

# University of Wollongong - Research Online

## Thesis Collection

Title: Performance of water recycling technologies

Author: Jawad Hilmi Al-rifai

Year: 2008

Repository DOI:

### Copyright Warning

You may print or download ONE copy of this document for the purpose of your own research or study. The University does not authorise you to copy, communicate or otherwise make available electronically to any other person any copyright material contained on this site.

You are reminded of the following: This work is copyright. Apart from any use permitted under the Copyright Act 1968, no part of this work may be reproduced by any process, nor may any other exclusive right be exercised, without the permission of the author. Copyright owners are entitled to take legal action against persons who infringe their copyright. A reproduction of material that is protected by copyright may be a copyright infringement. A court may impose penalties and award damages in relation to offences and infringements relating to copyright material.

Higher penalties may apply, and higher damages may be awarded, for offences and infringements involving the conversion of material into digital or electronic form.

**Unless otherwise indicated, the views expressed in this thesis are those of the author and do not necessarily represent the views of the University of Wollongong.**

Research Online is the open access repository for the University of Wollongong. For further information contact the UOW Library: [research-pubs@uow.edu.au](mailto:research-pubs@uow.edu.au)

*University of Wollongong Thesis Collections*

*University of Wollongong Thesis Collection*

---

*University of Wollongong*

*Year 2008*

---

# Performance of water recycling technologies

Jawad Hilmi Al-rifai  
University of Wollongong

Al-rifai, Jawad Hilmi, Performance of water recycling technologies, PhD thesis, School of Civil, Mining Environmental Engineering, University of Wollongong, 2008.  
<http://ro.uow.edu.au/theses/759>

This paper is posted at Research Online.  
<http://ro.uow.edu.au/theses/759>

## **NOTE**

This online version of the thesis may have different page formatting and pagination from the paper copy held in the University of Wollongong Library.

## **UNIVERSITY OF WOLLONGONG**

### **COPYRIGHT WARNING**

You may print or download ONE copy of this document for the purpose of your own research or study. The University does not authorise you to copy, communicate or otherwise make available electronically to any other person any copyright material contained on this site. You are reminded of the following:

Copyright owners are entitled to take legal action against persons who infringe their copyright. A reproduction of material that is protected by copyright may be a copyright infringement. A court may impose penalties and award damages in relation to offences and infringements relating to copyright material. Higher penalties may apply, and higher damages may be awarded, for offences and infringements involving the conversion of material into digital or electronic form.

# *Performance of Water Recycling Technologies*

A thesis submitted in fulfilment of the requirements for

Admission to the degree of

**DOCTOR OF PHILOSOPHY (Ph.D.)**

In

Environmental Engineering

by

**Jawad Hilmi Al-rifai**

Faculty of Engineering

School of Civil, Mining & Environmental Engineering



Wollongong, NSW, Australia.

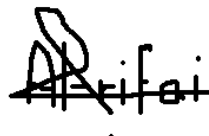
APRIL 2008



## **Declaration**

I hereby declare that this submission is my own work and to the best of my knowledge it contains no material previously published or written by another person, nor material which to a substantial extent has been accepted for the award of any other degree or diploma at the University of Wollongong or any other educational institution, except where due acknowledgement is made in the text. Any contribution made to the research by others, with whom I have worked at UoW or elsewhere, is explicitly acknowledged in the thesis.

I also declare that the intellectual content of this thesis is the product of my own work, except to the extent that assistance from others in the project's design and conception or in style, presentation and linguistic expression is acknowledged.



Jawad Al-Rifai

Date 18<sup>th</sup> of July 2008

## **Thesis supervisors/ advisors**

Professor William E. Price, School of Chemistry, Faculty of Science, University of Wollongong, Wollongong. [wprice@uow.edu.au](mailto:wprice@uow.edu.au)

Dr Hadi Khabbaz, Senior Lecturer in Geotechnical Engineering, Infrastructure and the environment group, Faculty of Engineering, university of Technology, Sydney, City Campus. [hadi.khabbaz@uts.edu.au](mailto:hadi.khabbaz@uts.edu.au)

# *Abstract*

---

Prolonged drought conditions and increased water consumption, especially in Australia, have forced water authorities, consumers and local councils to consider wastewater recycling as a supplementary water supply. As a consequence there is a growing momentum favouring reuse of wastewater. Due to a fear of the potential effects of micro-pollutants on wildlife and human health, there has been a concomitant increase in resistance to such schemes.

Three Australian wastewater recycling schemes have been studied for their ability to remove trace organic contaminants. Two of these schemes employ reverse osmosis (RO) technology and the other applies ozonation and biological activated carbon filtration (BAC). Contaminant concentrations were determined using a sensitive analytical method, developed in this study, comprising solid phase extraction (SPE), derivatization and gas chromatography (GC) with mass spectrometry detector (MS) using selected ion monitoring (SIM). In addition, a range of other standard characterization techniques including total organic carbon, total nitrogen, turbidity, UV absorbance and pH were used. In raw wastewaters, analgesics and non-steroidal anti-inflammatory medications present were similar in nature and concentration to those found in wastewaters around the world. Remarkably, removal efficiencies for the three schemes were superior to literature values and RO was responsible for the greatest proportion of contaminant removal.

A comprehensive one year study was conducted to investigate the occurrence, persistence and fate of a range of organic compounds at different processing points at the Luggage Point Water Reclamation Plant in Brisbane, Australia. The treatment applied consists of screening, grit removal and diffused activated sludge followed by microfiltration (MF) and reverse osmosis (RO). It was found that salicylic acid was the most abundant contaminant in the influent with a concentration range of 11,065 - 38,490 ng/L followed by bisphenol A with a range of 6,330 - 23,020 ng/L. The concentration of all analytes decreased on average by one order of magnitude during primary and secondary treatments. Gemfibrozil, primidone and carbamazepine were found to have relatively low removal efficiencies (74-78%) during these stages compared to the other compounds which would indicate lower biodegradability. Furthermore, a positive relation

was found between metal concentration and their removal from the wastewater treatment plant resulting in a concentration less than 0.05 mg/L for most metals in the secondary effluent.

The RO system was found to play an important role in further lowering these concentrations by another order of magnitude. The overall removal efficiencies in the final recycled water were between of 97-100% resulting in most compound concentrations in the product water being lower than 100 ng/L. An exception to this was bisphenol A (which was present at concentrations of up to 500 ng/L).

Notably, the RO membrane serves as a large reservoir for organic matter (i.e., high organic carbon, TN and absorbance measurements) as well as trace organic compounds such as PhACs and EDCs due to the adsorption of contaminants on membranes and their likely release in the brine. The concentrations of trace organic compounds reached  $\mu\text{g/L}$  levels. The concentration factor for the detected compounds ranged between one and five for all detected trace compounds. With regard to the metals content of the brine (anions, cations and heavy metals), the RO membrane concentrates these metals by a factor of between three and five.

The demonstrated ability of RO membranes to concentrate many of the compounds highlights the need for continued research into monitoring wastewater treatment, concentrate disposal, improved water recycling schemes and ultimately, safer water and a cleaner environment.

Fully investigation of the micropollutants fate in the wastewater treatment plants was impossible due to both time constraints and the fact that little systematic relationships were found between the removal of organic contaminants and water treatment processes. It was not possible to pursue studies of the mechanisms of removal for the treatment plants under investigation.



# *Acknowledgments*

---

The work presented in this thesis was carried out under the guidance and supervision of Prof. William Price and Dr Hadi Khabbaz. I would like to thank them for the time and resources that were committed to this project. I would particularly like to express my appreciation for their invaluable guidance and continuous support for my PhD project.

I am greatly indebted to Prof. Andrea Schafer for her guidance and support in the first part of my research and for the acceptance of my application to undertake this research. I also express my appreciation for Dr Stuart Khan for the considerable knowledge and skills I acquired in the Gas chromatography and chemical analysis.

Special thanks to Ms Joanne George and Mr Norm Gal for sharing their technical knowledge and assistance in this work and to the administrative staff of the Engineering for their support to me during my PhD research. I am also grateful for the invaluable advice, insight and assistance contributed by Dr Candace Gabelish during my research as well as for the proof reading of this manuscript.

The project was funded through the Australian Research Council (ARC) Linkage project. The author thanks the personnel of the water treatment plants namely Grahame Simpson and Christopher Irvine-Brownor (Brisbane Water), Jeff Kidd (Gerringong Gerroa Sewage Scheme) and Hugh Chapman (Water Reclamation and Management Scheme), and plant personnel for organizing sample collection and the provision of the required results.

The Australian Research Council (ARC) and Brisbane Water are acknowledged for the provision of scholarships and materials support for the PhD candidate through the Linkage Scheme project LP0454254.

Finally, thanks to my wife for her time, caring, warmth and understanding throughout the course of this research, to my kids: Dena and Ahmad for their patience during the months of hard works and to my mum, dad, brothers and sister for their sympathy and encouragement during the four years I spent away from them.

**Table of Contents**

<b>1</b>	<b>INTRODUCTION .....</b>	<b>1-1</b>
<b>2</b>	<b>PHARMACEUTICALS AND ENDOCRINE DISRUPTING COMPOUNDS .....</b>	<b>2-1</b>
2.1	INTRODUCTION .....	2-1
2.2	USES .....	2-2
2.3	METABOLISM AND EXCRETION .....	2-2
2.4	SOURCES IN THE ENVIRONMENT .....	2-3
2.5	PHYSICO-CHEMICAL PROPERTIES .....	2-3
2.6	ENVIRONMENTAL OCCURRENCE .....	2-4
2.7	EFFECTS .....	2-6
2.8	ANALYSIS .....	2-7
2.9	SUMMARY .....	2-12
<b>3</b>	<b>ANALYTICAL METHODS .....</b>	<b>3-1</b>
3.1	INTRODUCTION .....	3-1
3.2	EXPERIMENTAL .....	3-5
3.3	METHOD VALIDATION .....	3-15
3.4	PHYSICOCHEMICAL CHARACTERIZATION .....	3-18
3.5	SUMMARY .....	3-21
<b>4</b>	<b>COMPARATIVE ASSESSMENT OF THREE WATER RECYCLING PLANTS IN REMOVAL OF TRACE ORGANIC COMPOUNDS .....</b>	<b>4-1</b>
4.1	INTRODUCTION .....	4-1
4.2	CASE STUDIES .....	4-3
4.3	EXPERIMENTAL METHODS .....	4-13
4.4	RESULTS AND DISCUSSION .....	4-14
4.5	SUMMARY .....	4-28
<b>5</b>	<b>OCCURRENCE AND FATE OF MICROPOLLUTANTS IN THE LUGGAGE POINT WATER RECLAMATION PLANT .....</b>	<b>5-1</b>
5.1	INTRODUCTION .....	5-1
5.2	INORGANIC CONSTITUENTS .....	5-3
5.3	PHARMACEUTICALS AND ENDOCRINE- DISRUPTORS COMPOUNDS .....	5-4

## TABLE OF CONTENTS

5.4	REMOVAL MECHANISMS .....	5-5
5.5	MATERIALS AND METHODS .....	5-7
5.6	PHYSICOCHEMICAL CHARACTERISATION OF INFLUENT AND EFFLUENT .....	5-9
5.7	PERFORMANCE OF WASTEWATER TREATMENT PROCESSES OF LPWRP .....	5-12
5.8	OCCURRENCE OF PHACs AND EDCs IN WASTEWATER INFLUENTS AT LUGGAGE POINT WATER RECLAMATION PLANT .....	5-16
5.9	REMOVAL OF PHACs AND EDCs IN LPWRP .....	5-21
5.10	SUMMARY .....	5-24
<b>6</b>	<b>ROLE OF REVERSE OSMOSIS FOR THE REMOVAL OF TRACE COMPOUNDS IN RECYCLED WATER TREATMENT (LPWRP).....</b>	<b>6-1</b>
6.1	INTRODUCTION.....	6-1
6.2	MEMBRANE PROCESS .....	6-3
6.3	MEMBRANE APPLICATIONS .....	6-5
6.4	REMOVAL OF TRACE CONTAMINANTS .....	6-6
6.5	THE LUGGAGE POINT WATER RECLAMATION PLANT (LPWRP).....	6-7
6.6	MICROFILTRATION PROCESS .....	6-10
6.7	RO FILTRATION PROCESS .....	6-12
6.8	PRODUCT WATER .....	6-27
6.9	SUMMARY .....	6-30
<b>7</b>	<b>CONCLUSIONS AND RECOMMENDATIONS .....</b>	<b>7-1</b>
7.1	INTRODUCTION.....	7-1
7.2	RAW WASTEWATER .....	7-3
7.3	SECONDARY EFFLUENT .....	7-3
7.4	PRODUCT WATER .....	7-4
7.5	BACKWASH .....	7-5
7.6	CONCENTRATE .....	7-5
7.7	SUGGESTIONS FOR FURTHER STUDIES: .....	7-6
<b>8</b>	<b>APPENDICES .....</b>	<b>8-1</b>
<b>9</b>	<b>REFERENCES.....</b>	<b>9-1</b>

# *Chapter*

## *1 Introduction*

---

Membrane technology has become a technically and economically feasible alternative for water and wastewater treatment. This has come about due to the achievement of reliable, high removal efficiency at reasonable cost. A superior effluent quality not only allows an improved discharge quality, but also opens up the potential for direct and indirect reuse of industrial and municipal effluents.

The number of organic compounds that have been synthesized since the turn of the century is in excess of fourteen million. As a result, many synthetic compounds now occur in the wastewater from most municipalities and communities. Their occurrence presents many potential problems in terms of removal and discharge back to the environment and possible health effects to biota of the parent compounds or degradation products.

Different classes of trace contaminants have been detected in wastewater effluent, including pharmaceutical compounds, detergents, pesticides, polycyclic aromatics hydrocarbons, surfactants, chlorinated organic compounds, esters, alcohols, glycols, aliphatic aromatic amines and phenols. The trace contaminants, usually at ng/L levels, are generally greatly diverse in chemical properties and have complex matrices. Their occurrence in wastewater and behaviour during the production of drinking water and wastewater treatment are key environmental issues in the reuse of water resources.

There has been a worldwide increase in the number and size of wastewater treatment plants utilizing reverse osmosis (RO) membrane technology for the production of high quality recycled water over the past 10-15 years. As membrane plants continue to increase, so will the potential impact of RO concentrate disposal on the environment. The issue of concentrate disposal must be addressed as an integral part of the design and evaluation of any membrane process and the

method of disposal will ultimately be site specific. Disposal options for the RO concentrate are reintroduction to the wastewater treatment plant, ground water injection and evaporation pond. The cost of disposal and any treatment can have a considerable impact on the overall economic viability of a membrane plant. Neither the characteristics of the RO concentrate nor the environmental impacts of contaminants found are clear at present.

The occurrence and fate of both organic and inorganic trace contaminants in the aquatic environment have long been recognized as important issues of public health and environmental concern. A wide range of trace contaminants, organic and inorganic, synthetic or natural have been detected and identified as important contaminants in sewage and effluent impacted water bodies including surface and ground water.

The primary objective of this project was to investigate the performance of water recycling technologies in removal of organic trace contaminants particularly pharmaceuticals and endocrine disrupting compounds. The project was divided into three phases.

- Phase I was designed to develop a procedure for estimating concentrations of key pharmaceuticals in wastewater. This involved the identification and quantification of individual compounds.

- Phase II was designed to investigate the occurrence and fate of trace contaminants in three different water recycling plants in Australia. These plants implement different treatment technologies such as activated sludge, biological active carbon, ozonation, microfiltration and reverse osmosis. Investigated trace organic compounds belong to the most commonly detected compounds in wastewater, namely pharmaceuticals and endocrine disrupting compounds.

- Based on the outcomes of phase I, Luggage Point Water Reclamation Plant was selected for a comprehensive examination of the fate of the trace organic compounds for a year (Phase III). This involved the determination of removal percentages of pharmaceuticals and endocrine disrupting compounds by various treatment processes, and examination of the relationship with the physiochemical properties of these organic compounds. The quality of produced water was assessed using the general characteristics as well as the organic and inorganic contents in order to evaluate the treatment processes efficiencies. Furthermore, the concentrate and the backwash of the reverse osmosis were characterised to study the potential impact of disposal of these streams for the management of wastewater.

The body of the dissertation consists of six main chapters as follows:

Chapter 2 provides a literature review on pharmaceuticals and endocrine disrupting compounds with respect to their chemistry, usage and sources in the environment. Other aspects such as analytical methods, water recycling, removal mechanisms of trace contaminants and membrane technologies are discussed in later chapters.

Chapter 3 reviews current methods of analysis reported by other researchers, and describes the development of the procedure used for the analysis of target compounds, and validation of the developed method.

Chapter 4 reviews the current state of water recycling in Australia, the Australian guideline for “the use of reclaimed water” and the case studies of water recycling plants under investigation. A comparative analysis of the occurrence and fate of trace organic compounds was conducted and the results were discussed in relation to removal of trace compounds and the efficiency of the three water recycling schemes in producing high water quality for reuse.

Chapter 5 reviews wastewater contents, conventional wastewater treatment processes and mechanisms of trace contaminant removal through these treatment processes. A comprehensive investigation of the efficiency of the Luggage Point Water Reclamation Plant in producing a high water quality was carried out. The investigation detailed the efficiencies of wastewater treatment in removal of inorganic and organic compounds from the raw wastewater.

Chapter 6 reviews membrane technology and the principle of mass balance. This is followed by an investigation of the mass balance of the microfiltration and reverse osmosis processes and characterisation of the RO concentrate and backwash.

Chapter 7 summarizes the critical and fundamental findings of this study and makes suggestions for further research.



# Chapter

## 2 *Pharmaceuticals and Endocrine Disrupting Compounds*

---

### 2.1 Introduction

Effluent from wastewater treatment plants (WWTP) is increasingly being reclaimed, recycled and reused for various purposes in many countries. In some parts of the world, especially in arid areas reclaimed water is recognised as a valuable and essential resource for irrigation crops. For example, about 14% of treated effluents are reused for irrigation in Australia (Radcliffe, 2004). Wastewater effluents from waste water treatment plants (WWTPs) contain toxic inorganic and organic chemicals as well as pathogens and can potentially pose risks to the environment and public health and therefore need careful management.

Considering the scarce water resources in Australia, major environmental initiatives such as reuse of wastes and water are crucial for the future prosperity of the country.. Therefore, there is a need to remove any impediment that can potentially affect the implementation of such environmental programs in Australia. Emerging issues associated with EDCs and other organic wastewater contaminants therefore need adequate attention. A wide range of compounds have been identified as being potential contaminants in water sources such as surfactants, polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), persistent organic compounds, phthalates, endocrine disrupting compounds (EDCs), steroid hormones, pharmaceutically active compounds (PhACs), and pesticides. (Granier et al., 1988; Paxéus et al., 1992; Biziuk et al., 1996; Paxéus, 1996; Pham and Proulx, 1997; Ternes, 1998; Sekela et al., 1999; Stumpf et al., 1999; Bolz et al., 2000; Korner et al., 2000; Blanchard et al., 2001; Fromme



et al., 2002; Khan, 2002; Birkett and Lester, 2003; Koutsouba et al., 2003; Blanchard et al., 2004; Carballa et al., 2004; Katsoyiannis and Samara, 2004; Lee et al., 2004; Macia' et al., 2004; Bendz et al., 2005; Clara et al., 2005; Joss et al., 2005; Khan et al., 2005; Lindqvist et al., 2005; Vieno et al., 2005; Gomez et al., 2007)

A range of target analytes were selected as representatives of a number of categories based on previous detection in wastewater, anticipated health and environmental effects, bioaccumulation potential or known persistence in the environment (as discussed in this chapter). These included pharmaceutically active compounds (PhACs) and endocrine disrupting compounds (EDCs).

## **2.2 Uses**

Pharmaceuticals are used in large quantities throughout the world as prescription and non-prescription drugs. In developed countries, annual consumption rates of prescribed pharmaceuticals range from a few kilograms to hundreds of tonnes. The consumption of drugs purchased without a prescription is at least an order of magnitude greater than the amount of prescribed drugs consumed. For instance, patterns of drug use in Australia indicated that the acetylsalicylic acid (aspirin) and acetaminophen (paracetamol) sold over-the-counter ranked among the top ten most dispensed drugs with 4.5 million prescriptions for the year 2003 (Department of Health and Aging, 2005).

## **2.3 Metabolism and excretion**

Pharmaceuticals are administered to humans and animals for a variety of reasons including prevention and treatment of various types of disease. Most (if not all) administered pharmaceuticals are excreted to various degrees and discharged directly to the sewage system depending on the physiochemical properties of the compounds. Investigations carried out in many countries have detected more than 80 pharmaceuticals and their metabolites in the aquatic environment at concentrations in the  $\mu\text{g/L}$  range or lower. Reported compounds include wide range of classes of pharmaceuticals: Analgesics, antiinflammatory compounds, beta-blockers, lipid regulators, antiepileptics, antibiotics, X-ray media contrast agents and contraceptive drugs (Heberer, 2002b).

## 2.4 Sources in the environment

Pharmaceutical compounds primarily enter the aquatic environment through WWTP effluent discharges due to the large amount used as prescription or over the counter medication. Other sources of pharmaceuticals could be livestock waste, hospitals, industrial discharges and contribution from municipal sewage (Drewes, 2007).

The introduction of pharmaceuticals to the aquatic environment via wastewater treatment and effluent discharge is dependant on drug use, pharmacokinetic and physicochemical properties of the drug and on the water treatment processes involved (Daughton and Ternes, 1999). For example, Aspirin is readily metabolised to carbon dioxide and water so is unlikely to be detected in effluent (Richardson and Bowron, 1985) whereas, clofibrilic acid will remain in the aqueous phase and be detected in effluents (Halling-Sorensen et al., 1998). A large variety of drug residues have been detected in WWTP secondary effluent, such as antiphlogistics, lipid regulators and beta blockers, and the concentrations of these pharmaceuticals often exceeds several nanograms per litre (Heberer, 2002a).

## 2.5 Physico-chemical properties

The fate of organic micropollutants, once released in the environment, is, in part, determined by their physico-chemical and biodegradability properties, water solubility, hydrophobicity and tendency to volatilize (Drewes, 2007). Physico-chemical properties of target compounds are summarized in Table 2-1. These properties will influence whether compounds will remain in the aqueous phase or adsorb to sewage sludges. The tendency for organic compounds to accumulate in sludge solids can be assessed using octanol-water partition coefficient ( $K_{ow}$ ). Rogers (1996) proposed the following guide to assess the sorption potential for organic contaminants.

$\log K_{ow} < 2.5$	Low sorption potential
$2.5 < \log K_{ow} < 4.0$	Medium sorption potential
$\log K_{ow} > 4.0$	High sorption potential

Acidic pharmaceutical compounds are defined as carboxylic acids with solubility ranges from insoluble to slightly soluble. Acetyl salicylic acid is the most soluble in this group (see Table 2-1). Other pharmaceutical compounds are often considered as neutral pharmaceuticals, but have

in fact slight acidic groups such as phenolic moieties (e.g., acetaminophen) or amid groups (e.g., carbamazepine) (see Table 2-1).

These properties are also important from the analytical point of view since they largely determine the solvents and sorbents for extraction or analytical techniques for their determination.

## **2.6 Environmental occurrence**

The occurrence and fate of both organic and inorganic trace contaminants in the aquatic environment has long been recognized as an important issue of public health and environmental concern. A wide range of trace contaminants, organic and inorganic, synthetic or natural have been detected and identified as important contaminants in sewage and effluent impacted water bodies including surface and ground water.

The first data on pharmaceutical residues in the environment mainly focused on clofibric acid, the active metabolite of three lipid regulators (Garrison et al., 1976; Hignite and Azarnoff, 1977). In 1998, Duarte (Duarte et al., 1999) reported clofibric acid in the North Sea at concentrations between 1 and 2 ng/L, while in year 2002 clofibric acid concentration was as high as 19 ng/L.

Acidic drugs used as anti-inflammatories and analgesics either by prescription or available over the counter have been detected frequently in municipal wastewater and surface water (Soulet et al., 2002; Metcalfe et al., 2003; Macia' et al., 2004; Lindqvist et al., 2005; Tauxe-Wuersch et al., 2005; Thomas and Foster, 2005; Loraine and Pettigrove, 2006; Nakada et al., 2007). A variety of lipid-regulating agents and neutral anti-epileptics drug have also been widely identified in wastewater, surface water and ground water (Ternes et al., 2001; Metcalfe et al., 2003).

Until very recently, relatively little was known about the efficiency with which pharmaceutical residues are removed during wastewater and biosolids treatment processes. Conventional wastewater treatment facilities are not specifically designed to remove pharmaceutical residues, and the degree to which they are removed varies from nearly complete to very little (Ternes et al., 1999).

**Table 2-1: General characteristics of short listed compounds**

Compound	Classification	Mol. Weight	log $K_{ow}$	$pK_a$	Water Solubility (mg/L)	Solubility index <sup>(i)</sup>
<b>Acidic</b>						
diclofenac	Non-steroidal, anti-inflammatory	318.1, 296.2 (aq)	0.7 <sup>(b)</sup> , 4.51 <sup>(m)</sup>	4.0-4.2 <sup>(a,b,d,m)</sup>	2.4 <sup>(a)</sup> <sub>(PI)</sub>	PI
ibuprofen	Non-steroidal, anti-inflammatory	206.2	3.14-4.5 <sup>(a,b,c,f,h,g)</sup>	4.9-5.7 <sup>(a,b,c,d,g)</sup>	21 <sup>(c,a,g)</sup> , 10 <sup>(b)</sup> <sub>(PI)</sub>	PI
ketoprofen	Non-steroidal, anti-inflammatory	254.3	3.12 <sup>(a,h,m)</sup>	4.45 <sup>(a,d,m)</sup>	51 <sup>(a)</sup>	PI
naproxen	Non-steroidal, anti-inflammatory	230.2	3.18 <sup>(h,g,m)</sup>	4.15-4.5 <sup>(d,g,m)</sup>	16 <sup>(g)</sup> , 159 <sup>(a)</sup>	PI
clofibrilic acid	Antihyperlipidemics	214.5	2.57 <sup>(f,m)</sup>	N/A	583 <sup>(f)</sup>	VSS
gemfibrozil	Antihyperlipidemics	250.2	4.39-4.77 <sup>(a,g,m)</sup>	4.42-4.7 <sup>(a,g,m)</sup>	19 <sup>(a,g)</sup>	
salicylic acid	Analgesics	180.2	1.19 <sup>(b,m)</sup>	3.5 <sup>(b,m)</sup>	5000 <sup>(b)</sup>	SS
<b>Neutral</b>						
acetaminophen	Analgesics	151.2	0.46 -0.89 <sup>(b,g,m)</sup>	9.4-9.7 <sup>(b,g,m)</sup>	100 <sup>(b)</sup>	VSS
carbamazepine	Anticonvulsant	236.3	2.3-2.93 <sup>(b,h,g,m)</sup>	7 <sup>(b)</sup> , 13.9 <sup>(m)</sup>	10 <sup>(b)</sup> , 18 <sup>(g)</sup>	PI
phenytoin	Anticonvulsant	252.3	2.47 <sup>(k)</sup>	8.33 <sup>(k)</sup>	10 <sup>(i)</sup>	
primidone	Analgesics	218.3	0.85- 9.1 <sup>(a,m)</sup>	12.26 <sup>(a)</sup>	500 <sup>(b,a)</sup>	VSS
<b>Endocrine Disrupting chemicals (EDCs)</b>						
bisphenol A	Non-steroidal estrogenic	228.3	3.32 <sup>(c, h)</sup>	10.1 <sup>(e)</sup>	120 <sup>(c,e)</sup>	PI
nonylphenol	Non-steroidal estrogenic	220	4.48 <sup>(e,h)</sup>	10.3 <sup>(e)</sup>	5 <sup>(e)</sup>	PI

Solubility index: (PI): practically insoluble <100mg/L; (VSS): very slightly soluble 100-1000mg/L; (SS): slightly soluble: 1-10g/L

<sup>(a)</sup> (Xu et al., 2005) <sup>(b)</sup> (Jjemba, 2006) <sup>(c)</sup> (Kimura et al., 2003a) <sup>(d)</sup> (Lindqvist et al., 2005) <sup>(e)</sup> (Nghiem and Schäfer, 2006) <sup>(f)</sup> (Ternes et al., 2004) <sup>(g)</sup> (Snyder et al., 2007) <sup>(h)</sup> (Nakada et al., 2007) <sup>(k)</sup> (Khan, 2002) <sup>(i)</sup> (Kasim et al., 2004) and <sup>(m)</sup> (Barcelo, 2007)

aq: aqueous.

N/A: not applicable

The fate and transport of trace organic constituents in municipal wastewater treatment are of particular concern to many municipalities due to their possible adverse health effects on both humans and wildlife.

## **2.7 Effects**

In recent years evidence has emerged that certain chemicals (e.g. estradiols, nonylphenol, bisphenol A, PCB, POPs and pesticides) at elevated concentrations can interfere with the normal functioning of endocrine systems and can cause reproductive and immune system problems in wildlife. These chemicals are generally referred to as Endocrine Disrupting Chemicals (EDCs). However, the risks of EDCs for the Australian environment are not clear, as we have little knowledge of their fate and behaviour. .

