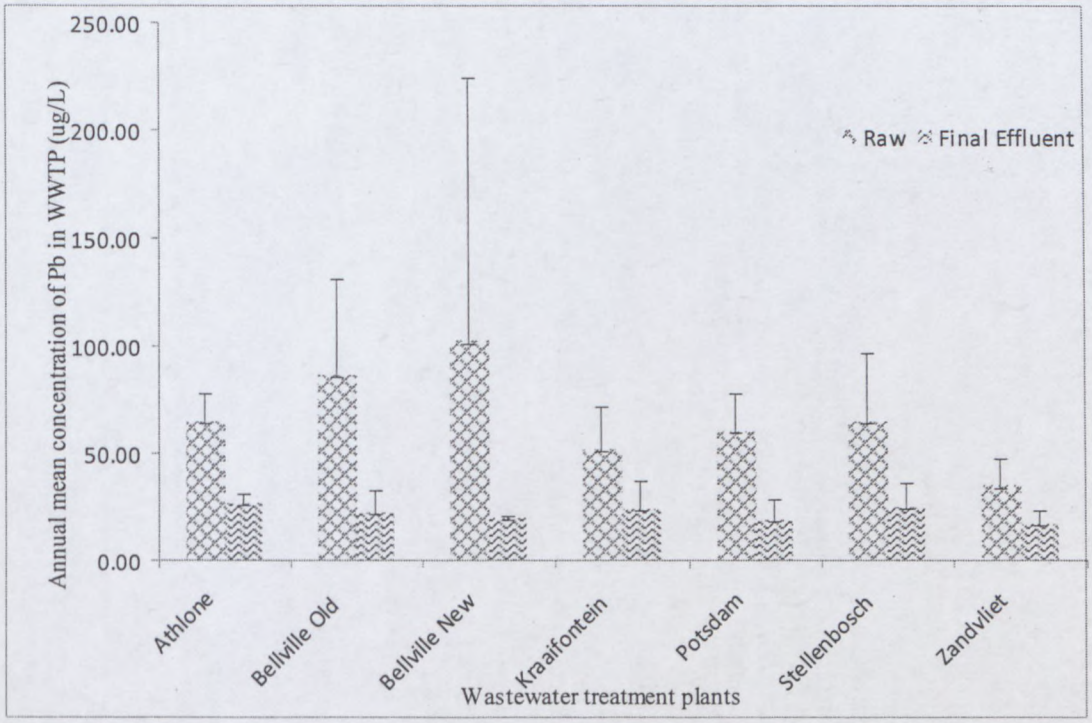


Figure 4.7: Annual mean (± SD) of influent and effluent concentration of lead in WWTPs

influent concentration at Stellenbosch plant but there was no significant difference for Zandvliet over the study period. The two plants had significant difference between the influent and effluent concentration due to plant treatment processes during the summer season.

4.2.1.4 Mercury

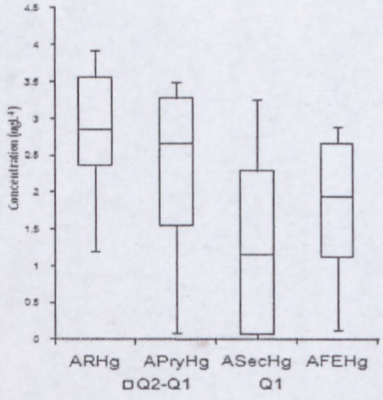
Mercury concentration in raw water into Athlone ranged from 2.20 to 3.34 μgl^{-1}, while in final effluent, it concentration ranged from 0.19 to 2.57 μgl^{-1} (Table 4.8). Percentage removal of mercury in the treatment plant ranged from 23.01 to 91.46 % while the annual mean influent, annual mean effluent and percentage removal were 2.82 μgl^{-1}, 1.74 μgl^{-1} and 41.93 % respectively.19.86 and 34.04 % of Hg was removed at the plant during the primary and secondary settling period (Figure 4.7 (a)) with annual removal efficiency of 41.93 % (Figure 4.8).There was no significant at the plant either due to seasonal difference or due to plant treatment process.

Concentration of mercury into Bellville treatment plants ranged from 1.77 to 3.74 μgl^{-1} for the old plant and 0.84 to 2.92 μgl^{-1} for the new plant. The effluent concentration varied between 0.38 and 1.90 μgl^{-1} in old plant and from 0.17 to 2.61 μgl^{-1} in the new plant. The annual mean influent concentration was 2.69 and 2.01 μgl^{-1} while mean annual effluent concentration was 1.22 and 1.40 μgl^{-1} for the old and new plant, respectively (Table 4.8). The annual distribution pattern and removal efficiency are presented in Figure 4.7 (b) and (c) and Figure 4.8. 17.91 % of the total Hg concentration was removed at the secondary settling tank into secondary sludge in the new plant, while 59.65 and 16.72 % were trapped into primary and secondary sludge of the old treatment plant. Significant difference observed was due to concentration change arising from the treatment process.

Table 4.8: Mean concentration (±SD) of Hg in the influent, primary, secondary and final effluent of WWTPs during the different seasons ($\mu g l^{-1}$) with removal efficiency.

WWTP	Season	Concentration ($\mu g l^{-1}$)				$\alpha_{concentration}$	Removal efficiency
		Influent	Primary Effluent	Secondary Effluent	Final Effluent		
Athlone	Summer '10	2.2 ± 1.2	0.4 ± 0.3	0.3 ± 0.2	0.19 ± 0.1		91.5
	Autum '10	3.2 ± 0.7	3.2 ± 0.3	2.9 ± 0.4	2.3 ± 0.8		26.5
	Winter '10	2.6 ± 0.4	2.2 ± 0.4	1.9 ± 0.2	1.9 ± 0.1		26.7
	Spring '10	3.3 ± 0.5	3.3± 0.3	N/A	2.27 ± 0.2		23.0
	α_{season}						
Old Bellville	Summer '10	1.77 ± 0.9	0.8 ± 0.3	0.1 ± 0.1	0.38 ± 0.1		78.9
	Autum '10	3.74 ± 2.0	1.4 ± 0.3	1.1 ± 0.1	0.7 ± 0.3		81.5
	Winter '10	2.6 ± 0.2	2.5 ± 0.3	2.2 ± 0.2	1.9 ± 0.1		25.4
	Spring '10	2.7 ± 0.6	2.7 ± 0.6	2.5 ± 0.3	2.2 ± 0.1		29.9
	α_{season}			*			
New Bellville	Summer '10	0.84 ± 0.3	NPST	0.3 ± 0.2	0.17		80.05
	Autum '10	1.5 ± 0.4	NPST	1.4 ± 0.6	0.8		47.8
	Winter '10	2.7 ± 0.3	NPST	2.2 ± 0.3	2.0 ± 0.2		26.3
	Spring '10	2.92 ± 0.9	NPST	2.6 ± 1.4	2.6 ± 0.1		10.6
	α_{season}	*					
Kraaifontein	Summer '10	0.6± 0.03	0.3± 0.1	N/A	0.1± 0.03		88.1
	Autum '10	1.5± 0.2	0.9± 0.1	0.8± 0.2	0.7± 0.1		50.4
	Winter '10	2.7± 0.3	2.4± 0.5	2.2± 0.7	1.8± 0.6		33.1
	Spring '10	4.0± 0.7	3.9± 0.7	3.9± 0.7	3.2± 0.1		20.9
	α_{season}	*	*	*	*		
Potsdam	Summer '10	0.8 ± 0.3	0.3 ± 0.1	0.1 ± 0.04	0.1 ± 0.1		87.3
	Autum '10	14.5 ± 5.1	12.1 ± 0.4	3.1 ± 1.2	1.5 ± 0.5		90.0
	Winter '10	2.6 ± 0.1	2.2 ± 0.1	2.1 ± 0.3	1.8 ± 0.2		30.7
	Spring '10	4.2 ± 0.5	4.4 ± 0.7	4.1 ± 0.6	3.9 ± 0.3		7.9
	α_{season}	*	*	*	*		
Stellenbosch	Summer '10	0.6 ± 0.02	0.5 ± 0.1	0.1 ± 0.03	0.3 ± 0.03		61.3
	Autum '10	3.0 ± 0.7	1.4 ± 0.2	1.4 ± 0.5	1.0 ± 0.5		65.2
	Winter '10	3.8 ± 1.1	2.2 ± 0.1	1.8 ± 0.3	1.4 ± 0.1		63.3
	Spring '10	4.3 ± 0.7	4.0 ± 0.2	3.7 ± 0.3	3.6 ± 0.8		15.7
	α_{season}						
Zandvliet	Summer '10	0.7 ± 0.1	NPST	0.3 ± 0.1	0.2 ± 0.02		77.60
	Autum '10	1.8 ± 0.3	NPST	1.4 ± 0.03	1.3 ± 0.2		29.48
	Winter '10	1.57 ± 0.1	NPST	1.56 ± 0.1	1.55 ± 0.03		1.5
	Spring '10	3.9 ± 1.2	NPST	3.0 ± 0.4	2.9 ± 0.7		25.1
	α_{season}	*		*	*		

NA = Not analysed; NPST = no primary settling tank; $\alpha_{concentration}$ denotes the significance of difference between the stages of WWTP, **: difference is significant at $\alpha = 0.05$; α_{season} denotes the significance of difference of seasonal differences, *: difference is significant at $\alpha = 0.05$.



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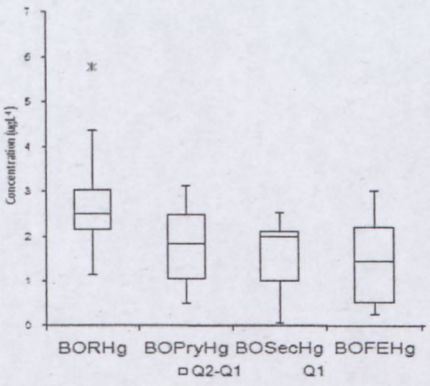

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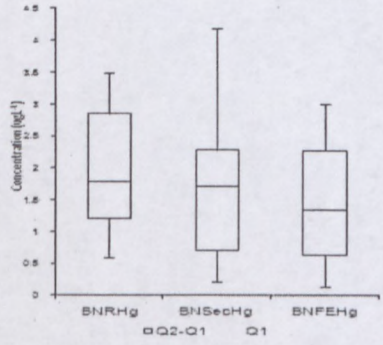

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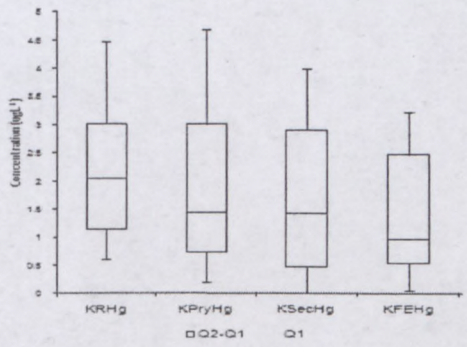

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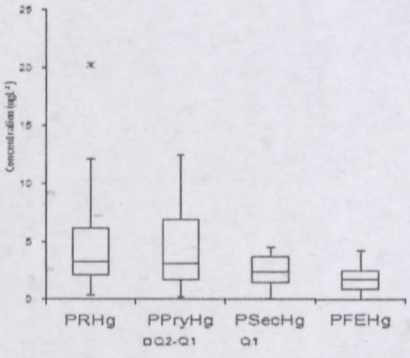

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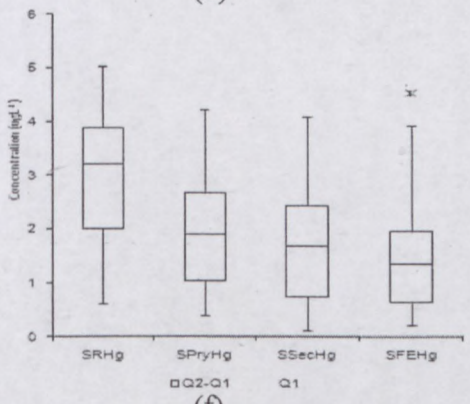

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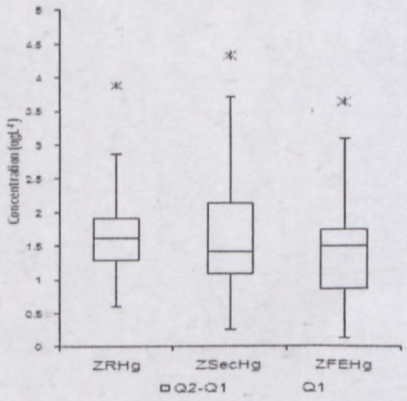


(g)

Figure 4.7

Box and whisker plot for the annual spread of mercury concentrations in WWTP: (a) Athlone WWTP, (b) Old Bellville WWTP, (c) New Bellville WWTP, (d) Kraaifontein WWTP, (e) Potsdam WWTP, (f) Stellenbosch WWTP and (g) Zandvliet WWTP.

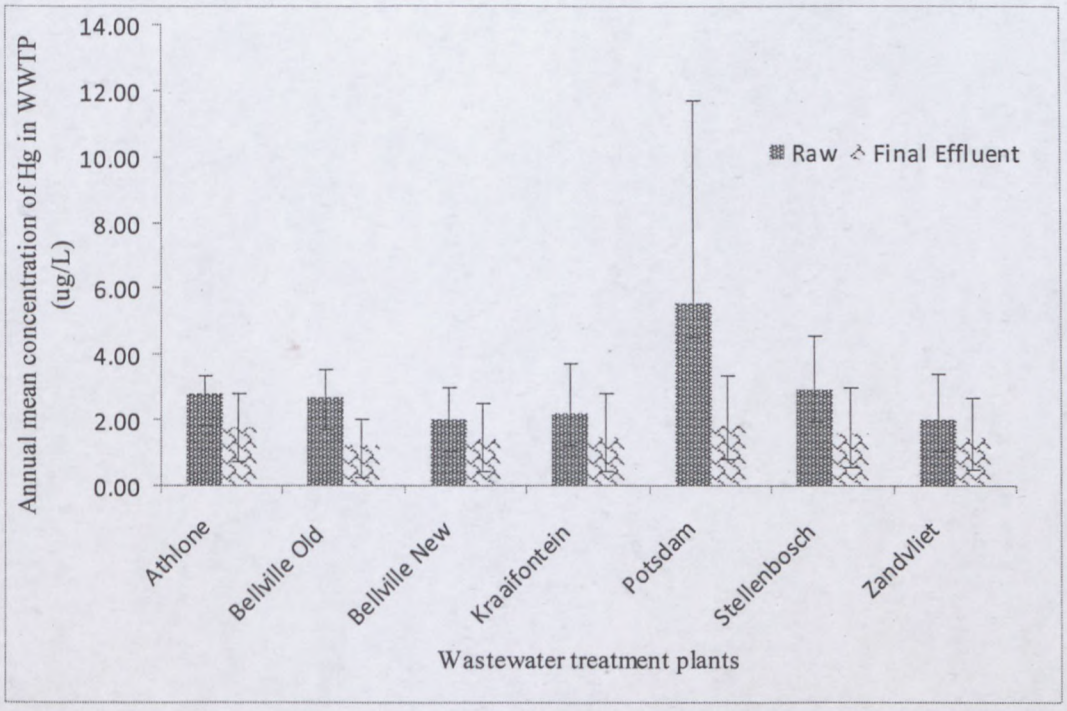


Figure 4.8: Annual mean (± SD) of influent and effluent concentration of mercury in WWTPs

Mercury concentration at the Kraaifontein WWT plant ranged from 0.64 to 4.07 μgl^{-1} with annual mean of 2.22 μgl^{-1}, while the final effluent concentration ranged from 0.08 to 3.17 μgl^{-1} with annual mean of 1.80 μgl^{-1} (Table 4.7). The seasonal removal efficiency of the plant ranged between 20.96 and 88.05 %. Annual spread (Figure 4.8 (d)) shows that 14.65 % was removed at the primary settling tank, while about 26 % was taken off at the secondary sedimentation tank. The annual mean removal efficiency of the plant was 48.13 % (Figure 4.8). There was significant difference due to seasonal change in influent concentration and due to concentration change from plant treatment process.

Potsdam WWTP received the highest mercury concentration. The annual mean concentration was 5.53 μgl^{-1} with corresponding effluent concentration of 1.80 μgl^{-1}. The percentage removal varied from 7.87 to 90.04 % (Table 4.8). The plant distribution trend shows that 13.56 and 44.3 % was removed at the primary and secondary sedimentation respectively (Figure 4.7 (e)). The annual mean removal efficiency was 53.38 %. There was significant difference due to seasonal change in influent concentration into the plant.

Stellenbosch and Zandvleit WWTPs received Hg concentration range of 0.64 to 4.26 μgl^{-1} and 0.69 to 3.99 μgl^{-1} respectively (Table 4.8). The final effluent in the two plants ranged from 0.25 to 3.59 μgl^{-1} for Stellenbosch and 0.15 to 2.99 μgl^{-1} for Zandvliet, 31.06 and 8.87 % of total mercury in the waste influent was removed at the primary and secondary tanks of Stellenbosch, while 22.39 % was removed at the secondary tank of Zandvliet plant (Figure 4.7 (f) and (g)). The annual removal efficiency of the plant was 51.38 % for Stellenbosch and 33.41 % for Zandvliet (Figure 4.8). There

was significant difference due to influent concentration and treatment process at Stellenbosch, however, Zanvliet plant showed only significant difference in mercury influent over the study period.

4.2.1.5 Zinc

Zinc was generally the highest trace metals in all the WWTPs investigated. The Athlone influent concentration ranged from 961.367 to 1431.95 μgl^{-1} with annual mean of 1236.71 μgl^{-1} (Table 4.8). The final effluent concentration varied between 222.68 and 298.44 μgl^{-1} with annual mean concentration of 251.47 μgl^{-1}. The seasonal percentage removal of the plant varied from 68.96 to 84.45 %. The annual distribution pattern in the plants showed that 44.99 % and 31.24 % of total annual concentration was removed through primary and secondary sedimentation tanks (Figure 4.9 (a)). The annual mean removal efficiency of the plant was 78.78% (Figure 4.10). There was significant difference in the plant due to seasonal variation and treatment process.

The old Bellville plant influent concentration ranged from 766.6 to 2079.12 μgl^{-1}, while the final effluent varied between 332.53 to 533.77 μgl^{-1} (Table 4.8). The annual spread is presented in Figure 4.9 (b). For the period investigated, 44.67 % of Zn concentration into the plant was removed at the primary and 18.51% was taken off at the secondary sedimentation tank. The seasonal removal efficiency ranged from 46.88 to 84.01 %, while the annual mean removal efficiency was 65.45 % (Figure 4.10). There was significant difference in the plant due to seasonal variation and treatment process.

On the other hand, the new Bellville plant influent concentration ranged from 400.94 to 1472.70 μgl^{-1} with annual mean concentration of 948.19 μgl^{-1} and the effluent concentration varied from 248.33 to 468.05 μgl^{-1} with annual mean of 351.86 μgl^{-1}. Seasonal plant removal efficiency ranged from 6.69 to 72.40 %. 34.16 % was trapped into the secondary sludge, while the balance was returned in the activated sludge (Figure 4.9). There was significant difference in the plant due to seasonal variation and treatment process.

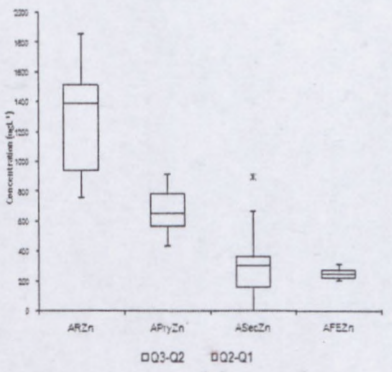
The influent concentration at Kraaifontein WWTP ranged from 638.43 to 1206 μgl^{-1} with annual mean of 933.21 μgl^{-1} and effluent concentration varied from 208.29 to 24.30 μgl^{-1} with annual mean of 222.80 μgl^{-1} (Table 4.8). The plant shows that 37.59 and 36.89 % of Zn influx into the plant was removed at the primary and secondary sedimentation tanks (Figure 4.9 (d)) for the studied period. The seasonal removal efficiency varied between 67.17 and 82.74 % while the annual mean removal efficiency was 74.47% (Figure 4.10).

Potsdam WWTP influent concentration ranged from 822.99 to 1065.72 μgl^{-1} with annual influent mean of 887.14 μgl^{-1}, while effluent concentration ranged from 183.79 to 410.82 μgl^{-1} with annual mean of 310.56 μgl^{-1} (Table 4.8). The distribution of Zn in the plants showed that 21.29 and 39.42% was removed into primary and secondary sludge, respectively. The seasonal removal efficiency ranged from 50.54 to 82.74 % with annual mean of 63.74 % (Figure 4.10). There was significant difference in the plant due to seasonal variation and treatment process.

Table 4.9: Mean concentration (±SD) of Zn in the influent, primary, secondary and final effluent of WWTPs during the different seasons ($\mu g l^{-1}$) with removal efficiency.

WWTP	Season	Concentration ($\mu g l^{-1}$)				$\alpha_{concentration}$	Removal efficiency
		Influent	Primary Effluent	Secondary Effluent	Final Effluent		
Athlone	Summer '10	1431.9 ± 16.8	912.5 ± 9.6	527.1 ± 324	222.7 ± 22	**	84.5
	Autum '10	1411.9 ± 252.3	517.0 ± 69	303.6 ± 121.8	255.1 ± 14	**	82.2
	Winter '10	1121.6 ± 611.1	644.5 ± 124	344.9 ± 74.6	229.7 ± 18	**	79.5
	Spring '10	961.4 ± 24.9	647.2 ± 12.1	N/A	298.4 ± 13.5	**	68.9
	α_{season}	*					
Old Bellville	Summer '10	1004.8 ± 0.8	883.5 ± 124.6	699.6 ± 8.5	533.8 ± 15.2	**	46.9
	Autum '10	2079.1 ± 134.4	832.3 ± 548.8	540.5 ± 115.2	332.5 ± 117	**	84.0
	Winter '10	766.7 ± 17.6	460.9 ± 18.7	295.6 ± 16.9	332.7 ± 36	**	56.61
	Spring '10	1455.5 ± 32.9	758.8 ± 37.1	417.7 ± 25.7	374.1 ± 22	**	74.3
	α_{season}	*					
New Bellville	Summer '10	1148.2 ± 10.7	NPST	932 ± 10.2	316.9±3.6	**	72.4
	Autum '10	1472.7 ± 288	NPST	929 ± 55	468 ± 53.9	**	68.2
	Winter '10	770.9 ± 9.3	NPST	253 ± 22.5	248 ± 16.9	**	67.8
	Spring '10	400.9 ± 5.1[fij]	NPST	383 ± 23.1	374 ± 22.4	**	6.7
	α_{season}	*					
Kraaifontein	Summer '10	1206.9 ±1.2	391.5 ± 4.6	N/A	208.3 ± 17.3	**	82.7
	Autum '10	638.4 ± 47.5	425.0 ± 51	356.5 ± 27.6	209.6 ± 53.6	**	67.2
	Winter '10	756.1 ± 35.9	560.1 ± 47	319.1 ±13.0	232.0 ± 13.3	**	69.3
	Spring '10	1131.5 ± 46.1	952.9 ±12	277.1 ± 10.0	241.3 ± 20.1	**	78.7
	α_{season}		*	*			
Potsdam	Summer '10	822.9 ± 1.5	626.3 ± 10.3	341.3 ± 7.6	260.1 ± 1.6	**	68.4
	Autum '10	1065.7 ± 47.8	846.3 ±45.9	250.1 ± 39.9	183.8 ± 10.8	**	82.8
	Winter '10	829.3 ± 29.2	727.8 ± 29.6	384.2 ± 11.0	387.6 ± 48.4	**	53.3
	Spring '10	830.6 ±13.9	592.8 ± 28.8	418.6 ± 5.9	410.8 ± 10.3	**	50.5
	α_{season}						
Stellenbosch	Summer '10	684.9 ± 16.6	351.2 ± 22.4	128.5 ± 13.9	133.7 ± 13.4	**	80.5
	Autum '10	581.1 ± 167.2	209.7 ± 43.2	247.9 ± 8.4	215.2 ± 2.9	**	62.9
	Winter '10	925.5 ± 39.1	754.2 ± 78.2	402.4 ± 191.8	353.8 ± 100.5	**	61.8
	Spring '10	734.2 ± 3.8	452.9 ± 15.1	195.2 ± 3.2	182.1 ± 4.8	**	75.2
	α_{season}						
Zandvliet	Summer '10	5128.3 ± 10.2	NPST	2119.9 ± 11.8	909.4 ± 23.1	**	82.3
	Autum '10	395.2 ± 19.8	NPST	277.2 ± 18.2	191.8 ± 10.9	**	51.5
	Winter '10	380.2 ± 14.8	NPST	223.9 ± 17.6	190.0 ± 5.2	**	50.0
	Spring '10	965.8 ± 19.8	NPST	340.6 ± 5.2	313.2 ± 1.5	**	67.6
	α_{season}						

NA = Not analysed; NPST = no primary settling tank; $\alpha_{concentration}$ denotes the significance of difference between the stages of WWTP, **: difference is significant at $\alpha = 0.05$; α_{season} denotes the significance of difference of seasonal differences, *: difference is significant at $\alpha = 0.05$.



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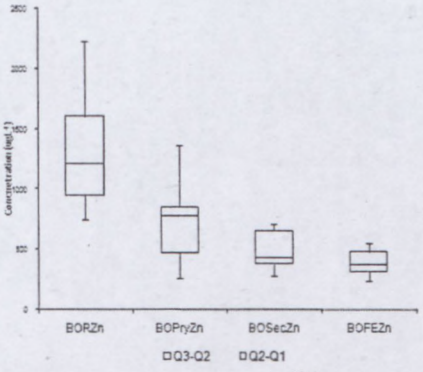

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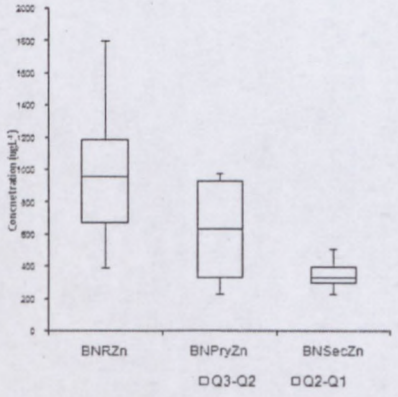

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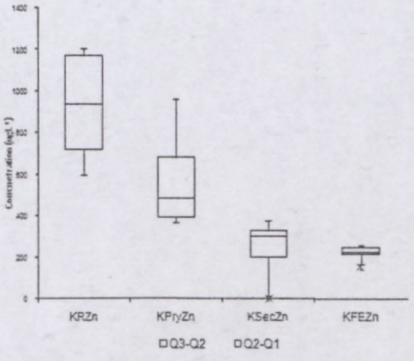

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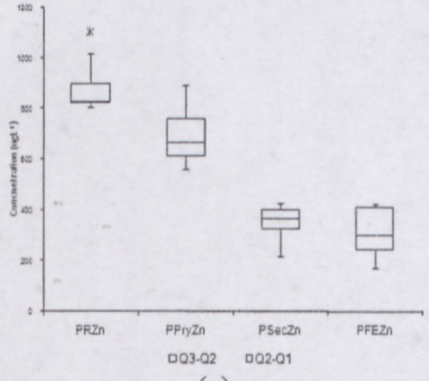

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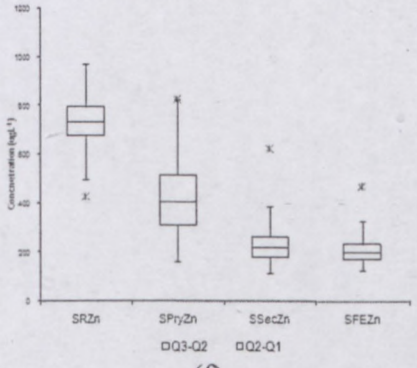

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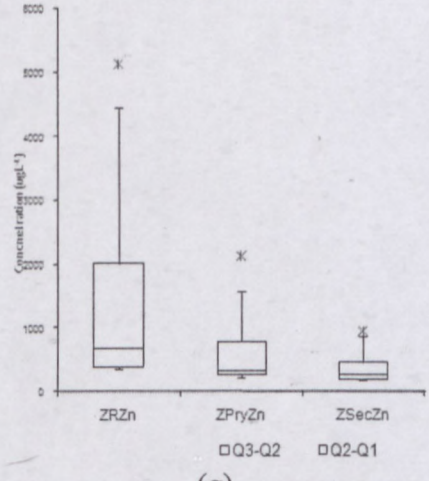


(g)

Figure 4.9

Box and whisker plot for the annual spread of zinc concentrations in WWTP: (a) Athlone WWTP, (b) Old Bellville WWTP, (c) New Bellville WWTP (d) Kraaifontein WWTP, (e) Potsdam WWTP, (f) Stellenbosch WWTP and (g) Zandvliet WWTP.

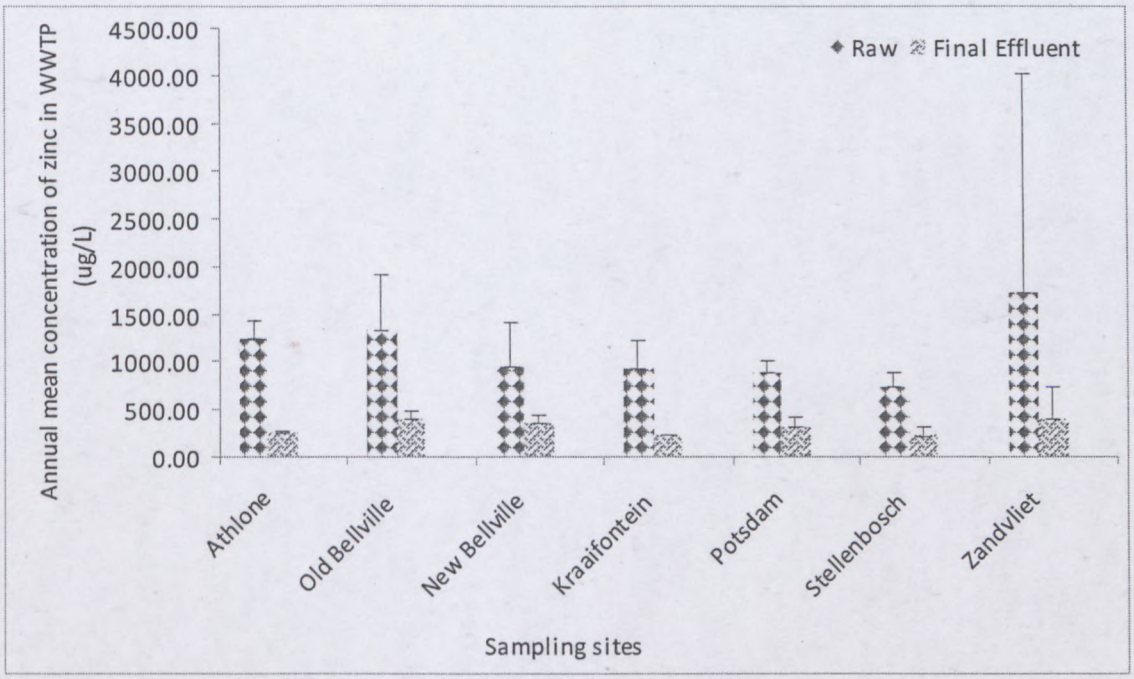


Figure 4.10: Annual mean (± SD) of influent, effluent and removal efficiency for Zn in WWTPs

Stellenbosch and Zandvliet plants received concentration range of 582.09 to 925.48 μgl^{-1} and 380.19 to 521.8 μgl^{-1}, respectively (Table 4.9). 39.57% and 27.14 % of total zinc concentration into Stellenbosch the plant was removed at the primary and settling tanks while 56.89 % was removed at the secondary tank of Zandvliet (Figure 4.10 (f) and (g)). Removal efficiency was 70.1 % for Stellenbosch and 62.83 % for Zandvliet. In the two plants, there was significant difference in the plant due to seasonal variation and treatment process.

4.2.2 Discussion on seasonal variability and percentage removal of metals from wastewater treatment plants investigated

Generally speaking, activated sludge process are designed for organic matter by activated sludge microorganisms and removal of heavy metals is considered as side benefit, and has been quite variable (Bussetti *et al.*, 2005; Usun, 2009; Chanpiwat *et al.*, 2010). In addition, metal removal efficiency is not only dependent on the metal influent concentrations, but also by other cfactors such as the operating parameters e.g. the retention time in the treatment plants, flowrate, physical, chemical and biological factors (Wang et al., 1999; Oliveira *et al.*, 2007). For example, metals removal is known to be dependent on dissolved organic matter (Oliveira *et al.*, 2007) and pH (Cheng *et al.*, 1975; Wang *et al.*, 1999), as removal efficiency increases with pH until they precipitate as hydroxides.

Activated WWTPs are usually conducted at pH 7-9. Thus, because of differing metal solubilities at these pH values, retention time in the WWTP, flow rate, and since wastewater composition is always complex, removal of heavy metals is attributed to these factors (Wang *et al.*, 1999). In this study, the pH values for the untreated influent and treated effluent

ranged from 6.5 to 8.03 ± 0.21 (Table 4.1) at a temperature range of 10 to 22 °C (Table 4.3). This variation in the pH and temperature contributed to the variation in removal efficiency for metals in the WWTPs investigated. Generally, the level of metal removal from the treatment plants remains unpredictable for the period investigated.

The seasonal dataset obtained from the WWTPs showed that the investigated WWTPs received varying concentrations of heavy metals in the raw influent water, of which Zn was the most abundant. The seasonal variations in the metals analyzed from all the treatment plants are presented from Table 4.5 to Table 4.9. The results showed that the wastewater treatment plants metals composition is complex and quite variable. The concentrations and distribution pattern of heavy metals in the raw wastewater were generally similar in WWTPs investigated. This could be attributed to the fact that all the WWTPs received a mixture of domestic wastewater, stormwater and industrial effluent except Kraaifontein WWTP.

Generally, the abundance distribution pattern of heavy metals in terms of concentration is Zn>Pb>As>Cd>Hg. The variation in wastewater metal content can further be attributed to diversity in economic activities and the living pattern in the province. Athlone, Potsdam, Bellville, Stellenbosch, and Zandvliet plants are known to receive high industrial waste when compared to Kraaifontein (Moeletsi *et al.*, 2004).

There are many catering, restaurants, sawmills, Ni-Cd battery centres and carwash industries in the province that release their waste for further treatment by the municipality. Generally, the influent values are higher than effluent values. The average removal efficiency for the plants could be rated effective on an annual basis as the effluent values are always lower than the influent values for all the metals in all the measurement. As shown in Figures 4.1 to 4.9, metals removal occurs both in the primary (where portion of metals adsorb to the particles) and in the secondary biological treatment (where metals are removed by biosorption) (Usun, 2009).

The relationship between influent and removal efficiency agreed with previous research findings (Kulbat *et al.*, 2003; Shomar *et al.*, 2004; Oliveira *et al.*, 2007), where it was observed that the removal of heavy metal in the wastewater is directly proportional to the influent concentrations. From this study, Potsdam treatment plant was the most effective at heavy metals removal ((Figure 4.11). On an average, Potsdam treatment plant like every treatment plants investigated received industrial, domestic and storm water had the best annual performance in terms of removal efficiency. The plant effectiveness at metal removal may be attributed to the people way of life and installation of new treatment plant to complement the old wastewater treatment plant.

4.2.2.1 Arsenic

The annual abundance pattern for arsenic in all treatment plants can be rated as the new Bellville > Stellenbosch > old Bellville > Athlone > Kraaifontein ≥ Potsdam > Zandvliet. The removal efficiency for arsenic was best at Potsdam plant for all the seasons except during the spring. Arsenic compounds are extensively used in the wood processing industries to protect the timbers. Two wood processing industries are functioning in the vicinity of Stellenbosch WWTP. These industries may use arsenic compounds to protect timbers, though uses of these chemicals which subsequently released in their waste. Generally, arsenic concentration in effluent from all the treatment plants investigated fell below the South Africa water quality guideline of 10 μgl^{-1}. However, it was above the CCME, 1999 recommendation. All the treatment plants could be rated high except for Athlone during the Autum and spring due to malfunctioning of the plants.

4.2.2.2 Cadmium

Generally, cadmium annual abundance pattern by plant could be rated as Potsdam > Kraaifontein > Athone ≥ old Bellville > Stellenbosch ≥ Zandvliet ≥ new Bellville. The possible sources of cadmium into water ways are laundrettes, electroplating workshops, plastic manufacturing, pigments, enamels, paints etc. Cadmium was well removed from Athlone, Bellville old, Kraaifontein and Potsdam while Bellville new and Sellenbosch plant were not very effective. The influent and effluent concentrations were within the reported values elsewhere (Table 4.10). Statistically, no significant difference was observed for raw effluent except for Kraaifontein and Potsdam during the winter season. The reported concentration fell below SWQG of 10 μgl^{-1} limit for irrigational and livestock purposes (DWAF, 1996; CCME, 1999) but higher than 0.017 μgl^{-1} (CCME, 1999) and 0.02 μgl^{-1} for human consumption application.

4.2.2.3 Lead

Pb removal efficiency in the plants could be rated effective as between 40 to 95 % of the toal influx was removed from the waste stream. The reported concentration range for the investigated treatment plants were collaborated by previous studies elsewhere (Table 4.11), while the plants abundance patter could be rated as new Bellville > old Bellville > Stellenbosch ≥ Athlone > Potsdam > Kraaifontein > Zandvliet. This abundance distribution pattern can largely be attributed to the industrial effluent being received at each of the treatment plant and the living pattern of the Capetonia. There was significant difference between the influent and effluent cocnetration for most the plants as the final effluent concentration was generally lower than the influent. The final effluent concentration fell below the SA waster quality guidelines for aquatic life, irrigation and livestock production purposes. However, the concentration was far above the CCME (1999) guidelines.

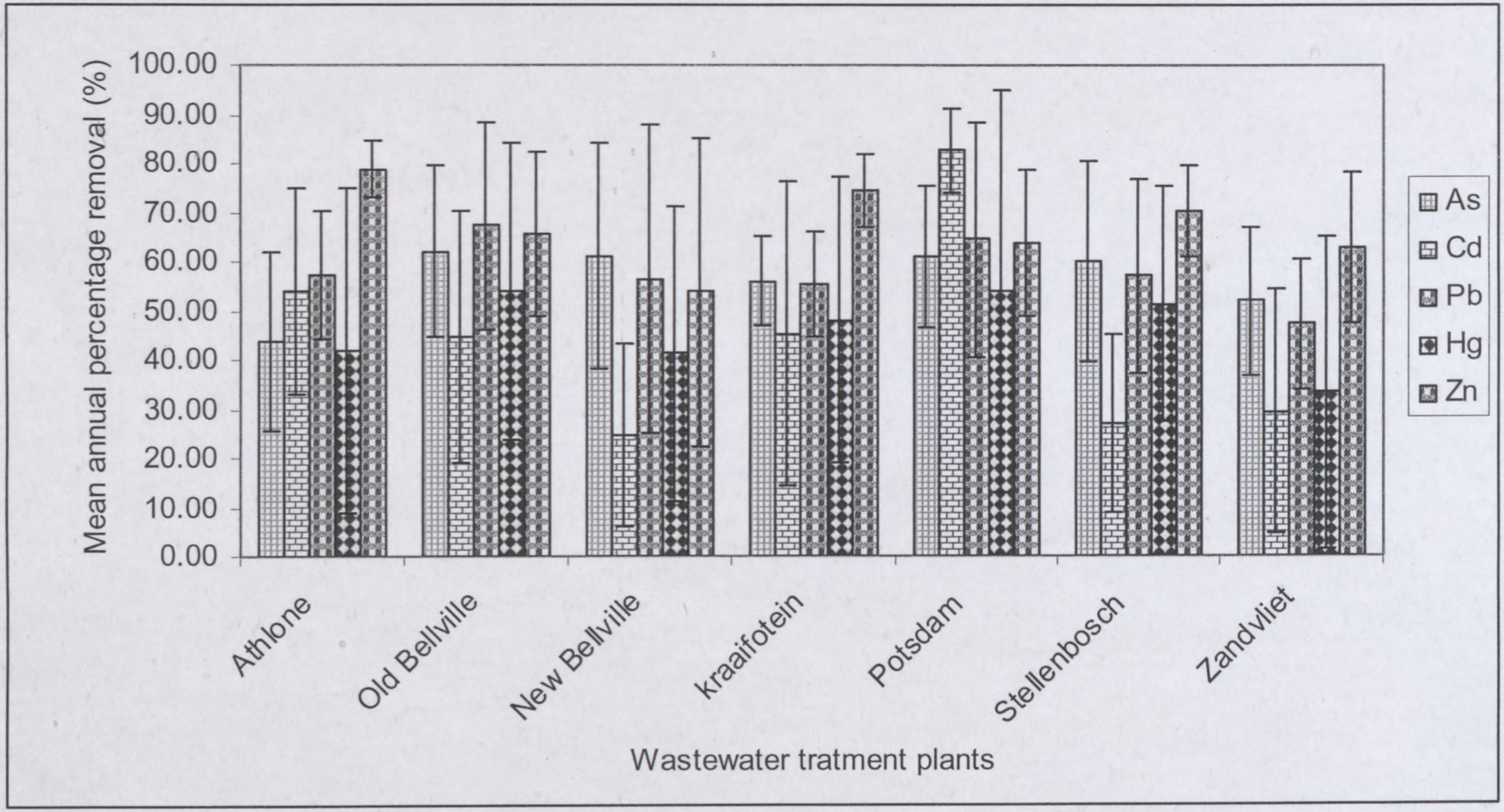


Figure 4.11: Comparison of annual removal efficiency for trace metals in wastewater treatment plants

4.2.2.4 Mercury

Sources of mercury to the environment include dental practices, clinical thermometers, glass mirrors among others. Mercury is known to be highly toxic and can affect human health at the lowest concentration of possible exposure. For the WWTPs, no significant difference was noticeable between the influent and effluent concentration. However, all the wastewater treatment plants could be rated effective with the exception of Athlone and Zandvliet where percentage removal fell below 30 % over the study period. The abundance distribution pattern of mercury in the WWTP can be described asPotsdam > Stellenbosch > Old Bellville > Athlone > Kraaifontein > Zandvliet > New Bellville. Potsdam was highly effective at Hg removal as for other metals except for the spring season. The poor performance of the plant for Hg removal could be attributed to plant overload, which is subsequently affected by the retention time of wastewater in the plant. The concentration reported in this study for mercury was higher than values reported in Austria, France, Spain and Germany (European Communities, 2001; Oliveira *et al.*, 2007), however, it was lower than the finding of Busetti *et al.* (2005).

4.2.2.5 Zinc

Sources of zinc include domestic wastes, galvanizing, batteries, paints, fungicides, textiles, cosmetics, pulp, papermills, and pharmaceutics. In this study, n was the most dominant metal in all the WWTPs investigated. The annual plant rating can be rated as Zandvliet > old Bellville > Athlone > new Bellville ≥ Kraaifontein > Potsdam > Stellenbosch. The range of zinc in this study was generally higher than findings in other studies (Table 4.11). In terms removal efficiency, Athlone treatment plant had the highest and can be rated above other plants. There was significant difference between the influent and effluent concentration over the study period. Considering the high concentration of Zn received at these plants, the final effluent concentration was within the national water act waste discharge standards, DWAF 2010 guidelines.

Table 4.10: Heavy metal concentrations in influent and effluents from other countries and investigated treatment plants in Cape Town

Metal	Country	Untreated influent (μgl^{-1})	Treated effluent (μgl^{-1})	References
As	Spain	2.2	-	European Communities, 2001
	Italy	0.3-31	0.5-9.2	Busetti *et al.*, 2005
	Israel	5.6	5.1	Shomar *et al.*, 2004
	South Africa	**5-43.76**	**1.12-5.69**	**this study**
Cd	Austria	<20-60	<20-60	European Communities, 2001
	Poland	<0.01	<0.01	Kulbat *et al.*, 2003
	France	6-85	-	European Communities, 2001
	Germany	0.4	-	European Communities, 2001
	Greece	<1-44	<1	Karvelas *et al.*, 2003
	Greece	0.56	0.34	Firfilionis *et al.*, 2004
	Israel	0.6	0.8	Shomar *et al.*, 2004
	Italy	0.2-1.8	0.1-1.6	Bussetti *et al.*, 2005
	Spain	0.06 – 1.19	0.04 – 0.11	Oliveira *et al.*, 2007
	Turkey	0-137	4-5	Usun, 2009
	South Africa	**1.07-17.39**	**0.52-2.58**	**this study**
Hg	Austria	<10	<10	European Communities, 2001
	Spain	0-0.5	0-0.24	Oliveira *et al.*, 2007
	France	1-8	-	European Communities, 2001
	Italy	<1	-	European Communities, 2001
	Germany	0.6	0.1	European Communities, 2001
	Italy	0.2-147	0.1-9.5	Busetti et al., 2005
	South Africa	**0.6-14.5**	**0.1-3.2**	**this study**
Zn	Poland	270-800	-	Chipasa *et al.*, 2003
	Poland	270-300	90-120	Kulbat *et al.*, 2003
	Austria	<20-3700	20-500	European Communities, 2001
	Greece	330-3200	20-900	Karvelas *et al.*, 2003
	Greece	456	268	Firfilionis *et al.*, 2004
	Israel	75	54	Shomar *et al.*, 2004
	Italy	100-900	-	European Communities, 2001
	Italy	61-833	24-238	Busetti *et al.*, 2005
	South Africa	**400.9-5128.3**		**this study**
Pb	Poland	37-148	-	Chipasa *et al.*, 2003
	Poland	15	<10	Kulbat et al., 2003
	Austria	<20-60	<20-60	European Communities, 2001
	Greece	28.6	13.1	Firfilionis *et al.*, 2004
	Republic of Korea	2.93-79.33	0.70-17.45	Chinpiwat *et al.*, 2010
	Spain	37.42	22.57	Oliveira *et al.*, 2007
	Turkey	6-358	22-30	Usun, 2009
	Italy	10-61	1.0-11	Busetti *et al.*, 2005
	South Africa	**10-61**	**1.0-11**	**this study**

4.3 Occurrence and level of heavy metals in sewage sludge

Due to the tremendous increases in wastewater treatment plants, the amount of sewage sludge produced had increased rapidly. During the wastewater treatment processes, about 70 to 90 % of the heavy metals in wastewater are transferred into the sewage sludge by adsorption or precipitation. Sewage sludge is produced at about 1- 4% of the wastewater treated (Tyagi et al., 1999). Since metals present in the wastewater become concentrated in the sludge, management of heavy metal-laden sludge represents one of the prime environmental issues (Fuentes *et al.*, 2004; Dai *et al.*, 2006; Hua *et al.*, 2008; Deng *et al.*, 2009). The metal composition of sludge can be extremely variable due to the irregular inputs from urban and industrial sources, with a time dependence on the industrial activities, weather and other factors.

Various method of sewage sludge disposal has been proposed and investigated either in the form of liquid slurry or dried sludge. Traditional sludge disposal include landfilling, agricultural use, incineration, ocean dumping and lagooning (Kim *et al.*, 2005; Dai *et al.*, 2006; Garcia-Delgado *et al.*, 2007; Deng *et al.*, 2009; Singh and Agrawal, 2010). Incineration of sewage sludge seems to be a good option for disposal; however, it can result in air pollution due to emissions and thus requires expensive off-gas treatment. Moreover, incineration contributes to the green house-gas effect and leads to the production of contaminated and hazardous slags and fly ashes which often requires further treatment. Considering the richness of sewage sludge in terms of organic carbon, nitrogen and phosphorus, land application as agricultural fertilizer is low cost and highly effective route of its disposal as landfilling could result in waste table pollution due to leachate production (Wang *et al.*, 2005; Jia-yin *et al.*, 2006; Hua *et al.*, 2008).

Cape Town is one of the most developed cities in South Africa. It is a highly populated area and also harbors many industrial zones. The 21 wastewater treatment plants (WWTPs) in Cape Town treat over 2.3 million tons of wastewater produce perday and approximately more than 150,000 (d.w) of sewage sludge are disposed through landfilling or agricultural fertilizer. In recent years, many countries have developed series of regulations to control disposal or use of sewage sludge as agricultural fertilizer. This is to allow for regulations of heavy metals in sewage sludge which could pose serious environmental challenges and human health risk. South Africa has also reviewed her acceptable limits for heavy metals in sewage sludge. This study is to provide additional insight into (i) to levels of their occurrence in selected wastewater treatment plants and (ii) to evaluate the suitability as agricultural fertilizer using South Africa guidelines.

In all the samples analysed, Zn was the most abundant, while Hg was the least. The general trend of abundance for heavy metals was Zn > Pb > As > Cd > Hg. The annual mean of heavy metal levels in sewage sludge samples collected from the six wastewater treatment plants i.e. Athlone (dewatered sludge), old and New Bellville (Activated sludge), Kraaifontein (activated sludge), Potsdam (dewatered sludge), Stellenbosch (primary and secondarysludge) and Zandvliet (activated and treated sludge) are shown in Figures 4.12-4.16.

4.3.1 Arsenic levels in sewage sludge

The annual mean concentrations of arsenic in the sludge samples varied between 37.86 $mgkg^{-1}$ and 88.44 $mgkg^{-1}$ (Figure 4.12). The lowest annual mean concentration was found at the Kraaifontein, while the highest was at the new Bellville plant. The difference is obvious as Kraaifontein received about 90 % domestic waste and the new Bellville plant received about 10% domestic waste and the re-circulated sludge from the old Bellville plant (Table 4.11).

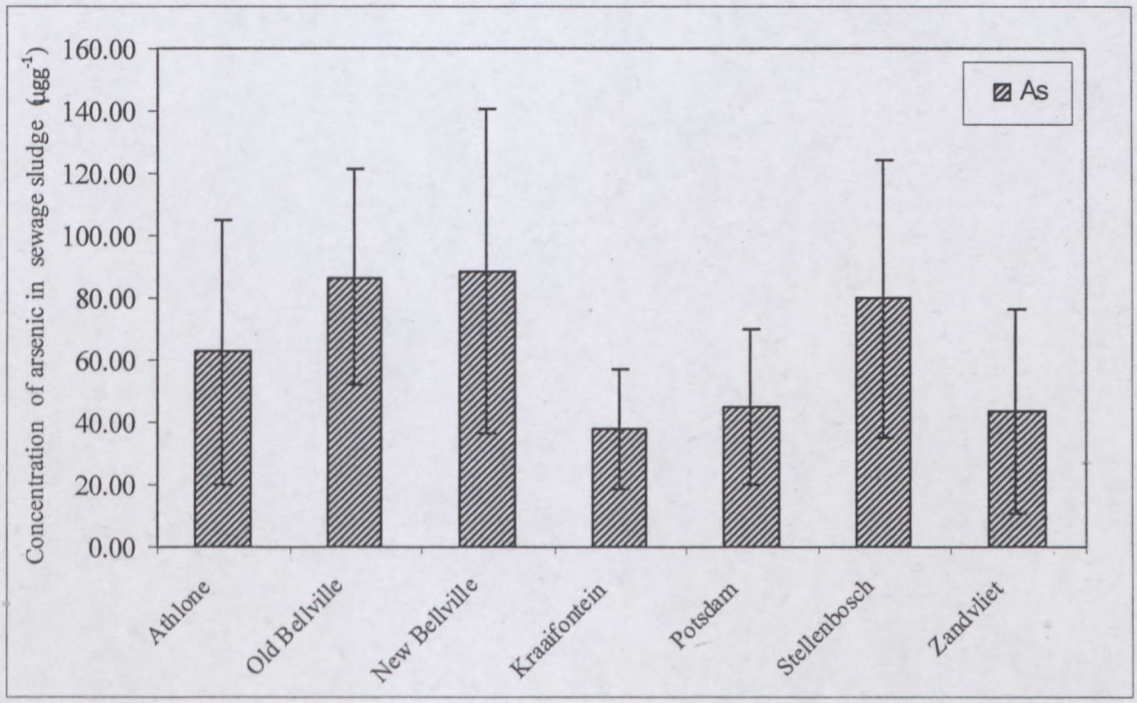


Figure 4.12: Annual mean (±SD) concentration of arsenic in sewage sludge from WWTP.

Other plants investigated also had high concentration of arsenic in the sewage sludge due to high anthropogenic input e.g. Stellenbosch plant received industrial wastes from about 160 industries (consisting of restaurants, cosmetics, sawmills and wood processing industries). The obtained result for arsenic in this study is significantly higher than values reported in sewage sludge from three plants in China by Dai *et al.* (2006). Comparing the result of this study with the South Africa, United State of America and the European Union guidelines for land application, the annual mean of all the plants of 63.37 $mgkg^{-1}$ was above the maximum limit of 15 $mgkg^{-1}$. Applying the sewage sludge as fertilizer in agricultural land could lead to bio-accumulation of arsenic and subsequent health risk problems.

4.3.2 Cadmium levels in sewage sludge

Cadmium concentration ranged from 0.12 $mgkg^{-1}$ to 2.08 $mgkg^{-1}$ (Figure 4.13). The lowest concentration of Cd was found at Kraaifontein, while the highest was found at the new Bellville plant. Cadmium in sewage sludge may have come from fertilizer producing industries and the use of cadmium based batteries (Ni-Cd). The highest value been recorded at the Bellville plant and lowest at the Kraaifontein was an indication that the source of Cd in the sewage sludge is anthropogenic (Industrial wastewater). No significant difference was noticeable in the seasonal concentration of Cd in all the treatment plants except for Athlone and Potsdam during raining seasons.

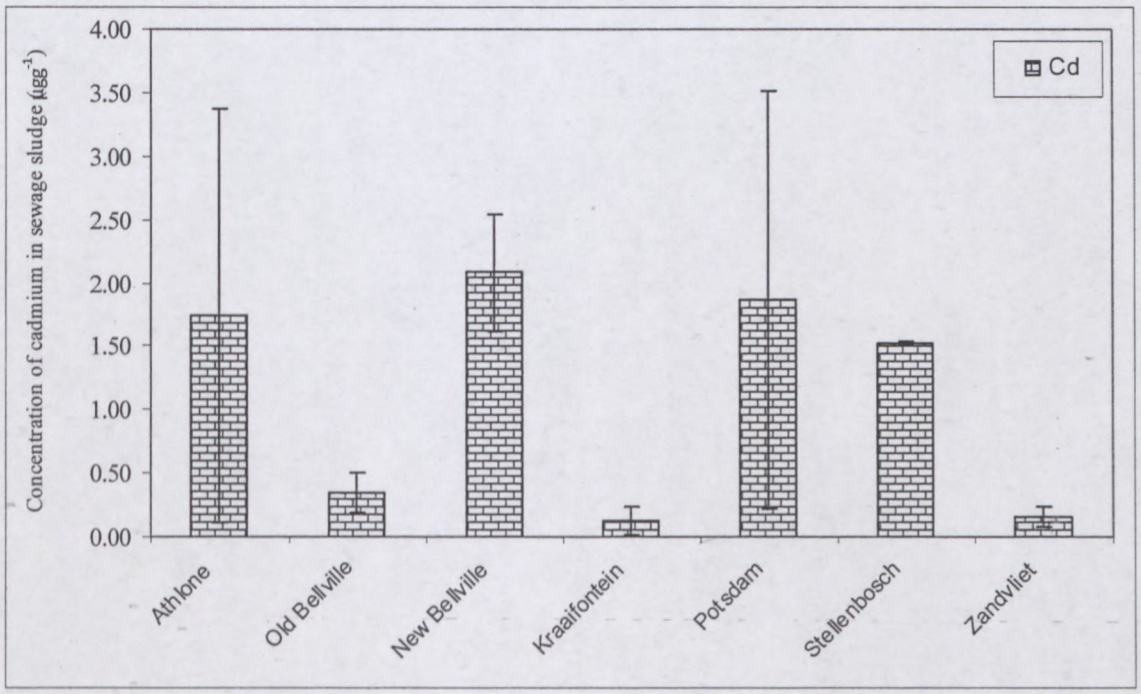


Figure 4.13: Annual mean (±SD) concentration of cadmium in sewage sludge from WWTPs

This may be attributed to high runoff during the seasons as Cd is known to wear off rubber tires, thus, contributed to significant increase in Cd concentration during the season. In previous studies in China, Cd levels in sludge had been reported to range from 0.90 to 112.3 $mgkg^{-1}$ (Wang *et al.*, 2005) and from 11.9 to 81.2 $mgkg^{-1}$ (Dai *et al.*, 2006). However, obtained results from this study for all the investigated treatment plants are not significantly different from study in Eastern Cape, South Africa (Morrisson *et al.*, 2004) and levels reported in other countries (Kadewa *et al.*, 2001; Kaonga *et al.*, 2010). The quantity of Cd in sewage sludge was way below the maximum acceptable limits from other countries and South Africa guidelines (Table 4.11).

4.3.3 Lead levels in sewage sludge

Sources of lead in sewage sludge may include fuel additive, lead batteries manufacturin, pigments and chemical manufacturing, roofing, fishing weights, melting and processing and secondary metals production (Moeletsi *et al.*, 2004). Other routes include dry and wet deposition into drainage systems by rain water. As with other metals, Kraaifontein treatment plant had the least concentration of Pb (23.48 $mgkg^{-1}$), while Athlone had the highest (211.88 $mgkg^{-1}$) (Figure 4.14). The values reported in this study was higher than result values reported by Jaganyi *et al.* (2005), Kadewa *et al.* (2001) and Koanga *et al.* (2010) but lower than than values reported by Morrisson *et al.* (2004) and Dai *et al.* (2006) except for Athlone and Old Bellville plants.

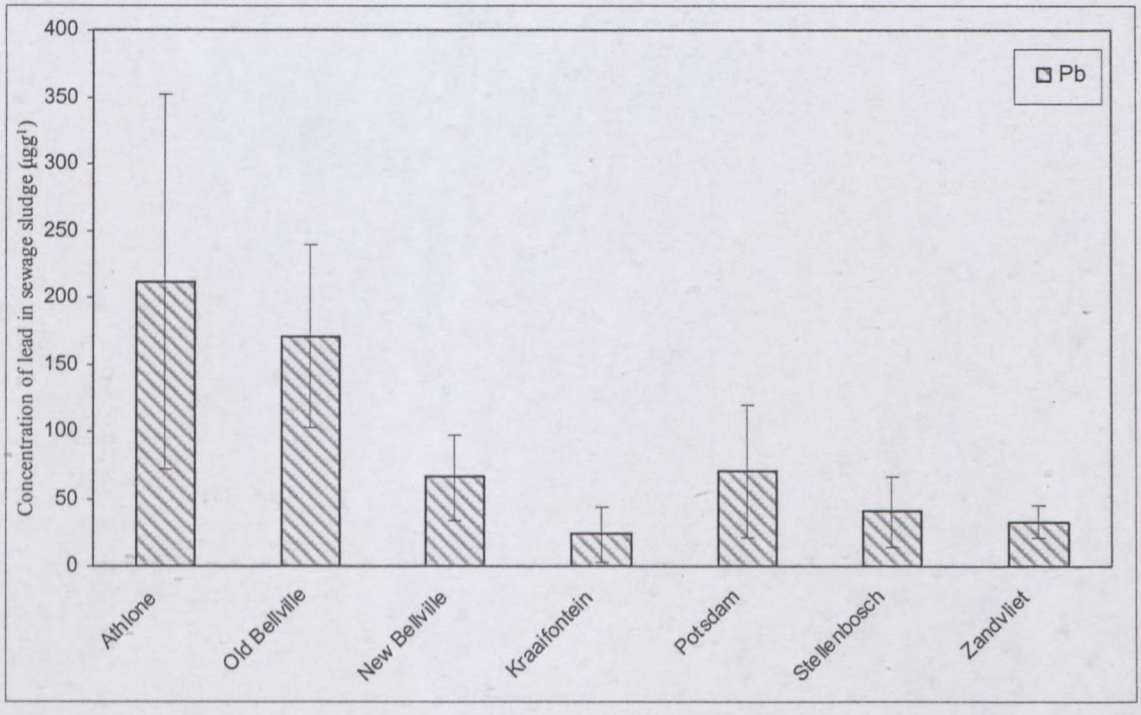


Figure 4.14: Annual mean of lead (±SD) concentration in sewage sludge from WWTPs

High level of Pb in sludge from these WWTPs compared to values reported in Malawi (Koanga *et al.*, 2010) could be attributed to continous use of leaded petrol in South Africa, while it has been banned in Malawi. The levels of Pb were extremely higher than the South Africa guidleines for land application as fertilizer at Athlone and old Bellville plants, while the levels in the new Bellville and Potsdam plants were slightly above the limit. However, Kraaifontein, Stellenbosch and Zandvliet were below the set standard. Comparing with internationally set limits, the reported values for all the WWTPs were lower. On the basis of South Africa limit, sewage sludge from Athlone, old and new Bellville and Potsdam WWTPs could pose serious environmental challenges when used continuously as soil suppliments.

4.3.4 Mercury levels in sewage sludge

Mercury concentration ranged from 0.6 $mgkg^{-1}$ (Zandvliet) to 3.17 $mgkg^{-1}$ (Athlone) (Figure 4.15). Sources of mercury into wastewater treatment plants include dental practices, clinical thermometers, glass mirrors among others (Moeletsi *et al.*, 2004). Tolosana and Ehrlich (2000) found that the effluent from medical institutions in South Africa contained high levels of metals, thus, this could have contributed to the level of mercury reported in the sludge across the plants. Generally, mercury concentration was not reported in the previous studies in South Africa. Though the reported levels in this study was way above the findings of Da *et al.* (2006), the concentration showed that Hg concentration was low and fall within the guidelines set by South Africa, USA and the European Union (Table 4.11).

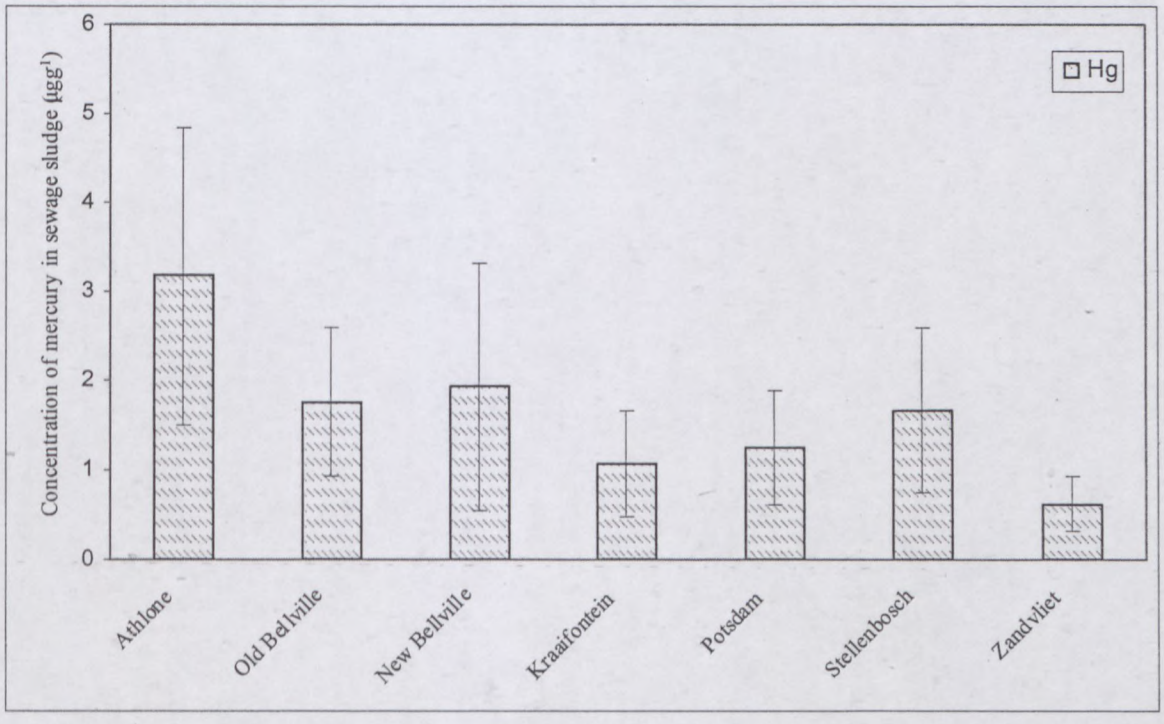


Figure 4.15: Annual mean (±SD) concentration of mercury in sewage sludge from WWTPs

4.3.5 Zinc levels in sewage sludge

Zinc is a phytotoxic metal, but it is important as a micronutrient at the appropriate levels (Sanders *et al.*, 1999). Sources of Zn in the environment are usually from natural and anthropogenic sources ranging from industrial effluents, domestic effluents, storm water runoff and spoil heaps. Concentration of Zn found in the sludge from WWTPs ranged from 381.95 $mgkg^{-1}$ at the new Bellville plant to 2674.93 $mgkg^{-1}$ at the old Bellville plant. Basically, concentrations were generally high at all the treatment plant with Kraaifontein still having the second least concentration. The levels of zinc in sludge were lower than the maximum permissible levels for other countries but higher than South Africa guidelines (Table 4.11).