Pharmaceuticals are, by design, biologically active compounds. Their potential to affect a range of physiological processes in a large variety of non-target organisms is inherent. For example, many common antidepressant drugs act by mechanisms that are known to disrupt a wide variety of physiological processes in a highly diverse number of aquatic species including fish, bivalve molluscs, gastropods and crustaceans. Biochemical processes, which regulate such actions as spawning (Fong et al., 1998), parturition (Fong et al., 1998) and metamorphosis (Couper and Leise, 1996) are affected by antidepressants at micromolar concentrations. The known toxicity of pharmaceuticals towards aquatic organisms has been comprehensively reviewed (Halling-Sorensen et al., 1998; Webb, 2001). It has been shown that some pharmaceuticals may influence both the structure and the function of algal communities in stream ecosystems receiving treated sewage effluents (Wilson et al., 2003). Such changes could affect both the nutrient processing capacity and the natural food web structure of the aquatic environment.

It is unlikely that most pharmaceutical compounds are present in the environment at high enough concentrations to cause significant harm (Jones et al., 2007). However, some have been observed at sufficient concentrations, to induce effects in both animals and plants and it is possible they may have other effects that have not yet to be uncovered. There is also possibility of chronic, long-term effects and it would therefore seem unwise to conclude that these compounds are having no effect at all until there is more proof (Jones et al., 2007).

While there is no evidence that most pharmaceuticals pose a human health risk their presence is of concern. This is especially important in potential indirect and direct water reuse situations.

From a toxicological point of view, traces of drug residues as they have been reported to occur in drinking water are, from today's scientific knowledge, not harmful for lifetime human consumption (Heberer et al., 2002; Heberer, 2007)

Residues of many pharmaceuticals are known to be prevalent throughout the aquatic environment (Halling-Sorensen et al., 1998; Daughton and Ternes, 1999; Heberer, 2002a). Environmental risk assessment of pharmaceuticals is still in its infancy. However, the conceptual considerations required for such an assessment have been discussed (Lange and Dietrich, 2002). It has been argued that the ecotoxicological actions of pharmaceuticals may be complex, unexpected and severe, even at concentrations significantly lower than normal (human) therapeutic doses (Seiler, 2002).

## **2.8 Analysis**

The increased concern globally toward trace organics has necessitated the development of highly sensitive and specific analytical tools for their determination in environmental samples. The diversity of chemical properties of trace organics, the complexity of environmental matrices and the ultra-trace detection limits make the analysis of trace organics a challenging task for many researchers. Most techniques involve a pre-concentration step, clean-up of the extracts and chromatographic separation by gas or liquid chromatography followed by high sensitivity detection.

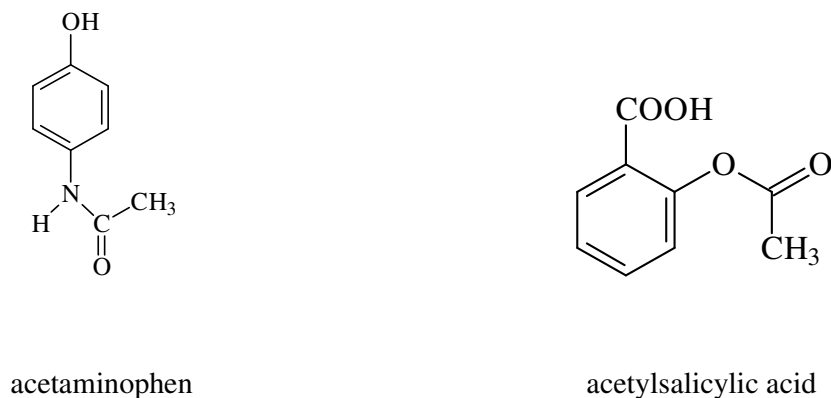
A range of target analytes were selected to represent a number of categories of current environmental contaminants known to be persistent through the sewage treatment processes to varying degrees. These included pharmaceutically active compounds (PhACs) and endocrine disrupting chemicals (EDCs). A description of the compounds and their sources is presented in the following sections.

### **2.8.1 Pharmaceutically Active Compounds**

#### **2.8.1.1 Analgesics**

Acetaminophen (paracetamol) and acetylsalicylic acid (aspirin) are two of the most prevalent pharmaceutical drugs in Australia. They are available to the consumer without a prescription and are most commonly used for their analgesic and in some cases, antipyretic properties. Structures

of some common analgesic agents are shown in Figure 2-1. When aspirin is ingested, it is quickly and effectively hydrolysed to the major excretion product, salicylic acid. Other non-conjugate metabolites of aspirin include gentisic acid and *o*-hydroxyhippuric acid.

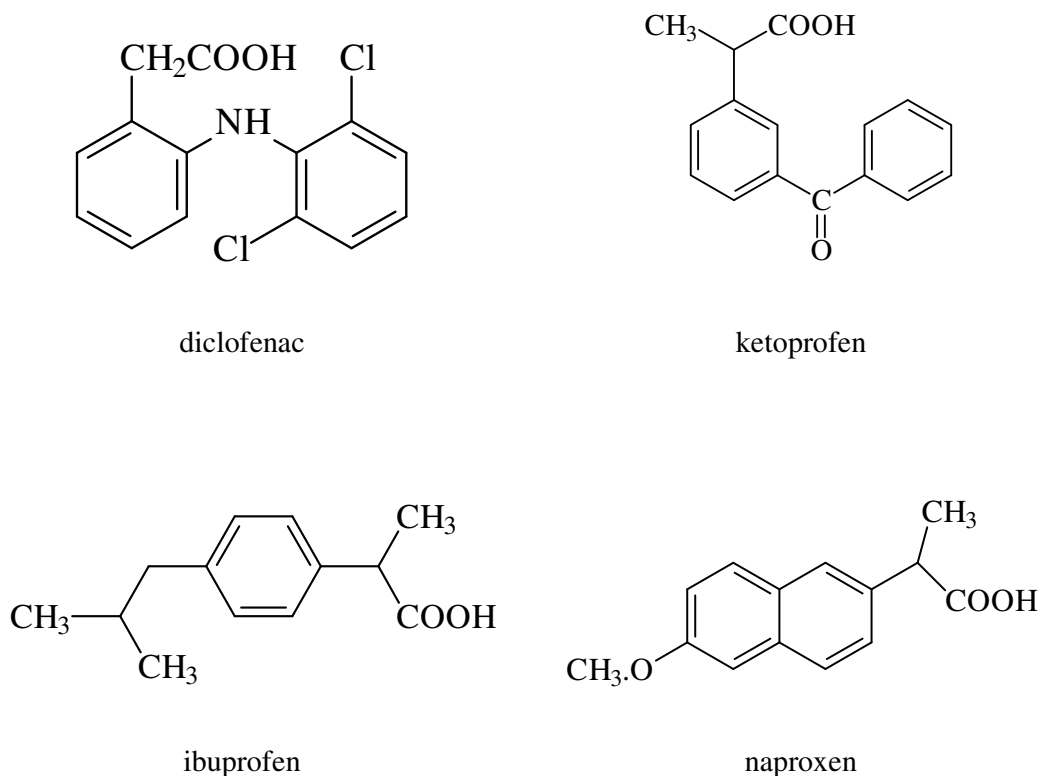


**Figure 2-1: Structures of some common analgesic agents**

In addition to the metabolism of aspirin, there are several other sources of salicylic acid in sewage. One example is the use of this compound as a food preservative. Excreted salicylic acid is predominantly conjugated with glucuronic acid and glycine to form acyl and ether glucuronides and salicyluric acid. Only 5%-10% of a dose is excreted as free salicylic acid. Most of the remainder is excreted as conjugates (Moffat, 1986).

#### 2.8.1.2 Non-steroidal anti-inflammatory (NSAI) agents

Non-steroidal anti-inflammatory (NSAI) drugs include diclofenac, ibuprofen, ketoprofen and naproxen (Figure 2-2). They are used to relieve some symptoms caused by arthritis (rheumatism), such as inflammation, swelling, stiffness, and joint pain. Some of these medicines are also used to treat other painful conditions such as gout attacks, menstrual cramps, bursitis, tendonitis, sprains, strains and other injuries. Ibuprofen and naproxen are also used to reduce fever (United States Pharmacopeia, 2000).

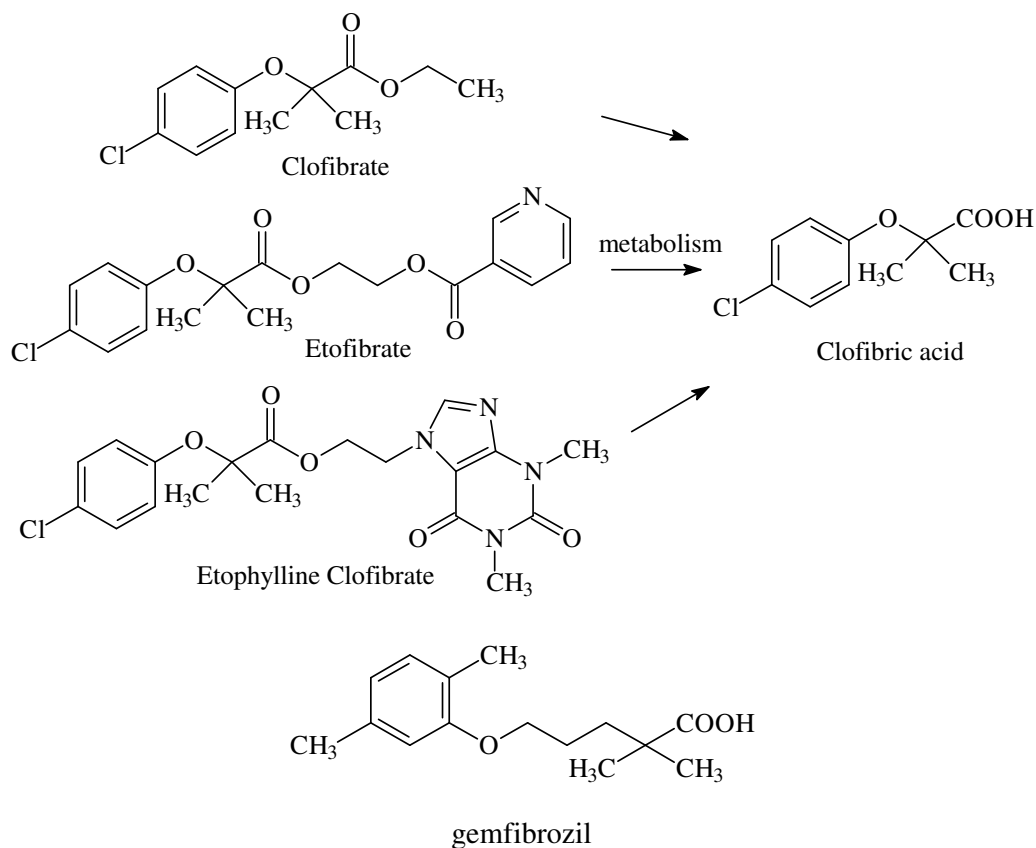


**Figure 2-2: Structures of some common NSAID agents**

### 2.8.2 Antihyperlipidemics

Antihyperlipidemics, including clofibrate, etofibrate, etophylline clofibrate, and gemfibrozil are used to lower cholesterol and triglyceride levels in the blood. Their purpose is to prevent clogging of the blood vessels (United States Pharmacopeia, 2000). Upon ingestion, clofibrate, etofibrate and etophylline clofibrate are rapidly hydrolysed to their biologically active metabolite, clofibric acid. Glucuronide conjugates of these polar metabolites are the predominant excretion products (Figure 2-3). The more polar compound, gemfibrozil, is excreted largely unchanged (United States Pharmacopeia, 2000).

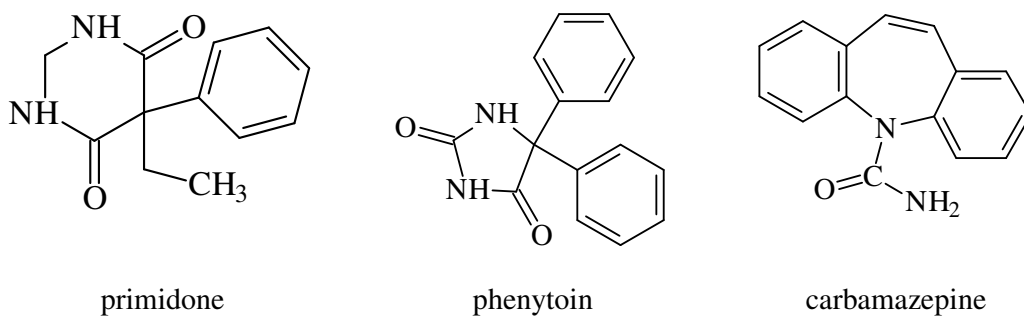




**Figure 2-3: Structures of some common antihyperlipidemic agents and metabolites**

#### 2.8.2.1 Anticonvulsants

Anticonvulsants are a structurally diverse group of drugs, used primarily for the treatment and prevention of epileptic seizures, and also for treatment of conditions such as bipolar disorder. Commonly prescribed anticonvulsants include carbamazepine, phenytoin and primidone (Figure 2-4).



**Figure 2-4: Structures of some common anticonvulsants**

### 2.8.3 Endocrine Disrupting Chemicals

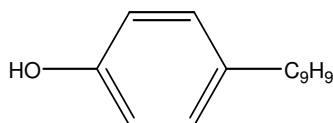
For several decades, scientists have reported that certain synthetic and natural compounds could mimic, block, simulate, or inhibit natural hormones in the endocrine systems of animals, including humans. These substances are collectively known as endocrine disrupting compounds (EDCs), and have been linked to a variety of adverse effects in both humans and wildlife. Chemicals classified as EDCs have a wide variety of origins including pharmaceuticals, personal care products (PCPs), herbicides and pesticides, industrial chemicals, household chemicals, disinfection by products, natural occurring hormones, and metals.

These synthetic and natural occurring chemicals have been discovered in various surface and groundwaters, some of which have been linked to ecological impacts at trace concentrations (Koplin et al., 2004). In this section, a brief discussion is provided.

#### 2.8.3.1 4-Nonylphenol

4-Nonylphenol is a degradation product of the surfactant, Nonylphenol-polyethoxylate. Alkylphenol-polyethoxylates (APnEO) are an important class of non-ionic surfactants that are widely used in many household and industrial detergent formulations. The occurrence and transformation of APnEOs in biological STPs has been studied in some detail (Ahel et al., 1994). Whilst the parent APnEO compounds are known to be eliminated efficiently during biological treatment, a range of major biodegradation products including alkylphenols (AP) are known to persist, sometimes in high concentrations. In detergent formulations, the APnEOs with 8-12 ethoxylate groups are most commonly used with nonylphenol polyethoxylates (NPnEO) accounting for about 80% of the total and octylphenol polyethoxylates (OPnEO) making up most of the remaining 20%. Consequently, the major degradation product of APnEOs is nonylphenol (NP) (White et al., 1994). The specific NP isomer 4-NP is typically the most abundant.

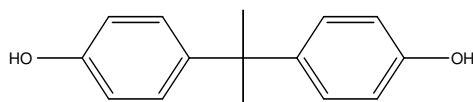
4-NP has been demonstrated to have estrogenic effects on fish, birds and mammals by a variety of bioassays including vitellogenesis, gene transcription in transfected cells and the growth of breast cancer cell lines (White et al., 1994). 4-NP has a relative estrogenic potency of around  $10^{-7}$  that of estradiol (E2) (Jobling and Sumpter, 1993).



**Figure 2-5: Structure of 4-Nonylphenol (4-NP)**

### 2.8.3.2 Bisphenol A (BPA)

Bisphenol A (BPA) is manufactured in large quantities with over 90% being used in the plastics industry for the production of polycarbonate and epoxy resins, unsaturated polyester-styrene resin and flame retardants. Because BPA is used widely in households and industry, it is expected to be present in raw sewage, wastewater effluents and in sewage sludge. Fromme et al (2002) found low concentrations of BPA in surface waters (0.0005 to 0.041 µg/L), sewage effluents (0.018 to 0.702 µg/L), sediments (0.01 to 0.19 mg/L) and sewage sludge (0.004 to 1.363 mg/L) (Birkett & Lester, 2003).



**Figure 2-6: Structure of bisphenol A**

BPA has been shown to induce estrogenic effects in fish by the induction of vitellogenesis (Hansen et al., 1998; Jobling et al., 1998). Bergeron et al (1999) have reported the estrogenic activity of BPA, with a potency of four to six orders of magnitude less than 17β-estradiol. Chen et al (2002) determined that other bisphenols used in industrial applications are also weakly estrogenic.

## 2.9 Summary

Chemicals classified as EDCs have a wide variety of origins. These synthetic and naturally occurring chemicals have been discovered in various surface and groundwaters, some of which have been linked to ecological impacts at trace concentrations.

The word “pharmaceutical” refers to a chemical prepared or dispensed in pharmacies and which treats or prevents or alleviates the symptoms of diseases. Pharmaceuticals are an extra-ordinarily diverse group of chemicals used in veterinary medicine, agricultural practices and human health.

Increasing awareness of the ecological and human risks posed by contamination of the environment with pharmaceutical residues is a challenge for the scientific community.

The presence of endocrine disrupting compounds (e.g., PhACs, BPA and NP) in the environment has raised concern among environmental scientists in recent years because of their potential to induce adverse biological effects, especially in the aquatic environment. Thus, knowing concentration levels of pharmaceuticals in different environmental media is likely important to understand the extent of the impact on the environment.

While there is no evidence that most EDCs pose a human health risk their presence is of concern. This is especially important in potential indirect and direct water reuse situations and this should be taken into account in new policies or regulations.



# Chapter

## 3 *Analytical Methods*

---

### 3.1 Introduction

Global awareness that organic contaminants can damage the environment, even at trace levels, has driven the development of more sophisticated and sensitive analytical tools for their detection in environmental samples. The diversity of organic pollutants, the complexity of environmental matrices and the ultra-trace detection limits required make the analysis of trace organics a challenging task for many researchers.

Several multi-residue analytical methods for measuring pharmaceutically active compounds (PhACs) and endocrine disrupting compounds (EDCs) in aqueous solution have been published. These methods have been reviewed for this study to aid development of an effective method. Amongst these, the predominant analytical techniques have incorporated gas chromatography-mass spectrometry (GC-MS) (Weigel et al., 2001; Koutsouba et al., 2003; Zafra et al., 2003; Quintana et al., 2004; Soliman et al., 2004; Thomas and Foster, 2005) and high- performance liquid chromatography-mass spectrometry (HPLC-MS) (Vanderford et al., 2003; Löffler et al., 2005). Less commonly used methods include gas chromatography / time of flight-mass spectrometry (GC/TOF-MS) (Hirsch et al., 2001), liquid chromatography / time of flight-mass spectrometry (LC-TOF-MS) (Ferrer and Thurman, 2003), capillary electrophoresis-mass spectrometry (CE-MS)(Ahrer and Buchberger, 2001), HPLC-Fluorometry(Gonzalez-Barreiro et al., 2003), as well as immunoassay techniques(Aherne et al., 1990).

For the purpose of this study, it was necessary to develop an analytical method that was accurate, precise and practical. The method needed to be relatively quick and inexpensive, requiring accessible instrumentation and the minimal use of hazardous reagents. Special emphasis was placed on low detection limits and on a wide range of determination. Compounds included seven acidic pharmaceuticals (i.e., diclofenac, ibuprofen, ketoprofen, naproxen, clofibric acid,

gemfibrozil and salicylic acid), four neutral pharmaceuticals (i.e., acetaminophen, primidone, carbamazepine and phenytoin) and two EDCS (i.e., bisphenol A and nonylphenol)

This chapter outlines the developed analytical procedure and describes the sampling procedure, sample preparation and the analytical procedure as well as the validation procedure carried out for measuring its performance.

### 3.1.1 Solid phase extraction (SPE)

Traditionally, in the environmental field, liquid-liquid extraction has been the preferred extraction method for organics from aqueous samples (Moeder et al., 2000). However, the pressure to reduce the use of organic solvents in laboratories has led to the development of various methods over the last decade (Hennion et al., 1998). Among these are solid phase extraction (SPE) (Koutsouba et al., 2003; Kosjek et al., 2005) and solid-phase micro-extraction (SPME)(Weigel et al., 2001). Furthermore, it may be noticed that the analysis of various polar groups contained in these chemicals (i.e., alcoholic, phenolic hydroxyl, carbonyls and polyethoxylates) may result in considerable solubility in water and are often poorly recovered by organic solvents.

The general procedure for SPE is to pass an aqueous solution (mobile phase) containing dissolved analyte through a granulated solid phase (stationary phase) to which the analyte is able to adsorb. Once this is complete, the solid phase is normally dried by drawing through air or nitrogen. Often, this is followed by a sample clean-up stage in which the cartridge containing the dried SPE phase is washed with a small volume of a very polar solvent, typically methanol. Finally, the analyte is removed from the solid phase by washing with a less polar solvent. Normally only 1-10 ml of solvent are required for extraction from a litre of water enabling high levels of concentration of the analytes of interest.

Among the most commonly used extraction sorbents in the field of environmental analysis have been octadecyl (C18) and octyl (C8) bonded silicas. The retention mechanism of these sorbents is primarily determined by hydrophobic interactions between the analyte and the carbonaceous alkyl chain of the sorbent. It has been demonstrated that extraction by C18 sorbents is generally appropriate for compounds exhibiting a log  $K_{OW}$  greater than 2 (Pichon, 2000). More recently, hydrophilic-lipophilic balance (HLB) phases supplied by Waters Corp. (Millford, MA) have

provided exceptional extractability across a diverse range of polar and non-polar analytes (Vanderford et al., 2003). These were selected for the current study.

### 3.1.2 Derivatization

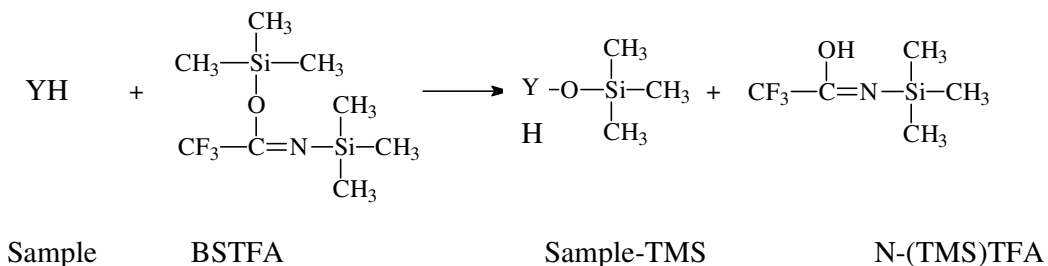
Most of the drugs analysed in this thesis contain functional groups prone to hydrogen bonding. These functional groups include carboxyl, phenol, alcohol, amino, amido and thiol. Hydrogen bonding as well as other dipole-dipole interactions decreases the volatility of compounds and therefore require higher temperatures for GC-MS analysis that increases the likelihood of thermal decomposition of many organic compounds.

Replacement of active hydrogen atoms in OH (e.g., alcohols, phenols and carboxylic acid), NH (e.g., amines and amides), and SH (e.g., thiols and thiolcarboxylic acid) groups by silyl group is the principle of derivatization. Derivatization of compounds prior to analysis may enhance performance by blocking protic sites, thereby reducing dipole interactions and increasing volatility. They can also serve to enhance the mass spectrometric properties and improve selectivity by producing more favourable diagnostic fragment patterns, including ions of increased  $m/z$  values.

Different reagents have been used to derivatize target compounds in order to improve their sensitivities and selectivities. These include pentafluorobenzyl bromide (PFBr), N,O-bis(trimethylsilyl) trifluoroacetamide (BSTFA), N-methyl -N-tert.- (butyldimethyl) trifluoroacetamide, hepta- fluorobutyryl, penta fluorobenzoyl and alkyl (e.g., methyl, ethyl, dimethyl, etc.) which have all been reported in literature (Halket and Zaikin, 2003).

BSTFA is a widely used silylating reagent in the displacement of an active proton in YH groups (i.e., OH, NH and SH) with a trimethylsilyl (TMS) group (Figure 3-1). Generally, amides, many secondary amines and some hindered hydroxyls could not be derivatised by BSTFA reagent alone. However, these functional groups can often be satisfactorily derivatized with the addition of a secondary agent acting as a catalyst such as trimethylchlorosilane (TMCS).





**Figure 3-1: Derivatization with BSTFA**

### 3.1.3 Deuterated internal standards

In order to accurately quantify analytes at the ng/L level using GC–MS procedures, internal (or surrogate) standards are commonly used. These standards are added to the sample prior to analysis and are used to correct for variations in the analytical procedure including the volume of sample injected onto the GC column, chromatographic performance and recoveries of the analytes. The present procedure comprised several chemical and physical processes including derivatization, volatilization, adsorption and desorption from SPE. Therefore, it was important that the standards had very similar physicochemical properties to the analytes. This problem was overcome by use of internal standards that differed from the analytes only in their isotopic composition, i.e., deuterated analogues of the analytes (stable isotope-labelled tracer compounds,  $^2\text{H}_{10}$  analogue). Since some of the hydrogen atoms in the native compounds are replaced with deuterium atoms, deuterated compounds would be expected to exhibit similar physicochemical behaviour to their non-deuterated analogues. Deuterated standards were reported to be used as internal standard for quantification of PhACs and nSECs (Spengler et al., 2001; Khan, 2002; Liu et al., 2004).

The use of deuterated internal standard was complicated by the existence of common fragment ions in the mass spectra of the deuterated compounds and their corresponding native analogues. It was therefore crucial to optimise the chromatographic separation between each analyte and the corresponding deuterated internal standard. At similar concentrations, their SPE recoveries should be identical, regardless of matrix or pH-related effects. In addition, their derivatization efficiencies should be the same, thus compensating for incomplete derivatization reactions. Mass spectral matrix-induced effects are also compensated for using this method. A further advantage of the co-elution of surrogate and analyte was associated with the observed retention time of the analyte that could take a more precise role in the confirmation of the correctly identified species.

### 3.1.4 Gas chromatography

Silyl derivatives are the most frequently used compounds in GC and GC/MS analysis. These silyl derivatives are particularly well resolved on capillary columns coated with non-polar polysiloxane stationary phases, such as 100% polymethylsiloxane (various commercial names e.g., HP-1, DB-1 and BP-1). These stationary phases possess good chemical and thermal stability, and provide excellent resolution of silyl derivatives.

## 3.2 Experimental

### 3.2.1 Standards preparation

Individual high purity standards (purity > 97%) including the following standards: salicylic acid, clofibric acid, ibuprofen, acetaminophen, primidone, 4-nonylphenol, gemfibrozil, naproxen, ketoprofen, bisphenol A, phenytoin, carbamazepine and diclofenac were all purchased from Sigma-Aldrich (Castle Hill, NSW). Individual stock solutions (ISS) of these standards were prepared in a volumetric flask. The stock solution was then wrapped in aluminium foil to prevent photo-catalytic degradation and stored in a refrigerator at 4°C. These standards were used to prepare the standard mixture solution (SMS) with a concentration of 50 mg/L, which were used to prepare the calibration standards.

Calibration curves were prepared to indicate the relationship between concentration (x-axis) and the ratio of the analyte response to the internal standard response (y-axis). The calibration curves were then used to undertake a linear regression analysis and thus derive linear expression for the conversion of measured analyte internal standard ratios to concentration within the experimental concentration range.

### 3.2.2 Deuterated internal standards

The following deuterated compounds: carbamazepine- $d_{10}$ , 2-hydroxybenzoic acid- $d_6$ , gemfibrozil- $d_6$ , (+/-) -Ibuprofen- $d_3$ , 5,5' diphenyl- $d_{10}$ -hydantoin, acetaminophen  $d_4$ , and nonylphenol 2,3,5,6- $d_6$ , O,D were purchased from Scientific Technology, Australia. Similarly to standard preparations (see Section 3.2.1), a 50 mg/L of the deuterated standard mixture were prepared.

A precise quantity of the deuterated standard mixture solution was added to each sample before extraction. Subsequent to derivatization and GC-MS analysis, calibration curves were prepared as described previously. The calibration curves were then used to derive the analyte concentrations in sewage from the analyte-to-deuterated ratios. This method compensated for any matrix-induced effects and other variability during extraction, derivatization and GC-MS analysis.

### **3.2.3 Sample collection**

Two modes of sample collection were used in the project. These were manually retrieved grab-samples and samples extracted with the aid of an auto-sampler. The decision as to which mode was appropriate for a particular sample was largely determined by the nature of the samples required. Manual grab-sample collection was accomplished by either pouring directly from a tap into a 2 L amber glass bottle or by the use of a small bucket and pouring into the bottle. Manual sampling was used for all samples except the raw wastewater. On the other hand, an auto-sampler was used to collect discrete samples, at preset time intervals into a single container. Samples contained in the auto-sampler were maintained at a constant 4°C until collected into a 2 L amber glass bottle. Collected samples were then transferred to the lab using an ice box to keep the samples cold during the transfer.

### **3.2.4 Sample filtration**

All samples were vacuum filtered using three different types of filters in the following order: GF/D (2.7µm) GF/F (0.7µm) filter papers and then by 0.48µm filter membrane. Filtered samples were either extracted the same day they were delivered to the lab or stored in the fridge at 4°C overnight. Sample filtration, extraction and analysis was conducted in batches. Each batch consisted of 8-12 samples, one recovery (spiked, see Section 3.2.6) sample and one blank (non-spiked see Section 3.2.7) sample.

### **3.2.5 Internal standards**

One litre of filtered sample was used for each sample extraction. This was adjusted to pH 2-3 with 4 M H<sub>2</sub>SO<sub>4</sub>. After adjustment, the pH was checked using litmus pH paper. A 100 µL of the deuterated standard mixture solution was added to each sample, recovery and blank for the purpose of internal standard calibration.

### 3.2.6 Recoveries

One litre of wastewater and recycled water was spiked at a concentration of 50ng/L of target standard. Recoveries were extracted in parallel with all other extraction. Recoveries were routinely run at a minimum frequency of every eight to ten samples.

### 3.2.7 Blanks

Non spiked samples of MilliQ water were analysed in order to determine whether sample contamination had occurred during sample preparation, extraction, derivatization and analysis, which were afterwards subtracted from the samples. At least one blank sample was run with each batch.

### 3.2.8 SPE cartridges

Oasis HLB SPE cartridges (6 ml, 200 mg) were purchased from Waters Australia. These cartridges were preconditioned by washing with 5 mL methyl tetra butyl ether (MTBE), 5 mL methanol and 5 mL MilliQ water. A one litre sample was extracted at a flow rate not greater than 5 mL/min. After sample-loading the cartridge was washed with 3 mL of 5% (v/v) methanol in water solution. In order to eliminate the presence of water from the eluate, a column of anhydrous sodium sulphate was prepared and fitted under the SPE column before the elution procedure started. The SPE cartridges were eluted with 3 x 1 mL of 10% methanol in MTBE (v/v). The extract was then evaporated to dryness at 39°C under a gentle nitrogen stream and reconstituted with 150 µL of acetonitrile into a 2 ml GC vial prior to derivatization.

A 24-port SPE cartridge manifold (manufactured by Visiprep and purchased from Supelco) was used for simultaneous extraction of up to 24 samples. Furthermore, precise flow control was provided through each cartridge by valves in the cover as well as a vacuum release valve and gauge control within the chamber of the manifold.

### 3.2.9 Derivatization

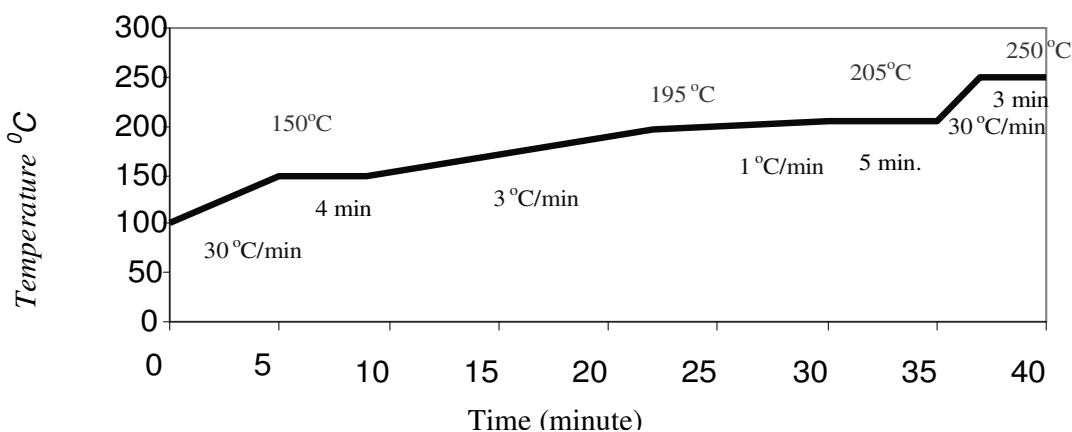
The BSTFA and TMCS (99:1) mixture was purchased from Sigma-Aldrich, Australia. A 100 µL volume of the derivatising mixture (BSTFA and TMCS (99:1)) was added to the sample extract in GC vial which was then capped immediately. The analytes were allowed to react for 1 h at

70°C a using Multi-BLOK® Heater (Branstead Lab Line, USA) before injection onto the GC-MS.

### 3.2.10 Gas chromatography – mass spectrometry (GC-MS)

For the qualitative and quantitative analysis of potential compounds a Shimadzu-GC 17A gas chromatograph equipped with an auto-injector (model AOC-20i), mass detector (model QP5000), and Split / Splitless injector was used.

To optimise the chromatographic separation, a series of preliminary experiments were performed by running each single target compound using different sets of parameters (i.e., injection, oven and detector temperatures, and carrier gas flow rate) to determine the best conditions for each compound. Furthermore, the 13 target compound mixture was injected using the best parameters. The oven temperature program was 100°C; 30°C /min.; 150°C (4 min); 3°C /min; 195°C; 1°C /min; 205°C (5 min); 30°C /min; 250 °C (3 min) (Figure 3-2). The injection port was maintained at 270°C and operated in splitless mode and the interface temperature was held at 270°C. Helium was used as a carrier gas at a flow rate of 1 mL /min and the gas line was equipped with a moisture, hydrocarbon and oxygen trap.

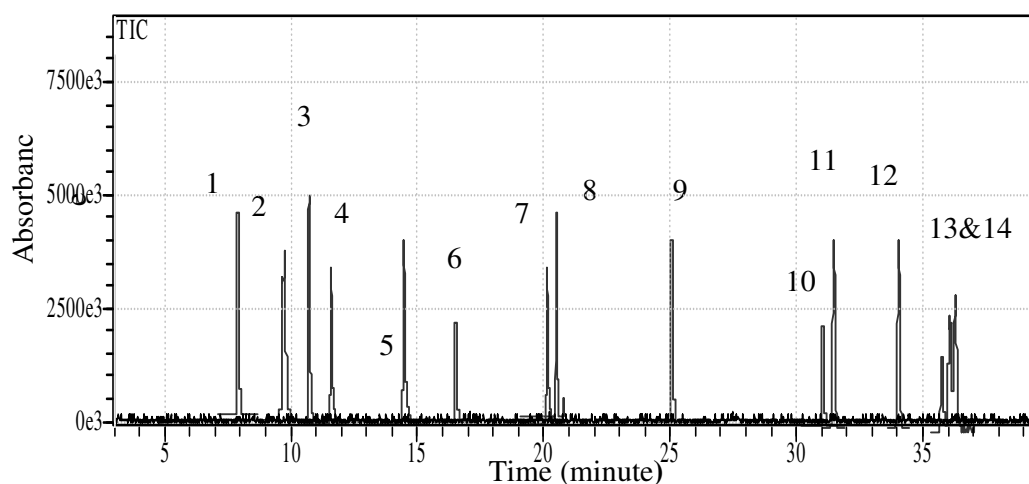


**Figure 3-2: Temperature program for the GC oven**

An appropriately selected GC-MS column was crucial for optimised separation and detection of target analytes. Many compounds under investigation required derivatization before analysis. However, many derivatized compounds, particularly silyl derivatives, are sensitive to and react with stationary phases containing active functional groups. Inevitably, this achieves unacceptable chromatographic results. Moreover, residual derivatising reagent can irreversibly damage the

performance of such a column. As reported by Khan (2002), unsatisfactory stationary phases for use with silyl derivatives include ethylene glycols and free fatty acid phases.

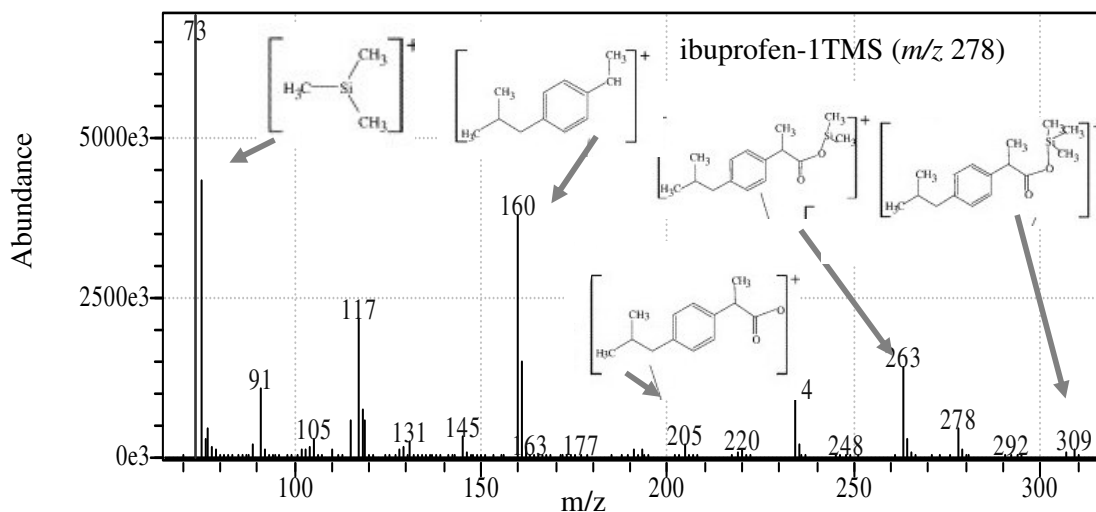
For the purpose of combined inertness and stability with good chromatographic separation characteristics for the potential compounds, a Phenomenex Zebron ZB-5 capillary column was selected. This column is a silicone-based phase column (non-polar phase), composed of 5% diphenyl and 95% dimethyl polysiloxane with a dimensions of 30 m  $\times$  0.25 mm (I.D.)  $\times$  0.25  $\mu$ m film thickness. A typical chromatogram for spiked sample with 1  $\mu$ g/ml per analyte using full-scan conditions after optimizing the GC MS parameters is shown in Figure 3-3.



**Figure 3-3: Total Ion Current for the potential analytes (Peak no. 1= salicylic acid, 2= clofibric acid, 3= ibuprofen, 4= acetaminophen, 5= acetaminophen mono, 6= primidone, 7= nonylphenol, 8= gemfibrozil, 9= naproxen, 10= ketoprofen, 11= bisphenol A, 12= phenytoin, 13= carbamazepine, 14= diclofenac).**

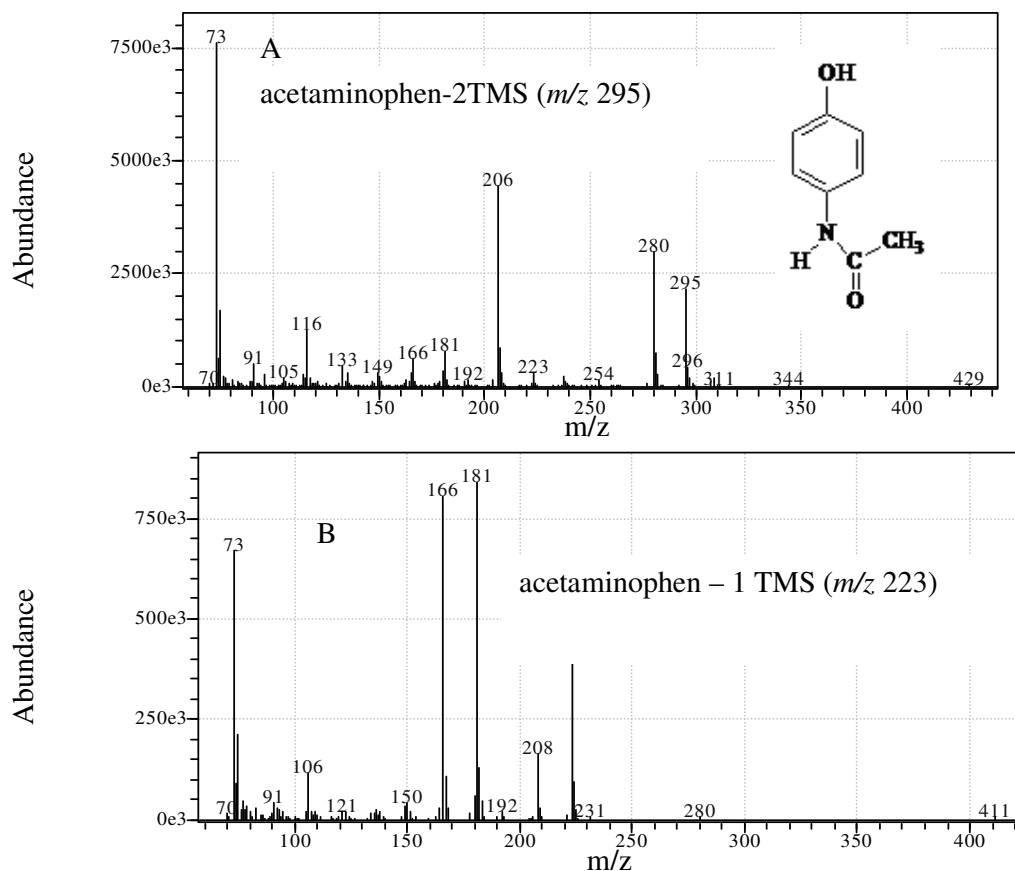
All qualitative analyses were undertaken with the mass spectrometric detector operating in full scan mode ( $m/z$  70-505) with an electron energy of 70eV. In many cases, the derivatization of the target compounds had a very favourable effect on the electron ionized mass spectrum ( $m/z$ ) with trimethylsilyl (TMS) group of  $[M-72]^+$  corresponding to base peak ( $M$ : molecular ion). Figure 3-4 is an example mass spectrum of the TMS ester of ibuprofen which was extracted from the total ion current trace with a retention time of 10.7 minutes (see Figure 3-3). It has a molecular ion at  $m/z$  = 228. The fragment ion at  $m/z$  = 263 represent the fragmentation of methyl group from molecular ion ( $[M-TMS-CH_3]^+$ ), while  $m/z$  = 205 shows the trimethylsilyl group fragmentation ( $[MTMS-SiMe_3]^+$ ). Ion at  $m/z$  = 160 is developed with sequential fragmentation

of trimethylsilyl and carboxyl groups. The base ion is present at  $m/z=73$  and is typical of BSTFA derivatization.



**Figure 3-4: EI mass spectrum of Ibuprofen**

For compounds having a single active H atom (e.g., ibuprofen;  $m/z$  282) derivatization results in mono substitution of the H atom with 1TMS ( $m/z$  278) (Figure 3-4). For other compounds, which have more than one active H atom, derivatization can form one or more substitutions. For example, Figure 3-5 shows the mass spectra of acetaminophen ( $m/z$ ) with two silylated products. The first results from derivatization of the OH group to form acetaminophen –TMS [ $M^+-72$ ] with a  $m/z$  of 223. The second product comes from simultaneous derivatization of both OH and C=O groups to form acetaminophen –2TMS [ $M^+-144$ ] with a  $m/z$  of 295 as shown in Figure 3-5. As seen in Figure 3-3, peak nos. 4 and 6 represent the Acetaminophen 2-TMS and 1-TMS, respectively.

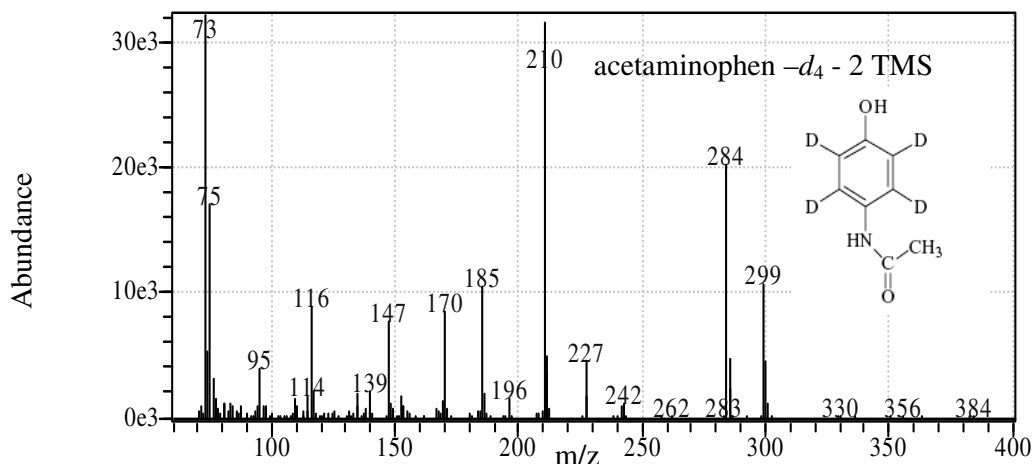


**Figure 3-5: EI mass spectrum of acetaminophen. (A) mono TMS [ $M^+-72$ ] and (B) double TMS [ $M^+-72$ ]**

Deuterated analogues of the analytes after derivatization have similar [ $M^+-TMS$ ] plus the number of deuterated hydrogen. For example, acetaminophen  $-d_4$  has  $m/z$  of 299 including 4 deuterated  $^2H_1$  in this particular compound as shown in Figure 3-6 (See Appendix 8-1 for the mass spectrum for all analytes). Since silylation reagents react with active hydrogen atoms, all solvents containing such groups were necessarily avoided. These included water, alcohols, primary and secondary amines, and enolisable ketones. While TMS esters are thermally stable, they are easily hydrolysed in the presence of water. It was therefore important to keep all TMS derivatives in anhydrous conditions at all stages of sample preparation and analysis.

It was not possible to measure the derivatization efficiency since derivatized standards of selected compounds were commercially unavailable. However, if derivatization was not complete, two distinct peaks could be seen in the chromatogram (Figure 3-7). For example, the non-derivatized carbamazepine was occasionally found with  $m/z$  of 236 and retention time of 35.8 minutes, while the TMS ester of carbamazepine was identified by the  $m/z$  of 308 at a retention time of 34.3 minutes (Figure 3-7).

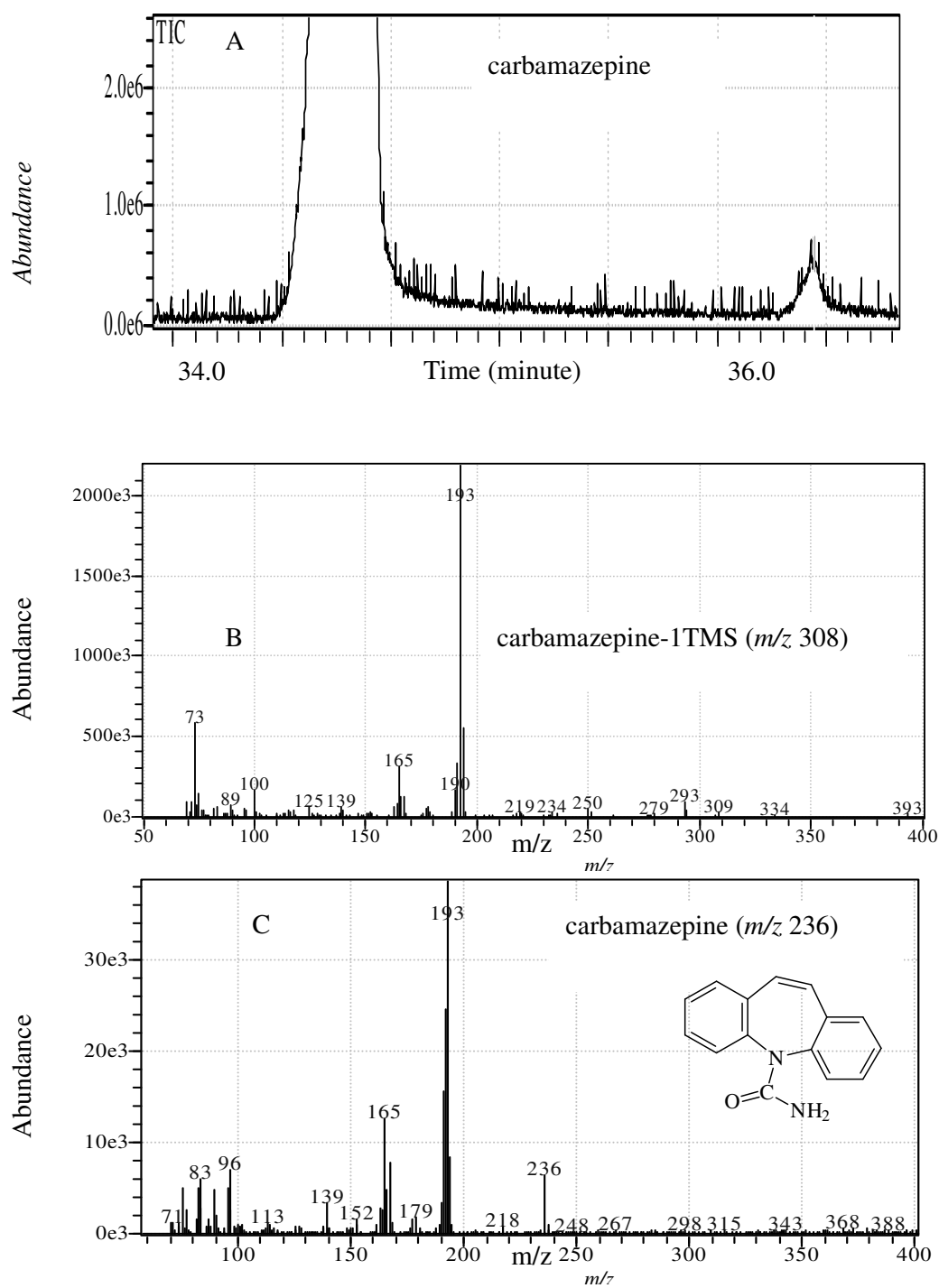




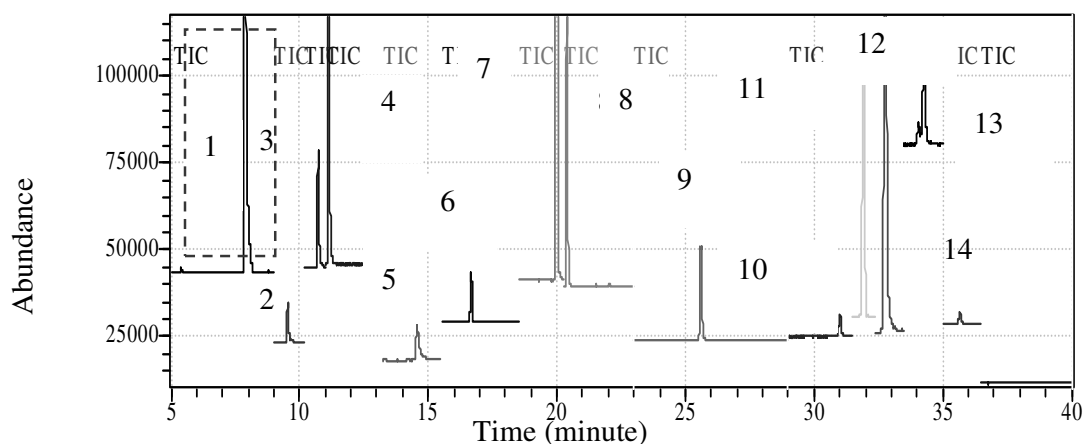
**Figure 3-6: EI mass spectrum of deuterated acetaminophen**

In a real sample the matrix ions at the GC-MS in full-scan mode overload the spectrum of the target analytes resulting in difficulties with detection. In order to reduce the background, reduce noise level and improve the signal to noise to ratio for all target analytes in the real sewage sample, single ion monitoring (SIM) technique was used (Figure 3-8). For SIM mode, ions were chosen on the basis of a number of criteria. Primarily, these were intensity and exclusivity. An optimal analyte was one that would fragment in a manner that provided few high intensity  $m/z$  peaks. Selecting peaks that were exclusive to the analyte required more care.

As a general rule, low mass ions are considerably less specific than high mass ions. The reason is that many molecules with varying masses may produce low mass ions, but only large, relatively stable molecules can produce high mass ions (see Table 3-1) Where possible, only fragments with  $m/z$  greater or close to 200 were used for quantification. Where this was not possible, the highest  $m/z$  ions of reasonable intensity were selected. There were a few exceptions as the Phenomenex Zebron ZB-5 capillary column is a silicone-based column, and typical silicone oxide molecules are known to bleed from the column at high temperatures. The resulting silicon oxide ions at  $m/z$  207, 281 and 355 are very common and were avoided for quantitative analysis. Ions normally associated with specific classes of derivatives were also avoided as these were not representative of an single analyte of interest. Examples include the common trimethylsilyl (TMS) derivative ions of  $m/z$  73 and 75. Representative ion chromatograms are shown for a spiked sewage sample with 1  $\mu\text{g/ml}$  per analyte.



**Figure 3-7: Carbamazepine in (A) as TIC, (B) EI of carbamazepine -1TMS and (C) EI of original carbamazepine.**



(Peak no. 1= salicylic acid, 2= clofibric acid, 3= ibuprofen, 4= acetaminophen, 5= acetaminophen mono, 6= primidone, 7= nonylphenol, 8= gemfibrozil, 9= naproxen, 10= ketoprofen, 11= bisphenol A, 12= phenytoin, 13= carbamazepine, 14= diclofenac).

**Figure 3-8: SIM chromatogram of spiked sample.**

**Table 3-1: Retention times and SIM ions (m/z) for potential analytes and deuterated**

Compound	Retention time	Ion 1	Ion 2	Ion 3
	(mins)			
salicylic acid	7.877	267	268	209
salicylic acid -d6	7.917	271	272	213
clofibric acid	9.533	286	288	243
ibuprofen	10.723	263	278	234
ibuprofen -d3	10.71	266	237	281
acetaminophen	11.127	206	280	295
acetaminophen d4	11.187	284	299	277
acetaminophen-mono	14.57	181	223	208
primidone	16.673	334	347	362
4-NP	19.987	292	179	293
4-NP -d6	19.997	183	296	297
gemfibrozil	20.39	201	194	202
gemfibrozil -d6	20.33	207	191	194
naproxen	25.60	243	287	302
BPA	31.907	357	358	372
phenytoin	34.057	281	381	253
phenytoin -d10	33.86	291	181	
carbamazepine	34.27	193	194	293
carbamazepine -d10	34.13	203	147	
diclofenac	35.677	277	367	369

### 3.3 Method Validation

#### 3.3.1 Calibration curves

Calibration curves for the determination of trace organic compounds were established by injecting various concentrations of 1, 10, 100 and 1000 ng/L of each compound together with a fixed concentration of the deuterated standard mix (dsm) into the GC-MS with the optimised conditions. Excellent linearity was obtained for all compounds using linear regression analysis and over the established concentration range, with determination coefficients,  $R^2$ , greater than 0.93 except for primidone ( $R^2 = 0.81$ ). As shown in Table 3-2, the linear ranges were found to be between 1 and 1000 ng/L for 4-nonylphenol and salicylic acid, 5 and 1000 ng/L for acetaminophen, bisphenol, carbamazepine, gemfibrozil and naproxen, 10 and 1000 ng/L for clofibric acid, ibuprofen and ketoprofen, 15 and 1000 ng/L for primidone, and 50 and 1000 ng/L for diclofenac and phenytoin.

#### 3.3.2 Method sensitivity

In order to determine the sensitivity of the method for each analyte, method detection limits (MDLs) and method quantification limits (MQLs) were determined according to Adams et al., (Adams et al., 2002). Five replicate blank analyses (sample blank with added deuterated standards) were carried out, and the peak areas of the “noise” peaks were integrated. The MDL was calculated as the mean peak area converted to a concentration (ng/L) plus three times the standard deviation (SD). MQL was calculated as the mean concentration plus 10 times the SD. Table 3-2 shows the MDLs and MQLs which ranged between 1 and 50 ng/L. Therefore, the method provides quite acceptable sensitivity for the investigated compounds.

#### 3.3.3 Recoveries

Extraction recoveries of the target compounds were carried out for product water using samples spiked at a concentration of 50 ng/L. Recoveries were determined comparing the concentrations obtained, calculated by internal standard calibration with the initial spiking levels. In each case, samples were analysed in five replicates. Blanks (non-spiked samples) were analysed in order to determine their concentrations, which were afterwards subtracted from the spiked waters. The average recoveries for the wastewater and recycled water obtained were ranged between 70% and 92% with a SD between 3 and 8, respectively (Table 3-3).

Table 3-2: Linearity and limits of target compounds

Compound	Linearity		SD	Limits (ng/L)	
	Range (ng/L)	R <sup>2</sup>		QL	MDL
salicylic acid	1-1000	0.94	15	1	0.5
clofibric acid	10-1000	0.94	23	10	8
ibuprofen	10-1000	0.97	20	10	6
acetaminophen	5-1000	0.94	13	5	2
primidone	15-1000	0.81	41	15	12
nonylphenol	1-1000	0.98	8	1	0.6
gemfibrozil	5-1000	0.98	8	5	2
naproxen	5-1000	0.98	7	5	4
ketoprofen	10-1000	0.94	15	10	9
BPA	5-1000	0.98	5	5	2
phenytoin	50-1000	0.93	17	50	50
carbamazepine	5-1000	0.98	11	5	5
diclofenac	50-1000	0.99	7	50	23

### 3.3.4 Method precision

The long-term reproducibility of the method was monitored using control charts. The control chart was constructed by applying the result of the deuterated internal standards in each sample and expressing it as the standard deviation of these measurements.

Table 3-4 shows the percentage recoveries and the standard deviation which were ranged between 62 and 99 %, and 2 and 6, respectively.

### 3.3.5 Matrix effects

One of the drawbacks in mass spectrometry quantitative analysis is the effect of the solution matrix on the values obtained. It occurs in this instance because the EI “electron ionization” source is highly susceptible to other components present in the matrix, which may result in a signal suppression or enhancement leading to significant error in the measured concentration of analyte.