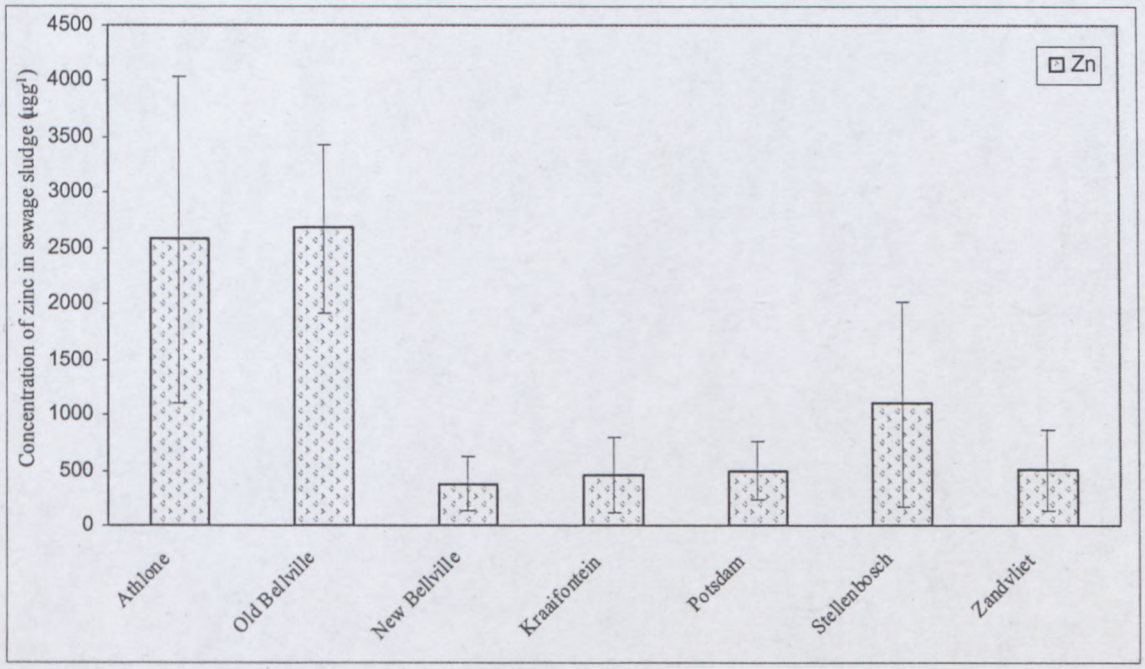


Figure 4.16: Annual mean (± SD) concentration of zinc in sewage sludge from WWTPs

This result is similar to the fndings of Morrisson *et al.* (2004) and Dai *et al.* (2006), but significantly higher than values reported by Kadewa *et al.* (2001) and Koanga *et al.* (2010). The presence of zinc in sewage sludge may be due to corrosion of galvanized iron in the domestic plumbing systems and this may be suggested for Kraaifontein treatment plant and industrial effluents sources for other plants (Koch and Rotard, 2001). The release of waste effluent from hospitals into the municipal sewer line, might also be contributing to zinc levels in sewage sludge. Tolosana and Ehrlich (2000) found that effluent from medical institutions in South Africa had higher levels of zinc. This is compounded by the use of shampoos to combat dandruff which can contain up to 0.5 % Zn as an active ingredient (Leeper, 1978). As the case, Cape Town had a lot of hair dressing saloons whose zinc contribution to wastewater may be significant.

Table 4.11: Sludge guidelines by South Africa, United State of America and European Union ($mgkg^{-1}$)

Elements	SA	USA	EU	Concentraton range in this study
As	15	41	10-75	37.86 - 88.44
Cd	15.7	39	20-40	0.12 – 2.08
Hg	10	17	16-25	0.62 – 3.17
Pb	50.5	300	750-1200	23.48 – 211.88
Zn	353.5	2800	2500-4000	494.96 – 2674.93

4.4 Seasonal variability in the concentrations of heavy metals in river water and sediment receiving wastewater effluents

4.4.1 Arsenic

In this study the seasonal concentrations of arsenic in water and sediment of the selected river systems receiving wastewater effluent were determined for samples taken from points about 1 – 2 km up and down stream from the point of final discharge into the rivers. The range of the annual mean of arsenic in water for all sampling sites in comparison with other studies is presented in Table 4.12. The graphical forms of the seasonal variation at each sampling point for water is presented in Figure 4.17. The average levels of arsenic in water samples obtained from the river system ranged from 0.56 μgl^{-1} to 23.78 μgl^{-1} for the nineteen sampling points. The highest level of arsenic was obtained at sampling point 7 (Bellville WWTP down stream) during winter and the lowest at sampling point 12 (Stellenbosch WWTP discharge point) as depicted in Figure 4.17. The annual mean concentration of arsenic from each sampling point ranged from 1.62 μgl^{-1} (Site 1) to 13.7 μgl^{-1} (Site 13).

Studies in several countries reported levels of arsenic in water ranging from 1.25 μgl^{-1} to 5114 μgl^{-1} (Chen *et al.*, 1994; William *et al.*, 1996; Welch *et al.*, 1996; Mukherjee and Bhattacharya, 2001; Jung *et al.*, 2002; Ikem *et al.*, 2003; Xia and Liu, 2004; Arain *et al.*, 2009) (Table 4.12). When comparising the findings of this study with other reported values, it was obvious that the result of this study was generally low except for sites 7, 11 and 13 where reported values were higher than the South Africa water quality guidelines and WHO (2002). Reported concentrations were within the human consumption (except for 7, 11 and 13), livestock watering, irrigation and aquacultural use (DWAF, 1996; CCME, 1999).

Generally, the wastewater treatment plants are believed to be one of the possible routes of organic and inorganic pollutants into the river systems. However, from this study, the annual mean values for arsenic at the discharge point was lower compared to the upstreams and downstreams values of the river, but higher than the values at the control site (Site 1). The natural and anthropogenic sources of arsenic have been discussed in Chapter Two of this thesis.

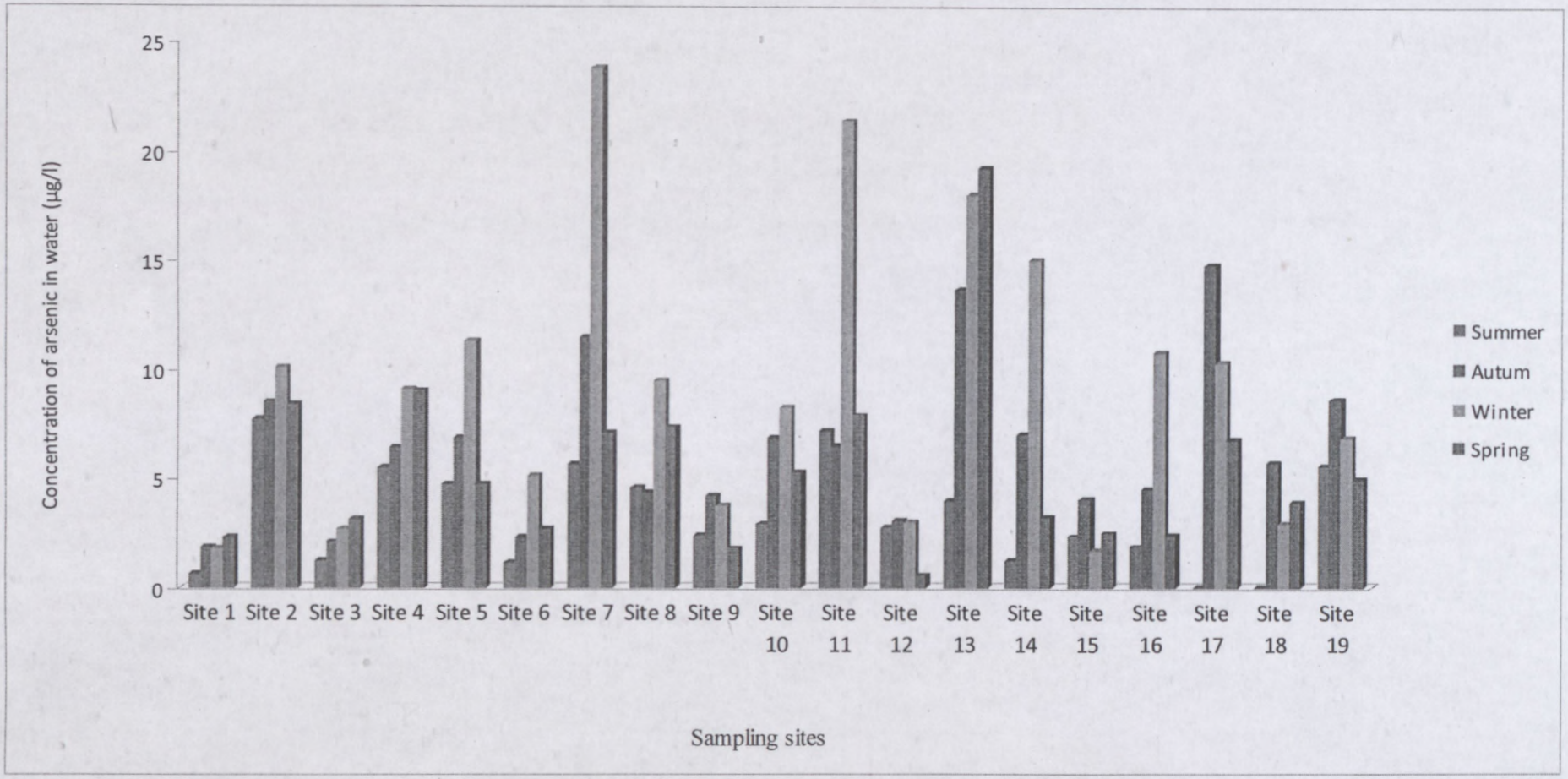


Figure 4.17: Seasonal trend in arsenic concentration (μgl^{-1}) in river water receiving waste effluent from WWTPs

Site 1: Kirstenbosch Botanical garden (Control Site); Site 2: Potsdam WWTP upstream; Site 3: Potsdam WWTP discharge point; Site 4: Potsdam WWTP downstream; Site 5: Bellville WWTP upstream; Site 6: Bellville WWTP discharge point; Site 7: Bellville WWTP downstream; Site 8: Kraaifontein WWTP upstream; Site 9: Kraaifontein WWTP discharge point; Site 10: Kraaifontein WWTP downstream; Site 11: Stellenbosch WWTP upstream; Site 12: Stellenbosch WWTP discharge point; Site 13: Stellenbosch WWTP downstream; Site 14: Zandvliet WWTP upstream; Site 15: Zandvliet WWTP discharge point; Site 16: Zandvliet WWTP downstream; Site 17: Athlone WWTP upstream; Site 18: Athlone WWTP discharge point; Site 19: Athlone WWTP downstream.

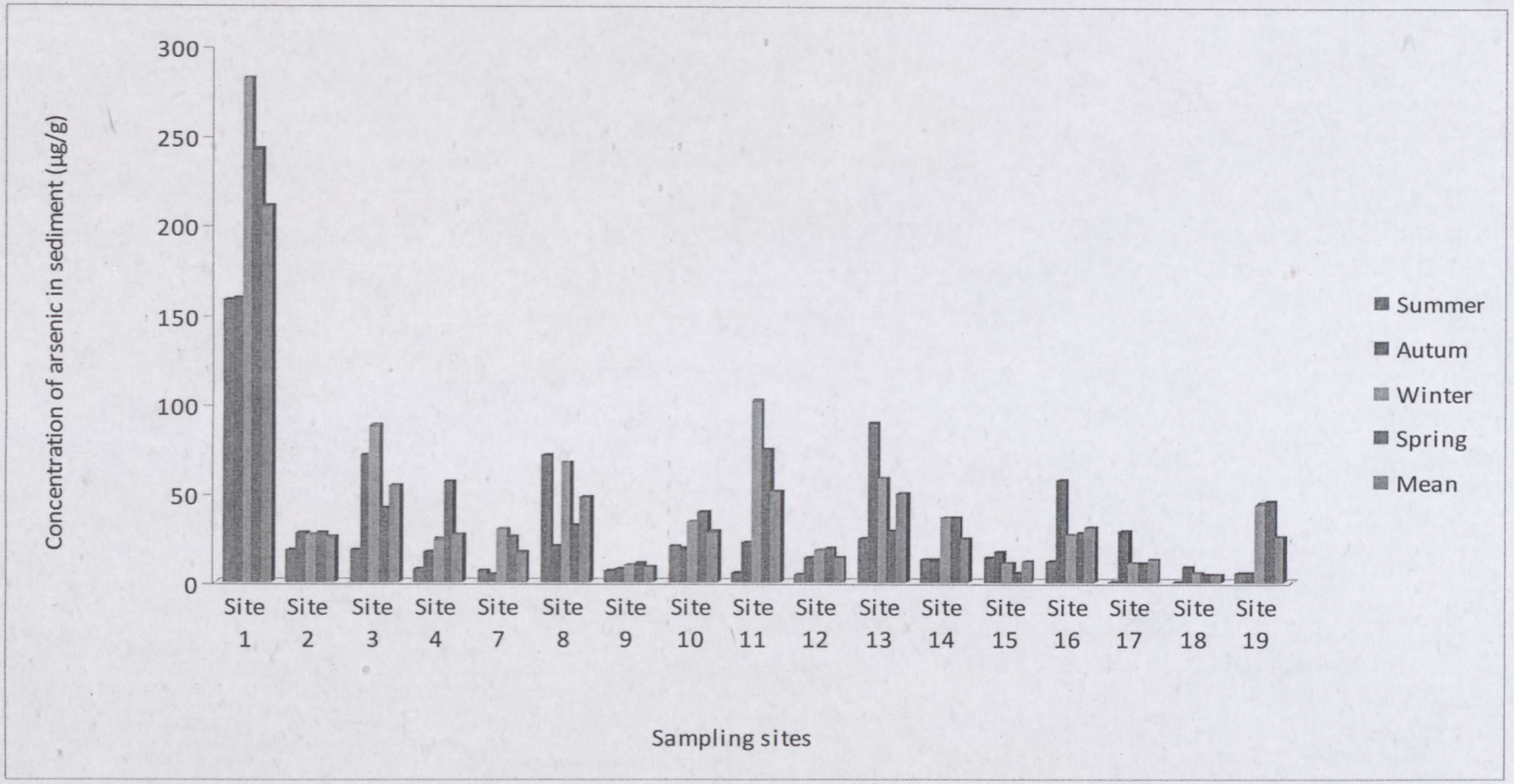


Figure 4.18: Seasonal trend in arsenic concentrations ($\mu g g^{-1}$) in river sediment receiving waste effluent from WWTPs

Site 1: Kirstenbosch Botanical Garden (Control Site); Site 2: Potsdam WWTP upstream; Site 3: Potsdam WWTP discharge point; Site 4: Potsdam WWTP downstream; Site 7: Bellville WWTP downstream; Site 8: Kraaifontein WWTP upstream; Site 9: Kraaifontein WWTP discharge point; Site 10: Kraaifontein WWTP downstream; Site 11: Stellenbosch WWTP upstream; Site 12: Stellenbosch WWTP discharge point; Site 13: Stellenbosch WWTP downstream; Site 14: Zandvliet WWTP upstream; Site 15: Zandvliet WWTP discharge point; Site 16: Zandvliet WWTP downstream; Site 17: Athlone WWTP upstream; Site 18: Athlone WWTP discharge point; Site 19: Athlone WWTP downstream.

Table 4.12: Range of arsenic concentration in the freshwater samples (μgl^{-1}) and sediment ($mgkg^{-1}$) and camparison with other globally published values

		Range	Mean (Mean±SD)	Reference
Water	WHO		10	WHO, 2002
	Cape Town	**1.62-13.70**	-	**this study**
	Pakistan	-	97.5±28.5	Arain *et al.*, 2009
	Tuskegee Lake	-	0.06±0.23	Ikem *et al.*, 2003
	USA	100->500	-	Welch *et al.*, 2000
	China	<100-1860	-	Xia and Liu, 2004
	Si Thammarat Province, Thailand	1.25-5114	503.4	William *et al.*, 1996
	Taiwan	up to 1800	-	Chen *et al.*, 1994
	Bangladesh	<2->900	-	Mukherjee and Bhattacharya, 2001
	Taiwan	1-50	21±10	Jung *et al.*, 2002
	Japan	0.24-0.68	0.48	Iwashita and Shimamura, 2001.
	China	8.33-28.81	-	Zhang *et al.*, 2010
	Mexico	70-160	-	Gutierrez *et al.*, 2008
Sediment	China	7.77-25.96	-	Bai *et al.*, 2011
	Cape Town	**4.31-210.34**	-	**this study**
	China	8.20-29.90		Yang *et al.*, 2009
	Denmark	18-73	-	Marcussen *et al.*, 2008
	Begium	2.3-140.2	-	Chapagain *et al.*, 2007
	Chile	119-2393	749±544	Oyarzun *et al.*, 2004
	Croatia	18.7-47.2	32.7±8.9	Bukvic *et al.*, 2010
	Bangladesh	16.23-444.02	-	Sarifuzzaman *et al.*, 2007
	Brazil	<20->2830	-	Borba *et al.*, 2000

Table 4.13: Limit values ($mgkg^{-1}$) for toxic elements in sediment

	Vietnamese limit value (Agriculture, Forestry, Residential, Commerce and Service, Industry)	Dutch Values (Target, Intervention)	CCME Values Interim sediment quality guidelines, Probable effect level
As	12 (all cases)	29, 55	5.9, 17
Cd	2, 2, 5, 5,10	1.1, 30	0.596, 3.35
Pb	70, 100, 120, 200, 300	85, 530	35, 91.3
Zn	200, 200, 200, 300, 300	140, 720	123, 315
Hg	NA	NA	0.174, 0.486

CCME= Canadian Councilof Minister on Environment; DOE: Depertment of Environment; NA = Not available

A possible means of arsenic in this section of the river may be attributed to the use of sodium salt of arsenous acid to treat tick infestations on cattle (Okonkwo, 2007) and waste tire dump. The high concentrations of arsenic at site 7 may be attributed to defeacating by cattle in the water as the water is used for livestock management in the area. At sites 11 and 13, the high concentration of arsenic recorded may be attributed to seepage of landfill leachate into the river systems at site 11. The high concentration at site 17 may be attributed to channelization of the upstream and informal seetlement around the sampling point. There is also possibility of storm water contamination as many rivers in Cape Town are known to receive storm water carrying industrial effluents, wastes from home and farms or seepage from groundwater (Synman *et al.*, 2002). Sites 7 (Bellville WWTP downstream) and 14 (Zandvliet WWTP upstream) are sampling points on Kuils River. Site 7 is located far upstream of site 14 which is about 2 km of Zandvliet point of discharge. High arsenic level at this portion of this river may be due to storm and wastewater effluent from the biggest informal settlement in Cape Town (Khayelitsha) with over 1.2 million inhabitants.

The arsenic concentration in sediments taken from the river and the control site were depicted in Figure 4.18 for the seventeen out the nineteen sampling locations. The upstream and point of discharge for Bellville treatment plant was channelized, thus, this made it impossible to get sediment samples from those sites. Apparently, the concentration of arsenic in the sediment taken from all the 17 sampling points ranged from 1.96 μgg^{-1} to 282.26 μgg^{-1}. The highest average concentration was obtained from sampling point 1 (Kirstenbosch Botanical Garden) during winter while the lowest concentration was obtained from sampling point 18 (Athlone discharge point). However, the annual mean value of arsenic obtained from the sediment of the control site and the river system ranged from 4.80 ugg^{-1} to 210 μgg^{-1}.

Previous studies elsewhere indicated that arsenic concentration in contaminated sediment ranged from 2.3 μgg^{-1} to 2393 μgg^{-1} (Marcussen *et al.*, 2008; Yang *et al.*, 2009; Bai *et al.*, 2011). The values in the river sediment reported in this study (Figure 4.18) were within values reported elsewhere. However, the value at the control was extremely high. This can be attributed to the source of the water in the dam being the Table Mountain. This dam is in the upper section of Liesbeck River. Aside the source been Table Mountain, Kirstenbosch botanical garden uses a lot of agrochemicals and pesticides to control weeds, pests and maintain the general outlook of the garden for tourist. Soils usually contain arsenic between 0.001 μgg^{-1} and 0.040 μgg^{-1} in the absence of industrial or agricultural contamination (Reilly, 1991). This clearly shows that the arsenic concentration obtained from the sediments of the receiving river system and the control site is highly polluted. Sediments normally contain considerably higher amounts of arsenic, compared to water. Sediments are always higher in arsenic than the waters with which they are associated.

There is no sediment quality guideline in South Africa, thus, comparing the values with international acceptable standard (Table 4.13), the concentration range was above the Vietnamese Limit Value of 12 $mgkg^{-1}$. According to the Dutch intervention value of 29 $mgkg^{-1}$, Sites 1, 3, 8, 11 and 13 were seriously polluted while Site 16 (30.83 ugg^{-1}) could be rated slightly polluted. However, comparing with the CCME (1999) guidelines, all sites except Site 18 (Athlone discharge point) were above the interim sediment quality guideline, while sites 7, 9, 12, 15 and 18 fell within the probable effect limits.

4.4.2 Cadmium

In this study, seasonal concentrations change of cadmium in water and sediment of the river systems receiving wastewater effluents and Kirstenbosch Botanical Garden are presented in graphical forms (Figures 4.19 and 4.20). For all the sites investigated, the average mean concentrations of Cd in water samples obtained from the river systems ranged from 0.09 μgl^{-1} to 14.78 μgl^{-1} for the 19 sampling points as placed in Figure 4.19. The highest level of cadmium in water was obtained at Site 17 (Athlone WWTP Upstream) during the autum sampling season and the lowest at Site 14 (Zandvliet WWTP Upstream) during autum. The annual average cadmium concentration found in this study ranged from 1.44 μgl^{-1} Site 15 (Zandvliet WWTP discharge point) to 7.96 μgl^{-1} Site (17 Athlone WWTP downstream).

In previous studies conducted in South Africa, Fatoki *et al.* (2002) reported concentration range of 0.01 to 26 mgl^{-1}, while Sanders *et al.* (1999) reported concentration range of between 2 and 4 μgl^{-1}. Cadmium concentration had not been previously reported in the selected river systems in Cape Town as attention had been focus on other toxic metals and expecially in sediment and soil samples. In a study conducted by Reinecke *et al.* (2003), cadmium was detected at about 6 μgl^{-1} for upstream and downstream samples collected in the Eerste River for two sampling seasons. Elsewhere in South Africa, it was reported that levels of cadmium in water ranged from 1.6 μgl^{-1} to 260 μgl^{-1} as placed in Table 4.14 (Sanders *et al.*, 1999; Awofolu *et al.*, 2005; Okonkwo and Mothiba, 2005). Annual values reported in this study were lower compared to previous finding in the Eastern Cape and Nigeria (Table 4.14). Cd concentrations in non-polluted natural waters usually are lower than 1 μgl^{-1}, have been reported (Hans, 1994).

On camparison with South Africa water quality guidelines, the reported levels of cadmium indicated that all sampling sites concentration were within the limits for human consumtion except for site 17 and 19, while all sites, 17 and 19 inclusive were below the set limits of 10 μgl^{-1} for livestock watering and irrigation of farmlands. However, in relation to protection of aquatic lifes, reported concentrations for all the 19 sites were above the 0.2 μgl^{-1} and 0.017 μgl^{-1} limits set byt DWAF, (1996) and CCME, (1999), respectively.

Figure 419: Seasonal trend in Cd concentrations (μgl^{-1}) in river water receiving waste effluent from WWTPs

Site 1: Kirstenbosch Botanical garden (Control Site); Site 2: Potsdam WWTP upstream; Site 3: Potsdam WWTP discharge point; Site 4: Potsdam WWTP downstream; Site 5: Bellville WWTP upstream; Site 6: Bellville WWTP discharge point; Site 7: Bellville WWTP downstream; Site 8: Kraaifontein WWTP upstream; Site 9: Kraaifontein WWTP discharge point; Site 10: Kraaifontein WWTP downstream; Site 11: Stellenbosch WWTP upstream; Site 12: Stellenbosch WWTP discharge point; Site 13: Stellenbosch WWTP downstream; Site 14: Zandvliet WWTP upstream; Site 15: Zandvliet WWTP discharge point; Site 16: Zandvliet WWTP downstream; Site 17: Athlone WWTP upstream; Site 18: Athlone WWTP discharge point; Site 19: Athlone WWTP downstream.

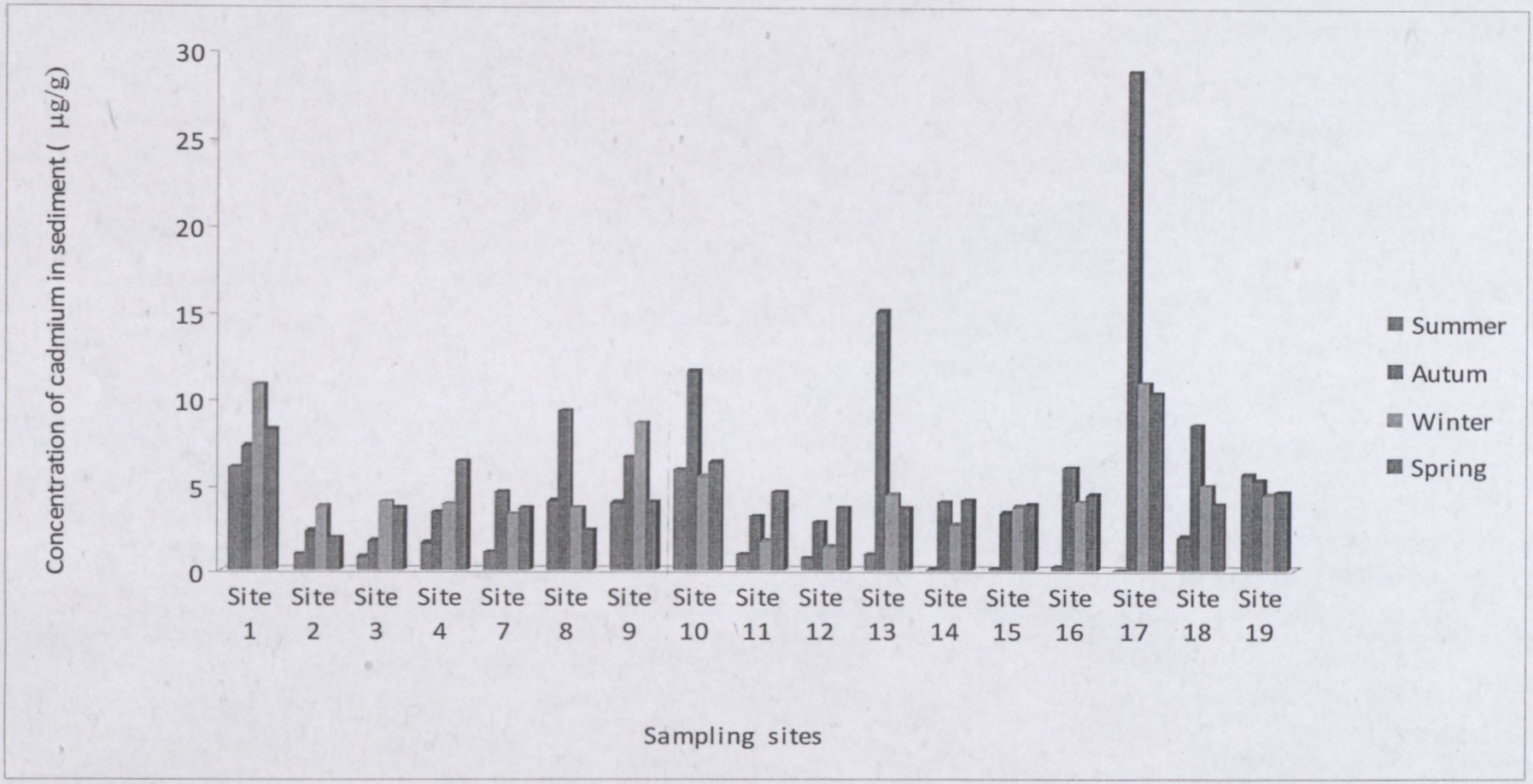


Figure 4.20: Seasonal trend in Cd concentrations ($\mu g g^{-1}$) in river sediment receiving waste effluent from WWTPs

Site 1: Kirstenbosch Botanical Garden (Control Site); Site 2: Potsdam WWTP upstream; Site 3: Potsdam WWTP discharge point; Site 4: Potsdam WWTP downstream; Site 7: Bellville WWTP downstream; Site 8: Kraaifontein WWTP upstream; Site 9: Kraaifontein WWTP discharge point; Site 10: Kraaifontein WWTP downstream; Site 11: Stellenbosch WWTP upstream; Site 12: Stellenbosch WWTP discharge point; Site 13: Stellenbosch WWTP downstream; Site 14: Zandvliet WWTP upstream; Site 15: Zandvliet WWTP discharge point; Site 16: Zandvliet WWTP downstream; Site 17: Athlone WWTP upstream; Site 18: Athlone WWTP discharge point; Site 19: Athlone WWTP downstream.

Table 4.14: Range of cadmium concentration in the freshwater samples (μgl^{-1}) and sediment ($mgkg^{-1}$) and camparison with other globally published values

		Range	Mean (Mean±SD)	Reference
Water	South Africa	2-4	-	Sanders *et al.*, 1999
	South Africa	10-260	-	Fatoki *et al.*, 2002
	Cape Town	**1.44-7.96**	-	**this study**
	South Africa	30-44	-	Awofolu *et al.*, 2005
	Mexico	-	14	Gutierrez *et al.*, 2008
	Egypt	<0.5-34	25	Bouraie *et al.*, 2010
	India	0.67-5.61	-	Ashokkumar *et al.*, 2009
	South Africa	-	6	Reinecke *et al.*, 2003
	South Africa	1.6-9.3	-	Okonkwo and Mothiba, 2005
	Nigeria	30-390	-	Ohiamain *et al.*, 2008
Sediment	Turkey	0.139-0.572	0.29	Duman *et al.*, 2007
	Cape Town	**2.15-12.49**	-	**this study**
	China	0.1-3.40	-	Yang *et al.*, 2009
	Vietnam	0.88-427	-	Marcussen *et al.*, 2009
	China	0.32-1.62	0.76±0.22	Bai *et al.*, 2011
	Uganda	0.81-3.81	-	Sekabira *et al.*, 2010
	Nigeria	7.34-19.34	-	Akan *et al.*, 2010
	South Africa	4.1-142.2	-	Sanders et al., 1999
	South Africa	0.002-0.005	-	Awofolu *et al.*, 2005
	South Africa (Stellenbosch)	0.43-0.45	-	Reneicke *et al.*, 2003
	South Africa (Cape Town)	7.12-19.2	-	Ayeni *et al.*, 2010

On the other hand, cadmium concentration in the sediment from the 17 sampling points showed a concentration range of 0.09 to 28.8 μgg^{-1}. The highest concentration was obtained at Site 17 during autum and the least was at Site 14 in summer. The annual mean concentration ranged from 2.15 μgg^{-1} (Site 12, Stellenbosch WWTP discharge point) to 12.49 μgg^{-1} (Site 17, Athlone WWTP Upstream). Previous study by Ayeni *et al.* (2010) on the lower section of Diep River had reported concentration range of 7.12 to 19.2 μgg^{-1} (Table 4.14), while other studies in South Africa had reported somewhat higher concentration in river sediment (Sanders *et al.*, 1999). Cd concentrations in this study were lower compared to other study in Cape Town (Ayeni *et al.*, 2010). The ranged of values reported in this study were higher than the Vietnamese limit value, Dutch target value and guidelines for threshold effect concentration and probable effect level of 2, 1.1, 0.596 and 3.35 $mgkg^{-1}$ (Table 4.13). However, the reported values were below the Dutch Intervention guidelines of 30 $mgkg^{-1}$.

4.4.3 Lead

The result of seasonal concentrations of lead in water and sediment of the selected river systems receiving wastewater effluent are presented in Figures 4.21 and 4.22. The average values of Pb in water samples obtained from the river system ranged from 4.18 μgl^{-1} to 86.73 μgl^{-1} for the 19 sampling points as shown in Figure 4.21. The highest level of lead was obtained at Site 16 (Zanvliet WWTP point of discharge) during summer and the lowest at Site 1(control site, Kirstenbosch Botanical Garden) during summer. Meanwhile, the annual mean value of lead at each sampling site in this study for water ranged from 17.64 μgl^{-1} to 52.99 μgl^{-1}.

Previous studies in South Africa had reported Pb concentration ranging below detection limit to 1110 μgl^{-1} (Fatoki *et al.*, 2002; Okonkwo and Mothiba, 2005) (Table 4.15). Meanwhile, another study Reinecke *et al.* (2003) reported 30 to 40 μgl^{-1} of lead in the Eerste River. Effluent discharges from sewage treatment plant and industries had been suggested as possible routes of Pb into river systems. Thus, considering the values reported in the study, wastewater effluent is a factor to high lead concentration in the river system. Though, the study showed that the final effluent concentrations were generally low for lead, and that the effluent helps to further dilute the river water concentration, possible contamination source could not be ruled out. The recommended threshold level of lead for South Africa Rivers is 10 μgl^{-1} (DWAF, 1996). The results showed that the annual average value of lead for all the sampling points of the river system and the control site were above the TWQR threshold level for human consumption and

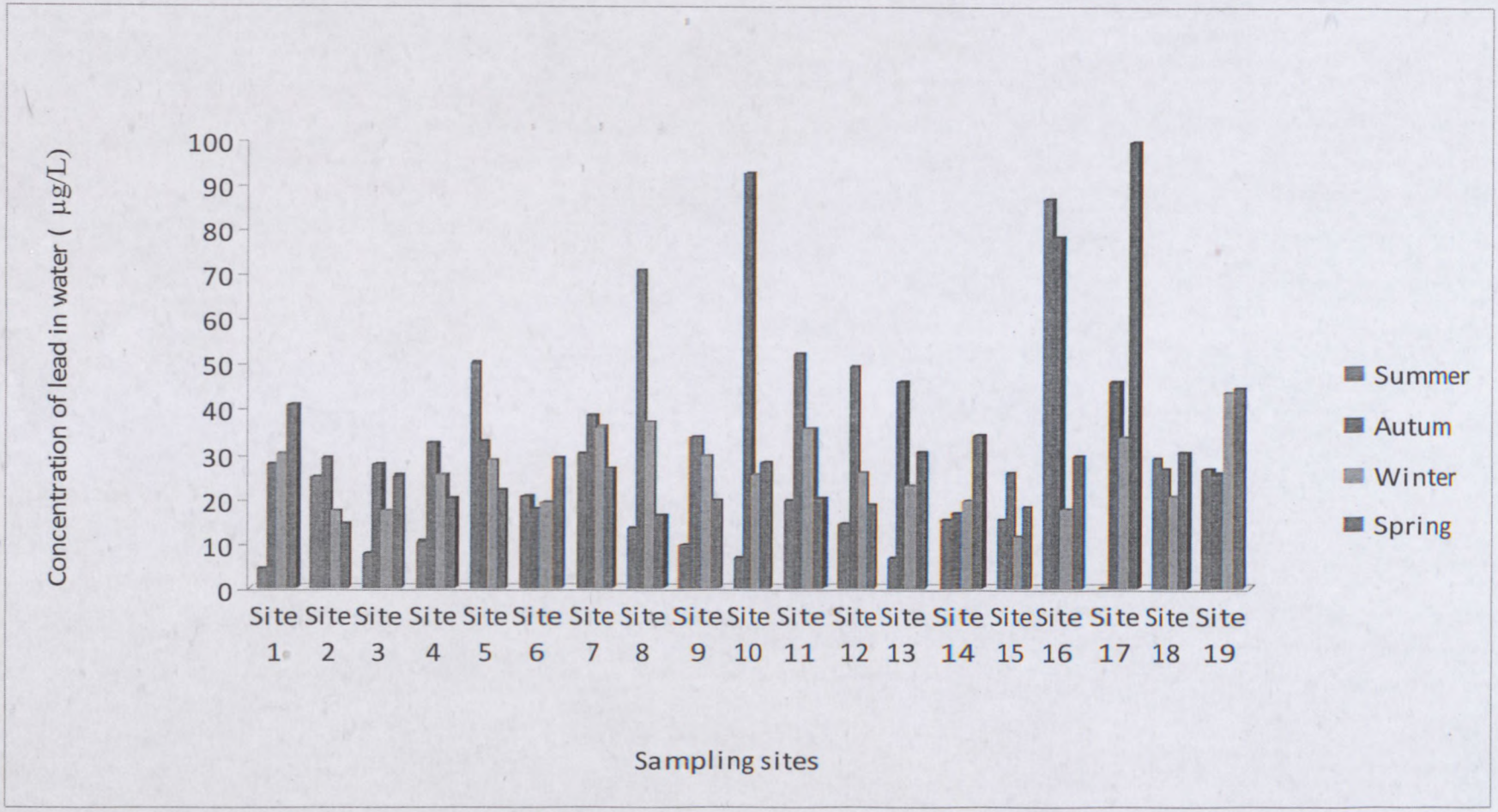


Figure 4.21: Seasonal trend in Pb concentrations (μgl^{-1}) in river water receiving waste effluent from WWTPs

Site 1: Kirstenbosch Botanical garden (Control Site); Site 2: Potsdam WWTP upstream; Site 3: Potsdam WWTP discharge point; Site 4: Potsdam WWTP downstream; Site 5: Bellville WWTP upstream; Site 6: Bellville WWTP discharge point; Site 7: Bellville WWTP downstream; Site 8: Kraaifontein WWTP upstream; Site 9: Kraaifontein WWTP discharge point; Site 10: Kraaifontein WWTP downstream; Site 11: Stellenbosch WWTP upstream; Site 12: Stellenbosch WWTP discharge point; Site 13: Stellenbosch WWTP downstream; Site 14: Zandvliet WWTP upstream; Site 15: Zandvliet WWTP discharge point; Site 16: Zandvliet WWTP downstream; Site 17: Athlone WWTP upstream; Site 18: Athlone WWTP discharge point; Site 19: Athlone WWTP downstream.

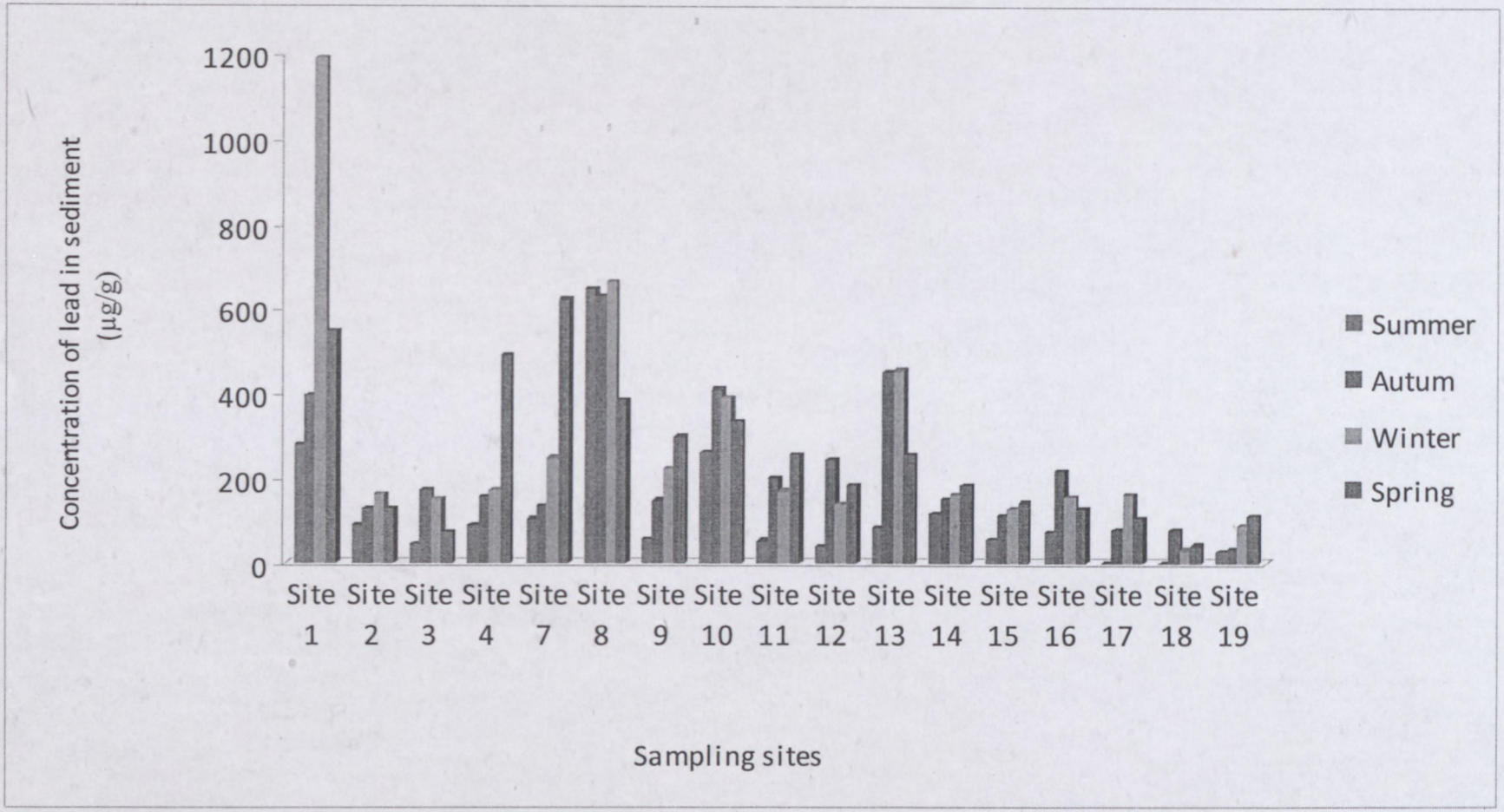


Figure 4.22: Seasonal trend in Pb concentrations ($\mu g g^{-1}$) in river sediment receiving waste effluent from WWTPs

Site 1: Kirstenbosch Botanical Garden (Control Site); Site 2: Potsdam WWTP upstream; Site 3: Potsdam WWTP discharge point; Site 4: Potsdam WWTP downstream; Site 7: Bellville WWTP downstream; Site 8: Kraaifontein WWTP upstream; Site 9: Kraaifontein WWTP discharge point; Site 10: Kraaifontein WWTP downstream; Site 11: Stellenbosch WWTP upstream; Site 12: Stellenbosch WWTP discharge point; Site 13: Stellenbosch WWTP downstream; Site 14: Zandvliet WWTP upstream; Site 15: Zandvliet WWTP discharge point; Site 16: Zandvliet WWTP downstream; Site 17: Athlone WWTP upstream; Site 18: Athlone WWTP discharge point; Site 19: Athlone WWTP downstream.

Table 4.15: Range of lead concentration in the freshwater samples (μgl^{-1}) and sediment ($mgkg^{-1}$) and camparison with otherglobal published values

		Range	Mean (Mean±SD)	Reference
Water	**Cape Town**	**17.64-52.99**	-	**this study**
	Nigeria	10-2570	-	Ohiamain *et al.*, 2008
	South Africa	10.5-20.1	-	Okonkow and Mothiba, 2005
	Greece	ND-12.61	-	Papafilippaki *et al.*, 2008
	South Africa	30-40	-	Reinecke *et al.*, 2003
	South Africa	24-350	-	Awofolu *et al.*, 2005
	South Africa	240-1110	-	Fatoki *et al.*, 2002
	Egypt	5-57	-	Bouraie *et al.*, 2010
Sediment	South Africa	5.3-7.0	-	Reinecke *et al.*, 2003
	Cape Town	**36.67-603.19**	-	**this study**
	China	30.71-88.96	53.19±11.73	Bai *et al.*, 2011
	Vietnam	58.9-168	-	Marcussen *et al.*, 2008
	India	4.8-156.20	32.88±21.93	Singh *et al.*, 2005
	China	20.00-142.00	-	Yang *et al.*,. 2009
	South Africa	2.6-71.7	-	Ayeni *et al.*, 2010
	China	22-3470	-	Wu *et al.*, 2010
	Philippines	2.20-1256.16	-	Roa *et al.*, 2010

aquacultural purposes. However, reported values were within the TWQR for irrigation and livestock watering. The water is unsuitable for the protection of aquatic ecosystems as TWQR limits of 0.2 μgl^{-1} was exceeded.

The seasonal concentrations for Pb in sediment samples from all the 17 sampling sites are presented in Figure 4.22, while the annual mean Pb concentration in the sediment samples ranged from 36.67μgg^{-1} to 603.19 μgg^{-1}. Site 1 was the most polluted while Site 18 was the least. The contamination pattern recorded in this study for lead was similar to the distribution pattern reported for lead. In previous studies as reported in Table. 4.15, Pb in contaminated sediment ranged from 2.2 μgg^{-1} to 3470 μgg^{-1} (Reinecke *et al.*, 2003; Singh *et al.*, 2005; Yang *et al.*, 2009; Marcussen *et al.*, 2008; Ayeni *et al.*, 2010; Roa *et al.*, 2010; Wu *et al.*, 2010; Bai *et al.*, 2011).

Comparing the Pb cocnetration in this study with Dutch target limits, all sites with the exception of Site 18 exceeded the limit of 85 μgg^{-1}, however, all sites except sites 1 and 8 were within the intervention guideline of 530 μgg^{-1}. Meanwhile, using the threshold and probable effect concentration by CCME (1999) as the bench mark, all sites exceeded the limits. Thus, the reported values for all the sampling sites clearly shows that the river river systems and the control site were highly contaminated and water from these sites were not suitable for the support of aquatic life and supply water for domestic uses.

4.4.4 Mercury

In this study, the seasonal concentrations of mercury in water of the selected river system and control site are depicted in Figure 4.23. The average levels of Hg in water samples obtained from the 19 sampling sites ranged from 0.1 μgl^{-1} to 8.09 μgl^{-1}, while the annual mean concentration for each sampling site ranged from 1.45 μgg^{-1} to 2.58 μgg^{-1}. The highest level of mercury was obtained at sampling site 15 (Zandvliet discharge point) during the spring season and the lowest at sampling point 2 (Potsdam WWTP upstream) as depicted in Figure 4.23. Previous study in Eastern Cape had reported concentration of Hg to be 0.003 mgl^{-1} (Fatokia and Awofolu, 2003), while Retief *et al.* (2009) reported Hg concentration range of 0.125 μgl^{-1} to 0.513 μgl^{-1} in the Vaal dam, South Africa.

Previous studies in several countries reported levels of mercury in water were ranged from not detetcted to 1502 μgl^{-1} (Fernandez *et al.*, 1992; Navarro *et al.*, 1993; Ayas and Kolankaya, 1996; Ramos *et al.*, 1999; Ashokkumar *et al.*, 2009) (Table 4.16). The recommended TWQR threshold level of mercury for South African rivers for human consumption is 1.00 μgl^{-1} (DWAF, 1996). The average values of mercury for all the samplings sites exceeded the limits, though there are instances during sampling period where Hg concentrations were below this guideline. Also, Hg concentration exceeded TWQR guideline for the protection of aquatic

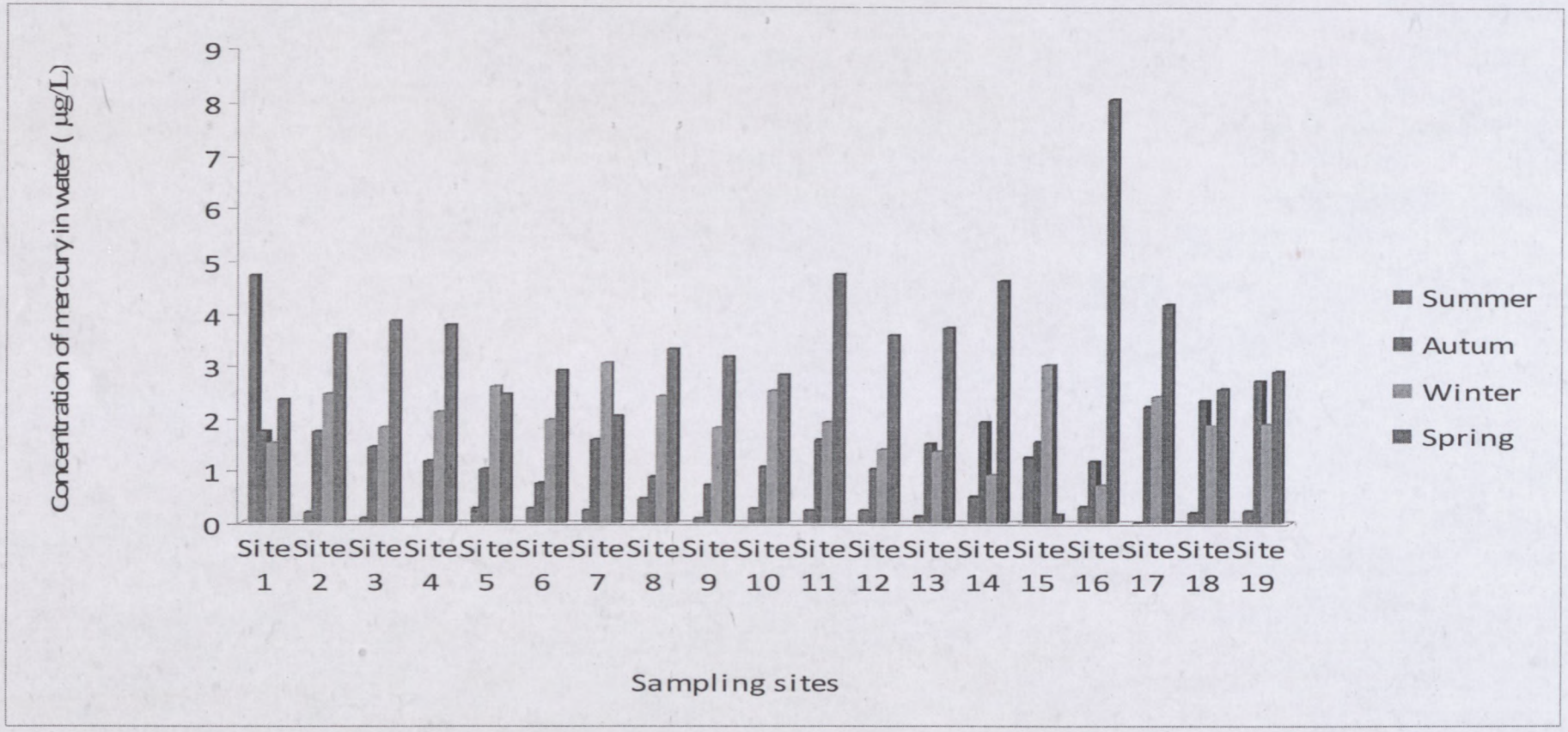


Figure 4.23: Seasonal trend in Hg concentration (μgl^{-1}) in river water receiving waste effluent from WWTPs

Site 1: Kirstenbosch Botanical garden (Control Site); Site 2: Potsdam WWTP upstream; Site 3: Potsdam WWTP discharge point; Site 4: Potsdam WWTP downstream; Site 5: Bellville WWTP upstream; Site 6: Bellville WWTP discharge point; Site 7: Bellville WWTP downstream; Site 8: Kraaifontein WWTP upstream; Site 9: Kraaifontein WWTP discharge point; Site 10: Kraaifontein WWTP downstream; Site 11: Stellenbosch WWTP upstream; Site 12: Stellenbosch WWTP discharge point; Site 13: Stellenbosch WWTP downstream; Site 14: Zandvliet WWTP upstream; Site 15: Zandvliet WWTP discharge point; Site 16: Zandvliet WWTP downstream; Site 17: Athlone WWTP upstream; Site 18: Athlone WWTP discharge point; Site 19: Athlone WWTP downstream.

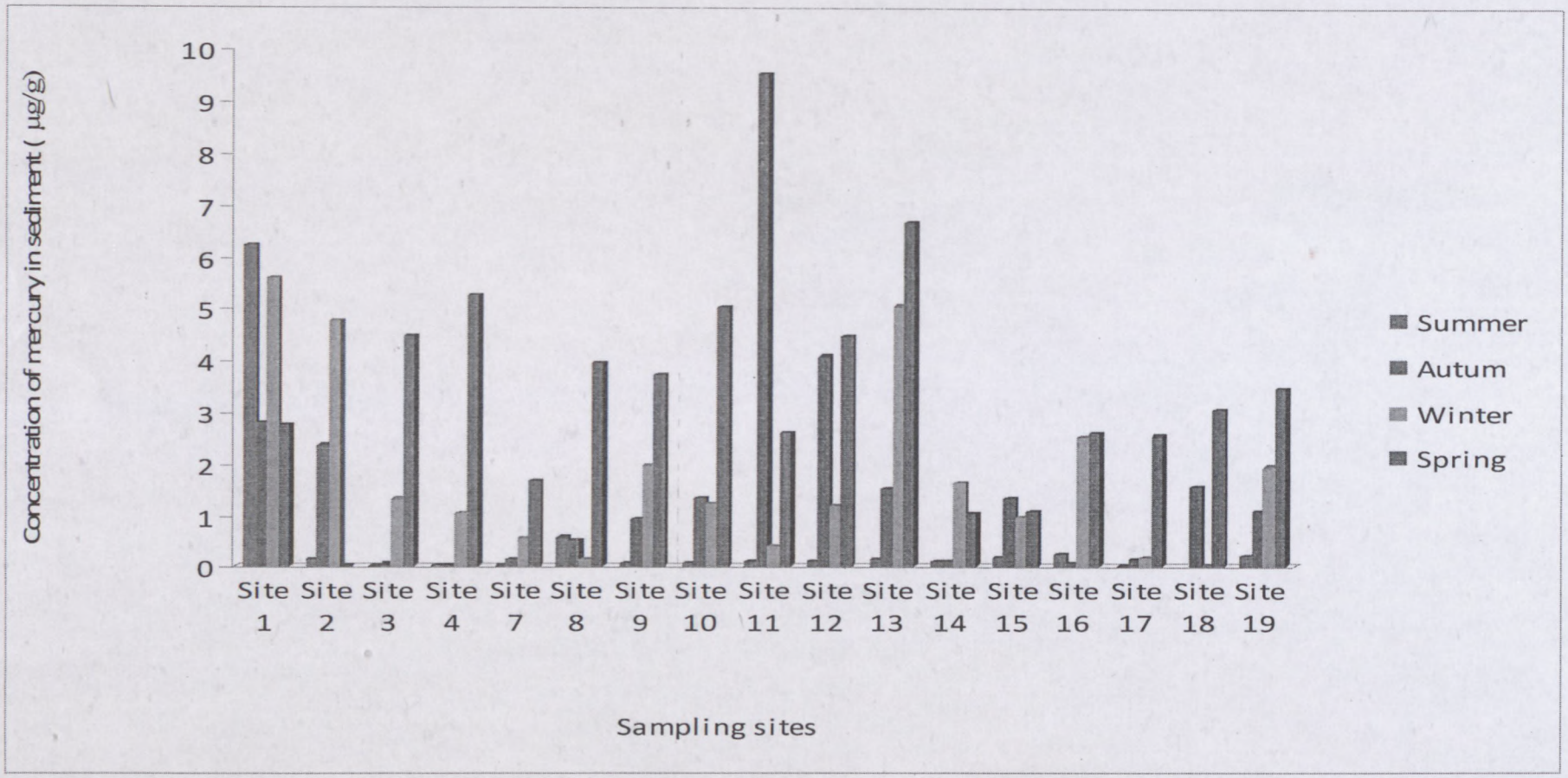


Figure 4.24: Seasonal trend in Hg concentration (μgg^{-1}) in river sediment receiving waste effluent from WWTPs

Site 1: Kirstenbosch Botanical Garden (Control Site); Site 2: Potsdam WWTP upstream; Site 3: Potsdam WWTP discharge point; Site 4: Potsdam WWTP downstream; Site 7: Bellville WWTP downstream; Site 8: Kraaifontein WWTP upstream; Site 9: Kraaifontein WWTP discharge point; Site 10: Kraaifontein WWTP downstream; Site 11: Stellenbosch WWTP upstream; Site 12: Stellenbosch WWTP discharge point; Site 13: Stellenbosch WWTP downstream; Site 14: Zandvliet WWTP upstream; Site 15: Zandvliet WWTP discharge point; Site 16: Zandvliet WWTP downstream; Site 17: Athlone WWTP upstream; Site 18: Athlone WWTP discharge point; Site 19: Athlone WWTP downstream.

Table 4.16: Range of mercury concentration in the freshwater samples (μgl^{-1}) and sediment ($mgkg^{-1}$) and camparison with otherglobal published values

		Range	Mean (Mean±SD)	Reference
Water	**Cape Town**	**1.45-2.58**	-	**this study**
	India	0.015-0.194	0.001	Ashokkumar *et al.*, 2009
	South Africa	trace-3	-	Fatoki and Awofolu, 2003
	Spain	ND	-	Ramos *et al.*, 1999
	Turkey	1.50-1502	-	Ayas and Kolankaya, 1996
	Spain	ND-2.09	-	Navarro *et al.*, 1993
	Spain	2.80-5.70	-	Fernandez *et al.*, 1992
Sediment	China	0.04-1.93	-	Yang *et al.*, 2009
	Cape Town	**0.58-4.33**	-	**this study**
	China	0.04-61.20	-	Wu *et al.*, 2010
	India	0.017-0.191	0.05±35	Ashokkumar *et al.*, 2009
	Philippines	2.85-341.06	-	Rao *et al.*, 2010
	Spain	0.05-1.46	-	Ramos *et al.*, 1999

ecosystem, livestock watering and aquacultural uses. Considering the effect of ingesting Hg through the river water, the water system is unsafe for domestic, agricultural, livestock and aquacultural uses.

The Hg concentrations in sediments from the river systems and control site are presented in Figure 4.24. The mercury concentration ranged from 0.004 μgg^{-1} to 9.52 μgg^{-1}. The highest concentration was obtained during autum at Site 11 (Stellensboch upstream) and the lowest concentration was obtained at Site 2 (Potsdam upstream) during the spring. Meanwhile the annual mean concentration of hg for the 17 sites ranged from 0.58 μgg^{-1} (Site 7, Bellville downstream) to 4.33 μgg^{-1} (Site 1, Kirstenboach Botanical Garden). Previous study by Retief *et al.* (2009), reported concentration range of 0.0014 μgg^{-1} to 0.95 μgg^{-1} in Vaal dam, South Africa.

Elsewhere, studies had indicated that Hg concentration in contaminated sediment ranged from 0.41 μgg^{-1} to 341.06 μgg^{-1} as placed in Table 4.4.8 (Ramos *et al.*, 1999; Ashokkukamr *et al.*, 2009; Yang *et al.*, 2009; Roa *et al.*, 2010; Wu *et al.*, 2010). Comparing the reported values in this study with international standard limits (CCME, 1999), the concentration exceeded both the interim sediment quality guideline and probable effect level of 0.174 μgg^{-1} and 0.486 μgg^{-1}. This clearly indicates that the overall Hg concentration obtained from the sediments of all the sampling point is polluted.

4.4.5 Zinc

Seasonal variation in the concentration of Zn in water samples from all the 19 sampling sites is presented in Figure 4.25. The average seasonal concentration ranged from 25.15 μgl^{-1} to 909.38 μgl^{-1}. The highest level of zinc was obtained at sampling site 15(Sandvliet discharge point) during summer and the lowest at sampling site 12 (Stellenbosch discharge point). Meanwhile, the annual mean zinc concentration found in this ranged from 172.79 μgl^{-1} (Site 1, Kirstenbosch Botanical Garden) to 722.07μgl^{-1}(Site 13, Stellenbosch downstream).

Previous study in the Western Cape Province had reported various concentration of Zn in river water. Jackson *et al.* (2007), reported zinc concentration range of 100 μgl^{-1} to 2100 μgl^{-1} in Berg River and Jackson *et al.* (2009), reported a concentration range of between 100 μgl^{-1} to 4400 $\mu gl^{-1}$for studies conducted on Plankenburg and Diep Rivers. However, studies elsewhere in South Africa had reported concentration range of 10 μgl^{-1} to 431 μgl^{-1} (Sanders *et al.*, 1999; Fatoki *et al.*, 2002; Fatoki and Awofolu, 2003; Awofolu *et al.*, 2005) (Table 4.17). Meanwhile, studies in several countries reported levels of zinc in water were ranged from <5 μgl^{-1} to 97 μgl^{-1} (Ashokkumar *et al.*, 2009; Bouraie *et al.*, 2010) (Table 4.4.10). The reported values in this study were lower compare to previous studies in Cape Town. Aside from the geology of the catchment, zinc concentration in the river systems pointed towards WWTPs and storm water carrying both industrial and domestic effluents.

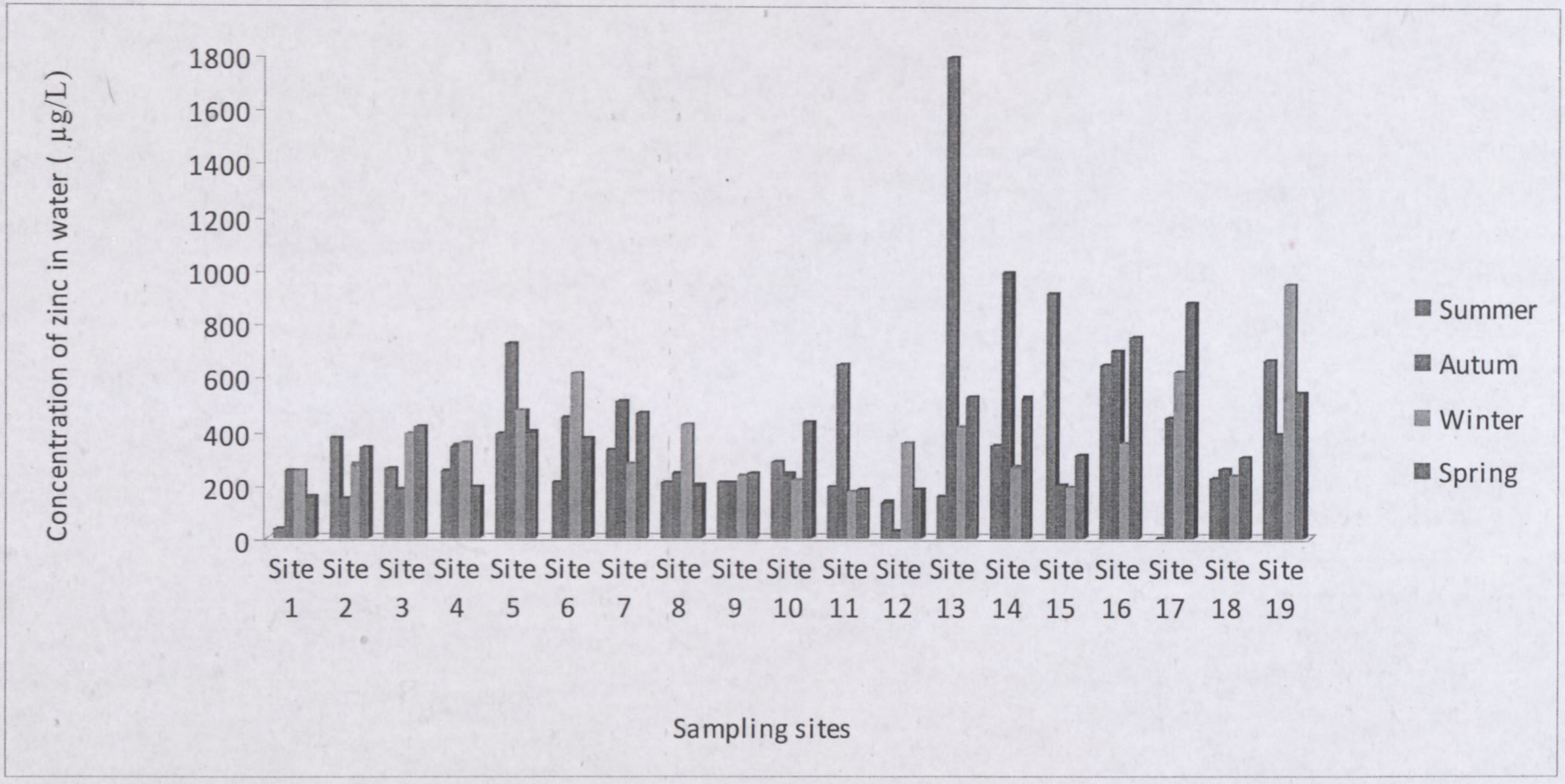


Figure 4.25: Seasonal trend in Zn concentrations (μgl^{-1}) in river water receiving waste effluent from WWTPs

Site 1: Kirstenbosch Botanical garden (Control Site); Site 2: Potsdam WWTP upstream; Site 3: Potsdam WWTP discharge point; Site 4: Potsdam WWTP downstream; Site 5: Bellville WWTP upstream; Site 6: Bellville WWTP discharge point; Site 7: Bellville WWTP downstream; Site 8: Kraaifontein WWTP upstream; Site 9: Kraaifontein WWTP discharge point; Site 10: Kraaifontein WWTP downstream; Site 11: Stellenbosch WWTP upstream; Site 12: Stellenbosch WWTP discharge point; Site 13: Stellenbosch WWTP downstream; Site 14: Zandvliet WWTP upstream; Site 15: Zandvliet WWTP discharge point; Site 16: Zandvliet WWTP downstream; Site 17: Athlone WWTP upstream; Site 18: Athlone WWTP discharge point; Site 19: Athlone WWTP downstream.