**Table 3-3: Recoveries of target analytes**

Compound	Recoveries (%)			
	Min.	Max.	Average	SD
salicylic acid	75	85	80	4
clofibric acid	81	92	87	4
ibuprofen	85	92	88	3
acetaminophen	76	84	79	3
primidone	71	82	77	4
nonylphenol	70	85	78	6
gemfibrozil	80	90	86	4
naproxen	84	92	89	3
ketoprofen	75	95	87	8
BPA	85	92	89	3
phenytoin	76	89	80	5
carbamazepine	75	91	82	8
diclofenac	75	92	84	7

**Table 3-4: Recoveries obtained for deuterated internal standards in wastewater and product water**

Compounds	% Recoveries for wastewater				% Recoveries For product water			
	Min	Max	Ave	SD	Min	Max	Ave	SD
salicylic acid - $d_6$	62	75	71	5	78	86	82	3
ibuprofen - $d_3$	67	75	69	4	79	95	86	4
acetaminophen $d_4$	75	81	78	4	79	98	88	6
4-NP - $d_6$	65	75	72	3	85	97	91	3
gemfibrozil - $d_6$	64	81	75	3	84	99	89	4
phenytoin - $d_{10}$	73	82	78	2	78	95	87	5
carbamazepine - $d_{10}$	69	75	71	3	78	95	87	5

As shown in Table 3.4, the recoveries of the wastewater samples were lower by 13% than the product water. From these results, it can be seen that using an internal standard improves the method validation. Gros et al. (2006) studied several strategies to reduce the matrix effects. Among these are selective extractions, effective sample clean up, improvement of the chromatographic separation, external calibration or standard addition. The use of internal standards is an efficient approach to assess the loss of signal intensity and therefore can be used for quantification purposes with the advantages of simplicity and efficiency.

### **3.4 Physicochemical Characterization**

Samples collected from various wastewater treatment schemes were characterized by measuring pH, conductivity, absorbance, turbidity, total organic carbon, nitrogen, phosphorus, major anions and cations and heavy metals. Methods of analysis and calibration were carried out according to the Standard Methods for the examination of water and wastewater, American Public Health Association Washington (APHA, 2005). A concise summary of the principle, procedures and method number of each technique used is described in the following section.

#### **3.4.1 Total organic carbon**

Total organic carbon (TOC) is a useful expression of the total organic content of a sample. It does not provide identification of species, though it does offer an indication of the level of organic carbon. The TOC is independent of the oxidation state of the organic matter and does not measure other organically bound elements such as nitrogen or phosphorous nor does it measure inorganic compounds.

A TOC-VCSH “Total Organic Carbon Analyser” equipped with autosampler (Shimadzu) was used. This method utilises heat and oxygen, to convert carbon to single carbon units of CO<sub>2</sub>. The CO<sub>2</sub> produced is then measured directly by a non-dispersive infrared analyser.

All samples were adjusted to pH 2 and purged with nitrogen to remove inorganic carbon and other purgables. The actual measured parameter was then non-purgable organic carbon (NPOC). The sample was injected into the total carbon (TC) port. The oven in the TC detector was set at 950°C where the carbon was oxidized to CO<sub>2</sub> and carried to the infrared analyser. Peak height on the recorder was directly related to the TC in the sample ((APHA, 2005) method No. 5310B).

For the preparation of standard stock solution (1000mg/L), a weight of 2.1254 g of anhydrous potassium bipthalates was dissolved in carbon free water and diluted to 1000 ml. The standard was acidified with H<sub>2</sub>SO<sub>4</sub> to pH 2 and stored at 4°C. This standard was used to prepare the working standard (100 mg/L) as well as the calibrating standards.

The standard stock solution of carbon was diluted to form a series of standard solutions of 100, 50, 20 and 5 mg/L to cover the expected range in samples. The standards were injected at least three times to obtain reproducibility of  $\pm 5\%$ . The recorded peak areas were plotted against the carbon concentrations in mg/L to establish a calibration curve.

An aliquot of 20 ml of each sample was transferred into a glass vial prewashed with acid and baked at 400°C for two hours. Samples were injected at least twice into the TOC-VCSH analyser. Every 10- 15 samples, a blank and a known concentration sample were analysed as a batch.

#### **3.4.2 Total nitrogen**

Total Nitrogen (TN) is a useful expression of the total nitrogen content of a sample. It does not provide identification of species, though it does offer an indication of the level of total nitrogen in the sample. TOC-VCSH Total Organic Carbon Analyzer equipped with TNM-1 “total nitrogen measuring unit” and ASI-V autosampler, Shimadzu was used for determination of TN. A nitrogen-based sample is decomposed to nitrogen monoxide and nitrogen dioxide. The nitrogen species are then reacted with ozone to form an excited state of nitrogen dioxide. Upon returning to the ground state, light energy is emitted. Then, TN is measured using a chemiluminescence detector (Sharp et al., 2004).

For the preparation of standard stock solution (1000mg/L), an amount of 7.219 g of potassium nitrate was dissolved in nitrogen free water, diluted to 1000 mL and stored at 4°C. This standard was used to prepare the working standard (100 mg/L) as well as the calibrating standards.

For the determination of TN, the same procedure as for determination of TOC was followed (see section 3.4)



### 3.4.3 UV absorbance

Some organic compounds commonly found in water and wastewater strongly absorb ultraviolet (UV) radiation. UV absorption has been used to monitor wastewater effluents. UV absorption measurements were reported in units of  $\text{cm}^{-1}$  ((APHA, 2005) method No. 5910 B)

A UV- Visible Spectrophotometer model UV 1700 Phara Spec, Shimadzu was used for the measurement of the UV absorbance. Calibration of the spectrophotometer was established according to the manufacturer's instructions. The wavelength was set at 245 nm. Absorbance for each sample was measured in comparison with the blank reagent.

### 3.4.4 Turbidity

Turbidity in water is caused by suspended and colloidal matter such as clay, slit, finely divided organic and inorganic matter. Turbidimeter measurement is based on a comparison of intensity of light scattered by the sample under defined conditions with the intensity of light scattered by a standard reference suspension (formazine polymer) under the same condition. Measurements were reported as nephelometric turbidity units (NTU) ((APHA, 2005) method No. 2130).

Turbidity meter model HACH 2100N, HACH, S.A/N.V, USA was used for the measurement of the turbidity. Calibration was conducted according to manufacturer's instructions. A portion of the sample was transferred into the sample vial and the turbidity reading was recorded for each sample. Turbidity for the reagent water was measured with every batch.

### 3.4.5 Conductivity and pH

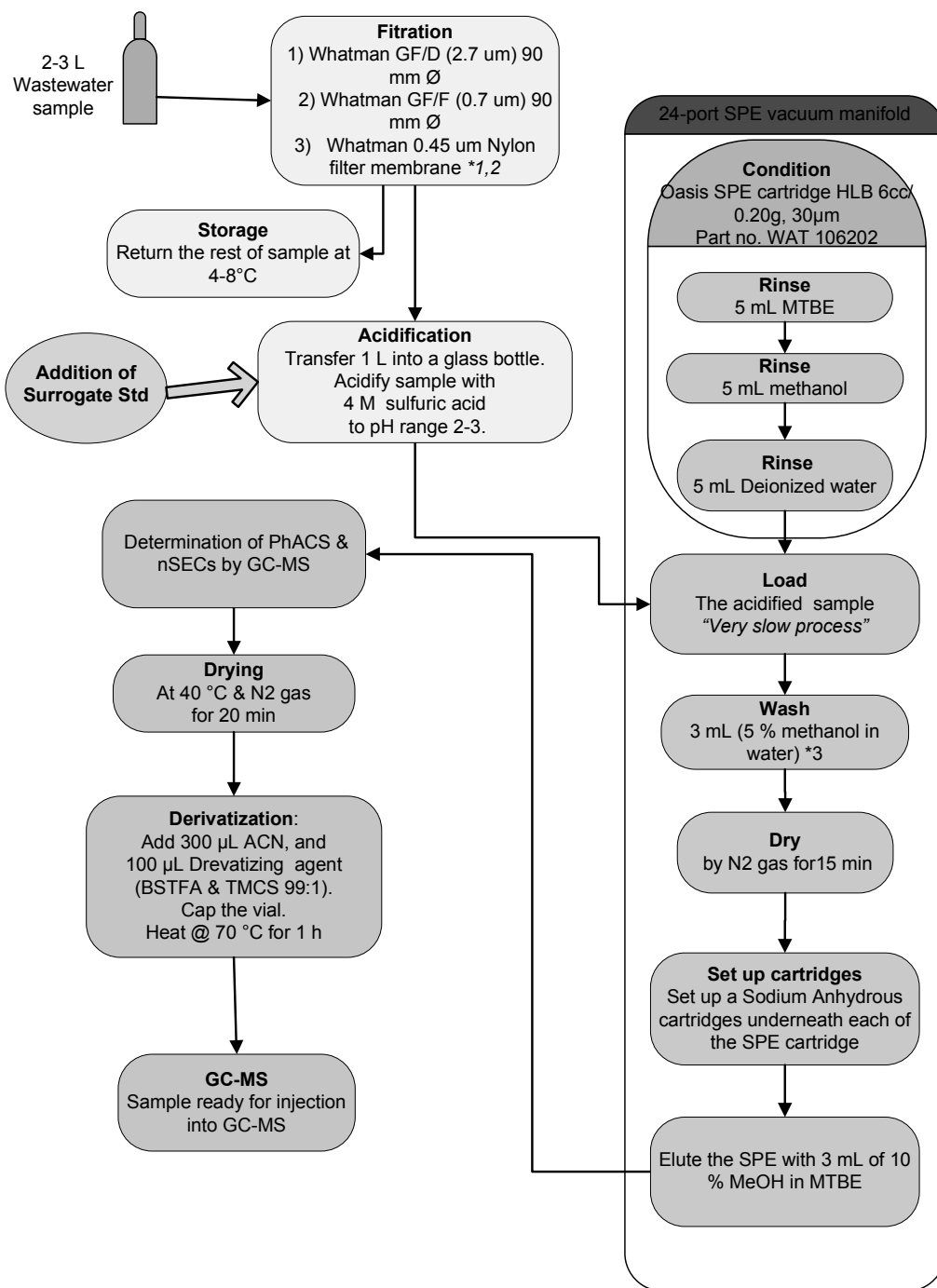
Conductivity,  $k$ , is a measurement of the ability of an aqueous solution to carry an electric current. This ability depends on the presence of ions; on their total concentration, mobility, and valence; and on the temperature of measurement. The conductivity measurements were reported as mS/cm (APHA, 2005) method No.2510 B).

Measurement of pH is one of the most important and frequently used tests in water chemistry. At a given temperature, the intensity of acidic or basic character of a solution is indicated by pH or hydrogen ion activity. Conductivity and pH were measured using a pH / ION meter Micron, CHK Engineering Courtcloud Ltd, Dove, England ((APHA, 2005) method no. 423).

### 3.5 Summary

The first part of this chapter included the analytical method that was developed for analysis of trace organic compounds in wastewater. Figure 3-9 summarises the various steps for the developed method. Furthermore, the performance of the analytical method in determining the trace organic contaminants was evaluated using different techniques (e.g., recovery, minimum detection limits and maximum detection limits). Recovery results were excellent and ranged from 70 to 92%. Limits of detection for the trace organic compounds was ranged between 1 and 50 ng/L. The overall data validation indicated that the developed method can deliver accurate and precise results, producing more confidence in the analysis of actual samples.

The second part of the chapter discussed the various methods used for measuring the physicochemical characteristics of different types of samples collected. These methods have generally been obtained from the Standard Methods for examination of water and wastewater.



\*1) Filtered samples stored overnight in the refrigerator at temp 4-8 °C

\*2) Under vacuum to accelerate flow

\*3) SPE cartridges kept in desiccators overnight for the next step.

**Figure 3-9: Schematic diagram for the validated analytical procedure for determination of TOCs**

# *Chapter*

## *4 Comparative Assessment of Three Water Recycling Plants in Removal of Trace Organic Compounds*

---

### **4.1 INTRODUCTION**

Water has emerged as the one of the most important issues facing Australia currently. Australia has the third-highest per capita water consumption rate in the world after the USA and Canada (Radicliffe, 2004). Furthermore, the Australian average use of water for agriculture, industry and domestic purposes are 75%, 20% and 5%, respectively. Most of the water used in Australia (79%) comes from rivers and dams and about 21% is derived from groundwater sources, but these percentage vary greatly from state to state (Australian Government: National Water Commission).

Although Australia is a very large continent, it is the driest of the world's inhabited continents with the lowest percentage of rainfall, the lowest amount of water in rivers and the smallest area of permanent wetland. As a result of drought and a strong reduction in water storage levels, water restrictions have been applied across Australian capital cities since 2002 to reduce water use in the domestic sector as well as other recreation sectors. Some of these restrictions have been voluntary others mandatory. Water conservation measures have been applied to homes and outdoor use. Sydney, Melbourne, Perth, Hobart and Canberra all experienced mandatory water restrictions. Darwin was the only capital city not affected by water restrictions during 2002-2004.

With many communities approaching the limits of their readily available water supplies, recycling water has become an increasingly attractive option for extending water supplies. The greatest water recycling occurs in world regions suffering water scarcity, such as the Middle East, Australia, US south-west, or in regions with severe restrictions on disposal of treated wastewater effluents such as Florida and most of European Union countries.

Untreated municipal wastewater typically contains a variety of biological and chemical constituents that may be hazardous to human health and the environment including microbial (e.g., bacteria, viruses, helminths and protozoa) or chemical hazards (e.g., endocrine disrupting chemicals, pharmaceuticals and disinfection by-products). For health assurance standards, few indicators such as faecal coliforms and *E. coli* have been chosen by Water Recycling Quality Regulators to correlate the possibility of presence of various bacterial pathogens. Furthermore, physico-chemical water quality indicators, such as turbidity, suspended solids and pH are not in themselves health concerns. However, they can be used as a measure of water treatment process performance as their presence may indicate the presence of contaminants of concern.

The Australian Guideline “Use of Reclaimed Water” sets out the quality required of reclaimed water and extent of monitoring that might be anticipated for secondary and tertiary treated effluents for various potential uses. These include indirect potable, urban (non-potable), agricultural, aquaculture, recreational impoundment, environmental and industrial uses. These National Australian Reclaimed Water Guidelines (i.e., NSW (NWQMS 2000); Victoria (EPA Victoria 2003); South Australia (DHS-SA 1999) and Tasmania (Dettrick 2002)) vary from one State to another and generally place primary emphasis on bacteriological standards in spite of referencing turbidity and pH (Table 4-1). There is only limited consideration of protozoa, viruses and chemicals (Radcliffe, 2004).

Over five hundred sewage treatment plants (STPs) across Australia are now engaging in the recycling of at least part of their treated effluent for beneficial purposes. Approximately 166 GL/yr of reclaimed water were used in Australia in 2001-2002, which represented 10% of the total discharge effluent (Radcliffe, 2004; Bixio et al., 2008). Three case studies of water recycling plants in Australia are summarised in Table 4-2 and are discussed in the following section.

## **4.2 Case Studies**

### **4.2.1 Gerringong Gerroa Sewage Scheme (GGSS)**

Owned by Sydney Water and operated by Veolia Australia, the Gerringong Gerroa Sewage Scheme (GGSS) is located 120 km south of Sydney on the southeast coast of Australia, near the town of Kiama and is adjacent to the Crooked River. It serves a population of about 4000 with a capacity of 2.2 ML/day (see Table 4-2). The average discharge volume is 0.7 ML/day and the surplus flows are discharged to sand dune systems. Once the sand dunes reach capacity, the excess is discharged to the Crooked River (Thomas and Foster, 2005; Boake, 2006). A minimum of 80% of treated wastewater is used by adjacent dairy farmers for pasture production and currently irrigates 70 hectares (Radcliffe, 2004).

The GGSS consists of screens, a biological reactor, clarifier, sand filtration, ozonation, biological activated carbon (BAC), MF, UV disinfection and chlorination (Figure 4-1 and Table 4-2).

### **4.2.2 Water Reclamation and Management Scheme (WRAMS)**

The Water Reclamation and Management Scheme is owned by Sydney Olympic Park Authority (SOPA). WRAMS integrates sewage treatment and storm water collection. It serves the Olympic Park as well as the adjacent suburb of Newington through a dual reticulation system in which households are connected to a potable tap water as well as a recycled water supply. The treated wastewater is used for all non-drinking purposes by residents, commercial premises, sport venues, parklands and playing fields. WRAMS has capacity of 2.2 ML/day and can treat up to 7.0 ML/day ((Chapman, 2006).

WRAMS consists of screen, grit removal, an activated sludge process, UV disinfection, MF (microfiltration), RO (reverse osmosis) and chlorination (See Table 4-2 and Figure 4-2). The MF back flush is sent to the brick pit for dilution while the RO brine is sent to the Sydney sewer. It should be noted that the RO plant is only used for storm water treatment, which is supplied via a brickpit. Sewage is treated by MF only as no salt removal is intended.







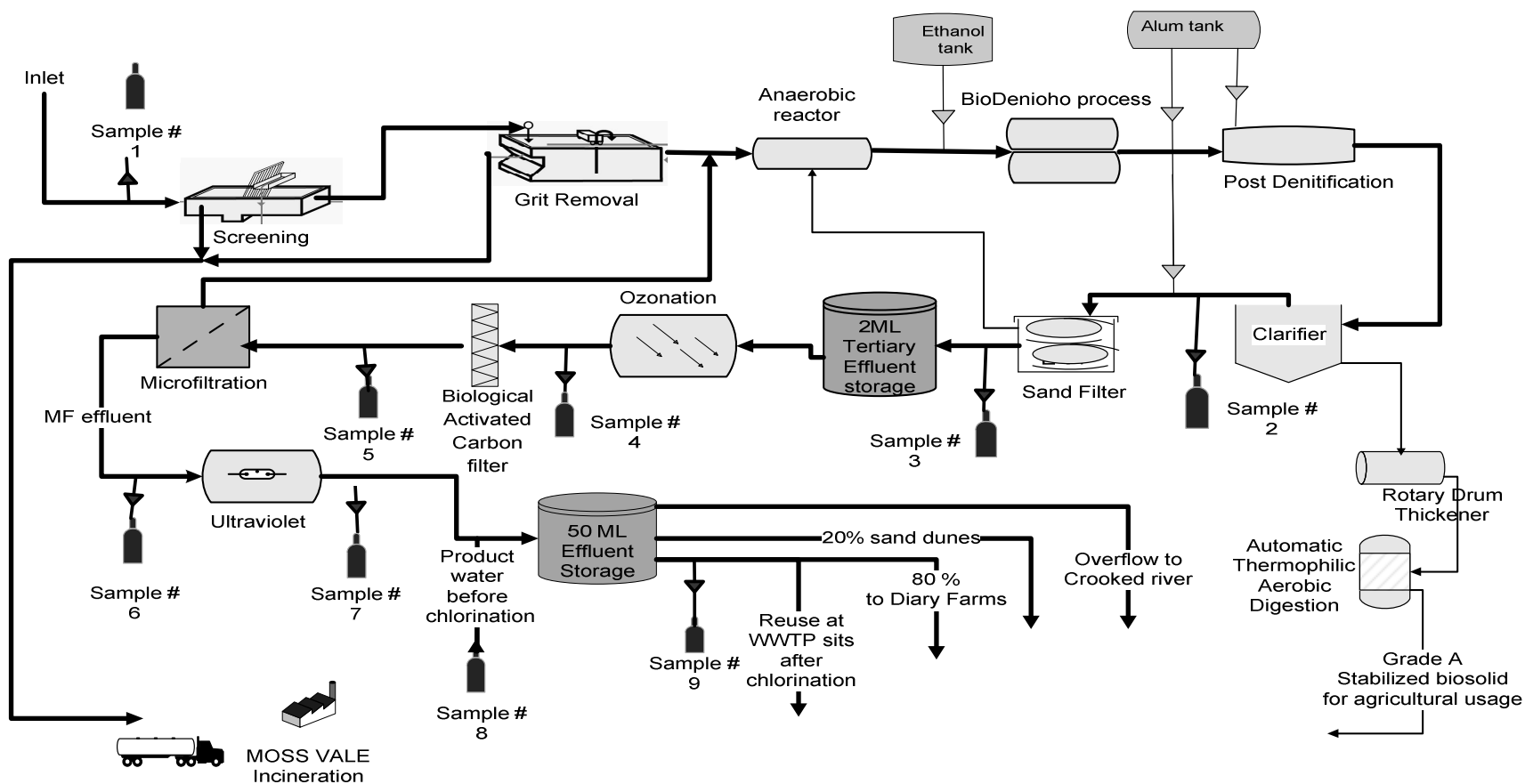




**Table 4-2: Summaries of the water recycling plants**

Case Study	Designed for	Reuse Purposes	Capacity	Key Element for		Waste Disposal	
				WWTP	WRP	MF Back flush	RO Concentrate
Gerringong Gerroa, South Coast, NSW	Treating sewage comes from domestic sources and small amount from commercial and industrial contributors	Local Dairy Farmer (pasture irrigation) (80%), disposed into the Crooked River through a sand dune system	2.2 ML/day**	Screening, Grit, Biological treatment (Return Activated Sludge RAS), Sand filter	Ozonation, Biological Activated Carbon Column (BAC), Microfiltration (MF) (0.2microns) and UV disinfection		
Sydney Olympic Park, Sydney, NSW	Conserve and reuse water for the Olympic Park	Olympic Park Site and Newington Village for toilet flushing,  Irrigation, Fire fighting	2.2 ML/day**	Screening, Sludge Activation Process, UV disinfections	Microfiltration, Reverse Osmosis (RO)*, Chlorination	Back flush recirculated to the Brickpit Reservoir	Discharged to Sydney sewerage system
Luggage Point, Brisbane, Queensland	Cleaning of Brisbane household and industrial waters	Supply BP refinery	150 ML/day**	Screening, grit removal, diffused air activated sludge	Filtration (300 µm), MF (0.1 µm), RO and chlorination	Routed back to the WWTP	Routed back to the WWTP

\*RO is used only when TDS exceeds a certain value ; \*\* An average flow of dry weather for the Wastewater Reclamation Plant



**Sampling key:** (1) Raw wastewater (2) Clarifier effluent (3) Sand filter effluent (4) Ozonation effluent (5) Biological active carbon filter effluent (6) Microfiltration effluent (7) Ultraviolet effluent (8) Product water before chlorination (9) Product water after chlorination

**Figure 4-1: Schematic of Gerringong Gerroa Sewage Scheme (GGSS)**

### 4.2.3 Luggage Point Water Reclamation Plant (LPWRP)

Brisbane Council has ten sewage treatment plants, from which it discharges 285 ML/day into the environment (adjacent to the environmentally sensitive Moreton Bay). 2.0 ML/Day are used on golf courses and more than 10.0 ML/Day are recycled through LPWRP (see Table 4-2). The LPWRP is located near the mouth of the Brisbane River. The LPWRP produces 8.8 ML/Day of very high quality water and is capable of producing of 10.6 ML/Day. The product water is delivered to the British Petroleum (BP) refinery (4 km away) for cooling tower make up, boiler feed water and other process uses. The LPWRP returns the reject flows (MF back flush and RO brine) back to the head of the wastewater treatment plant. The reject flows are 30% or approximately 3.6 ML/Day when the plant is producing 8.8 ML/Day (Simpson, 2006). The LPWRP process includes automatic backwashing of 300  $\mu\text{m}$  screens, MF, RO and chlorination (Figure 4-3).

The primary objective of this chapter was to assess three different water recycling plants with different technology in removal of trace organic compounds. In addition to that, this study will investigate the occurrence and fate of trace organic compounds in the three plants. Acetaminophen, carbamazepine, clofibric acid, diclofenac sodium, gemfibrozil, ibuprofen, ketoprofen, naproxen, primidone, phenytoin and salicylic acid represent PhACs and BPA and NP represent EDCs. These compounds were selected based on the previous detection in wastewater combined with their anticipated health and environmental effects or bioaccumulation potential. The results of this chapter will indicate the benefit of the technology implemented in waste water recycling schemes.

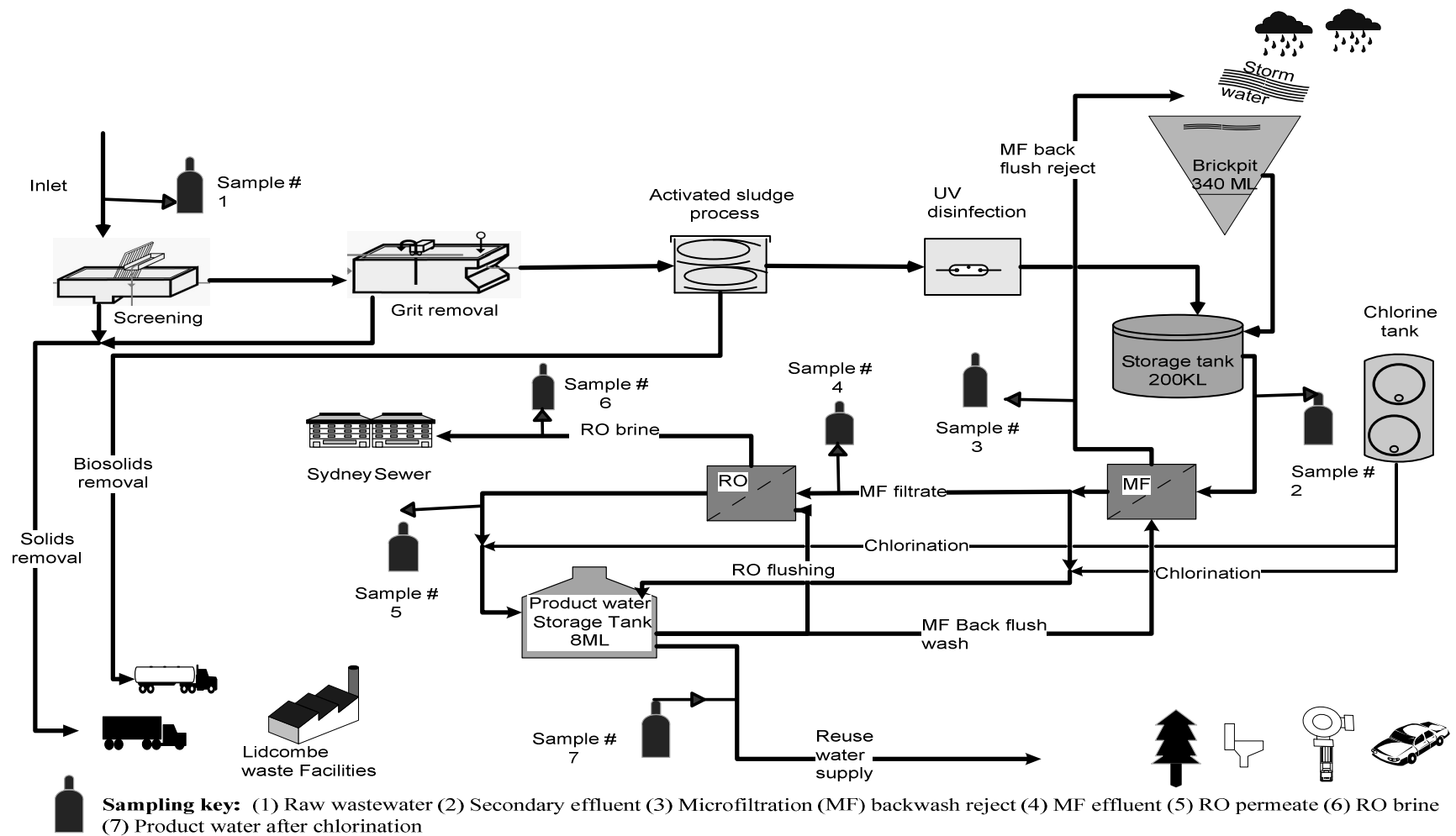
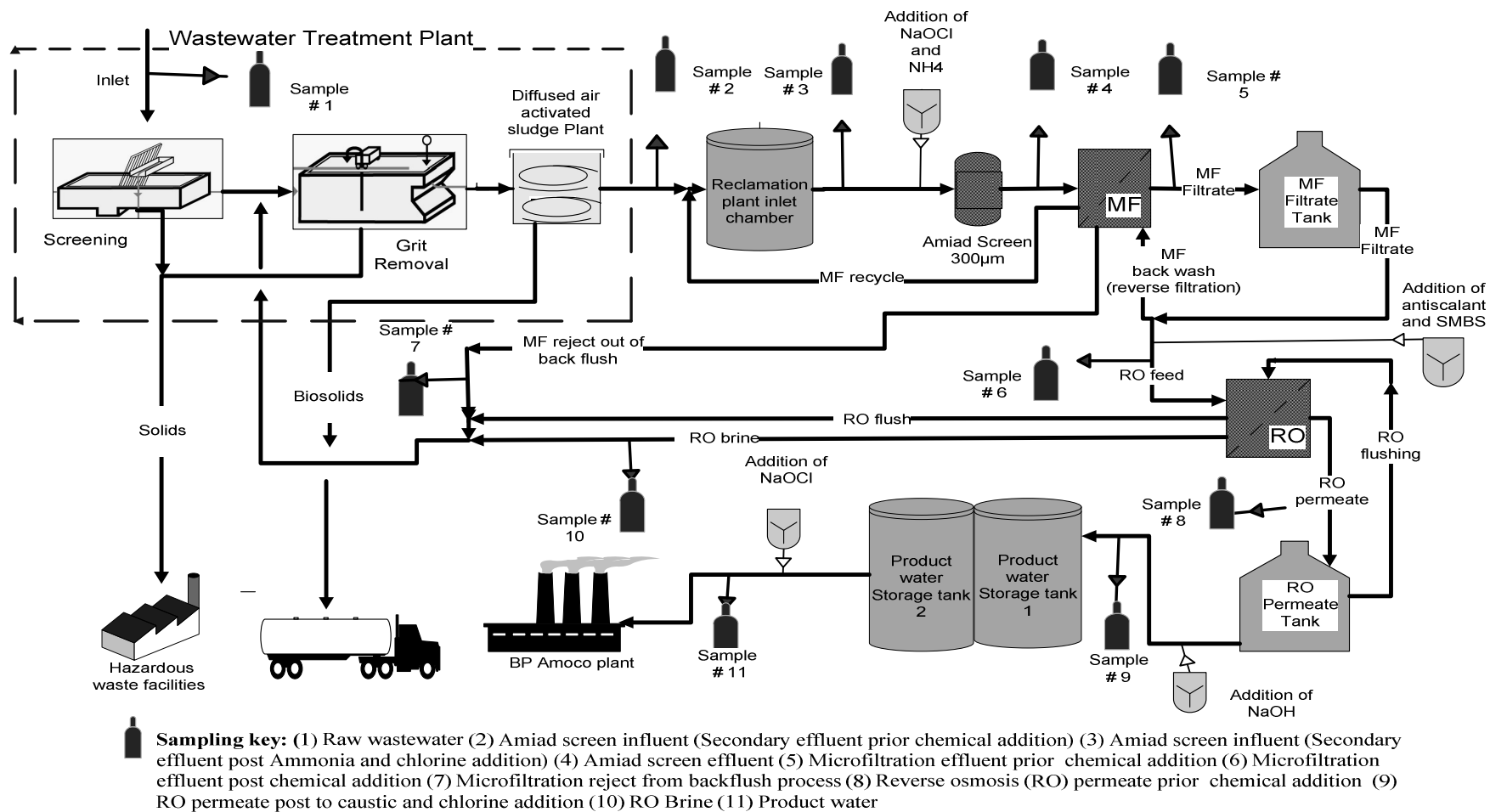


Figure 4-2: Schematic of Water Reclamation and Management Scheme (WRAMS)



**Figure 4-3: Schematic of Luggage Point Water Reclamation Plant (LPWRP)**

## **4.3 Experimental Methods**

### **4.3.1 Sampling Protocol**

Composite raw wastewater samples and grab samples from the feed and effluent of the various unit operations were taken at each scheme. Sampling points are shown in (see Figures 4-1 to 4-3). For additional information on sampling points see Appendix 8-2. Samples were taken in May, September and December 2005 for WRAMS, LPWRP and GGSS, respectively. All samples were collected in 2.5 L amber glass bottles, transferred overnight and processed immediately. Sampling collection and transfer procedures were as detailed in section 3.2.

### **4.3.2 Physicochemical Characterisation:**

Total organic concentrations, nitrogen content, turbidity, ultraviolet absorption, pH were measured. Analysis were carried according to the Standards Methods for the examination of water and wastewater, American Public Health Association Washington (APHA, 2005). Details of measurement procedures have been described in section 3.4.

### **4.3.3 Trace Organic Contaminants Analysis**

The samples were filtered, adjusted to pH 2-3, and extraction was carried out using SPE. Extracts were analysed by GC-MS after derivatization. Details of the experimental works have been described previously in Section 3.2.

### **4.3.4 Determination of Concentration Factor in Reverse Osmosis**

The concentration factor is a ratio of the concentration of a component in the brine compared to the RO feed, which depends on the recovery of water and retention of individual compounds. It can be represented as shown in Equation (4-1).

$$F = \frac{C_c}{C_f} \quad (4-1)$$

where  $C_f$  and  $C_c$  ( $\text{g/m}^3$ ,  $\text{mg/L}$ ) are the solute concentration in the feed and in the brine, respectively.



## 4.4 Results and Discussion

### 4.4.1 Physicochemical Characteristics

The physicochemical characteristics provided by the scheme operators for the influent and effluent streams are shown in Table 4-3. The composition of untreated wastewater (e.g., TSS, BOD, COD, nitrogen and phosphorus) varies between the three schemes (see Table 4-3). This variation in the quality of influent among various communities depends on the number and type of commercial and industrial establishments in the area, and the condition of the wastewater collection system.

The aggregate constituents (e.g., biological oxygen demand (BOD) and chemical oxygen demand (COD)) were used to characterize the bulk of the organic matter in wastewater (see Table 4-3). The uncertainty associated with these aggregate organic parameters - in both the untreated influent and reclaimed water - is that they do not relate any information regarding the specific compounds that make up the measured parameters.

According to the collected results and observation, it can be seen that the current schedule for monitoring of the recycling schemes are not sufficient and it would be useful if one or more surrogate (indicator) parameters were available and included to characterize the safety and suitability of reclaimed water for human and environmental exposure. The majority of providers of recycled water monitor the quality parameters specified by EPA licenses. Higgins et al. (2002) found that less than 10% of users and providers of recycled water monitor components other than those required for the license compliance such as cations, sulphate, bicarbonate, alkalinity, turbidity and chlorine. However, most current wastewater discharge and reuse guidelines are limited to bulk parameters (see Table 4-1). Specific organic contaminants are to date not regulated in Australia and monitoring is hence neither economic nor encouraged with any incentives. Research and development support for companies and monitoring of the performance of the key contaminants would, in all likelihood, provide great insight for the operation.

To understand performance of the scheme in more detail, a number of analyses were carried out in the laboratory. These parameters are pH, conductivity, turbidity, TOC, absorbance at 245 nm and total nitrogen TN. In GGSS, water quality generally increases during treatment. A dramatic decrease in turbidity (97%), absorbance (92%), TN (98%) and TOC (90%) occurred during the secondary treatments which consist of activated sludge bioreactors (see Table 4-3). A typical

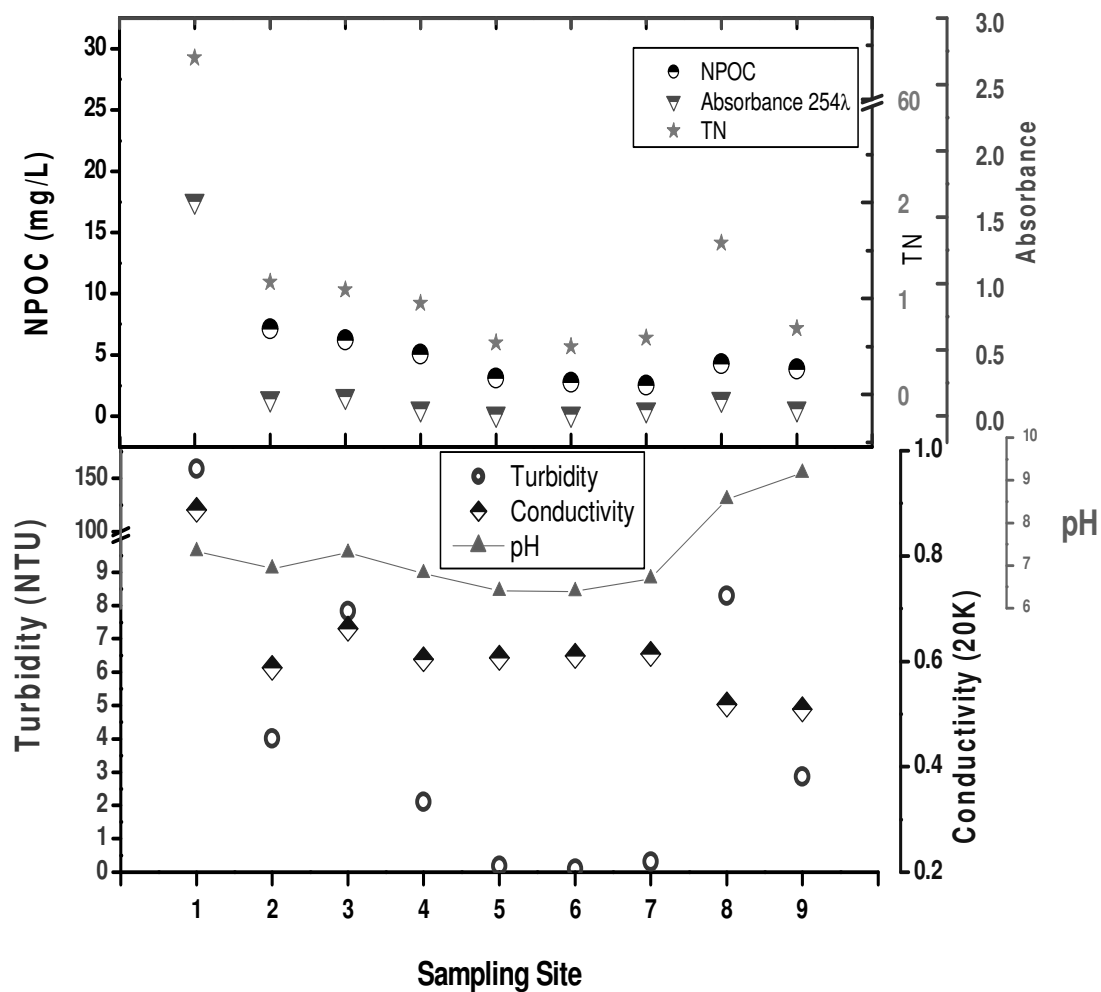
activated sludge effluent has TOC, TN and turbidity in a range of 10-40 mg/L, 15-35 mg/L and 2-15 NTU, respectively (see Table 4-4). This indicated that most of the organic matter and total suspended solids removal was achieved during the secondary treatment.

Slight decreases in organic matter and TSS occurred during the sand filter, ozonation, biological activated carbon filter, microfiltration and UV disinfection treatments. Thus, the cumulative removal of these parameters with various treatments was between 95% and 99% (see Table 4-3 ). On the other hand, the reclaimed water had a high content of total dissolve solids (311 mg/L) (see Figure 4-4) due to the inability of MF to remove soluble solids and the lack of a reverse osmosis process in the plant that could cause an environmental risk issue.

In LPWRP the trend was also one of increased water quality. Total nitrogen, organic carbon, turbidity and absorbance parameter values dropped between 81 % and 100 % during the activated sludge, resulting in a secondary effluent of a typical characteristics of organic content of 12 for both organic carbon (mg/L) and turbidity (NT) (see Figure 4-5). Furthermore, slight reductions were found for these parameters through amiad screen, microfiltration and reverse osmosis treatment (Figure 4-5). The final water quality was superior with regard to organic carbon, conductivity, turbidity and TN, which were  $\leq 1$  for the RO permeate (see Figure 4-5) in comparison to typical effluent processed under similar treatments (see Figure 4-4). However, with membrane processes there is an obvious production of waste streams such as the MF backwash water (high turbidity, TOC, TN and absorbance) as well as the RO brine (elevated conductivity, organic carbon, absorbance and TN).

**Table 4-3: Characteristics of raw wastewater and product water of the three schemes. ( n.m : not measured)**

Characteristics	Schemes	GGSS		WRAMS		LPWRP	
	Unit	Raw wastewater	Product water	Raw wastewater	Product water	Raw wastewater	Product water
Sample ID		1	8	1	7	1	11
pH		7.6	7.3	7.5	7.7	7.36	n.m.
Alkalinity as CaCO <sub>3</sub>	mg L <sup>-1</sup>	241	n.m.	n.m.	n.m.	n.m.	n.m.
Conductivity at 25 °C	µS cm <sup>-1</sup>	n.m.	564.	n.m.	431	2398	n.m.
Turbidity	NTU	n.m.	n.m.	n.m.	0.11	n.m.	n.m.
Solids Content							
TSS	mg L <sup>-1</sup>	248	2	200	< 2	262	n.m.
TDS	mg L <sup>-1</sup>	n.m	311	350	n.m.	n.m.	n.m.
Organic Content							
BOD	mg L <sup>-1</sup>	235	2	200	5	258	n.m.
COD	mg L <sup>-1</sup>	525	10	470	57	583	n.m.
TN	mg L <sup>-1</sup>	53.5	0.79	40	5.7	n.m.	0.40
Ammonia as N	mg L <sup>-1</sup>	41.5	0.01	30	2.9	36.5	< 0.004
Nitrate as N	mg L <sup>-1</sup>	n.m.	n.m.	0.05	n.m.	n.m.	n.m.
Nitrite as N	mg L <sup>-1</sup>	n.m.	n.m.	0.27	n.m.	n.m.	n.m.
Total Phosphorus	mg L <sup>-1</sup>	10.8	0.017	7.00	0.84	10.57	< 0.010
Anions & cations							
Aluminum	mg L <sup>-1</sup>	n.m.	0.13	n.m.	n.m.	0.50	< 0.005
Calcium	mg L <sup>-1</sup>	n.m.	99	n.m.	n.m.	45	n.m.
Chlorine (free residual)	mg L <sup>-1</sup>	n.m.	n.m.	n.m.	0.15	n.m.	8.5
Magnesium	mg L <sup>-1</sup>	n.m.	18	n.m.	n.m.	46	n.m.
Potassium	mg L <sup>-1</sup>	n.m.	86	n.m.	n.m.	31	n.m.
Sodium	mg L <sup>-1</sup>	n.m.	368	n.m.	n.m.	394	n.m.
Sulphides	mg L <sup>-1</sup>	n.m.	n.m.	n.m.	n.m.	6.8	n.m.
Microorganisms							
Faecal Coliforms (MF)	CFU 100 mL <sup>-1</sup>	n.m.	0	n.m.	0	n.m.	n.m.



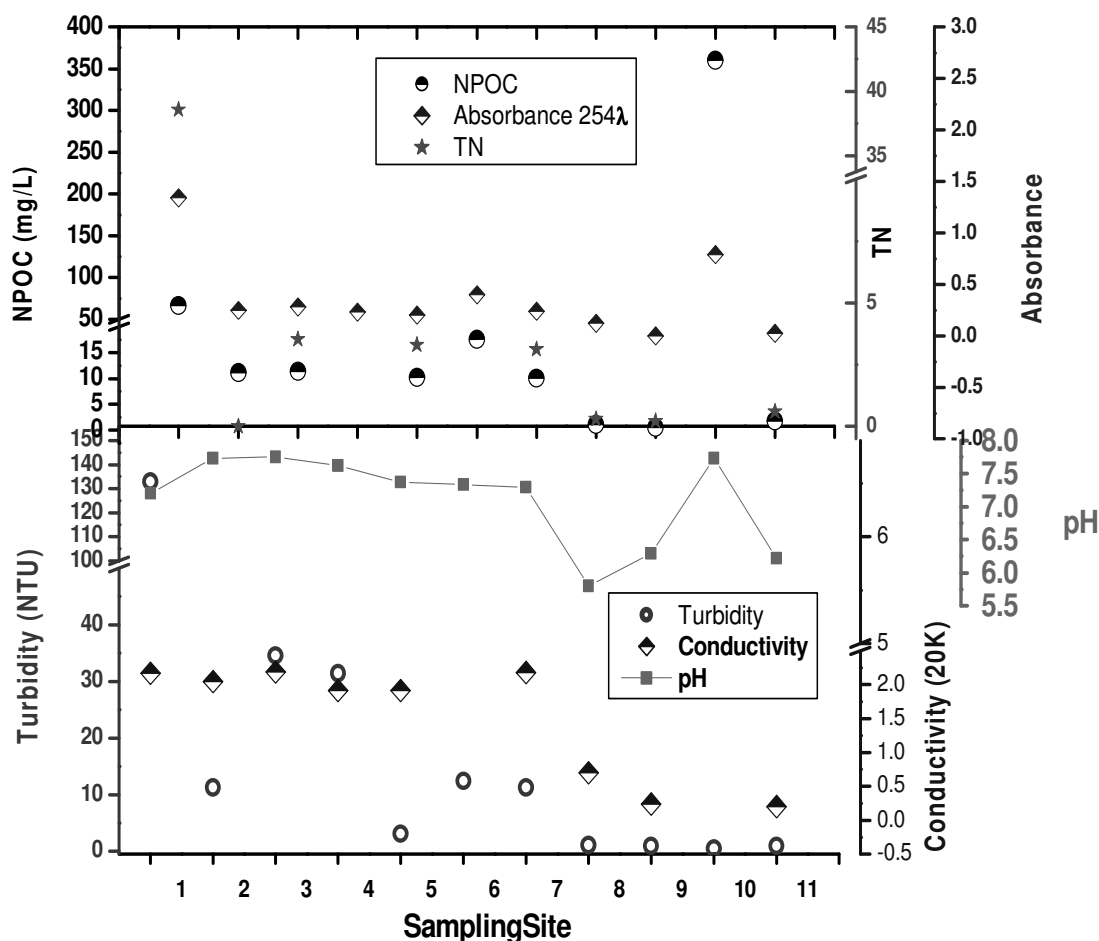
**Figure 4-4: Physicochemical measurements for samples collected from GGSS: (TOC (mg/L), TN (mg/L), pH (unit) and absorbance at 245λ (1/cm), conductivity (mS/cm) and turbidity (NTU)).**

**Table 4-4: Typical range of effluent quality**

Adapted from (Metcalf & Eddy, 2007)

#### **4.4.2 Occurrence of Trace Contaminants in Raw Wastewaters**

The results from the analysis of samples collected from the Gerringong Gerroa Sewage Treatment are presented in Table 4-5. Only three compounds were detected in the raw wastewater above the detection limits of the method. The concentrations of detected compounds were 0.7 µg /L, 0.2 µg/L and 0.05 µg/L, for ibuprofen, ketoprofen, and gemfibrozil, respectively (see Table 4-5). These concentrations are in the lower range of those reported by other authors for similar raw wastewaters (Soulet et al., 2002; Lindqvist et al., 2005; Vieno et al., 2005)(Table 4-6). Compounds not detected in the raw wastewater may have been present at concentrations lower than the detection limit (n.d).



**Figure 4-5: Physicochemical measurements for samples collected from LPWRP: TOC (mg/L) and TN (mg/L), pH and absorbance at 245λ (1/cm), conductivity (mS/cm) and turbidity (NTU).**

These low levels of detected compounds may be explained by the small population (i.e., 4000 people in 2005) living in the area served by the Gerringong Gerroa Sewage Scheme as well as the possible dilution of domestic sewage with other waste streams entering the system such as local businesses and light industries. The presence of ibuprofen and ketoprofen (non-steroidal anti-inflammatory compounds) and gemfibrozil (blood lipid regulator) could reflect the extensive usage of pharmaceuticals by substantial elderly population living in the Gerringong and Gerroa area in the retirement homes (Al-rifai et al., 2007). Surprisingly, no other

contaminants (like bisphenol A and nonylphenol) common indicators of industrial and commercial activity were detected in the Gerringong Gerroa Sewage Scheme as it is common in various industrial areas (Al-rifai et al., 2007).

**Table 4-5: Concentrations of trace organic compounds (ng/L) in samples collected from GGSS.**

Compounds	Raw Sewage	Clarifier	Sand filter	Ozonation	BAC	CMF	UV	Product water
	1	2	3	4	5	7	6	8
bisphenol A	n.d	n.d	n.d	n.d	n.d	30	20	n.d
nonylphenol	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d
clofibric Acid	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d
gemfibrozil	50	n.d	n.d	n.d	n.d	n.d	n.d	n.d
diclofenac	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d
ibuprofen	700	n.d	n.d	n.d	n.d	n.d	n.d	n.d
ketoprofen	200	n.d	n.d	n.d	n.d	n.d	n.d	n.d
naproxen	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d
salicylic acid	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d
acetaminophen	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d
carbamazepine	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d
phenytoin	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d
primidone	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d

*n.d: not detected (less than the detection limits, see section 3.3.2)*

In WRAMS, seven pharmaceuticals and BPA were found in the influent above the detection limits of the method (Table 4-7). Pharmaceuticals were detected in the ranges 0.22–23.33 µg/L. Acetaminophen and salicylic acid were the most abundant compounds with concentrations of 23.33 and 8.97 µg/L, respectively. These two compounds are the two most popular pain killers sold around the world.

According to the results reported by other authors, these two compounds were frequently detected in the raw wastewater of most wastewater treatment plants either with one order of magnitude higher or lower than that detected in WRAMS (Pham and Proulx, 1997; Blanchard et al., 2004). Furthermore, a low level of bisphenol A (0.14 µg/L) was detected as an indication of the level of contamination from the local industries.

**Table 4-6: PhACs and EDCs levels reported in the literature\***

PhACs	Concentration range
Analgesics and anti-inflammatory compounds	
acetaminophen (Paracetamol)	1-291.9 <i>a,b,c</i>
acetylsalicylic acid (ASA)(Aspirin)	0.22 – 54 <i>a,b,c,d,i</i>
Non-steroidal anti-inflammatory compounds	
diclofenac	0.035-510 <i>a,d,g,k,j,m,q,r</i>
ibuprofen	0.3 - 990 <i>b,c,e,k,g,m,p,q,r</i>
ketoprofen	0.13-3 <i>b,m,p,q,r</i>
naproxen	3.84- 8 <i>b,c,e,m,n,q,r</i>
Anti-epileptics (Anti-convulsants)	
carbamazepine	0. 1-1.85 <i>b,d,c,k,l,q</i>
Beta-blockers (anti-drenergenics)	
clofibric acid*	0.47-170 <i>d,g,m</i>
gemfibrozil	1.50 - 3.00 <i>b,c,m,q</i>
bezafibrate	1.55-7.60 <i>d,k,m,p,r</i>
Oral Contraception	
phenytoin	0.18 - 0.29 <i>b,c</i>
EDCs	
bisphenol A	0.16-28.1 <i>h,k</i>
nonylphenol	0.5-3 - 16.7 <i>f,h,k,o,q</i>
nonylphenol ethoxylate	0.5-31-868 <i>f,h,k</i>
octylphenol	0.44-1.05 <i>h,k</i>
octylphenol ethoxylate	0.04-0.2 <i>f,k</i>

\* *Degradation products, a (Pham and Proulx, 1997), b (Blanchard et al., 2004), c (Granier et al., 1988), d (Khan, 2002), e (Carballa et al., 2004), f (Paxéus, 1996), g (Soulet et al., 2002), h (Lee et al., 2004), I (Ternes, 1998), j (Koutsouba et al., 2003), k (Clara et al., 2005), l (Joss et al., 2005), m (Stumpf et al., 1999), n (Macia' et al., 2004), o (Sekela et al., 1999), p (Vieno et al., 2005), q (Bendz et al., 2005) and r (Lindqvist et al., 2005).*

In LPWRP, eight of the pharmaceuticals and the two EDCs were detected in the influent. The highest detected pharmaceuticals were salicylic acid, ibuprofen and acetaminophen with concentrations of 38.5, 10.34, 8.14 and 23.3 µg/L respectively (See Table 4-8). Generally, these results are comparable with published data for cities with large populations where there is a high consumption of over the counter pain relief medication (Granier et al., 1988; Ternes, 1998). Ibuprofen is determined in the intermediate range, acetaminophen falls in the lower range, while all other compounds tested were either not detected or detected at concentrations below those found elsewhere (Pham and Proulx, 1997; Blanchard et al., 2004; Bendz et al., 2005; Clara et al., 2005) (see Table 4-6). Bisphenol A and nonylphenol were detected at the highest concentrations in the LPWRP, where local industry may have contributed, compared to the other two schemes.



Table 4-7: Concentrations of trace organic compounds in samples collected from WRAMS (ng/L)

Compounds	Raw wastewater	Second effluent	MF back wash	MF permeate	RO concentrate	RO permeate	Product water
	1	2	3	4	5	6	7
bisphenol A	140	nd	nd	nd	nd	nd	nd
nonylphenol	Nd	nd	nd	nd	nd	nd	nd
clofibric acid	Nd	nd	nd	nd	nd	nd	nd
gemfibrozil	790	650	210	520	930	130	nd
diclofenac	220	nd	nd	nd	nd	nd	nd
ibuprofen	2810	310	50	90	50	15	nd
ketoprofen	570	250	70	120	250	50	nd
naproxen	3110	980	390	450	1270	110	nd
salicylic acid	8970	110	50	70	160	nd	nd
acetaminophen	23330	220	50	250	820	80	nd
carbamazepine	nd	nd	nd	nd	20	nd	nd
phenytoin	nd	nd	nd	nd	nd	nd	nd
primidone	nd	nd	nd	nd	nd	nd	nd

**Table 4-8: Concentrations of trace organic compounds in LPWRP (ng/L)**

Compounds	Raw wastewater	Sec. effluent	Amiad feed	MF feed	MF permeate	RO feed	MF backwash	RO permeate	RO permeate post-Chem	RO concentrate.	Product water
	1	2	3	4	5	6	7	8	9	10	11
bisphenol A	23020	1950	1650	1750	1790	1153	450	545	549	3790	464
nonylphenol	230	25	25	20	18	15	n.d	15	14	25	15
clofibric acid	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d
gemfibrozil	2420	690	450	300	350	290	n.d	22	22	950	28
diclofenac	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d
ibuprofen	10340	350	350	350	250	260	45	54	53	500	30
ketoprofen	1540	105	121	115	125	115	92	25	22	380	20
naproxen	7840	150	110	100	120	115	97	69	40	310	35
salicylic acid	38490	250	250	210	120	100	n.d	70	72	320	60
acetaminophen	8140	150	120	150	100	140	96	50	55	500	40
carbamazepine	1480	350	340	380	330	370	410	120	100	1000	80
phenytoin	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d
primidone	1470	520	420	590	360	449	185	45	53	480	49

#### 4.4.3 Removal of Trace Organics in Secondary Treatments

The concentrations of trace contaminants in the secondary effluent of all schemes are shown in Tables 4-5, 4-7 and 4-8. The results revealed that secondary treatments including activated sludge were effective at removing most of the target compounds in the influent. A final conclusion on the effectiveness of these treatments can not be drawn as some of these compounds were detected further down the schemes of GGSS, WRAMS and LPWRP as seen in Tables 4-5, 4-7 and 4-8. The author was not able to identify why these compounds were not detected in the secondary effluent. Other authors have also reported the incomplete removal of various micropollutant by conventional wastewater treatment plants employing activated sludge processes (Kim et al., 2007).

Furthermore, the contaminant concentrations in the influent, effluent and backwash of the microfiltration for LPWRP and WRAMS showed that the microfiltration did not contribute to the removal of these compounds as seen in Tables 4-7 & 4-8. Conversely, the results obtained for microfiltration backwash indicated detectable analytes (see Tables 4-7 and 4-8), which could be explained by the release during the backwash process of adsorbed micropollutants from the membrane. For GGSS, all organic contaminants were removed to below detection limits prior to MF and so a comparison with the other schemes could not be made. Furthermore, MF backwash water was not accessible for sampling so potential concentration of contaminants could not be determined.

#### 4.4.4 Trace Organics Removal in Reverse Osmosis (RO)

A comparison of the results obtained from the influent, effluent and the brine of the RO revealed that RO was a very effective treatment in removing the PhACs and EDCs (see Tables 4-9 and 4-10). Rejection rates varied between each wastewater treatment plants (see Table 4-9 and 4-10). In LPWRP, the highest rejection rates were between 30 and 92% for salicylic acid and gemfibrozil, respectively (see Table 9). However, salicylic acid was rejected completely by the RO membrane system in the WRAMS.

**Table 4-9: Removal and rejection percentages, and concentration factor for detected compounds in LPWRP**

Compounds	WWTP Removal %	RO rejection %	Conc. Factor (CF)	Total Removal Efficiency
bisphenol A	91.5	53	3.3	98.0
nonylphenol	89.1	N.A	N.A	93.5
gemfibrozil	71.5	92	3.3	98.8
ibuprofen	96.6	79	1.9	99.7
ketoprofen	93.2	78	3.3	98.7
naproxen	98.1	40	2.7	99.6
salicylic acid	99.4	30	3.2	99.8
acetaminophen	98.2	64	3.6	99.5
carbamazepine	76.4	68	2.7	94.6
primidone	64.6	90	1.1	96.7

**Table 4-10: Removal and rejection percentages, and concentration factor for detected compounds in WRAMS**

Compounds	WWTP Removal %	RO Rejection %	Conc. Factor (FC)	Total Removal Efficiency
bisphenol A	100	N.A	N.A	100
gemfibrozil	17.7	75	1.8	100
ibuprofen	89.0	83.3	0.6	100
diclofenac	100	N.A	N.A	100
ketoprofen	56.1	58.3	2.1	100
naproxen	68.5	75.6	2.8	100
salicylic acid	98.8	100	2.2	100
acetaminophen	99.1	68.0	3.3	100

Retention is dependant on many factors such as chemical characteristics of the compound, membrane characteristics, water matrix and adsorption interactions between compounds and the

membrane. The retention mechanism of target compounds represents a complex interaction of steric hindrance, electrostatic repulsion, solution effects on the membrane, and solute membrane properties. Some mechanisms are fairly well understood, while others are not (i.e. electrostatic exclusion and hydrophobic-hydrophobic interaction).