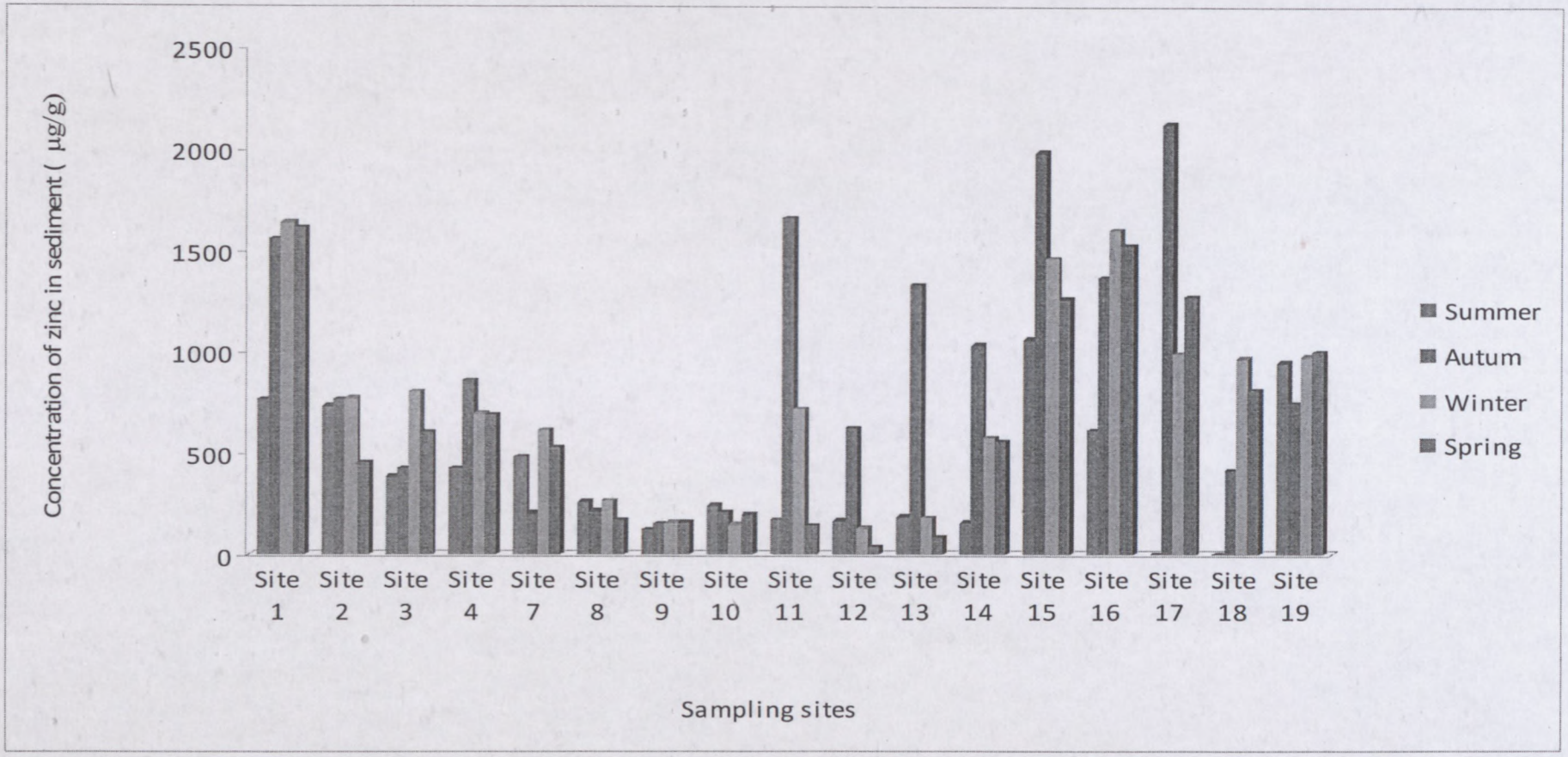


Figure 4.26: Seasonal trend in Zn concentrations ($\mu g g^{-1}$) in river sediment receiving waste effluent from WWTPs

Site 1: Kirstenbosch Botanical Garden (Control Site); Site 2: Potsdam WWTP upstream; Site 3: Potsdam WWTP discharge point; Site 4: Potsdam WWTP downstream; Site 7: Bellville WWTP downstream; Site 8: Kraaifontein WWTP upstream; Site 9: Kraaifontein WWTP discharge point; Site 10: Kraaifontein WWTP downstream; Site 11: Stellenbosch WWTP upstream; Site 12: Stellenbosch WWTP discharge point; Site 13: Stellenbosch WWTP downstream; Site 14: Zandvliet WWTP upstream; Site 15: Zandvliet WWTP discharge point; Site 16: Zandvliet WWTP downstream; Site 17: Athlone WWTP upstream; Site 18: Athlone WWTP discharge point; Site 19: Athlone WWTP downstream.

Table 4.17: Range of zinc concentration in the freshwater samples (μgl^{-1}) and sediment ($mgkg^{-1}$) and camparison with otherglobal published values

		Range	Mean (Mean±SD)	Reference
Water	**Cape Town**	**172.79-722.07**	-	**this study**
	Egypt	<5-97	-	Bouraie *et al.*, 2010
	South Africa	70-120	-	Faoki *et al.*, 2002
	South Africa	10-358	-	Sanders *et al.*, 1999
	South Africa	18-431	-	Awofolu *et al.*, 2005
	India	15.46-34	-	Ashokkumar *et al.*, 2009
	South Africa	0-2100	-	Jackson *et al.*, 2007
	South Africa	100-4400	-	Jackson *et al.*, 2009
	South Africa	220	-	Reinecke *et al.*, 2003
	South Africa	26-350	-	Faoki and Awofolu, 2003
Sediment	China	49.00-1142	-	Yang et al., 2009
	Cape Town	**144.46-1443.13**	-	**this study**
	China	29.6-121.68	86.82±30.05	Bai *et al.*, 2011
	Denmark	362-1240	-	Marcussen *et al.*, 2008
	Egypt	146.6-742	-	Bouraie *et al.*, 2010
	South Africa	578-15240	-	Sanders *et al.*, 1999
	Turkey	39.02-75.31	-	Duman *et al.*, 2007
	Uganda	44.27-1968.43	-	Sekabira *et al.*, 2010
	India	128.66-308.02	210.10	Ashokkumar *et al.*, 2009
	India	8.47-343.47	-	Singh *et al.*, 2005
	South Africa	269.5-1081.2	-	Jackson *et al.*, 2009
	South Africa	44.7-77.5	-	Reinecke *et al.*, 2003
	South Africa	2.9-211.3	-	Ayeni *et al.*, 2010

The recommended TWQR for Zn in water for domestic purposes is 3000 μgl^{-1} (DWAF, 1996). Thus, from the reported values, no health effect is expected from domestic use of the water from the sampling sites. However, the TWQR for the protection of aquatic ecosystem, aquacultural purposes, livestock watering and irrigation of are 2 μgl^{-1}, 30 μgl^{-1}, 0 to 20 mgl-1 and 100 μgl^{-1}. From this study, water from the river systems and the control site is not suitable for the protection of aquatic ecosystem or use for aquacultural purposes.

Apparently, the seasonal variation in the concentrations of Zn in sediment taken from the 17 sampling sites is presented in Figure 4.26. The concentration ranged from 35.62 μgg^{-1} to 1986.72 μgg^{-1}. The highest seasonal average concentration was obtained from sampling site 15 (Zandvliet discharge point) during autum and the lowest concentration was obtained from sampling site 12 (Stellenbosch discharge point). Meanwhile, the annual mean concentration of Zn obtained in the sediment from each sampling site ranged from 144.46 (Site 9, Kraaifontein discharge) to 1443.13 (Site 15, (Zandvliet discharge point).

Several studies on Zn in the sediment from different sections of Diep, Plankenburg and Berg Rivers in Cape Town had reported concentration range of 2.9 to 1081.2 (Reinecke *et al.*, 2003; Jackson *et al.*, 2007; Jackson *et al.*, 2009; Ayeni *et al.*, 2010) (Table 4.17). Elsewhere in South Africa, concentration range of 0.08 μgg^{-1} to 15,240 μgg^{-1} had been reported (Sanders *et al.*, 1999; Fatoki *et al.*, 2002; Awofolu *et al.*, 2005; Singh *et al.*, 2005; Marcussen *et al.*, 2008; Sekabirat *et al.*, 2010). However, studies in several countries like Egypt, Uganda, Vietnam, India and China had reported concentration of 29.6 μgg^{-1} to 1968.43 μgg^{-1} in river sediment (Duman *et al.*, 2007; Ashokkumar *et al.*, 2009; Yang *et al.*, 2009; Bouraie *et al.*, 2010; Bai *et al.*, 2011)(Table 4.17).

Comparing the reported values of Zn in this study with internationally acceptable values, all sampling sites exceeded the target level for Zn in river sediment by Dutch standard. However, zinc levels at site 1, 14, 17 and 19 were above the intervention limits guideline. Meanwhile, using the CCME benchmark, all the sites exceeded the interim sediment quality guideline of 123 and sites 8, 9, 10 and 12 were within the probable effect limit.

4.5 Results and discussion on method development on HPLC and GC-MS

4.5.1 Method development on Agillent 1100 HPLC

4.5.1.1 Chromatographic separation

The SPE-HPLC-DAD chromatograms of a standard mixture of all the eleven priority phenols and surrogate standard (2, 4, 6-TBP) under the chromatographic conditions described in the experimental section are presented in Figures 4.27 and 4.28. As can be seen in Figure 4.5.1 and 4.5.2, the chromatographic conditions used yielded an adequate resolution of the target compounds in less than 14 min (Acetonitrile/water) and 25 min (methanol/water). Methanol/water take longer time thus not in conformity with the aim of reducing organic solvent used for analysis.

4.5.1.2 Linearity and precision

An in-house validation of the proposed analytical method was performed in order to establish essential parameters, linearity range, detection limits, quantification limits, precision and accuracy. Because no certified reference material was available, the trueness of the analytical method was assessed through the recovery of a standard mixture target analyte. For all the analytes investigated, external calibration method as described by Zakeri-Milani *et al.* (2005) was used. Calibration plots were built reporting the peak area (relative units as given by the integrator) versus standard concentration in a concentration range between 0.1 and 30 $ng\mu l^{-1}$ for all the analytes except for 4-nitrophenol (2.5 to 30 $ng\mu l^{-1}$). Straight lines were obtained for the regression parameters reported in Table 4.18. The goodness of fit (R^2) for all analytes was > 0.99 demonstrating method suitability for the analysis (Chawla *et al.*, 2006; Campo *et al.*, 2006). The calibration plots for all the analytes are presented in Appendix 1.

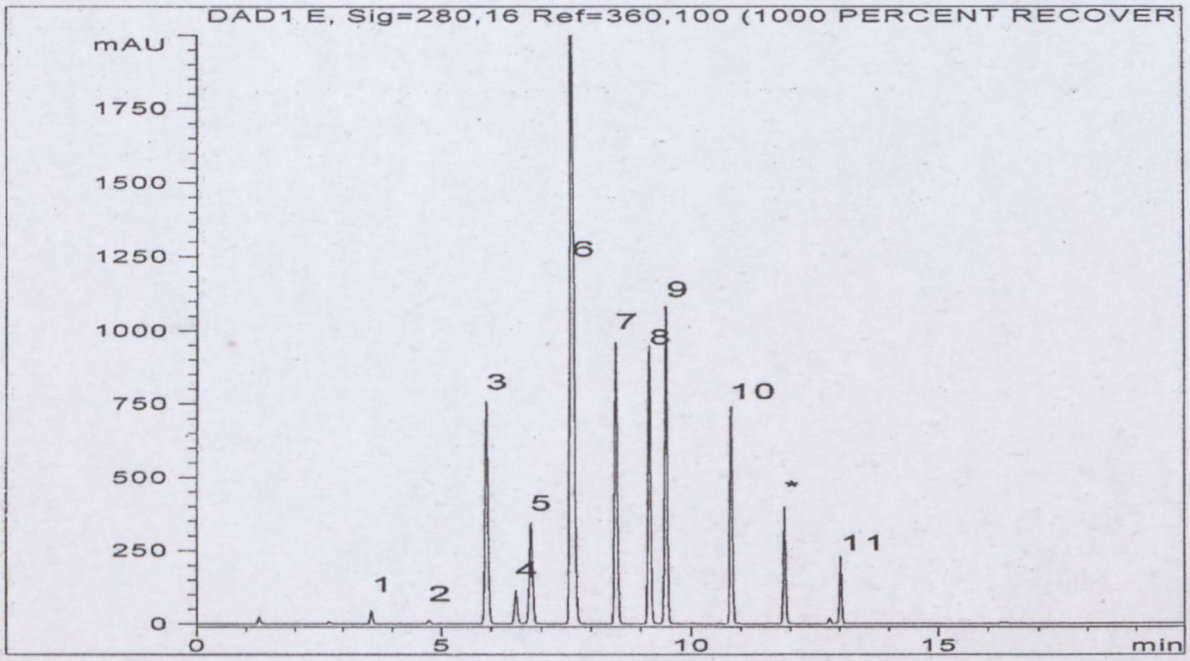


Fig. 4.27: Acetonitrile/water separation of phenol; (1) phenol (2) 4-nitrophenol (3) 2-chlorophenol (4) 2,4-dinitrophenol, (5) 2-nitrophenol (6) 2,4-dimethyl phenol (7) 4-chloro, 3-methyl phenol (8) 2,4-dichlorophenol (9)2-methyl, 4,6-dinitrophenol (10) 2,4,6-trichlorophenol, (*) 2,4,6-tribromophenol (11) pentachlorophenol.

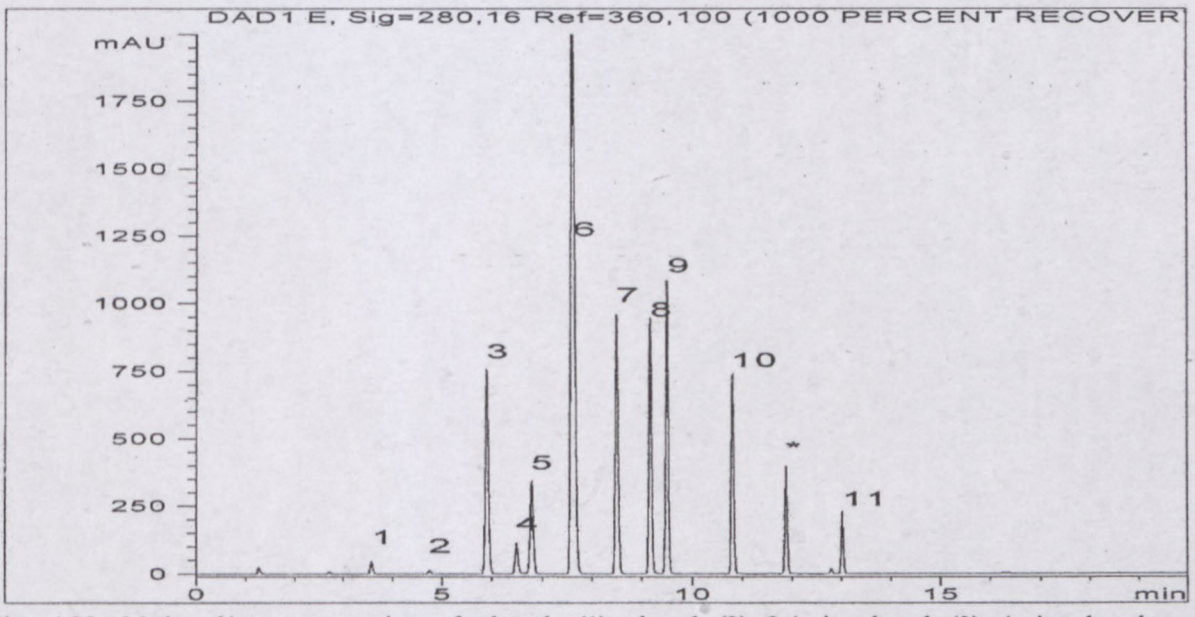


Fig. 4.28: Methanol/water separation of phenol; (1) phenol (2) 2,4-nitrophenol (3) 4-nitrophenol (4) 2-dinitrophenol (5) 2-chlorophenol (6) 2,4-dimethyl phenol (7) 2-methyl, 4,6-dinitrophenol (8) 4-chloro, 3-methyl phenol (9) 2,4-dichlorophenol (10) 2,4,6-trichlorophenol, (*) 2,4,6-tribromophenol (11) pentachlorophenol.

Table 4.18: Calibration plot equations: peak area (y, relative units) versus standard concentration (x, ngμl^{-1}), correlation coefficients, retention times and linearity.

Analyte	Retention time	Calibration Plot	r^2	Linearity (ngμl^{-1})
P-OH	3.543	y = 10.28493x + 0.38296	0.99972	0.30 – 30
4-NP	4.706	y = 0.85740x + 0.00285	0.99919	2.5 – 30
2-CP	5.865	y = 204.50267x – 9.7233	0.99986	0.20 – 30
2,4-DNP	6.452	y = 38.36583x – 4.4209	0.99976	0.20 – 30
2-NP	6.746	y = 27.76183x – 4.22382	0.99979	0.20 – 30
2,4-DP	7.550	y = 185.29596x – 9.60877	0.99989	0.20 – 30
4-C-3-MP	8.464	y = 11.28097x - 0.51992	0.99990	0.30 – 30
2,4-DCP	9.127	y = 11.77682x - 0.53496	0.99991	0.30 – 30
2-M, 4,6-DNP	9.450	y = 49.8612x – 3.12107	0.99990	0.20 – 30
2,4,6-TCP	10.738	y = 9.19452x – 0.61745	0.99991	0.20 – 30
2,4,6-TBP	11.778	y = 5.16817x + 0.16299	0.99990	0.20 – 30
PCP	12.911	y = 3.124950x + 0.26393	0.99985	0.30 – 30

The precision of the method, based on measurement of repeatability, was obtained from the repeatable standard deviation expressed as the co-efficient of variation (% CV) by replicates injections (n=7) of standard mixture (prepared in the laboratory) and the internal standard (IS), by taking into consideration the concentration and the retention time of each compound (Table 4.5.1). Repeatability results showed good precision with mean RSD values range of 0.97% and 10.49% for the 11 phenols (Zakeri-Milani *et al.* 2005; Leon *et al.*, 2006; Opeolu *et al.*, 2010).

4.5.1.3 Limit of detection and limit of quantification

In this study, LOD and LOQ were calculated by multiplying the standard deviation of the lowest detectable concentration by 3 and 10 respectively (Kuselman and Shenhar, 1995; Huber, 2003). The detection limit ranged from 4 μgl^{-1} to 166 μgl^{-1}, while the limit of quantification ranged from 15 to 502 μgl^{-1} as shown in Table 4.19. The obtained values for both LOD and LOQ for the analytes were low, indicating that the method is capable of not only quantifying all the used standards, but also of detecting traces of these phenolic compounds in different water samples. The result proved to be 100 times better than result obtained on HPLC Waters 2210 in our laboratory (Opeolu et al., 2010) and previous studies elsewhere (Angelino and Gennaro, 1997; Andrade *et al.*, 2006).

4.5.1.4 Accuracy

Some experiments of recovery yield were performed by analyzing, under the same chromatographic conditions (acetonitrile/water), MilliQ water samples was spiked to obtain 10 mgl^{-1} of each analyte. Apparently, recovery was calculated as the ratio of measured concentration to the spiked concentration and expressed as percentage (Andrade *et al.*, 2006; Polo *et al.*, 2006). No significant matrix interference was observed. The obtained recoveries were

within the same order of magnitude as reported by other researchers (Angelino and Gennaro, 1997; Alonso *et al.*, 1998; Kostrhounova *et al.*, 2003; Jeon *et al.*, 2007; Huang *et al.*, 2009). The result reported in Tables 4.19 provided evidences that the optimized method for all the analytes have acceptable repeatability (RSD $\leq$ 11%). This was further confirmed by the prepared standard of the analytes mixture supplied by Sigma Aldrich, South Africa at known concentration.

4.5.1.5 Real water analysis

The developed analytical method was applied to analyze phenolic congeners from real water samples. The result of water analysis from laboratory, student residence, surface water and bottled water is presented in Table 4.20 while the chromatogram of tap water and brand 2 table water are presented in Figures 4.29 and 4.30. Due to their toxicity on drinking surface waters, aquatic and human lives, the European Commission (EC) and the United State Environmental Protection Agency (USEPA) have classified some of them as EDCs.

The minimum admissible levels set by the EC and USEPA for water intended for human consumption are 0.5 μgl^{-1} and 0.1 μgl^{-1} for total and individual compounds, respectively and 5 μgl^{-1} for bathing water (Galceran and Jauregui *et al.*, 1995; Angelino and Gennaro, 1997; Llompart *et al.*, 2002; Fattahi *et al.*, 2007). The world health organization suggest a guide level concentration lower than 200 $\mu gl^{-1}$for 2,4,6-trichlorophenol and 9 μgl^{-1} for pentachlorophenol (Simoes et al., 2007). The International Agency for Research on Cancer (IARC) has classified 2,4,6-trichlorophenol in Group 2B (possibly carcinogenic to human) while Environmental Protection Agency (EPA, 2004) has classified 2,4,6-trichlorophenol as a probable carcinogen.

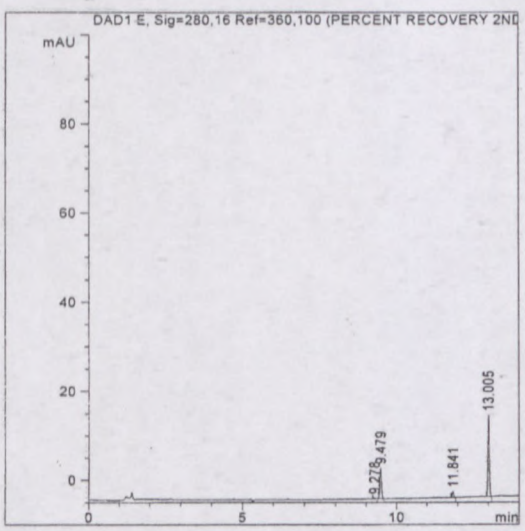


Fig. 4.29: Tap water analyzed in the laboratory

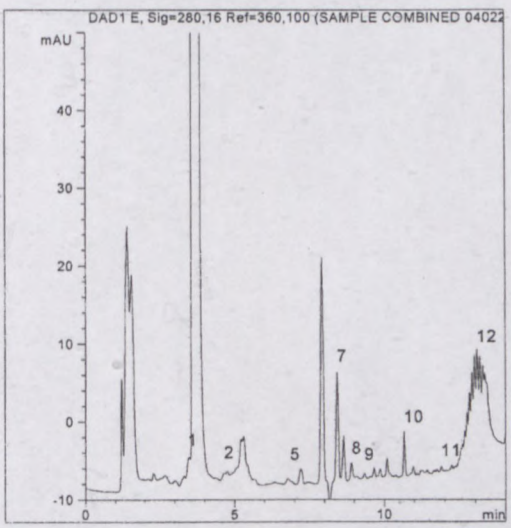


Fig. 4.30: Brand 2 water from grocery shop

Analysis showed that most of the analytes were not detected in the water samples; however, 4-nitrophenol, 2-methyl, 4,6-dinitrophenol (O-cresol), pentachlorophenol, and 2,4-dichlorophenol were found in some of the samples. These compounds have been used either as raw materials or intermediate products in the agro-chemical industry and wood preservation

(Ribeiro *et al.*, 2002; Santana *et al.*, 2002; Bestamin, 2005). While chlorophenols are also formed as metabolites of agricultural pesticides (e.g. chlorophenoxy acids and lindane), in pulp bleaching processes, due to inefficient removal of these congeners from wastewater treatment plants waste effluent and as by-products of the chlorination of drinking water (Heberer and Stan, 1997). On the other hand, nitrophenols are formed from reaction of atmospheric oxides with aromatic hydrocarbons which subsequently accumulates in precipitate.

This proposes the possible sources of 2,4-dichlorophenol and pentachlorophenol contamination in the water samples. The brand 2water is branded phenolic water and this could be responsible for the presence of almost all the target phenolic congeners present in the water. The reported concentration of phenol and phenol derivatives were far higher than the values recommended by EU, USEPA and WHO for individual, total, 2,4,6-trichlorophenol and pentachlorophenol. Results are consistent with those reported by Opeolu *et al.* (2010) who analyzed eleven priority phenols in water samples from some selected informal settlements in Cape Town.

Table 4.19: Limit of detection, limit of quantification, percent recovery, precision and concentration used for precision analysis

Analyte	LOD ($ng\mu l^{-1}$)	LOQ ($ng\mu l^{-1}$)	Percent recovery (%)			Precision	Concentration
			Average ± SD	Min	Max	(%CV)	(used for precision) ($ng\mu l^{-1}$)
Phenol	0.052	0.158	81.52 ± 0.43	81.05	81.90	7.43	0.2
4-Nitrophenol	0.166	0.502	71.73 ± 1.07	70.50	72.30	2.08	2.4
2-Chlorophenol	0.005	0.015	81.43 ± 0.65	80.80	82.10	1.49	0.1
2,4-Dinitrophenol	0.018	0.158	72.97 ± 0.47	72.60	73.50	1.99	0.2
2-Nitrophenol	0.025	0.502	72.40 ± 1.11	71.40	73.60	2.35	0.3
2,4-Dimethylphenol	0.004	0.015	89.35 ± 0.31	89.10	89.70	1.19	0.1
4-Chloro-3-methylphenol	0.044	0.055	76.53 ± 1.00	76.90	77.30	4.61	0.3
2,4-Dichlorophenol	0.056	0.076	69.43 ± 1.76	67.80	71.30	6.29	0.2
4,6- Dinitro-o-cresol	0.021	0.011	78.00 ± 0.61	78.00	79.21	5.51	0.1
2,4,6-Trichlorophenol	0.009	0.135	101.87 ± 0.45	101.40	102.3	0.97	0.2
2,4,6-Tribromophenol*	0.019	0.064	101.57 ± 0.91	100.60	102.4	1.56	0.3
Pentachlorophenol	0.131	0.028	92.03 ± 2.19	90.30	94.50	10.49	0.3

LOD = 3.3 x δ; LOQ = 10 x δ; δ = the standard deviation of the signal to noise ratio.

Table 4.20: Levels of priority phenols in drinking and surface water samples from difference locations in Cape Town.

	Potable water samples								Freshwater samples		
	PG	FT-LAB	BD1	BD2	BD3	Khayelitsha	Langa	Guguletu	DAM	POND	POOL
P-OH	nd	nd	nd	2.36±0.02	nd	nd	nd	nd	nd	nd	nd
4-NP	nd	nd	nd	16.79±0.00	nd	nd	nd	nd	nd	nd	4.57±0.16
2-CP	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
2,4-DNP	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
2-NP	nd	nd	nd	0.43±0.01	nd	nd	nd	nd	nd	nd	nd
2,4-DMP	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
4-C,3MP	nd	nd	nd	11.31±0.0	nd	nd	nd	nd	nd	nd	nd
2,4-DCP	nd	0.11	nd	5.13±0.012	nd	nd	nd	nd	nd	nd	nd
4,6- Dinitro-o-cresol	0.08	0.56	nd	0.543±0.05	0.10±0.0	nd	nd	nd	nd	nd	nd
2,4,6-TCP	nd	nd	nd	2.33±0.03	nd	nd	nd	nd	nd	nd	nd
PCP	0.31	1.16	nd	0.17±0.01	nd	nd	0.291±0.001	4.79±0.36	nd	nd	nd

PG = Postgraduate residence; FT-LAB = Food tech laboratory; BD1 = Brand water 1; BD2 = Brand water 2; BD3 = Brand water 3; nd = not detected

4.5.2 Method development on GC-MS

4.5.2.1 Selection of derivatization reagent

Preliminary experiment explored for derivatization using acetylation showed that the nitro-groups were not well derivatized with acetic anhydride as compared to the silylation method. Therefore, derivatization with acetic anhydride was not pursued further. Results are consistent with previous studies on acetylation of nitrophenol where unsatisfactory result had been reported (Heberer and Stan, 1997).

Yield from derivatization using block heater was not acceptable. Thus, derivatization was successfully carried out at 90°C (20 mins) as described in the method development. Stability of the derivatized products was investigated by keeping the products in the dark at 4°C for 7, 14 and 21 days. The products were stable after 21 days as no significant difference in the intensity of the products was observed. The quantifier ions were mostly the ion peaks with the largest abundance (Table 4.21). The chromatogram of the silylated phenol, chlorophenols and nitrophenols is shown in Figure 4.31. The target analytes were well separated with exception of 4-NP and 2,4,6-TCP with close retention and often eluted at 20.75 min. The result agreed with the findings of Heberer and Stan (1997). The mass spectra of some of the derivatized phenols are presented in Figures 4.32 (a) to 4.32 (h). Phenols and phthalates were usually determined separately using standard protocols. However, the derivatization of priority phenols in this study showed that the intensity and the stability of the phthalates are not affected by the drivatization procedure used.

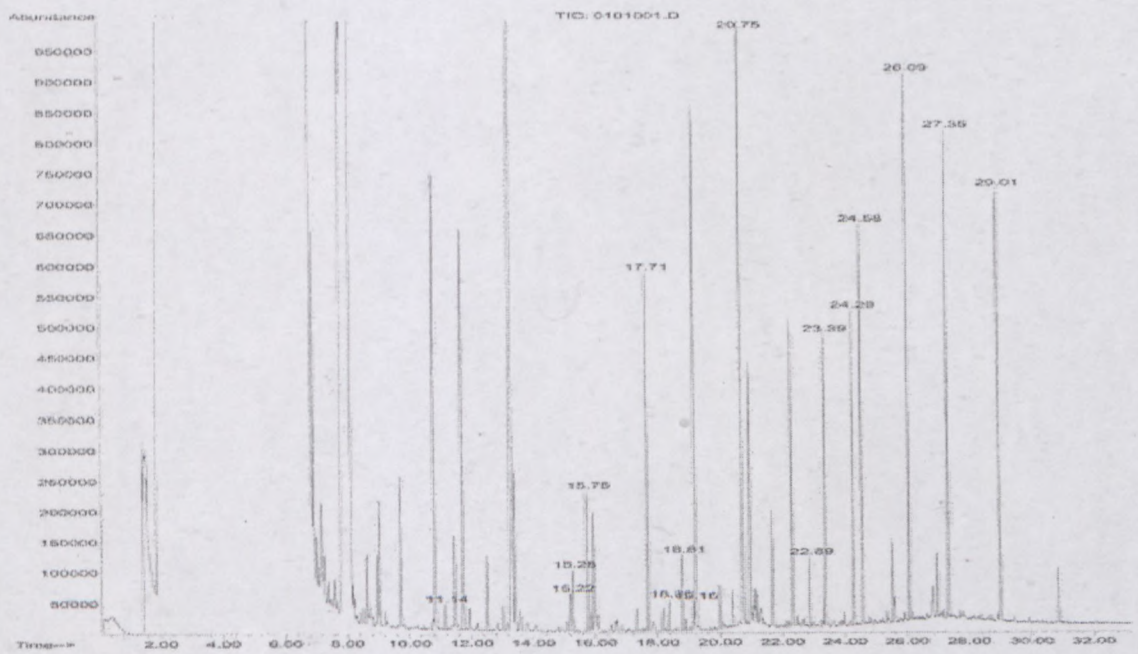


Fig 4.31: Chromatogram of derivatized phenols and phthalate esters

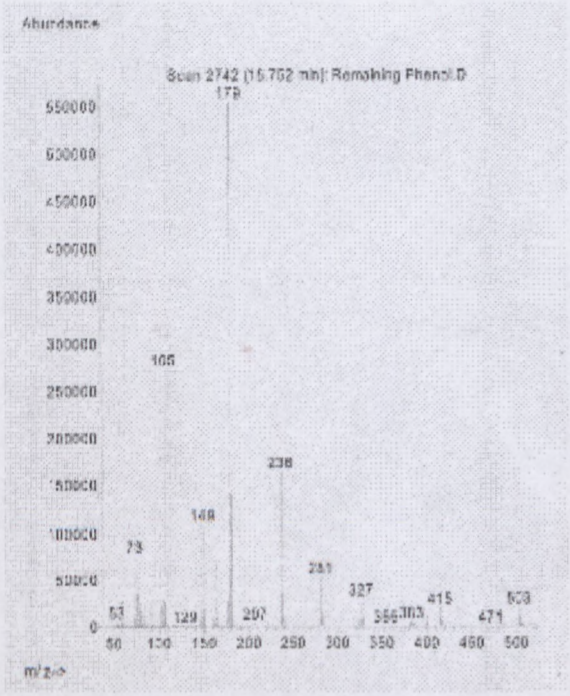


Figure 4.32a: 2,4-Dimethyl phenol

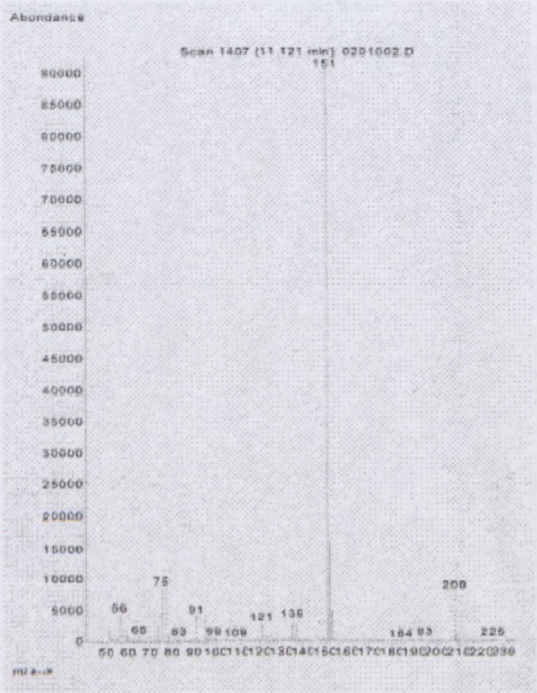


Figure 4.32b: Phenol

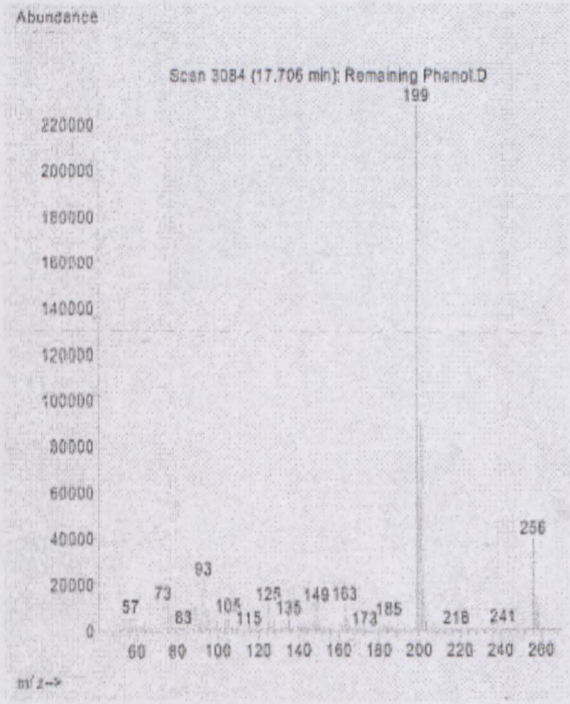


Figure 4.32c: 4-Chloro, 3-Methyl phenol

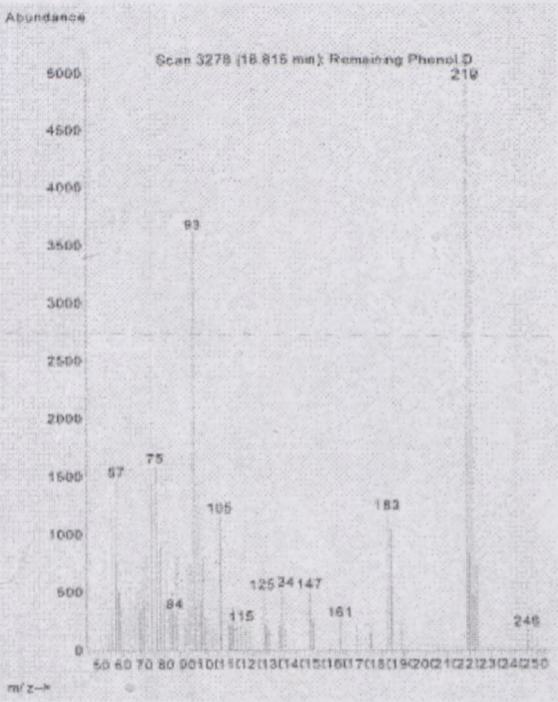


Figure 4.32d: 2,4-Dichloro phenol

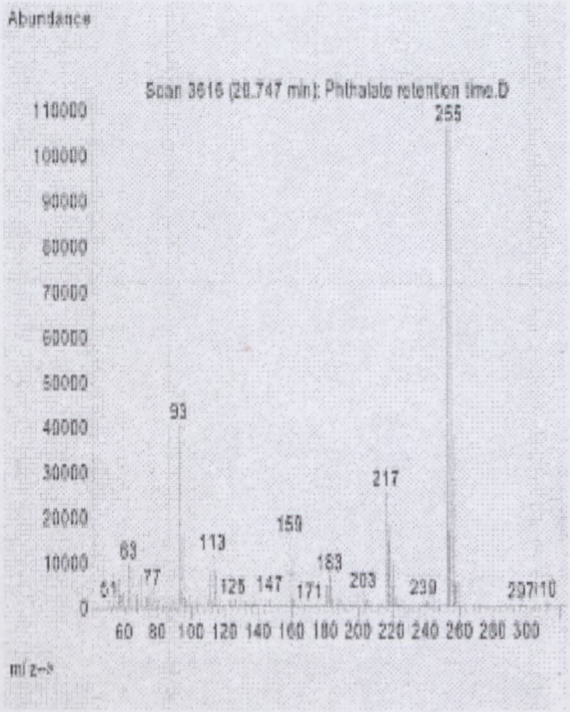


Figure 4.32e: 2,4,6-Trichloro phenol

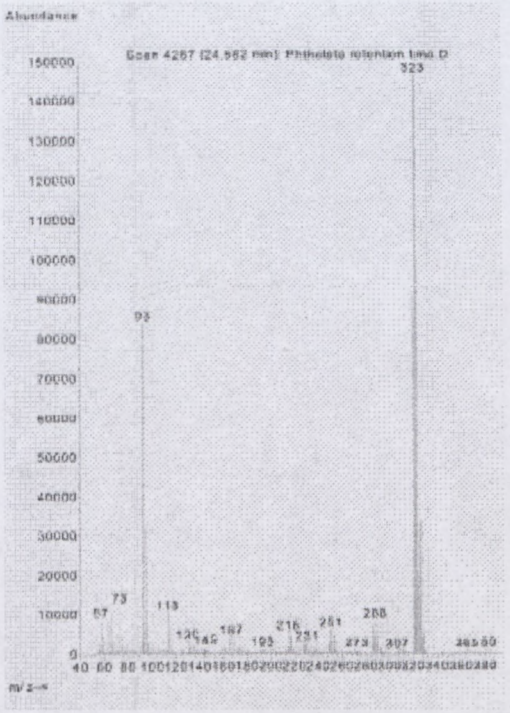


Figure 4.32f: Pentachlorophenol

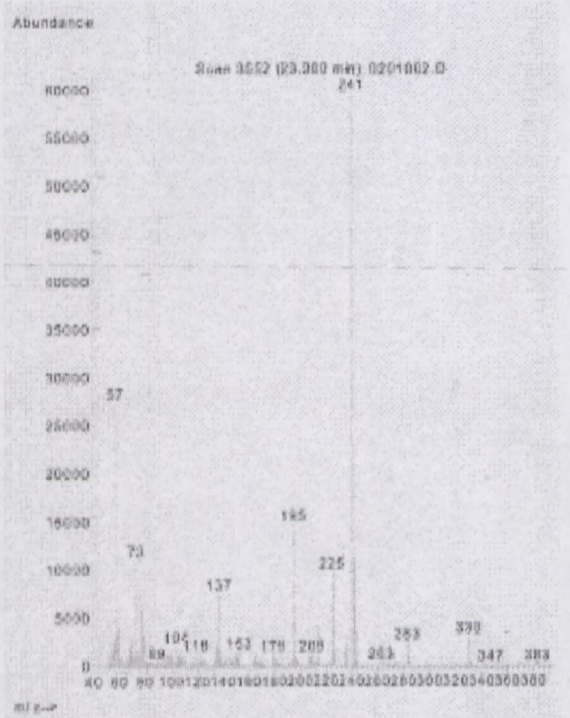


Figure 4.32g: 2,4-Dinitrophenol

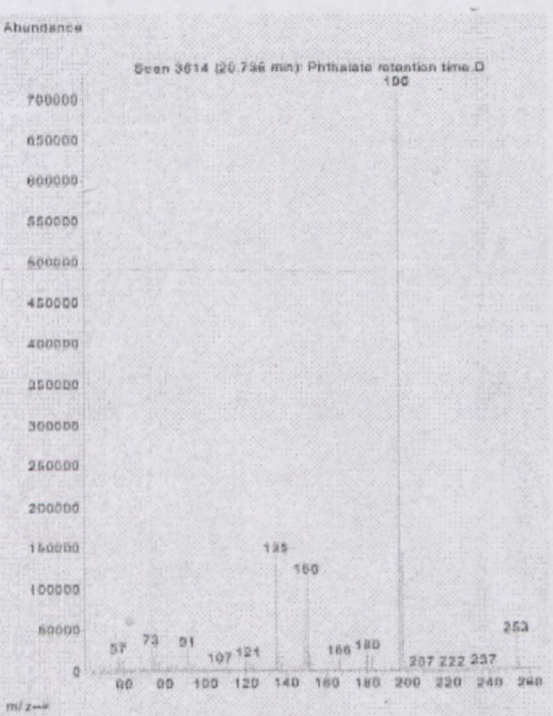


Figure 4.32h: 4-Nitro phenol

4.5.2.2 Optimal elution conditions for phenols and phthalate from SPE cartridges

Solvent are used to remove target analytes from SPE cartridges. Types and volume of solvents also plays an important role in the recoveries of target congeners. Solvent selection depends on target analyte to be eluted from the cartridges and elution strength of the solvent. Different solvent like ethyl acetate, acetone, methanol, dichloromethane, hexane have been used for elution of target analytes from varying forms of SPE cartridges (Fatoki and Noma, 2002; Tan et al., 2008; Clara *et al.*, 2010). Since the target compounds covered a range of polarity, combination of three solvents namely hexane and acetone and methanol were examined based on literatures reviewed (Cepedes *et al.*, 2005; Tan *et al.*, 2008; Clara *et al.*, 2010).

The eluent was derivatized, measured with GC-MS and the relative response was quantified for compound. The ratio of hexane to acetone that gave the best recovery was 50:50. The elution combination ratio was similar to values of methanol and dichloromethane combination ratio reported by Fatoki and Noma (2002). For surface water analysis, recovery ranged from 75 % to 113 %.

4.5.2.3 Calibration and validation of analytical method

Five point calibration curves were constructed using triplicate injections of the phthalate standards with the derivatized phenols standard. The retention time, target ion monitored, and the SPE recovery of the selected phenols and phthalates are presented in Table 4.21. Analysis of the result demonstrated the concordance of the response with a linear model as shown in Table 4.22, where the regression coefficient ranged from 0.976 to 1.000. The method precision and accuracy were satisfactory. The calibration concentration ranged was from 2.5 to 1000 μgl^{-1}. Due to non-availability of reference materials, the trueness of the analytical method for extraction and elution was assessed through recovery of additions of standard mixtures of the target analytes in Milli-Q. For the efficient quantification of the target compounds, analysis was performed within the linear portion of the calibration curve.

Table 4.21: Retention time, target ion in GC-MS detection of the selected phenols and phthalates recoveries (n = 7)

Compound	Retention Time (min)	Target ion (m/z)	Reference ion (m/z)	SPE Recovery (%)
Phenol	11.14	151	208	93.43 ± 0.05
2-Chlorophenol	15.21	185	149, 93	98.21 ± 4.38
Dimethyl phthalate (DMP)*	15.27	163	77	83.72 ± 6.03
2,4-Dimethylphenol	15.74	179	163, 149, 105	98.69 ± 8.43
4-chloro, 3-methylphenol	17.71	199	93	76.21 ± 5.28
Diethyl phthalate (DEP)*	18.38	149	177, 104, 77	98.46 ± 11.31
2,4-Dichlorophenol	18.81	219	183, 125,93	94.1 ± 7.16
2-Nitrophenol	19.15	196	180, 151, 136, 91	95.39 ± 11.68
4-Nitrophenol	20.74	196	150, 135	88.19 ± 10.29
2,4,6-Trichlorophenol	20.76	255	217, 159, 93	73.21 ± 0.05
Dibutyl phthalate (DBP)*	22.89	149	207	98.99 ± 8.27
2,4-Dinitrophenol	23.39	241	225, 195, 137	96.34 ± 2.93
2-methyl, 4,6-dinitrophenol	24.29	255	239, 209 179, 149	90.33 ± 6.18
Pentachlorophenol	24.58	323	93	92.64 ± 11.39
Benzybutyl phthalate (BBP)*	26.09	149	206, 91	97.43 ± 18.31
Diethylhexylphthalate (DEHP)*	27.35	149	279, 167	101.32 ± 0.21
Dioctyl phthalate (DOP)*	29.01	149	279, 57	90.77 ± 5.39

*Compound not affected by MTBSTFA derivatization

4.5.2.4 Limits of detection and quantification

The LOD of each compound for the 17 analytes was determined as three times the standard deviation of seven independent replicate analyses. Limits of quantification (LOQs) were determined as 3.3 times of LODs. Instrument detection limits ranged from 0.6 μgl^{-1} (DEHP) to 3.16 ugl^{-1} (4-NP) and the LOQs varied from 1.9 ugl^{-1} (DEHP) to 10.44 ugl^{-1} (4-NP) as presented in Table 4.22. The method detection limit values for LODs and LOQs are adequate for environmental monitoring of the target compounds and low enough compared to previous work on the analytes of interest (Fatoki and Noma, 2002; Yuan *et al.*, 2002; Cortazar *et al.*, 2005; Zhou *et al.*, 2005; Kayali *et al.*, 2006; Ling *et al.*, 2007) taking into account the complexity of the samples and the low sample amounts used. For wastewater and river samples, the LODs achieved in the present work were at similar levels or lower than those obtained in previous studies with GC–MS (Yuan *et al.*, 2002; Cortazar *et al.*, 2005; Kayali *et al.*, 2006).

Table 4.22: Limit of detection, limit of quantification and correlation coefficient of analytes

Compound	IDL (μgl^{-1})	LOQ (μgl^{-1})	Correlation coefficient (R^2)
Phenol	2.2	7.18	1.000
2-Chlorophenol	1.9	6.34	0.988
Dimethyl phthalate (DMP)*	2.2	7.43	0.993
2,4-Dimethylphenol	1.4	4.78	0.987
4-chloro, 3-methylphenol	2.96	9.77	0.989
Diethyl phthalate (DEP)*	1.58	5.22	0.993
2,4-Dichlorophenol	1.11	3.66	1.000
2-Nitrophenol	1.36	4.47	1.000
4-Nitrophenol	3.16	10.44	0.999
2,4,6-Trichlorophenol	2.81	9.63	0.999
Dibutyl phthalate (DBP)*	0.9	2.9	0.987
2,4-Dinitrophenol	1.63	5.36	0.986
2-methyl, 4,6-dinitrophenol	1.48	4.87	0.976
Pentachlorophenol	2.23	7.37	0.998
Benzybutyl phthalate (BBP)*	0.9	2.9	0.987
Diethylhexylphthalate (DEHP)*	0.6	1.9	0.989
Dioctyl phthalate (DOP)*	1.41	4.65	0.988

4.6 Seasonal occurrence and annual distribution pattern of phenolic and phthalic acid esters congeners in wastewater and river water

4.6.1 Levels of phenolic compounds and phthalate esters congeners in Athlone WWTP and Vygekraal River

Activated sludge process successfully removed the bulk of the organic compounds that enters the wastewater treatment plant. However, not all the compounds are usually broken down or converted into biomass (i.e. sludge) by microorganisms (Wang *et al.*, 2005). For the phenols and phthalate esters investigated, the results of seasonal mean for the Athlone WWTP is presented in Table 4.23, while Figure 4.33 depicted the summation of the annual mean distribution pattern in both the freshwater systems and the wastewater treatment plant. During the first quarter sampling campaign, all the investigated phenols were not detected in the upstream samples except for 2-NP which was below the instrument quantification limit. With the exception of 2,4-DMP and 2,4,6-TCP, all other phenols were present in the influent waste for all the sampling seasons while 2,4-DCP was neither detected in the freshwater nor in the WWTP effluents. Generally, the seasonal mean concentration (standard deviation) of phenolic congeners ranged from < LOD to 143 (2) μgl^{-1} (2,4-DMP), < LOD to 843 (39) μgl^{-1} (PCP), < LOD to 184 (3) μgl^{-1} (2,4-DMP), and < LOD to 506 (4) μgl^{-1} (2-NP) for upstream, influent water, effluent water and downstream water, respectively.

The distribution pattern for phenolic congeners is PCP > 2NP > 2,4-DMP > POH > 2CP > 2,M,4,6-DNP > 4C-3MP > 4NP > 2,4,6-TCP > 2,4-DNP > 2,4-DCP. PCP accounted for 34 % of the total annual phenolic concentrations, while POH, 2CP and 2,4-DMP accounted for 11.58, 10.08 and 11.89 % of the total annual phenols investigated. The concentration of 2,4-DNP, 2,4,6-TCP, 4-NP and 2,4-DCP concentration were negligible, while other could be ranged in comparison to phthalate esters as PCP > 2-NP > POH with percentage composition of 16%, 11 %, 5 %, 2 % and 1 %, respectively. This distribution pattern in the wastewater treatment plant could be attributed to the wide use of chemicals containing the phenolic congeners of interest in many industrial processes, such as production of plastics, dyes, drugs, pesticides, antioxidants and paper, as well as petrochemical processes (Czaplicka, 2001; Zhou *et al.*, 2005). The level and distribution patterns of phenolic compounds in the river and waste treatment reported in this study were generally higher than the finding reported in similar matrix in Oman, Italy and Spain (Czaplicka, 2001; Riberio *et al.*, 2002; Zhou *et al.*, 2005; Suliman *et al.*, 2006; Bagheri *et al.*, 2007; Zhao *et al.*, 2009). The result could not be compared to any previous study in South Africa as no data is available for review on levels of phenolic congeners in wastewater and freshwater systems in the country.

Table 4.23: Seasonal Mean (± SE) (μgl^{-1}) of phenolic compounds and phthalates in Athlone WWTP's and Vygekraal River (grab sample n =108)

Compound	Upstream				Influent				Effluent				Downstream			
	Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4
P-OH	nd	nd	69(6)	64(3)	115±3	235±7	163±3	163±1	nd	nd	nd	nd	nd	nd	nd	nd
2-CP	nd	nd	nd	nd	217±10	174±10	140±12	173±1	nd	nd	nd	nd	nd	nd	nd	nd
DMP*	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
2,4-DMP	nd	143(2)	57±24	102±2	nd	nd	nd	nd	86±2	184±3	10±1	8±1	79±7	93±2	40±5	28±2
4-C, 3-MP	nd	nd	nd	nd	30±1	31±2	29±1	29±5	nd	nd	nd	nd	nd	nd	nd	nd
DEP*	nd	652(8)	427±7	539±1	1506(13)	459±12	460±12	752±2	26±4	165±8	89±2	272±204	113±3	56±5	nd	9
2,4-DCP	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
2NP	bdl	110(6)	100±6	108±1	115±10	109±14	140±12	123±1	79±1	48±1	29±2	29±3	56±4	nd	109±81	48±5
4NP	nd	20±1	20±1	22±2	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
2,4,6-TCP	nd	21±1	17	18	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
DBP*	nd	nd	nd	nd	113	110±12	140±6	129±2	83±3	nd	nd	nd	nd	nd	nd	nd
2,4-DNP	nd	nd	nd	nd	10±1	nd	9.6±0.3	11±1	nd	nd	nd	nd	nd	nd	nd	nd
2-M,4,6-DNP	nd	nd	nd	nd	20±1	40±1	140±60	11±1	nd	nd	nd	nd	nd	nd	nd	nd
PCP	nd	10±1	nd	14	526±22	362±153	673±3	843±39	nd	nd	nd	nd	nd	nd	nd	nd
BBP*	nd	10±1	nd	9.6±1	61±2	80±12	846±22	733±13	nd	nd	nd	nd	nd	9±2	nd	9±1
DEHP*	blq	40±1	41±1	41±1	60±7	50±12	60±1	57±4	20±1	15.6	18.7	16.7	10±1	18±1	62±1	6±1
DOP*	nd	10±1	nd	13	37±26	9±1	11±1	11	nd	nd	nd	nd	nd	nd	nd	nd

Q1 = Summer; Q2 = Autumn; Q3 = Winter; Q4 = Spring; P-OH = Phenol; 2-CP = 2 Chlorophenol; DMP=Dimethyl phthalate; 2,4-DMP = 2,4-Dimenthyl phenol; 4-C, 3-MP = 4 Chloro 3methyl phenol; DEP = Diethyl phthalates; 2,4-DCP = 2,4 Dichlorophenol; 2-NP = 2 Nitrophenol; 4-NP = 4 Nitrophenol; 2,4,6-TCP = 2,4,6 Trichlorophenol; DBP = Dibutyl phthalate; 2,4-DNP = 2,4 Dinitrophenol; 2-M, 4,6-DNP = 2 Methyl 4,6-Dinitrophenol; PCP = Pentachlorophenol; BBP = Benzylbutyl phthalate; DEHP = Diethylhexyl phthalate; DOP = Dioctyl phthalate; nd = not detected; bdl = below detection limits; blq = below quantification limit; *Compound not affected by MTBSTFA derivatization.

For phthalate esters, of all the six substances that were assessed, diethylhexyl phthalate (DEHP), dimethyl phthalate (DMP), diethyl phthalate (DEP), di-n-butyl phthalate (DnBP), di-octyl phthalate (DOP) and benzylbutyl phthalate (BBP), only DMP was not detected in the raw wastewater and the freshwater systems. The result was in agreement with the findings of Fromme *et al.* (2002) and Vogelsang *et al.* (2006). DEHP was detectable in all samples tested and accounted for

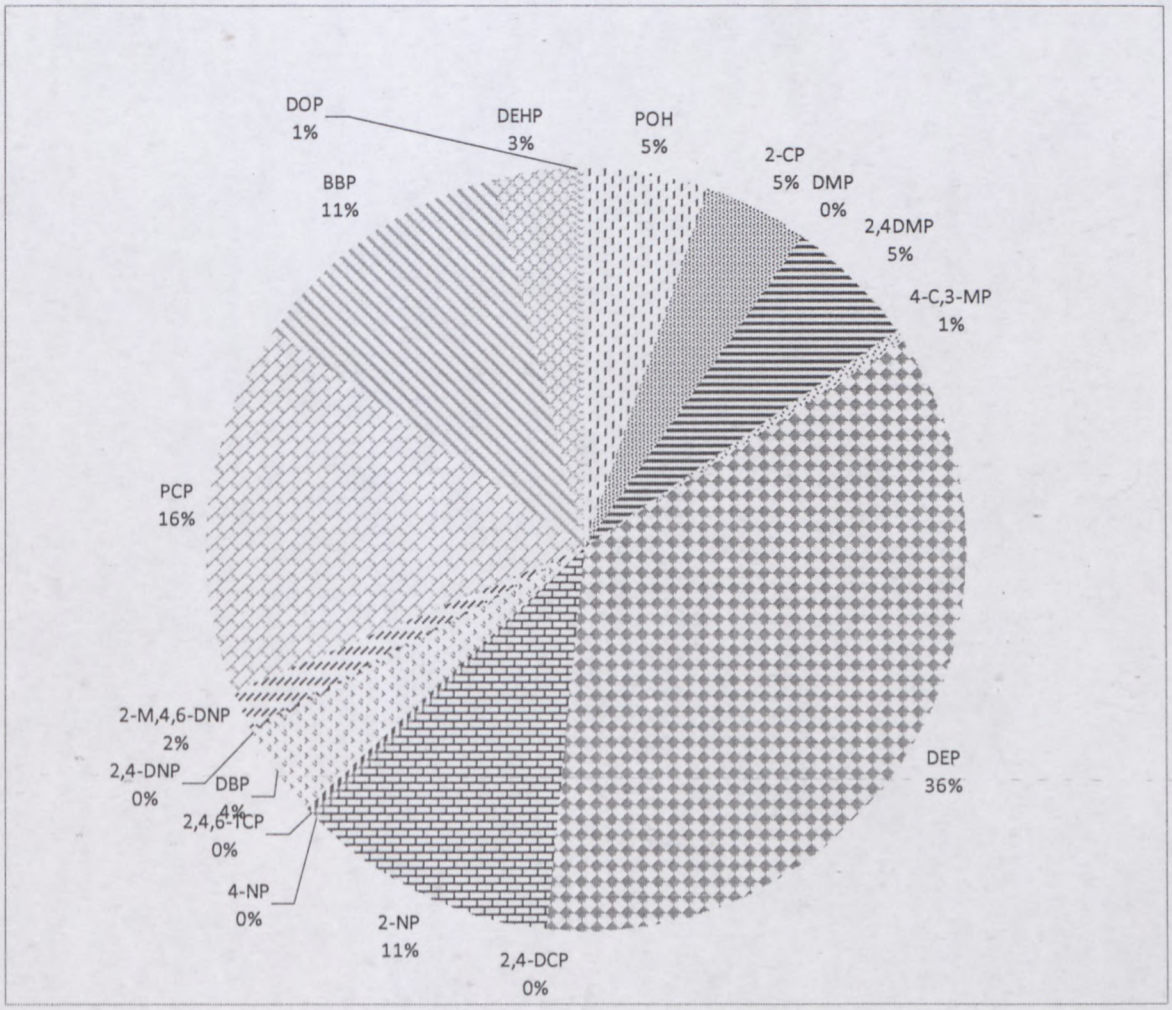


Figure 4.33: Annual distribution pattern of phenolic and phthalate esters congeners in Vygekraal River and Athlone WWTP

3 % of the total congeners investigated in the fresh and WWTP systems. Levels of DEHP in this study ranged from 6 to 62 μg l^{-1} and 10 to 60 μg l^{-1} for freshwater and WWTP, respectively. These values were higher than what was reported in the literatures (Fromme *et al.*, 2002; Vogelsang *et al.*, 2006). However, the trend and seasonal distribution pattern from the chemical analysis revealed that DEP had an occurrence frequency of 87.5 % and accounted for 36 % of the total congeners on an annual basis. DEHP, BBP, DOP and DBP had occurrence frequencies of 100, 16.7, 12.5 and 8.33 % with total annual distribution percentages of 3, 11, 1 and 4%, respectively. This results trend agreed with those reported in the literature for sewage effluent and

for oxidation pond by Ogunfowokan *et al.* (2006) where DEP and DBP have been reported with higher concentration compared to DEHP.

The presence of phthalates was expected since these compounds are widely used throughout the industry and within households, particularly as additives in plastics, including pipes used for plumbing purposes. This pattern of PEs is complex and deviate from the general norms of higher molecular congeners most especially DEHP having the dominant concentration. This pattern could be as a result of source compositions, sedimentary dispersion/accumulation patterns, environmental degradation, or metabolism by sedimentary communities. Considering the array of industries in this zone and usage to which PEs of lower molecular weight (DMP, DEP, DBP) are put to e.g. in production of cosmetics and personal care products, while longer chain or branched structure is used as plasticizers, this could have been a major route of the lower congeners into the environment and the freshwater system.

Though, there are a number studies on phthalate esters in the developed world, studies on their availability are very few in Africa with South Africa having reported some levels in water, soil and sediment samples (Fatoki and Noma, 2002; Adeniyi *et al.*, 2008; Fatoki *et al.*, 2010). The concentration of PEs reported in this study for Athlone WWTP and Vygekraal river was similar to values reported in literatures (Tan, 1995; Vitali *et al.*, 1997; Fromme *et al.*, 2002; Yuan *et al.*, 2002; Vethaak *et al.*, 2005; Zeng *et al.*, 2008).

The removal efficiency calculated using detectable concentration of analytes showed that 2-nitrophenol and DEHP were poorly removed from the waste stream for all the seasons (Figure 4.34). The removal efficiency was less than 80 %, while DBP was poorly removed during the summer sampling season. The reported removal efficiency agreed with the removal pattern of some nonyl-phenols and DBP by Wang *et al.* (2005). It is noteworthy to state the occurrence of 2,4-dimethylphenol, which was not initially detected in the influent water into the WWTP. This could be due to the breakdown of higher compounds that were present in the waste stream into the WWTP by microorganisms.

There was strong correlation between the wastewater effluent concentration and concentration of the target analytes downstream of the receiving river. Though a significant concentration of the analytes were detected upstream of the plant and most of the analytes was not detected in the final effluent, DEHP, DEP, 2-NP and 2,4- DMP from the WWTP contributed to further contamination of the downstream water. The highest concentration of phthalates detected downstream was DEP. This treatment plant is located in the heart of the city where a significant amount of the plastic materials including wall papers, floor lacquers, titles, wire coating, restaurant and hospitals released their waste into the sewers for further treatment.

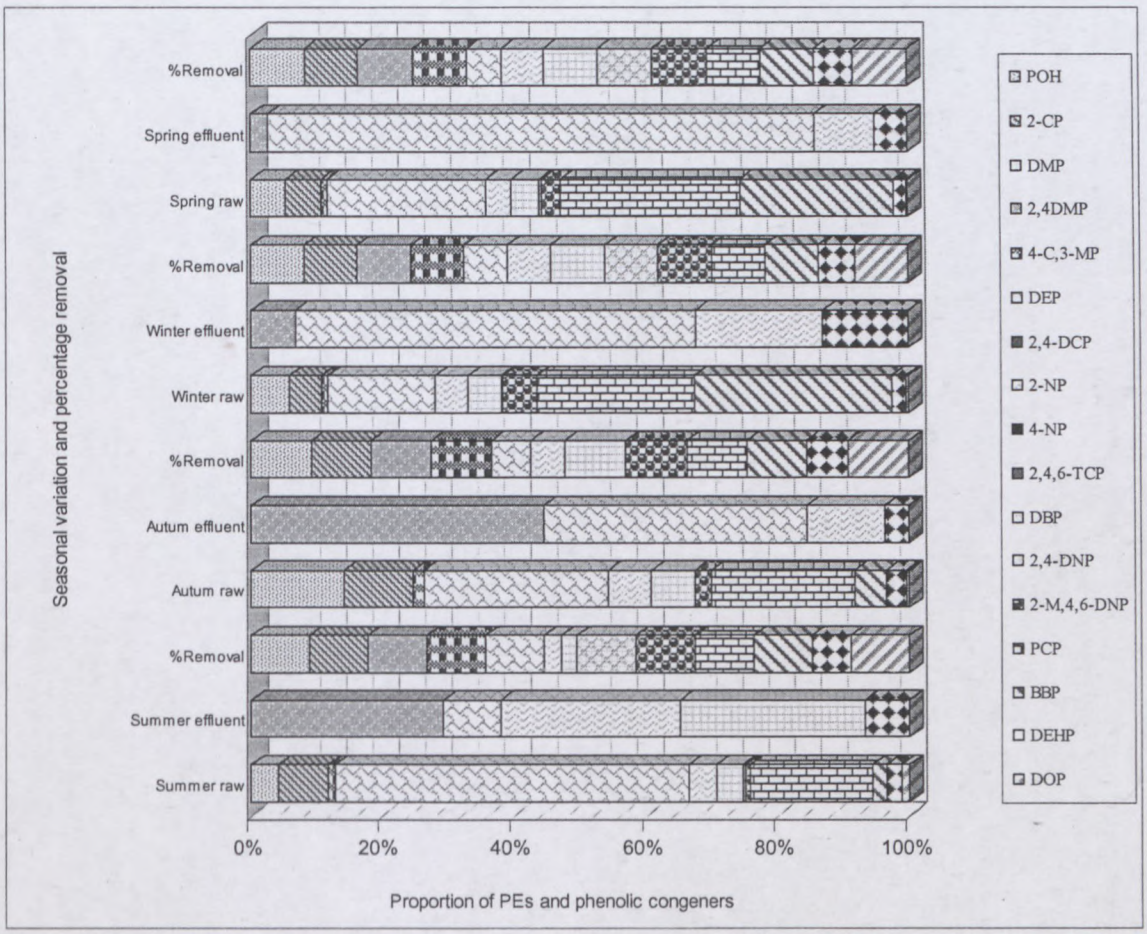


Figure 4.34: Proportion of PEs to phenolic congeners and removal efficiency of Athlone WWTP in summer, autumn, winter and spring

Furthermore, PEs deposited on the roadside as result oil and chemical spillage from vehicles, vehicles components, car care products and tire ware can be washed out during raining events into the river systems. Additionally, close to the downstream section is a golf course that uses different kinds of pesticides for weed and pest control as well as informal settlement and low cost housing estate just below the wastewater treatment plant discharge point.