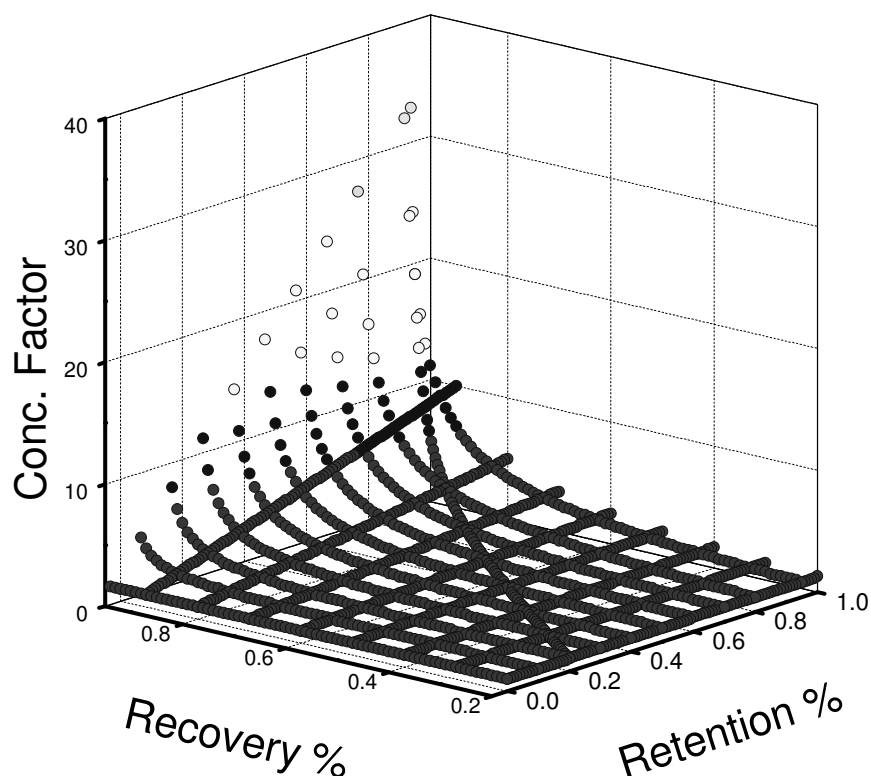
#### 4.4.5 Concentration of Trace Organics in Reverse Osmosis Concentrate

Generally water recycling plant using RO systems are usually operated at a recovery of between 80 and 95% and the retention of trace organics varies from zero to 100% (Metcalf & Eddy, 2007). Tables 4-7 and 4-8 show concentrations of pharmaceuticals and EDCs in the RO concentrate. The maximum concentrations were 0.545 and 0.13 µg/L for the LPWRP and the WRAMS, respectively. The concentration factor for the detected compounds in the LPWRP indicated that primidone, nonylphenol, ibuprofen, naproxen and carbamazepine have concentration factors of between 1 and 3 while salicylic acid, gemfibrozil, bisphenol A, ketoprofen and acetaminophen have concentration factors greater than 3 (Table 4-9). According to equations 1-3, a theoretical concentration factor of 40 times can hence be expected if a compound is fully retained and system recovery is high (see Figure 4-6 ).

The RO modules may further serve as a large reservoir for the PhACs and EDCs due to the adsorption of contaminants on membranes and their release is likely in the brine or during membrane cleaning processes. In addition, compounds may be released to permeate following cleaning or erratic pH variations. Treatment strategies for the brine and the spent solution need to be considered particularly when organic trace contaminants are of concern (Nghiem and Schäfer, 2006).

#### 4.4.6 Comparison of Trace Organic Removal in Water Recycling Schemes

When comparing the product waters of the three schemes, the concentrations of the trace contaminants were lower than the detection limits for most of the compounds except for ketoprofen (0.11 µg/L), primidone (0.05 µg/L) and naproxen (0.03 µg/L) in the LPWRP. This is consistent with a previous study by Ternes (1998) that reported diclofenac, ibuprofen, indometacine, naproxen, ketoprofen and phenazone were present in more than 50% of the investigated STP discharge and the 90 % of diclofenac and ibuprofen concentrations exceeded 1 µg/L. Salicylic acid and acetaminophen were detectable only in some STP effluents. They are known to be entirely degraded in sewage treatment plants (Ternes, 1998).



**Figure 4-6: Effect of recovery and retention on the concentration of compounds in the RO concentrate**

The removal efficiencies of PhACs and EDCs in the three schemes were determined by comparing the results of the raw wastewater and the recycled water. The removal efficiencies of these compounds during passage through the different processes were between 65% and 99% (see Table 4-9) despite high concentrations in the raw wastewater. In this study, the removal efficiencies were found to be superior to values reported in the literature. For ibuprofen, naproxen, ketoprofen and diclofenac previously reported removal rates were 75 to 100%, 55 to 98%, 23 to 100% and 3 to 75%, respectively (Ternes, 1998; Stumpf et al., 1999; Heberer, 2002a; Soulet et al., 2002; Lindqvist et al., 2005). The main reasons this variability in efficiency are; different treatment processes and variation in the functioning of these processes (Soulet et al., 2002; Tixier et al., 2003). The hybrid processes such as ozonation and BAC as well as the MF and RO used to treat municipal wastewater are the most advanced available technology to date.

The water quality produced was excellent and potentially too good for many applications. Unfortunately, the existing guidelines, Use of Reclaimed Water, are not sufficient and do not give adequate consideration to the various usage applications by including specific parameters for each category

The results of this study indicate, without doubt, the effectiveness of advanced and more recently implemented technology in different schemes such as ozonation, biological activated carbon, membranes (such as MF and RO) and UV disinfection in the removal of trace contaminants. These results are consistent with studies that found the majority of the influent load was removed during secondary treatment; 51 to 99% yielding expected surface water concentrations of 0.013 to 0.056 µg/L (Thomas and Foster, 2005) and 55 to 99% yielding 0.01 to 17.3 µg/L in the sewage effluent (Lee et al., 2004).

The specific mechanisms responsible for the elimination of these compounds remain to be elucidated. These could include abiotic degradation induced by solar irradiation, biotransformation, physical sequestration or a combination of these, (Sekela et al., 1999; Bendz et al., 2005).

## **4.5 Summary**

To date the quality of municipal wastewater has been elevated in terms of removal of conventional chemical parameters, i.e., nutrients, organic matter and suspended solids. However, the occurrence of micro-contaminants (e.g., pharmaceuticals, EDCs, hormones and disinfecting by products) in the effluent and receiving waters has been a matter of concern.

Three wastewater recycling plants have been investigated and analysed for the presence of eleven pharmaceuticals and two endocrine disrupting compounds, most of which have been detected in the influent of the three studied schemes. Some of these compounds were detected in other process streams such as MF backwash or RO brine which is indicative of an effective retention process and also demonstrates the possible creation of a new disposal problem. Despite the absence of currently detectable levels of micropollutants in water recycled from GGSS, the fact that this water is subsequently used for irrigation, raises the potential for negative environmental impacts to occur over long periods where concentration of these compounds to higher levels occurs through partitioning to soil and possibly plants, persistence and bioconcentration.

The comparative assessment of the three water recycling plants- discussed in this chapter- led to the next phase of the study. This was a comprehensive and detailed analysis of trace organic compounds in raw wastewater / water recycling processes over a whole year. This research was conducted in order to investigate the occurrence and seasonal variation, fate and removal of these micropollutants in wastewater treatment plants (Chapter 5) and mass balance of reverse osmosis, removal of micropollutants by membrane technologies and the overall removal by the wastewater / water recycling processes (Chapter 6). The Luggage Point Water Reclamation Plant (LPWRP) was chosen to investigate the fate of trace organics for the whole year as it is employing dual membrane systems and has a high water production. Furthermore, the concentrations of micropollutants in the MF and RO side streams (i.e., MF backwash and RO concentrate) were analysed to draw conclusions regarding the management of these streams (Chapter 7)





# *Chapter*

## *5 Occurrence and Fate of Micropollutants in the Luggage Point Water Reclamation Plant*

---

### **5.1 INTRODUCTION**

Wastewater contains a mixture of both organic and inorganic constituents. Its composition varies from time to time and place to place, basically depending on economic aspects, social behaviour, type and number of industries located in the collection area, climatic conditions, water consumption, the type and conditions of the sewer system, and so forth (Metcalf & Eddy, 2003). Figure 5-1 shows the proportions of the organic and inorganic constituents to the total wastewater volume. Organic matter typically consists of protein, carbohydrate, oils and fat and small quantities of a large number of synthetic organic molecules.

Provisions for the appropriate handling of sewage date as far as the forth century B.C., judging by the ‘Athenian Constitution’ written by Aristotle (Seghezzo et al., 1998). Thousands of years ahead, direct discharge to the environment would still be the most common way of dealing with sewage and domestic wastewater, particularly in the developing countries (Seghezzo et al., 1998).

Yet several technological options are available today in the field of wastewater treatment, including conventional aerobic treatment in ponds, trickling filters and activated sludge plants (Metcalf & Eddy, 2003).

**Figure 5-1: Composition of domestic sewage, modified after (Tebbutt, 1992).**

The efficiency of modern sewage treatment is such that the overall organic loading of receiving waters is low, indeed significant improvements in water quality have been achieved over the past 50-100 years, particularly with the introduction of the activated sludge process in 1913 (Cooper and Downing, 1998; Johnson and Sumpter, 2001).

Essentially, sewage treatment systems, such as activated sludge and biological (trickling) filters, rapidly convert aqueous organic compounds into biomass that are then separated from the aqueous phase by settlement. An influent biological oxygen demand of 300 mg/L could be converted to less than 10 mg/L in only a few hours (Cooper and Downing, 1998; Johnson and Sumpter, 2001). Such rapid treatment of a wastewater should be acknowledged as a remarkable achievement. As reported by Johnson and Sumpter (2001) biological treatment times in European activated sludge sewage treatments are often in the range of 4-14 hour (hydraulic retention time, HRT).

Conventional wastewater treatments are based on primary treatments, secondary treatments and - in some cases- tertiary treatments. The primary treatments aim to separate suspended solids and grease. The secondary treatment allows removal of dissolved organic matter. The tertiary treatments of wastewater treatment plants (WWTPs) include chemical processes to decrease nutrients and ultraviolet light to decrease micro-organisms. These conventional treatments are not

specifically designed to remove trace organic compounds. The presence of these widely used compounds have been reported in WWTPs from different countries around the world such as Canada (Gagne et al., 2006), Spain (Carballa et al., 2004) and Sweden (Ferrari et al., 2003) among others.

In the previous chapter, the residues of most of the investigated pharmaceuticals and endocrine disrupting compounds were detected in the influent of the three wastewater treatment plants. Furthermore, the implementation of advance technologies indicates the effectiveness in removal of these trace organic compounds. The variation in concentrations of these compounds between the different wastewater / recycling plants as well their removal percentage by various treatment processes led to a comprehensive study.

The key objectives of this chapter are to investigate the following in the Luggage Point Water Reclamation Plant (PWRP): 1) the seasonal variation of target compounds in influent, 2) the effectiveness of treatment in terms of conventional physiochemical parameters and 3) the occurrence and removal of metals and selected trace organic compounds (TOCs) over a period of a year. The physiochemical properties of the trace organic compounds were used to investigate the relationship between these compounds and their removal.

## **5.2 Inorganic constituents**

The inorganic constituents of wastewater are derived from either natural water or added through domestic, commercial and industrial usage. The presence of these inorganic solutes in water can cause significant concern with respect to drinking water quality, aesthetics and industrial use. The concerns over inorganic solutes range from their toxicity to their impact on process operation, product operation and product quality in industrial processes. The Environmental Protection Agency (EPA) has defined an array of primary and secondary drinking water standards to control and limit the overall impact of inorganic solutes (Eichenberger and Chen, 1982; U.S. Environmental Protection Agency, 2002).

According to Sörme and Lagerkvist (2002) households are an important source of Cu (tap water system and food), Hg (amalgam) and Zn (food and tap water systems), Pb, Cr, Ni and Cd in sewage water. Karvelas et al., (2003) investigated the occurrence and the fate of eight heavy metals (Cd, Pb, Mn, Cu, Cr, Zn, Fe, and Ni) during wastewater treatment processing in the city

of Thessaloniki in Northern Greece. They found that the heavy metals were detectable in the wastewater samples in a range of  $\mu\text{g/L}$  with frequency of occurrence of about 90-100%.

During the last two decades, the presence of heavy metal concentrations and their bioavailability in wastewater and sludge have received increased attention from scientific communities. Many studies have been performed on heavy metals speciation in wastewater, sewage sludge and its compost (Fuentes et al., ; Lester et al., 1979; Granier et al., 1990; Sörme and Lagerkvist, 2002; Karvelas et al., 2003; Buzier et al., 2006). Assessment of concentrations and chemical speciation of heavy metals enables evaluation their mobility, bioavailability or phytotoxicity. A significant part of the anthropogenic production of heavy metals ends up in wastewater. Major industrial sources include surface treatment processes with elements such as Cu, Zn, Ni, and Cr, as well as industrial products that at the end of their life are discharged in wastes. Waste treatment plants are expected to control the discharge of heavy metals to the environment. Cai et al (2007) has reported that the total heavy metals content in sewage sludge is about 0.5 – 2.0 % on a dry weight basis and in some cases may rise up to 4%, especially for metals such as Cu and Zn. In this study the concentrations of inorganic metals will be investigated for the determination of removal efficiencies by wastewater treatment processes. Moreover, a comparison will be conducted to compare these results with other work.

### **5.3 Pharmaceuticals and Endocrine- Disruptors Compounds**

The existence of micro-pollutants in the aquatic environment and their possible effects on living organisms have been discussed in Chapter 2. In wastewater treatment plants, organic pollutants could be removed partially or totally (Golet et al., 2002). While it is not feasible to remove all micro-contaminants to a level below the detection limits of modern analytical instrumentation, some treatment processes are clearly more effective than others at reducing the concentration of a broad range of trace contaminants. Coagulation, flocculation, and precipitation processes have been shown to be largely ineffective for removing organic contaminants from wastewater (Ternes et al., 2002; Westerhoff et al., 2005). Oxidative processes such as chlorination and ozonation are effective for reducing the concentrations of several classes of micro-contaminants (Adams et al., 2002; Snyder et al., 2003; Ternes et al., 2003; Pinkston and Sedlak, 2004; Huber et al., 2005a; Huber et al., 2005b).

Biological processes, such as activated sludge, biofiltration, and soil aquifer treatment, have been shown to greatly reduce the concentration of compounds which are biodegradable and/or readily bind to particles (Alcock et al., 1999; Ternes et al., 1999; Drewes et al., 2002; Snyder et al., 2004; Joss et al., 2005). Activated carbon can remove nearly all organic contaminants; however, removal capacity is limited by contact time, competition from natural organic matter, contaminant solubility, and carbon type (Ternes et al., 2002; Snyder et al., 2007). Reverse osmosis (RO) and nanofiltration (NF) membranes provide effective barriers for rejection of contaminants, while microfiltration (MF) and ultrafiltration (UF) membranes provide selective removal for contaminants with specific properties (Snyder et al., 2007).

## **5.4 Removal Mechanisms**

The removal of constituents from wastewater relies on two types of processes, which are based on mass transfer separation and chemical and biological transformation. The removal by mass transfer is accomplished by the transfer of mass from one phase to another (e.g., membrane, ion exchange, and distillation). On the other hand, transformation of specific constituents from one form to another occurs through chemical reactions (i.e., ozone, chlorine and UV) and biological conversion (i.e., activated sludge and biological activated carbon). Metal removal in biological treatment processes is mainly by adsorption and complexation of the metals with the microorganisms and the activated sludge floc (Lester, 1987). In addition, metals may also be complexed by carboxyl groups found in microbial polysaccharides and other polymers, or adsorbed by protein materials in the biological cell (Metcalf & Eddy, 2003).

The mechanisms of trace organic compound removal can strongly be influenced by the physicochemical characteristics of the compounds with the properties of the wastewater treatment process. These interactions are complex, which to date, are not fully understood due to their extremely small concentrations in the environment. In this study the mechanisms of organic pollutant removal from wastewater are briefly reviewed.

### **5.4.1 Biological degradation and transformation**

Parameters influencing the degradation efficiency are not yet fully understood, and include solid retention time (SRT), sludge age, substrate availability, redox conditions (aerobic, anoxic or anaerobic), sorption and reactor configuration (number of compartments, biofilm growth

surfaces and filtration). The effect of SRT on different pharmaceutical compounds is shown in Figure 5-2.

**Figure 5-2: Biological degradation and transformation of pharmaceuticals based on the aerobic solids retention time, SRT (Larsen et al., 2004).**

#### **5.4.2 Chemical oxidation**

The reaction mechanisms of oxidation during ozonation have been studied (Deborde et al., 2005; Huber et al., 2005a). During ozonation, micro-pollutants are oxidised through attack by either the ozone molecule itself or the hydroxyl radical, derived from ozone decomposition. Von Gunten (2003) believes that ozone molecules react selectively with certain functional groups, but oxidation with hydroxyl radicals is indiscriminate. However, Nakada *et al* (2007) suggest that molecular ozone attacks structures with high electron density, such as C=C, activated aromatic systems, and non protonated amines, but not aromatic rings with ethylene, amide or carboxylic groups. By and large, exact information on transformation products is still lacking.

#### **5.4.3 Sorption**

Sorption of organic micro-pollutants to the sludge in the treatment plant depends on two main mechanisms: absorption and adsorption as shown in Figure 5-3. Absorption is the result of the hydrophobic interaction of the aliphatic and aromatics groups of a compound with the lipophilic cell membrane of the microorganisms and with the lipid fraction of the sludge. Adsorption is the electrostatic interactions of positively charged groups of the chemicals with negatively charged surfaces of the biomass (Schwarzenbach et al., 2003). Since sorption only involves a phase shift to the pollutants and no degradation or even transformation, the fate of the sewage sludge is central to the environmental evaluation of this process.

**Figure 5-3: Adsorption and desorption of TOCs to particulate matter (Larsen et al., 2004).**

#### **5.4.4 Stripping**

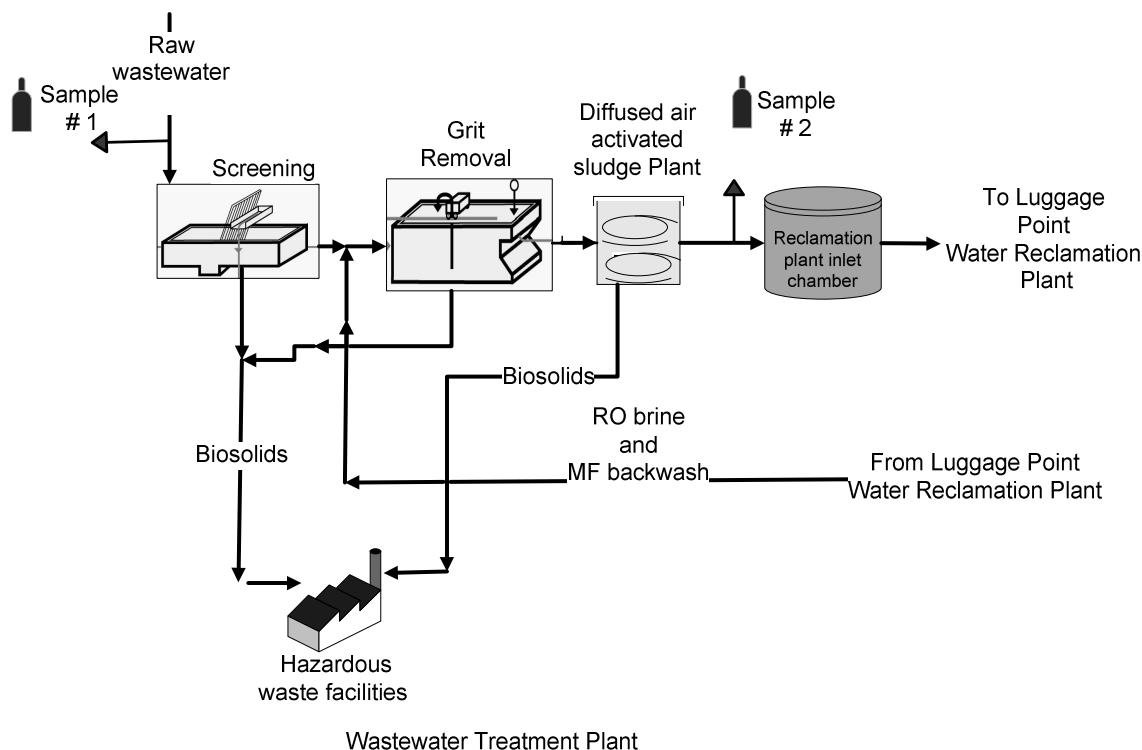
Stripping is an important removal mechanism for low molecular weight compounds. It takes place in the aerobic part of the wastewater treatment plant due to the intensive aeration of the mixed liquor. Stripping depends on the aeration intensity and the Henry coefficient of a given compound. Since the majority of pharmaceuticals have a molecular mass of above 250 mg/ mol with a Henry coefficient below 0.005, stripping is not likely to be a practical removal mechanism for these compounds (Larsen et al., 2004).

### **5.5 Materials and Methods**

#### **5.5.1 Sampling**

Wastewater treatment at Luggage Point Water Reclamation Plant (LPWRP) employs primary and secondary treatment using activated sludge with a solid retention time of 14 days. A complete description for the LPWRP was given in Section 4.2.3. Samples were collected from the influent and effluent of the wastewater treatment processes (Figure 5-4). Two campaigns of sampling were conducted for this study between May 2005 and July 2006. For analysis of anions, cations and heavy metals, sampling was conducted monthly and for analysis of trace organic compounds (TOCs) and physicochemical parameters (e.g., pH, electrical conductivity (EC), suspended solids (SS), chemical oxygen demand (COD) and biological oxygen demand (BOD)), sampling was conducted in May, September, November and December 2005, as well as February, April and June 2006 (see Table 5-1).





**Figure 5-4: Scheme of Wastewater Treatment Processes of Luggage Point Water Reclamation Plant (LPWRP)**

### 5.5.2 Sample Preparation

Samples were collected during the period May 2005 and July 2006 using pre-cleaned amber glass containers. For analysis of TOCs, samples were kept on ice during transit to the laboratory and adjusted to pH between 2 and 3 by addition of sulphuric acid. The samples were subsequently filtered using three different filters before being stored at 4°C until extraction. More details are given in Section 3.2.

For analysis of physicochemical parameters, different procedures were used. Appendix 8-3 summarises various methods used for the characterisation of influent and effluent of wastewater treatment and their method detection limit.

### 5.5.3 Analytical Methods

In brief, filtered samples were loaded onto pre-conditioned Waters Oasis HLB SPE cartridges. After loading, the cartridges were rinsed with reagent and dried with nitrogen. Compounds were eluted using methanol in water (5% v/v) solution. Extracts were concentrated and derivatized

using BSTFA and TMCS (99:1) before injection onto a gas chromatograph with mass detector for identification and quantification of compounds. More detail can be found in Sections 3.2 and 3.3.

## 5.6 Physicochemical Characterisation of Influent and Effluent

### 5.6.1 Characterization of Influent

The inflow of the wastewater was monitored during the period between May 2005 and July 2006. These data showed that the inflow of the wastewater ranged between 113 and 160 ML/day with an average of 135 ML/day during dry season, while it reached up to 438 ML/day during the high rainfall. The accumulated rainfall for each month, plus the minimum and maximum temperatures during the sampling period are presented in Table 5-1.

**Table 5-1: Monthly rainfall and minimum and maximum temperature**

Sampling date	Influent flow (ML/day)	Monthly rainfall (mm)	Temp (°C)	
			Min	Max
30th May, 2005	153	53	14	25
13th Sep., 2005	140	15	11	23
1st Nov., 2005	158	133	20	28
13 <sup>th</sup> Dec., 2005	162	78	22	32
1st Feb., 2006	159	107	22	31
6 <sup>th</sup> Apr., 2006	141	48	17	28
8 <sup>th</sup> June, 2006	133	44	11	22

Table 5-2 shows the variations of the physico-chemical parameters of the influent during the sampling period. These values exhibit large variations throughout the sampling period. The pH values varied from 7.2 to 7.26 and fall within the optimal range of pH for development of bacteria (6.0 to 7.5) and fungi (5.5 to 8.0) (Cai et al., 2007). The values of nitrogen, phosphorous, chemical oxygen demand (COD), EC and suspended solids (SS) declined occasionally by more than fifty percent which was associated with the incidence of high rainfall (Table 5-1).

**Table 5-2: Physico-chemical characteristics of the influent and secondary effluent**

Characteristic	May	Sep	Nov	Dec	Feb	Apr	June
pH	7.3 (7.8)*	7.4 (7.9)	7.5 (7.9)	7.4 (7.7)	7.4 (7.8)	7.2 (7.8)	7.3 (7.8)
BOD	243 (2.5)	208 (2.5)	277 (2.5)	257 (2.5)	229 (2.5)	241 (2.5)	401 (2.5)
COD	610 (32)	518 (30)	598 (27)	500 (25)	568 (31)	617 (24)	808 (29)
EC (µS/cm)	2515 (2688)	2254 (2198)	1851 (1694)	2712 (2120)	3038 (2927)	1598 (1718)	2415 (2334)
SS	216 (6)	230 (7)	320 (3)	245 (6)	252 (16)	392 (3)	304 (13)
Total Kjeldahl Nitrogen as N	46 (2.7)	55 (1.6)	49 (1.7)	46 (3)	46 (3.1)	47 (1.4)	57 (6)
Total Phosphorus	9 (5)	12 (6)	11 (9)	10 (5)	9 (9)	9 (5)	11 (5)
Calcium	56 (47)	45 (43)	36 (35)	38 (40)	47 (46)	36 (34)	44 (44)
Magnesium	77 (54)	46 (44)	32 (31)	39 (41)	57 (58)	29 (33)	43 (44)
Potassium	39 (31)	30 (29)	23 (23)	25 (35)	33 (23)	23 (24)	31 (31)
Sodium	670 (479)	394 (384)	260 (255)	347 (369)	484 (500)	216 (271)	317 (346)
Total Sulphide	6 (nm)	11 (nn)	8 (nm)	15 (nm)	17 (nm)	5 (nm)	8 (nm)

All units are mg/L unless otherwise noted

\*: Data between the parenthesis ( ) represents the concentration in the effluent; nm: not measured

**Table 5-3: Range of influent and effluent quality in (mg/L) after secondary and advanced treatments**

Components	Influent		Influent *		Effluent		Effluent **	
Cations	Min	Max	Min	Max	Min	Max	Min	Max
calcium	36	56	74		34	47	66	
magnesium	29	77	38		31	58	39	
potassium	30	39	-		23	35	-	
sodium	216	670	198		255	500	198	
Heavy metals								
aluminum	0.415	0.826			0.025	0.053		
arsenic	<0.025		0.0032		0.025	0.025	<0.0005	0.05
barium	0.02	0.052			0.0025	0.022	0.5	
cadmium	0.0025		0.02	0.16	<0.0025		<0.0002	0.05
chromium	0.005	0.023	0.003	8.12	<0.005		<0.001	
copper	0.051	0.111	0.04	0.63	0.0025	0.01	0.001	0.07
iron	0.577	4.463	0.04	8.8	0.089	0.170		
lead	0.025		0.04	0.19	<0.025		0.007	
manganese	0.163	0.173	0.07	105	0.096	0.163	0.008	
mercury	0.05	0.316			<0.05		<0.0002	0.02
molybdenum	0.012	0.015			0.005	0.015		
nickel	0.005	0.019	0.3	0.77	<0.005		0.0007	0.12
zinc	0.06	0.198	0.15	1.8	0.029	0.062	0.023	0.1

\*(Orhon *et al.*, 1997; Singh *et al.*, 2004),(Karvelas *et al.*, 2003) , \*\*: minimum achievable residual concentrations by advanced treatment as reported by (Metcalf & Eddy, 2003, 2007).

By comparing the properties of the influent with the reported range of wastewater by other researchers from around the world, it shows that the magnitude of the contents was in the lower ranges (Table 5-3). The dilute contents of the influent, as in this case, could be due to the high rate of water usage in Australia.

The concentration of the major anions and cations including Ca, Mg, Na, S, and K were investigated in the influent of wastewaters. These concentrations were found to fluctuate during the sampling time with two sharp peaks during the dry seasons. Their relative abundance was in

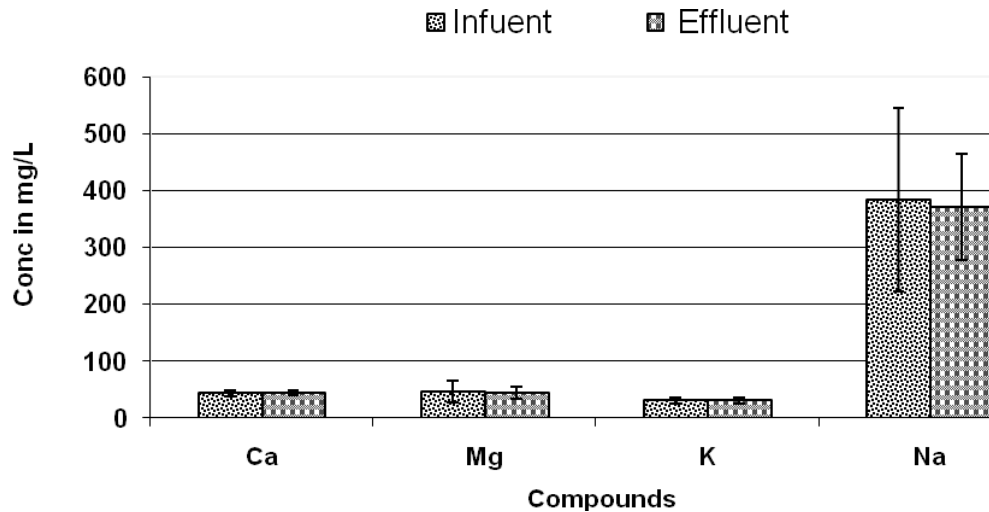
the following order:  $\text{Na} \gg \text{Mg} > \text{Ca} > \text{K} > \text{S}$  (Table 5-2) with the maximum concentration for Na up to 670 mg/L.