4.6.2 Levels of phenolic and phthalate esters congeners in Bellville wastewater treatment plant and Kuils River

The new Bellville wastewater treatment was investigated of the two WWTPs. The plant received majorly industrial effluent from the northern suburb. Industries in the southern suburb of the City of Cape Town include: paper mills, wood processing plants, tannery and garages, after-shave, metals processing, tannery, paints, table water production plant and pharmaceuticals. The seasonal mean of the phenols and phthalates in the freshwater and wastewater effluents is presented in Table 4.24, while the annual mean distribution pattern of each of the 17 congeners is presented in Figure 4.35. For the phenolic congeners investigated, none of the 11 congeners

Table 4.24: Seasonal Mean (± SE) ($\mu g l^{-1}$) of phenolic compounds and phthalates in new Bellville WWTP and Kuils River (grab sample n =108)

Compound	Upstream				Influent				Effluent				Downstream			
	Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4
P-OH	nd	nd	nd	663±89	282±1	13±1	431±1	1130±89	39±1	nd	72±0.3	250±27	nd	nd	nd	260±2
2-CP	nd	nd	nd	437±20	163±9	177±7	424±1	790±324	nd	nd	69±1	307±62	nd	nd	nd	450±0.3
DMP*	nd	nd	nd	3±0.3	30±1	nd	10±1	40±1	nd	nd	nd	10±1	nd	nd	nd	nd
2,4-DMP	nd	nd	nd	170±25	nd	54±1	nd	3253± 2165	26±13	6±0.3	195±0.3	473±167	nd	20±0.3	nd	133±19
4-C, 3-MP	nd	nd	nd	200	9±1	nd	47	160±6	nd	nd	20±0.3	10	nd	nd	nd	nd
DEP*	nd	nd	nd	393±123	820±6	750±6	2472±1	4373± 205	431±1	nd	845	210±29	nd	nd	nd	153±9
2,4-DCP	nd	nd	nd	nd	nd	nd	233±9	nd	nd	nd	163±3	nd	nd	nd	nd	nd
2NP	nd	nd	nd	603±38	190±6	46±4	413±1	313±38	123±3	nd	217±9	9	nd	30±1	nd	533±32
4NP	nd	nd	nd	nd	nd	nd	10±1	10±1	nd	nd	nd	nd	nd	nd	nd	nd
2,4,6-TCP	nd	nd	nd	nd	nd	nd	10±1	10	nd	nd	nd	nd	nd	nd	nd	nd
DBP*	70±6	443±1	nd	16653 ±886	150±8	1363±6	1343±9	17596± 499	nd	807±3	770±6	9766± 95	nd	399±9	827±3	2266± 195
2,4-DNP	nd	nd	nd	10	63±3	nd	29	23±3	nd	nd	nd	nd	nd	nd	nd	33±0.03
2-M,4,6-DNP	nd	nd	nd	nd	483±3	157±8	27±3	23±3	nd	nd	9±1	nd	nd	nd	nd	nd
PCP	nd	nd	nd	23±15	680±6	173±3	1513±1	2626±14	23	nd	53	330±177	nd	nd	nd	3
BBP*	nd	nd	nd	20	80±6	403±6	48±1	110±30	9±1	nd	13	43±13	nd	nd	nd	20±10
DEHP*	nd	nd	nd	90±10	117±7	193±1	197±2	457±26	70±1	nd	36±1	43±13	nd	nd	nd	3±0.3
DOP*	nd	nd	nd	10	230±6	14	61±1	97±7	nd	nd	nd	13±3	nd	nd	nd	7±3

Q1 = Summer; Q2 = Autumn; Q3 = Winter; Q4 = Spring; P-OH = Phenol; 2-CP = 2 Chlorophenol; DMP=Dimethyl phthalate; 2,4-DMP = 2,4-Dimenthyl phenol; 4-C, 3-MP = 4 Chloro 3methyl phenol; DEP = Diethyl phthalates; 2,4-DCP = 2,4 Dichlorophenol; 2-NP = 2 Nitrophenol; 4-NP = 4 Nitrophenol; 2,4,6-TCP = 2,4,6 Trichlorophenol; DBP = Dibutyl phthalate; 2,4-DNP = 2,4 Dinitrophenol; 2-M, 4,6-DNP = 2 Methyl 4,6-Dinitrophenol; PCP = Pentachlorophenol; BBP = Benzylbutyl phthalate; DEHP = Diethylhexyl phthalate; DOP = Dioctyl phthalate; nd = not detected; bdl = below detection limits; blq = below quantification limit; *Compound not affected by MTBSTFA derivatization.

were detected upstream of the treatment plant during the first three quarters of sampling, while the downstream contains high concentration of POH, 2CP, 2,4-DMP, and PCP among others.

The frequency of occurrence ranged from 12.5 % for 2,4-DCP to 56.25 % for POH and PCP. Unlike in the Athlone WWTP where 2,4-DMP was only detected in the effluent wastewater, it was substantially detected during the last sampling season (summer, 2011). The seasonal mean concentration of phenols ranged from < LOD to 663 (89) μgl^{-1} (POH), < LOD to 3253 (2165) μgl^{-1} (2,4-DMP), < LOD to 473 (167) μgl^{-1} (2,4-DMP) and < LOD to 450 (0.3) μgl^{-1} (2CP) for upstream, influent, effluent and downstream waster, respectively. For the phenolic congeners, 2,4-DMP accounted for about 70 % while PCP accounted for about 11 %. However, on annual basis in comparison to phthalate esters, the distribution of phenolic congeners could be rated as 2,4-DMP > PCP > POH > 2CP = 2NP > 2-M, 4,6- DNP > 4-C,3-MP = 2,4-DNP = 2,4,6-TCP = 4NP = 2,4-DCP.

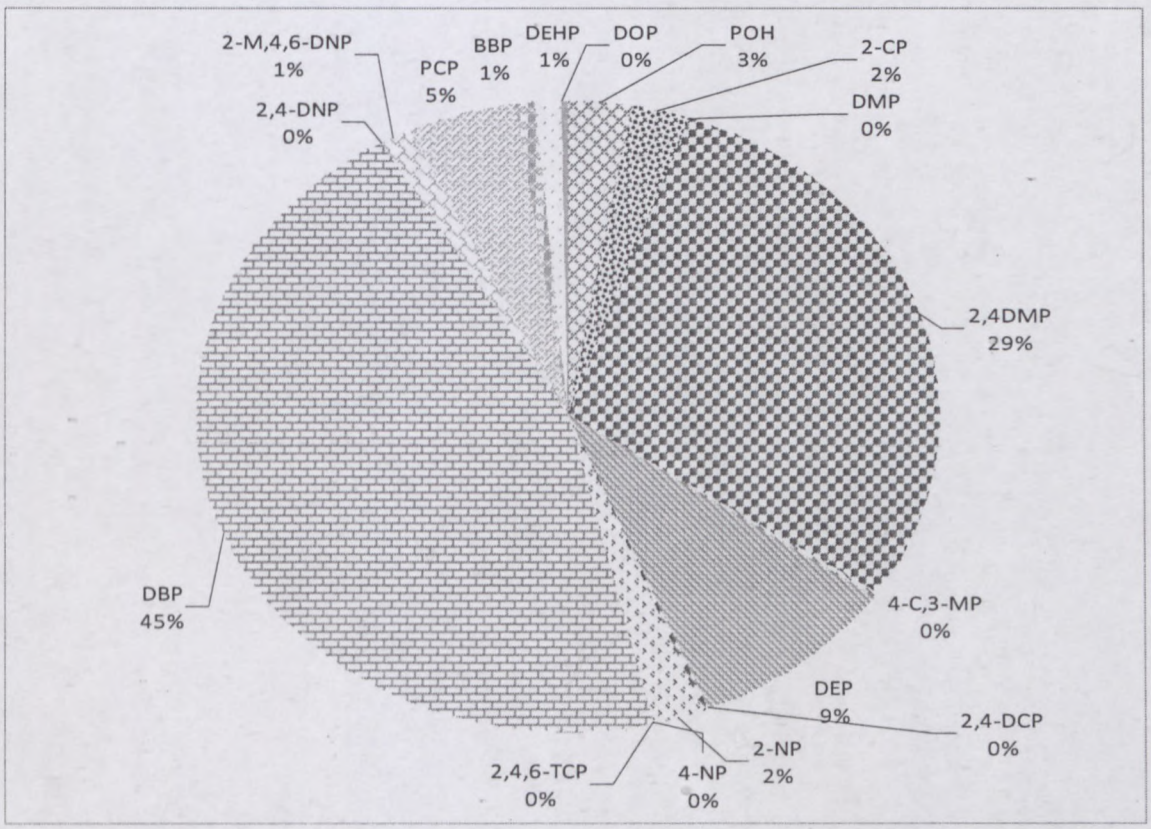


Figure 4.35: Annual distribution pattern of phenolic and phthalate esters congeners in Kuils River and Bellville WWTP

The occurrence frequency of phthalate esters over the sampling period is DEP (56.3 %), DBP (81.3 %), DOP (43.8 %), DEHP (56.3 %), BBP (56.3 %) and DMP (31.3 %). The frequency of DBP in the wastewater and the freshwater samples is a clear indication of possible sources of DBP in relation to the industrial setup in the suburb. The distribution pattern (Figure 4.5.9) showed that DBP accounted for 45 %, while DEHP, BBP, DEP, DOP and DMP accounted for 1 %, 1 %, 9 %, 0% and 0%, respectively in comparison to phenolic congeners. This trend of

distribution where DBP had the dominant concentration instead of DEHP as reported agreed with the trend reported by Adeniyi *et al.* (2011) and by Ogunfowokan *et al.* (2006).

The general trend for DBP in both freshwater and WWTP is alarming. Considering the possible health risk this could pose to aquatic life and for the domestication purposes water could be put to. The reported ranges of < LOD to 16653 μgl^{-1} (886) and 150 μgl^{-1} (8) to 17596 μgl^{-1} (499) for the upstream and the downstream, respectively, were higher compared to reported concentration in Europe and in some other countries (Zeng *et al.*, 2009; Adeniyi *et al.*, 2011). However, the values agreed with values reported by Ogunfowokan *et al.* (2006). Removal efficiency of the WWTP (Figure 4.36) shows that DEHP, 2-NP and DEP were poorly removed from the waste effluent during the summer season, while DBP was not well removed for all the seasons under study. Generally, the removal efficiency of the treatment plant could be said to be effective for most of the congeners under study as between 80 and 90 % were removed from the waste stream except for 2-NP phenols.

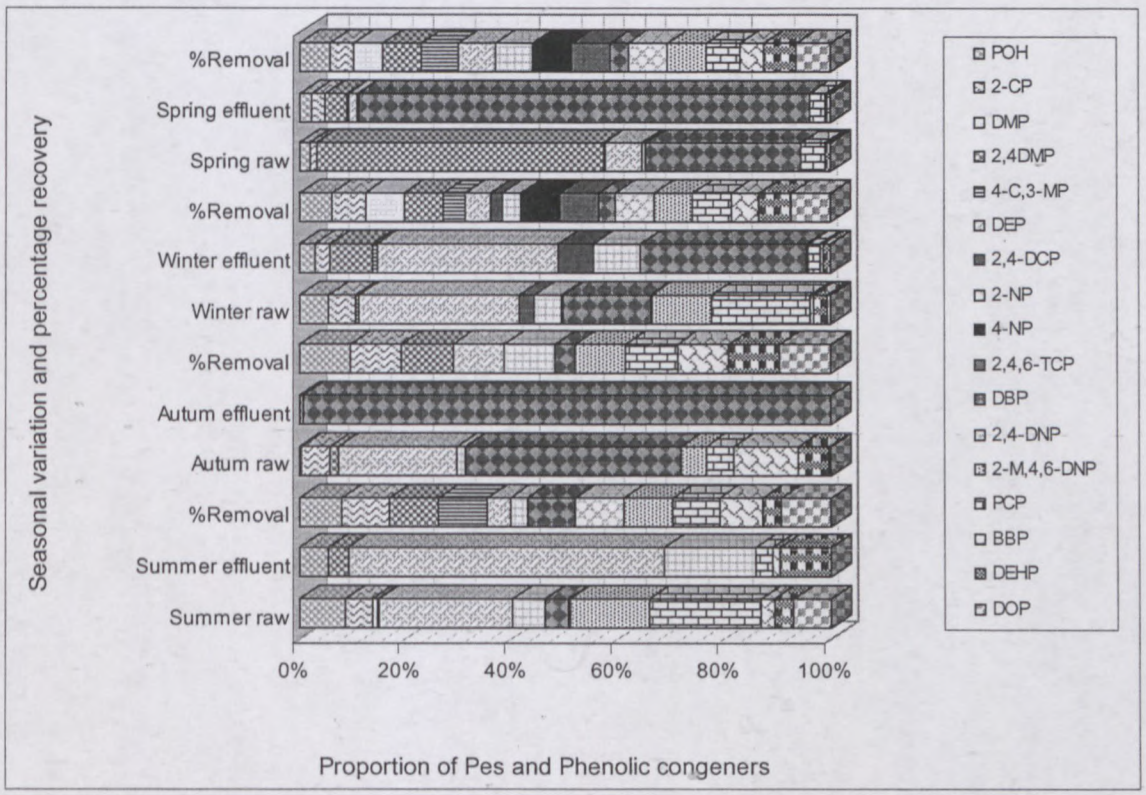


Figure 4.36: Proportion of PEs to phenolic congeners and removal efficiency of Bellville WWTPT in summer, autumn, winter and spring

The WWTP was very efficient during the autumn sampling as nearly all the congeners were totally removed except for DBP. The removal efficiency for DBP is directly proportional to the concentration of DBP received at the WWTP. The ineffective removal efficiency of the WWTP during the spring correlate significantly with the high concentration of the congeners detected in the water downstream of the plant. The ineffective removal during the spring could be attributed to WWTP overload and constant breakdown of the plant. In addition, high

concentration of congeners during the sampling seasons can be attributed to direct waste disposal of industrial effluent into inlet source without preliminary treatment.

4.6.3 Levels of phenolic and phthalate esters congeners in Kraaifontein and Mosselbank River

Kraaifontein treatment plant is known to receive mainly household waste with about 10% industrial effluent. The seasonal concentrations of the 17 congeners in this study are presented in Table 4. 25, while the annual distribution percentage for each congener is shown in Figure 4.37. The relative contributions of the 11 phenolic congeners during summer, autumn, winter and the spring seasons is presented in Table 4.28 showing clearly that POH was the most abundant. In the freshwater and the wastewater effluent, concentration of phenol increased significantly due to seasonal change (Figure 4.38).

The occurrence trend of phenolic congeners shows that 2-CP, 4-C, 3-MP, 4-NP, 2,4,6-TCP and PCP were mainly detected in wastewater influent while o-cresol, 2,4-DCP, and 2-NP were not detected in the freshwater and the wastewater effluent. The occurrence frequency is in the order of POH(100 %), 2-CP (56.3 %), 4-NP (25 %), PCP (18.8 %), 2,4,6-TCP (18.8 %) and 2,4-DNP (6.3 %).The annual distribution pattern (Figure 4.37) gave the annual percentage of phenolic congeners in comparison with PEs as POH (8%), 2,4-DMP (2 %), 2-CP (2 %) and PCP (1 %).

Of the six PEs, DBP and DEHP were present in all the water samples analyzed (Table 4.25). The occurrence frequencies for these two congeners were 100 % while others were mainly present in the waste influent. DMP was detected once in the influent waste into the plant during the autum sampling season. The relative contributions of the six PE congeners to the total phenolic congeners concentration in the dissolved water samples during the sampling seasons clearly showed that DBP was the most abundant with concentration (standard error) ranges of 1766 (7) μgl^{-1} to 8683 (3) μgl^{-1}, 1950 (6) μgl^{-1} to 5267 (39) μgl^{-1}, 417 (3) μgl^{-1} to 1049 (1) μgl^{-1} and 517 (46) μgl^{-1} to 1143 (3) $\mu gl^{-1}$for the upstream, influent, effluent and the downstream water samples.

Given the earlier reports of plasticizers in water samples (Fromme *et al.*, 2002; Fauser *et al.*, 2003; Marttinen *et al.*, 2003), this finding was not unexpected; however, the relative quantities of the DBP plasticizers in the upstream samples were surprising. The highest levels of PEs congeners upstream were detected in winter and the lowest in summer. These results agreed

Table 4.25: Seasonal Mean (± SE) (ugl^{-1}) of phenolic compounds and phthalates in Kraaifontein WWTP's and Mosselbank River (grab sample n =108)

Compound	Upstream				Influent				Effluent				Downstream			
	Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4
P-OH	127±3	159±3	226±3	176±8	823±4	650±6	483±3	710±12	150	123±3	127±3	128±2	130±6	120	273±3	170±15
2-CP	nd	157±117	29	42	69±1	323±3	30±3	423±202	nd	nd	18±	30±1	nd	nd	nd	nd
DMP*	nd	nd	nd	nd	nd	40	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
2,4-DMP	nd	nd	nd	nd	397±3	443±3	187±3	333±7	nd	nd	nd	nd	nd	nd	nd	nd
4-C, 3-MP	nd	nd	nd	nd	21±8	nd	nd	96±82	nd	nd	nd	nd	nd	nd	nd	nd
DEP*	nd	nd	nd	nd	nd	253±29	217±3	6596± 393	nd	nd	29±6	100	nd	38±1	nd	23±2
2,4-DCP	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
2NP	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
4NP	nd	nd	nd	nd	9±1	19±1	9	10±6	nd	nd	nd	nd	nd	nd	nd	nd
2,4,6-TCP	nd	nd	nd	nd	50±1	13	9±1	nd	nd	nd	nd	nd	nd	nd	nd	nd
DBP*	2597±7	1766±7	8683±3	3400±40	5267±39	1063±7	1950±6	1633±133	1049±1	763±3	417±3	749±3	1143±3	897±3	1437±3	517±46
2,4-DNP	nd	nd	nd	nd	nd	8±1	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
2-M,4,6-DNP	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
PCP	nd	nd	nd	nd	nd	76±57	10±1	394±171	nd	nd	nd	nd	nd	nd	nd	nd
BBP*	nd	nd	19	9	nd	nd	nd	69	nd	nd	nd	10	nd	nd	nd	nd
DEHP*	131±1	141±1	140±1	167±3	1177±9	1040±35	3917±177	127±3	123±3	10±1	107±3	83	163±3	189	139±1	147±4
DOP*	nd	nd	nd	nd	40±17	8	nd	430±170	nd	nd	nd	nd	nd	nd	nd	nd

Q1 = Summer; Q2 = Autumn; Q3 = Winter; Q4 = Spring; P-OH = Phenol; 2-CP = 2 Chlorophenol; DMP=Dimethyl phthalate; 2,4-DMP = 2,4-Dimenthyl phenol; 4-C, 3-MP = 4 Chloro 3methyl phenol; DEP = Diethyl phthalates; 2,4-DCP = 2,4 Dichlorophenol; 2-NP = 2 Nitrophenol; 4-NP = 4 Nitrophenol; 2,4,6-TCP = 2,4,6 Trichlorophenol; DBP = Dibutyl phthalate; 2,4-DNP = 2,4 Dinitrophenol; 2-M, 4,6-DNP = 2 Methyl 4,6-Dinitrophenol; PCP = Pentachlorophenol; BBP = Benzylbutyl phthalate; DEHP = Diethylhexyl phthalate; DOP = Dioctyl phthalate; nd = not detected; bdl = below detection limits; blq = below quantification limit; *Compound not affected by MTBSTFA derivatization.

with other reports for polycyclic aromatic hydrocarbons (PAHs), organochlorine pesticides (OCPs) and polychlorinatedbiphenyls (PCBs), mainly caused by urban storm water runoff and atmospheric deposition (Kim and Kannan, 2007; Gevao *et al.*, 2008).

This result is consistent with the commonly reported findings that DBP, DEP and DEHP are the dominant components of the PEs congeners often found in water (Suzuki *et al.*, 2001; Fatoki and Noma, 2002), sediment (Tan *et al.*, 1995; Yuan *et al.*, 2002; Mackintosh *et al.*, 2006; Sha *et al.*, 2007; Barnabe *et al.*, 2008) and biota (Silva *et al.*, 2004). This trend was also supported by Vitali *et al.* (1997) observation that DEHP and DBP are the most commonly produced PEs. However, this does not reflect the usual pattern of the plastic industry production dominated by DEHP reported in other studies (Tan *et al.*, 1995; Gómez-Hens *et al.*, 2003; Mackintosh *et al.*, 2006).

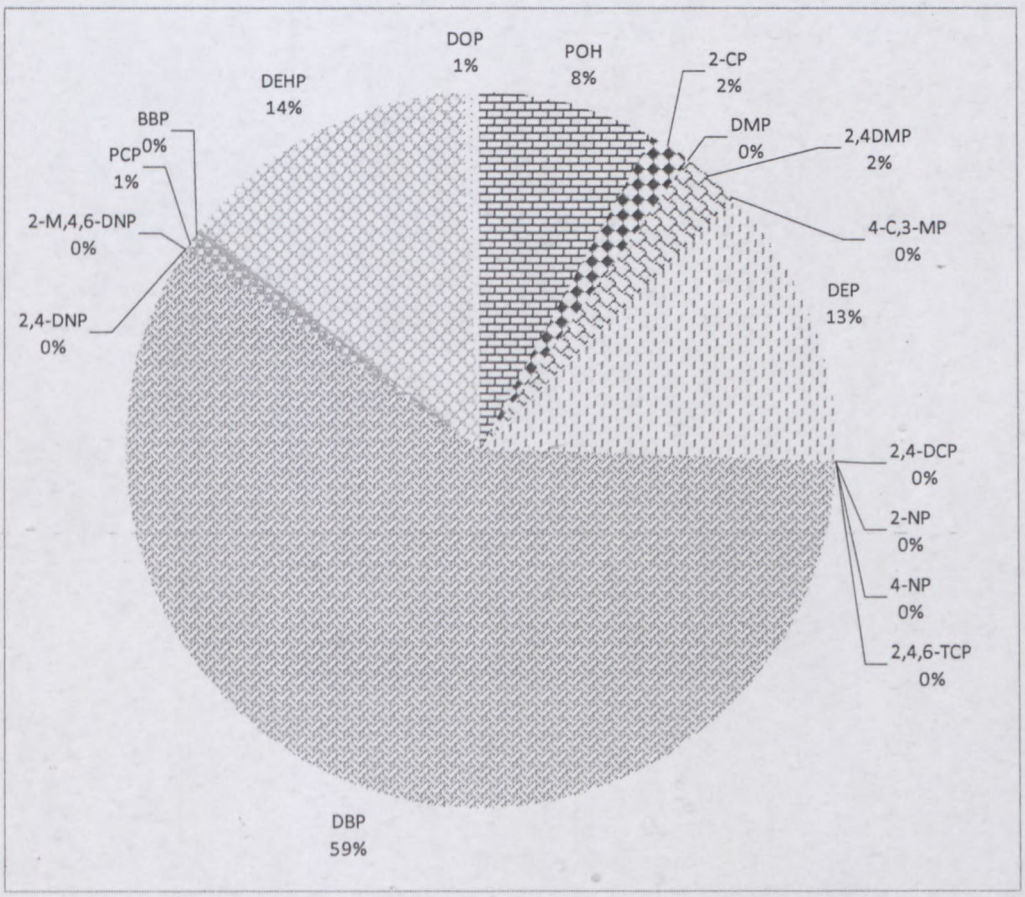


Figure 4.37: Annual distribution pattern of phenolic and phthalate esters congeners in Mosselbank River and Kraaifontein WWTP

The annual distribution pattern showed that DBP accounted for 59 % of the total congeners followed by DEHP (14 %) and DEP (13 %) in comparison to other PEs and phenolic congeners under study. As shown in Figure 4.38, there was significant difference in the seasonal concentration of PEs most especially for DBP for winter and summer in the upstream and in the influent samples.

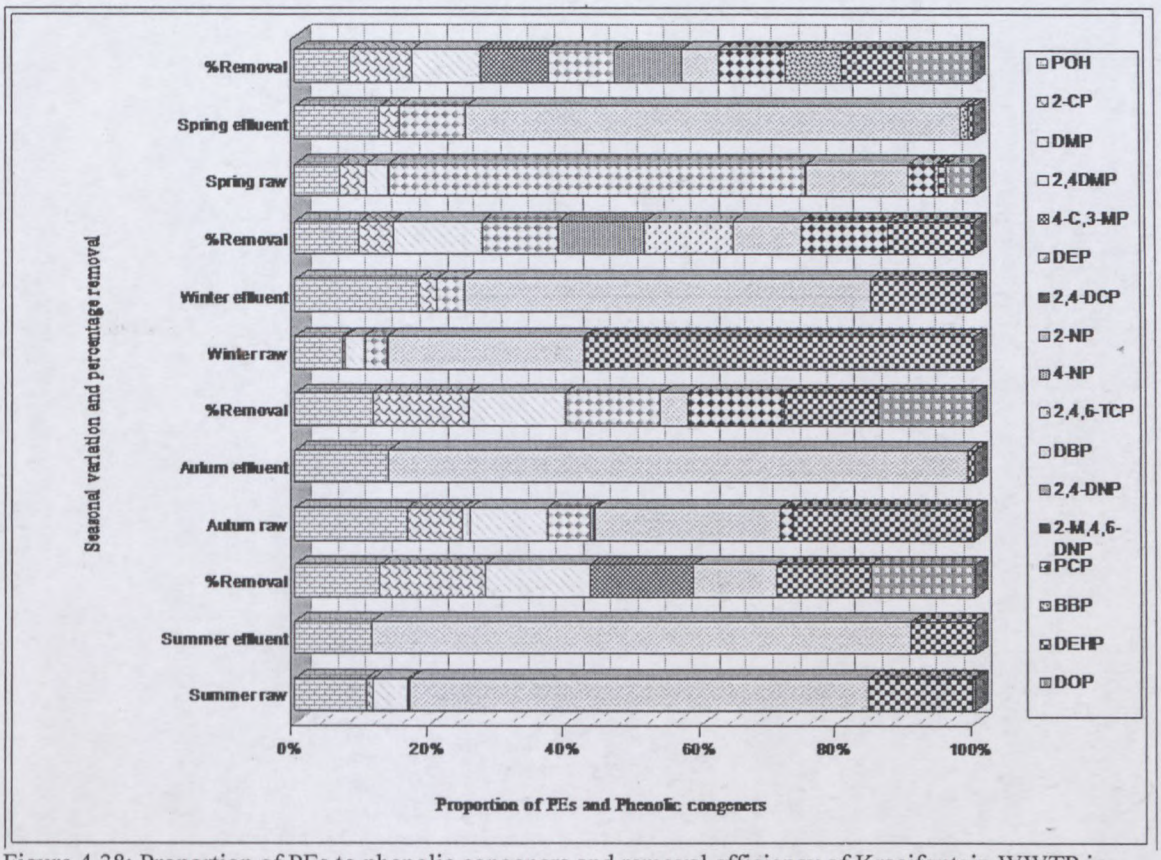


Figure 4.38: Proportion of PEs to phenolic congeners and removal efficiency of Kraaifontein WWTP in summer, autumn, winter and spring

4.6.4 Levels of phenolic and phthalate esters congeners in Potsdam WWTP and Diep River

Two congeners (2-NP and 2,4-DMP) out of the 11 phenolic congeners were detected in the upstream samples of the WWTP for all the sampling seasons. The levels of the detected congeners are presented in Table 4.26, while the annual distribution pattern in relation to PEs is presented in Figure 4.39. For the all the seasons, 2,4-DCP, 2,4,6-TCP, 4-NP and 2,4-DNP were not detected. The occurrence frequency of the phenolic congeners reveals as 2-NP (100 %), PCP (50 %), 2,4-DMP (43.75 %), POH (37.5 %) 2-CP and 2-M, 4,6-DNP (25 %). The trend of the phenolic congeners upstream of the WWTP is similar to the trend recorded upstream of Athlone, Bellville and Kraaifontein treatment plants. In comparison to other phenolic congeners on an annual basis, 2-NP accounted for about 41% while others are in the order PCP (35 %), POH (9 %), 2-M,4,6-DNP (6 %), 2-CP (4 %), 2,4-DMP (2 %) and 4-C,3-MP (2 %).

Table 4.26: Seasonal Mean (± SE) ($\mu g l^{-1}$) of phenolic compounds and phthalates in Potsdam WWTP's and Diep River (grab sample n =108)

Compound	Upstream				Influent				Effluent				Downstream			
	Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4
P-OH	nd	nd	nd	nd	59	nd	79±2	75±4	nd	nd	nd	nd	59±1	nd	71±1	52±4
2-CP	nd	nd	nd	nd	19	49±1	112	23±2	nd	nd	nd	nd	nd	nd	nd	nd
DMP*	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
2,4-DMP	nd	6	10±1	8±1	nd	nd	nd	nd	12±1	18	29	20±3	nd	nd	nd	nd
4-C, 3-MP	nd	nd	nd	nd	19±1	15±1	22±2	20±6	nd	nd	nd	nd	nd	nd	nd	nd
DEP*	413±3	131	190	315±16	5281±1	2353±20	543±2	1826±46	112	128±1	78	50±2	264±2	193±2	342±1	307±5
2,4-DCP	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
2NP	103±3	60±1	39±	136±4	315±3	86±2	294±1	309±4	39	37	66	47	39	39	28	39
4NP	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
2,4,6-TCP	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
DBP*	nd	nd	nd	nd	1863±7	1144±1	1214±1	1429±4	nd	nd	nd	nd	nd	nd	nd	nd
2,4-DNP	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
2-M,4,6-DNP	nd	nd	nd	nd	113	40±1	71±1	53±2	nd	nd	nd	nd	nd	nd	nd	nd
PCP	nd	nd	nd	nd	474±1	317±2	195±2	228±9	nd	nd	nd	nd	31±2	323	31±1	41±5
BBP*	nd	nd	nd	nd	526±2	273±1	379±6	384±43	nd	nd	nd	nd	41±5	18±1	50±2	29±2
DEHP*	9±1	10±1	9±1	10±1	155±2	72±1	139±8	105±3	19	nd	9	12	9±1	7±1	7±1	9±1
DOP*	nd	nd	nd	nd	23±2	11±1	21±3	nd	nd	nd	nd	nd	nd	nd	nd	nd

Q1 = Summer; Q2 = Autumn; Q3 = Winter; Q4 = Spring; P-OH = Phenol; 2-CP = 2 Chlorophenol; DMP = DMP=Dimethyl phthalate; 2,4-DMP = 2,4-Dimenthyl phenol; 4-C, 3-MP = 4 Chloro 3methyl phenol; DEP = Diethyl phthalates; 2,4-DCP = 2,4 Dichlorophenol; 2-NP = 2 Nitrophenol; 4-NP = 4 Nitrophenol; 2,4,6-TCP = 2,4,6 Trichlorophenol; DBP = Dibutyl phthalate; 2,4-DNP = 2,4 Dinitrophenol; 2-M, 4,6-DNP = 2 Methyl 4,6-Dinitrophenol; PCP = Pentachlorophenol; BBP = Benzylbutyl phthalate; DEHP = Diethylhexyl phthalate; DOP = Dioctyl phthalate; nd = not detected; bdl = below detection limits; blq = below quantification limit; *Compound not affected by MTBSTFA derivatization.

However, the distribution pattern of the listed phenolic congeners on annual basis in comparison to the PEs is in the order of 2-NP (7 %), PCP (6 %), POH (2 %) 2-CP and 2M,4,6-DNP (1 %), while others are negligible (Figure 4.39). Considering the living pattern and clusters of informal settlements around this area, the level of 2-NP and 2,4-DMP in the water may be attributed to gray water and household wastewater from the informal settlement further upstream of the treatment plant. The reported values were higher than values reported in literatures (Czaplicka, 2001; Riberio *et al.*, 2002; Zhao *et al.*, 2009).

DEP concentration ranged from 50 to 413 μgl^{-1} and 78 to 5281 μgl^{-1} for the freshwater and WWTP effluents, respectively. The corresponding concentration range for DBP were <LOD and 1144-1863 μgl^{-1}, respectively. Other phthalate ester congeners detected were BBP (<LOD to 50 μgl^{-1} in freshwater; <LOD to 526 μgl^{-} for wastewater effluents); DEHP (7-10 μgl^{-1} and <LOD to 155 for freshwater and effluent, respectively) and DOP (<LOD and <LOD to 23 μgl^{-1} for freshwater and effluent, respectively).

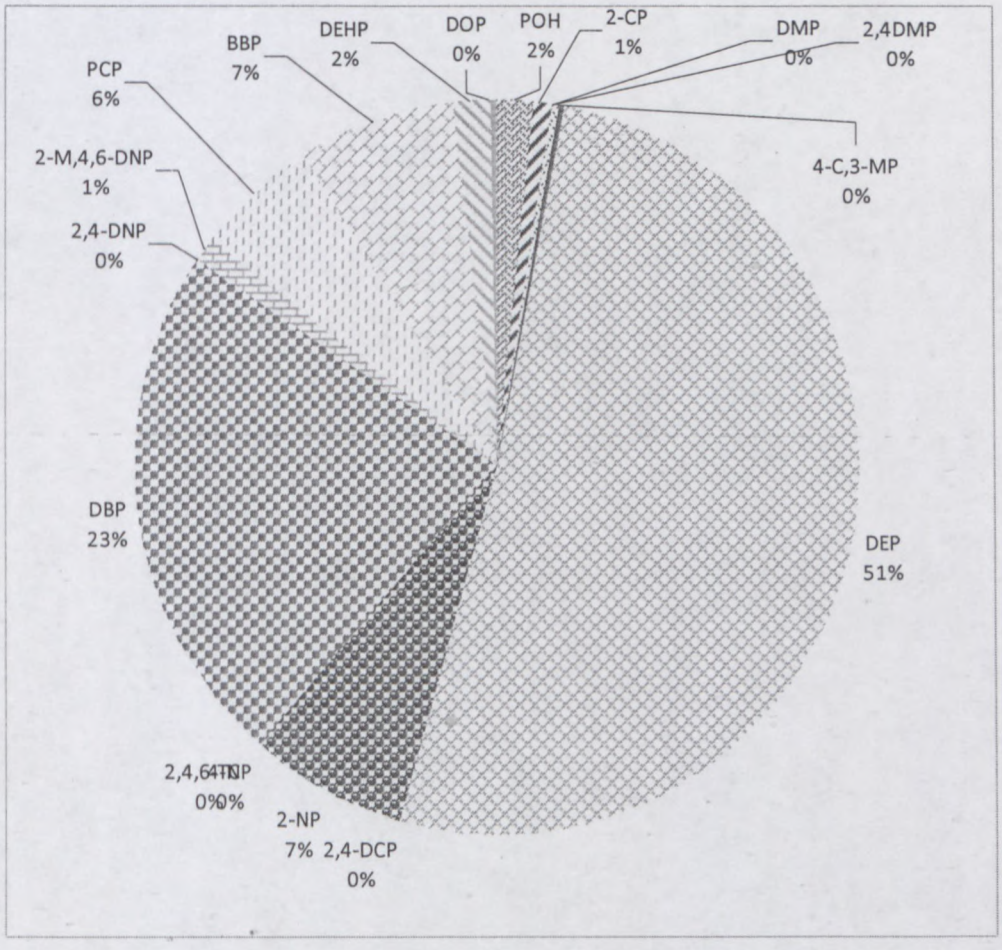


Figure 4.39: Annual distribution pattern of phenolic and phthalate esters congeners in Diep River and Potsdam WWTP

The occurrence and distribution trend in PEs congeners in the freshwater and the treatment plant was similar to the observed trend at the Athlone WWTP and the Vygekraal river. DEP was the dominant congener with 51% on an annual basis followed by DBP (23 %), BBP

(7 %) and DEHP (2 %) in relation to the 11 phenolic congeners determined (Figure 4.39). The occurrence frequency is listed as DEP (100 %), DBP (50 %), DBP (25 %), DEHP (61 %), DOP (18 %) and DMP (0 %). Concentrations of the PEs congeners in the influent, effluent and freshwater systems are comparably higher than concentration found in other studies (Makepeace *et al.*, 1995; Boutrup and Plesner *et al.*, 2001; Marttinen *et al.*, 2003; Roslev *et al.*, 2007; Clara *et al.*, 2010; Zgheib *et al.*, 2011). However, concentration in this study was lower for effluent and freshwater compared to studies in Nigeria and South Africa (Fatoki and Noma, 2002; Ogunfowokan *et al.*, 2006; Adeniyi *et al.*, 2011). The occurrence pattern of phthalates in the wastewater effluent may be attributed to an array of industries in the zone releasing the waste into the sewer for further treatment.

Wastewater treatment plants represent a significant route of PEs into their environment. From Figure 4.40, the removal efficiency of Potsdam treatment plant was not excellent for DEP and DEHP. Although, high removal efficiency was obtained for the plant, there was a strong

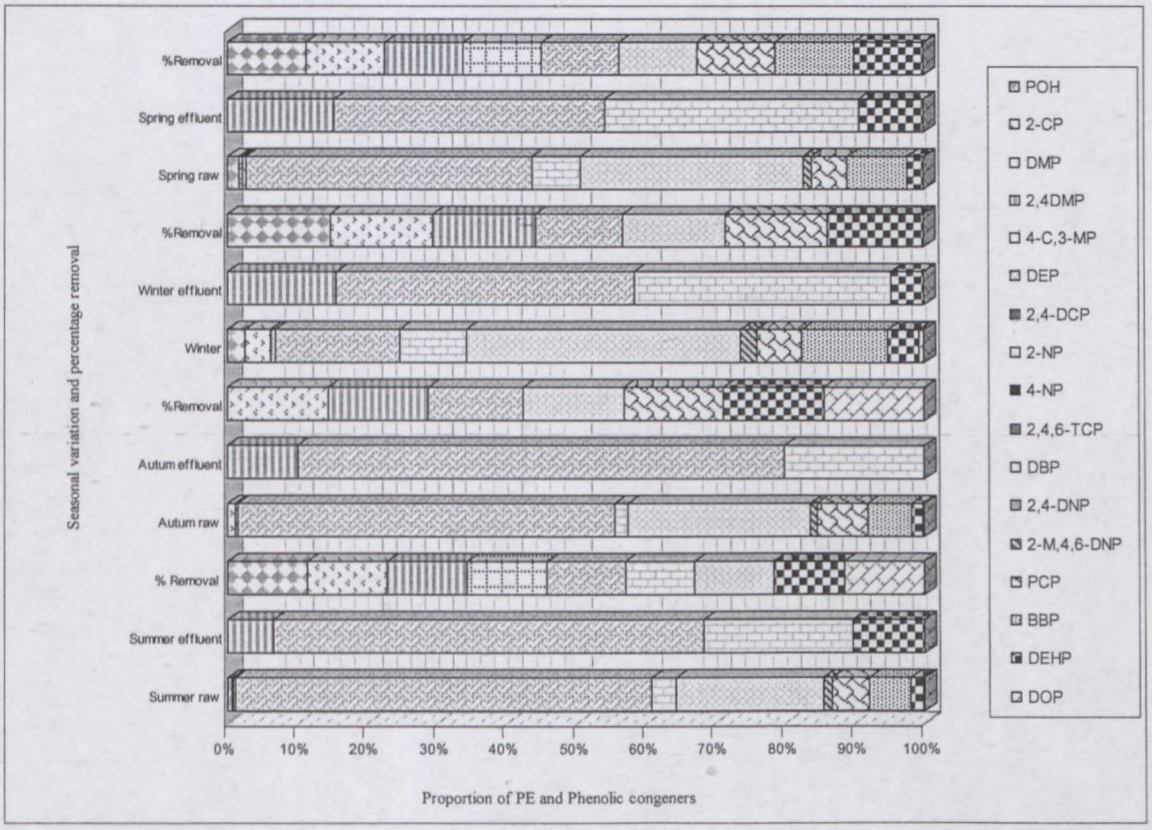


Figure 4.40: Proportion of PEs to phenolic congeners to percent removal efficiency of Potsdam WWTP in summer, autumn, winter and spring

correlation between the treatment plant and the freshwater samples. In addition, DBP and BBP, though were not detected in the final effluent from the plants, high occurrence downstream of the WWTP may be attributed to storm water from a petroleum refinery close to the WWTP. Although DBP has been the most widely used lower molecular weight phthalate congener, its production had showed a decreasing trend around the world (KemI, 2010).

4.6.5 Levels of phenolic and phthalate esters congeners in Stellenbosch WWTP and Vedlwachters River

The summary of data for all the analyzed phenolic congeners in the river water, influent and effluents from the Stellenbosch WWTP is presented in Table 4.27. Aside from 2,4-DCP, 2,4-DNP and 2-M,4,6-DNP, all the phenolic congeners were detected in the upstream water samples. Phenol was the dominant congeners with a concentration that ranged from 233 to 1063 μgl^{-1}, followed by PCP with a concentration range of 10 to 118 μgl^{-1}. There was a significant difference ($P < 0.05$) in the phenolic congener concentration most especially POH, 2,4-DMP, 2-NP and PCP (Figure 4.41) over the study period.

The level of phenolic congeners reported in the upstream section may be attributed to pollution by landfill leachate from a landfill site adjacent to the sampling site and dumping of demolished building wastes in this section of the river. Some levels of phenols had been reported in leachate samples in Europe (Bestamin, 2005). The occurrence frequency for the phenolic congeners is listed as POH (85%), 2-CP (95.83%), 2,4-DMP (75%), 2,4-DCP (18.75%), 2-NP (100%), PCP (100%), 4-NP (37.5%), 2,4,6-TCP (31.25%), 2,4-DNP (50%) and 2-M,4,6-DNP (68.75%). The annual distribution pattern with respect to PEs congeners showed that PCP accounted for 17% followed by 2,4-DMP (10%), POH (9%), 2-NP (3%), 2-M,4,6-DNP and 4-C,3-MP (1% each), while others are negligible (Figure 4.42).

From this study, removal efficiency showed that 2-NP was ineffectively removed from the wastewater. Also, statistical analysis showed strong correlation (0.896) between the final effluent and downstream concentration, an indication that wastewater treatment plant acts a source of river water pollution. There was significant change in phenolic compounds concentration over the seasons studied (Figure 4.42). To date, no work had reported on the level of 11 phenolic congeners investigated in this study in river water or WWTP in South Africa, thus making comparison difficult. However, the results clearly suggested that the volume of influx of these compounds into the treatment plant and surface water is mainly due to anthropogenic activites.

The result trend for PEs congeners in the freshwater system upstream of the WWTP over the study period showed that all the PEs congeners were frequently detected in all samples except DMP that was detected during winter and spring seasons. This trend of occurrence is similar to other studies reported elsewhere (Fromme *et al.*, 2002; Oliver *et al.*, 2005) where DMP has been not frequently detected in the freshwater compare to other PEs congeners. The frequency of occurrence (% of samples above the LOD) for the congeners is listed as DBP (100 %), DEHP (100 %), DEP (93.75 %), BBP (87.5 %), DOP (37.5 %) and DMP (12.5%). The concentration of PEs congeners in the upstream section was higher than expected in a natural river system. This may be attributed to point source contamination by leachate from Stellenbosch landfill site that drains into the river system.

Table 4.27: Seasonal Mean (± SE) (μgl^{-1}) of phenolic compounds and phthalates in Stellenbosch WWTP's and Veldwachters River (grab sample n =108)

Compound	Upstream				Influent				Effluent				Downstream			
	Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4
P-OH	1063±1	233±1	413±9	653±82	1257±4	1578±2	1038±4	2063±429	36±1	150±2	nd	1040±401	19±3	nd	9	10
2-CP	28±1	18±1	27±1	20±12	165±2	653	313±1	430±140	108±2	128±1	nd	253±52	nd	20±2	nd	387±3
DMP*	nd	nd	nd	nd	nd	nd	6±6	26±15	nd	nd	nd	nd	nd	nd	nd	nd
2,4-DMP	894±2	nd	370±2	513±172	nd	nd	4271±1	nd	1379±1	1160±2	1589±2	377±75	828±4	560±2	449±1	327±20
4-C, 3-MP	nd	nd	nd	6±3	124±2	172±2	125±2	107±12	70±1	10±2	17±1	20	19±3	nd	9	10
DEP*	289±4	122±1	nd	123±31	1848±42	3353±1	7413±2	1357±219	310±1	70±2	146	117±12	189±4	813±15	103±3	53±9
2,4-DCP	nd	nd	nd	nd	nd	39±1	nd	27±20	nd	nd	nd	nd	nd	156±117	nd	nd
2NP	63±32	27±1	26±1	250±55	164±6	223±1	218±6	237±32	49±1	177±1	69±2	78±41	201±1	180±2	67±2	58±15
4NP	nd	nd	nd	3	13	11±2	9±1	10	nd	nd	nd	nd	nd	nd	14	nd
2,4,6-TCP	nd	nd	nd	3	9±1	7±1	11±1	10	nd	nd	nd	nd	nd	nd	nd	nd
DBP*	7059±9	1014±2	3312±22	1877±284	1042±1	1541±2	13101±1	6163±361	639±2	729±3	897±3	707±67	5600±1	3278±3	2131±1	1343±78
2,4-DNP	nd	nd	nd	nd	31±1	21±1	320±2	23±3	6±1	nd	7±1	nd	11±1	nd	21±1	nd
2-M,4,6-DNP	nd	nd	nd	nd	143±1	162±2	1021±1	167±21	39±1	38±1	265±197	6±3	18±2	nd	3	39±1
PCP	118±85	nd	10±1	33±9	4823±5	11680±35	312±2	4557±540	468±2	280±2	149±2	90±20	140±3	131±1	30±2	13±3
BBP*	57±2	nd	11±1	13±9	898±4	2392±6	1678±4	100±12	118±50	346±7	138±2	23±3	140±2	nd	10	20
DEHP*	431±3	263±3	215±2	80±17	562±2	1151±2	1451±2	383±38	296±1	391±2	353±1	150±12	361±2	296±4	280±8	107±7
DOP*	nd	nd	nd	nd	193±1	91±1	59±2	10	6±1	nd	nd	nd	5±3	nd	nd	nd

Q1 = Summer; Q2 = Autumn; Q3 = Winter; Q4 = Spring; P-OH = Phenol; 2-CP = 2 Chlorophenol; DMP=Dimethyl phthalate; 2,4-DMP = 2,4-Dimenthyl phenol; 4-C, 3-MP = 4 Chloro 3methyl phenol; DEP = Diethyl phthalates; 2,4-DCP = 2,4 Dichlorophenol; 2-NP = 2 Nitrophenol; 4-NP = 4 Nitrophenol; 2,4,6-TCP = 2,4,6 Trichlorophenol; DBP = Dibutyl phthalate; 2,4-DNP = 2,4 Dinitrophenol; 2-M, 4,6-DNP = 2 Methyl 4,6-Dinitrophenol; PCP = Pentachlorophenol; BBP = Benzylbutyl phthalate; DEHP = Diethylhexyl phthalate; DOP = Dioctyl phthalate; nd = not detected; bdl = below detection limits; blq = below quantification limit; *Compound not affected by MTBSTFA derivatization.

Furthermore, high levels of PEs congeners recorded during the study period, aside from the landfill leachate may be attributed to dumping of demolished building wastes in this section of the river and the channelization of storm water runoff from the landfill site. PEs congener had been widely reported in storm water across Europe (Zgheib *et al.*, 2011). However, no study had reported their levels in storm water in South Africa to the best of our knowledge. Average concentrations of phthalates in pretreated water, from autumn 2010 to summer 2011, are presented in Table 4.27. DBPP was the most abundant compound (1042 to 13101 μg l^{-1}). DEP came next (1357 to 7413 μgl^{-1}). Other phthalates were found in the range of < LOD to 26 μgl^{-1}, 100 to 2392 μgl^{-1}, 383 to 1451 μgl^{-1}, 10 to 193 μgl^{-1} for DMP, BBP, DEHP and DOP, respectively. A similar distribution pattern with higher concentration range was described in sewage oxidation pond at Obafemi Awolowo University, Ile Ife in Nigeria (Ogunfowokan *et al.*, 2006). The distribution pattern in this study where DEP was more dominant than DEHP is consistent with the prevalence of DEP in Marne Aval wastewater treatment plant in France (Dargnat *et al.*, 2009).

Levels of PEs congeners in wastewater to WWTP from other countries showed wide discrepancies with this study as comparatively lower concentration had been reported. In the developed countries where there are regulation and environmental control on the use and disposal of PEs containing chemical and pharmaceutical industrial wastes e.g. in the United Kingdom, Canada, Australia and France, DEHP had been reported to range from 2.83 to 44 μgl^{-1} (Oliver *et al.*, 2005; Barnabe *et al.*, 2008; Dargnet *et al.*, 2008; Tan *et al.*, 2009).

Other phthalates in this study were higher than reported values in The Netherlands, Finland, China, France and United Kingdom (Marttinen *et al.*, 2003; Oliver *et al.*, 2005; Vethaak *et al.*, 2005; Zeng *et al.*, 2009; Dargnat *et al.*, 2009). The high level of PEs in this WWTP could be linked to a wide number of industries that released their waste effluent into the plant for further treatment prior to discharge into the river system or use for irrigation purposes.

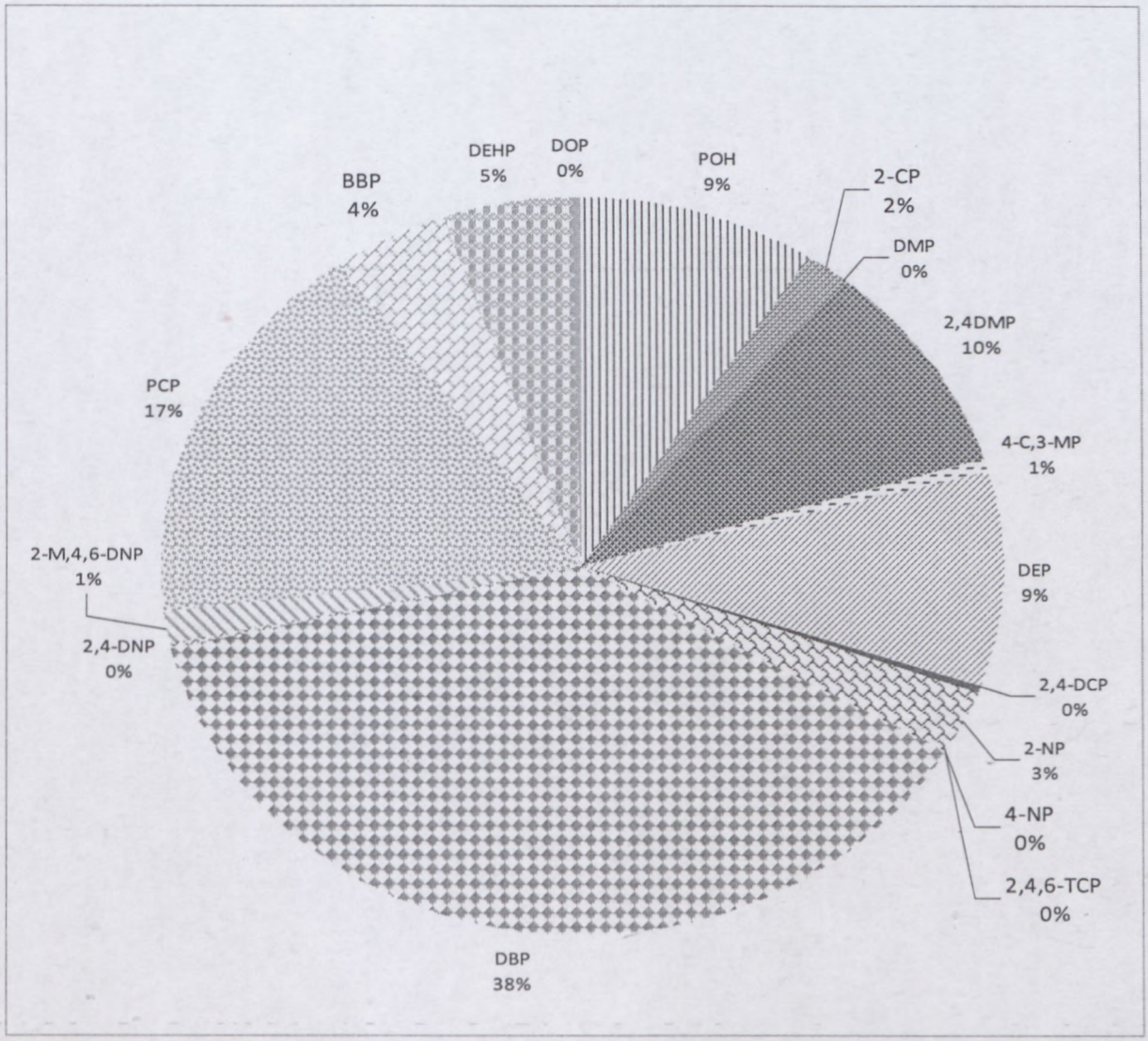


Figure 4.41: Annual distribution pattern of phenolic and phthalate esters congeners in Veldwatchers River and Stellenbosch WWTP

Throughout the sampling period, DEP, BBP, DBP, DEHP and DOP were detected in the final effluent (Figure 4.42). Though the removal efficiency was high (above 80%), the removal efficiency for DEHP was generally low ranging from 47.36% (summer) to 75.7% (winter). This is directly proportional to the influent concentration. Despite the high removal efficiency recorded by the plant, levels of PEs congeners in the plant were higher than values reported elsewhere. For example, Marttinen *et al.* (2003) reported 6 μgl^{-1} of DEHP in Finland, while Paxeus (1996) reported concentration range of 3–8 μgl^{-1}; 6–22 μgl^{-1}; 6–17 μgl^{-1}; 10–17 μgl^{-1} for DEP, DBP, BBP and DEHP, respectively in Sweden. However, Ogunfowokan *et al.* (2006) reported higher concentration in South West, Nigeria.

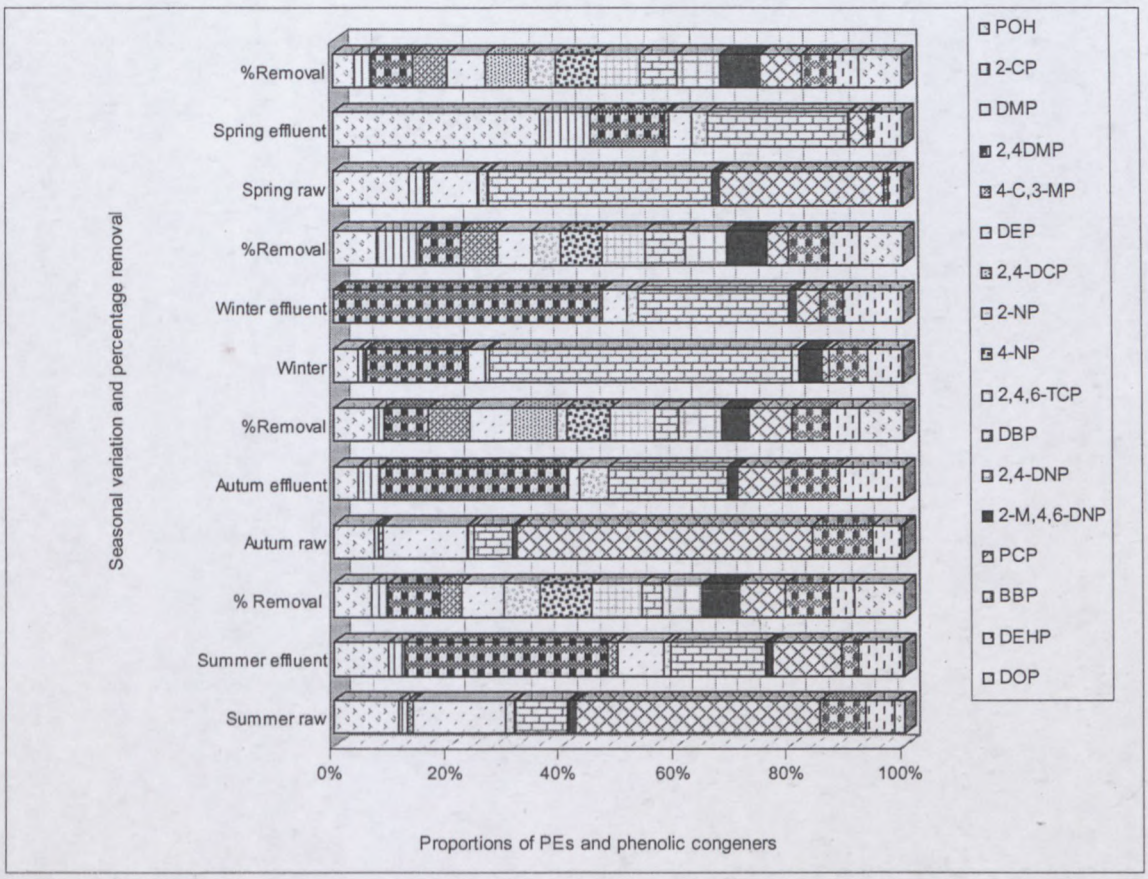


Figure 4.42: Proportion of PEs to phenolic congeners to removal efficiency of congeners in Stellenbosch WWTP in summer, autumn, winter and spring.

There was significant difference ($P < 0.05$) in the concentrations of most of the PEs congeners over the study period in both the surface water and the WWTP. The WWTP acted as a pollution source to the water downstream, though the water has been polluted upstream by the leachate and demolition material. The impact of the effluent on the levels of PEs congeners was very pronounced during autum and winter where DEP, DBP and DEHP concentrations increased by a factor of 3, 4 and 0.25, respectively.

4.6.6 Level of phenolic and phthalate esters congeners in Zandvliet WWTP and Kuils River

During the sampling campaigns 108 samples were collected comprising of influents, effluent and receiving river water samples. The data obtained from all the analyzed samples are presented in Table 4.28. Regarding the surface water samples, the occurrence of the phenolic congeners in the upstream samples was similar to the pattern observed in the Diep River. Most of the phenolic congeners were detected during the spring with the exception of POH, 2,4-DMP and 2-NP that were detected all over the studied seasons. The upstream section of the treatment plant is the lower section of Bellville WWTP and is adjacent to the largest informal settlement in Cape Town. The high level of phenolic congeners recorded may directly be connected to the storm water runoff and direct dumping of refuse material on the river course. Statistical analysis shows that there was significant difference ($P < 0.05$) in the concentration of the congeners over the study period upstream.

With respect to untreated water, all the phenolic congeners were detected except for 2,4-DMP. This trend in 2,4-DMP concentration was similar to other WWTPs investigated (Table 4.28). The WWTP received both industrial and domestic wastewater, thus the concentration of phenolic congners ranged from < LOD to 3260 μgl^{-1} for POH during summer sampling season. The concentration of phenolic comopound in the influent wastewater was higher than other WWTPs investigated in this study. The congeners were not totally eliminated by the applied processes and as a result, they were detected in the final effluent samples (Table 4.28). In the effluent wastewater, phenol was the dominat congeners and was detected in all the samples. This probably may be a result of its high concentrations in the untreated wastewater or due to degradation actions by microorganisms of higher molecular compounds present in the untreated wastewater not included in this study during the treatment process.

The effect of incomplete removal of the phenolic congeners was felt downstream of the treatment plant. Though the upstream shows some level of contamination, the wastewater effluent also contributed to the high level of congeners detected downstream. In some instances, the WWTP acted as a dilution factor on high concentration detected upstream, e.g. 2-NP, the WWTP effluent helped to further dilute the congener concentration which ranged from 23 to 4681μgl^{-1} upstream to < LOD to 927 μgl^{-1} downstream. The annual distribution pattern of the phenolic congeners in respect to the PEs (Figure 4.43) showed that 2NP was the dominant congener (25 %) followed by POH, PCP and 2,4-DMP with 6 %, 5 % and 1 %, respectively, while others are negligible.

Table 4.28: Seasonal Mean (± SE) ($\mu g l^{-1}$) of phenolic compounds and phthalates in WWTP's F and Kuils River (grab sample n =108)

Compound	Upstream				Influent				Effluent				Downstream			
	Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4
P-OH	102±6	713±15	373±82	620±156	3260±30	563±114	760±242	2433±187	686±21	324±145	180±15	590±32	251±19	370±60	50±25	500±56
2-CP	nd	nd	nd	303±26	609±39	1205±64	467±182	613±	nd	311±8	17±2	223±35	223±6	120±10	nd	237±19
DMP*	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
2,4-DMP	133±3	15±2	27±12	207±32	nd	nd	nd	nd	20±10	90±10	173±75	317±43	86	11	3	223±19
4-C, 3-MP	nd	nd	nd	7±3	130	130±20	87±9	110±10	nd	nd	nd	13±3	nd	nd	nd	10
DEP*	nd	nd	nd	115±51	909±13	737±5	657±400	2103±109	nd	nd	nd	93±9	8±1	nd	340±34	120±20
2,4-DCP	nd	nd	nd	nd	nd	nd	100±10	137±20	nd	nd	83	nd	36±5	nd	nd	63±3
2NP	23±3	310±22	110±40	4681±2345	610±53	741±15	423±3	890±40	nd	nd	nd	nd	nd	nd	53±29	927±69
4NP	nd	nd	nd	nd	10	10	6±3	10	nd	nd	nd	nd	nd	nd	nd	nd
2,4,6-TCP	nd	nd	nd	nd	10	10	10	10	nd	nd	nd	nd	nd	nd	nd	nd
DBP*	4286±31	3350±178	7623±811	6567±1421	16143±131	6950±1221	34520±754	3580±321	3227±20	788±27	7363±119	830±55	250±42	518±3	320±1205	897±43
2,4-DNP	nd	nd	nd	nd	10±1	27±3	27±12	20	nd	nd	nd	nd	nd	nd	nd	nd
2-M,4,6-DNP	nd	nd	nd	nd	20±5	408±266	87±9	21±1	nd	nd	nd	nd	nd	nd	nd	nd
PCP	nd	nd	nd	10±6	3160±312	1277±285	2150±60	3257±259	nd	nd	43±13	nd	nd	nd	3	13±7
BBP*	23±3	10	7±3	80±12	2465±76	1213±116	4434±90	87±1	10	7	7±3	86±3	25±9	20	367±36	27±22
DEHP*	11±1	45±4	100±6	190±10	1227±9	495±63	2093±34	380±12	286±39	93±1	73±3	133±35	29±6	26±4	360±310	77±12
DOP*	nd	nd	nd	nd	25±3	8	27±3	10±3	nd	nd	nd	nd	nd	nd	283±28	nd

Q1 = Summer; Q2 = Autumn; Q3 = Winter; Q4 = Spring; P-OH = Phenol; 2-CP = 2 Chlorophenol; DMP=Dimethyl phthalate; 2,4-DMP = 2,4-Dimenthyl phenol; 4-C, 3-MP = 4 Chloro 3methyl phenol; DEP = Diethyl phthalates; 2,4-DCP = 2,4 Dichlorophenol; 2-NP = 2 Nitrophenol; 4-NP = 4 Nitrophenol; 2,4,6-TCP = 2,4,6 Trichlorophenol; DBP = Dibutyl phthalate; 2,4-DNP = 2,4 Dinitrophenol; 2-M, 4,6-DNP = 2 Methyl 4,6-Dinitrophenol; PCP = Pentachlorophenol; BBP = Benzylbutyl phthalate; DEHP = Diethylhexyl phthalate; DOP = Dioctyl phthalate; nd = not detected; bdl = below detection limit; blq = below quantification limit; *Compound not affected by MTBSTFA derivatization.

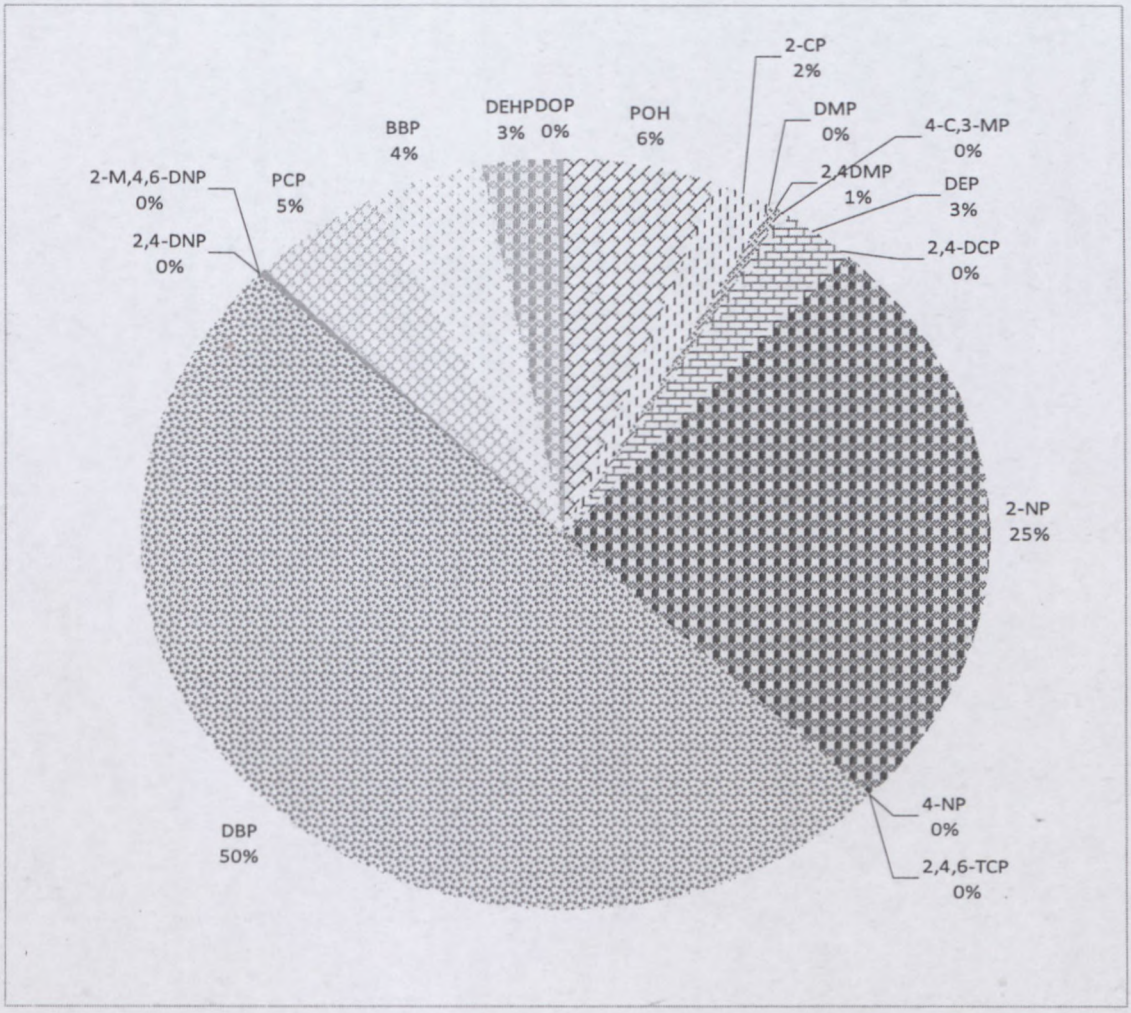


Figure 4.43: Annual distribution pattern of phenolic and phthalate esters congeners in Kuils River and Zandvliet WWTP

Like other WWTPs investigated, of all the six PEs congeners, DMP was not detected in surface water and wastewater effluents samples analyzed. The frequency of occurrence above LOD indicated that DBP, BBP and DEHP were the most detected PEs congeners followed by DEP and DOP (Table 4.28). The pattern of occurrence on an annual basis is similar to the trend observed for Bellville, kraaifontein and Stellenbosch with DBP accounting for 50% followed by BBP, DEHP and DEP with 4 %, 3 % and 3 %, respectively. The removal efficiency of the wastewater showed that DBP, BBP and DEHP were not totally removed from the wastewater. The concentration PEs congeners were significantly higher ($P < 0.05$) during the summer and the winter seasons compared to the other two seasons (Figure 4.44). Though PEs was detected upstream, however, the ineffective removal of PEs congeners from the wastewater effluent showed that WWTP acted as the major route of PEs congeners into the river systesm.

The ranged of DBP (3500 to 34,520 μgl^{-1}) reported in Table 4.28 was the highest for the PEs investigated for all the WWTPs in this study. The reported concentrations were similar to values reported in sewage sludge oxidation pond in Nigeria (Ogunfowokan *et al.*, 2006) but

higher than levels detected in Eastern Cape, South Africa; Ogun River, Nigeria and sewage treatment plants in Sweden, Finland, China and Australia (Fatoki and Noma, 2002; Tan *et al.*, 2008; Fatoki *et al.*, 2010; Adeniyi *et al.*, 2011).

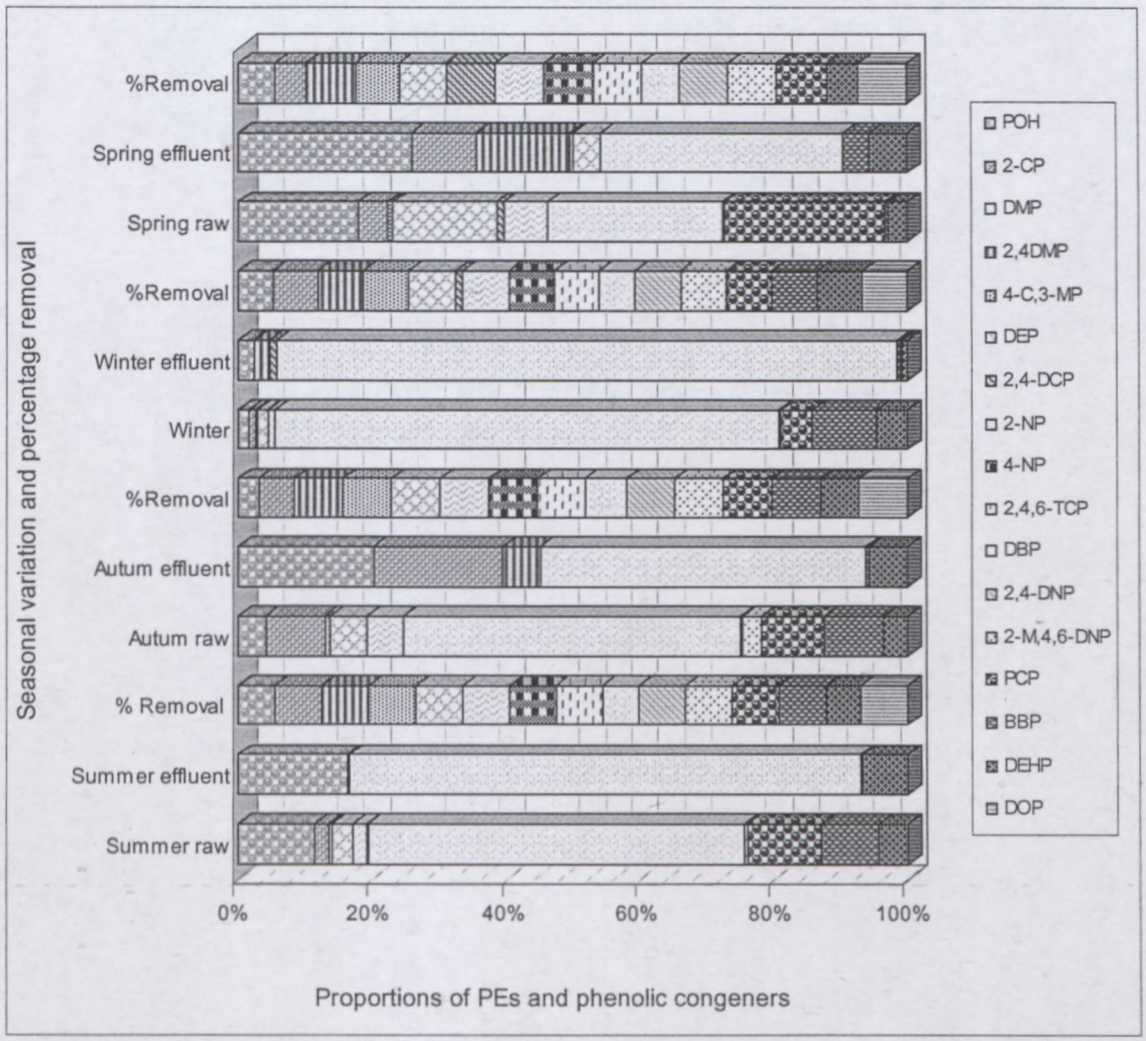


Figure 4.44: Proportion of PEs to phenolic congeners to removal efficiency of congeners in Zandvliet WWTP in summer, autumn, winter and spring

Although there was no previous study on the seasonal variability of PEs in WWTPs and surface waster in South Africa, considering the seasonal variation in concentration of PEs in the WWTP and river water, it is not possible to determine if this is an isolated case or if it typical of Western Cape. However, it is clear from this study that lower molecular phthalates congeners are often released into the environment compared to the higher molecular congeners.

4.5.3.7Kirstenbosch Botanical Garden (KBG)

Levels and distribution pattern of phenolic and phthalate ester congeners at the control site are presented in Table 4.29 and Figure 4.45. The data showed that most of the analytes were below the detection limit in water samples except for 2-CP, 2-NP, BBP and DEHP while DEP and PCP were detected during the summer season only. Comparing the results obtained at the control site to the surface water samples from other investigated sites (WWTP and river water), it clearly showed that the reported concentrations detected from all the sites are mainly from anthropogenic sources. Although, high level of DEHP is reported in the site, this may be attributed to aerial transportation through dry and wet deposition while 2-CP and 2-NP may be attributed to the use of treated sludge, inorganic fertilizer and pesticides for garden beautification. Also, nitro-phenols may probably come from the aerial transportation after the formation through atmospheric processes (Luttke *et* al., 1997; Sirvent *et* al., 2004; Minero *et al.*, 2007)

Table 4.29: Seasonal Mean (± SE) (μgl^{-1}) of phenolic compounds and phthalates in Kirstenbosch Botanical Garden

Compound	Q1	Q2	Q3	Q4
POH	nd	nd	nd	nd
2CP	101±44	113±4	125±13	100
DMP*	nd	nd	nd	nd
2,4-DMP	10	nd	10	10
4C-3MP	nd	nd	nd	nd
DEP*	50	nd	nd	nd
2,4-DCP	nd	nd	nd	nd
2NP	19±3	nd	29±1	19±1
4NP	nd	nd	nd	nd
2,4,6-TCP	nd	nd	nd	nd
DBP	nd	nd	nd	nd
2,4-DNP	nd	nd	nd	nd
PCP	6±1	nd	nd	nd
BBP	18±1	nd	10	10
DEHP	30	1163±15	1527±100	266±3
DOP	nd	nd	nd	nd

Q1=Summer; Q2=Autumn; Q3=Winter; Q4=Spring; P-OH=Phenol; 2-CP=2 Chlorophenol; DMP=Dimethyl phthalate 2,4-DMP=2,4-Dimenthyl phenol; 4-C,3-MP= 4Chloro 3methyl phenol; DEP=Diethyl phthalates; 2,4-DCP = 2,4 Dichlorophenol; 2-NP=2 Nitrophenol; 4-NP=4 Nitrophenol; 2,4,6-TCP=2,4,6 Trichlorophenol; DBP=Dibutyl phthalate; 2,4-DNP=2,4 Dinitrophenol; 2-M, 4,6-DNP=2 Methyl 4,6-Dinitrophenol; PCP=Pentachlorophenol; BBP=Benzylbutyl phthalate; DEHP=Diethylhexyl phthalate; DOP=Dioctyl phthalate; nd=not detected; bdl=below detection limits; bql = below quantification limits.; *Compound not affected by MTBSTFA derivatization.

Figure 4.5.19 showed the annual distribution pattern with DEHP accounting for 81 %, while 2-CP and 2-NP accounted for 13 % and 2 %, respectively. 2,4-DMP and BBP accounted for 1 %, while others are negligible.

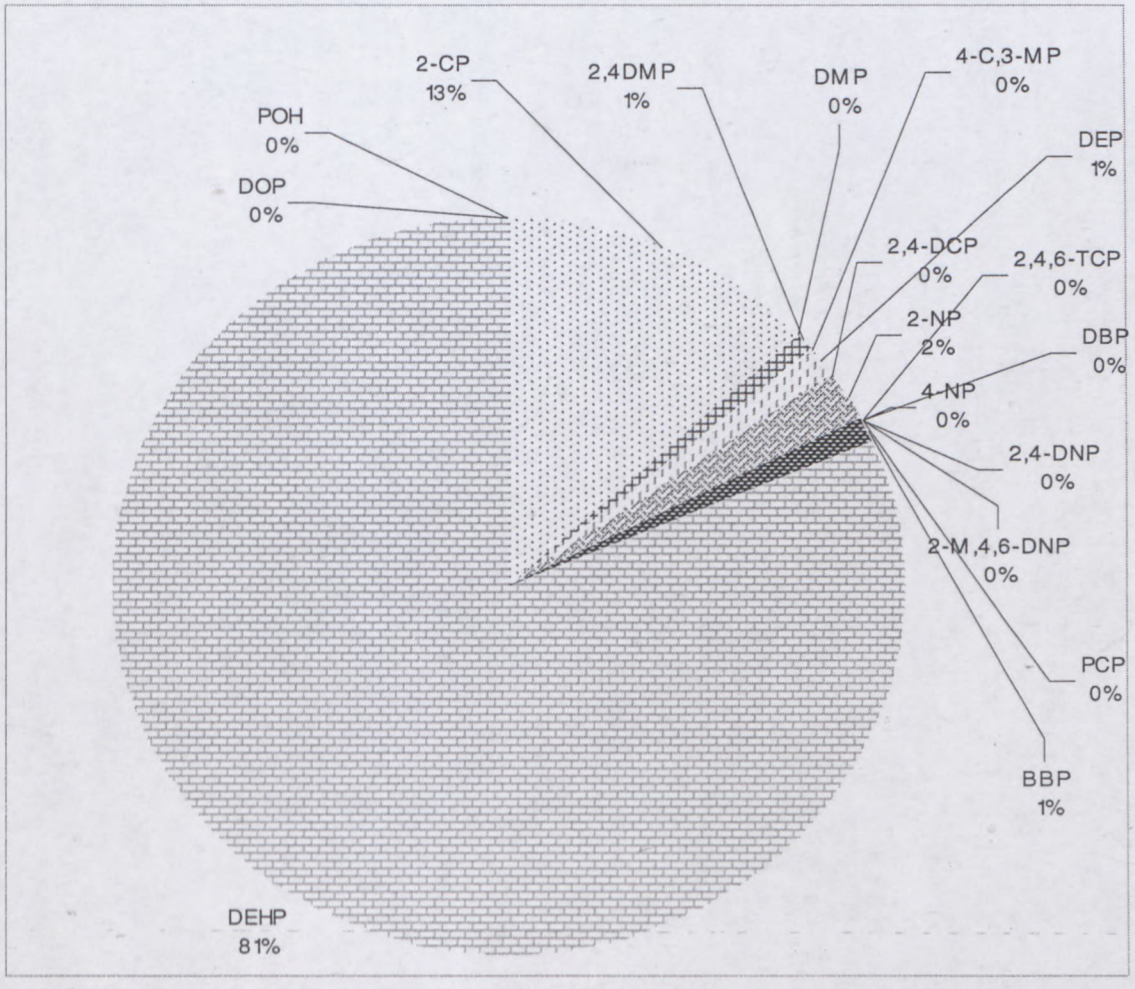


Figure 4.45: Annual distribution pattern of phenolic and phthalate esters congeners in Kirstenbosch water

4.6 General discussion on the phenolic and phthalate esters congeners in water

On the basis of this research finding, it was established that the river system is contaminated with the congeners of interest, it is however obvious that the wastewater treatment plants acted as one of the major routes of these congeners into the freshwater systems. Comparing the results presented in Table 4.23 to Table 4.28 with results from the control site (Kirstenbosch Botanical Garden), it was obvious that the possible routes of the congeners into the environment are mainly through anthropogenic soruces.

This study had revealed that the PEs congeners of lower molecular weight were the most detectable and dominant in both the WWTPs and the river systems. DBP is the most dominant of the PEs accounting for 50 % of the total congeners in the studied systems, followed by DEP. On the other hand, POH, 2CP and PCP were the dominanting congeners among the phenolics group over the studied period. As previously discussed, the profiling of the PEs congeners from the two

systems (WWTP and river water) failed to align with the widely reported distribution pattern, where DEHP is reported as the most dominant. Though, past studies in Nigeria, and South Africa had reported a similar trend (Fatoki and Noma, 2002; Ogunfowokan *et al.,* 2006; Adeniyi, *et al.*, 2011), however, the most profiling had it that DEHP is the dominant congeners in environmental samples.

Interms of the congener's abundance and concentrations, Zandvliet WWTP and the associated river system accounted for the highest concentrations of congeners especially for phthalate esters with respect to other WWTPs investigated. The trend of DEHP at the control site is a source of worry as the concentration was actually higher than values reported in the river systems for most of the sites investigated.

Also, it noteworthy to state that 2,4-DCP was scarcely detected in the WWTPs and the river water over the study period unlike other phenolics congeners. It was only detected once in Bellville WWTP and Kuils river (winter) and twice in Zandvliet WWTP. The profiling pattern for 2,4-DMP showed that they are often detected in the final effluent rather than in the influent wastewater. This may be attributed to the degradation of higher organic congeners present in the WWTP during the treatment processes. This occurrence pattern is common to all the wastewater treatment plants investigated.

4.7 Health risk assessment of endocrine disruptive metals and organic compounds

4.7.1 Results on health risk assessment

There are many associated adverse health effects if people are exposed to these chemical contaminants in excess doses. Where possible the study looked at whether people might be exposed to excessive concentrations through various pathways, such as if water were used for domestic purposes, if the water were used to irrigate vegetables, if fish living in the water were eaten on a regular basis, if the rivers were used for recreational swimming and lastly if meat were consumed from the area making use of the water. The classic example of a population that differs from the norm is subsistence fishers, who may consume as much as 10 times the amount of freshwater fish that most citizens do.

This population is of particular concern when evaluating surface water contamination in areas that are economically depressed or if the immune systems of the people in the area are compromised. The methodology used to asses this potential human health risk was that described by the US-EPA (1988, 1996) and the WHO (2002), making use of the risk assessment programme, Risk Assistant ^{TM} (Thistle Publishers, 1996). Metals included in this study were arsenic, cadmium, lead and mercury. Although the adverse health effects caused by these metals are known, the human dose response data available only allowed for the risk assessment to include arsenic and cadmium. Similarly, DEHP and DBP were the only organic chemicals of those tested that could be included in the quantitative health risk assessment.

The average concentrations detected in all the sample sites over the sampling period of a year was used as a most likely scenario to determine what risks (if any) were involved as a screening risk assessment. If a chemical was found to be responsible for risks considered by the US-EPA and WHO to be unacceptably high, a more detailed assessment for that chemical was investigated, making use of the spread of the data, averages, and identifying which sampling site was responsible for the highest concentrations detected. The following graphs (Figures 4.46 to 4.48) illustrates the average concentrations of the chemicals detected at the sampling sites used in the primary screening for human health risk assessment.

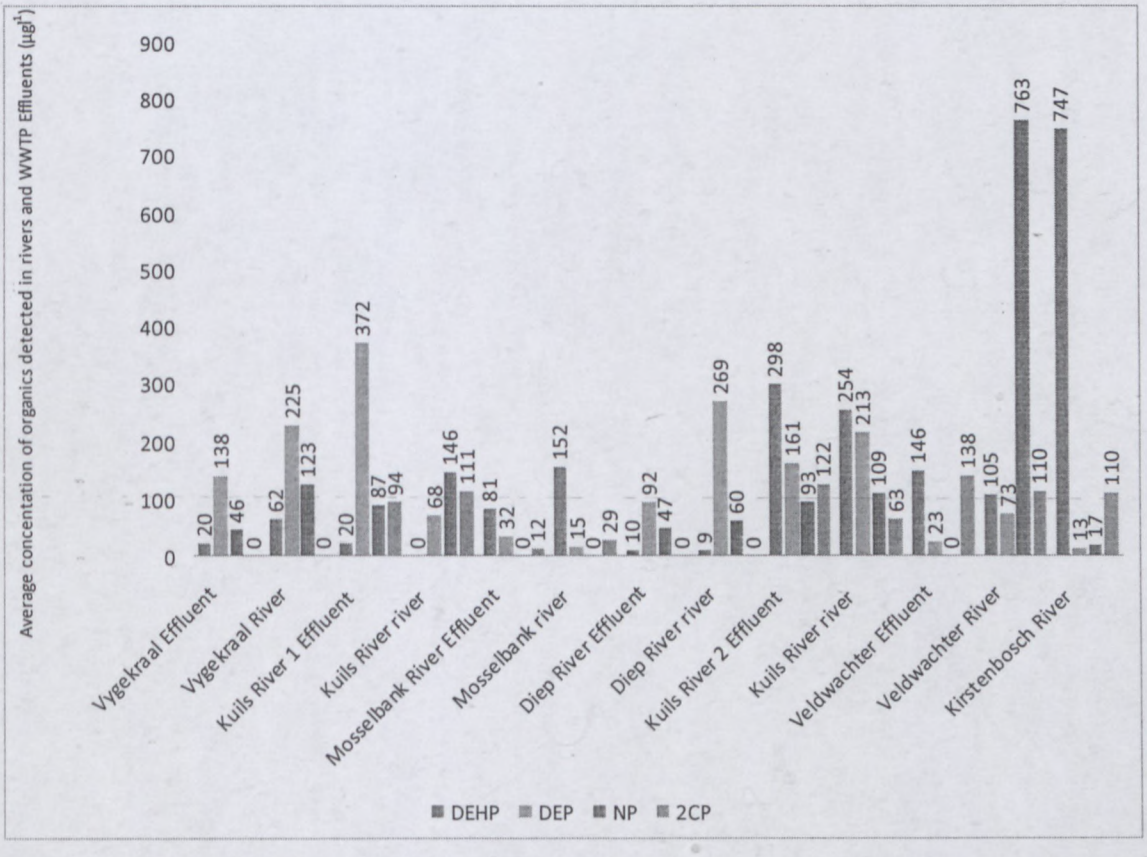


Figure 4.46: Concentrations (µg/l) of phthalate and phenolic congeners detected in river and WWTP effluents at different sites (excluding DBP)

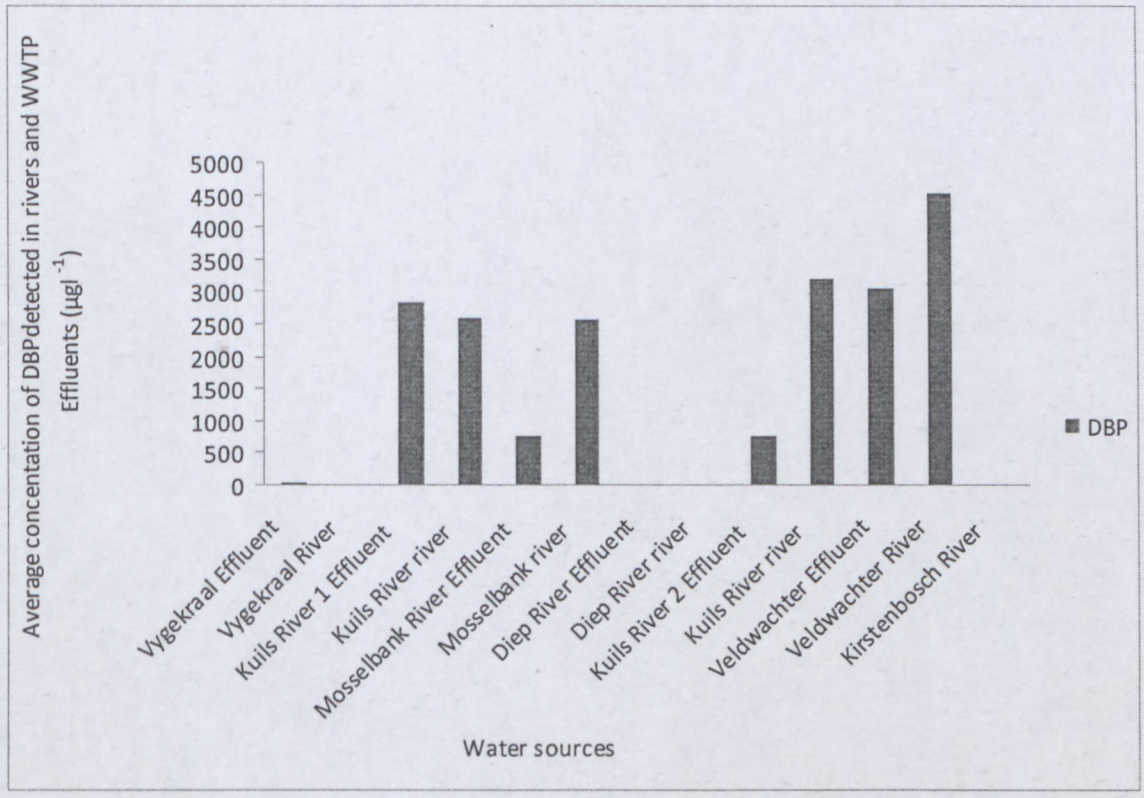


Figure 4.47: DBP concentrations (µg/l) detected in effluent and river water samples at the different sites

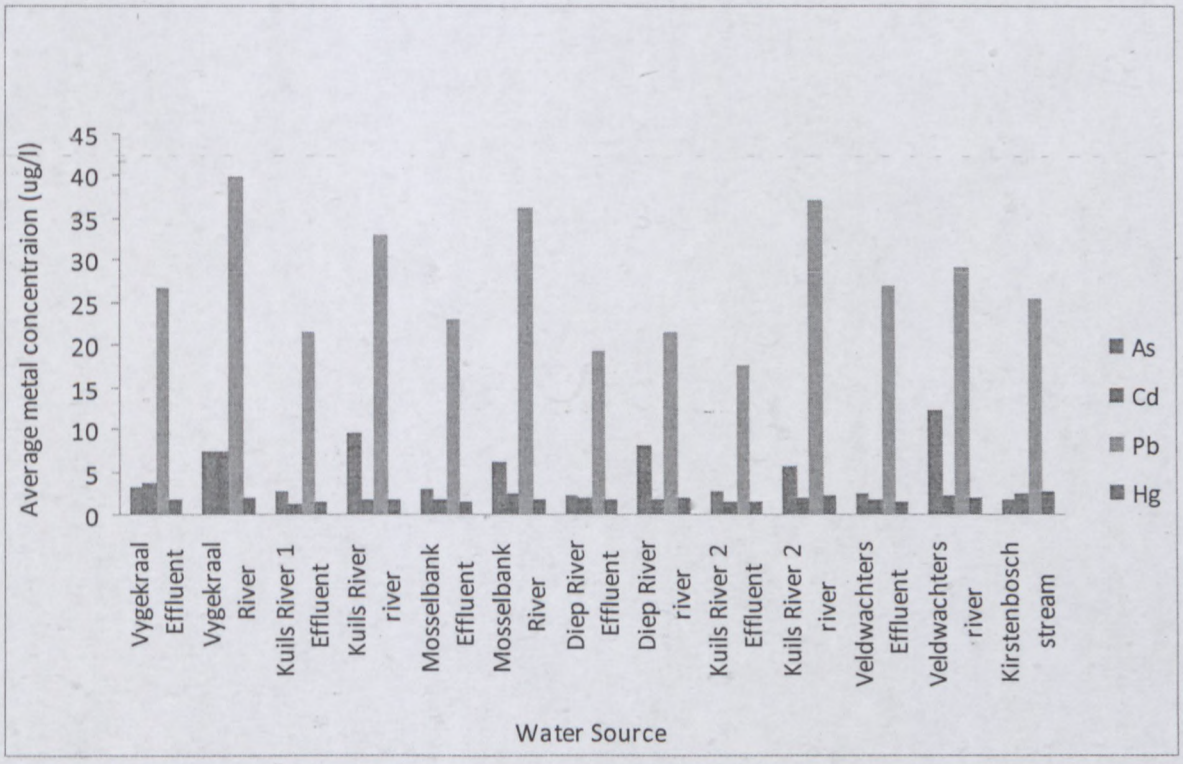


Figure 4.48: Average metal concentrations detected in effluent and river samples at the different sites

DBP was found at highest concentrations in both river water samples and wastewatereffluents, followed by nitro-phenol (NP) and DEP (Figures 4.46 & 4.47). Human dose-response data was available for DEHP and DBP to allow a quantitative health risk assessment to be performed. Lead was detected at the highest concentrations of the metals, but could not be included in the quantitative human health risk assessment due to a lack of dose-response data. Arsenic and cadmium were included in the quantitative health risk assessment (while unavailable data for mercury did not allow it to be included).

4.7.2 Discussion on health risk assessment

The results of the exposure calculations are given in the table below (Tables 4.30 and 4.31) and are presented as both Average Daily Dose (ADD) and Lifetime Average Daily Dose (LADD) in mg/kg/d. The detailed results for each of the possible scenarios are given in appendix II. Exposure Estimates expressed as Average Daily Dose (ADD) and Lifetime Average Daily Dose (LADD).

Table 4.30: Predicted total average daily doses and lifetime average daily doses, based on average concentrations of phthalates

Site	Chemical	ADD mg/kg/d	LADD mg/kg/d
Vygekraal River	DEPH	0.02474	0.0106
	DBP	0	0
Vygeraal Effluent	DEHP	0.007983	0.0003421
	DBP	0.003242	0.001389
Kuils River 1	DEHP	0	0
	DBP	0.3895	0.1708
Kuils River (1) Effluent	DEHP	0.007982	0.003421
	DBP	0.4377	0.1876
Mosselbank River	DEHP	0.06066	0.0206
	DBP	0.3943	0.169
Mosselbank Effluent	DEHP	0.03233	0.01385
	DBP	0.115	0.04927
Diep River	DEHP	0.003592	0.001539
	DBP	0	0
Diep River Effluent	DEHP	0.003991	0.00171
	DBP	0	0
Kuils River (2)	DEHP	0.1014	0.0435
	DBP	0.4941	0.2118
Kuils River (2) Effluent	DEHP	0.1189	0.05097
	DBP	0.1147	0.04914
Veldwachter River	DEHP	0.04191	0.1796
	DBP	0.6986	0.02497
Veldwachter Effluent	DEHP	0.05827	0.02497
	DBP	0.471	0.2019
Kirstenbosch Stream	DEHP	0.1278	0.1278
	DBP	0	0

Vygekraal Effluent = Athlone WWTP effluent; Kuils River (1) Effluent = Bellville WWTP Effluent; Mosselbank Effluent = Kraaifontein WWTP Effluent; Kuils River (2) Effluent = Zandvliet WWTP Effluent Veldwachter Effluent = Stellenbosch WWTP Effluent; Kirstenbosch Stream = Control Site.

Table 4.31: Predicted Average Daily Dose of metals as a result of exposure through drinking water and fish

Site	Chemical	ADD mg/kg/d	LADD mg/kg/d
Vygekraal River	Arsenic	0.000235	1.4
	Cadmium	0.000431	1.3
Vygeraal Effluent	Arsenic	0.000101	0.6
	Cadmium	0.000216	0.6
Kuils River 1	Arsenic	0.000306	1.9
	Cadmium	0.000102	0.3
Kuils River (1) Effluent	Arsenic	0.000091	0.6
	Cadmium	0.000078	0.2
Mosselbank River	Arsenic	0.000199	1.2
	Cadmium	0.000210	0.6
Mosselbank Effluent	Arsenic	0.000098	0.6
	Cadmium	0.000096	0.3
Diep River	Arsenic	0.000264	1.6
	Cadmium	0.000102	0.3
Diep River Effluent	Arsenic	0.000075	0.5
	Cadmium	0.000120	0.4
Kuils River (2)	Arsenic	0.000186	1.1
	Cadmium	0.000108	0.3
Kuils River (2) Effluent	Arsenic	0.000085	0.5
	Cadmium	0.000084	0.3
Veldwachter River	Arsenic	0.000398	2.4
	Cadmium	0.000126	0.4
Veldwachter Effluent	Arsenic	0.000075	0.5
	Cadmium	0.000102	0.3
Kirstenbosch Stream	Arsenic	0.000052	0.3
	Cadmium	0.000150	0.4

Vygekraal Effluent = Athlone WWTP effluent; Kuils River (1) Effluent = Bellville WWTP Effluent; Mosselbank Effluent = Kraaifontein WWTP Effluent; Kuils River (2) Effluent = Zandvliet WWTP Effluent Veldwachter Effluent = Stellenbosch WWTP Effluent; Kirstenbosch Stream = Control Site.

Based on the exposure assumptions described in the section above risks of developing cancer and toxic effects were calculated for the various phthalate chemicals where sufficient data was available. Most of the chemicals were found at concentrations to be at below those where "unacceptable" risks, as defined by both the WHO and US-EPA, are anticipated. However, risks of developing cancer may be as high as 2 in one thousand resulting from exposure to DEHP (Figure 4.49) resulting predominantly from exposure through vegetables that have been irrigated with the contaminated water, and to a lesser extent, through the consumption of fish from the contaminated water. The details of this are presented in the appendix II.

DEHP was detected at high concentrations at Kirstenbosch, Kuilsriver, Mosselbank river and Vygekraal river. In general, river waters contained higher concentrations than treated effluents of the waste water treatment works (Figure 4.49). This risk would result if the water were used to irrigate vegetables or if fish from the water were consumed on a regular basis (appendix 2).

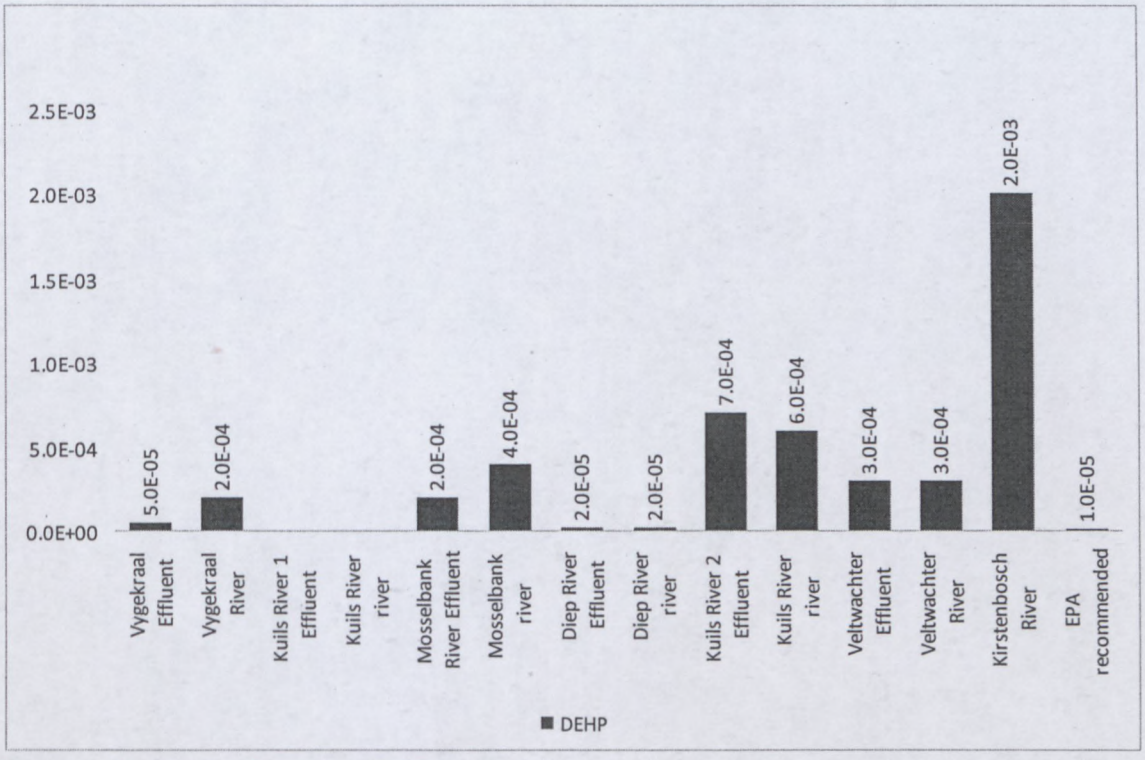


Figure 4.49: Cancer risks from DEHP exposure

Toxic risks could be anticipated resulting from exposure to both DEHP and DBP with individual exposure concentrations predicted at up to 14 times that considered to be safe for a lifetime exposure (Figure 4.50 & 4.51). However, the certainty of the reference dose, or the dose considered to be safe, has a safety factor of 100 built into it for both DEHP and DBP (ATSDR, 2002; ATSDR, 2001). The safety factors built into the reference doses for DEHP and DBP are to allow for extrapolation from animals to humans (a factor of 10) and to allow for variability within humans (another factor of 10) (ATSDR 2001 & 2002). The predicted risks indicate that a possible risk exists and does not indicate a definite risk as the exposures are modelled and not based on actual measurements.

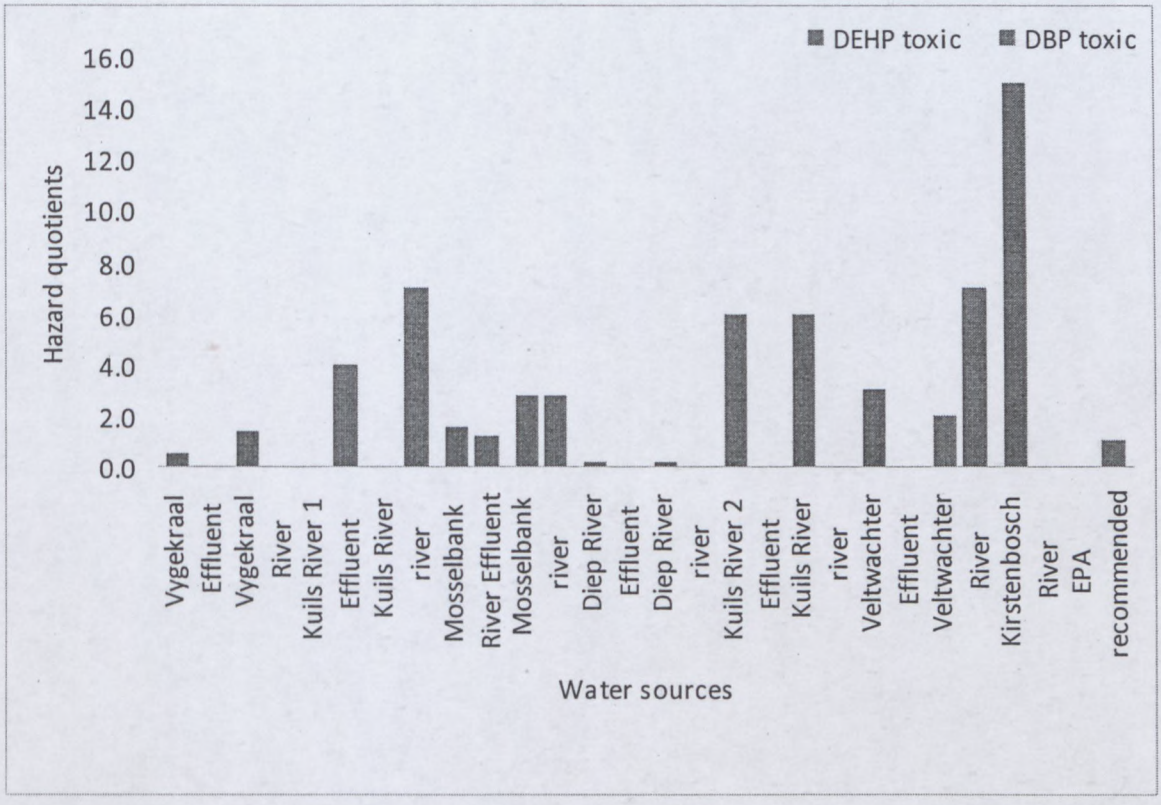


Figure 4.50: Hazard quotients for individual phthalates

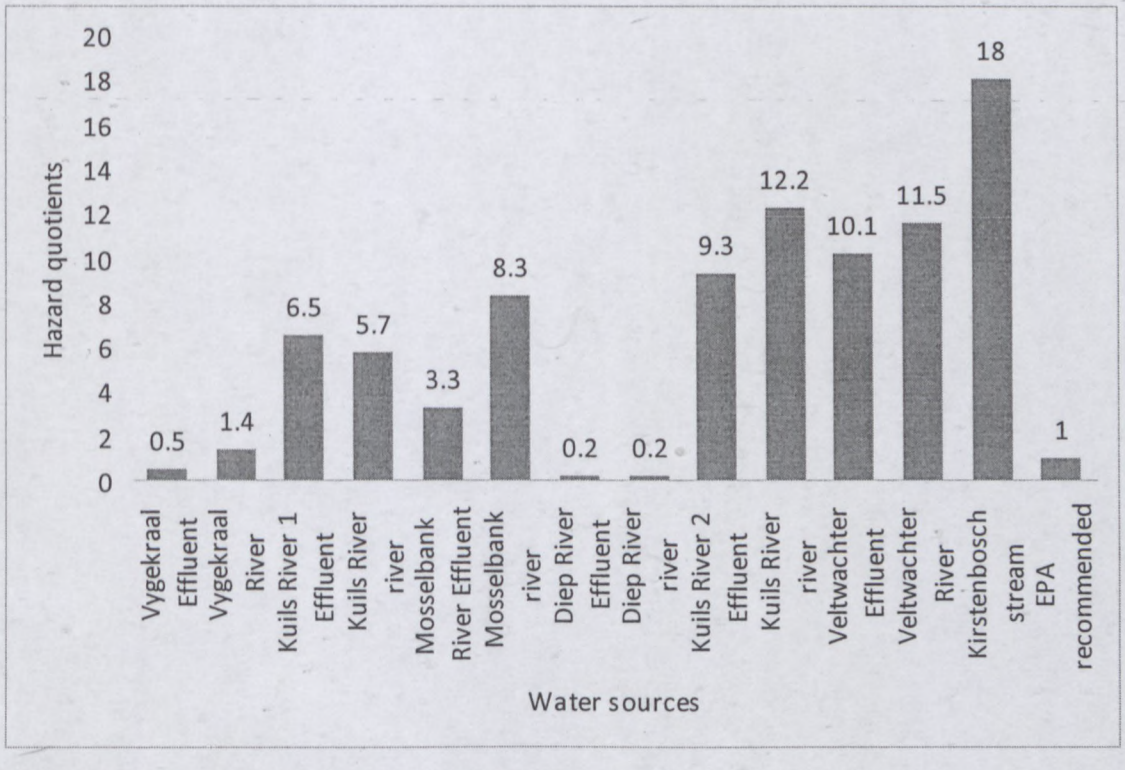


Figure 4.51: Hazard quotients for total phthalates

The doses calculated for possible exposure to arsenic and cadmium showed that it may be twice that considered safe for arsenic, whereas cadmium was measured at concentrations considered to be safe. The reference dose for arsenic is much more certain than that for the phthalates, with the low uncertainty factor of 3 used (Figures 4.53 &4.54).

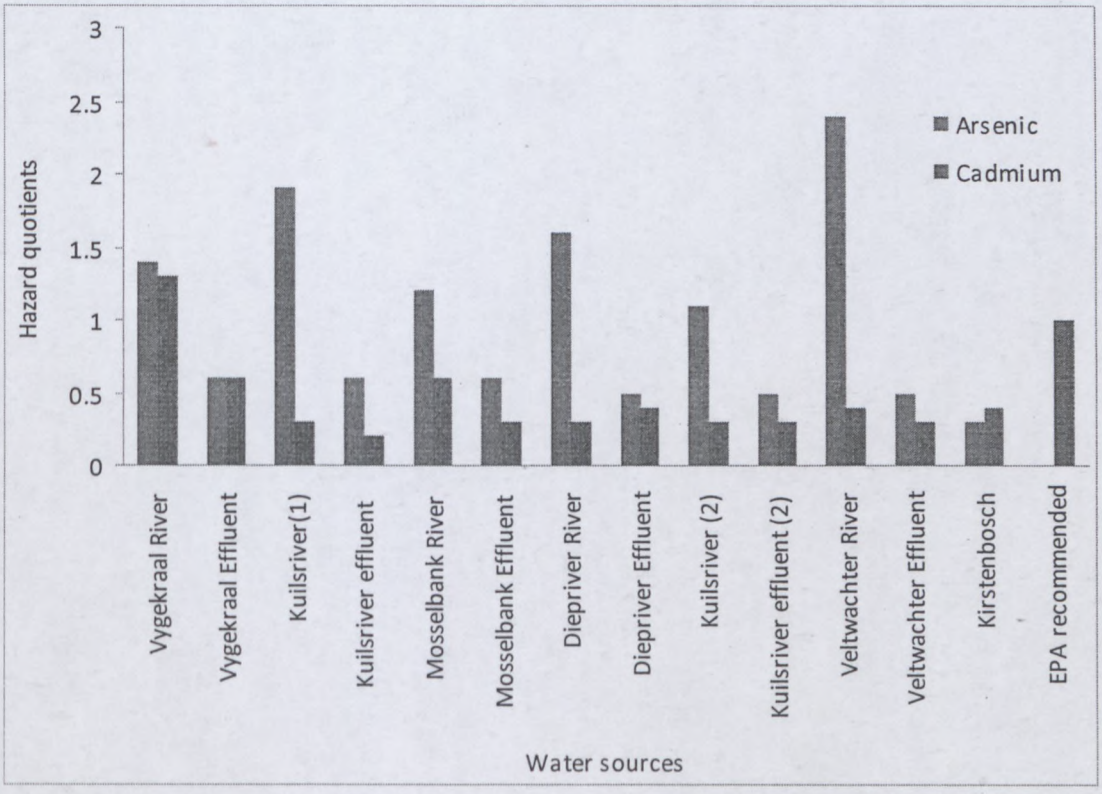


Figure 4.52: Individual metal hazard quotients

The driver of the human health risk was identified through this exercise. The chemicals responsible for the risks include DEHP and to a lesser extent, DBP (Figures 4.48 & 4.49). DEHP was found to be the major contributor of risk of developing cancer in this screening health risk assessment. The highest potential risks were observed at Kirstenbosch resulting from DEHP detected in the river water. The potential risk through the use of this water is if it were used to irrigate vegetables.

This section examined whether possible human health effects might be anticipated based on chemical contaminants detected in wastewater effluents and in rivers throughout the Western Cape, South Africa. In order to determine whether this is possible, a human health risk assessment modelling was conducted using the chemical contaminant concentrations expected in vegetables, fruit, fish and meat based on levels detected in water. Trans-media calculations (water to fish; water to fruit and vegetables and water to meat) were conducted based on individual chemical parameters described in the earlier sections.

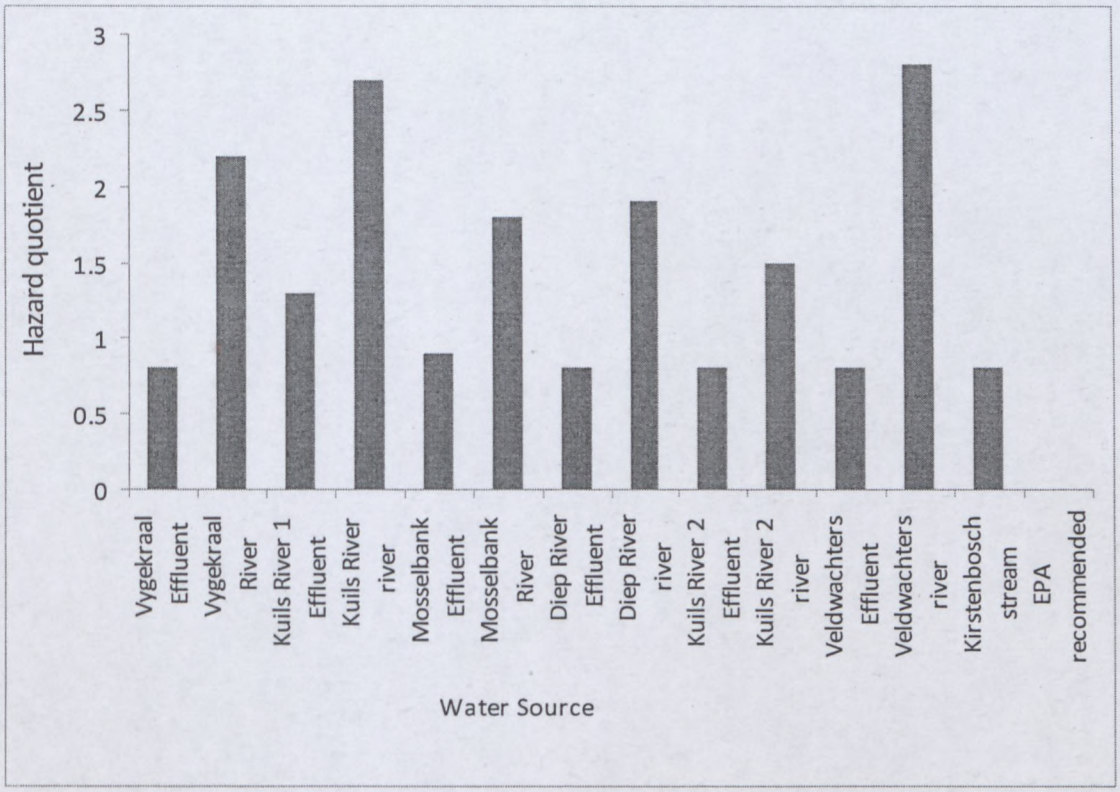


Figure 4.53: Total risks resulting through exposure to metals (Arsenic and Cadmium)

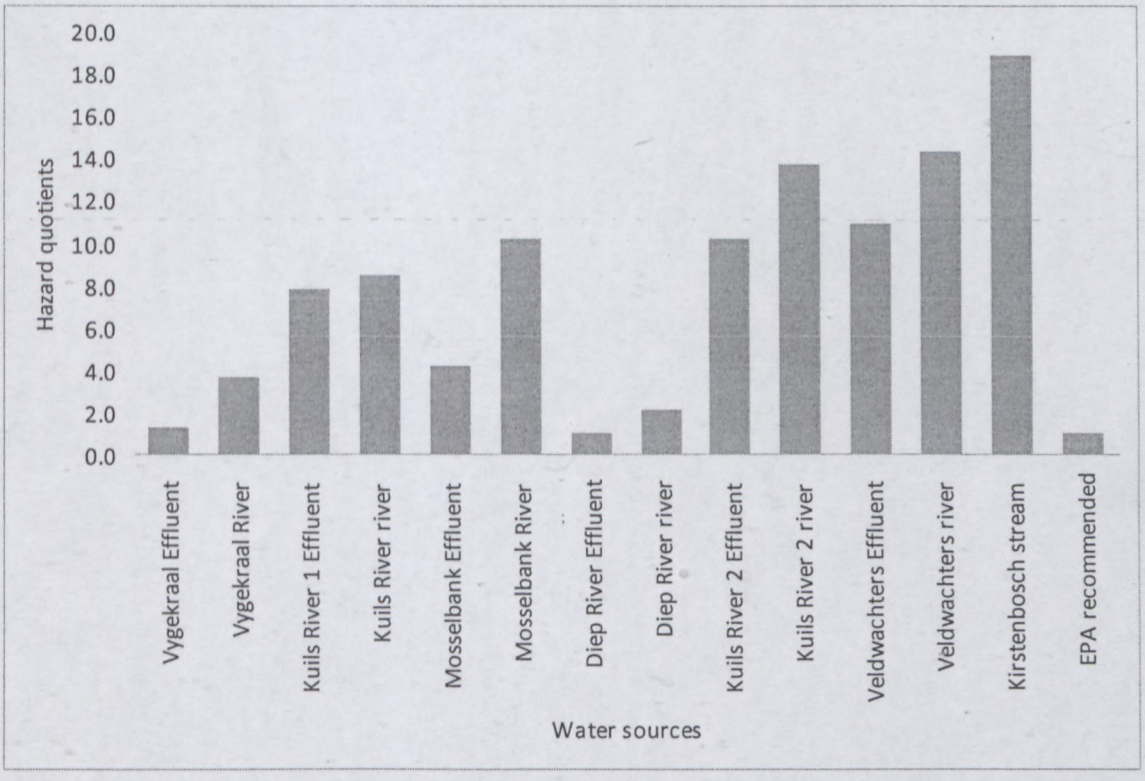


Figure 4.54: Total toxic risks including metals and phthalates

The screening risk assessment identified the chemicals that could be responsible for adverse health effects if drinking the untreated water or eating fish , fruit, vegetables or meat , over a 30 year period were to occur. Although not present at the highest concentrations, the chemicals that were of principal concern were identified as DEHP and to a lesser degree, DBP and arsenic. The type of adverse effect that might result was also identified as predominantly carcinogenic, with possible reproductive system toxic effects being anticipated, as the predicted doses were well below those considered safe by the WHO and US EPA.

This screening risk assessment has highlighted that possible health risks can be anticipated resulting from ingestion of vegetables irrigated with the water and ingestion of fish from the rivers on a regular basis. There are many uncertainties in any health risk assessment, and this study presents a screening or rapid human health risk assessment. Seasonal and spatial variations were considered in this health risk assessment as the average concentrations tested over the 4 seasons were used in the average daily dose calculations. In addition to sample variation, dose calculations also represent uncertainty, based on the assumption of the number of times a year that people eat certain foods and the amount of that food eaten.

Future investigations need to focus on verifying the uptake of phthalates into vegetables and fish via water as this has highlighted that although levels were considered to be safe in the water, bio-accumulation is possible into both fish and vegetables to levels considered to be unacceptable by the US EPA and WHO.

5.1 CONCLUSION

The physicochemical parameter assessed in this study, conductivity and total dissolved solids exceeded the acceptable limits according DWAF (1996d) water quality standard except for effluents from the wastewater treatment plants. This is a clear indication that the WWTPs though might act as a possible source of physicochemical parameters pollution, the river water physicochemical parameters indicated that wastewater effluents from the investigated WWTPs are not responsible for the contamination observed. The possible source of pollution might be from non-point source like stormwater runoff and indiscriminate discharge of industries.

The general abundance and distribution pattern for the metals is Zn > Pb > Cd > As > Hg for all the treatment plants. From this study, it was established that the influent concentration of the heavy metals and arsenic in wastewater into the WWTP is proportional to the activities around each of the WWTP. Though exceptional cases were recorded, the prominent trend for all the metals and arsenic revealed that Kraaifontein WWTP received the lowest concentration of metals investigated. This was attributed to being a majorly domestic treatment plant. Significant difference due to the influent concentrations and the treatment plants processes was noticeable over the study period.

The levels of metals and metalloid reported in this study were within the reported values in European Countries (Table 4.10) except for Zn at Bellville WWTP in the summer of 2010. As nocetiable from Figure 4.11, Potsdam WWTP is the most eefective out of the six WWTPs investigated, while other WWTPs are frequently overloaded resulting in frequent mechanical faults and impacts on their removal efficiency. All the metals and metalloid were within the South Africa water quality guidelines, however, cadmium concentration exceeded the 0.17 μgl^{-1} and 0.02 μgl^{-1} for human and livestock application according to CCME (1999).

As excepted and widely reported in the literatures, sewage sludge and sediments acted as a sink for heavy metals. The range of heavy metals reported in the sewage sludge is directly proportional to the concentration determined in the influent wastewater into the WWTP. The level of heavy metals except for arsenic and lead in the sewage sludge was within the South Africa, United States of America and European guidelines. The concentration of arsenic and lead reported in the sewage sludge could pose serious health risk if used as agricultural fertilizer.

In the river water, arsenic and cadmium were within the normal level for human consumption but exceeded the limits for the aquatic life prorection. Also, lead and mercury exceeded both limits for human consumption and sustainable aquatic lifes. In the sediment samples, for most of the sites investigated, arsenic, mercury and zinc exceeded the interim water

quality guideline of CCME (1999), while cadmium and lead fell within the intervention values. The sediment acted generally as a sink for the waterbodies.

The trend in the levels of metals and arsenic in the river systems showed that the upstreams and downstreams are more polluted compared to the WWTP discharge points. This is an indication that the WWTPs might not completely be the pollution source of the river systems in the City of Cape Town. The reported trend may be attributed to waste dumping on the river course, indiscriminate wastewater discharge from industries, stormwater, run off from agricultural lands and grey and domestic wastewater.

The general trend of the organic compounds, most especially the PEs congeners showed that DBP was the dominant congeners in the water samples analyzed. This trend is similar to reported trend by Fatoki et al. (2010), Adeniyi et al. (2011) and Zgheib et al. (2011). The paradigm shift in the commonly reported distribution pattern from DEHP to DBP may be attributed to increasing wide usage of DBP ingredients in a non-plasticizer (Swan, 2008).

For the organic congeners investigated, there are no limits in South Africa to compare our results with the levels of individuals or all the total congeners. However, the reported concentrations were higher than 3 μgl^{-1} limit set by USEPA (1980) for PEs for the protection of aquatic life and fish. Also, DEHP and DBP exceeded the Canadian interim standing water quality guidelines of 1 μgl^{-1} and 19 μgl^{-1}, respectively for freshwater aquatic life protection. The reported concentration for the phenolic congeners like the PEs exceeded the 0.5 μgl^{-1} and 0.1 μgl^{-1} for the total and individual phenols acceptable limits set by USEPA. Also, the concentrations exceeded the 5 acceptable limits for bathing water. Though not frequent like the PEs, they are very persistent environmental pollutant and could trigger various health effects in lower aquatic lifes.

Human health risk assessment showed clearly that arsenic (metalloid), cadmium (metal) and DBP and DEHP of the organic congeners could results in health related problems. Considering the uncertainty in risks assessment, DEHP showed that using the water from the river most importantly water from Kirstenbosch Botanical Garden could lead to cancer, while non-cancer effect can also be anticipated. However, for metals, a cancer effect was not anticipated, but, non-cancer effects may result from vegetable watering and human consumption of fish.

5.2 RECOMMENDATION FOR FUTURE RESEARCH

This project has served as an introduction to the assessment of the endocrine disrupting compounds research in the wastewater treatment plants in Western Cape, and will hopefully provide a platform from which future research can be conducted. The most logical progression from this project would be to conduct a study on the modeling of the fate of the suspected endocrine disrupting compounds in the wastewater treatment plants and to assess the extent of bioaccumulation of metals in biota, particularly filter feeding and burrowing organisms

downstream of the wastewater treatment plants. This is a necessary step that must be followed as attempt to assess levels of bioaccumulation of heavy metals in freshwater snails and earthworms proved futile due to assumed poor water quality to sustain freshwater aqutic lifes.

Ecotoxicology and use of bioindicators and biomarkers has emerged as a powerful means of assessing the effects of contaminants on living organisms and ecosystem health, and a combination of chemical and biological monitoring allows scientists to better assess environmental risk. It is advised that future research focuses on identifying the most suitable bioindicators within Western Cape freshwater systems that can be used alongside chemical monitoring to assess ecosystem health.

Wastewater treatment plants using constructed wetlands systems for further treatment of effluent prior to discharge into the river systems would be interesting systems on which to conduct such studies. Some of the wastewater treatment plants appriopriate for the study may include but not limited to Cape Flat WWTP, Borchery quarry WWTP, Kraaifontein WWTP among others. Most countries have well established chemical monitoring programmes for heavy metals and organic compounds classified as endocrine disrupting chemicals, and it is imperative that such long term monitoring programs are initiated on the South African by the Department of Environmental Affairs to strengthen the water quality of the Republic. Chemical monitoring alone cannot, however, be used to assess the environmental risks imposed by chemical contamination.

Finally, it is recommended that an integrated approach must be developed in the Republic for water quality monitoring to have an interim water quality guidelines for river sediment. The government of South Africa must also strive to set up lmits for the PEs, the phenolic congeners investigated in this study and other organic chemicals that have been enlisted as endocrine disrupting chemicals. Also, the government should further monitor and fund research into the efficiency of the WWTPs at removing these compounds and set targets for the WWTPs to ensure protection of the freshwater systems receing effluents from the WWTPs.

REFERENCES

Abboo, S. and Pletschke, B.I. 2010. Effect of phenolic compounds on the rapid direct enzymatic detection of β-D-galactosidase and β-D-glucuronidase. *Water SA* 36 (1): 133-138.

Adeniyi, A.A., Okedeyi, O. O. and Yusuf, K.A. 2011. Flame ionization gas chromatographic determination of phthalate esters in water, surface sediment and fish species in the Ogun river catchments, Ketu, Lagos, Nigeria. *Environ. Monit. Assess.* 172:561-569.

Adeniyi, A., Dayomi, M., Siebe, P. and Okedeyi, O. 2008. An assessment of the levels of phthalate esters and metals in the Muledane open dump, Thohoyandon, Limpopo province, South Africa. *Chemistry Central Journal* doi:10.1186/1752.153X-2-9.

Ahel, M., Schaffner, C. and Giger, W. 1996. Behaviour of alkylphenol polyethoxylate surfactants in the aquatic environment—III. Occurrence and elimination of their persistent metabolites during infiltration of river water to groundwater, *Water Research.* 30:37–46.

Ahel, M., Giger, W. and Koch, W. 1994. Behaviour of alkylphenol polyethoxylate surfactants in the aquatic environment--I. Occurrence and transformation in sewage treatment. *Water Research* 28, pp. 1131-1142.

Akan, J.C., Abdulrahman, F.I., Sodipo, O.A., Ochanya, A.E. and Askira, Y.K. 2010. Heavy metals in sediments from River Ngada, Maiduguri Metropolis, Borno State, Nigeria. *Journal of Environmental Chemistry and Ecotoxicology.* 2(9): 131-140.

Akan, J.C., Abdulrahaman, F.I., Dimari, G.A. and Ogugbuaja, V.O. 2008. Physicochemical determination of pollutants in wastewater and vegetables samples along the Jakara wastewater channel in kano metropolis Kano State, Nigeria. *European Journal of Scientific Research.* 23 (1): 122-133.

Alatriste-Mondragon, F., Iranpourb, R. and Ahringa, B.K. 2003. Toxicity of di-(2-ethylhexyl) phthalate on the anaerobic digestion of wastewater sludge. *Water Research.* 37: 1260–1269.

Alonso, M.C., Puig, D., Silgonerb, I., Grasserbauerb, M. and Barcelo, D.1998. Determination of priority phenolic compounds in soil samples by various extraction methods followed by liquid chromatography–atmospheric pressure chemical ionisation mass spectrometry. *Journal of Chromatography A*, 823: 231–239.

Andrade, L.S., Laurindo, E.A., de Oliviera, R.V., Rocha-Filho, R.C., Cass, Q.B. 2006. Development of a HPLC method to follow the degradation of phenol by electrochemical treatment. *Journal of Brazil Chemical Society* 17(2): 369-373.

Aneck-Hahn, N.H., Bornman, M.S. and de Jager, C. 2009. Oestrogenic activity in drinking waters from rural area in the waterberg district, Limpopo province, South Africa. *Water SA.* 35 (3): 245 – 252.

Angelino, S. and Gennaro, M.C.1997. An ion-interaction RP-HPLC method for the determination of eleven priority pollutant phenols. *Analytica Chimica Acta* 346: 61-71.

Arain, M.B, Kazi, T.G., Baig, J.A., Jamali, M.K. Afridi, H.I., Shah, A.Q. Jalbani, N., and Sarfraz, R.A. Determination of arsenic levels in lake water, sediment, and foodstuff from selected area of Sindh, Pakistan: Estimation of daily dietary intake. *Food and Chemical Toxicology* 47:242-248.

Arbab-zavar, M.H., Rounaghi, G.H., Chamsaz, M. and Masrournia, M. 2003. Determination of Mercury(II) Ion by Electrochemical Cold Vapor Generation Atomic Absorption Spectrometry. *Analytical Science* 19: 743-746.

Arditsoglou, A. and Voutsa, D. 2008. Determination of phenolic and steroid endocrine disrupting compound in environmental matrices. *Envinronmental Science Pollution Research* 15(3): 228-236.

Ashokkumar, S., Mayavu, P., Sampathkumar, P., Manivasagam, P. and Rajaram, G. 2009. Seasonal distribution of heavy metals in the Mullipallam creek of Muthupettai mangroves (Southeast coast of India). *American-Eurasian Journal of Scientific Research* 4(4): 308-312.

Awofolu, O.R., Mbolekwa, Z., Mtshemla, V. and Fatoki, O.S. 2005. Levels of trace metals in water and sediment from Tyume river and its effects on an irrigated farmland. *Water SA* 31(1):87-94.

Ayas, Z. and Kolankaya, D. (1996). Accumulation of some heavy metals in various environments and organisms at Goksu Delta, Turkey. *Bulletin of Environmental Contamination and Toxicology*. 56: 65-72.

ATSDR, (1995). Agency for Toxic Disease Registry. Toxicological profile for Diethyl phthalate. . Public Health Service Agency for Toxic Substances and Disease Registry.

ATSDR (2001) Toxicological profile Di-n-butyl phthalate. Public Health Service Agency for Toxic Substances and Disease Registry.

ATSDR (2002). Toxicological profile for D2-(2 ethylhexyl) phthalate. . Public Health Service Agency for Toxic Substances and Disease Registry

Ayeni, O. O., Ndakidemi, P. A., Snyman, R. G. and Odendaal, J. P. 2010. Metal contamination of soils collected from four different sites along the lower Diep River, Cape Town, South Africa. *International Journal of the Physical Sciences* 5(13): 2045-2051.

Bagheri, H., Saber, A. and Mousavi, S.R. 2004. Immersed solvent microextraction of phenol and chlorophenols from water samples followed by gas chromatography-mass spectrometry. *Journal of Chromatography* 1046: 27-33.

Bai, J., Cui, B., Chen, B., Zhang, K., Deng, W., Gao, H. and Xiao, R. 2011. Spatial distribution and ecological risk assessment of heavy metals in surface sediments from a typical plateau lake wetland, China. *Ecological Modeling* 222:301-306.

Baldwin, D.A. and Debowski, J.K. 1988. Determination of phenols by HPLC to PPT levels. *Chromatographia* 26:186-190.

Baltussen, E., David, F., Sandra, P., Janssen, H. and Cramers, C. 1999. Automotive sorptive extraction thermal desorption-gas chromatography mass spectrometry analysis: Determination of phenols in water samples. *Journal Microcolumn Separations* 11(6): 471-474.

Barcelo, D. and Kettrup, A. 2004. Endocrine disruptors. *Anal Bioanal Chem.* 378: 547-548.

Barnabé, S., Beauchesne, I., Cooper, D.G. and Nicell, J.A. 2008. Plasticizers and their degradation products in the process streams of a large urban physicochemical sewage treatment plant. *Water Research* 42: 153–162.

Barnhoorn, I.E.J., Bornman, M.S., Pieterse, G.M. and van Vuren, J.H.J. 203. Histological evidence of intersex in feral sharptooth catfish (*Clarias gariepinus)* from an estrogen-polluted water source in Gauteng, South Africa. *Water SA* DOI 10.1002/tox.20068

Barrico, M.L., Nabais, C., Martins, M.J. and Freitas, H. 2006. Sources of phenolic compounds in two catchments of southern Portugal – Effect of season,land use and soil type. *Chemosphere* 65:482–488.

Baskan, M.B. and Pala, A. 2009. Determination of arsenic removal efficiency by ferric ions using response surface methodology. *Journal of Hazardous Materials* 166:796-801.

Bauer, M., Fulda, B. and Blodau, C. 2008. Groundwater derived arsenic in high carbonate wetland soils: Sources, sinks and mobility. *Science of the Total Environment* 401:109-120.

Bennion, H., Hilton, J., Hughes, M., Clark, J., Hornby, D., Fozzard, I., Phillips, G. and Reynolds C. 2005The use of a GIS-based inventory to provide a national assessment of standing waters at risk from eutrophication in Great Britain. *Science of the Total Environment* 344: 259-273.

Bestamin, O. 2005. Chlorophenols in leachates originating from different landfills and aerobic composting plants. *Journal of Hazardous Materials* 124: 107-112.

Bhattacharya, P., Welch, A.H. Stollenwerk., K.G., McLaughlin, M.J., Bundschuh, J. and Panaullah, G. 2007. Arsenic in the environment: Biology and Chemistry. *Science of the Total Environment* 379:109-120

Bi, X., Feng, X., Yang, Y., Li, X., Shin, G.P.Y., Li, G., Liu, T. and Fu, Z. 2009. Allocation and source attribution of lead and cadmium in maize (Zea mays L.) impacted by smelting emissions. *Environmental Pollution* 157:834-839.

Borba, R.P., Figueiredo, B.R., Rawlins, B.G. and Matschullat, J. 2000. Arsenic in water and sediment in the Iron Quadrangle, Minas Gerais state, Brasil. *Revista Brasileira de Geociências*, 20, 554-557.

Bornman, R., Van Vuren, J., Bouwman, H., De Jager, T., Genthe, B. and Barnhoorn, I. 2007. Endocrine disruptive activity and the potential health risk in the Rietvlei Nature Reserve. Report to the Water Research Committee on the project "Endocrine disruptive activity and the potential health risk in the Rietvlei Nature Reserve (RNR)."

Botes, P.J. and van Staden, J.F. 2005. Investigation of trace element mobility in river sediments using ICP-OES. *Water SA* 31 (2) 183-191.

Bouraie, M.M., El Barbary, A.A., Yehia, M.M. and Motawea, E.A. 2010. Heavy metal concentrations in surface river water and bed sediments at Nile Delta in Egypt. *Finnish Peatland Society* 61(1): 1–12.