The occurrence and fate of heavy metals including aluminium (Al), arsenic (Ar), barium (Ba), cadmium (Cd), chromium (Cr), cobalt (Co), copper (Cu), iron (Fe), lead (Pb), manganese (Mn), mercury (Hg), molybdenum (Mo), nickel (Ni) and zinc (Zn) were investigated in the WWTP (Table 5-3). Compounds namely, lead, cadmium and arsenic were not detected in the raw wastewater, while other compounds were detected in all wastewater samples with relative abundance in the following order:  $\text{Fe} > \text{Al} > \text{Hg} > \text{Mn} > \text{Zn} > \text{Cu} > \text{Ba} > \text{Mo} > \text{Cr} > \text{Ni}$  (Table 5-3) the data shows that the concentration of heavy metals are in the lower concentrations range of previous works. According to Chipasa (2003) the heavy metals content in wastewater influent were  $\leq 0.02$  mg/L for cadmium,  $\leq 0.05$  mg/L for lead,  $\leq 0.1$  mg/L for copper and  $\leq 0.5$  mg/L for zinc. He reported that the heavy metals influent concentration in wastewater cannot be either predicted or monitored hourly or monthly.

## 5.7 Performance of wastewater treatment processes of LPWRP

The physico-chemical properties of the effluent are presented in Table 5-2. The total nitrogen content and the total phosphorus content decreased from 57 mg/L to 6 mg/L and 9 to 5 mg/L, respectively. The primary and secondary treatments of the wastewater effectively reduced the nitrogen by 89%. Nitrogen and phosphorus are commonly known as limiting nutrients for eutrophication in natural waterways. Therefore, careful control of their release is important to prevent excessive algal growth (Andersen et al., 2006). It is clear that the effluent had a better quality in regards to the organic and nitrogen contents due to the efficiency of the activated sludge process in the WWTP. In the secondary effluent, the suspended solids, the levels are much lower than the untreated concentrations, 93%.

A comparison of major cations in the influent and effluent is presented in Figure 5-5. During the primary and secondary treatments, these concentrations did not change significantly (less than 5% variation) (see Figure 5-5). This also, can be seen by the only slight marginal change in the electrical conductivity between the influent and effluent with a maximum reduction of 12% which is comparable to other researcher's results (7%) as reported by Tchobanoglous et al. (2007) (see Table 5-3)

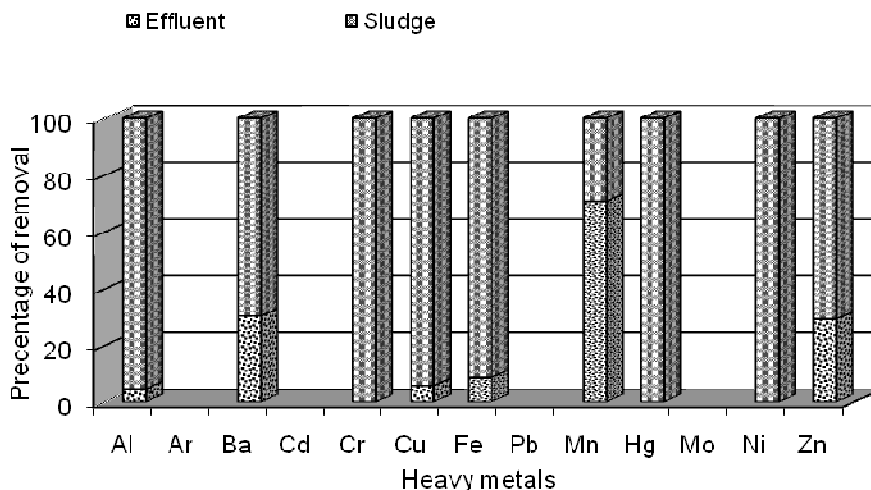


**Figure 5-5: Concentrations of major cations in the influent and effluent**

The concentration of heavy metals found in wastewater samples are presented in Table 5-3. These concentrations in treated effluent indicating that Cr, Ni and Hg were removed totally, while 70 -95% of Cu, Fe, Zn, Al, and Ba, and 30% of Mn were removed (Figure 5-6). The total metals concentrations markedly decreased after primary and secondary treatments, suggesting a strong impact of both treatments. Heavy metals removal occurred both in primary treatments (where a portion of metals absorb on to particles) and in secondary biological treatment (where metals are removed by sorption). Biological treatment systems are designed for removal of organic matter by activated sludge microorganisms. Therefore, removal of heavy metals by these systems may be regarded as a side benefit, and has been found to be very variable. Such removal of total metals by activated sludge has long been reported (Nielsen and Hrudey, 1983; Buzier et al., 2006). On the other hand, Buzier et al. (2006) found that removal of Cr, Cu and Fe were highly positively correlated with the removal of suspended solids.

Assuming no biodegradation, the total heavy metal loading of raw wastewater will end up in the sludge or remain in the treated effluent (Figure 4-6). Santarsiero et al. (1998) reported that primary sedimentation affected to a great degree the distribution of Zn, Pb and Cr, while the biological processes and secondary sedimentation affected mostly the distribution of Cu, Cd, and

Ni. Other researchers have reported that Mn and Cu are primarily (>70%) accumulated in sludge, while 47-63% of Cd, Cr, Pb, Fe, Ni, and Zn remain in the treated effluent (Karvelas et al., 2003).

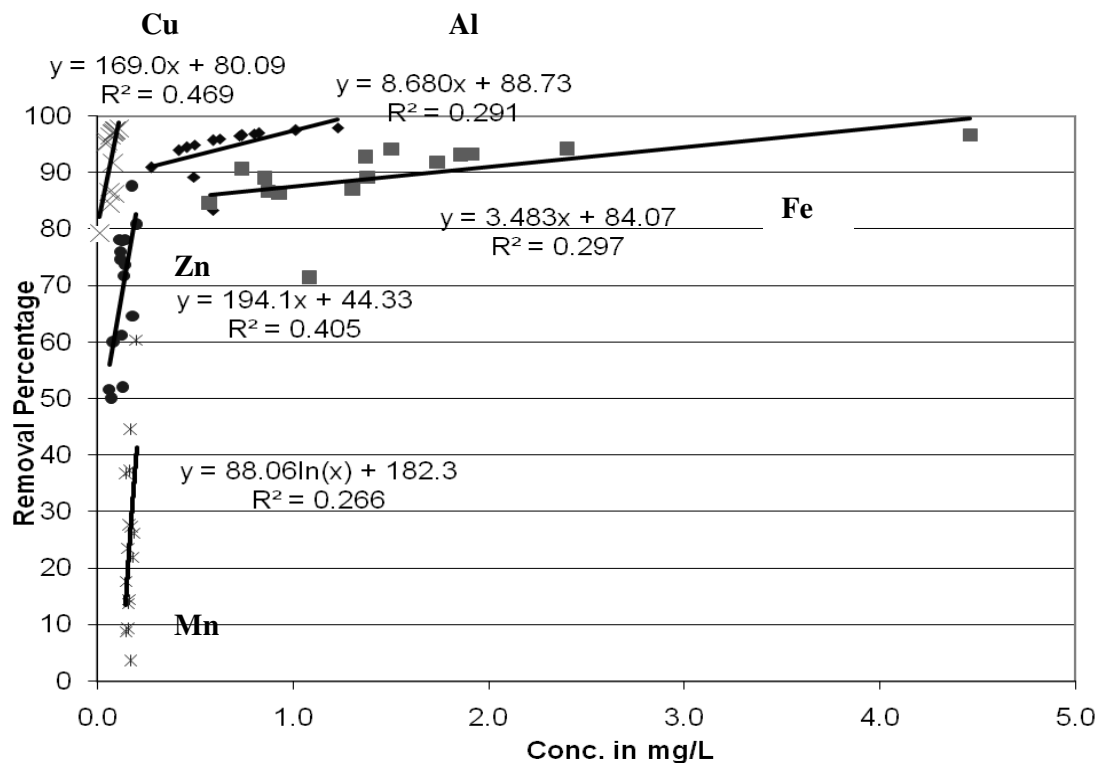


**Figure 5-6: Percentage removal of heavy metals**

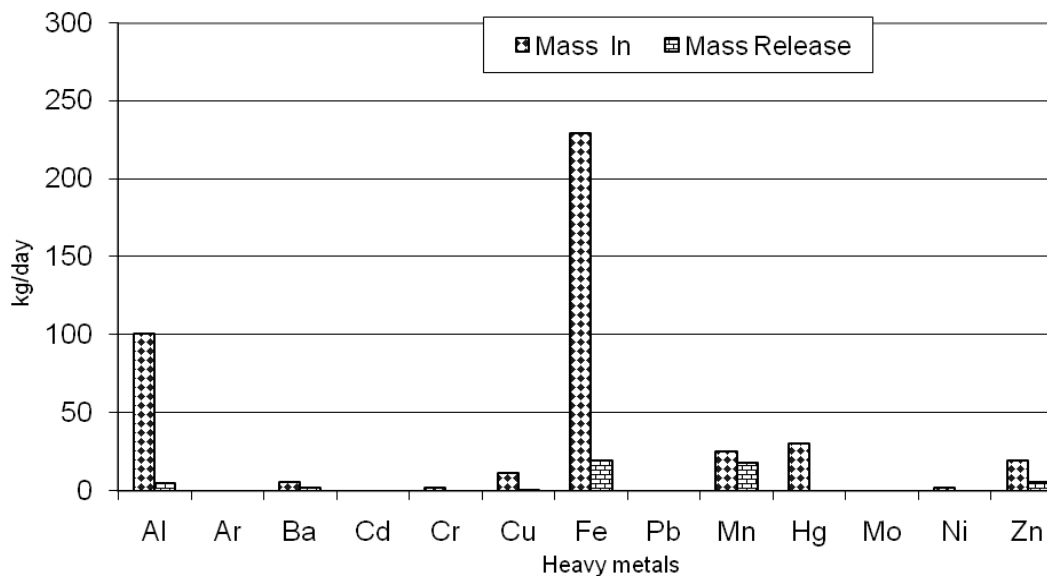
A correlation has been found between the concentration of heavy metals and their removal as shown in (Figure 5-7). Removals of aluminum and iron have shown a strong relation with increasing concentrations. Karvelas and their co-worker (2003) determined the partition coefficient ( $K_p$ ) for heavy metals in wastewater. The partition coefficient is defined as the ratios of the dissolved to the solid phase concentration, which is indicative of the process (sorption, desorption, etc.) that takes place and specifies the presence of each element in the two phases.

The mass balance of heavy metals in the wastewater treatment was calculated from their concentrations in the influent and the effluent. Figure 5-8 presents the mean amounts of heavy metals that daily enter and exit the treatment plant. In theory, there should be very good accordance between the input and output loads for conservation pollutants like metals that cannot be degraded but settle out in the sludge or remain in the water stream (Karvelas et al., 2003).

The total amount of metal in the influent and effluent was found to be more than 425 kg/day and 50 kg/day, respectively (Figure 5-8). This indicates that more than 88% of these metals were primarily removed through sludge. Iron and aluminium represented more than 54% and 23% of the total amount. Karvelas et al. (2003) suggested that wastewater may be a significant source of heavy metals such as aluminium; therefore concentration of the heavy metal should be taken into account when discharging effluent to the aquatic environment.



**Figure 5-7: Correlation between concentration and removal of heavy metals**



**Figure 5-8: Mass balance of heavy metals in wastewater treatment plant**



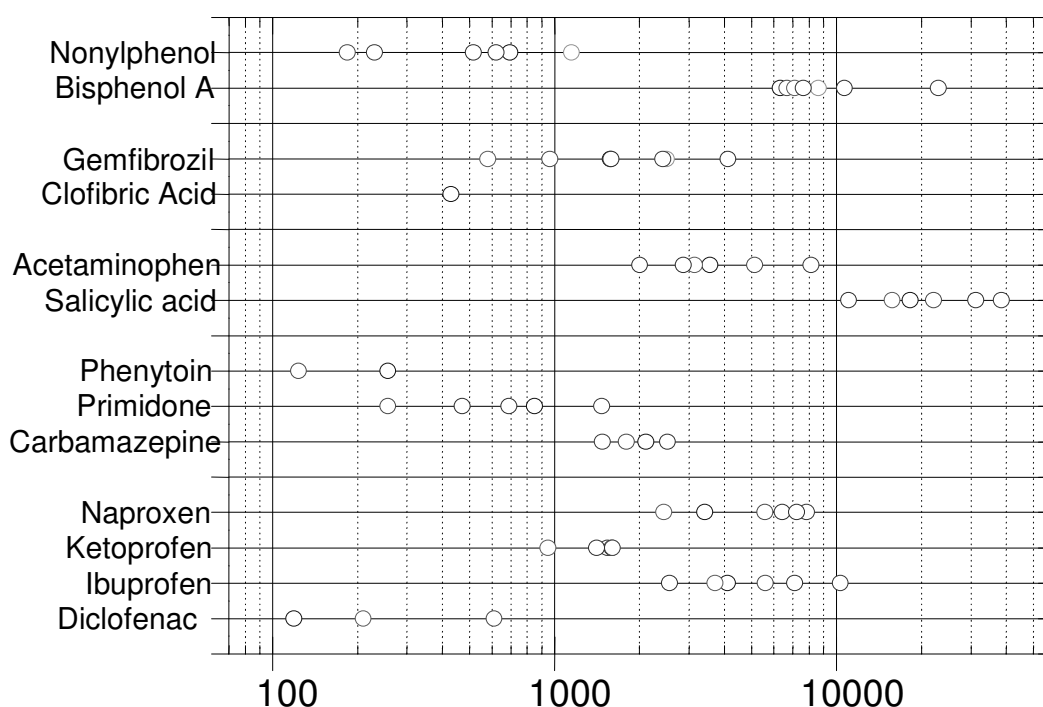
## 5.8 Occurrence of PhACs and EDCs in wastewater influents at Luggage Point Water Reclamation Plant

The concentrations of the target compounds in the influent over the year long sampling period at LPWRP are summarized in (Figures 5-9 and 5-10). Gemfibrozil, naproxen, acetaminophen and salicylic acid were found in all influent samples. Acetylsalicylic acid (aspirin) is one of the top ten pharmaceuticals dispensed in Australia (Department of Health and Aging, 2005), and is easily degraded by deacetylation into a more active form, salicylic acid (Ternes, 1998; Roberts and Thomas, 2006). Salicylic acid was found in the influent at concentrations significantly higher than other target compounds ranging from 11,065 to 38,490 ng/L with an average of 7 positive samples of 22,470 ng/L (Figure 5-9). This high occurrence of salicylic acid can be correlated with its high solubility and low pKa value. These concentrations are consistent with other studies with concentrations of  $3.2 \times 10^3 - 54 \times 10^3$  ng/L in Canada (Pham and Proulx, 1997), Germany (Ternes, 1998), France (Blanchard et al., 2004) and Australia (Khan, 2002). Variations of one order of magnitude in concentration of salicylic acid were detected during this survey. The high concentrations of salicylic acid were most likely indicative of higher rate of consumption of salicylic acid in conjunction with other medicines recorded during September 2005. During this time of the year, the recorded minimum and maximum temperatures, and rainfall were 10.6°C, 23.0°C and 14.6 mm, respectively. Decreased degradation rates of target compounds could be a result of low temperatures (Figure 5-9).

Ibuprofen had the second highest concentration in this study, among the pharmaceuticals, with a maximum concentration of 10,340 ng/L (average: 5570 ng/L, n = 6) (Figure 5-9). These concentrations are consistent with other reports from Japan (Nakada et al., 2006) and Finland (Lindqvist et al., 2005; Vieno et al., 2005), but higher by one order of magnitude than observations in Switzerland (Joss et al., 2005), Brazil (Stumpf et al., 1999) and Sweden (Bendz et al., 2005). According to Roberts and Thomas(2006), the occurrence of ibuprofen in environmental water is frequently reported and is considered one of the most common drug residues in surface water.

Acetaminophen (paracetamol) was ranked third among the top ten most dispensed drugs in Australia with 4.5 million prescriptions in the year 2003 (Department of Health and Aging, 2005). Acetaminophen was detected in all of the wastewater samples at concentrations ranging from 1,500-8,140 ng/L (average: 3,760 ng/L, n=7) with the highest concentrations in September

2005 and lowest concentrations in May 2005 and April 2006. These concentrations were to some extent lower than those reported previously (Pham and Proulx, 1997; Blanchard et al., 2004)



**Figure 5-9: Variation of concentration of various target compounds (ng/L) in the influent- each circle in line represents one sample**

Carbamazepine was present in the wastewater at concentrations up to 2,500 ng/L (average 2080 ng/L, n=5). These concentrations were the same order of magnitude found in Austria (Clara et al., 2005) and Sweden (Bendz et al., 2005). However, it was reported at one order of magnitude lower in Australia (Khan, 2002), France (Blanchard et al., 2004) and Switzerland (Joss et al., 2005). Since only 2-3% of the carbamazepine dose is excreted in urine in unchanged form, the presence of the primary metabolite- 10, 11 epoxide- (Gomez et al., 2007) should be addressed in future investigations.

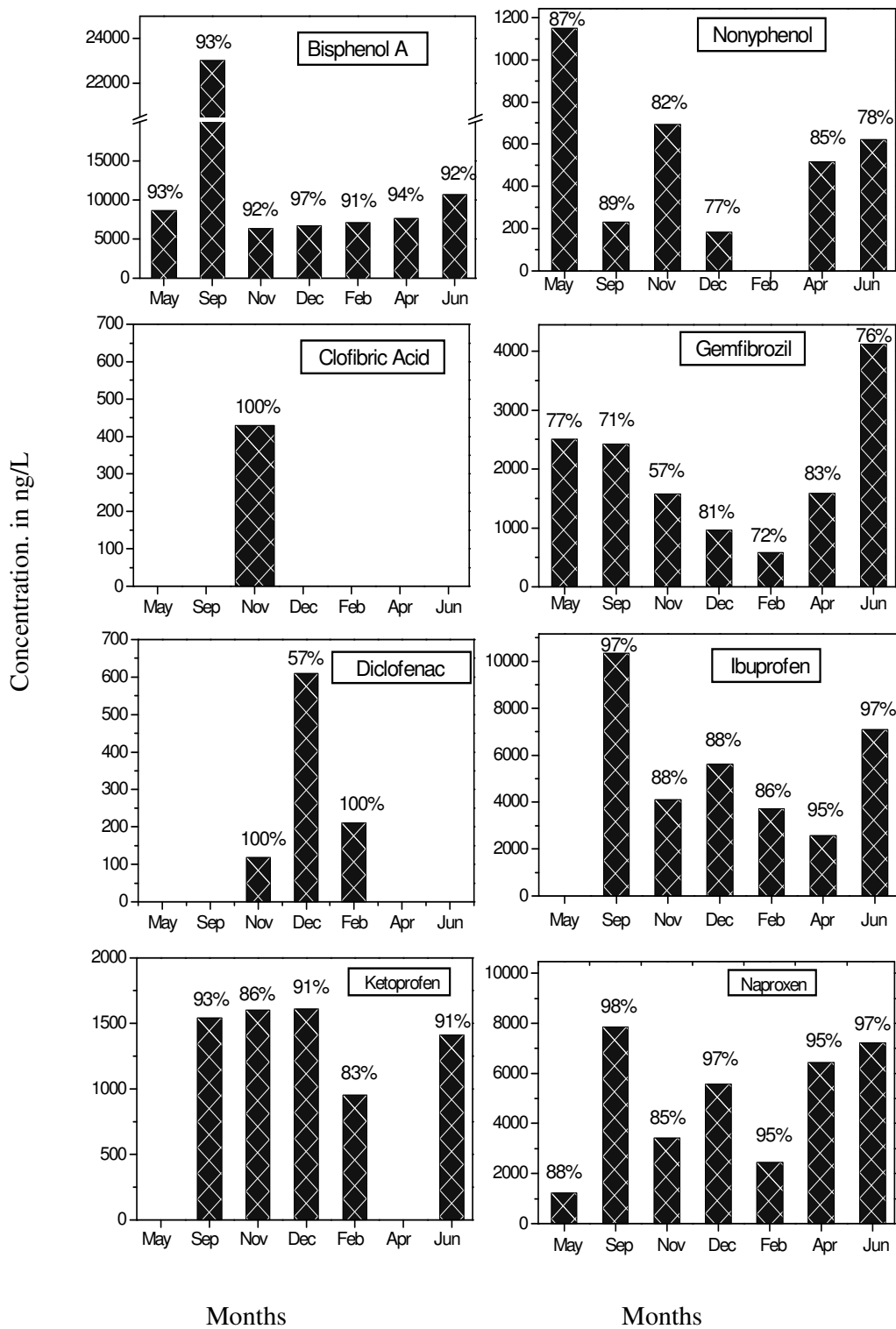
Clofibric acid, phenytoin and diclofenac showed the lowest concentration ranging from 120 to 610 ng/L. These concentrations were comparable to other reports for clofibric acid in Brazil (Stumpf et al., 1999) and Australia (Khan, 2002) and for diclofenac in Australia (Khan, 2002), Sweden (Bendz et al., 2005), Finland (Lindqvist et al., 2005), Germany (Ternes, 1998) and Brazil (Stumpf et al., 1999). Clofibric acid was the least frequently detected compound (430 ng/L), which was not detected in STPs of France, Greece and Italy (Ferrari et al., 2003).

In conclusion, the September influent sample had the highest total concentration of the studied compounds ( $\Sigma 95.0 \mu\text{g/L}$ ) of the influent samples collected around the year. The reason for this discrepancy is that there is a higher consumption of drugs during winter time (for example, because of the flu epidemics). Furthermore, September was one of the driest months through the year (total rain during September < 14 mm) which leads to less dilution of the compounds and can be seen through the lowest flow level of the influent during the year.

Among the EDCs, BPA showed the highest concentrations and ranged from 6,330 to 23,020 ng/L (average 10,010 ng/L,  $n=7$ ). These concentrations were higher than in Austria (Clara et al., 2005) while consistent with another report from Canada (Lee et al., 2004). BPA is a well-known industrial chemical and has been reported as slightly to moderately toxic and easily biodegradable (Staples et al., 1998), but its importance lies in its well documented estrogenic activity. It is considered as a priority hazardous compound (Bergeron et al., 1999).

Furthermore, the concentration of NP reached 1150 ng/L (average 570 ng/L,  $n=6$ ). Other researchers have found greatly varying concentrations of NP with both one order of magnitude lower to a one order of magnitude higher than the present results (Lee et al., 2004; Nakada et al., 2006; Clara et al., 2007). As reported by Sekela et al. (1999), the nonylphenol ethoxylates ( $\text{NP}_n\text{EO}_s$ ) under anaerobic conditions biodegrade to yield the most toxic 4-substituted monoalkylphenol (4-nonylphenol, NP). The amount of measured NP represents only 27% of the  $\text{NP}_n\text{EO}_s$  (nonionic surfactants which are used in household and industrial applications.), while the remainder represents 61% as  $\text{NP}_1\text{EO}$  (nonylphenol mono-ethoxylate) and 12% as  $\text{NP}_2\text{EO}$  (nonylphenol diethoxylate) in the influent of WWTPs.

The European Commission proposals for a Directive on Environmental Quality Standards (EQS) in the field of water policy report a limit of an average of  $0.3 \times 10^3 \text{ ng/L/year}$  of NP. Besides the EQS, the Commission proposal also defines a maximum allowable concentration of  $2.0 \times 10^3 \text{ ng/L}$  for NP (COM (2006)). According to EQS, the effluent reached a concentration above the



**Figure 5-10: Concentrations of PhACs and EDCs (ng/L) in the influent and the removal percentage by the treatment processes of LPWRP**

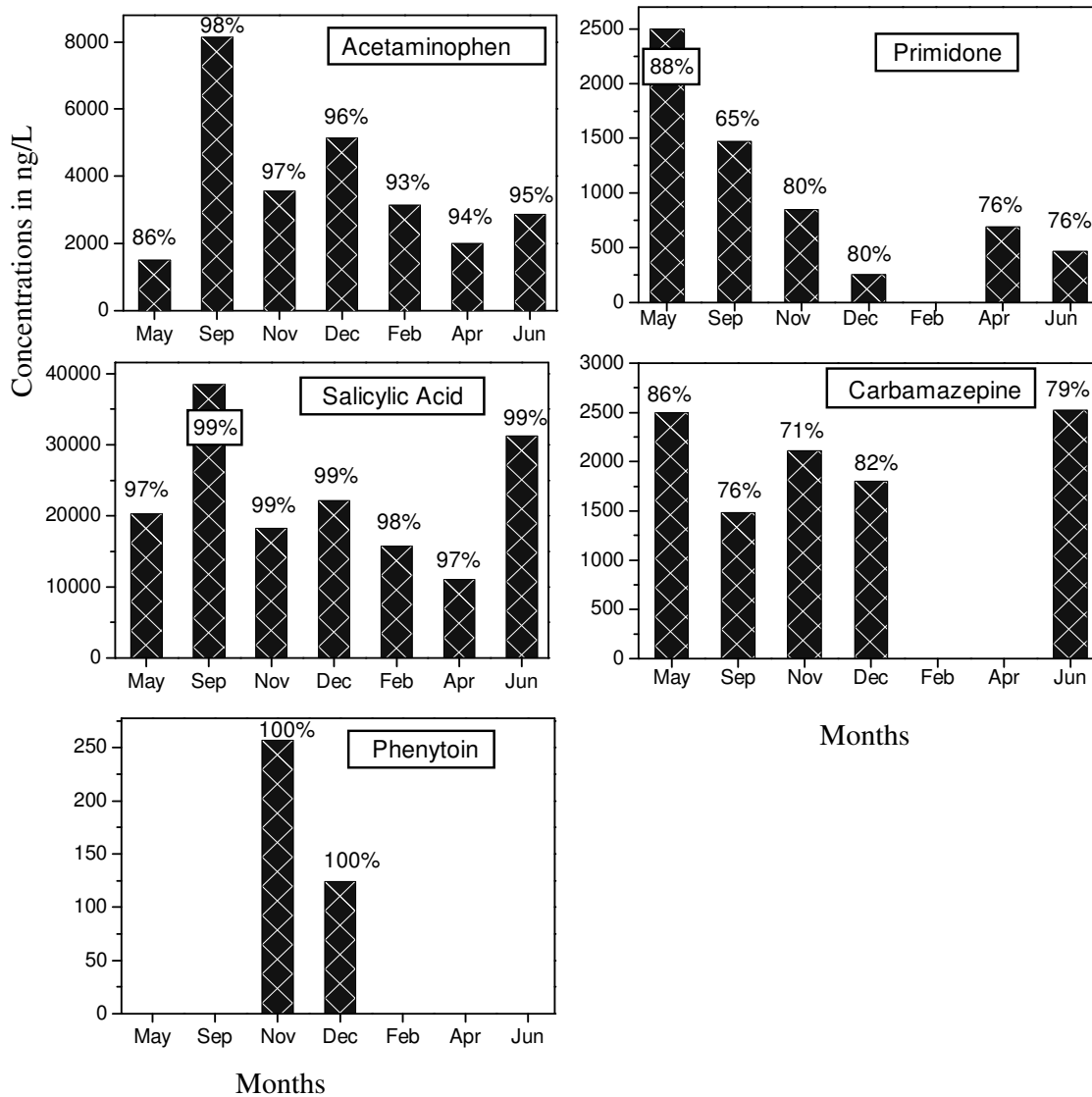


Figure 5-10 (Continued): Concentrations of PhACs and EDCs (ng/L) in the influent and the removal percentage by the treatment processes of LPWRP

limit value. In order to keep to the proposed limit a reduction of the concentration is necessary through implementing an efficient wastewater treatment process.

Considering the average temperature during the sampling campaigns, September 2005 and June 2006 had the lowest mean temperature, 23.0 °C and 21.8 °C, respectively. This fact might indicate that the concentrations of PhACs in the influent may be related to higher consumption of pharmaceutical products in the community during the cold periods of the year when more illness occurs. Comparable results were obtained by Clara et al.(2005).

## 5.9 Removal of PhACs and EDCs in LPWRP

Concentrations of the target micro-pollutants in the effluent of wastewater treatment plant are presented in Figure 5-10. Most target chemicals were detected in the WWTP effluent in a range of 100-1000ng/L. This is in agreement with Ternes et al (1998), who reported that many PhACs were detected in the effluents and measured at high concentrations due to incomplete elimination in German sewage treatment plants. In addition, the concentrations of the compounds detected in effluent were much lower by one order of magnitude than those in the influent (Figure 5-10).

Treatment efficiencies of the targeted compounds in the WWTP were calculated as relative amounts compared with the intake concentration using the following equation:

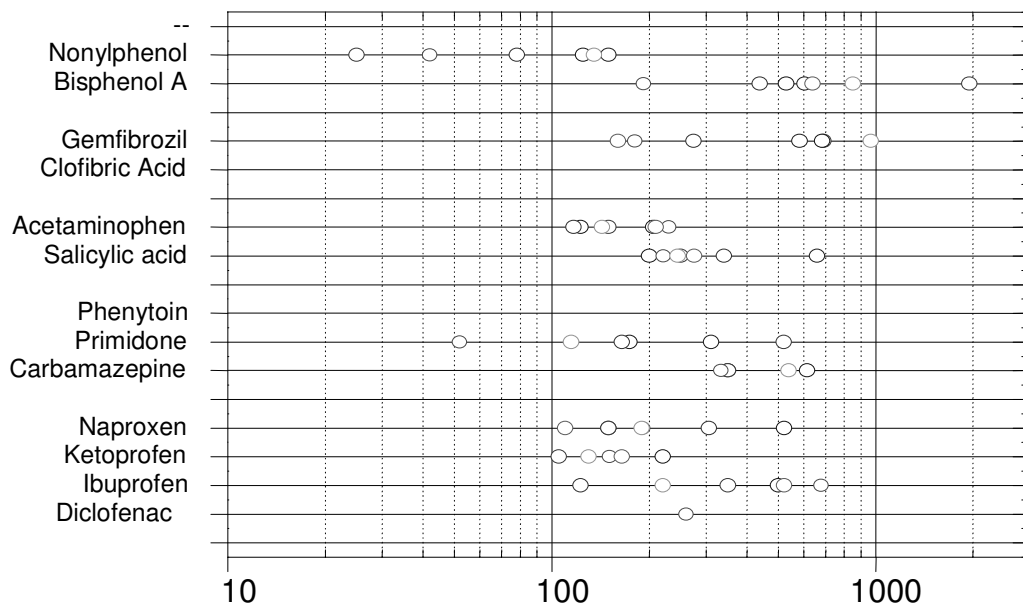
$$\text{Efficiency} = \left( \frac{C_i - C_e}{C_i} \right) \times 100 \quad (5-1)$$

where  $C_i$  and  $C_e$  are the concentrations measured in the influent and effluent of wastewater treatment processes, respectively.