Bradlow, H.L., Davis, D.L., Lin, G., Sepkovic, D., Tiwari, R. 1995. Effects of pesticides on the ratio of 16alpha/2-hydroxyestrone: A biological marker of breast cancer risk. *Environmental Health Perspective* 103:143-150.

Brasher, A.M.D., and Wolff, R. H. 2004. Relations between land use and Organochlorine Pesticides, PCBs, and Semi-Volatile Organic Compounds in streambed sediment and fish on the Island of Oahu, Hawaii. *Archieve of Environmental Contamination Toxicology* 46: 385–398.

Brzoska, M.M. and Moniuszko-Jakoniuk, J. 2001. Interactions between cadmium and zinc in the organism. *Food and Chemical Toxicology* 39:967-980.

Bukvic, V., Dusak, V., Kucinic, M., Delic, A., Dulcic, J., Senta, I. and Glamuzina, B. 2010. Arsenic in the water, sediment and fish in the Neretva River Delta, Croatia. *Journal of Applied Ichthyol.* 1–4 doi: 10.1111/j.1439-0426.2010.01604.x

Burger, A.E.B. and Moolman, A.P.M. 2006. First phase of an endocrine reseach programme for South Africa water system. *Water Practice and Technology* 1(2): 1-8.

Burger, A.E.C. and Nel, A. 2008. Report to the water research commission on the project: Scoping study to determine the potential impact of agricultural chemical substances (pesticides) with endocrine disruptor properties on water resources of South Africa. WRC Report no 1774/1/08 ISBN 978-1-77005-714-2.

Busetti, F., Badoer, S., Cuomo, M., Rubino, B. and Traverso, P. 2005. Occurrence and removal of potentially toxic metals and heavy metals in the wastewater treatment plant of Fusina (Venice, Italy). *Ind. Eng. Chem. Res.* 44: 9264 – 9272.

Cabrera, C., Ortega, E., Gallego, C., Lopez, M.C., Lorenzo, M.L. and Assensio, C. 1994. Cadmium concentration in farmlands in southern Spain: possible sources of contamination. *Science of the Total Environment* 153:261-265.

Cai, Y., Jiang, G. and Liu, J. 2003. Solid-phase extraction of several phthalate esters from environmental water samples on column packed with polytetrafluoroethylene turning. *Analytical Sciences* 19: 1491-1494.

Campbell, C.G., Borglin, S.E., Green, F.B., Grayson, A., Wozei, E. and Stringfellow, W.T. 2006. Biologically directed environmental monitoring, fate, and transport of estrogenic endocrine disrupting compounds in water: A review. *Chemosphere* 65:1265–1280.

Campo, P., Sorial, G.A., Suidan, M.T., Venosa, A.D. 2006. Statistical evaluation of an analytical GC/MS method for the determination of long chain fatty acids. *Talanta*.68: 888-894.

Canadian Council of Ministers of the Environment. 1999. Canadian water quality guidelines for the protection of aquatic life: Cadmium. In: Canadian environmental quality guidelines, 1999, Canadian Council of Ministers of the Environment, Winnipeg.

Canadian Council of Ministers of the Environment. 1999. Canadian sediment quality guidelines for the protection of aquatic life: Lead. In: Canadian environmental quality guidelines, 1999, Canadian Council of Ministers of the Environment, Winnipeg.

Canadian Council of Ministers of the Environment. 2001. Canadian water quality guidelines for the protection of aquatic life: Arsenic. Updated. In: Canadian environmental quality guidelines, 1999, Canadian Council of Ministers of the Environment, Winnipeg.

Capdevila, F., Nadal, M., Schuhmacher, M. and Domingo, J.L. 2003. Intake of lead and cadmium from edible vegetables cultivated in Tarragona Province, Spain. *Trace Elements and Electrolytes* 20: 256-261.

Castillo, M., Puig, D. and Barcelo, D. 1997. Determination of priority phenolic compounds in water and industrial effluents by polymeric liquid-solid extraction cartridges using automated sample preparation with extraction columns and liquid chromatography. Use of liquid-solid extraction cartridges for stabilization of phenols. *Journal of Chromatography A* 778:301-311.

Cespedes, R., Lacorte, S., Demetrio Raldua, D., Ginebreda, A., Barcelo, D., Pin, B. 2005. Distribution of endocrine disruptors in the Llobregat River basin (Catalonia, NE Spain) *Chemosphere* 61:1710–1719.

Chanpiwat, P., Sthiannopkao, S. And Kim, K-W. 2010. Metal content variation in wastewater and biosludge from Bangkok's central wastewater treatment plants. *Microchemical Journal* 95:326-332.

Chapagain, S. K., Du Laing, G., Verloo, M., Shrestha, S. and Kazama, F. Monitoring of arsenic occurrence in intertidal sediments of River Scheldt (Belgium). Agricultural Engineering International: the CIGR Ejournal. Manuscript LW 07 009. Vol. IX. October, 2007. Chemicals Agency (KemI), Sundbyberg, Sweden.

Chapman, D. 1996. Water quality assessments: A guide to the use of biota, sediments and water in environmental monitoring 2nd Ed. UNESCO, World Health Organization, United Nations Environment Programme, London.

Chawla, S., Ghosh, S., Sihorkar, V., Nellore, R., Shanta, K.T.R., Srinivas, N.R. 2006. High performance liquid chromatography method development and validation for simultaneous determination of five model compounds, antipyrine, metoprolol, ketoprofen, furosemide and phenol red, as a tool for the standardization of rat in situ intestinal permeability studies using timed wavelength detection. *Biomedical Chromatography* 20: 349-357.

Chen, S.L., Dzeng, S.R., Yang, M., Chiu, K., Shieh, G. and Wai. C.M. 1994. Arsenic Species in Groundwaters of the Blackfoot Disease Area, Taiwan." *Environmental Science and Technology* 32: 877-881.

Cheng, M. H., Patterson, E. R., Minear, R. A. 1975. Heavy metals uptake by activated sludge. *Water Pollution Control Federation Journal* 47: 362-376.

Chipasa, K.B. 2003. Accumulation and fate of selected heavy metals in a biological wastewater treatment systems. *Waste Management* 23:135-143.

Choe, S., Kim, S., Kim, H., Lee, J.H., Choi, Y., Lee, H. and Kim, Y. 2003. Evaluation of estrogenicity of major heavy metals. *Science of the Total Environment* 312:15-21

Chojnacka, K., Chojnacki, A., Gorecka, H. and Gorecki, H. 2005. Bioavailability of heavy metals from polluted soils to plants. *Science of the Total Environment* 337: 175-182.

Clara, M., Windhofer, G., Hartl, W., Braun, K., Simon, M., Gans, O., Scheffknecht, C. and Chovanec, A. 2010 Occurrence of phthalates in surface runoff, untreated and treated wastewater and fate during wastewater treatment. *Chemosphere* 78(9), 1078-1084.

Cledera-Catro, M., Santos-Montes, A. and Izquierdo-Hornillos, R. 2005. Comparison of the performance of conventional microparticulates and monolithic reversed-phase columns for lipid chromatography separation of eleven pollutants phenols. *Journal of Chromatography A* 1087: 57-63.

Cledera-Catro, M., Santos-Montes, A. and Izquierdo-Hornillos, R. 2006. Method development and validation for phenol and nitrophenols in tap water by HPLC using a monolithic column. http//www.license.icopyright.net/user 06/10/2008.

Clotfelter, E.D., Bell, A.M. and Levering, K.,R. 2004. The role of animal behaviour in the study of endocrine-disrupting chemicals. *Animal Behaviour* 68: 665 – 676.

Cortazar, E., Bartolome, L., Delgado, A., Etxebarria, N., Fern´andez, L.A., Usobiaga, A. and Zuloaga, O. 2005. Optimisation of microwave-assisted extraction for the determination of nonylphenols and phthalate esters in sediment samples and comparison with pressurised solvent extraction. *Analytica Chimica Acta* 534: 247–254.

Czaplicka, M. 2001, Determination of Phenols and Chlorophenols in Bottom Sediments. *Suppl.* 53: 470-473.

Czaplicka, M. 2004. Sources and transformations of chlorophenols in the natural environment. *Science of the Total Environment* 322: 21–39.

Cuypersa, F., De Dobbelaereb, C., Hardy, A., Van Baelb, M.K. and Helsena, L. 2009. Thermal behaviour of arsenic trioxide adsorbed on activated carbon. *Journal of Hazardous Mater*ials doi:10.1016/j.jhazmat.2008.12.048.

Dai, J., Xu, M., Chen, J., Yang, X. and Ke, Z. 2007. PCDD/F, PAH and heavy metals in the sewage treatment plants in Beijing, China. *Chemosphere* 66: 353-361.

Dai, J., Chen, L., Zhao, J. and Na, M.A. 2006. Characteristics of sewage sludge and distribution of heavy metal in plans with amendment of sewage sludge. *Journal of Environmental Sciences* 18(6): 1094-1100.

Dallas, H.F. and Day, J.A. 2004. The effect of water quality variables on aquatic ecosystems, a review. WRC Report No TT 224/04. Water Reseach Commission, Pretoria.

Dargnat, C., Teil, M., Chevrevil, M. and Blanchard, M. (2009) Phthalate removal throughout wastewater treatment plant case study of Marne Aval station (France). *Science of the Total Environment* 407: 1235-1244.

Das, P., SAmantaray, S. and Rout, G.R. 1997. Studies of cadmium toxicity in plants: a review. *Environmental Pollution* 98(1):29-36.

Dawson, A. 2000. Mechanism of Endocrine disruption with particular reference to occurrence in avian wildlife: A Review. *Ecotoxicology* 9: 395-399.

Deng, J., Feng, X. and Qiu, X. 2009. Extraction of heavy metal from sewage sludge using ultrasound-assisted nitric acid. *Chemical Engineering Journal* 152: 177-182.

De Jager, C., Bornman, M. S., Vorster, H., Burger, A. E. C., Apps, P. J. A. 1998. p-Nonylphenol in food packing material: an absorption study. *International symposium on human reproduction and male subfertility*, 22-25 April, Genk, Belgium.

De Sousa, J. P. B., da Silva Filho, A. A., Bueno, P. C. P., Gregório, L. E., Furtado, N. A. J. C., Jorgea, R. F. and Bastosa, J. K. 2009. A validated reverse-phase HPLC analytical method for the Quantification of Phenolic compounds in *Baccharis dracunculifolia. Phytochemical Analytical* 20:24-32.

Demirak, A., Yilmaz, F., Tuna, A.L. and Ozdemir, N. 2006. Heavy metals in water, sediment and tissues of Leuciscus cephalus from a stream in southwestern Turkey. *Chemosphere* 63: 1451–1458.

Diniz. M.S., Peres, L., Pihan, J.C. 2005. Comparative study of the estrogenic responses of minor carp (*Cyprinus carpio)* exposed to treated municipal sewage effluent (Lisbon) during two periods in different seasons. *Science of the Total Environment.* 349: 129-139.

Dowshen, M. D. 2007. Endocrine disruptor: A review. http://www.hormone.org/endo101 04/02/2009

Duker, A.A., Carranza, E.J.M. and Hale, M. 2005. Arsenic geochemistry and health. *Environmental International* 31:631-641.

Duman, F., Aksoy, A. and Demirezen, D. 2007. Seasonal variability of heavy metals in surface sediment of Lake Sapanca, Turkey. *Environmental Monitoring Assessment* 133:277–283

Dural, M., Goksu, M.Z.L. and ozak, A.A. 2007. Investigation of heavy metals levels in economically important fish species captured from the Tuzla lagoon. *Food chemistry* 102:415-421.

Duty, S.M., Ackerman, R.M., Calafat, A.M. and Hauser, R. 2005. Personal care product use predicts urinary concentrations of some phthalate monoesters. *Environmental Health Perspectives* 113 (11): 1530-1535.

DWAF (1996b) Water quality Guidelines, aquatic ecosystem Use (1st edition.). Vol. 7. Department of Water Affairs and Forestry, Pretoria.

DWAF. 1996b. Water quality guidelines, field guide (1st edition) Vol. 8. Department of Water Affairs and Forestry, Pretoria.

DWAF. 1996d. South African water quality guidelines, Agricultural water use irrigation (2nd edition.). Vol. 7. Department of Water Affairs and Forestry, Pretoria.

DWAF; WRC, (1995). South Africa water quality guideline management series. Procedures to assess effluent discharge impacts. WRC Report No. TT 64/94. Department of Water Affairs and Forestry and Water Research Commission, Pretoria.

Eberlin, M.N. and Cesar de saliva, R. 2008. Faster and simpler determination chlorophenols in water by fiber introduction mass spectrometry. *Analytica Chimica Acta* 620: 97-102

Edwards, J.R. and Prozialeck, W.C. 2009. Cadmium, diabetes and chronic kidney disease. *Toxicology and Applied Pharmacology* 238:289-293.

European Communities. 2001. Pollutants in urban wastewater and sewage sludge. Final Report, ISBN 92-894-1735-8; Office for Official Publications of the European Communities: Luxembourg.

Evanko, C.R. & Dzombak, D.A. 1997. Remediation of Metals-Contaminated Soils and Groundwater. Technology Evaluation Report, Carnegie Mellon University, Pittsburgh, PA.

Falconer, I.R., Chapman, H.F., Moore, M.R. and Ranmuthygela, G. 2006. Endocrine-disrupting compounds: A review of their challenge to sustainable safe water supply and water reuse. *Environmental Toxicology*. DOI 10.1002/tox.

Fatoki, O.S., Bornman, M., Ravandhalala, L., Chimuka, L., Genthe, B. and Adeniyi, A. 2010. Phthalate ester plasticizers in freshwater systems of Venda, South Africa and potential health effects. *Water SA* 36(1): 117-126.

Fatoki, O. S., Lujiza, N. and Ogunfowokan A, O. 2002. Trace metal pollution in the Umtata River. *Water SA* 28 (2): 183-190.

Fatoki, O.S. and Awofolu, R. 2003. Level of Cd, Hg and Zn in some surface waters from Eastern Cape Province, South Africa. *Water SA*. 29(4): 375-380.

Fatoki, O.S. and Mathabatha, S. 2001. An assessment of heavy metal pollution in the East London and Port Elizabeth harbours. *Water SA* 27 (2): 233-240.

Fatoki, O.S., Muyiwa, N.Y.O. and Lujiza. 2001. Situation analysis of water quality in the Umtata River catchment. *Water SA* 27 (4): 467 - 474

Fatoki, O.S. and Noma, A. 2002. Solid phase extraction method for selective determination of phthalate esters in the aquatic environment. *Water, Air and Soil Pollution* 140: 85-98.

Fatoki, O.S. Awofolu, O.R. and Genthe, B. 2004. Cadmium in the Umtata River and the associated health impact on rural communities whose are primary users of water from the river. *Water SA* 30(4):507-513.

Fatoki, O.S. and Vernon, F. 1990. Phthalate esters in rivers of the greater Manchester area, U.K. *Sciernce of the Total Environment* 95: 227-232.

Fattahi, D., Canna-Michaelidou, S., Michael, C., Georgiou, E.D., Christodoulidou, M. Achilleos, A., Vasquez, M. 2007. Organochlorine and organophosphoric insecticides, herbicides and heavy metals residue in industrial wastewaters in Cyprus. *Journal of Hazardous Materials* 145: 169–179.

Fattahi, N., Assadi, Y., Hosseini, M.R.M. and Jahromi, E.Z. 2007. Determination of chlorophenols in water samples using simultaneous dispersive liquid–liquid microextraction and derivatization followed by gas chromatography-electron-capture detection. *Journal of Chromatography A* 1157: 23–29.

Fauser, P., Vikelsoe, J., Sorensen, P.B. and Carlsen, L. 2003. Phthalates, nonylphenols and LAS in an alternately operated wastewater treatment plant fate modeling based on measured concentrations in wastewater and sludge. *Water Research* 37: 1288–1295.

Fernandez M.A., Hernandez, L.M., Gonzalez, M.J. and Tabera, M.C. (1992). Organochlorine compounds and selected metals in waters and soils from Donana National Park (Spain). *Water Air and Soil Pollution* 65: 293-302.

Ferraz, N., Carnevia, D., Nande, G., Rossotti, M., Miguez, M.N., Last, J. A. and Gonzalez-Sapienza, G. 2007. Specific immunoassays for endocrine disruptor monitoring using recombinant antigenscovered by degenerated primer PCR. *Anal Bioanal Chem* 389: 2195-2202.

Fiamegos, Y.C., Nanos, C.G., Pilidis, G.A. and Stalikas, C.D. 2003. Phase-transfer catalytic determination of phenols as methylated derivatives by gas chromatography with flame ionization and mass-selective detection. *Journal of Chromatography A* 983:215-223.

Filali-Meknasi, Y., Tyagi, R.D., Surampali, R.Y., Barata, C., Riva, M.C. 2004. Endocrine-disrupting compounds in wastewater, sludge-treatment processes and receiving water: overview. *Practice Periodical of Hazardous Toxicology and Radioactive Waste Management* 8:39-56.

Firfilionis, G., Paraskevopoulou, V., Vilioti, G. and Dassenakis, M. 2004. The removal of trace metals at the wastewater treatment plant of Psyttalia. *Meditrranean Marine Science* 5(1): 71-81.

Flinn, J.M., Hunter, M., Linkous, D.H., Lanzirotti, A, Smith, L.N., Brightwell, J. and Jones, B.F. *Physiology and Behavior* 83:793-803.

Fromme, H., Kuchler, T., Otto, T., Pilz, K., Mu¨ller, J. and Wenzel, A. 2002. Occurrence of phthalates and bisphenol A and F in the environment. *Water Research* 36:1429–38.

Fuentes, A., Llorens, M., Saez, J., Soler, A., Aguilar, M.I., Ortuno, J.F. and Meseguer, V.F. 2004. Simple and sequential extractions of heavy metals from different sewage sludges. *Chemosphere* 54: 1039-1047.

Gabriel, L.P.F., Cyris, M., Giger, W. and Kohler, H.E. 2007. Ipso-substitution: A general biochemical and biodegradation mechanicsm to a cleave a-Quartenary alkyl phenols and bisphenol A. *Chemistry and Biodiversity* 4: 2123-2137.

Galceran, M.T. and Jauregui, O. 1995. Determination of phenols in sea water by liquid chromatography with electrochemical detection after enrichment by using solid-phase extraction cartridges and disks. *Analytica Chimica Acta* 304: 75-84.

Game, C., Gagnon, M.M., Dianne, W. and Richard, L. 2006. Endocrine disruption in male mosquito fish (Gambusia holbrooki) inhabiting wetland in Western Australian. *Ecotoxicology*. 15: 665 – 672.

García-Delgado, M., Rodríguez-Cruz, M.S., Lorenzo, L.F., Arienzo, M. and Sánchez-Martín, M..J. 2007. Seasonal and time variability of heavy metal content and its chemical forms in sewage sludges from different wastewater treatment plants. *Science of the Total Environment* 383: 82–92.

Gartner, S., Balski, M., Koch, M. and Nehls, I. 2009. Analysis and migration of phthalates in infant food packed in recycled paperboard. *Journal of Agricultural Food Chemistry* 57: 10675–10681.

Ge, J., Cong, J., Sun, Y., Li, G., Zhou, Z., Qian, G. and Liu, F. 2010. Determination of Endocrine Disrupting Chemicals in Surface Water and Industrial Wastewater from Beijing, China. *Bulletin of Environmental Contamination and Toxicology* 84: 401–405.

Gelbke, H.P., Hofmann, A., Owens, J.W. and Freyberger, A. 2007. The enhancement of the sub acute repeat dose toxicity test OECD TG 407 for the detection of endocrine active chemicals: Comparison with toxicity tests of longer duration. *Archieve of Environmental Toxicology* 81: 227-250

Gevao, B., Muzaini, S. and Helaleh, M. 2008. Occurrence and concentrations of polybrominateddiphenyl ethers in sewage sludge from three wastewater treatment plants in Kuwait. *Chemosphere* 71 (2008) 242–247.

Gómez-Hens, A. and Aguilar-Caballos, M.P. 2003. Social and economic interest in the control of phthalic acid esters, *Trends in Analytical Chemistry* 22: 847–857.

Goyer, R.A. Toxic and essential metals interactions. 1997. *Annual. Review of Nutrition* 17:37-50.

Govender, S., Jacobs, E.P., Bredenkamp, M.W. and Swart, P. 2007. Affinity chromatography using biocompatible and reusable biotinylated membranes. *Journal Chromatography* B 859: 1-8.

Government Gazette. 1984. Requirements for the purification of wastewater or effluent. Gazette No. 9225, Regulation, 991.

Grynkiewicz, E., Polkowska, Z., Kot-Wasik, A. and Namiesnik, J. 2002. Determination of phenols in runoff. *Polish Journal of Environmental Studies* 11(1), 85-89.

Gsapar, I.F., Polese, L., Minelli, E.V., Ribeiro, M.L. and Jardim, E.F.G. 1997. Determination of pentachlorophenol in drinking water. *Journal of Brazilian Chemical Society* 8(5): 515-518.

Guo, G.L., Zhou, Q.X., Koval, P.V. and Belogolova, G.A. 2006. Speciation, distribution of Cd, Pb, Cu and Zn in contaminated Phaeozem in north-east China using single and sequential extraction procedures. *Australian Journal of Soil Research* 44: 135-142.

Gutierrez, R., Rubio-Arias, H., Quintana, R., Ortega, J.A. and Gutierrez, M. 2008. Heavy metals in water of the San Pedro River in Chihuahua, Mexico and it potential health ris. *International Journal of Environmental Research and Public Health* 5 (2): 91-98.

Haase, H., Overbeck, S. and Rink, L. 2008. Zinc supplementation for the treatment or prevention of disease: current status and future perspectives. *Experimental Gerontology* 43:394-408

Halim, M.A., Majumder, R.K., Nessa, S.A., hiroshiro, Y., uddin, M.J., Shimada, J. and Jinno, K. 2009. Hydrogeochemistry and arsenic contamination of groundwater in the Ganges Delta Plain Bangladesh. *Journal of Hazardous Materials* 164:1335-1345.

Handy, R.D. 2003. Chronic effects of copper exposure versus endocrine toxicity: two sides of the same toxicological process? *Comparative Biochemistry and Physiology part A* 135:25-38.

Harris C.A., Henttu P., Parker M.G. and Sumpter J.P. 1997. The estrogenic activity of phthalate esters in vitro. *Environmental Health Perspectives* 105: 802-811.

Hashem, A.R. 1995. Microbial and heavy metals analysis of sewage sludge from Saudi Arabia. *Journal King Saudi University* 7(2):207-213.

Hauser and Calafat, . 2005. Phthalates and human health. *Occupational Environmental Medical* 62, 806-818.

Hays, S.M., Nordberg, M., Yager, J.W. and Aylward, L.L. 2008. Biomonitoring Equivalents (BE) dossier for cadmium (Cd) (CAS No. 7440-43-9). *Regulatory Toxicology and Pharmacology* 51: 49–56.

Heberer, T. and Stan, H. 1997. Detection of more than 50 substituted phenols as their t-butyldimethylsilyl derivatives using gas chromatography-mass spectrometry. *Analytica Chimica Acta* 341: 21-34.

Hecker, M. and Giesy, J. P. 2008. Novel trends in endocrine disrupting testing: The H295R steroidogenesis assay for identification of inducers and inhibitors of hormone production. *Anal Bioanal Chem.* 390: 287-291.

Heijerick, D.G. Jansen, C.R., Karlen, C., Wallinder, I.O. and Leygraf, C. 2002. Bioavailability of zinc in runoff water from roofing materials. *Chemosphere* 47:1073-1080.

Helaleh, M.I.H., Fuji, S., Korenaga, T. 2001. Column Silylation method for determining endocrine disruptors from environmental water samples by solid phase micro-extraction. *Talanta* 54:1039-1047.

Hellstrom, L., Jarup, L., Persson, B. and Axelson, O. 2004. Using environmental concentrations of cadmium and lead to assess human exposure and close. *Journal of Exposure Analysis and Environmental Epidemiology* 14: 416-423.

Hill, S.S., Shawa, B. R. and Wuc, A.H.B. 2001. The clinical effects of plasticizers, antioxidants, and other contaminants in medical polyvinylchloride tubing dusring respiratory and non-respiratory exposure. *Review Clinica Chimica Acta* 304: 1–8.

Hjelmborg, P.S., Ghisari, M. and Bonefeld-Jorgensen, E.C., 2006. SPE-HPLC purification of endocrine disruoting compounds from human serum for assessment of xenoestrogenic activity. *Anal Bioanal Chem.* 385: 875-887.

Hogberg, J., Hanberg, A., Berglund, M., Skerfving, S., Remberger, M., Calafat, A.M., Filipsson, A.F., Jansson, B., Johansson, N., Appelgren M. and Hakansson, H. 2008. Phthalate diesters and their metabolites in human breast milk, blood or serum, and urine as biomarkers of exposure in vulnerable populations. *Environmental Health Perspectives* 116 (3): 334-339.

Horng, C., Wang, S. and Cheng, I. 2009. Effects of sediment-bound Cd, Pb, and Ni on the growth, feeding, and survival of *Capitella* sp. I. *Journal of Experimental Marine Biology and Ecology* 371:68–76.

Hossain, M.F. 2006. Arsenic contamination in Bangladesh-An overview. *Agriculture, Ecosystems and Environment* 113:1-16.

Hua, L., WU, W., Liu, Y., Tientchen, C.M., and Chen, Y. 2008. Heavy Metals and PAHs in Sewage Sludge from Twelve Wastewater Treatment Plants in Zhejiang Province. *Biomedical and Environmental Sciences* 21: 345-352.

Huang, J., Wang, H., Jin, Q., Liu, Y. and Wang, Y. 2007. Removal of phenol from aqueous solution by adsorption onto OTMAC-modified attapulgite. *Journal Environmental Management* 84: 229-236.

Huang, P-C., Tien, C-J., Sun, Y-M, Hsieh, C-Y. and Lee, C-C. 2008. Occurrence of Phthalates in sediment and biota: Relationship to aquatic factors and the biots-sediment accumulation factor. *Chemosphere* 73: 539-544.

Ikem, A. Egiebor, O. and k. Nyavor. 2003. Trace elements in water, fish and sediment from Tuskegee lake, Southeastern USA. *Water, Air, and Soil Pollution* 149: 51–75.

Igbinosa, E.O. and Okoh, A.I. 2009. Impact of discharge wasterwater effluents on the physic-chemical qualities of a receiving watershed in a typical rural community. *International Journal of Environmental Science Technology* 6 (2): 175-182.

Iwashita, M. and Shimamura, T. 2003. Long-term variations in dissolved trace elements in the Sagami River and its tributaries (upstream area), Japan. *Science of the Total Environment* 312: 167–179.

ITER 2010 International Toxicity Estimates for Risk (ITER) database. Bethesda, MD,National Institutes of Health, National Library of Medicine, Toxicology Data Network (TOXNET) (http://toxnet.nlm.nih.gov/, accessed 23 August 2010).

Jackson, V. A., Paulse, A. N., Stormbroek, T., Odendaal, J. P. and Khan, W. 2007.Investigation into metal contamination of the Berg River, Western Cape, South Africa. *Water SA* 33(2): 175-182.

Jackson, V.A., Paulse, A.N., Odendaal, J.P. and Khan, W. 2009. Investigation into the metal contamination of the Plankenburg and Diep Rivers, Western Cape, South Africa. *Water SA* 35 (3): 289-299.

Jaganyi, D., Tesfai, F.K., Southway, C. and Mamabolo, M. 2005. Determination of inorganic pollutants and assessment of the current South African guidelines on permissible utilisation of sewage sludges. *Water SA* 31(3): 359-368.

Jaji, M.O., Bamgbose, O., Odukoya, O.O. and Arowolo, T.A. 2007. Water quality assessment of Ogun river, South West, Nigeria. *Environmental Monitoring Assessment* 133: 473-482.

Jansen, J., Karges, W. and Rink, L. 2009. Zinc and diabetes-clinical links and molecular mechanisms. *Journal of Nutritional Biochemistry* 20:399-417.

Jeon, C.W., Lee, J.H., Ko, K.S., Lee, H.K. and Lee, S.H. 2007. SPE and SPME extraction of phenols from water followed by Gas chromatography-FID and MSD. *Applied Chemistry* 11(1): 317-320.

Jiao, B. and Cheng, C.H.K. 2008. Disruption actions of bisphenol A and malachite green on growth hormone receptor gene expression and signal transduction in seabeam. *Fish Physiol Biochem:* doi 10.1007/s10695-008-9227-0.

Jing, S., Lianqing, L. and Genxing, PAN. 2009. Variation or grain Cd and Zn concentration of 110 hybrid rice cultivars grown in a low-Cd paddy soil. *Journal of Environmental Sciences* 21: 168-172.

Jones, J.J., Nichols, P.D., John, R.B. and Smith, J.D. 1987. The effect of mercury and cadmium on the fatty acid and sterol composition of the marine diatom asterionella glacialis. *Phytochemistry* 26(5):1343-1348.

Joseph, P. 2009. Mechanism of cadmium carcinogenesis. *Toxicology and Applied Pharmacology* doi:10.1016/j.taap.2009.01.11.

Jung, M.C., Thorntonb, I. and Chonc, H. 2002. Arsenic, Sb and Bi contamination of soils, plants, waters and sediments in the vicinity of the Dalsung Cu–W mine in Korea. *Science of the Total Environment* 295: 81–89.

Juvancy, Z., Barna, S., Gyarmathy, D. and Konorot, F. 2008. Study of endocrine disrupting chemicals in environment. *Acta Polytechnic Hungarica* 5 (3): 49-58.

Kadewa, W. W.; Henry, E. M.; Masamba, W. R. M.; Kaunda, C. C. 2001. Impact of sewage sludge application to horticulture: A case of the city of Blantyre, in: Proceedings of the First Chancellor College Research Dissemination Conference. Zomba, Malawi

Kaonga, C.C., Kumwenda, J. and Mapoma, H.T. 2010. Accumulation of lead, cadmium, manganese, copper and zinc by sludge worms; Tubifex tubifex in sewage sludge. *International Journal of Environmental Science and Technology* 7 (1): 119-126.

Karvelas, M., Katsoyiannis, A. and Samara, C. 2003. Occurrence and fate of heavy metals in the wastewater treatment process *Chemosphere* 53: 1201–1210.

Kayali, N., Tamayo, F.G. and Polo-Diez, L.M. 2006. Determination of dimethylhexyl phthalate in water by solid phase microextraction coupled to high performance liquid chromatography. *Talanta* 69: 1095-1099.

Kazi, T.G., Jamali, M.K., Arain, M.B., Afridi, H.I., Jalbani, N., Sarfraz, R.A. and Ansari, R. 2009. Evaluation of an ultrasonic acid digestion procedure for total heavy metals determination in environmental and biological samples. *Journal of Hazardous Materials* 161: 1391-1398.

KemI .2010. KemI-stat (statistical information based on data in the Swedish Chemicals Agency's products register and pesticides register).

Khairiah, J., Yu, H.Y., Khairal, N.I. and Ang, W.W., Aminah, A., Maimon, A., Zalifah, M. K. and Geri, A. K. 2002. Bioavailability of chromium in vegetables of selected Agricultural areas of Malaysia. *Pakistan Journal of Biological Sciences* 5(4): 471-473.

Kim, S.K. and Kannan, K. 2007. Perfluorinated acids in air, rain, snow, surface runoff, and lakes: relative importance of pathways to contamination of urban lakes. *Environmental Science Technology* 41: 8328–8334.

Kim, S., Lee, J.U. and Jong, A. 2005. Bioleaching of heavy metals from dewatered sludge by *Acidthiobacillus ferrooxidans*. *Journal of Chemical Techology and Biotechnology* 80: 1339–1348.

Kim, S.W., Choi., S.H. Min., J. and Gu, M.B. 2000. Toxicity monitoring of endocrine disrupting chemicals (EDCs) using free-dried recombinant bioluminescent bacteria. *Biotechnology Bioprocess Engineering* 5: 395-399.

King, J.M., Scheepers, A.C.T., Fisher, R.C., Reinecke, M.K. and Smith, L.B. 2003. River rehabilitation: Literature review, case studies and emerging principles. WRC No 1161/1/03. Water Reseach Commission, Pretoria.

Kitano, T., Koyanagi, T., Adachi, R., Sakimura, N., Takamune, K. and Abe, S.I. 2006. Assesment of estrogenic chemicals using estrogen receptor α(ER α)- and ERβ –mediated reporter gene assay in fish. *Marine Biology* 149: 49-55.

Koch, M. and Rotard, W. 2001. On the contribution of background sources to the heavy metal content of municipal sewage sludge. *Water Science Technology* 43 (2): 67-74

Kostrhounova, R., Hrdlicka, A. and Sommer, L. 2003. Solid Phase Extraction of Phenol and Chlorophenols on Octadecylsilica and Amberlite XAD 2 Sorbents in the Presence of Cationic Surfactant. *Microchimita Acta* 142: 95–99.

Kovacs, A., Kende, A., Morti., Volk, G., Rikker and Torkos, K. 2008. Determination pf phenols and chlorophenols as trimethylsilyl derivatives using gas chromatography-mass spectrometry. *Journal of Chromatography A* 1194: 139-142

Krijgsheid, K.R. and Van der Gen, A. 1986. Assessment of the impact of the emission of certain Organochlorine compounds on the aquatic environment. Part 1: Monochlorophenols and 2,4-dichlorophenol. *Chemosphere* 15 (7): 825-860.

Krishnamurti, G.S.R. and Naidu, R. 2000. Speciation and phytoavailability of cadmium in selected surface soils of South Australian. *Australian Journal of Soil Research* 38: 991-1004.

Kuban, P., Houserova, P., Kuban, P., Hauser, P.C. and Kuban, V. 2007. Mercury speciation by CE: A review. *Electrophoresis* 28:58-68.

Kulbat, E., Olanczuk-Neyman, K., Quant, B., Geneja, M. and Haustein, E. 2003. Heavy metals removal in the mechanical-biological wastewater treatment plant "Wschod" in Gdansk. *Polish Journal of Environmental Studies* 12 (5): 635-641.

Kumar, V., Kumar, M., Jha, K.M., Jeong, J. and Lee, J-C. 2009. Solvent extraction of cadmium from sulfate solution with di-(2-ehtylhexyl) phosphoric acid diluted in kerosene. *Hydrometallurgy* 96:230-234.

Lafuente, A. Marquez, N., Perez-Lorenzo, M., Pazo, D. and Esquifino, A.I. 2000. Pubertal and postpubertal cadmium exposure differentially affects the hypothalamic-pituitary-testicular axis function in the rat. *Food and Chemical Toxicology* 38: 913-923.

Lalor, G.C. 2008. Review of cadmium transfers from soil to human and its health effects in the Jamaican environment. *Science of the Total Environment* 400:162-172.

Lascombe, I., Beffa, D., Ruegg, U., Tarradellas, J., Wahli, W. 2000. Estrogenic activity assessment of the environmental chemicals using in vitro assays: identification of two new estrogenic compounds. *Environmental Health Perspective* 108:621-629.

Latini, G., Wittassek, M., DelVechio, A., Presta, G., De Felice, C. and Angerer, J. 2009. Lactational exposure to phthalates in southern Italy. *Environment International* 35:236-239.

Lavado, R., Thibaut, R., Raldua, D., Martin, R., Porte, C. 2004. First evidence of endocrine disruption in feral carp from Ebro River. *Toxicolology Application Pharmacology* 196: 247-257.

Lazaier, C. and Mackay, M.E. 1993. Vitellogenin gene expression in teleost. In: Hochachka, P.W., Mommsen, T.P. (Eds.), Biochemistry and molecular biology. Elsevier Amsterdam, pp. 391-405.

Leeper, G. W., (1978). Managing the heavy metals on the land. Pollution. Engineering and Tech., Vol. 6. Marcel Dekker Inc., New York, USA.

Leon, V.M., Llorca-Porcel, J., Alvarez, B., Cobollo, M.A., Munoz, S., Valor, I. 2006. Analysis of 35 priority semivolatile compounds in water by stir bar sorptive extraction-thermal desorption-gas chromatography-mass spectrometry Part II: Method validation. *Analytical Chimita Acta* 558: 261-266.

Leuch, F.D.L., Chapman, H.F., van den Heuvel, M.R., Tan, B.L.L., Gooneratne, S.R., Tremblay, L.A. 2006a. Bioassay-derived androgenic and estrogenic activity in municipal sewage in Australia and New Zealand. *Ecotoxicology Environmental Safety* 65: 403-411.

Li, D. and Park, J. 2001. Silyl derivatization of alkylphenols, chlorophenols and bisphenol A for simultaneous GC/MS determination. *Analytical Chemistry* 73: 3089-3095.

Li, X., Zhong, M., Xuc, S. and Sun, C. 2006. Determination of phthalates in water samples using polyaniline-based solid-phase microextraction coupled with gas chromatography. *Journal of Chromatography A.* 1135:101–108.

Liao C-M., Shen, H-H., Chen, C-L., Hsu, L-I., Lin, T-L., Shen, S-C. and Chen, C-J., 2009. Risk assessment of arsenic-induced internal cancer at long-term low dose exposure. *Journal of Hazardous Materials,* 165:652-663.

Limei, Z., Xiaoyong, L., Tongbin, C., Xiulan, Y., Hua, X., Bin, W. and Lixia, W. 2008. Regional assessment of cadmium pollution in agricultural lands and the potential risk related to intensive mining activities: A case study in Chenzhou City, China. *Journal of Environmental Science* 2002: 696-703.

Ling, W., Gui-bin, J., Ya-qi, C., Bin, H., Ya-wei, W. and Da-zhong, S. (2007) Cloud point extraction coupled with HPLC-UV for the determination of phthalate esters in environmental water samples. *Journal of Environmental Sciences* 19:874–878.

Liu, R., Zhou, J.L., Wilding, A., 2004. Simultaneous determination of endocrine disrupting phenolic compounds and steroid in water by solid phase extraction-gas chromatography-mass spectrometry. *Journalof Chromatography A* 1022: 179-189.

Llompart, M., Lourido, M., Landın, P., Garcıa-Jares, C. and Cela, R. 2002. O ptimization of a derivatization–solid-phase microextraction method for the analysis of thirty phenolic pollutants in water samples. *Journal of Chromatography A* 963:137–148.

Luks-Betlej, K., Popp, P., Janoszka, B and Paschke, H. 2001. Solid-phase microextraction of phthalates from water. *Journal of Chromatography A* 938: 93-101.

Luttke, J., Scheer, V., Levsen, K., Wfjnsch, G., Cape, J.N., Hargreaves, K.J., Robert L., West, S., Acker, K., Wieprechv, W. and Jones, B. 1997. Occurrence and formation of nitrated phenols in and out of cloud. *Atmospheric Environment* 31(16): 2637-2648.

Macintosh, C. E., J. A. Maldonado, M. G. Ikonomou and F. A. P. C. Gobas. 2006. Sorption of Phthalate Esters and PCBs in a Marine Ecosystem. *Environmental Science Technology* 40(11); 3481-3488.

Madungwe, E. and Sakuringwa, S. 2007. Greywater reuse: A strategy for water demand management in Harare. *Physics and Chemistry of the Earth* 32: 1231-1236.

Mahomed, S.I. Voyi, K.V.V., Aneck-Hahn, N.H. and de Jager, C. 2008. Oestrogenicity and chemical target analysis of water from small-sized industries in Pretoria, South Africa. *Water SA* 3 (3): 357-364.

Makepeace, D. K., Smith D. W. and Stanley S. J. 1995. Urban stormwater quality: Summary of contaminant data. *Critical Review in Environmental Science Technology* 25(2): 93-139.

Mandal, B.K. and Suzuki, K.T. 2002. Arsenic round the world: a review. *Talanta* 58: 201-235

Marcussen, H., Dalsgaard, A. and Holm, P.E. 2008. Content, distribution and fate of 33 elements in sediments of rivers receiving wastewater in Hanoi, Vietnam. *Environmental Pollution* 155: 41-51.

Maret, W. and Sandstead, H.H. 2006. Zinc requirements and the risks and benefits of zinc supplementation. *Journal of Trace Elements in Medicine and Biology* 20:3-18.

Marttinen, S.K., Kettunen, R.H. and Rintala, J.A. 2003. Occurrence and removal of organic pollutants in sewages and landfill leachates. *Science of the Total Environ*, 301(1-3), 1-12.

Matschullat, J. 2000. Arsenic in the geosphere. *Science of the Total Environment* 249:297-312.

Matthiessen, P. 2000. Is endocrine disruption a significant ecological issue? *Ecotoxicology* 9: 21-24.

Mauricio, R., Diniz, M., Petrovic, M., Amaral, L., Peres, I., Barcelo, D. and Santana, F. 2006. A characterization of selected endocrine disruptor compounds in a Portuguese wastewater treatment plant. *Environmental Monitoring and Assessment* 118: 75-87.

McArdle, M., Elskus, A., McElroy, A., Larsen, B., Benson, W., Schlenk, D. 2000. Estrogenic and CYPIA response of mummichogs and sunshine bass to sewage effluent. *Marine Environmental Research.* 50: 175-179.

McKinlay, R., Plant, J.A., Bell, J.N.B. and Voulvoulis, N. 2008. Calculating human exposure to endocrine disrupting pesticides via agricultural and non-agricultural exposure routes. *Science of the Total Environment* 398: 1 – 12.

McNeely, R.N., V.P. Neimanis, and L. Dwyer. 1979. Phenolic compounds. In: Water quality sourcebook: A guide to water quality parameters. Environment Canada, Inland Waters Directorate, Water Quality Branch, Ottawa. Method for the analysis of sulfluramid and its isomers in ant bait by capillary column gas chromatography. *Journal Separation Science* 24: 406–410.

MDH (Minnesota Department of Health). 2006. Copper in drinking water, health effects and how to reduce exposure. [http://healthstate.mn.us/dirs/eh/water/com/fs/copper.html], (Accessed 2009 May 11).

Minero, C., Maurino, V., Pelizzetti, E. and Vione, D. 2007. Assessing the steady-state [NO_2] in environmental samples. implication for aromatic photonitration processes induced by nitrate and nitrite. *Environmental Science Pollution Research* 14 (4): 241-243.

Mirlean, N., Andrus, V.E. and Baisch, P. 2003. Mercury pollution sources in sediments of Patos Lagoon Estuary, Southern Brazil. *Marine Pollution Bulletin* 46(3): 331-334.

Moder, M., Braun, P., Lange, F., Schrader, S. and Lorenz, W. 2007. Determination of endocrine disrupting compounds and acidic drugs in water by coupling of derivatization, Gas Chromatograpgy and Negative Chemical ionization Mass Spectrometry. *Clean* 35 (5): 444-451.

Moeletsi, M. Mazema, H. and Halday, I. Strategy for mitigating the impacts of heavy metals in wastewater and the economic and environmental implications for the city of Cape Town. Proceedings of the 2004 Water Institute of Southern Africa (WISA) Biennial Conference 2-6 May 2004 ISBN: 1-920-01728-3 Cape Town, South Africa.

Moghadam, M., Tangestaninejad, S., Mirkhani, V., Mohammadpoor-Baltork, I., Chahardahcheric, S. and tavakoli, Z. 2008. Rapid and highly efficient trimethylsilylation of alcohols and phenols with hexamethyldisilazane (HDMS) catalyzed zirconyl triflate, [$ZrO(OTf)_2$]. *Journal of Organometallic Chemistry* 693: 2041-2046

Molisani, M.M., Salomo, M.S.M.B., Ovalle, A.R.C., Rezende, C.E. Lacerda, L.D. amd Carvalho, C.E.V. 1999. Heavy metals in sediments of the lover Paraibado Sul River and Estuary, River in Brazil. *Bulletin Envronmental Contamination and Toxicology* 63: 682-690.

Montero, L., Concradi, S., Weiss, H. and popp, P. 2005. determination of phenols in lake and ground water samples by stir bar sorptive extraction-thermal desorption-gas chromatography-mass spectrometry. *Journal of chromatography* A 1071:163-169

Moore, C.J. 2000. A review of mercury in the environment. www.heads-up.net/sci/Hg_review_080905.pdf, accessed 3rd July, 2009.

Morrison, G., Fatoki, O.S., Linder, S. and Lundehn, C. 2004. Determination of heavy metal concentrations and metal fingerprints of sewage sludge from Eastern Cape Province, South Africa by Inductively Coupled Plasma – mass spectrometry (ICP-MS) and Laser Ablation-Inductively Coupled Plasma-Mass Spectrometry (LA-ICP-MS). *Water, Air, and Soil Pollution* 152: 111–127.

Morrison, G., Fatoki, O.S., Persson, L. and Ekberg, A. 2001. Assessment of the impact of point source pollution from the Keiskammahoek Sewage Treatment Plant on the Keiskammahoek River – pH, electrical conductivity, oxygen demand substances (COD) and nutrients. *Water SA* 27 (4): 475-480

Morville, S. Scheyer, A., Mirabel, P. and Millet, M. 2004. A multiresidue method analysis of phenols and nitrophenols in the atmosphere. *Journal of Environmental Monitoring* DOI:10.1039/b408756a

Mukherjee, A. B. and Bhattacharya, P. 2001. Arsenic in groundwater in the Bengal Delta Plain: Slow poisoning in Bangladesh. *Environmental Reviews* 9: 189-220

Muszkat, L., Bir, L. and Raucher, D. 1997. Identification of mixed O-phenyl alkyl phthalate esters in an agricultural land. *Bulletin of Environmental Contamination and Toxicology* 58: 348-355

Navarro, M., Lopez, H., Sanchez, M. and Lopez M.C. 1993. The effect of industrial pollution on mercury levels in water, soil, and sludge in the costal area of Motril, Southeast Spain, *Archives of Environmental Contamination and Toxicology* 24: 11-15

NRC. 1983. Risk Assessment in the Federal Government: Managing the Process. National Research Council, National Academy Press. Washington, DC, USA.

NRC. 1993. Issues in Risk Assessment. National Research Council, National Academy Press. Washington, DC, USA.

Odendaal, J. P. and Reinecke, A. J. 2004. Bioaccumulation of Cadmium and Zinc, and Field Validation of a Histological Biomarker in Terrestrial Isopods. *Bulletin of Environmental Contamination and Toxicology* 72: 769–776.

Oehmen, A., Fradinho, J., Serra, S., Carvalho, G., Capelo, J.L., Velizarov, S., Crespo, J.G. and Reis, M.A.M. 2009. The effect of carbon source on the biological reduction of ionic mercury. *Journal of Hazardous Materials* 165:1040-1048.

Ogunfowokan, A.O., Torto, N., Adenuga, A.A. and Okoh, E.K. 2006. Survey of levels of phthalate ester pasticizers in a sewage lagoon effluent and a receing stream. *Environmental Monitoring and Assessment* 118:457-480.

Ohimain, E.I., Jonathan, G. and Abah, S.O. 2008. Variations in heavy metal concentrations following the dredging of an oil well access canal in the Niger Delta. *Advances in Biological Research* 2 (5-6): 97-103

Okonkwo, J.O. 2007. Arsenic status and distribution in soils at disused cattle dip in South Africa. *Bulletin of Environmental Contamination and Toxicology* 79:380-383.

Okonkwo, J.O. and Mothiba, M. 2005. Physico-chemical characteristics and pollution levels of heavy metals in the rivers in Thohoyandou, South Africa. *Journal of Hydrology* 308: 122–127

Oliveira, A. D., Bocio, A, Trevilato, T.M. B., Takayanagui, A.M.M., Domingo, J.L. and Segura-Muniz, S.I. 2007. Heavy metals in untreated/treated urban effluent and sludge from biological wastewater treatment plant. *Environmental Science and Pollution Research* 14 (7):483 – 489.

Oliver, R., May, E. and Williams, J. (2005) The occurrence and removal of phthalates in a trickle filter STW. *Water Research* 39: 4436-4444.

OMOE (Ontario Ministry of Environment). 2008. Cobalt in the environment. [http://www.ene.gov.on.ca/en/], (Accessed 2009 May 11).

Opeolu, B. O., Fatoki, O. S. and Odendaal, J.. 2010. Development of a solid-phase extraction method followed by HPLC-UV detection for the determination of phenols in water. *International Journal of the Physical Sciences* 5(5): 576-581.

Oyarzuna, R., Lillob, J., Higuerasc, P., Oyarzun, J. and Maturana, H. 2004. Strong arsenic enrichment in sediments from the Elqui watershed, Northern Chile: industrial (gold mining at El Indio–Tambo district) vs. geologic processes. *Journal of Geochemical Exploration* 84: 53–64.

Oymak, T., Tokalioglu, S., Yimaz, V., Kartal, S. and Aydin, D. 2009. Determination of lead and cadmium in food samples by coprecipitation method. *Food Chemistry* 113:1314-1317.

Pagliarussi RS, Freitas LAP and Bastos JK. 2002. A quantitative method for the analysis of xanthine alkaloids in Paullinia cupana (guaraná) by capillary column gas chromatography. *Journal Separation Science* 25: 371–374.

Pandey, P.K., Yadav, S. Nair, S. and Bhui, A. 2002. Arsenic contamination of the environment, A new perspective from central-east India. *Environment International* 28-245:235.

Papafilippaki, A. K., Kotti, M. E., & Stavroulakis, G. G. (2008). Seasonal variations in dissolved heavy metals in the Keritis River, Chania, Greece. *Global NEST Journal,* 10: 320–325.

Parketon, T.F. and Konkel, W.J. (2000) Application of quantitative structure-activity relationships for assessing the aquatic toxicity of phthalate esters. *Ecotoxicology and Environmental Safety* 45: 61-78

Patandin, S., Lanting, C.I., Mulder, P.G., Boersma, E.R., Sauer, P.J. and Weisglas-Kuperus, N. 1999. Effects of environmental exposure to polychlorinated biphenyls and dioxins on cognitive abilities in Dutch children at 42 months of age. *Journal of Pediatrics* 134 (1): 33 - 41

Patrolecco, I., Capri, S., De Angelis S., Polesello, S., Valsecchi, S. 2004. Determination of endocrine disrupting chemicals in environmental solid matrices by extraction with a non-ionic surfactant (Tween 80). *Journal of Chromatography A* 1022: 1-7.

Paustenbach DJ, Panko JM, Fredrick MM, Finley BL, Proctor DM. 1997. Urinary chromium as a biological marker of environmentaleExposure: What are the limitations? *Regulatory Toxicology and Pharmacology* 26: 23-34.

Paxeus, N. 1996. Organic pollutants in the effluent of large wastewater treatment plants in Sweden. *Water Research* 30(5): 1115-1122.

Peng, X., Wang, Z., Yang, C., Chena, F. and Maia, B. 2006. Simultaneous determination of endocrine-disrupting phenols and steroid estrogens in sediment by gas chromatography–mass spectrometry. *Journal of Chromatography A* 1116: 51–56

Petrovic, M., Eljarrat, E., Lopez de Alda, M.J. and Barcelo, D. 2001. Analysis and environmental levels of endocrine-disrupting compounds in fresh water sediments. *Trends in Analytical Chemistry* 20 (11): 637-648

Petrovic, M., Lacorte, S., Viana, P. and Barcelo, D. 2002. Pressurized liquid extraction followed by liquid chromatography–mass spectrometry for the determination of alkylphenolic compounds in river sediment. *Journal of Chromatography A* 959:15–23.

phthalate esters and PCBs in a marine ecosystem, Environ. Sci. Technol. 40: 3481–3488.

Polo, M., Llompart, M., Garcia-Jares, C. and Cela, R. 2005. Multivariate optimization of a solid-phase microextraction method for the analysis of phthalate esters in environmental waters. *Journal of Chromatography A* 1072: 63–72

Psillakis, E., Mantazavinos, D., Kalogerakis, N. 2004. Monitoring the sonochemical degradation of phthalate esters in water using solid-phase microextraction. *Chemosphere* 54: 849 – 857.

Puig, D. and Barcelo, D. 1996. Determination of phenolic compounds in water and waste water. *Trends Anal. Chem.* 15 (8): 362-375.

Radojevic, M. and Baskin, V.N. 1999. Organic matter in practical environmental analysis. *The Royal Society of Chemistry* 325-329.

Rajapakse, N., Ong, D., Kortenkamp, A., 2001. Defining the impact of weakly estrogenic chemicals on the action of steroidal estrogens. *Toxicology Sci.* 60: 296-304.

Ramos, L., Fernandez, M.A., Gonzalez, L. And Hernandez, L.L. 1999. Heavy metal pollution in water, sediment and earthworms from the Ebro River, Spain. *Bulletin of Environmental Contamination and Toxicology* 63:305-311.

Renberg, L., Marell, E., Sundstrom, G. and Adolfsson-Erici, M. 1983. Levels of chlorophenol in natural waters and fish after an accidental discharge of a wood-impregnating solution. *Environmental Research and Management* 12 (2): 121-123.

Retief, N-R., Avenant-Oldewage, A. and Du-Preez, H.H. 2009. Seasonal study on *Bothriocephalus* as indicator of metal pollution in yeloowfish, South Africa. *Water SA* 35(3): 315-322.

Reyes, L.H., Mar, J.L.G., G.M., Rahman, M., Fahrenholz, B.T. and Skip Kingston, H.M. 2009. Simultaneous determination of arsenic and selenium species in fish tissues using microwave-assisted enzymatic extraction and ion chromatography–inductively coupled plasma mass spectrometry. *Talanta* 78(3): 983-990.

Ribeiro, A., Neves, M.H., Almeida, M.F., Alves, A. and Santos, L. 2002. Direct determination of chlorophenols in landfill leachates by solid-phase micro-extraction-gas chromatography-mass spectrometry. *Journal of Chromatography* 975: 267-274

Rice, C., Birnabaum, L.S., Cogliano, J., Mahaffey, K., Needham, L., Rogan, W. J., and Vom Saal, F.S., 2003. Exposure assessment for endocrine disruptors: Some consideration in the design of studies. *Environmental Health Perspectives* 111 (3): 1683-1690.

River-Moore, N.A, Jewitt, G.P.W., Weeks, D.C. and O'keeffe, J.H. 2004. Water temperatureand fish distribution in the Subie River system: towards the development of an adaptive management tool. WRC Report No 1065/1/04. Water Reseach Commission, Pretoria.

Reilly.C. 1991. Metal Contamination of Food. *Applied Science* 3-10.

Reinecke, A.J., Snyman, R.G. and Nel, J.A.J. 2003. Uptake and distribution of lead (Pb) and cadmium (Cd) in the freshwater Crab, *Potamonautes Perlatus* (Crustacea) in the Eerste River, South Africa. *Water, Air, and Soil Pollution* 145:395-408.

Rikken, M.G.J. and Lijzen, J.P.A. 2004. Update of risk assessment models for the indirect human exposure. RIVM report No 601516011/2004. National Institute for Public Health and the Environment. Bilthoven, The Netherlands.

Roa, E.C., Capangpangan, M.B. and Schultz, M. 2010. Modification and validation of a microwave-assisted digestion method for subsequent ICP-MS determination of selected heavy metals in sediment and fish samples in Agusan River, Philippines *Journal of Environmental Chemistry and Ecotoxicology*, *2*(9): 141-151.

Rodriguez, V.M., Jimenez-Capdeville, M.E. and Giordano, M. 2003. The effects of arsenic exposure on the nervous system. *Toxicology Letters*:1-18

Rompa, M., Kremer, E. and Zygmunt, B. 2003. Derivatisation in gas chromatographic determinationof acidic herbicides in aqueous environmental samples. *Anaytical and Bioanalytical Chemistry* 377: 590–599

Roslev, P., Vorkamp, K., Aarap, J., Frederiksen, K. and Nielsen, P.H. 2007. Degradation of phthalate esters in an activated sludge wastewater treatment plant. *Water Research* 41: 969-976

Routledge, E.J., Sheahan, D., Desbrow, C., Brighty, G.C., Waldock, M., Sumpter, J.P., 1998. Identification of estrogenic chemicals in STW effluent. 2. In vivo responses in trout and roach. *Environmental Toxicology and Chemistry* 32: 1559–1565

Rudel, R.A. and Perovich L.J. 2009. Endocrine disrupting chemicals in indoor and outdoor air. *Atmospheric Environment* 43: 170–181

Safarzadeh, M.S., Bafghi, M.S., Moradkhani, D. and Ilkhchi, M.O. 2007. A review on hydrometallurgical extraction and recovery of cadmium from various resources. *Minerals Engineering* 20:211-220

Salgueiro, M.J., Zubillaga, M., Lysionek, A., Sarabia, M.I., Caro, R., De Paoli, T., Hager, A., Weill, R. and Boccio, J., 2000. Zinc as an essential microelement: a review. *Nutrional Research* 20(5):737-755

Salgueiro, M.J., Zubillaga, M.B., Lysionek, A.E., Caro, R.A., Weill, R. and Boccio, J.R, 2002. The role of zinc in the growth and development of children. *Nutrition* 18(6):510-519.

Sanchez-Avila, J., Bonet, J., Velasco, G. and Lacorte, S. 2009. Determination and occurrence of phthalates, alkylphenols, bisphenol A, PBDEs, PCBs and PAHs in an industrial sewage grid discharging to a municipal wastewater treatment plant. *Science of the Total Environment* 407: 4157-6167.

Sanders, M.J., Du Preez, H.H. and Van Vuren, J.H.J. 1999. Monitoring of cadmium and zinc contamination in freshwater systems with the use of the freshwater river crab, *Potamonautes warreni*. *Water SA* 25(1): 91-98

Santana, C.M., Ferrera, Z.S., Padron, M.E.T. and Rodriguez, J. J. S. 2009. Methodologies for the extraction of phenolic compounds from environmental samples: New approaches. *Molecules* 14: 298-320.

Santana, C.M., Ferrera, Z.S. and Rodriguez, J.J.S. 2005. An environmentally friendly method for the extraction and determination of priority phenols in soils using micro-assisted micellar extraction. *Analyticaland Bioanalytical Chemistry* 382: 125-133.

Santana, C.M., Ferrera, Z.S., Rodriguez, J.J.S. 2002. Use of non-ionic surfactant solutions for the extraction and pre-concentration of phenolic compounds in water prior to their HPLC-UV detection. *Analyst* 127: 1031-1037.

Saraji, M. and Bakhshi, M. 2005. Determination of phenols in water samples by single-drop microextraction followed by insyringe derivatization and gas chromatography-mass spectrometric detection. *Journal of Chromatography A* 1098: 30-36.

Saraji, M. and Marzban, M. 2010. Determination of 11 priority pollutant phenols in wastewater using dispersive liquid-liquid microextraction followed by high-performance liquid chromatography-diode-array detection. *Analyticaland Bioanalytical Chemistry* 396: 2685-2693

Sarifuzzaman, M., Siddique, M.N.A., Ferdousi, F.K., Ahmed, E., Alam, A.M.S. and Ullah, S.M. Studies of Arsenic Mobilization with Iron, Manganese and Copper in Borehole Sediments of the River Padma. *Pakistani Journal of Analytical and Environmental Chemistry* 8 (1 & 2): 91- 95

Sathyanarayana, S. 2008. Phthalates and Children's Health. *Current Problems in Pediatric Adolescent Health Care* 38: 34-49

Schmidt, K., Steinberg, C.E.W. and Staaks, G.B.O., Pfugmacher, S. 2005. Infleunce of a zenobiotic mixture (PCB & TBT) compared to single substances on swimming behavior or reproduction Daphnia magna. *Acta Hydrochimica et Hydrobiologica* 33 (4): 287-300

Schmidt-Baumler, Heberer, T. and Stan, H.J. 1999. Occurrence and distribution of organic contaminants in the aquatic sytem in Berlin part II: Substituted phenols in Berlin surface water. *Acta Hydrochimica et Hydrobiologica 27*(3): 143-149

Schummer, C., Delhomme, O., Appenzeller, B.M.R., Wennig, R., and Millet, M. (2009) Comparison of MTBSFA and BSTFA in derivation reaction of polar compounds prior to GC/MS analysis. *Talanta* 77, 1473-1482

Schummer, C., Sadiki, M., Mirabel, P. and Millet, M. 2006. Analysis of t-burtyldimethylsilyl derivatives of chlorophenols in the atmosphere of urban and rural areas in east of France. *Chromatographia* 63: 189-195

Scrippo, M., Argiris, L., Van De Weerdt, C., Muller, M., Willemsen, P., Martial, J. and Maghuin-Rogister, G. 2004. Recombinant human estrogen, Androgen and progesterone receptors for detection of potential of potential endocrine disruptors. *Analytical and Bioanalytical Chemistry* 378: 664-669

Seckin, E., Fromme, H. and Volekl, W. 2009. Determination of total and free mono-butyl phthalate in human urine samples after medication of di-n-butyl phthalate containing capsule. *Toxicology Letters* 188: 33 -37.

Sekabira, K., Origa, H.O., Basamba, T.A., Mutumba, G. and Kakudidi, E. 2010. Assessment of heavy metal pollution in the urban stream sediment and its tributaries. *International Journal of Environmental Science and Technology* 7 (3): 435-446

Segner, H. 2005. Developmental, reproductive, and demographic alterations in aquatic wildlife: Establishing causality between exposure to endocrine-active compounds (EACs) and effects. *Acta Hydrochimica et Hydrobiologica* 33(1): 17-26.

Sexton, K., Callahan, M.A., Bryan, E.F. 1995. Estimating exposure and dose to characterize health risks: The role of human tissue monitoring in exposure assessment. *Environmental Health Perspectives.* 103: 13-29.

Sha, Y., Xia , X. Yang, Z. and Huang, G.H. 2007. Distribution of PAEs in the middle and lower reaches of the Yellow River, China. *Environmental Monitoring Assessment* 124: 277–287.

Sharma, R.K., Agrawal, M. and Marshall, F. M. 2009. Heavy metals in vegetables collected from production and market sites of a tropical urban area of India. *Food and Chemical Toxicology* 47: 583-591

Sharpe, R. and Skakkebeak N.E. (1993). Are estrohens involved in falling sperm counts and disorders of the male reproductive tract? *The Lancet* 341: 1259-1266

Shomar, B.H., Muller, G. and Yahya, A. 2004. Potential use of treated wastewater sludge in the agricultural section of the Gaza Strip. *Clean Technologies and Environmental Policy* 6:128-137

Shuping L.S. 2008. Biomonitoring of metal contamination in the lower Diep River, Milnerton, Western Cape. (MTech Dissertation, Cape Peninsula University of Technology), pp. 60-64.

Silva,M.J., Reidy, J.A., Herbert, A.R., Preau, J.L., Needham, L.L. and Calalipid, A.M. 2004. Determination of phthalatemetabolites in human amniotic fluid. *Bulletin of Environmental Contamination and Toxicology* 72: 1226–1231.

Simoes, N.G., Cardoso, V.V., Ferreira, E., Benoliel, M.J. and Almeida, M.M. 2007. Experimental and statistical validation of SPME-GC-MS analysis of phenol and chlorophenols in raw and treated water. *Chemosphere* 68: 501-510

Singh, R.P. and Agrawal, M. 2010. Effect of different sewage sludge applications on growth and yield of *Vigna radiata* L. field crop: metal uptake by plant. *Ecol. Eng.* 36: 969–972.

Singh, K.P, Mohan, D., Singh, V.K. and Malik, A. 2005. Studies on distribution and fractionation of heavy metals in Gomti river sediments—a tributary of the Ganges, India. *Journal of Hydrology* 312: 14–27

Sirivithayapakorn, S. and Thuyviang, K. 2010. Dispersion and ecological risk assessment of Di (2-ethylhexyl) phthalate (DEHP) in the surface waters of Thailand. *Bulletin of Environmental Contamination and Toxicology* 84:503-506.

Sirvent, G., Sanchez, J.M. and Salvado, V. (2004) Preconcentration and determination of priority pollutant phenols in waters at trace levels using a polymeric solid-phase extraction cartridge. *Journal of Separation Science* 27: 1524-1530

Smith, L.A., Means, J.L., Chen, A., Alleman, B., Chapman, C.C. and Tixier, J.S. 1995. Remedial Options for Metals-Contaminated Sites. Boca Raton, FL: Lewis Publishers.

Snyman, R. G., Reinecke, A. J. and Nel, J. A. J. 2002. Uptake and distribution of copper in the freshwater crab, *Potamonautes perlatus* (Crustacea) in the Eerste River, South Africa. *African Zoology* 81–89.

Solomon, G.M. and Schetter, T. 2000. Endocrine disruption and potential health implications. *Environment and Health* 163(11): 1471-1476

Soto, A.M., Sonnenschein, C., Chung, K.L., Fernandez, M.F., Olea, N., Olea-Serrano, M.F. 1995. The E-Screen assay as a tool to identify estrogens, an update on estrogenic environmental pollutants. *Environmental Health Perspective* 103(7): 113-122.

Spinks, A.T., Dunstan, R.H., Harrison, T., Coombes, P. & Kuczera, G. (2006). Thermal inactivation of waterborne pathogenic and indicator bacteria at subboiling temperatures. *Water Research*, **40**, 1326-1332.

Sprynskyy, M., Lebedynets, M., Namiesnik, J. and Buszewski, B. 2007. Phenolics occurrence in surface water of the Dniester river basin (West Ukraine): natural background and industrial pollution. *Environmental Geology* 53:67–75

Suzuki, T., Yaguchi, K. and Suzuki, S. 2001. Monitoring of phthalic acid monoesters in river water by solid-phase extraction and GC–MS determination. *Environmental Science Technology* 35: 3757–3763.

Suliman, F.E.O., Al-Kindi, S.S., Al-kindy, S.M.Z., Al-Lawati, H.A.J. 2006. Analysis of phenols in water by high-performance using -6-sulfonyl chloride as a fluorogenic pre-column. *Journal of Chromatography A* 1101:179-184

Sumpter J.P. 2005. Endocrine disruptor in the aquatic environment: A review. *Acta Hydrochimca et Hydrobiologica* 33 (1) 9-16.

Sun, Q., Deng, S., Huang, J., Shen, G. and Yu, G. 2008. Contributors to estrogenic activity in wastewater from a large waterwater treatment plant in Beijing, China. *Environmental Toxicology and Pharmacology* 25: 20-26.

Sun, W.L., Ni, J.R. and Liu, T.T. 2006. Effect of sediment humic substances on sorption of selected endocrine disruptors. *Water, Air and Soil Pollution* 6:583-591

Swan, S.H. 2008. Environmental phthalate exposure in relation to reproductive outcomes and other health end points in humans. *Environmental Research* 108:177-184.

Szollosi, R., Varga, I.S., Erdei, L. and Mahalik, E. 2009. Cadmium-induced oxidative stress and oxidative mechanisms in germinating Indian mustard *(Brassica junceaL.)* seeds. *Ecotoxicology and Environmental Safety* 72: 1337-1342.

Tan, G.H. 1995. Residue levels of phthalate esters in water and sediment samples from the Klang River basin. *Bulletin of Environmental Contamination and Toxicology* 54: 171–176.

Ternes, T.A., Stumpf, M., Muller, J., Haberer, K., Wilken, R.D. and Servos, M. 1999a. behavior and occurrence of estrogens in municipal sewage treatment plants – I. Investigations in Germany, Canada and Brazil. *Science of the Total Environment* 225: 81-90.

Tolosana, S. and Erhlich, R. 2000. Composition of liquid effluent discharged by medical institutions in Cape Town. *South Africa Journal of Science* 96 (8): 417-420.

Toniolo, R., Pizzariello, A., Susmel, S., Dossi, N., Doherty, A.P. and Bontempelli, G. 2007. An anionic-liquid based probe for sequential preconcentration from headspace and direct voltammetric detection of phenols in wastewater. *Electrolysis* 19 (19-20): 2141-2148

Toppari, J., Larsen, J.C., Christiansen, P., Giwercman, A., Grandjean, P., Guilette, L.J., Jegou, B., Jensen, T.K., Jouannet, P., Keiding, N., Leffers, H., McLachlan, J.A., Meyer, O., Muller, J., Rajpert-De Meyts, E., Scheike, T., Sharpe, R., Sumpter, J., Skakkebaek, N.E. 1996. Male reproductive health and environmental xenoestrogens. *Environmental Health Perspectives.* 104(4):741-803.

Trenholm, R.A., Vanderford, B.J., Holady, J.C., Rexing, D.J. and Snyder, S.A. 2006. Broad range analysis of endocrine disruptors and pharmaceuticals using gas chromatography and liquid chromatography tandem mass spectrometry. *Chemosphere*, 65:1990-1998

US EPA (1989a) *Exposure Factors Handbook.* EPA/600/P-03/002A. National Center for Environmental Assessment, US Environmental Protection Agency. Washington, DC.

United State Environmental Protection Agency (US EPA). 1992. Guidelines for exposure assessment. EPA/600/Z-92/001. Risk assessment forum, US EPA, Washington, DC.

US Environmental Protection Agency (EPA), (1996) Method 8061A: phthalate esters by gas chromatography with electron capture detection (GC/ECD) revision 1, online test for evaluating solid waste physical/chemical methods (SW-846), Office of solid waste, Washington, DC.

US-EPA. (1996). Method 3050B, Acid digestion of sediment sludges and soils. Revision 2, 1-12. United States Environmental Protection Agency.

US EPA. 1997. Guiding Principles for Monte Carlo Analysis. Risk Assessment Forum. US Environmental Protection Agency. Washington, DC.

US EPA. 2001. Risk Assessment Guidance for Superfund: Volume I. Human Health Evaluation Manual (Part D). Publ 285.7–47, US Environmental Protection Agency. Washington, DC.

US EPA 1990. Office of Toxic Substances.Methods of Assessing exposure to Chemical Substances. Vol 8:Methods for Assessing Environmental Pathways of Food Contamination. EPA 560/5-85-008.

Usero, J., Izquierdo, C., Morillo, J. and Gracia, I. 2003. Heavy metals in fish (*Solea vulgaris, Anguilla anguilla* and *Liza aurata*) from salt marshes on the southern Atlantic coast of Spain. *Environment International* 29: 949– 956

Ustun, G.E. 2009. Occurrence and removal of metals in urban wastewater treatment plants. *Journal of Hazardous Materials*, 172: 833-838

Van Aardt, W.J. and Erdmann, R. 2004. Heavy metals (Cd, Pb, Cu, Zn) in mudfish and sediments from three hard-water dams of the Mooi River catchment, South Africa. *Water SA* 30 (2):211-213

Van Den Berg, M., Sanderson, T., Kurihara, N. and Katayam, A. 2003. Role of metabolism in the endocrine-disrupting effects of chemicals in aquatic and terrestrial systems. *Pure and Applied Chemistry* 75: (11-12) 1917-1932.

Van Leeuwen, C.J., Hermens, J.L.M. 1995. Risk assessment of chemicals: an introduction. Kluwer academic publishers, The Netherlands, 374.

Van Wyk, J.H. and Pieterse, G.M. 2008. A histo-morphological study of the testis of sharptooth catfish (*Clarias gariepinus*) as reference for future toxicological assessments. *Journal of Applied Ichthyology* 24: 415 – 422.

Van Wyk, J.H., Pool, E.J. and Leslie, A.J. 2003. The effects of anti-androgenic and estrogenic disrupting cominants on breeding gland (nuptial pad) morphology, plasma testosterone levels, and plasma vitellogenin in male Xenopus laevis (Africa clawed frog). *Archieve of Environmental Contamination Toxicology* 44: 247 – 256.

Vethaak, A.D., Lahr, J., Schrap, S.M., Belfroid, A.C., Rijs, G.B.J., Gerritsen, A., Boer, J.D. Bulder, A.S., Grinwis, G.C.M., Kuiper, R.V., Legler, J., Murk, T.A.J., Peijnenburg, W., Verhaar, H.J.M. and Voog, P.D. 2005. An integrated assessment of estrogenic contamination and biological effects in the aquatic environment of the Netherlands. *Chemosphere* 59: 511–524.

Vidal, J.L., Vega, A.B., Frenich, A.G. Gonzalez, F.J.E. and Liebana, F.J.A. 2004. Determination of fifteen priority phenolic compounds in environmental samples from Andalusia (Spain) by liquid chromatography–mass spectrometry. *Analytical and Bioanalytical Chemistry* 379: 125-130.

Vitali, M. Guidotti, M. Macilenti, G. and Cremisini, C. 1997. Phthalate esters in freshwaters as markers of contamination sources e a site study in Italy. *Environmental International* 23: 337–347.

Vogel, J.M. 2004. Tunnel Vision: The regulation of endocrine disruptors. *Policy Sciences* 37: 277-303.

Vogelsang, C., Grung, M., Jantsch, T.G., Tollefsen, K.E. and Liltved, H. 2006. Occurrence and removal of selected organic micropollutants at mechanical, chemical and advanced wastewater treatment plants in Norway. *Water Research*, 40, 3559-3570.

Voutsa, D., Hartman, P., Schaffner, C. and Giger, W. 2006. Benzotriazoles, Alkylphenols and Bisphenol A in Municipal Wastewaters and in the Glatt River, Switzerland. *Environmental Science and Pollution Research* 13 (5): 333–341.

Waalkes, M.P. 2000. Cadmium carcinogenesis in review. *Journal of Inorganic Biochemistry* 79:241-244.

Wang, D-Z., Jiang, X., Rao, W. and He, J-Z. 2009. Kinetics of soil cadmium under stimulated acid rain. *Ecological complexity* doi.10.1016/j.ecocom.2009.03.010.

Wang, I, Cai Y.Q., He, B., Yuan, C.G., shen, D.Z., Shao J. and Jiang, G.B. 2006. Determination of estrogens in water by Hplc-uv using cloud point extraction. *Talanta* 70: 47-51.

Wang, C., Hu, X., Chen, M. and Wu, Y. 2005. Total concentrations and fractions of Cd, Cr, Pb, Cu, Ni and Zn in sewage sludge from municipal and industrial wastewater treatment plants. *Journal of Harzardous Materials* B119:245-249.

Wang, C., Hu, X., Chen, M. and Wu, Y. 2005. Total concentrations and fractions of Cd, Cr, Pb, Cu, Ni and Zn in sewage sludge from municipal and industrial wastewater treatment plants. *Journal of Hazardous Materials*. 119 (1-3): 245-249

Wang, Q., kim, D., Dionysiou, D.D., Sorial, G.A. and Timberlake, D. 2004. Sources and remediation for mercury contamination in aquatic systems-a literature review. *Environmental Pollution* 131:323-336.

Wang, S. and Mulligan, C.N. 2006. Occurrence of arsenic contamination in Canada: Sources, behavior and distribution. *Science of the Total Environment* 366:701-721.

Wang, S. and Zhao, X., 2009. On the potential of biological treatment of arsenic contaminated soils and groundwater. *Journal of Environmental Management* 90:2367-2376.

Wang, Y., Hu, W., Cao, Z., Fu, X. and Zhu, T. 2005. Occurrence of endocrine-disrupting compounds in reclaimed water from Tiajin, China. Anal. Bioanal Chem 383:857-863.

Wang, J., Huang, C. P., Herber, E. A., Poesponegoro, I., Poesponegoro, H. and Takiyama, L. R. 1999. Effects of dissolved organic matter and pH on heavy metal uptake by sludge particulates exemplified by copper(II) and nickel(II): Three-variable model. *Water Environment Research* 71: 139-147.

Welch, A.H., Westjohn, D.B., Helsel, D.R. and Wanty, R.B. 1996. Arsenic in ground water of the United States: Occurrence and geochemistry. *Ground Water* 38(4): 589-604.

Welch, R.M., Levin, W., Conney, A.H. 1969. Estrogenic properties of DDT and its analogs. *Toxicol. Appl. Pharmacol.* 14:358-367.

Williams, P.R.D. 2004. Health risk communication using comparative risk analyses. *Journal of Exposure Analysis and Environmental Epidemiology* 14: 498-515.

Williams, W., Fordyce, F., Paijitprapapon, A. and Charoenchaisri, P. 1996. Arsenic contamination in surface drainage and groundwater in part of the southeast Asian tin belt, Nakhon Si Thammarat Province, southern Thailand. *Environmental Geology* 27:16–33.

Wong, C.S.C., Duzgore-Aydin, N.S., Aydin, A, and Wong, M.H. 2006. Sources and trends of environmental mercury emissions in Asia. *Science of the Total Environmental* 368: 649-662.

World Health Organization (WHO). 2003. State of the art report: health risks in aquifer recharge using reclaimed water. SDE/WSH/03.08. Geneva.

World Health Organization (WHO). 1984. Guildelines for drinking – Water quality, Vol. 1: Recommendations, WHO, Geneva.

World Health Organization (WHO). 2001. Water Quality: Guidelines, Standards and Health. Edited by Lorna Fewtrell and Jamie Bartram. Published by IWA Publishing, London, UK. ISBN: 1 900222 28 0

World Health Organization (WHO). 2006. Concise International Chemical Assessment Document 70: HEPTACHLOR. World Health Organisation, Geneva, Switzerland.

World Health Organization (WHO). 2010. Human Health Risk Assessment Toolkit

Wu, Y., Xu, Y., Zhang, J. and Hu, S. 2010. Evaluation of ecological risk and primary empirical research on heavy metals in polluted soil over Xiaoqinling gold mining region, Shaanxi, China. *Trans. Nonferrous Met. Soc. China* 20: 688-694.

Xia, Y. and Liu, J. 2004. An overview on chronic arsenism via drinking water in PR China, *Toxicology* 198 (1-3): 25–29

Xue, N and Xu, X. 2006. Composition, Distribution and Characterization of suspected endocrine-disrupting pesticides in Beying GuanTing Reservoir (GTR). *Archieve of Environmental Contamination and Toxicology* 50: 463-473.

Xue, X., Wu, F., Zhang, X. and Deng, N. (2008) Occurrence of endocrine disrupting compounds in rivers and lakes of Wuhan City, China. *Fresenius Environmental Bulletin* 17(2), 203-210.

Yadav, N. and Khandelwal, S. 2009. Therapeutic efficacy of picroliv in chronic cadmium toxicity. *Food and Chemical Toxicology* 47:871-879

Yang, Y., Zang, F-S., Li, H-F. and Jiang, J-Z. 2009. Accumulation of cadmium in the edible parts of six vegetable species grown in Cd-contaminated soils. *Journal of Environmental Management* 90:1117-1122

Yang, Z., Wang, Y., Shen, Z., Niu, J. and Tang, Z. 2009. Distribution and speciation of heavy metals in sediments from the mainstream, tributaries, and lakes of the Yangtze River catchment of Wuhan, China. *Journal of Hazardous Materials* 166: 1186-1194.

Yao, Li-X., Li, G-L., Dang, Z., He, Z-H, Zhou, C-M. and yang, B-M. 2009 Arsenic uptake by two vegetables grown in two soils amended with A-bearing animal manures. *Journal of Hazardous Materials* 164:904-910.

Yılmaz, F., Ozdemir, N., Demirak, A. and Tuna, A.L. 2007. Heavy metal levels in two fish species *Leuciscus cephalus* and *Lepomis gibbosus. Food Chemistry* 100:830–835

Ying, G-G., Kookana, R., and Waite, T.D. 2004. Endocrine disrupting chemicals and pharmaceuticals and personal products (PPCPs) in reclaimed water in Australia. Australia Water Conservation and Research Program Report.

Ying, G.G., Kookana, R.S. and Ru, Y.J. 2002. Occurrence and fate of hormone steroids in the environment, *Environment International* 28: 545–551.

Yuan, B., Li, Z., and Graham, N. 2008. Aqueous oxidation of dimethyl phthalate in a Fe(VI)-TiO_2-UV reaction system. *Water Research* 42: 1413-1420.

Yuan, S.Y., Liu, C., Liao, C.S. and Chang, B.V. 2002. Occurrence and microbial degradation of phthalate esters in Taiwan river sediments. *Chemosphere*, 49, 1295-1299.

Zahir, F., Rizwi, S.J. Haq, S.K. and Khan, H.R. 2005. Low dose mercury toxicity and human health. Environmental Toxicology and Pharmacology 20:351-360.

Zakeri-Milani, P., Barzegar-Jalali, M., Tajerzadeh, H., Azarmi, Y., Valizadeh, H. 2005. Simultaneous determination of naproxen, ketoprofen and phenol red in samples from rat intestinal permeability studies: HPLC method development and validation. *Journal of . Pharmaceutical and BiomedicalAnalysis*. 39: 624-630.

Zala, S.M. and Penn, D. J. 2004. Abnormal behavours induced by chemical pollution: a review of the evidence and new challenges. *Animal Behaviour* 68: 649-664.

Zang, S., Hu, F. and Li, H. 2009. Effects of Earthworms mucus and amino acids on cadmium subcellular distribution and chemicals forms in tomato seedlings. *Bioresource Technology* 100:4041-4046.

Zeng F, Cui K, Xie Z, Liu M, Li Y, Lin Y, Zeng Z and Li F. 2008. Occurrence of phthalate esters in water and sediment of urban lakes in a subtropical city, Guangzhou, South China. *Environment International*, 34(3), 372-380.

Zeng, F., Cui, K., Xie, Z., Wu, L., Luo, D., Chen, L., Lin, Y., Liu, M. and Sun, G. 2009. Distribution of phthalate esters in urban soils of subtropical city, Guangzhou, China. *Journal of Hazardous Materials* 164: 1171-1178

Zeng, X., Jin, T., Zhou, Y and Nordberg, G. F. 2003. Changes of serum sex hormone and MT and mRNA expression in rats orally exposed to cadmium. Toxicology 186: 109-118

Zgheib S, Moilleron R, Saad M and Chebbo G. 2011. Partition of pollution between dissolved and particulate phases: what about emerging substances in urban stormwater catchments? *Water Res*, 45(2): 913-925.

Zhang, Y. Wang, W., Lia, L. Huang, Y. and Cao, J. 2010. Eggshell membrane-based solid-phase extraction combined with hydride generation atomic fluorescence spectrometry for trace arsenic (V) in environmental water samples, *Talanta* 80: 1907–1912.

Zhang, W. And Xu, C. 2009. Calcium sensing receptor and heart diseases. *Pathology.* Doi:10.1016/j.pathophys.2009.02.013.

Zhao, J., Ying, G., Wang, L., Yang, J., Yang, X., Yang, L. and Li, X. 2009. Determination of phenolic endocrine disrupting chemicals and acidic pharmaceuticals in surface water of the Pearl Rivers in south China by gas chromatography –negative chemical ionization-mass spectrometry. *Science of the Total Environment* 407:962-974.

Zhou, F., Li, X. and Zeng, Z. 2005. Determination of phenolic compounds in wastewater samples using a novel fiber by solid-phase microextraction coupled to gas chromatography. *Analytica Chimica Acta* 538: 63-70.

Zuccato, E., Castiglioni, S., Fanelli, R., Reitano, G., Bagnati, R., Chiabrando, C., Pomati, F., Rossetti, C. and Calamari, D. 2006. Pharmaceuticals in the Environment in Italy: Causes, Occurrence, Effects and Control. *Environmental Science and Pollution Research* 13 (1): 15–21.

APPENDIX I

Calibration tables and curves for phenolic congeners using HPLC

Method C:\CHEM32\1\METHODS\LANREFINAL2CALIBRATION.M

Calibration Table

Calib. Data Modified : 24 November 2009 11:22:30

Calculate : External Standard Percent
Based on : Peak Area

Rel. Reference Window : 5.000 %
Abs. Reference Window : 0.000 min
Rel. Non-ref. Window : 5.000 %
Abs. Non-ref. Window : 0.000 min
Use Multiplier & Dilution Factor with ISTDs
Uncalibrated Peaks : not reported
Partial Calibration : Yes, identified peaks are recalibrated
Correct All Ret. Times: No, only for identified peaks

Curve Type : Linear
Origin : Included
Weight : Equal

Recalibration Settings:
Average Response : Average all calibrations
Average Retention Time: Floating Average New 75%

Calibration Report Options :
Printout of recalibrations within a sequence:
Calibration Table after Recalibration
Normal Report after Recalibration
If the sequence is done with bracketing:
Results of first cycle (ending previous bracket)

Signal 1: DAD1 E, Sig=280,16 Ref=360,100

RetTime [min]	Sig	Lvl	Amount [ng/ul]	Area	Amt/Area	Ref	Grp	Name
3.535	1	13	3.00000e-1	1.27313	2.35640e-1			PHENOL
		12	4.00000e-1	3.06020	1.30710e-1			
		11	5.00000e-1	3.59255	1.39177e-1			
		10	1.00000	9.83840	1.01643e-1			
		9	2.50000	24.84568	1.00621e-1			
		8	5.00000	48.75606	1.02551e-1			
		7	7.50000	78.46980	9.55782e-2			
		6	10.00000	104.70651	9.55050e-2			
		5	12.50000	130.15059	9.60426e-2			
		4	15.00000	156.64328	9.57590e-2			
		3	20.00000	203.00449	9.85200e-2			
		2	25.00000	261.02780	9.57752e-2			
		1	30.00000	303.22522	9.89364e-2			
4.695	1	9	2.50000	1.93150	1.29433			4-NITROPHENOL
		8	5.00000	4.03223	1.24001			
		7	7.50000	6.66131	1.12590			
		6	10.00000	8.66928	1.15350			
		5	12.50000	11.45047	1.09166			
		4	15.00000	12.76373	1.17520			
		3	20.00000	16.66200	1.20034			
		2	25.00000	21.25213	1.17635			
		1	30.00000	25.92448	1.15721			
5.833	1	14	2.00000e-1	29.21518	6.84576e-3			2-CHLOROPHENOL
		13	3.00000e-1	45.99628	6.52227e-3			
		12	4.00000e-1	63.26014	6.32310e-3			
		11	5.00000e-1	77.64234	6.43979e-3			
		10	1.00000	178.39645	5.60549e-3			
		9	2.50000	482.34897	5.18297e-3			
		8	5.00000	971.80188	5.14508e-3			
		7	7.50000	1556.46655	4.81861e-3			
		6	10.00000	2077.86011	4.81264e-3			
		5	12.50000	2581.86328	4.84146e-3			
		4	15.00000	3109.48657	4.82395e-3			

Method C:\CHEM32\1\METHODS\LANREFINAL2CALIBRATION.M

RetTime [min]	Sig	Lvl	Amount [ng/ul]	Area	Amt/Area	Ref	Grp	Name
		3	20.00000	4046.50391	4.94254e-3			
		2	25.00000	5151.69043	4.85278e-3			
		1	30.00000	6066.70703	4.94502e-3			
6.416	1	14	2.00000e-1	4.48457	4.45974e-2			2,4-DINITROPHENOL
		13	3.00000e-1	4.16164	7.20869e-2			
		12	4.00000e-1	10.67206	3.74811e-2			
		11	5.00000e-1	10.99498	4.54753e-2			
		10	1.00000	32.44516	3.08212e-2			
		9	2.50000	87.42685	2.85953e-2			
		8	5.00000	177.55466	2.81603e-2			
		7	7.50000	288.13467	2.60295e-2			
		6	10.00000	384.30527	2.60210e-2			
		5	12.50000	472.93323	2.64308e-2			
		4	15.00000	585.11865	2.56358e-2			
		3	20.00000	760.95044	2.62829e-2			
		2	25.00000	969.89105	2.57761e-2			
		1	30.00000	1128.34119	2.65877e-2			
6.712	1	14	2.00000e-1	3.22453	6.20245e-2			2-NITROPHENOL
		13	3.00000e-1	3.89537	7.70145e-2			
		12	4.00000e-1	6.71220	5.95930e-2			
		11	5.00000e-1	7.51152	6.65644e-2			
		10	1.00000	23.68077	4.22284e-2			
		9	2.50000	63.18327	3.95674e-2			
		8	5.00000	130.09628	3.84331e-2			
		7	7.50000	205.66389	3.64673e-2			
		6	10.00000	277.11938	3.60855e-2			
		5	12.50000	345.24149	3.62065e-2			
		4	15.00000	412.92270	3.63264e-2			
		3	20.00000	546.94482	3.65668e-2			
		2	25.00000	675.68127	3.69997e-2			
		1	30.00000	841.02686	3.56707e-2			
7.567	1	14	2.00000e-1	24.22145	8.25715e-3			2,4-DIMETHYLPHENOL
		13	3.00000e-1	43.58943	6.88240e-3			
		12	4.00000e-1	58.69980	6.81433e-3			
		11	5.00000e-1	71.64242	6.97911e-3			
		10	1.00000	162.47198	6.15491e-3			
		9	2.50000	442.25500	5.65285e-3			
		8	5.00000	876.11346	5.70702e-3			
		7	7.50000	1405.61304	5.33575e-3			
		6	10.00000	1875.89832	5.33078e-3			
		5	12.50000	2322.34766	5.38248e-3			
		4	15.00000	2813.52954	5.33138e-3			
		3	20.00000	3672.56372	5.44579e-3			
		2	25.00000	4659.52002	5.36536e-3			
		1	30.00000	5497.34766	5.45718e-3			
8.461	1	13	3.00000e-1	2.85007	1.05260e-1			4-CHLORO,3-METHYLPHENOL
		12	4.00000e-1	3.72131	1.07489e-1			
		11	5.00000e-1	4.46233	1.12049e-1			
		10	1.00000	9.97085	1.00292e-1			
		9	2.50000	26.72554	9.35435e-2			
		8	5.00000	53.43599	9.35699e-2			
		7	7.50000	85.58223	8.76350e-2			
		6	10.00000	114.34470	8.74549e-2			
		5	12.50000	141.50058	8.83389e-2			
		4	15.00000	170.89856	8.77714e-2			
		3	20.00000	223.84312	8.93483e-2			
		2	25.00000	283.47351	8.81917e-2			
		1	30.00000	335.05353	8.95379e-2			
9.118	1	13	3.00000e-1	2.72128	1.10242e-1			2,4-DICHLOROPHENOL
		12	4.00000e-1	4.01107	9.97240e-2			
		11	5.00000e-1	4.93606	1.01295e-1			
		10	1.00000	10.97874	9.10852e-2			
		9	2.50000	28.36415	8.81394e-2			
		8	5.00000	55.66023	8.98307e-2			
		7	7.50000	88.88954	8.43744e-2			
		6	10.00000	118.99547	8.40368e-2			
		5	12.50000	147.55298	8.47153e-2			
		4	15.00000	178.39577	8.40827e-2			
		3	20.00000	232.95610	8.58531e-2			
		2	25.00000	295.90524	8.44865e-2			

Method C:\CHEM32\1\METHODS\LANREFINAL2CALIBRATION.M

RetTime [min]	Sig	Lvl	Amount [ng/ul]	Area	Amt/Area	Ref	Grp	Name
		1	30.00000	350.59695	8.55683e-2			
9.426	1	14	2.00000e-1	7.00243	2.85615e-2			2-METHYL 4,6-DINITROPHENOL
		13	3.00000e-1	11.16360	2.68730e-2			
		12	4.00000e-1	15.50419	2.57995e-2			
		11	5.00000e-1	19.00664	2.63066e-2			
		10	1.00000	43.22135	2.31367e-2			
		9	2.50000	117.25833	2.13204e-2			
		8	5.00000	235.29333	2.12501e-2			
		7	7.50000	377.46155	1.98696e-2			
		6	10.00000	504.84015	1.98083e-2			
		5	12.50000	624.61499	2.00123e-2			
		4	15.00000	755.47754	1.98550e-2			
		3	20.00000	986.18420	2.02802e-2			
		2	25.00000	1251.45142	1.99768e-2			
		1	30.00000	1481.67712	2.02473e-2			
10.738	1	14	2.00000e-1	1.80869	1.10577e-1			2,4,6-TRICHLOROPHENOL
		13	3.00000e-1	2.06894	1.45002e-1			
		12	4.00000e-1	2.82069	1.41809e-1			
		11	5.00000e-1	3.40527	1.46831e-1			
		10	1.00000	7.83456	1.27640e-1			
		9	2.50000	21.56251	1.15942e-1			
		8	5.00000	43.32739	1.15400e-1			
		7	7.50000	69.54494	1.07844e-1			
		6	10.00000	92.32266	1.08316e-1			
		5	12.50000	115.39389	1.08325e-1			
		4	15.00000	139.31300	1.07671e-1			
		3	20.00000	181.60799	1.10127e-1			
		2	25.00000	230.27362	1.08566e-1			
		1	30.00000	273.82190	1.09560e-1			
11.797	1	14	2.00000e-1	7.82766e-1	2.55504e-1			2,4,6-TRIBROMOPHENOL
		13	3.00000e-1	2.03201	1.47637e-1			
		12	4.00000e-1	2.29544	1.74258e-1			
		11	5.00000e-1	2.96988	1.68357e-1			
		10	1.00000	4.84013	2.06606e-1			
		9	2.50000	12.46626	2.00541e-1			
		8	5.00000	24.96464	2.00283e-1			
		7	7.50000	39.82705	1.88314e-1			
		6	10.00000	52.42277	1.90757e-1			
		5	12.50000	65.49405	1.90857e-1			
		4	15.00000	78.75526	1.90463e-1			
		3	20.00000	102.70557	1.94731e-1			
		2	25.00000	130.16373	1.92066e-1			
		1	30.00000	154.07059	1.94716e-1			
13.169	1	13	3.00000e-1	2.27380	1.31938e-1			PENTACHLOROPHENOL
		12	4.00000e-1	1.53219	2.61063e-1			
		11	5.00000e-1	1.86610	2.67938e-1			
		10	1.00000	3.02501	3.30577e-1			
		9	2.50000	7.67109	3.25899e-1			
		8	5.00000	14.98194	3.33735e-1			
		7	7.50000	23.90218	3.13779e-1			
		6	10.00000	31.66340	3.15822e-1			
		5	12.50000	39.79721	3.14092e-1			
		4	15.00000	47.63996	3.14862e-1			
		3	20.00000	62.06618	3.22237e-1			
		2	25.00000	78.86377	3.17002e-1			
		1	30.00000	93.71767	3.20110e-1			

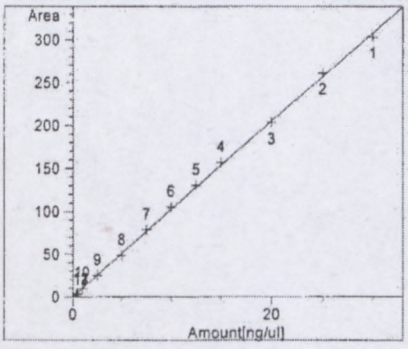
2 Warnings or Errors :

Warning : Overlapping peak time windows at 6.416 min, signal 1
Warning : Overlapping peak time windows at 9.118 min, signal 1

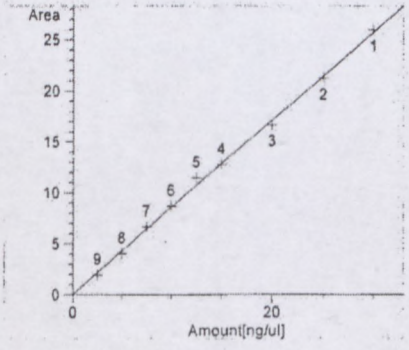
Peak Sum Table

No Entries in table

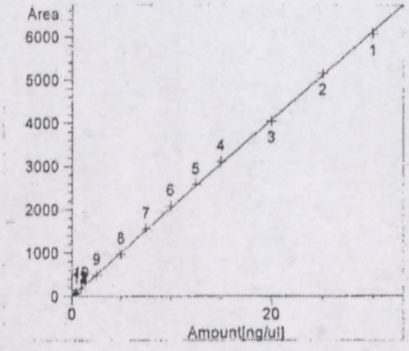
Calibration Curves



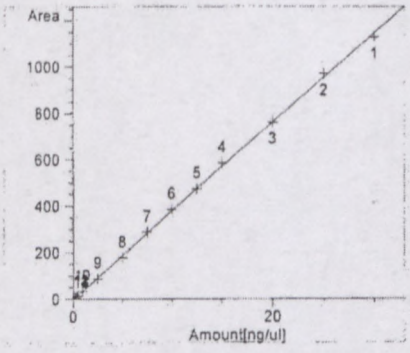
PHENOL at exp. RT: 3.535
DAD1 E, Sig=280,16 Ref=360,100
Correlation: 0.99972
Residual Std. Dev.: 2.53335
Formula: y = mx + b
m: 10.28493
b: -3.82963e-1
x: Amount[ng/ul]
y: Area



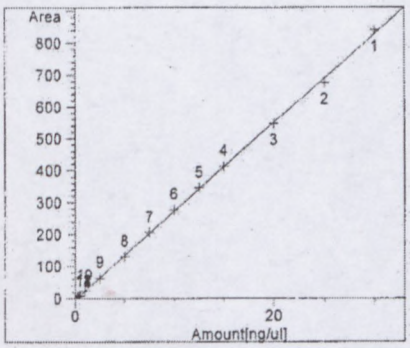
4-NITROPHENOL at exp. RT: 4.695
DAD1 E, Sig=280,16 Ref=360,100
Correlation: 0.99919
Residual Std. Dev.: 0.35872
Formula: y = mx + b
m: 8.57401e-1
b: 2.85376e-3
x: Amount[ng/ul]
y: Area



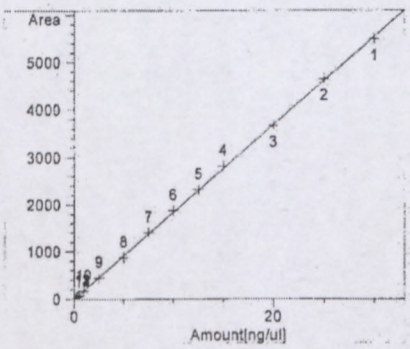
2-CHLOROPHENOL at exp. RT: 5.833
DAD1 E, Sig=280,16 Ref=360,100
Correlation: 0.99986
Residual Std. Dev.: 35.55479
Formula: y = mx + b
m: 204.65811
b: -9.72333
x: Amount[ng/ul]
y: Area



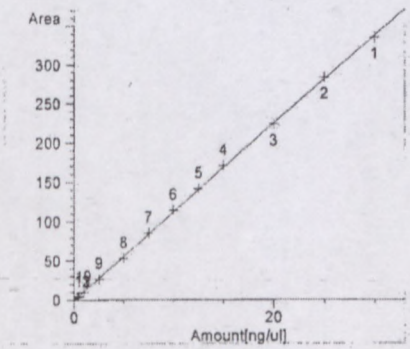
2,4-DINITROPHENOL at exp. RT: 6.416
DAD1 E, Sig=280,16 Ref=360,100
Correlation: 0.99976
Residual Std. Dev.: 8.66689
Formula: y = mx + b
m: 38.36588
b: -4.42091
x: Amount[ng/ul]
y: Area



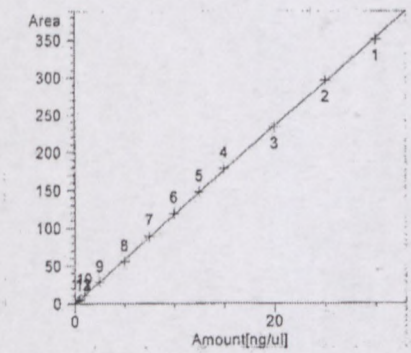
2-NITROPHENOL at exp. RT: 6.712
DAD1 E, Sig=280,16 Ref=360,100
Correlation: 0.99979
Residual Std. Dev.: 5.84146
Formula: y = mx + b
m: 27.76183
b: -4.22382
x: Amount[ng/ul]
y: Area



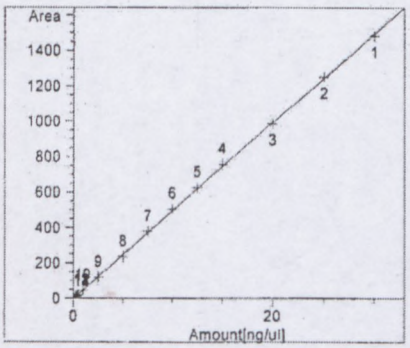
2,4-DIMETHYLPHENOL at exp. RT: 7.567
DAD1 E, Sig=280,16 Ref=360,100
Correlation: 0.99989
Residual Std. Dev.: 28.70786
Formula: y = mx + b
m: 185.29596
b: -9.60877
x: Amount[ng/ul]
y: Area



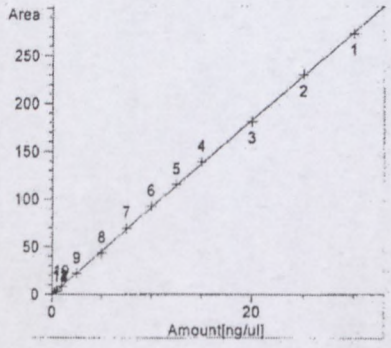
4-CHLORO,3-METHYLPHENOL at exp. RT: 8.461
DAD1 E, Sig=280,16 Ref=360,100
Correlation: 0.99990
Residual Std. Dev.: 1.68960
Formula: y = mx + b
m: 11.28097
b: -5.19919e-1
x: Amount[ng/ul]
y: Area



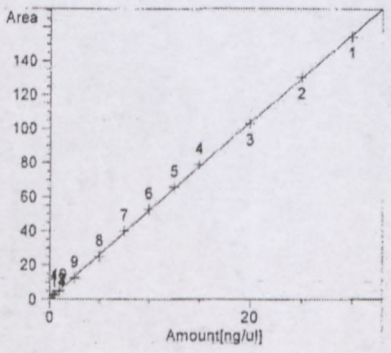
2,4-DICHLOROPHENOL at exp. RT: 9.118
DAD1 E, Sig=280,16 Ref=360,100
Correlation: 0.99991
Residual Std. Dev.: 1.61800
Formula: y = mx + b
m: 11.77682
b: -5.34962e-1
x: Amount[ng/ul]
y: Area



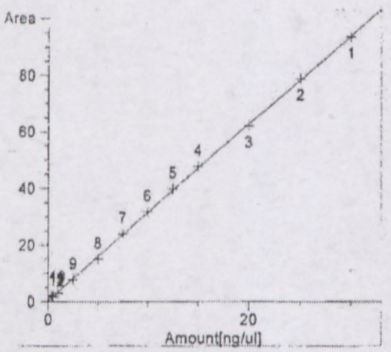
2-METHYL 4,6-DINITROPHENOL at exp. RT: 9.426
DAD1 E, Sig=280,16 Ref=360,100
Correlation: 0.99990
Residual Std. Dev.: 7.25181
Formula: y = mx + b
m: 49.86122
b: -3.12107
x: Amount[ng/ul]
y: Area



2,4,6-TRICHLOROPHENOL at exp. RT: 10.738
DAD1 E, Sig=280,16 Ref=360,100
Correlation: 0.99991
Residual Std. Dev.: 1.23618
Formula: y = mx + b
m: 9.19452
b: -6.17452e-1
x: Amount[ng/ul]
y: Area



2,4,6-TRIBROMOPHENOL at exp. RT: 11.797
DAD1 E, Sig=280,16 Ref=360,100
Correlation: 0.99990
Residual Std. Dev.: 0.75864
Formula: y = mx + b
m: 5.16817
b: 1.62990e-1
x: Amount[ng/ul]
y: Area



PENTACHLOROPHENOL at exp. RT: 13.169
DAD1 E, Sig=280,16 Ref=360,100
Correlation: 0.99985
Residual Std. Dev.: 0.55350
Formula: y = mx + b
m: 3.12495
b: 2.63929e-1
x: Amount[ng/ul]
y: Area

APPENDIX II

Data of risk assessment calculated using tested concentration from environmental samples

Vygekraal River

Calculated Average Daily Dose (ADD)

Chemical / Medium / Scenario	Oral ADD mg/kg/d	Inhalation Concentration mg/cu m	Dermal ADD mg/kg/d
117-81-7 DEHP			
Surface Water			
Drinking Water	0.001699		
Showering		0.62	0.003314
Outdoor Air		0.000977	
Vegetables	0.01771		
Fruits	0.000108		
Fish and Shellfish	0.005228		
Dairy	0.000001		
Meat	0.000001		
TOTALS	0.02474	0.621	0.003314
84-66-2 DIETHYL PHTHALATE			
Surface Water			
Drinking Water	0.006164		
Showering		2.25	0.000538
Outdoor Air		0.003547	
Vegetables	0.000796		
Fruits	0.000136		
Fish and Shellfish	0.01947		
Dairy	Outside Model Bounds		
Meat	Outside Model Bounds		
TOTALS	0.02657	2.254	0.000538
25154-55-6 NITROPHENOL			
Surface Water			
Drinking Water	0.00337		
Showering		Missing Data	0.000007
Outdoor Air		Missing Data	
Vegetables	Missing Data		
Fruits	Missing Data		
Fish and Shellfish	Missing Data		
Dairy	Missing Data		
Meat	Missing Data		
TOTALS	0.00337		0.000007
84-74-2 DIBUTYL PHTHALATE			
Surface Water			
Drinking Water	0		
Showering		0	0
Outdoor Air		0	
Vegetables	0		
Fruits	0		
Fish and Shellfish	0		
Dairy	0		
Meat	0		
TOTALS	0	0	0
95-57-8 CHLOROPHENOL, 2-			
Surface Water			
Drinking Water	0		
Showering		0	0
Outdoor Air		0	
Vegetables	0		
Fruits	0		
Fish and Shellfish	0		
Dairy	Outside Model Bounds		
Meat	Outside Model Bounds		
TOTALS	0	0	0

Calculated Lifetime Average Daily Dose (LADD)

Chemical	Oral	Inhalation	Dermal
Medium	LADD	Adj.Concentration	LADD
Scenario	mg/kg/d	ug/cu m	mg/kg/d
117-81-7 DEHP			
Surface Water			
Drinking Water	0.000728		
Showering		2.294	0.00142
Outdoor Air		0.1007	
Vegetables	0.007589		
Fruits	0.000046		
Fish and Shellfish	0.002241		
Dairy	5.5e-007		
Meat	4.8e-007		
TOTALS	0.0106	2.395	0.00142
84-66-2 DIETHYL PHTHALATE			
Surface Water			
Drinking Water	0.002642		
Showering		8.325	0.000230
Outdoor Air		0.3653	
Vegetables	0.000341		
Fruits	0.000058		
Fish and Shellfish	0.008346		
Dairy	Outside Model Bounds		
Meat	Outside Model Bounds		
TOTALS	0.01139	8.691	0.000230
25154-55-6 NITROPHENOL			
Surface Water			
Drinking Water	0.001444		
Showering		Missing Data	0.000003
Outdoor Air		Missing Data	
Vegetables	Missing Data		
Fruits	Missing Data		
Fish and Shellfish	Missing Data		
Dairy	Missing Data		
Meat	Missing Data		
TOTALS	0.001444		0.000003
84-74-2 DIBUTYL PHTHALATE			
Surface Water			
TOTALS	0	0	0
95-57-8 CHLOROPHENOL, 2-			
Surface Water			
TOTALS	0	0	0

Cancer Risk (Odds): Individual Probability of Getting Cancer from this Exposure Alone

	Oral	**Inhalation**	**Dermal**
117-81-7 DEHP			
Weight of Evidence: B2	Oral Slope (mg/kg/d): 0.014	No Unit Risk	Source: IRIS(05/30/95)
Surface Water			
Drinking Water	1 in 100,000 (1e-005)		
Showering		Missing Unit Risk	2 in 100,000 (2e-005)
Outdoor Air		Missing Unit Risk	
Vegetables	**1 in 10,000 (1e-004)**		
Fruits	< 1 in 1,000,000 (6e-007)		
Fish and Shellfish	3 in 100,000 (3e-005)		
Dairy	< 1 in 1,000,000 (8e-009)		
Meat	< 1 in 1,000,000 (7e-009)		
MEDIUM TOTALS	1 in 10,000 (1e-004)		2 in 100,000 (2e-005)
84-66-2 DIETHYL PHTHALATE			
Weight of Evidence: No Slope		No Unit Risk	Source: IRIS(05/30/95)
25154-55-6 NITROPHENOL			

Weight of Evidence:	No Slope	No Unit Risk	Source: IRIS(05/30/95)
95-57-8 CHLOROPHENOL, 2-			
Weight of Evidence:	No Slope	No Unit Risk	Source: IRIS(05/30/95)

Hazard Quotient: Ratio of Average Dose to 'Safe' Daily Dose

Scenario	Oral	Inhalation	Dermal
117-81-7 DEHP			
	RfD (mg/kg/d):0.02	No RfC	Source: IRIS(05/30/95)
Surface Water			
Drinking Water	0.08493		
Showering		Missing RfC	0.1657
Outdoor Air		Missing RfC	
Vegetables	0.8854		
Fruits	0.00539		
Fish and Shellfish	0.2614		
Dairy	0.000064		
Meat	0.000056		
ALL MEDIA TOTALS	1.237		0.1657

84-66-2 DIETHYL PHTHALATE			
	RfD (mg/kg/d):	0.8 No RfC	Source: IRIS(05/30/95)
Surface Water			
Drinking Water	0.007705		
Showering		Missing RfC	0.000672
Outdoor Air		Missing RfC	
Vegetables	0.000995		
Fruits	0.000170		
Fish and Shellfish	0.02434		
Dairy	Outside Model Bounds		
Meat	Outside Model Bounds		
ALL MEDIA TOTALS	0.03321		0.000672

TOTALS FOR ALL CHEMICALS

	Hazard Quotient	Risk (Odds):Individual Probability of Getting Cancer from this Exposure Alone
Oral	1.27	
Dermal	0.1664	
Surface Water	1.437	
TOTAL		2 in 10,000 (2e-004)

Vygekraal Effluent

Calculated Average Daily Dose (ADD)

Chemical Medium Scenario	Oral ADD mg/kg/d	Inhalation Concentration mg/cu m	Dermal ADD mg/kg/d
117-81-7 DEHP			
Surface Water			
Drinking Water	0.000548		
Showering		0.2	0.001069
Outdoor Air		0.000315	
Vegetables	0.005712		
Fruits	0.000035		
Fish and Shellfish	0.001687		
Dairy	4.1e-007		
Meat	3.6e-007		
Swimming	7.4e-007		0.000079
TOTALS	0.007983	0.2003	0.001147

84-66-2 DIETHYL PHTHALATE			
Surface Water			
Drinking Water	0.003781		
Showering		1.38	0.000330
Outdoor Air		0.002176	
Vegetables	0.000488		
Fruits	0.000083		

Fish and Shellfish	0.01194		
Dairy	Outside Model Bounds		
Meat	Outside Model Bounds		
Swimming	0.000005		0.000024
TOTALS	0.0163	1.382	0.000354

25154-55-6 NITROPHENOL

Surface Water			
Drinking Water	0.00126		
Showering	Missing Data		0.000003
Swimming	0.000002		7.1e-007
TOTALS	0.001262		0.000003

95-57-8 CHLOROPHENOL, 2-

Surface Water			
TOTALS	0	0	0

84-74-2 DIBUTYL PHTHALATE

Surface Water			
Drinking Water	0.000575		
Showering		0.21	0.000511
Outdoor Air	0.000331		
Vegetables	0.002314		
Fruits	0.000026		
Fish and Shellfish	0.000325		
Dairy	2.3e-007		
Meat	2.0e-007		
Swimming	7.8e-007		0.000038
TOTALS	0.003242	0.2103	0.000549

Calculated Lifetime Average Daily Dose (LADD)

	Oral LADD mg/kg/d	Inhalation Adj.Concentration ug/cu m	Dermal LADD mg/kg/d
117-81-7 DEHP			
Surface Water			
Drinking Water	0.000235		
Showering		0.74	0.000458
Outdoor Air		0.03247	
Vegetables	0.002448		
Fruits	0.000015		
Fish and Shellfish	0.000723		
Dairy	1.8e-007		
Meat	1.5e-007		
Swimming	3.2e-00	7	0.000034
TOTALS	0.003421	0.7725	0.000492
84-66-2 DIETHYL PHTHALATE			
Surface Water			
Drinking Water	0.00162		
Showering		5.106	0.000141
Outdoor Air		0.2241	
Vegetables	0.000209		
Fruits	0.000036		
Fish and Shellfish	0.005119		
Dairy	Outside Model Bounds		
Meat	Outside Model Bounds		
Swimming	0.000002		0.000010
TOTALS	0.006986	5.33	0.000152
25154-55-6 NITROPHENOL			
Surface Water			
Drinking Water	0.000540		
Showering		Missing Data	0.000001
Outdoor Air		Missing Data	
Vegetables	Missing Data		

Fruits	Missing Data			
Fish and Shellfish	Missing Data			
Dairy	Missing Data			
Meat	Missing Data			
Swimming	7.3e-007			3.0e-007
TOTALS	0.000541			0.000001

95-57-8 CHLOROPHENOL, 2-			
TOTALS	0	0	0

84-74-2 DIBUTYL PHTHALATE				
Surface Water				
Drinking Water	0.000247			
Showering		0.777		0.000219
Outdoor Air		0.0341		
Vegetables	0.000992			
Fruits	0.000011			
Fish and Shellfish	0.000139			
Dairy	1.0e-007			
Meat	8.7e-008			
Swimming	3.3e-007			0.000016
TOTALS	0.001389	0.8111		0.000235

Cancer Risk (Odds): Individual Probability of Getting Cancer from this Exposure Alone

	Oral	**Inhalation**	**Dermal**
117-81-7 DEHP			
Weight of Evidence: B2	Oral Slope (mg/kg/d): 0.014	No Unit Risk	Source: IRIS(05/30/95)
Surface Water			
Drinking Water	3 in 1,000,000 (3e-006)		
Showering	Missing Unit Risk		6 in 1,000,000 (6e-006)
Outdoor Air	Missing Unit Risk		
Vegetables	**3 in 100,000 (3e-005)**		
Fruits	< 1 in 1,000,000 (2e-007)		
Fish and Shellfish	1 in 100,000 (1e-005)		
Dairy	< 1 in 1,000,000 (2e-009)		
Meat	< 1 in 1,000,000 (2e-009)		
Swimming	< 1 in 1,000,000 (4e-009)		< 1 in 1,000,000 (5e-007)
MEDIA TOTALS	**5 in 100,000 (5e-005)**		7 in 1,000,000 (7e-006)

84-66-2 DIETHYL PHTHALATE			
Weight of Evidence:	No Slope	No Unit Risk	Source: IRIS(05/30/95)
Surface Water			
ALL MEDIA TOTALS			

25154-55-6 NITROPHENOL			
Weight of Evidence:	No Slope	No Unit Risk	Source: IRIS(05/30/95)
Surface Water			
Drinking Water	Missing Slope		

95-57-8 CHLOROPHENOL, 2-			
Weight of Evidence:	No Slope	No Unit Risk	Source: IRIS(05/30/95)
Surface Water			

84-74-2 DIBUTYL PHTHALATE			
Weight of Evidence:	No Slope	No Unit Risk	Source: IRIS(05/30/95)

Hazard Quotient: Ratio of Average Dose to 'Safe' Daily Dose

Scenario	Oral	Inhalation	Dermal
117-81-7 DEHP			
RfD (mg/kg/d):	0.02	No RfC	Source: IRIS(05/30/95)
Surface Water			
Drinking Water	0.0274		
Showering		Missing RfC	0.05345
Outdoor Air		Missing RfC	
Vegetables	0.2856		
Fruits	0.001739		
Fish and Shellfish	0.08433		
Dairy	0.000021		
Meat	0.000018		
Swimming	0.000037		0.003927
ALL MEDIA TOTALS	0.3991		0.05737
84-66-2 DIETHYL PHTHALATE			
RfD (mg/kg/d):	0.8	No RfC	Source: IRIS(05/30/95)
Surface Water			
Drinking Water	0.004726		
Showering		Missing RfC	0.000412
Outdoor Air		Missing RfC	
Vegetables	0.000610		
Fruits	0.000104		
Fish and Shellfish	0.01493		
Dairy	Outside Model Bounds		
Meat	Outside Model Bounds		
Swimming	0.000006		0.000030
ALL MEDIA TOTALS	0.02038		0.000442
25154-55-6 NITROPHENOL			
No RfD		No RfC	Source: IRIS(05/30/95)
95-57-8 CHLOROPHENOL, 2-			
RfD (mg/kg/d):	0.005	No RfC	Source: IRIS(05/30/95)
Surface Water			
ALL MEDIA TOTALS	0		0
84-74-2 DIBUTYL PHTHALATE			
RfD (mg/kg/d):	0.1	No RfC	Source: IRIS(05/30/95)
Surface Water			
Drinking Water	0.005753		
Showering		Missing RfC	0.005111
Outdoor Air		Missing RfC	
Vegetables	0.02314		
Fruits	0.000263		
Fish and Shellfish	0.003245		
Dairy	0.000002		
Meat	0.000002		
Swimming	0.000008		0.000376
ALL MEDIA TOTALS	0.03242		0.005487

TOTALS FOR ALL CHEMICALS

	Hazard Quotient	Risk (Odds):Individual Probability of Getting Cancer from this Exposure Alone
Oral	0.4519	
Dermal	0.0633	
Surface Water	0.5152	
TOTAL		5 in 100,000 (5e-005)

Kuils River Effluent

Calculated Average Daily Dose

Chemical Medium Scenario	Oral ADD mg/kg/d	Inhalation Concentration mg/cu m	Dermal ADD mg/kg/d
117-81-7 DEHP			
Surface Water			
Drinking Water	0.000548		
Showering		0.2	0.001069
Outdoor Air		0.000315	
Vegetables	0.005712		
Fruits	0.000035		
Fish and Shellfish	0.001687		
Dairy	4.1e-007		
Meat	3.6e-007		
TOTALS	0.007982	0.2003	0.001069
84-66-2 DIETHYL PHTHALATE			
Surface Water			
Drinking Water	0.01019		
Showering		3.72	0.000889
Outdoor Air		0.005865	
Vegetables	0.001316		
Fruits	0.000224		
Fish and Shellfish	0.0322		
Dairy	Outside Model Bounds		
Meat	Outside Model Bounds		
TOTALS	0.04393	3.726	0.000889
25154-55-6 NITROPHENOL			
Surface Water			
Drinking Water	0.002384		
Showering		Missing Data	0.000005
Outdoor Air		Missing Data	
Vegetables	Missing Data		
Fruits	Missing Data		
Fish and Shellfish	Missing Data		
Dairy	Missing Data		
Meat	Missing Data		
TOTALS	0.002384		0.000005
84-74-2 DIBUTYL PHTHALATE			
Surface Water			
Drinking Water	0.0777		
Showering		28.360	0.06903
Outdoor Air		0.04471	
Vegetables	0.3125		
Fruits	0.003546		
Fish and Shellfish	0.04382		
Dairy	0.000031		
Meat	0.000027		
TOTALS	0.4377	28.40	0.06903
95-57-8 CHLOROPHENOL, 2-			
Surface Water			
Drinking Water	0.002575		
Showering		0.94	0.000267
Outdoor Air		0.001482	
Vegetables	0.000228		
Fruits	0.000055		
Fish and Shellfish	0.001408		
Dairy	Outside Model Bounds		
Meat	Outside Model Bounds		
TOTALS	0.004266	0.9415	0.000267

Calculated Lifetime average daily dose

Chemical	Oral	Inhalation	Dermal
Medium	LADD	Adj.Concentration	LADD
Scenario	mg/kg/d	ug/cu m	mg/kg/d
117-81-7 DEHP			
Surface Water			
Drinking Water	0.000235		
Showering		0.74	0.000458
Outdoor Air		0.03247	
Vegetables	0.002448		
Fruits	0.000015		
Fish and Shellfish	0.000723		
Dairy	1.8e-007		
Meat	1.5e-007		
TOTALS	0.003421	0.7725	0.000458
84-66-2 DIETHYL PHTHALATE			
Surface Water			
Drinking Water	0.004368		
Showering		13.764	0.000381
Outdoor Air		0.604	
Vegetables	0.000564		
Fruits	0.000096		
Fish and Shellfish	0.0138		
Dairy	Outside Model Bounds		
Meat	Outside Model Bounds		
TOTALS	0.01883	14.368	0.000381
25154-55-6 NITROPHENOL			
Surface Water			
Drinking Water	0.001022		
Showering		Missing Data	0.000002
Outdoor Air	Missing Data		
Vegetables	Missing Data		
Fruits	Missing Data		
Fish and Shellfish	Missing Data		
Dairy	Missing Data		
Meat	Missing Data		
TOTALS	0.001022		0.000002
84-74-2 DIBUTYL PHTHALATE			
Surface Water			
Drinking Water	0.0333		
Showering		104.935	0.02958
Outdoor Air		4.605	
Vegetables	0.1339		
Fruits	0.00152		
Fish and Shellfish	0.01878		
Dairy	0.000013		
Meat	0.000012		
TOTALS	0.1876	109.540	0.02958
95-57-8 CHLOROPHENOL, 2-			
Surface Water			
Drinking Water	0.001104		
Showering		3.478	0.000114
Outdoor Air		0.1526	
Vegetables	0.000098		
Fruits	0.000024		
Fish and Shellfish	0.000603		
Dairy	Outside Model Bounds		
Meat	Outside Model Bounds		
TOTALS	0.001828	3.631	0.000114

Cancer Risk (Odds): Individual Probability of Getting Cancer from this Exposure Alone

Scenario	Oral	Inhalation	Dermal

117-81-7 DEHP

Weight of Evidence: B2	Oral Slope (mg/kg/d): 0.014	No Unit Risk	Source: IRIS(05/30/95)
Surface Water			
Drinking Water	3 in 1,000,000 (3e-006)		
Showering		Missing Unit Risk	6 in 1,000,000 (6e-006)
Outdoor Air		Missing Unit Risk	
Vegetables	**3 in 100,000 (3e-005)**		
Fruits	< 1 in 1,000,000 (2e-007)		
Fish and Shellfish	1 in 100,000 (1e-005)		
Dairy	< 1 in 1,000,000 (2e-009)		
Meat	< 1 in 1,000,000 (2e-009)		
MEDIUM TOTALS	**5 in 100,000 (5e-005)**		6 in 1,000,000 (6e-006)

84-66-2 DIETHYL PHTHALATE

Weight of Evidence:	No Slope	No Unit Risk	Source: IRIS(05/30/95)

25154-55-6 NITROPHENOL

Weight of Evidence:	No Slope	No Unit Risk	Source: IRIS(05/30/95)

84-74-2 DIBUTYL PHTHALATE

Weight of Evidence:	No Slope	No Unit Risk	Source: IRIS(05/30/95)

95-57-8 CHLOROPHENOL, 2-

Weight of Evidence:	No Slope	No Unit Risk	Source: IRIS(05/30/95)

Hazard Quotient: Ratio of Average Dose to 'Safe' Daily Dose

Scenario	Oral	Inhalation	Dermal

117-81-7 DEHP

RfD (mg/kg/d):	0.02	No RfC	Source: IRIS(05/30/95)
Surface Water			
Drinking Water	0.0274		
Showering		Missing RfC	0.05345
Outdoor Air		Missing RfC	
Vegetables	0.2856		
Fruits	0.001739		
Fish and Shellfish	0.08433		
Dairy	0.000021		
Meat	0.000018		
MEDIUM TOTALS	0.3991		0.05345

84-66-2 DIETHYL PHTHALATE

RfD (mg/kg/d):	0.8	No RfC	Source: IRIS(05/30/95)
Surface Water			
Drinking Water	0.01274		
Showering		Missing RfC	0.001111
Outdoor Air		Missing RfC	
Vegetables	0.001646		
Fruits	0.000281		
Fish and Shellfish	0.04024		
Dairy	Outside Model Bounds		
Meat	Outside Model Bounds		
MEDIUM TOTALS	0.05491		0.001111

25154-55-6 NITROPHENOL

No RfD	No RfC	Source: IRIS(05/30/95)

84-74-2 DIBUTYL PHTHALATE

RfD (mg/kg/d):	0.1	No RfC	Source: IRIS(05/30/95)
Surface Water			
Drinking Water	0.777		
Showering		Missing RfC	0.6903
Outdoor Air		Missing RfC	
Vegetables	**3.125**		
Fruits	0.03546		
Fish and Shellfish	0.4382		
Dairy	0.000314		
Meat	0.000275		
MEDIUM TOTALS	**4.377**		0.6903

95-57-8 CHLOROPHENOL, 2-

RfD (mg/kg/d): 0.005	No RfC		
Surface Water			
Drinking Water	0.5151		
Showering		Missing RfC	0.05342
Outdoor Air		Missing RfC	
Vegetables	0.04554		
Fruits	0.01097		
Fish and Shellfish	0.2815		
Dairy	Outside Model Bounds		
Meat	Outside Model Bounds		
MEDIUM TOTALS	0.8531		0.05342

TOTALS FOR ALL CHEMICALS

	Hazard Quotient	Risk (Odds):Individual Probability of Getting Cancer from this Exposure Alone
Oral	**5.684**	
Dermal	0.7983	
	6.482	
TOTAL		5 in 100,000 (5e-005)

Kuils River - River water

Calculated Average Daily Dose (ADD)

Chemical Medium Scenario	Oral ADD mg/kg/d	Inhalation Concentration mg/cu m	Dermal ADD mg/kg/d
117-81-7 DEHP			
Surface Water			
TOTALS	0	0	0
84-66-2 DIETHYL PHTHALATE			
Surface Water			
Drinking Water	0.001863		
Showering		0.68	0.000162
Outdoor Air		0.001072	
Vegetables	0.000241		
Fruits	0.000041		
Fish and Shellfish	0.005885		
Dairy	Outside Model Bounds		
Meat	Outside Model Bounds		
TOTALS	0.00803	0.6811	0.000162
25154-55-6 NITROPHENOL			
Surface Water			
Drinking Water	0.004		
Showering		Missing Data	0.000008
Outdoor Air		Missing Data	
Vegetables	Missing Data		
Fruits	Missing Data		
Fish and Shellfish	Missing Data		
Dairy	Missing Data		
Meat	Missing Data		
TOTALS	0.004		0.000008
84-74-2 DIBUTYL PHTHALATE			
Surface Water			
Drinking Water	0.07074		
Showering		25.820	0.06285
Outdoor Air		0.04071	
Vegetables	0.2845		
Fruits	0.003229		
Fish and Shellfish	0.0399		
Dairy	0.000029		
Meat	0.000025		
TOTALS	0.3985	25.861	0.06285

95-57-8 CHLOROPHENOL, 2-			
Surface Water			
Drinking Water	0.003041		
Showering		1.11	0.000315
Outdoor Air		0.00175	
Vegetables	0.000269		
Fruits	0.000065		
Fish and Shellfish	0.001662		
Dairy	Outside Model Bounds		
Meat	Outside Model Bounds		
TOTALS	0.005037	1.112	0.000315

Calculated Lifetime Average Dose (LADD)

Chemical	Oral	Inhalation	Dermal
Medium	LADD	Adj.Concentration	LADD
Scenario	mg/kg/d	ug/cu m	mg/kg/d
117-81-7 DEHP			
Surface Water			
TOTALS	0	0	0
84-66-2 DIETHYL PHTHALATE			
Surface Water			
Drinking Water	0.000798		
Showering		2.516	0.000070
Outdoor Air		0.1104	
Vegetables	0.000103		
Fruits	0.000018		
Fish and Shellfish	0.002522		
Dairy	Outside Model Bounds		
Meat	Outside Model Bounds		
TOTALS	0.003441	2.626	0.000070
25154-55-6 NITROPHENOL			
Surface Water			
Drinking Water	0.001714		
Showering		Missing Data	0.000004
Outdoor Air		Missing Data	
Vegetables	Missing Data		
Fruits	Missing Data		
Fish and Shellfish	Missing Data		
Dairy	Missing Data		
Meat	Missing D	ata	
TOTALS	0.001714		0.000004
84-74-2 DIBUTYL PHTHALATE			
Surface Water			
Drinking Water	0.03032		
Showering		95.537	0.02693
Outdoor Air		4.192	
Vegetables	0.1219		
Fruits	0.001384		
Fish and Shellfish	0.0171		
Dairy	0.000012		
Meat	0.000011		
TOTALS	0.1708	99.729	0.02693
95-57-8 CHLOROPHENOL, 2-			
Surface Water			
Drinking Water	0.001303		
Showering		4.107	0.000135
Outdoor Air		0.1802	
Vegetables	0.000115		
Fruits	0.000028		
Fish and Shellfish	0.000712		
Dairy	Outside Model Bounds		
Meat	Outside Model Bounds		
TOTALS	0.002159	4.287	0.000135

Cancer risks (Odds): Individual Probability of Getting Cancer from this Exposure Alone

Scenario	Oral	Inhalation	Dermal
117-81-7 DEHP			
Weight of Evidence: B2	Oral Slope (mg/kg/d):	0.014 No Unit Risk	Source: IRIS(05/30/95)
Surface Water			
Drinking Water	0 in 1 (0e+000)		
Showering		Missing Unit Risk	0 in 1 (0e+000)
Outdoor Air		Missing Unit Risk	
Vegetables	0 in 1 (0e+000)		
Fruits	0 in 1 (0e+000)		
Fish and Shellfish	0 in 1 (0e+000)		
Dairy	0 in 1 (0e+000)		
Meat	0 in 1 (0e+000)		
MEDIUM TOTALS	0 in 1 (0e+000)		0 in 1 (0e+000)
84-66-2 DIETHYL PHTHALATE			
Weight of Evidence:	No Slope	No Unit Risk	Source: IRIS(05/30/95)
25154-55-6 NITROPHENOL			
Weight of Evidence:	No Slope	No Unit Risk	Source: IRIS(05/30/95)
84-74-2 DIBUTYL PHTHALATE			
Weight of Evidence:	No Slope	No Unit Risk	Source: IRIS(05/30/95)
95-57-8 CHLOROPHENOL, 2-			
Weight of Evidence:	No Slope	No Unit Risk	Source: IRIS(05/30/95)

Hazard Quotient: Ratio of Average Dose to 'Safe' Daily Dose

Scenario	Oral	Inhalation	Dermal
117-81-7 DEHP			
RfD (mg/kg/d):	0.02	No RfC	Source: IRIS(05/30/95)
Surface Water			
Drinking Water	0		
Showering		Missing RfC	0
Outdoor Air		Missing RfC	
Vegetables	0		
Fruits	0		
Fish and Shellfish	0		
Dairy	0		
Meat	0		
MEDIUM TOTALS		0	0
84-66-2 DIETHYL PHTHALATE			
RfD (mg/kg/d):	0.8	No RfC	Source: IRIS(05/30/95)
Surface Water			
Drinking Water	0.002329		
Showering		Missing RfC	0.000203
Outdoor Air		Missing RfC	
Vegetables	0.000301		
Fruits	0.000051		
Fish and Shellfish	0.007357		
Dairy	Outside Model Bounds		
Meat	Outside Model Bounds		
MEDIUM TOTALS	0.01004		0.000203
25154-55-6 NITROPHENOL			
No RfD		No RfC	Source: IRIS(05/30/95)
Missing data			
84-74-2 DIBUTYL PHTHALATE			
RfD (mg/kg/d):	0.1	No RfC	Source: IRIS(05/30/95)
Surface Water			
Drinking Water	0.7074		
Showering		Missing RfC	0.6285
Outdoor Air		Missing RfC	
Vegetables	**2.845**		
Fruits	0.03229		
Fish and Shellfish	0.399		
Dairy	0.000286		
Meat	0.000250		

MEDIUM TOTALS	**3.985**		0.6285

95-57-8 CHLOROPHENOL, 2-

RfD (mg/kg/d): 0.005 No RfC Source: IRIS(05/30/95)

Surface Water			
Drinking Water	0.6082		
Showering		Missing RfC	0.06308
Outdoor Air		Missing RfC	
Vegetables	0.05377		
Fruits	0.01296		
Fish and Shellfish	0.3324		
Dairy	Outside Model Bounds		
Meat	Outside Model Bounds		
MEDIUM TOTALS	1.007		0.06308

TOTALS FOR ALL CHEMICALS

	Hazard Quotient	Risk (Odds):Individual Probability of Getting Cancer from this Exposure Alone
Oral	5.002	
Dermal	0.6917	
Surface Water	**5.694**	
TOTAL		0 in 1 (0e+000)

Mosselbank River

Calculated Average Daily Dose (ADD)

Scenario	Oral ADD mg/kg/d	Inhalation Concentration mg/cu m	Dermal ADD mg/kg/d
117-81-7 DEHP			
Surface Water			
Drinking Water	0.004164		
Showering		1.52	0.008124
Outdoor Air		0.002396	
Vegetables	0.04341		
Fruits	0.000264		
Fish and Shellfish	0.01282		
Dairy	0.000003		
Meat	0.000003		
TOTALS	0.06066	1.522	0.008124
84-66-2 DIETHYL PHTHALATE			
Surface Water			
Drinking Water	0.000411		
Showering		0.15	0.000036
Outdoor Air		0.000236	
Vegetables	0.000053		
Fruits	0.000009		
Fish and Shellfish	0.001298		
Dairy	Outside Model Bounds		
Meat	Outside Model Bounds		
TOTALS	0.001771	0.1502	0.000036
25154-55-6 NITROPHENOL			
Surface Water			
TOTALS	0	0	
84-74-2 DIBUTYL PHTHALATE			
Surface Water			
Drinking Water	0.07		
Showering		25.550	0.06219
Outdoor Air		0.04028	
Vegetables	0.2816		
Fruits	0.003195		
Fish and Shellfish	0.03948		
Dairy	0.000028		
Meat	0.000025		

TOTALS	0.3943	25.590	0.06219
95-57-8 CHLOROPHENOL, 2-			
Surface Water			
Drinking Water	0.000795		
Showering		0.29	0.000082
Outdoor Air		0.000457	
Vegetables	0.000070		
Fruits	0.000017		
Fish and Shellfish	0.000434		
Dairy	Outside Model Bounds		
Meat	Outside Model Bounds		
TOTALS	0.001316	0.2905	0.000082

Calculated Lifetime Average Daily Dose (LADD)

	Oral LADD mg/kg/d	Inhalation Adj.Concentration ug/cu m	Dermal LADD mg/kg/d
117-81-7 DEHP			
Surface Water			
Drinking Water	0.001785		
Showering		5.624	0.003482
Outdoor Air		0.2468	
Vegetables	0.01861		
Fruits	0.000113		
Fish and Shellfish	0.005493		
Dairy	0.000001		
Meat	0.000001		
TOTALS	0.026	5.871	0.003482
84-66-2 DIETHYL PHTHALATE			
Surface Water			
Drinking Water	0.000176		
Showering		0.555	0.000015
Outdoor Air		0.02435	
Vegetables	0.000023		
Fruits	0.000004		
Fish and Shellfish	0.000556		
Dairy	Outside Model Bounds		
Meat	Outside Model Bounds		
TOTALS	0.000759	0.5794	0.000015
25154-55-6 NITROPHENOL			
TOTALS	0		0
84-74-2 DIBUTYL PHTHALATE			
Surface Water			
Drinking Water	0.03		
Showering		94.538	0.02665
Outdoor Air		4.148	
Vegetables	0.1207		
Fruits	0.001369		
Fish and Shellfish	0.01692		
Dairy	0.000012		
Meat	0.000011		
TOTALS	0.169	98.686	0.02665
95-57-8 CHLOROPHENOL, 2-			
Surface Water			
Drinking Water	0.000341		
Showering		1.073	0.000035
Outdoor Air		0.04708	
Vegetables	0.000030		
Fruits	0.000007		
Fish and Shellfish	0.000186		
Dairy	Outside Model Bounds		
Meat	Outside Model Bounds		

TOTALS	0.000564	1.12	0.000035

Cancer Risk (Odds): Individual Probability of Getting Cancer from this Exposure Alone

	Oral	Inhalation	Dermal
117-81-7 DEHP			
Weight of Evidence: B2	Oral Slope (mg/kg/d): 0.014	No Unit Risk	Source: IRIS(05/30/95)
Surface Water			
Drinking Water	2 in 100,000 (2e-005)		
Showering		Missing Unit Risk	5 in 100,000 (5e-005)
Outdoor Air		Missing Unit Risk	
Vegetables	**3 in 10,000 (3e-004)**		
Fruits	2 in 1,000,000 (2e-006)		
Fish and Shellfish	**8 in 100,000 (8e-005)**		
Dairy	< 1 in 1,000,000 (2e-008)		
Meat	< 1 in 1,000,000 (2e-008)		
MEDIUM TOTALS	**4 in 10,000 (4e-004)**		5 in 100,000 (5e-005)

84-66-2 DIETHYL PHTHALATE			
Weight of Evidence:	No Slope	No Unit Risk	Source: IRIS(05/30/95)
25154-55-6 NITROPHENOL			
Weight of Evidence:	No Slope	No Unit Risk	Source: IRIS(05/30/95)
84-74-2 DIBUTYL PHTHALATE			
Weight of Evidence:	No Slope	No Unit Risk	Source: IRIS(05/30/95)
95-57-8 CHLOROPHENOL, 2-			
Weight of Evidence:	No Slope	No Unit Risk	Source: IRIS(05/30/95)

Hazard Quotient: Ratio of Average Dose to 'Safe' Daily Dose

	Oral	Inhalation	Dermal
117-81-7 DEHP			
RfD (mg/kg/d):	0.02	No RfC	Source: IRIS(05/30/95)
Surface Water			
Drinking Water	0.2082		
Showering		Missing RfC	0.4062
Outdoor Air		Missing RfC	
Vegetables	**2.171**		
Fruits	0.01321		
Fish and Shellfish	**0.6409**		
Dairy	0.000157		
Meat	0.000137		
MEDIUM TOTALS	**3.033**		0.4062

84-66-2 DIETHYL PHTHALATE			
RfD (mg/kg/d):	0.8	No RfC	Source: IRIS(05/30/95)
Surface Water			
Drinking Water	0.000514		
Showering		Missing RfC	0.000045
Outdoor Air		Missing RfC	
Vegetables	0.000066		
Fruits	0.000011		
Fish and Shellfish	0.001623		
Dairy	Outside Model Bounds		
Meat	Outside Model Bounds		
MEDIUM TOTALS	0.002214		0.000045

25154-55-6 NITROPHENOL			
No RfD		No RfC	Source: IRIS(05/30/95)

84-74-2 DIBUTYL PHTHALATE			
RfD (mg/kg/d):	0.1	No RfC	Source: IRIS(05/30/95)
Surface Water			
Drinking Water	0.7		
Showering		Missing RfC	0.6219
Outdoor Air		Missing RfC	
Vegetables	**2.816**		
Fruits	0.03195		
Fish and Shellfish	0.3948		

Dairy	0.000283			
Meat	0.000247			
MEDIUM TOTALS	**3.943**			0.6219

95-57-8 CHLOROPHENOL, 2-

RfD (mg/kg/d): 0.005 No RfC Source: IRIS(05/30/95)

Surface Water			
Drinking Water	0.1589		
Showering		Missing RfC	0.01648
Outdoor Air		Missing RfC	
Vegetables	0.01405		
Fruits	0.003385		
Fish and Shellfish	0.08685		
Dairy	Outside Model Bounds		
Meat	Outside Model Bounds		
MEDIUM TOTALS	0.2632		0.01648

TOTALS FOR ALL CHEMICALS

	Hazard Quotient	Risk (Odds):Individual Probability of Getting Cancer from this Exposure Alone
Oral	**7.242**	
Dermal	1.045	
Surface Water	**8.286**	
TOTAL		4 in 10,000 (4e-004)

Mosselbank Effluent

Calculated Average Daily Dose (ADD)

Medium / Scenario	Oral ADD mg/kg/d	Inhalation Concentration mg/cu m	Dermal ADD mg/kg/d
117-81-7 DEHP			
Surface Water			
Drinking Water	0.002219		
Showering		0.81	0.004329
Outdoor Air		0.001277	
Vegetables	0.02313		
Fruits	0.000141		
Fish and Shellfish	0.006831		
Dairy	0.000002		
Meat	0.000001		
TOTALS	0.03233	0.8113	0.004329
84-66-2 DIETHYL PHTHALATE			
Surface Water			
Drinking Water	0.000877		
Showering		0.32	0.000076
Outdoor Air		0.000504	
Vegetables	0.000113		
Fruits	0.000019		
Fish and Shellfish	0.00277		
Dairy	Outside Model Bounds		
Meat	Outside Model Bounds		
TOTALS	0.003779	0.3205	0.000076
25154-55-6 NITROPHENOL			
Surface Water			
TOTALS	0	0	
84-74-2 DIBUTYL PHTHALATE			
Surface Water			
Drinking Water	0.02041		
Showering		7.45	0.01813
Outdoor Air		0.01175	
Vegetables	0.0821		

Fruits	0.000932		
Fish and Shellfish	0.01151		
Dairy	0.000008		
Meat	0.000007		
TOTALS	0.115	7.462	0.01813

95-57-8 CHLOROPHENOL, 2-

Surface Water			
Drinking Water	0.000329		
Showering		0.12	0.000034
Outdoor Air		0.000189	
Vegetables	0.000029		
Fruits	0.000007		
Fish and Shellfish	0.000180		
Dairy	Outside Model Bounds		
Meat	Outside Model Bounds		
TOTALS	0.000545	0.1202	0.000034

Calculated Lifetime Average Daily Dose(LADD)

	Oral LADD mg/kg/d	Inhalation Adj.Concentration ug/cu m	Dermal LADD mg/kg/d
117-81-7 DEHP			
Surface Water			
Drinking Water	0.000951		
Showering		2.997	0.001855
Outdoor Air		0.1315	
Vegetables	0.00991		
Fruits	0.000060		
Fish and Shellfish	0.002927		
Dairy	7.2e-007		
Meat	6.3e-007		
TOTALS	0.01385	3.129	0.001855
84-66-2 DIETHYL PHTHALATE			
Surface Water			
Drinking Water	0.000376		
Showering		1.184	0.000033
Outdoor Air		0.05196	
Vegetables	0.000049		
Fruits	0.000008		
Fish and Shellfish	0.001187		
Dairy	Outside Model Bounds		
Meat	Outside Model Bounds		
TOTALS	0.001619	1.236	0.000033
25154-55-6 NITROPHENOL			
Surface Water			
TOTALS	0	0	
84-74-2 DIBUTYL PHTHALATE			
Surface Water			
Drinking Water	0.008748		
Showering		27.566	0.007771
Outdoor Air		1.21	
Vegetables	0.03519		
Fruits	0.000399		
Fish and Shellfish	0.004934		
Dairy	0.000004		
Meat	0.000003		
TOTALS	0.04927	28.775	0.007771
95-57-8 CHLOROPHENOL, 2-			
Surface Water			
Drinking Water	0.000141		
Showering		0.444	0.000015
Outdoor Air		0.01948	

Vegetables	0.000012		
Fruits	0.000003		
Fish and Shellfish	0.000077		
Dairy	Outside Model Bounds		
Meat	Outside Model Bounds		
TOTALS	0.000233	0.4635	0.000015

Cancer Risk (Odds): Individual Probability of Getting Cancer from this Exposure Alone

	Oral	Inhalation	Dermal
117-81-7 DEHP			
Weight of Evidence: B2	Oral Slope (mg/kg/d): 0.014	No Unit Risk	Source: IRIS(05/30/95)
Surface Water			
Drinking Water	1 in 100,000 (1e-005)		
Showering		Missing Unit Risk	3 in 100,000 (3e-005)
Outdoor Air		Missing Unit Risk	
Vegetables	**1 in 10,000 (1e-004)**		
Fruits	< 1 in 1,000,000 (8e-007)		
Fish and Shellfish	4 in 100,000 (4e-005)		
Dairy	< 1 in 1,000,000 (1e-008)		
Meat	< 1 in 1,000,000 (9e-009)		
TOTALS	**2 in 10,000 (2e-004)**		3 in 100,000 (3e-005)

84-66-2 DIETHYL PHTHALATE			
Weight of Evidence:	No Slope	No Unit Risk	Source: IRIS(05/30/95)
25154-55-6 NITROPHENOL			
Weight of Evidence:	No Slope	No Unit Risk	Source: IRIS(05/30/95)
84-74-2 DIBUTYL PHTHALATE			
Weight of Evidence:	No Slope	No Unit Risk	Source: IRIS(05/30/95)
95-57-8 CHLOROPHENOL, 2-			
Weight of Evidence:	No Slope	No Unit Risk	Source: IRIS(05/30/95)

Hazard Quotient: Ratio of Average Dose to 'Safe' Daily Dose

Scenario	Oral	Inhalation	Dermal
117-81-7 DEHP			
RfD (mg/kg/d):	0.02	No RfC	Source: IRIS(05/30/95)
Surface Water			
Drinking Water	0.111		
Showering		Missing RfC	0.2165
Outdoor Air		Missing RfC	
Vegetables	1.157		
Fruits	0.007041		
Fish and Shellfish	0.3415		
Dairy	0.000083		
Meat	0.000073		
MEDIUM TOTALS	1.616		0.2165

84-66-2 DIETHYL PHTHALATE			
RfD (mg/kg/d):	0.8	No RfC	Source: IRIS(05/30/95)
Surface Water			
Drinking Water	0.001096		
Showering		Missing RfC	0.000096
Outdoor Air		Missing RfC	
Vegetables	0.000142		
Fruits	0.000024		
Fish and Shellfish	0.003462		
Dairy	Outside Model Bounds		
Meat	Outside Model Bounds		
MEDIUM TOTALS	0.004723		0.000096

25154-55-6 NITROPHENOL			
No RfD		No RfC	Source: IRIS(05/30/95)
Surface Water			
Drinking Water	Missing RfD		
MEDIA TOTALS			

84-74-2 DIBUTYL PHTHALATE			
RfD (mg/kg/d):	0.1	No RfC	Source: IRIS(05/30/95)

Surface Water			
Drinking Water	0.2041		
Showering		Missing RfC	0.1813
Outdoor Air		Missing RfC	
Vegetables	0.821		
Fruits	0.009316		
Fish and Shellfish	0.1151		
Dairy	0.000082		
Meat	0.000072		
MEDIUM TOTALS	1.15		0.1813

95-57-8 CHLOROPHENOL, 2-

RfD (mg/kg/d): 0.005 No RfC Source: IRIS(05/30/95)

Surface Water			
Drinking Water	0.06575		
Showering		Missing RfC	0.006819
Outdoor Air		Missing RfC	
Vegetables	0.005813		
Fruits	0.001401		
Fish and Shellfish	0.03594		
Dairy	Outside Model Bounds		
Meat	Outside Model Bounds		
MEDIUM TOTALS	0.1089		0.006819

Risk (Odds):Individual Probability of

	Hazard Quotient	Getting Cancer from this Exposure Alone
Oral	**2.88**	
Dermal	**0.4047**	
Surface Water	**3.284**	
TOTAL		**2 in 10,000 (2e-004)**

Diepriver River water

Calculated Average Daily Dose (ADD)

Medium	Oral ADD	Inhalation Concentration	Dermal ADD
Scenario	mg/kg/d	mg/cu m	mg/kg/d
117-81-7 DEHP			
Surface Water			
Drinking Water	0.000247		
Showering		0.09	0.000481
Outdoor Air		0.000142	
Vegetables	0.00257		
Fruits	0.000016		
Fish and Shellfish	0.000759		
Dairy	1.9e-007		
Meat	1.6e-007		
TOTALS	0.003592	0.09014	0.000481

84-66-2 DIETHYL PHTHALATE

Surface Water			
Drinking Water	0.00737		
Showering		2.69	0.000643
Outdoor Air		0.004241	
Vegetables	0.00095		
Fruits	0.000162		
Fish and Shellfish	0.02328		
Dairy	Outside Model Bounds		
Meat	Outside Model Bounds		
TOTALS	0.03177	2.694	0.000643

25154-55-6 NITROPHENOL

Surface Water			
Drinking Water	0.001644		
Showering		Missing Data	0.000003
Outdoor Air		Missing Data	
Vegetables	Missing Data		

Fruits	Missing Data			
Fish and Shellfish	Missing Data			
Dairy	Missing Data			
Meat	Missing Data			
TOTALS	0.001644			0.000003

84-74-2 DIBUTYL PHTHALATE

Surface Water			
TOTALS	0	0	0

95-57-8 CHLOROPHENOL, 2-

Surface Water			
TOTALS	0	0	0

Calculated Lifetime Average Daily Dose (LADD)

Scenario	Oral LADD mg/kg/d	Inhalation Adj.Concentration ug/cu m	Dermal LADD mg/kg/d
117-81-7 DEHP			
Surface Water			
Drinking Water	0.000106		
Showering		0.333	0.000206
Outdoor Air		0.01461	
Vegetables	0.001102		
Fruits	0.000007		
Fish and Shellfish	0.000325		
Dairy	7.9e-008		
Meat	7.0e-008		
TOTALS	0.001539	0.3476	0.000206
84-66-2 DIETHYL PHTHALATE			
Surface Water			
Drinking Water	0.003159		
Showering		9.953	0.000275
Outdoor Air		0.4367	
Vegetables	0.000408		
Fruits	0.000070		
Fish and Shellfish	0.00998		
Dairy	Outside Model Bounds		
Meat	Outside Model Bounds		
TOTALS	0.01361	10.390	0.000275
25154-55-6 NITROPHENOL			
Surface Water			
Drinking Water	0.000705		
Showering		Missing Data	0.000001
Outdoor Air		Missing Data	
Vegetables	Missing Data		
Fruits	Missing Data		
Fish and Shellfish	Missing Data		
Dairy	Missing Data		
Meat	Missing Data		
TOTALS	0.000705		0.000001
84-74-2 DIBUTYL PHTHALATE			
Surface Water			
TOTALS	0	0	0
95-57-8 CHLOROPHENOL, 2-			
Surface Water			
TALS	0	0	0

Cancer Risk (Odds): Individual Probability of Getting Cancer from this Exposure Alone

	Oral	Inhalation	Dermal
117-81-7 DEHP			
Weight of Evidence: B2	Oral Slope (mg/kg/d): 0.014	No Unit Risk	Source: IRIS(05/30/95)
Surface Water			
Drinking Water	1 in 1,000,000 (1e-006)		
Showering		Missing Unit Risk	3 in 1,000,000 (3e-006)
Outdoor Air		Missing Unit Risk	
Vegetables	2 in 100,000 (2e-005)		
Fruits	< 1 in 1,000,000 (9e-008)		
Fish and Shellfish	5 in 1,000,000 (5e-006)		
Dairy	< 1 in 1,000,000 (1e-009)		
Meat	< 1 in 1,000,000 (1e-009)		
MEDIUM TOTALS	2 in 100,000 (2e-005)		3 in 1,000,000 (3e-006)
84-66-2 DIETHYL PHTHALATE			
Weight of Evidence: No Slope		No Unit Risk	Source: IRIS(05/30/95)
25154-55-6 NITROPHENOL			
Weight of Evidence: No Slope		No Unit Risk	Source: IRIS(05/30/95)
84-74-2 DIBUTYL PHTHALATE			
Weight of Evidence: No Slope		No Unit Risk	Source: IRIS(05/30/95)
95-57-8 CHLOROPHENOL, 2-			
Weight of Evidence: No Slope		No Unit Risk	Source: IRIS(05/30/95)

Hazard Quotient: Ratio of Average Dose to 'Safe' Daily Dose

	Oral	Inhalation	Dermal
117-81-7 DEHP			
RfD (mg/kg/d): 0.02		No RfC	Source: IRIS(05/30/95)
Surface Water			
Drinking Water	0.01233		
Showering		Missing RfC	0.02405
Outdoor Air		Missing RfC	
Vegetables	0.1285		
Fruits	0.000782		
Fish and Shellfish	0.03795		
Dairy	0.000009		
Meat	0.000008		
MEDIUM TOTALS	0.1796		0.02405
84-66-2 DIETHYL PHTHALATE			
RfD (mg/kg/d): 0.8		No RfC	Source: IRIS(05/30/95)
Surface Water			
Drinking Water	0.009212		
Showering		Missing RfC	0.000803
Outdoor Air		Missing RfC	
Vegetables	0.00119		
Fruits	0.000203		
Fish and Shellfish	0.0291		
Dairy	Outside Model Bounds		
Meat	Outside Model Bounds		
MEDIUM TOTALS	0.03971		0.000803
25154-55-6 NITROPHENOL			
No RfD		No RfC	Source: IRIS(05/30/95)
MEDIA TOTALS			
84-74-2 DIBUTYL PHTHALATE			
RfD (mg/kg/d): 0.1		No RfC	Source: IRIS(05/30/95)
ALL MEDIA TOTALS 0			0
95-57-8 CHLOROPHENOL, 2-			
RfD (mg/kg/d): 0.005		No RfC	Source: IRIS(05/30/95)
ALL MEDIA TOTALS 0			

TOTALS FOR ALL CHEMICALS

Hazard Quotient	Risk (Odds):Individual Probability of Getting Cancer from this Exposure Alone

Oral	0.2193
Dermal	0.02485
Surface Water	0.2442
TOTAL	2 in 100,000 (2e-005)

Diepriver Effluent

Calculated Average Daily Dose (ADD)

	Oral ADD mg/kg/d	Inhalation Concentration mg/cu m	Dermal ADD mg/kg/d
117-81-7 DEHP			
Surface Water			
Drinking Water	0.000274		
Showering		0.1	0.000534
Outdoor Air		0.000158	
Vegetables	0.002856		
Fruits	0.000017		
Fish and Shellfish	0.000843		
Dairy	2.1e-007		
Meat	1.8e-007		
TOTALS	0.003991	0.1002	0.000534
84-66-2 DIETHYL PHTHALATE			
Surface Water			
Drinking Water	0.002521		
Showering		0.92	0.000220
Outdoor Air	0.00145		
Vegetables	0.000326		
Fruits	0.000056		
Fish and Shellfish	0.007962		
Dairy	Outside Model Bounds		
Meat	Outside Model Bounds		
TOTALS	0.01086	0.9215	0.000220
25154-55-6 NITROPHENOL			
Surface Water			
Drinking Water	0.001288		
Showering		Missing Data	0.000003
Outdoor Air		Missing Data	
Vegetables	Missing Data		
Fruits	Missing Data		
Fish and Shellfish	Missing Data		
Dairy	Missing Data		
Meat	Missing Data		
TOTALS	0.001288		0.000003
84-74-2 DIBUTYL PHTHALATE			
Surface Water			
TOTALS	0	0	0
95-57-8 CHLOROPHENOL, 2-			
TOTALS	0	0	0

Calculated Lifetime Average Daily Dose (LADD)

	Oral LADD mg/kg/d	Inhalation Adj.Concentration ug/cu m	Dermal LADD mg/kg/d
117-81-7 DEHP			
Surface Water			
Drinking Water	0.000117		
Showering		0.37	0.000229
Outdoor Air		0.01624	
Vegetables	0.001224		
Fruits	0.000007		

Fish and Shellfish	0.000361		
Dairy	8.8e-008		
Meat	7.7e-008		
TOTALS	0.00171	0.3862	0.000229

84-66-2 DIETHYL PHTHALATE

Surface Water			
Drinking Water	0.00108		
Showering		3.404	0.000094
Outdoor Air		0.1494	
Vegetables	0.000140		
Fruits	0.000024		
Fish and Shellfish	0.003412		
Dairy	Outside Model Bounds		
Meat	Outside Model Bounds		
TOTALS	0.004656	3.553	0.000094

25154-55-6 NITROPHENOL

Surface Water			
Drinking Water	0.000552		
Showering		Missing Data	0.000001
Outdoor Air		Missing Data	
Vegetables	Missing Data		
Fruits	Missing Data		
Fish and Shellfish	Missing Data		
Dairy	Missing Data		
Meat	Missing Data		
TOTALS	0.000552		0.000001

84-74-2 DIBUTYL PHTHALATE			
TOTALS	0	0	0
95-57-8 CHLOROPHENOL, 2-			
TOTALS	0	0	0

Cancer Risk (Odds): Individual Probability of Getting Cancer from this Exposure Alone

	Oral	Inhalation	Dermal
117-81-7 DEHP			
Weight of Evidence: B2	Oral Slope (mg/kg/d): 0.014	No Unit Risk	Source: IRIS(05/30/95)
Surface Water			
Drinking Water	2 in 1,000,000 (2e-006)		
Showering		Missing Unit Risk	3 in 1,000,000 (3e-006)
Outdoor Air		Missing Unit Risk	
Vegetables	2 in 100,000 (2e-005)		
Fruits	< 1 in 1,000,000 (1e-007)		
Fish and Shellfish	5 in 1,000,000 (5e-006)		
Dairy	< 1 in 1,000,000 (1e-009)		
Meat	< 1 in 1,000,000 (1e-009)		
MEDIUM TOTALS	2 in 100,000 (2e-005)		3 in 1,000,000 (3e-006)
ALL MEDIA TOTALS	2 in 100,000 (2e-005)		3 in 1,000,000 (3e-006)

84-66-2 DIETHYL PHTHALATE			
Weight of Evidence:	No Slope	No Unit Risk	Source: IRIS(05/30/95)
25154-55-6 NITROPHENOL			
Weight of Evidence:	No Slope	No Unit Risk	Source: IRIS(05/30/95)
84-74-2 DIBUTYL PHTHALATE			
Weight of Evidence:	No Slope	No Unit Risk	Source: IRIS(05/30/95)
95-57-8 CHLOROPHENOL, 2-			
Weight of Evidence:	No Slope	No Unit Risk	Source: IRIS(05/30/95)

Hazard Quotient: Ratio of Average Dose to 'Safe' Daily Dose

	Oral	Inhalation	Dermal
117-81-7 DEHP			
RfD (mg/kg/d):	0.02	No RfC	Source: IRIS(05/30/95)
Surface Water			
Drinking Water	0.0137		
Showering		Missing RfC	0.02672
Outdoor Air		Missing RfC	
Vegetables	0.1428		
Fruits	0.000869		
Fish and Shellfish	0.04216		
Dairy	0.000010		
Meat	0.000009		
MEDIUM TOTALS	0.1996		0.02672
84-66-2 DIETHYL PHTHALATE			
RfD (mg/kg/d):	0.8	No RfC	Source: IRIS(05/30/95)
Surface Water			
Drinking Water	0.003151		
Showering		Missing RfC	0.000275
Outdoor Air		Missing RfC	
Vegetables	0.000407		
Fruits	0.000069		
Fish and Shellfish	0.00995		
Dairy	Outside Model Bounds		
Meat	Outside Model Bounds		
MEDIUM TOTALS	0.01358		0.000275
25154-55-6 NITROPHENOL			
No RfD		No RfC	Source: IRIS(05/30/95)
Surface Water			
Drinking Water	Missing RfD		
84-74-2 DIBUTYL PHTHALATE			
RfD (mg/kg/d):	0.1	No RfC	Source: IRIS(05/30/95)
MEDIA TOTALS	0	0	
95-57-8 CHLOROPHENOL, 2-			
RfD (mg/kg/d):	0.005	No RfC	Source: IRIS(05/30/95)
MEDIA TOTALS	0	0	

TOTALS FOR ALL CHEMICALS

	Hazard Quotient	Risk (Odds):Individual Probability of Getting Cancer from this Exposure Alone
Oral	0.2131	
Dermal	0.027	
Surface Water	0.2401	
TOTAL		3 in 100,000 (3e-005)

Kuilsriver 2 Riverwater

Calculated Average Daily Dose (ADD)

Chemical	Oral	Inhalation	Dermal
Medium	ADD	Concentration	ADD
Scenario	mg/kg/d	mg/cu m	mg/kg/d
117-81-7 DEHP			
Surface Water			
Drinking Water	0.006959		
Showering		2.54	0.01358
Outdoor Air		0.004004	
Vegetables	0.07254		
Fruits	0.000442		
Fish and Shellfish	0.02142		
Dairy	0.000005		
Meat	0.000005		
TOTALS	0.1014	2.544	0.01358

84-66-2 DIETHYL PHTHALATE

Surface Water			
Drinking Water	0.005836		
Showering		2.13	0.000509
Outdoor Air		0.003358	
Vegetables	0.000754		
Fruits	0.000129		
Fish and Shellfish	0.01843		
Dairy	Outside Model Bounds		
Meat	Outside Model Bounds		
TOTALS	0.02515	2.133	0.000509

25154-55-6 NITROPHENOL

Surface Water			
Drinking Water	0.002986		
Showering		Missing Data	0.000006
Outdoor Air		Missing Data	
Vegetables	Missing Data		
Fruits	Missing Data		
Fish and Shellfish	Missing Data		
Dairy	Missing Data		
Meat	Missing Data		
TOTALS	0.002986		0.000006

84-74-2 DIBUTYL PHTHALATE

Surface Water			
Drinking Water	0.08773		
Showering		32.020	0.07794
Outdoor Air		0.05048	
Vegetables	0.3529		
Fruits	0.004004		
Fish and Shellfish	0.04948		
Dairy	0.000035		
Meat	0.000031		
TOTALS	0.4941	32.070	0.07794

95-57-8 CHLOROPHENOL, 2-

Surface Water			
Drinking Water	0.001726		
Showering		0.63	0.000179
Outdoor Air		0.000993	
Vegetables	0.000153		
Fruits	0.000037		
Fish and Shellfish	0.000943		
Dairy	Outside Model Bounds		
Meat	Outside Model Bounds		
TOTALS	0.002859	0.631	0.000179

Calculated Lifetme Average Daily Dose

Medium	Oral LADD mg/kg/d	Inhalation Adj.Concentration ug/cu m	Dermal LADD mg/kg/d
117-81-7 DEHP			
Surface Water			
Drinking Water	0.002982		
Showering		9.398	0.005818
Outdoor Air		0.4124	
Vegetables	0.03109		
Fruits	0.000189		
Fish and Shellfish	0.00918		
Dairy	0.000002		
Meat	0.000002		
TOTALS	0.04345	9.811	0.005818

84-66-2 DIETHYL PHTHALATE

Surface Water

Drinking Water	0.002501		
Showering		7.881	0.000218
Outdoor Air		0.3458	
Vegetables	0.000323		
Fruits	0.000055		
Fish and Shellfish	0.007901		
Dairy	Outside Model Bounds		
Meat	Outside Model Bounds		
TOTALS	0.01078	8.227	0.000218

25154-55-6 NITROPHENOL

Surface Water			
Drinking Water	0.00128		
Showering		Missing Data	0.000003
Outdoor Air		Missing Data	
Vegetables	Missing Data		
Fruits	Missing Data		
Fish and Shellfish	Missing Data		
Dairy	Missing Data		
Meat	Missing Data		
TOTALS	0.00128		0.000003

84-74-2 DIBUTYL PHTHALATE

Surface Water			
Drinking Water	0.0376		
Showering		118.478	0.0334
Outdoor Air		5.199	
Vegetables	0.1512		
Fruits	0.001716		
Fish and Shellfish	0.02121		
Dairy	0.000015		
Meat	0.000013		
TOTALS	0.2118	123.676	0.0334

95-57-8 CHLOROPHENOL, 2-

Surface Water			
Drinking Water	0.000740		
Showering		2.331	0.000077
Outdoor Air		0.1023	
Vegetables	0.000065		
Fruits	0.000016		
Fish and Shellfish	0.000404		
Dairy	Outside Model Bounds		
Meat	Outside Model Bounds		
TOTALS	0.001225	2.433	0.000077

Risk (Odds): Individual Probability of Getting Cancer from this Exposure Alone

Scenario	Oral	Inhalation	Dermal
117-81-7 DEHP			
Weight of Evidence: B2	Oral Slope (mg/kg/d): 0.014	No Unit Risk	Source: IRIS(05/30/95)
Surface Water			
Drinking Water	4 in 100,000 (4e-005)		
Showering		Missing Unit Risk	8 in 100,000 (8e-005)
Outdoor Air		Missing Unit Risk	
Vegetables	4 in 10,000 (4e-004)		
Fruits	3 in 1,000,000 (3e-006)		
Fish and Shellfish	**1 in 10,000 (1e-004)**		
Dairy	< 1 in 1,000,000 (3e-008)		
Meat	< 1 in 1,000,000 (3e-008)		
MEDIUM TOTALS	6 in 10,000 (6e-004)		8 in 100,000 (8e-005)
ALL MEDIA TOTALS	6 in 10,000 (6e-004)		8 in 100,000 (8e-005)

84-66-2 DIETHYL PHTHALATE

Weight of Evidence:	No Slope	No Unit Risk	Source: IRIS(05/30/95)

25154-55-6 NITROPHENOL

Weight of Evidence:	No Slope	No Unit Risk	Source: IRIS(05/30/95)

84-74-2 DIBUTYL PHTHALATE
Weight of Evidence: No Slope No Unit Risk Source: IRIS(05/30/95)
95-57-8 CHLOROPHENOL, 2-
Weight of Evidence: No Slope No Unit Risk Source: IRIS(05/30/95)

Hazard Quotient: Ratio of Average Dose to 'Safe' Daily Dose

Scenario	Oral	Inhalation	Dermal
117-81-7 DEHP			
RfD (mg/kg/d):	0.02	No RfC	Source: IRIS(05/30/95)
Surface Water			
Drinking Water	0.3479		
Showering		Missing RfC	0.6788
Outdoor Air		Missing RfC	
Vegetables	**3.627**		
Fruits	0.02208		
Fish and Shellfish	1.071		
Dairy	0.000262		
Meat	0.000229		
MEDIUM TOTALS	**5.069**		0.6788
84-66-2 DIETHYL PHTHALATE			
RfD (mg/kg/d):	0.8	No RfC	Source: IRIS(05/30/95)
Surface Water			
Drinking Water	0.007295		
Showering		Missing RfC	0.000636
Outdoor Air		Missing RfC	
Vegetables	0.000942		
Fruits	0.000161		
Fish and Shellfish	0.02304		
Dairy	Outside Model Bounds		
Meat	Outside Model Bounds		
MEDIUM TOTALS	0.03144		0.000636
ALL MEDIA TOTALS	0.03144		0.000636
25154-55-6 NITROPHENOL			
No RfD		No RfC	Source: IRIS(05/30/95)
Drinking Water	Missing RfD		
84-74-2 DIBUTYL PHTHALATE			
RfD (mg/kg/d):	0.1	No RfC	Source: IRIS(05/30/95)
Surface Water			
Drinking Water	0.8773		
Showering		Missing RfC	0.7794
Outdoor Air		Missing RfC	
Vegetables	**3.529**		
Fruits	0.04004		
Fish and Shellfish	0.4948		
Dairy	0.000354		
Meat	0.000310		
MEDIUM TOTALS	**4.941**		0.7794
95-57-8 CHLOROPHENOL, 2-			
RfD (mg/kg/d):	0.005	No RfC	Source: IRIS(05/30/95)
Surface Water			
Drinking Water	0.3452		
Showering		Missing RfC	0.0358
Outdoor Air		Missing RfC	
Vegetables	0.03052		
Fruits	0.007354		
Fish and Shellfish	0.1887		
Dairy	Outside Model Bounds		
Meat	Outside Model Bounds		
MEDIUM TOTALS	0.5718		0.0358
ALL MEDIA TOTALS	0.5718		0.0358

TOTALS FOR ALL CHEMICALS

	Hazard Quotient	Risk (Odds):Individual Probability of Getting Cancer from this Exposure Alone
Oral	10.613	
Dermal	1.495	
Surface Water	12.108	
TOTAL		7 in 10,000 (7e-004)

KuilsRiver 2 Effluent

Calculated Average Daily Dose (ADD)

Chemical / Medium / Scenario	Oral ADD mg/kg/d	Inhalation Concentration mg/cu m	Dermal ADD mg/kg/d
117-81-7 DEHP			
Surface Water			
Drinking Water	0.008164		
Showering		2.98	0.01593
Outdoor Air		0.004698	
Vegetables	0.08511		
Fruits	0.000518		
Fish and Shellfish	0.02513		
Dairy	0.000006		
Meat	0.000005		
TOTALS	0.1189	2.985	0.01593
84-66-2 DIETHYL PHTHALATE			
Surface Water			
Drinking Water	0.000438		
Showering		0.16	0.000038
Outdoor Air		0.000252	
Vegetables	0.000057		
Fruits	0.000010		
Fish and Shellfish	0.001385		
Dairy	Outside Model Bounds		
Meat	Outside Model Bounds		
TOTALS	0.001889	0.1603	0.000038
25154-55-6 NITROPHENOL			
Surface Water			
Drinking Water	0.002548		
Showering		Missing Data	0.000005
Outdoor Air		Missing Data	
Vegetables	Missing Data		
Fruits	Missing Data		
Fish and Shellfish	Missing Data		
Dairy	Missing Data		
Meat	Missing Data		
TOTALS	0.002548		0.000005
84-74-2 DIBUTYL PHTHALATE			
Surface Water			
Drinking Water	0.02036		
Showering		7.43	0.01808
Outdoor Air		0.01171	
Vegetables	0.08188		
Fruits	0.000929		
Fish and Shellfish	0.01148		
Dairy	0.000008		
Meat	0.000007		
TOTALS	0.1147	7.442	0.01808
95-57-8 CHLOROPHENOL, 2-			
Surface Water			
Drinking Water	0.003342		
Showering		1.22	0.000347
Outdoor Air		0.001923	

Vegetables	0.000296		
Fruits	0.000071		
Fish and Shellfish	0.001827		
Dairy	Outside Model Bounds		
Meat	Outside Model Bounds		
TOTALS	0.005536	1.222	0.000347

Calculated Lifetime Average Daily Dose (LADD)

Chemical	Oral	Inhalation	Dermal
Medium	LADD	Adj.Concentration	LADD
Scenario	mg/kg/d	ug/cu m	mg/kg/d
117-81-7 DEHP			
Surface Water			
Drinking Water	0.003499		
Showering		11.026	0.006826
Outdoor Air		0.4838	
Vegetables	0.03648		
Fruits	0.000222		
Fish and Shellfish	0.01077		
Dairy	0.000003		
Meat	0.000002		
TOTALS	0.05097	11.510	0.006826
84-66-2 DIETHYL PHTHALATE			
Surface Water			
Drinking Water	0.000188		
Showering		0.592	0.000016
Outdoor Air		0.02598	
Vegetables	0.000024		
Fruits	0.000004		
Fish and Shellfish	0.000593		
Dairy	Outside Model Bounds		
Meat	Outside Model Bounds		
TOTALS	0.000810	0.618	0.000016
25154-55-6 NITROPHENOL			
Surface Water			
Drinking Water	0.001092		
Showering		Missing Data	0.000002
Outdoor Air		Missing Data	
Vegetables	Missing Data		
Fruits	Missing Data		
Fish and Shellfish	Missing Data		
Dairy	Missing Data		
Meat	Missing Data		
TOTALS	0.001092		0.000002
84-74-2 DIBUTYL PHTHALATE			
Surface Water			
Drinking Water	0.008724		
Showering		27.492	0.00775
Outdoor Air		1.206	
Vegetables	0.03509		
Fruits	0.000398		
Fish and Shellfish	0.004921		
Dairy	0.000004		
Meat	0.000003		
TOTALS	0.04914	28.70	0.00775
95-57-8 CHLOROPHENOL, 2-			
Surface Water			
Drinking Water	0.001432		
Showering		4.514	0.000149
Outdoor Air		0.1981	
Vegetables	0.000127		
Fruits	0.000031		
Fish and Shellfish	0.000783		

Dairy	Outside Model Bounds		
Meat	Outside Model Bounds		
TOTALS	0.002373	4.712	0.000149

Risk (Odds): Individual Probability of Getting Cancer from this Exposure Alone

Scenario	Oral	Inhalation	Dermal
117-81-7 DEHP			
Weight of Evidence: B2	Oral Slope (mg/kg/d): 0.014	No Unit Risk	Source: IRIS(05/30/95)
Surface Water			
Drinking Water	5 in 100,000 (5e-005)		
Showering		Missing Unit Risk	1 in 10,000 (1e-004)
Outdoor Air		Missing Unit Risk	
Vegetables	5 in 10,000 (5e-004)		
Fruits	3 in 1,000,000 (3e-006)		
Fish and Shellfish 2 in 10,000 (2e-004)			
Dairy	< 1 in 1,000,000 (4e-008)		
Meat	< 1 in 1,000,000 (3e-008)		
MEDIUM TOTALS	**7 in 10,000 (7e-004)**		1 in 10,000 (1e-004)

84-66-2 DIETHYL PHTHALATE			
Weight of Evidence:	No Slope	No Unit Risk	Source: IRIS(05/30/95)
25154-55-6 NITROPHENOL			
Weight of Evidence:	No Slope	No Unit Risk	Source: IRIS(05/30/95)
84-74-2 DIBUTYL PHTHALATE			
Weight of Evidence:	No Slope	No Unit Risk	Source: IRIS(05/30/95)
95-57-8 CHLOROPHENOL, 2-			
Weight of Evidence:	No Slope	No Unit Risk	Source: IRIS(05/30/95)

Hazard Quotient: Ratio of Average Dose to 'Safe' Daily Dose

Scenario	Oral	Inhalation	Dermal
117-81-7 DEHP			
RfD (mg/kg/d):	0.02	No RfC	Source: IRIS(05/30/95)
Surface Water			
Drinking Water	0.4082		
Showering		Missing RfC	0.7963
Outdoor Air		Missing RfC	
Vegetables	**4.256**		
Fruits	0.0259		
Fish and Shellfish	1.256		
Dairy	0.000307		
Meat	0.000269		
MEDIUM TOTALS	**5.947**		0.7963

84-66-2 DIETHYL PHTHALATE			
RfD (mg/kg/d):	0.8	No RfC	Source: IRIS(05/30/95)
Surface Water			
Drinking Water	0.000548		
Showering		Missing RfC	0.000048
Outdoor Air		Missing RfC	
Vegetables	0.000071		
Fruits	0.000012		
Fish and Shellfish	0.001731		
Dairy	Outside Model Bounds		
Meat	Outside Model Bounds		
MEDIUM TOTALS	0.002362		0.000048

25154-55-6 NITROPHENOL			
No RfD		No RfC	Source: IRIS(05/30/95)

84-74-2 DIBUTYL PHTHALATE			
RfD (mg/kg/d):	0.1	No RfC	Source: IRIS(05/30/95)
Surface Water			
Drinking Water	0.2036		
Showering		Missing RfC	0.1808
Outdoor Air		Missing RfC	
Vegetables	0.8188		

Fruits	0.009291		
Fish and Shellfish	0.1148		
Dairy	0.000082		
Meat	0.000072		
MEDIUM TOTALS	1.147		0.1808

95-57-8 CHLOROPHENOL, 2-

RfD (mg/kg/d): 0.005 No RfC Source: IRIS(05/30/95)

Surface Water			
Drinking Water	0.6685		
Showering		Missing RfC	0.06933
Outdoor Air		Missing RfC	
Vegetables	0.0591		
Fruits	0.01424		
Fish and Shellfish	0.3654		
Dairy	Outside Model Bounds		
Meat	Outside Model Bounds		
MEDIUM TOTALS	1.107		0.06933
ALL MEDIA TOTALS	1.107		0.06933

TOTALS FOR ALL CHEMICALS

	Hazard Quotient	Risk (Odds):Individual Probability of Getting Cancer from this Exposure Alone
Oral	8.203	
Dermal	1.047	
Surface Water	9.25	
TOTAL		8 in 10,000 (8e-004)

Veldwachter River

Calculated Average Daily Dose (ADD)

Chemical / Medium / Scenario	Oral ADD mg/kg/d	Inhalation Concentration mg/cu m	Dermal ADD mg/kg/d
117-81-7 DEHP			
Surface Water			
Drinking Water	0.002877		
Showering		1.05	0.005612
Outdoor Air		0.001655	
Vegetables	0.02999		
Fruits	0.000183		
Fish and Shellfish	0.008855		
Dairy	0.000002		
Meat	0.000002		
TOTALS	0.04191	1.052	0.005612
84-66-2 DIETHYL PHTHALATE			
Surface Water			
Drinking Water	0.002		
Showering		0.73	0.000174
Outdoor Air		0.001151	
Vegetables	0.000258		
Fruits	0.000044		
Fish and Shellfish	0.006318		
Dairy	Outside Model Bounds		
Meat	Outside Model Bounds		
TOTALS	0.00862	0.7312	0.000174
25154-55-6 NITROPHENOL			
Surface Water			
Drinking Water	0.0209		
Showering		Missing Data	0.000044
Outdoor Air		Missing Data	
Vegetables	Missing Data		
Fruits	Missing Data		
Fish and Shellfish	Missing Data		

Dairy	Missing Data		
Meat	Missing Data		
TOTALS	0.0209		0.000044

84-74-2 DIBUTYL PHTHALATE

Surface Water			
Drinking Water	0.124		
Showering		45.270	0.1102
Outdoor Air		0.07137	
Vegetables	0.4989		
Fruits	0.005661		
Fish and Shellfish	0.06996		
Dairy	0.000050		
Meat	0.000044		
TOTALS	0.6986	45.341	0.1102

95-57-8 CHLOROPHENOL, 2-

Surface Water			
Drinking Water	0.003014		
Showering		1.1	0.000313
Outdoor Air		0.001734	
Vegetables	0.000266		
Fruits	0.000064		
Fish and Shellfish	0.001647		
Dairy	Outside Model Bounds		
Meat	Outside Model Bounds		
TOTALS	0.004992	1.102	0.000313

Calculated Lifetime Average Daily Dose)

Chemical	Oral	Inhalation	Dermal
Medium	LADD	Adj.Concentration	LADD
Scenario	mg/kg/d	ug/cu m	mg/kg/d
117-81-7 DEHP			
Surface Water			
Drinking Water	0.001233		
Showering		3.885	0.002405
Outdoor Air		0.1705	
Vegetables	0.01285		
Fruits	0.000078		
Fish and Shellfish	0.003795		
Dairy	9.3e-007		
Meat	8.1e-007		
TOTALS	0.01796	4.056	0.002405

84-66-2 DIETHYL PHTHALATE

Surface Water			
Drinking Water	0.000857		
Showering		2.701	0.000075
Outdoor Air		0.1185	
Vegetables	0.000111		
Fruits	0.000019		
Fish and Shellfish	0.002708		
Dairy	Outside Model Bounds		
Meat	Outside Model Bounds		
TOTALS	0.003694	2.82	0.000075

25154-55-6 NITROPHENOL

Surface Water			
Drinking Water	0.008959		
Showering		Missing Data	0.000019
Outdoor Air		Missing Data	
Vegetables	Missing Data		
Fruits	Missing Data		
Fish and Shellfish	Missing Data		
Dairy	Missing Data		
Meat	Missing Data		

TOTALS	0.008959		0.000019

84-74-2 DIBUTYL PHTHALATE

Surface Water			
Drinking Water	0.05315		
Showering		167.504	0.04722
Outdoor Air		7.35	
Vegetables	0.2138		
Fruits	0.002426		
Fish and Shellfish	0.02998		
Dairy	0.000021		
Meat	0.000019		
TOTALS	0.2994	174.854	0.04722

95-57-8 CHLOROPHENOL, 2-

Surface Water			
Drinking Water	0.001292		
Showering		4.07	0.000134
Outdoor Air		0.1786	
Vegetables	0.000114		
Fruits	0.000028		
Fish and Shellfish	0.000706		
Dairy	Outside Model Bounds		
Meat	Outside Model Bounds		
TOTALS	0.002139	4.249	0.000134

Risk (Odds): Individual Probability of Getting Cancer from this Exposure Alone

Scenario	Oral	Inhalation	Dermal
117-81-7 DEHP			
Weight of Evidence: B2	Oral Slope (mg/kg/d): 0.014	No Unit Risk	Source: IRIS(05/30/95)
Surface Water			
Drinking Water	2 in 100,000 (2e-005)		
Showering		Missing Unit Risk	3 in 100,000 (3e-005)
Outdoor Air		Missing Unit Risk	
Vegetables	**2 in 10,000 (2e-004)**		
Fruits	1 in 1,000,000 (1e-006)		
Fish and Shellfish	5 in 100,000 (5e-005)		
Dairy	< 1 in 1,000,000 (1e-008)		
Meat	< 1 in 1,000,000 (1e-008)		
MEDIUM TOTALS	**3 in 10,000 (3e-004)**		3 in 100,000 (3e-005)

84-66-2 DIETHYL PHTHALATE			
Weight of Evidence:	No Slope	No Unit Risk	Source: IRIS(05/30/95)
25154-55-6 NITROPHENOL			
Weight of Evidence:	No Slope	No Unit Risk	Source: IRIS(05/30/95)
84-74-2 DIBUTYL PHTHALATE			
Weight of Evidence:	No Slope	No Unit Risk	Source: IRIS(05/30/95)
95-57-8 CHLOROPHENOL, 2-			
Weight of Evidence:	No Slope	No Unit Risk	Source: IRIS(05/30/95)

Chemical **Hazard Quotient: Ratio of Average Dose to 'Safe' Daily Dose**

Scenario	Oral	Inhalation	Dermal
117-81-7 DEHP			
RfD (mg/kg/d):	0.02	No RfC	Source: IRIS(05/30/95)
Surface Water			
Drinking Water	0.1438		
Showering		Missing RfC	0.2806
Outdoor Air		Missing RfC	
Vegetables	1.499		
Fruits	0.009128		
Fish and Shellfish	0.4427		
Dairy	0.000108		
Meat	0.000095		
MEDIUM TOTALS	2.095		0.2806

84-66-2 DIETHYL PHTHALATE			
RfD (mg/kg/d):	0.8	No RfC	Source: IRIS(05/30/95)

Surface Water
Drinking Water 0.0025
Showering Missing RfC 0.000218
Outdoor Air Missing RfC
Vegetables 0.000323
Fruits 0.000055
Fish and Shellfish 0.007898
Dairy Outside Model Bounds
Meat Outside Model Bounds
MEDIUM TOTALS 0.01078 0.000218

25154-55-6 NITROPHENOL
No RfD No RfC Source: IRIS(05/30/95)
Surface Water
Drinking Water Missing RfD

84-74-2 DIBUTYL PHTHALATE
RfD (mg/kg/d): 0.1 No RfC Source: IRIS(05/30/95)
Surface Water
Drinking Water 1.24
Showering Missing RfC 1.102
Outdoor Air Missing RfC
Vegetables 4.989
Fruits 0.05661
Fish and Shellfish 0.6996
Dairy 0.000501
Meat 0.000438
MEDIUM TOTALS **6.986** 1.102

95-57-8 CHLOROPHENOL, 2-
RfD (mg/kg/d): 0.005 No RfC Source: IRIS(05/30/95)
Surface Water
Drinking Water 0.6027
Showering Missing RfC 0.06251
Outdoor Air Missing RfC
Vegetables 0.05329
Fruits 0.01284
Fish and Shellfish 0.3294
Dairy Outside Model Bounds
Meat Outside Model Bounds
MEDIUM TOTALS 0.998 0.06251

TOTALS FOR ALL CHEMICALS

	Hazard Quotient	Risk (Odds):Individual Probability of Getting Cancer from this Exposure Alone
Oral	10.091	
Dermal	1.445	
Surface Water	11.536	
TOTAL		3 in 10,000 (3e-004)

Veldwachter Effluent

Calculated Average Daily Dose (ADD)

Chemical / Medium / Scenario	Oral ADD mg/kg/d	Inhalation Concentration mg/cu m	Dermal ADD mg/kg/d
117-81-7 DEHP			
Surface Water			
Drinking Water	0.004		
Showering		1.46	0.007803
Outdoor Air		0.002302	
Vegetables	0.0417		
Fruits	0.000254		
Fish and Shellfish	0.01231		
Dairy	0.000003		
Meat	0.000003		

TOTALS	0.05827	1.462	0.007803

84-66-2 DIETHYL PHTHALATE

Surface Water			
Drinking Water	0.000630		
Showering		0.23	0.000055
Outdoor Air		0.000363	
Vegetables	0.000081		
Fruits	0.000014		
Fish and Shellfish	0.001991		
Dairy	Outside Model Bounds		
Meat	Outside Model Bounds		
TOTALS	0.002716	0.2304	0.000055

25154-55-6 NITROPHENOL

Surface Water			
TOTALS	0		0

84-74-2 DIBUTYL PHTHALATE

Surface Water			
Drinking Water	0.08362		
Showering		30.520	0.07429
Outdoor Air		0.04812	
Vegetables	0.3363		
Fruits	0.003816		
Fish and Shellfish	0.04716		
Dairy	0.000034		
Meat	0.000030		
TOTALS	0.471	30.568	0.07429

95-57-8 CHLOROPHENOL, 2-

Surface Water			
Drinking Water	0.003781		
Showering		1.38	0.000392
Outdoor Air		0.002176	
Vegetables	0.000334		
Fruits	0.000081		
Fish and Shellfish	0.002067		
Dairy	Outside Model Bounds		
Meat	Outside Model Bounds		
TOTALS	0.006262	1.382	0.000392

Calculated Lifetime Average Daily Dose)

Chemical	Oral	Inhalation	Dermal
Medium	LADD	Adj.Concentration	LADD
Scenario	mg/kg/d	ug/cu m	mg/kg/d
117-81-7 DEHP			
Surface Water			
Drinking Water	0.001714		
Showering		5.402	0.003344
Outdoor Air		0.237	
Vegetables	0.01787		
Fruits	0.000109		
Fish and Shellfish	0.005277		
Dairy	0.000001		
Meat	0.000001		
TOTALS	0.02497	5.639	0.003344

84-66-2 DIETHYL PHTHALATE

Surface Water			
Drinking Water	0.000270		
Showering		0.851	0.000024
Outdoor Air		0.03734	
Vegetables	0.000035		
Fruits	0.000006		
Fish and Shellfish	0.000853		
Dairy	Outside Model Bounds		

Meat	Outside Model Bounds		
TOTALS	0.001164	0.8884	0.000024

25154-55-6 NITROPHENOL

Surface Water			
TOTALS	0		0

84-74-2 DIBUTYL PHTHALATE

Surface Water			
Drinking Water	0.03584		
Showering		112.927	0.03184
Outdoor Air		4.955	
Vegetables	0.1441		
Fruits	0.001636		
Fish and Shellfish	0.02021		
Dairy	0.000014		
Meat	0.000013		
TOTALS	0.2019	117.883	0.03184

95-57-8 CHLOROPHENOL, 2-

Surface Water			
Drinking Water	0.00162		
Showering		5.106	0.000168
Outdoor Air		0.2241	
Vegetables	0.000143		
Fruits	0.000035		
Fish and Shellfish	0.000886		
Dairy	Outside Model Bounds		
Meat	Outside Model Bounds		
TOTALS	0.002684	5.33	0.000168

Risk (Odds): Individual Probability of Getting Can from this Exposure Alone

Scenario	Oral	Inhalation	Dermal

117-81-7 DEHP

Weight of Evidence: B2 Oral Slope (mg/kg/d): 0.014 No Unit Risk Source: IRIS(05/30/95)

Surface Water			
Drinking Water	2 in 100,000 (2e-005)		
Showering		Missing Unit Risk	5 in 100,000 (5e-005)
Outdoor Air		Missing Unit Risk	
Vegetables	**3 in 10,000 (3e-004)**		
Fruits	2 in 1,000,000 (2e-006)		
Fish and Shellfish	7 in 100,000 (7e-005)		
Dairy	< 1 in 1,000,000 (2e-008)		
Meat	< 1 in 1,000,000 (2e-008)		
MEDIUM TOTALS	**3 in 10,000 (3e-004)**		5 in 100,000 (5e-005)

84-66-2 DIETHYL PHTHALATE

Weight of Evidence: No Slope No Unit Risk Source: IRIS(05/30/95)

25154-55-6 NITROPHENOL

Weight of Evidence: No Slope No Unit Risk Source: IRIS(05/30/95)

84-74-2 DIBUTYL PHTHALATE

Weight of Evidence: No Slope No Unit Risk Source: IRIS(05/30/95)

95-57-8 CHLOROPHENOL, 2-

Weight of Evidence: No Slope

Chemical Hazard Quotient: Ratio of Average Dose to 'Safe' Daily Dose

Scenario	Oral	Inhalation	Dermal

117-81-7 DEHP

RfD (mg/kg/d): 0.02 No RfC Source: IRIS(05/30/95)

Surface Water			
Drinking Water	0.2		
Showering		Missing RfC	0.3902
Outdoor Air		Missing RfC	
Vegetables	2.085		

Fruits	0.01269		
Fish and Shellfish	0.6156		
Dairy	0.000150		
Meat	0.000132		
MEDIUM TOTALS	2.914		0.3902
ALL MEDIA TOTALS	2.914		0.3902

84-66-2 DIETHYL PHTHALATE

RfD (mg/kg/d):	0.8	No RfC	Source: IRIS(05/30/95)
Surface Water			
Drinking Water	0.000788		
Showering		Missing RfC	0.000069
Outdoor Air		Missing RfC	
Vegetables	0.000102		
Fruits	0.000017		
Fish and Shellfish	0.002488		
Dairy	Outside Model Bounds		
Meat	Outside Model Bounds		
MEDIUM TOTALS	0.003395		0.000069
ALL MEDIA TOTALS	0.003395		0.000069

25154-55-6 NITROPHENOL

No RfD		No RfC	Source: IRIS(05/30/95)
Surface Water			
Drinking Water	Missing RfD		
Showering		Missing Data	Missing RfD

84-74-2 DIBUTYL PHTHALATE

RfD (mg/kg/d):	0.1	No RfC	Source: IRIS(05/30/95)
Surface Water			
Drinking Water	0.8362		
Showering		Missing RfC	0.7429
Outdoor Air		Missing RfC	
Vegetables	**3.363**		
Fruits	0.03816		
Fish and Shellfish	0.4716		
Dairy	0.000338		
Meat	0.000295		
MEDIUM TOTALS	**4.71**		0.7429

95-57-8 CHLOROPHENOL, 2-

RfD (mg/kg/d):	0.005	No RfC	Source: IRIS(05/30/95)
Surface Water			
Drinking Water	0.7562		
Showering		Missing RfC	0.07842
Outdoor Air		Missing RfC	
Vegetables	0.06685		
Fruits	0.01611		
Fish and Shellfish	0.4133		
Dairy	Outside Model Bounds		
Meat	Outside Model Bounds		
MEDIUM TOTALS	1.252		0.07842

TOTALS FOR ALL CHEMICALS

	Hazard Quotient	Risk (Odds):Individual Probability of Getting Cancer from this Exposure Alone
Oral	8.879	
Dermal	1.211	
Surface Water	10.091	
TOTAL		4 in 10,000 (4e-004)

Kirstenbosch River

Calculated Average Daily Dose (ADD)

	Oral ADD mg/kg/d	Inhalation Concentration mg/cu m	Dermal ADD mg/kg/d
117-81-7 DEHP			
Surface Water			
Drinking Water	0.02047		
Showering		7.47	0.03992
Outdoor Air		0.01178	
Vegetables	0.2133		
Fruits	0.001299		
Fish and Shellfish	0.06299		
Dairy	0.000015		
Meat	0.000013		
TOTALS	0.2981	7.482	0.03992
84-66-2 DIETHYL PHTHALATE			
Surface Water			
Drinking Water	0.000356		
Showering		0.13	0.000031
Outdoor Air		0.000205	
Vegetables	0.000046		
Fruits	0.000008		
Fish and Shellfish	0.001125		
Dairy	Outside Model Bounds		
Meat	Outside Model Bounds		
TOTALS	0.001535	0.1302	0.000031
25154-55-6 NITROPHENOL			
Surface Water			
Drinking Water	0.000466		
Showering		Missing Data	0.000001
Outdoor Air		Missing Data	
Vegetables	Missing Data		
Fruits	Missing Data		
Fish and Shellfish	Missing Data		
Dairy	Missing Data		
Meat	Missing Data		
TOTALS	0.000466		0.000001
84-74-2 DIBUTYL PHTHALATE			
Surface Water			
Drinking Water	0		
Showering		0	0
Outdoor Air		0	
Vegetables	0		
Fruits	0		
Fish and Shellfish	0		
Dairy	0		
Meat	0		
TOTALS	0	0	0
95-57-8 CHLOROPHENOL, 2-			
Surface Water			
Drinking Water	0.003014		
Showering		1.1	0.000313
Outdoor Air		0.001734	
Vegetables	0.000266		
Fruits	0.000064		
Fish and Shellfish	0.001647		
Dairy	Outside Model Bounds		
Meat	Outside Model Bounds		
TOTALS	0.004992	1.102	0.000313

Calculated Average Daily Dose (LADD)

Chemical / Medium / Scenario	Oral LADD mg/kg/d	Inhalation Adj.Concentration ug/cu m	Dermal LADD mg/kg/d
117-81-7 DEHP			
Surface Water			
Drinking Water	0.008771		
Showering		27.640	0.01711
Outdoor Air		1.213	
Vegetables	0.09144		
Fruits	0.000557		
Fish and Shellfish	0.027		
Dairy	0.000007		
Meat	0.000006		
TOTALS	0.1278	28.853	0.01711
84-66-2 DIETHYL PHTHALATE			
Surface Water			
Drinking Water	0.000153		
Showering		0.481	0.000013
Outdoor Air		0.02111	
Vegetables	0.000020		
Fruits	0.000003		
Fish and Shellfish	0.000482		
Dairy	Outside Model Bounds		
Meat	Outside Model Bounds		
TOTALS	0.000658	0.5021	0.000013
25154-55-6 NITROPHENOL			
Surface Water			
Drinking Water	0.000200		
Showering		Missing Data	4.2e-007
Outdoor Air		Missing Data	
Vegetables	Missing Data		
Fruits	Missing Data		
Fish and Shellfish	Missing Data		
Dairy	Missing Data		
Meat	Missing Data		
TOTALS	0.000200		4.2e-007
84-74-2 DIBUTYL PHTHALATE			
TOTALS	0	0	0
95-57-8 CHLOROPHENOL, 2-			
Surface Water			
Drinking Water	0.001292		
Showering		4.07	0.000134
Outdoor Air		0.1786	
Vegetables	0.000114		
Fruits	0.000028		
Fish and Shellfish	0.000706		
Dairy	Outside Model Bounds		
Meat	Outside Model Bounds		
TOTALS	0.002139	4.249	0.000134

Risk (Odds): Individual Probability of Getting Cancer from this Exposure Alone

Scenario	Oral	Inhalation	Dermal
117-81-7 DEHP			
Weight of Evidence: B2	Oral Slope (mg/kg/d): 0.014	No Unit Risk	Source: IRIS(05/30/95)
Surface Water			
Drinking Water	**1 in 10,000 (1e-004)**		
Showering		Missing Unit Risk	**2 in 10,000 (2e-004)**
Outdoor Air		Missing Unit Risk	
Vegetables	**1 in 1,000 (1e-003)**		
Fruits	8 in 1,000,000 (8e-006)		
Fish and Shellfish	4 in 10,000 (4e-004)		

Dairy	< 1 in 1,000,000 (9e-008)		
Meat	< 1 in 1,000,000 (8e-008)		
MEDIUM TOTALS	**2 in 1,000 (2e-003)**		2 in 10,000 (2e-004)

84-66-2 DIETHYL PHTHALATE

Hazard Quotient: Ratio of Average Dose to 'Safe' Daily Dose

Scenario	Oral	Inhalation	Dermal
117-81-7 DEHP			
RfD (mg/kg/d):	0.02	No RfC	Source: IRIS(05/30/95)
Surface Water			
Drinking Water	1.023		
Showering		Missing RfC	1.996
Outdoor Air		Missing RfC	
Vegetables	**10.667**		
Fruits	0.06494		
Fish and Shellfish	3.15		
Dairy	0.000769		
Meat	0.000673		
MEDIUM TOTALS	**14.907**		1.996

84-66-2 DIETHYL PHTHALATE			
RfD (mg/kg/d):	0.8	No RfC	Source: IRIS(05/30/95)
Surface Water			
Drinking Water	0.000445		
Showering		Missing RfC	0.000039
Outdoor Air		Missing RfC	
Vegetables	0.000058		
Fruits	0.000010		
Fish and Shellfish	0.001406		
Dairy	Outside Model Bounds		
Meat	Outside Model Bounds		
MEDIUM TOTALS	0.001919		0.000039

25154-55-6 NITROPHENOL			
No RfD		No RfC	Source: IRIS(05/30/95)
Surface Water			
Drinking Water	Missing RfD		
Showering		Missing Data	Missing RfD
Outdoor Air		Missing Data	
Vegetables	Missing Data		
Fruits	Missing Data		
Fish and Shellfish	Missing Data		
Dairy	Missing Data		
Meat	Missing Data		
MEDIUM TOTALS			
ALL MEDIA TOTALS			

84-74-2 DIBUTYL PHTHALATE			
RfD (mg/kg/d):	0.1	No RfC	Source: IRIS(05/30/95)
Surface Water			
Drinking Water	0		
Showering		Missing RfC	0
Outdoor Air		Missing RfC	
Vegetables	0		
Fruits	0		
Fish and Shellfish	0		
Dairy	0		
Meat	0		
MEDIUM TOTALS	0		0
ALL MEDIA TOTALS	0		0

95-57-8 CHLOROPHENOL, 2-			
RfD (mg/kg/d):	0.005	No RfC	Source: IRIS(05/30/95)
Surface Water			
Drinking Water	0.6027		
Showering		Missing RfC	0.06251

Outdoor Air		Missing RfC	
Vegetables	0.05329		
Fruits	0.01284		
Fish and Shellfish	0.3294		
Dairy	Outside Model Bounds		
Meat	Outside Model Bounds		
MEDIUM TOTALS	0.998		0.06251

TOTALS FOR ALL CHEMICALS Kirstenbosch

	Hazard Quotient	Risk (Odds):Individual Probability of Getting Cancer from this Exposure Alone
Oral	15.907	
Dermal	2.059	
Surface Water	17.966	
TOTAL		2 in 1,000 (2e-003)