These removal rates are shown in Figure 5-. All the acidic pharmaceuticals were removed efficiently by the WWTP, at an average range of 77-100% with a range of variability of 3.5–8%, with the exception of diclofenac which was removed at 57-100% with range of variability of 40%.

This high variability of diclofenac removal was related to infrequent detection at low concentrations. Furthermore, this compound has the largest molecular weight, the lowest aqueous solubility and is one of the most hydrophobic acidic compounds tested. This may affect its biodegradability. In general, the removal rates found in this study were consistent with other plants using primary and secondary treatment with activated sludge. For example, 75% removal rate in German (Ternes, 1998; Stumpf et al., 1999), up to 90% in Spain (Santos et al., 2007) and

up to 99% in Japan (Nakada et al., 2006) were reported. These removal rates for a single compound can vary greatly from one WWTP to another depending on the type of treatment (e.g. biological and physico-chemical) and the residence time of water in the primary sedimentation tank (Santos et al., 2007).



**Figure 5-11 Variation of Concentration of various target compounds (ng/L) in the secondary effluent of LPWRP; each circle in line represents one sample**

Removal efficiency of naproxen and ketoprofen have been reported with a large variability range from 40–65% and 40–90% in Spain (Santos et al., 2007) and 51–100% in Finland (Lindqvist et al., 2005). This variability can be partly ascribed to the low hydrophilic nature of naproxen and ketoprofen ( $\log K_{ow} < 3$ ) (Nakada et al., 2006), their persistence under microbial attack (Bendz et al., 2005) and different hydraulic retention times of the WWTPs (Santos et al., 2007).

Salicylic acid had the highest removal rates of  $99 \pm 1\%$  which could be ascribed to the microbial and chemical degradation processes incurred during the treatment as has been described by Nakada (2006). Acetaminophen was found to be eliminated efficiently at  $95 \pm 3.5\%$  ( $95 \pm 3.5\%$ ) due to its biodegradability. In Germany, acetaminophen was detected in less than 10% of all

sewage effluents and not detected in river water (Ternes, 1998; Kolpin et al., 2004; Roberts and Thomas, 2006).

Carbamazepine was found to have a relatively low removal efficiency compared to the other compounds averaging  $79 \pm 5\%$ , which is probably due to its hydrophilic nature ( $\log K_{ow} < 3$ ) and chemical stability (Nakada et al., 2006). Clofibric acid and phenytoin were totally removed from the WWTP, but due to infrequent detection at low concentrations no conclusions could be drawn.

Bisphenol A was almost completely removed, 91-97% (mean  $93 \pm 2\%$ ) (Figure 5-10) which is consistent with other reports from Japan ( $>92\%$ ) (Nakada et al., 2006) and Austria ( $>95\%$ ) (Clara et al., 2005). Clara and co-workers, (2005) concluded that the almost complete removal of BPA is attributable to the biodegradation / transformation with dependence on solid retention time (SRT) where no removal was observed in other WWTP with highly loaded plants, operating at SRTs between 1 and 2 days.

Nonylphenol had a comparatively low removal rate (78-89%, mean  $83 \pm 4$ ) with comparable results reported in Japan (61-75%) (Nakada et al., 2006) and Austria (79%) (Clara et al., 2005). More recently, Clara et al. (2007) reported that 90% of the NP and its ethoxylates (NPnEO) were removed, with more than 85% due to biotransformation. Conversely, the removal of NP in the WWTP which implemented an activated sludge process, was ascribed to its accumulation onto sewage sludge as a result of its lipophilic nature (Lee et al., 2004). With a Log  $K_{ow}$  of 4.5, NP is a hydrophobic molecule (Ahel et al., 1994), between 60% and  $> 90\%$  of spiked NP went into the sludge (Tanghe et al., 1998).

The efficiency of modern sewage treatments has increased the removal of micro-organic compounds from sewage influent with the introduction of the activated sludge process. Losses of pharmaceuticals in the activated sludge process occur due to adsorption to and removal in waste sludge and or biological or chemical degradation and biotransformation. Ternes (1998) suggested that activated sludge removes greater amounts of PhACs than other treatment (i.e. percolating filters), probably due to the bacterial activity in the activated sludge. The results of this study showed there was not complete elimination of trace organic compounds in the sewage effluent. Therefore implementing other technologies such as membrane systems would be necessary for complete removal of micropollutant compounds.



Although the total concentrations of target compounds in the influent samples through-out the yearly sampling fluctuated between 32.5 and 95.0 µg/L, the elimination process (i.e., activated sludge) in the treatment plant worked as efficiently during the summer months as during the winter months - average elimination ranged between 91 and 95% with ambient temperature range between 16 and 27°C). This conclusion contradicts other researchers who found that the elimination processes in treatment plants was higher in summer than in winter (Vieno et al., 2005). They suggested that the reason was the lower biodegradation in the plant because of low temperature in winter (~1 °C). The main elimination processes in the wastewater- as reported in the literature are sorption (i.e., ibuprofen (Tixier et al., 2003)), biodegradation (i.e., ibuprofen (Buser et al., 1999), and photodegradation (i.e., naproxen (Tixier et al., 2003; Vieno et al., 2005); ketoprofen and diclofenac (Buser et al., 1999; Tixier et al., 2003).

## 5.10 Summary

The combination of primary treatment with activated sludge treatment gave efficient removal of most of target metals (>70%) with the remaining concentration less than 0.05 mg/L for most metals (except for Fe and Mn). A positive relation was found between their concentrations and removal from the WWTP. The fate of metals in the sewage sludge should be considered when the sludge is disposed of on agriculture land or near water resources.

The wastewater treatment gave moderate to high removal efficiencies of trace organic compounds (PhACs & EDCS) (>70%). However, the effluent still had considerable concentrations of some of these compounds. These concentrations were in the range of 100-1000 ng/L, which indicate the need for further treatments to produce high quality water.

Most of the TOCs present in the influent were found in the effluent, with the exception of clofibric acid and pheytoin. The wastewater treatment plant was not able to completely remove all the TOCs, which may not be surprising considering the polar nature of the TOCs. However none of these compounds is currently regulated according to the guidelines.

In this chapter, an investigation was made to compare the level of pollutants between the influent and effluent of a wastewater treatment plant as well as the determination of removal percentage of these pollutants by the wastewater treatment processes. In the next chapter, the mass balance of reverse osmosis and the removal of micropollutants by advance technologies of water recycling processes of LPWRP will be described.

# *Chapter*

## *6 Role of Reverse Osmosis for the Removal of Trace Compounds in Recycled Water Treatment (LPWRP)*

---

### **6.1 INTRODUCTION**

For many water reuse applications, the removal of residual particulate matter by secondary treatment (e.g., activated sludge, trickling filter and membrane bioreactor) and even tertiary treatment (filter technologies such as depth, surface and membrane filtrations) meets the intended reuse water quality requirements. But with increased use of reclaimed water for applications where quality and reliability are critical, such as indirect potable reuse and some industrial uses, the increased removal of dissolved solids and trace constituents becomes essential.

The development of membrane technologies has provided practical means of achieving high removals of constituents such as dissolved solids, organic carbon, organic nitrogen and inorganic ions, while previous studies have demonstrated effective rejection of regulated organic compounds, nitrogen compounds and pathogens during membrane treatment. However little research has been conducted on the removal efficiency of trace organic compounds (TOCs) using reverse osmosis systems.

Membranes are classified either by the size of the largest particles (molecules) that can permeate a membrane or by the separation principle employed and the aggregation state of the fluids contacting the membrane (Table 6-1 and Figure 6-1 ). In this section, the focus is on the

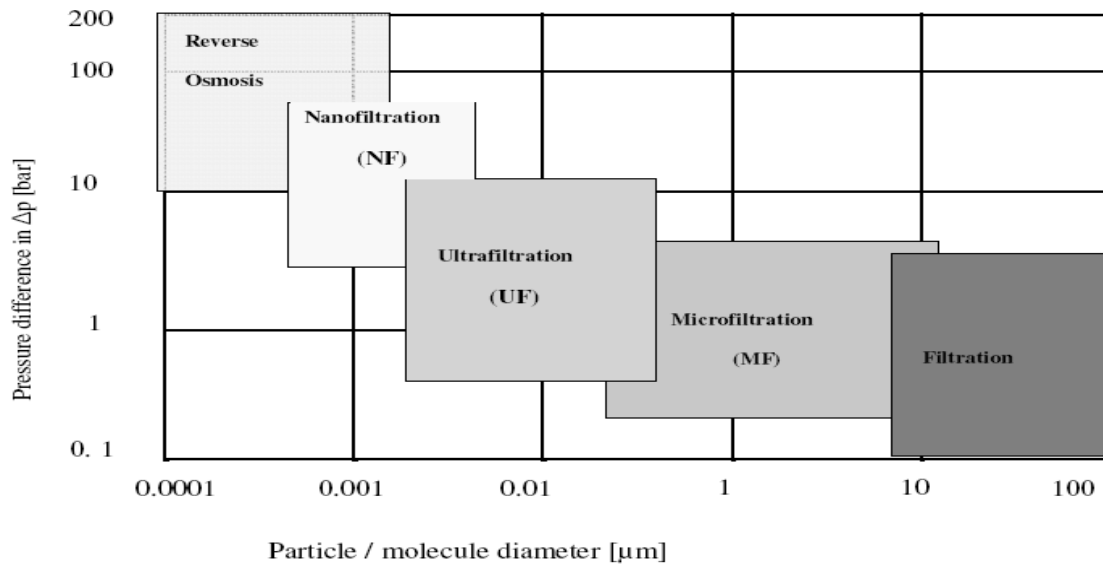
transmembrane pressure for the purpose of removing dissolved solids and trace constituents including microfiltration, ultrafiltration, nanofiltration and reverse osmosis.

Pressure driven membranes use trans-membrane pressure differences as driving forces (i.e., microfiltration, ultrafiltration, nanofiltration and reverse osmosis). Porous membranes with pore diameters over 0.1 $\mu$ m diameter are called microfiltration membranes (MF), and those with smaller pores are called ultrafiltration membranes (UF).

Table 6-1: General characteristics of membrane processes

Process	Driving Force	Separation mechanism	Aggregation
			State Liquid/ liquid
Microfiltration	Transmembrane pressure	Sieve	
Ultrafiltration	Transmembrane pressure	Sieve	
Nanofiltration	Transmembrane pressure	Sorption and diffusion	
Reverse Osmosis	Transmembrane pressure	Sorption and diffusion	
Dialysis	Concentration difference	Sorption and diffusion	
Diffusion Dialysis	Concentration difference		
Electrodialysis	Electromotive	Electrical potential difference	
Pervaporation	Partial pressure difference	Sorption and diffusion	Liquid / gas
Vapour permeation	Partial pressure difference	Sorption and diffusion	Gas/gas
Gas permeation	Partial pressure difference	Sorption and diffusion	

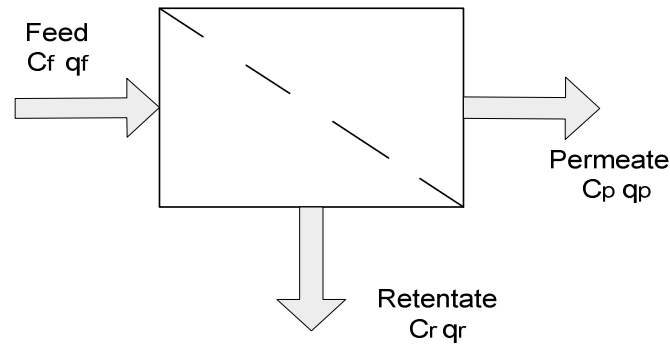
The dense membranes used in nanofiltration retain molecules over 300 Daltons and allow separation of mono- and divalent ions, due to electrostatic interactions between dissolved ions and the charged membrane matrix. Only the smallest molecules, primarily water molecules, can pass through reverse osmosis (RO) membranes. RO has become one of the standard technologies for the production of drinking water from seawater.



**Figure 6-1: Classification of pressure driven membrane processes (Schäfer and Wintgens, 2002).**

## 6.2 Membrane process

The principle of membrane separation relies on the membrane's ability to transport one component from the feed mixture to the receiving solution permeate more readily than any other component or components. In essence, the pores in the membrane are large enough to allow some molecules to pass through, but too small to permit the passage of others. A schematic representation of a membrane separation is given in (Figure 6-2) with feed water (f), permeate (p) and retentate (concentrate) (r).



**Figure 6-2: Sketch for operation of a membrane process**

### 6.2.1 Recovery Ratio

The recovery ratio ( $r$ ) is defined as the fraction of the feed flow, which passes through the membrane (Noble and Alexander Stern, 1995):

$$r = \frac{q_p}{q_f} \times 100 \quad (6-1)$$

where  $q_p$  and  $q_f$ , (L/h), ( $m^3/h$ ), or ( $m^3/s$ ), are the permeate and feed flow rates, respectively, The typical recovery is in the range of 60 to 90 percent, depending on feed water quality.

### 6.2.2 Rejection Efficiency

The retention efficiency expresses the extent to which the solute is retained by the membrane is also important. The percentage of retention ( $R$ ) is defined as (Noble and Alexander Stern, 1995):

$$R = 1 - \left[ \frac{C_p}{C_f} \right] \times 100 \quad (6-1)$$

where  $C_f$  and  $C_p$  are the solute concentration in the feed and in the permeate, respectively. The rejection efficiency can range from 85 to 99.5 percent for specific membranes and species.

### 6.2.3 Mass Balance

The concept of mass balance is that the total mass of the materials entering a system must equal the total leaving it. Typically, the mass flowrate in the concentrate (brine) can be represented by subtracting the mass flowrate of permeate from the total mass flowrate of the feed, as given in Equation 6-3.

$$C_c Q_c = C_f Q_f - C_p Q_p \quad (6-2)$$

### 6.2.4 Concentration Factors

The concentration factor is a measure of the concentration of solute that is retained (in brine) or does not pass through the membrane (in brine) to the concentration of solute in the feed. It can be represented as shown in Equation (6-4).

$$Cf = \left( \frac{C_r}{C_f} \right) \quad (6-3)$$

where  $C_p$  and  $C_r$  ( $\text{g/m}^3$ ,  $\text{mg/L}$ ) are the solute concentration in the feed and in the brine, respectively.

## 6.3 Membrane applications

Membrane technology has been established in many areas such as drinking water, industrial water, municipal wastewater treatment and water recycling. Microfiltration membranes with a pore size below  $0.2 \mu\text{m}$  can be considered as a barrier for bacteria. Viruses can also be retained by microfiltration membranes to a certain degree. This is due to the filtration effect of the cake layer forming to the membrane surface during filtration and due to the fact that viruses tend to adsorb on large particles. Nevertheless, other membrane processes (i.e., ultrafiltration, nanofiltration and RO) offer a sufficient rejection of viruses (Otaki et al., 1998). From an engineering point of view, ultrafiltration and microfiltration are basically alike. Therefore, the most important factor for ultrafiltration and microfiltration membranes is a complete rejection of solids. The core of every municipal wastewater treatment is the biological stage, where micro-organisms metabolise the biodegradable wastewater constituents and fulfill the main wastewater treatment objectives.

## 6.4 Removal of trace contaminants

Trace contaminants are a key factor in water recycling. In wastewater treatment, trace pollutants are of concern as they are removed partially in conventional treatment processes and thus subsequently are discharged into receiving waters. Persistent compounds may accumulate in the environment. Therefore, the removal of trace pollutants is a pressing issue for the Water Industry and may be achieved by introducing RO or NF membranes into a water recycling plant.

Advanced water treatment systems combine a microporous membrane process such as ultrafiltration (UF) and microfiltration (MF), followed by reverse osmosis. This combination has become the industry standard practice for the reclamation of municipal wastewater for industrial and indirect portable reuse applications.

Many attempts have been made to estimate the performance of membrane separation in order to predict the mass balance through membranes (Williams et al., 1999; Bowen et al., 2002). Most of these models are based on one or more compounds in base water and require sophisticated solution techniques. However, prediction of removal efficiencies for organic constituents is much more challenging than calculations for inorganic compounds since the physico-chemical properties of the compounds and interactions with membrane properties significantly affect the compound's mass transfer (Williams et al., 1999; Van der Bruggen and Vandecasteele, 2002). Bellona et al., (2004) have conducted a comprehensive survey in order to identify factors affecting the rejection of organic compounds in NF or RO membranes. A complete understanding of the solute and membrane characteristics that influence rejection could lay the foundation for modelling the fate of specific compounds during a high-pressure membrane application (Bellona et al., 2004).

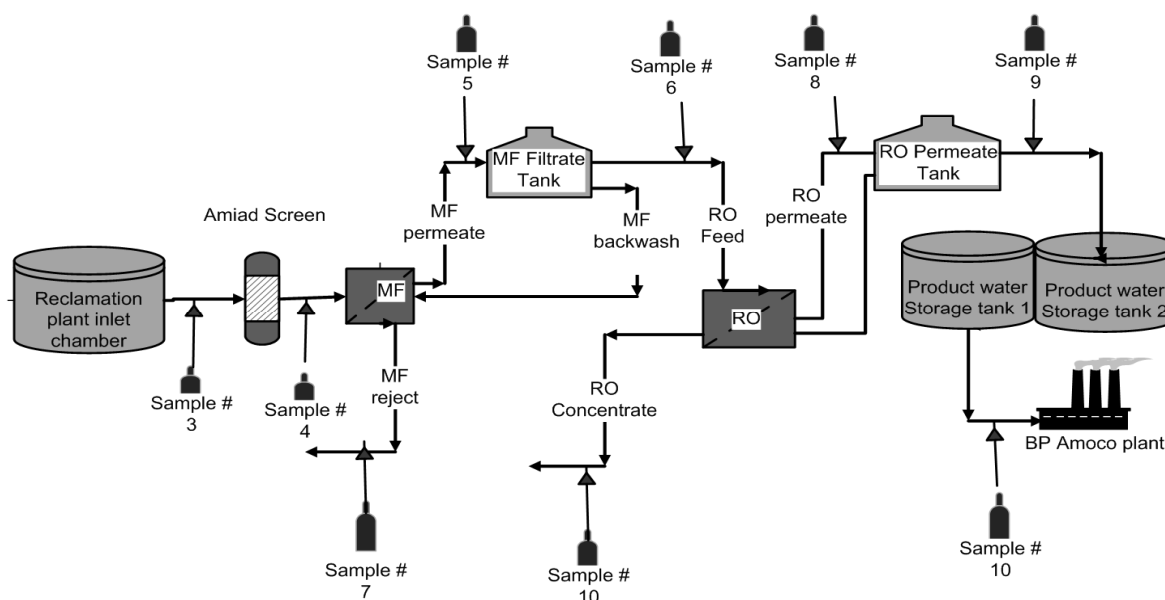
Recent research investigating the viability of NF/RO membranes has reported the incomplete rejection of organic micropollutants such as endocrine disrupting chemicals, pharmaceutically active compounds and others (Kimura et al., 2003b; Schäfer et al., 2003; Kimura et al., 2004; Nghiem et al., 2004). Most of these studies examined the rejection of micropollutants from a bench-scale flat sheet membrane unit or by using a dead end filtration module and high feed water solute concentrations. In addition, these experiments utilized deionized water spiked with one or more target solutes and a virgin membrane neglecting solution matrix effects and fouling commonly observed in full scale applications.

This chapter attempts to reveal the fate of both organic and inorganic trace contaminants in dual membrane processes through the water recycling plant at Luggage Point Water Reclamation Plant (LPWRP). For this purpose, this water recycling plant operating with the MF and RO was selected. The mass balances of the bulk organic constituents, anions and cations and trace organic compounds (TOCs) through the RO membrane were evaluated. The partition between RO permeates and brine in the RO was investigated. Mass rejections were also assessed in relation to physicochemical properties of the compounds.

To evaluate the performance of LPWRP, several physicochemical parameters were measured in the three RO streams including pH, chemical oxidation demand (COD), nitrogen, phosphorus, various anions and cations, and heavy metals.

## 6.5 The Luggage Point Water Reclamation Plant (LPWRP)

The feed water for the recycled scheme is taken from the secondary effluent of the wastewater treatment plant; which consists of screens and grit removal as a primary treatment and diffused air activated sludge as a secondary treatment. Furthermore, the recycling scheme consists of automatic backwashing of 300  $\mu\text{m}$  screens, MF and RO systems (Figure 6-3)



**Figure 6-3: A Schematic diagram for the Water Recycling processes at LPWRP**

\* Sample numbers referred to Figure 4-3 for more details. (3) Effluent feed for Amiad screen (Post to ammonia & chlorine addition); (4) MF Feed; (5) MF permeate; (6) MF permeate/ RO feed (post to chemical condition); (7) MF Backwash; (8) RO Permeate; (9) RO permeate (Post to Chemical Conditioning (Caustic & Chlorine)); (10) RO Concentrate; (11) Product water



### **6.5.1 Microfiltration**

The microfiltration system at LPWRP accepts screened water from the effluent channel as a feed, filters the water to produce the permeate and sends the MF permeate to the next stage of treatment, the reverse osmosis as shown in Figure 6-3. The MF itself is protected from gross solids by the 300 µm screens (called Amiad screens). Six microfiltration racks are fitted with 66 filter modules installed in each rack. The micro filtration uses 0.1 micron membranes, with a typical recovery of 97%. It is operated in cross-flow mode with 5-10% recirculation flow to maximise membrane usage and flux. Backwashing is carried out at 20-minute intervals. Compressed air bubbling precedes every backwashing cycle, shaking off accumulated materials. A clean in place (CIP) process is carried out with a caustic solution (NaOH) / NaOCl and citric solutions on a monthly basis (Leslie et al., 2002). More details of the MF membrane technical data, chemical dosing and cleaning protocol are described in Appendices 8-5 to 8-7.

The primary role of the MF system is to perform a pre-treatment stage for the RO system and to protect the RO from accumulation of particulates on the membrane surface or in clogging its pores (known as fouling), resulting in pressure build up on the feed side and decreases in membrane flux and the percent of rejection.

### **6.5.2 Reverse Osmosis**

Reverse osmosis (RO) is the next stage taken up after microfiltration. The RO system consists of six RO blocks (see Appendix 8-8). Each RO block has thirty-one pressure vessels. Each pressure vessel houses six RO membrane elements. The elements are formed from a large flat sheet membrane rolled into a cylinder approximately 203 mm (8 inches) diameter by 1016 mm (40 inches) long. This type of element is known as Spiral Wound. The RO system is operated in a 5 duty (5 RO block in operation) single stand-by configuration. The RO treatment is a 3-stage process per block with an array of 18, 8 and 5 pressure vessels in first, second and third stage, respectively. The membranes are periodically cleaned by flushing water across the membrane and by a chemical clean-in-place (CIP) process which involves the flushing of a hydrochloric acid (HCl) and caustic solution through the RO pressure vessels (Brisbane Water, 2002). More details are given in Appendix 8-7.

The overall recovery from the reverse osmosis system is 85%. The RO membranes are progressively fouled and therefore a CIP procedure is carried out approximately every 6 months

initiated by the operators. In order to prevent bio-fouling, chlorine is added to the microfiltration filtrate in order to maintain it at about 1-3 mg/L. The reverse osmosis membranes do not have a high tolerance level to free chlorine. Hence, ammonia is added to the microfiltration filtrate to convert free chlorine to chloramine with a level of 2 mg/L. Finally, a post chlorination of the RO permeate is performed to maintain a chlorine residual to meet the product water specification. Furthermore, additional chemical treatment is used to adjust water pH and chlorination (see Appendix 8-7).

The RO membrane used in the plant is BW30 365 FR manufactured by DOW/ Filmtec in a flat sheet configuration (see Appendix 8-8). The BW30 365 (FR fouling resistant RO) is a polyamide thin film with 99.995% solute rejection. Specifications, configuration and operating conditions during the normal plant operation are presented in Appendix 8-8.

### **6.5.3 Sample Campaigns**

Samples were taken from various inlets/outlets of the recycling water processes of LPWRP as shown in (Figure 6-3). The samples were collected in glass bottles and placed on ice and transferred overnight to the laboratory for determination of trace organic compounds. The sampling was carried out during the following months: May, September, November and December 2005, as well as February, April and June 2006. For more details on sampling procedure see section 3.3.

Furthermore, to understand the performance of the RO system in more detail, samples collected from LPWRP were characterized chemically by measuring pH, conductivity, absorbance at 245 nm, turbidity, total organic carbon (TOC), total nitrogen (TN), heavy metals, as well as various anions and cations.

For determination of trace organic contaminants- 11 pharmaceutically active compounds (PhACs) and two endocrine disrupting compounds (EDCs), aqueous samples were filtered through three different filters, GF/D (2.7µm), GF/F (0.7µm) Whatman filters, and 0.48 µm Nylon filter membranes and subsequently enriched by solid-phase extraction on polymeric cartridges (Oasis HLB, Waters). Prior to analysis, the analytes were derivatized by a mixture of N,O-bis (trimethylsilyl) trifluoroacetamide (BSTFA) and trimethylchlorosilane (TMCS) (99:1). Separation and identification were performed by GC/MS in Single Ion Mode (SIM).

The efficiency of extracting (recovery) and minimum quantification limits for the analysed compounds were in the range of 70 - 92% and 1-50 ng/L, respectively (Tables 3.2 and 3.3). Complete details of experimental method for determination of these trace contaminants has been reported in Section 3.

## 6.6 Microfiltration process

### 6.6.1 Physicochemical Characteristics

The physicochemical characteristics of the feed and permeate for the MF process (sample numbers 1-4, Figure 6-3) are presented in Table 6-2. The maximum removal efficiencies of the microfiltration process were 77%, 61% and 30% for the turbidity, total organic carbon and total nitrogen measurements, while there were no significant changes in the conductivity measurements. Thus, the MF process provides an essential pre-treatment for the RO by removing particulate and colloidal material from the feed but the removal is limited to particles larger than the membrane pore size (Van der Bruggen et al., 2003a).

**Table 6-2: Characteristics of MF feed, permeate and backwash of MF process**

Characteristics	Amiad feed		MF Feed		MF permeate		MF backwash	
Sample no.	3		4		5		7	
	Min.	Max.	Min.	Max.	Min.	Max.	Min.	Max.
Turbidity (NTU)	3.1	34.6	1.4	31.4	0.3	7.9	7.7	337.0
Conductivity $\mu\text{S}/\text{cm}$	1.6	3.0	1.6	3.0	1.5	3.0	1.0	3.1
pH	7.6	7.8	7.3	7.6	7.4	7.7	6.9	7.5
Total organic carbon (mg/L)	6.5	154.7	6.6	211.8	5.7	82.7	7.3	176.0
Total nitrogen (mg/L)	3.5	5.7	4.6	5.7	3.3	4.7	3.4	25.6
Absorbance 245nm ( $1/\text{cm}^3$ )	0	2.8	0	0.3	0	0.2	0.2	2.4

### 6.6.2 Removal of Trace Organic Compounds

The concentration of TOCs was measured at Amiad screen feed, MF feed, MF permeate and MF backwash (Table 6-3). These concentrations ranged between 200 and 1950 ng/L in the Amiad feed and there was no significant difference between Amiad feed, MF feed and the MF permeate.

**Table 6-3: Concentration of trace organic compounds (ng/L) in the MF process**

Compounds		Secondary effluent (2)	Amald screen feed (3)	MF feed (4)	MF permeate (5)	MF backwash (7)
		Range	Range	Range	Range	Range
bisphenol A	BPA	192 - 1950	100 - 1650	102 - 1750	140 - 1790	ND - 450
nonylphenol	NP	ND- 150	ND - 130	ND - 119	ND - 120	ND - 97
clofibric acid	CLB	ND	ND	ND	ND	ND
gemfibrozil	GFZ	160 - 968	165 - 899	154 - 876	140 - 855	ND - 550
diclofenac	DCF	ND- 260	ND - 220	ND - 156	ND - 123	ND - 97
ibuprofen	IBU	ND -679	170 - 850	ND - 723	163 - 680	ND - 150
ketoprofen	KPF	ND -220	ND - 199	ND - 180	ND - 180	ND - 500
naproxen	NPX	110- 523	110 - 263	100 - 324	60 - 295	ND - 290
acetaminophen	ACM	117- 230	111 - 250	120 -250	100 - 158	19 - 617
primidone	PMD	ND-520	ND - 420	ND - 590	ND - 360	ND - 250
salicylic acid	SCA	200-660	134 - 307	150 - 620	120 - 283	ND - 500
carbamazepine	CMZ	ND- 614	ND - 568	ND - 585	ND - 555	ND -536
phenytoin	PHT	ND	ND	ND	ND	ND - 90

The Amiad filter and the MF membrane with pore size 300  $\mu\text{m}$  and 0.1  $\mu\text{m}$ , respectively, did not show any significant removal of trace organic contaminants through the filtration processes (see Table 6-3). For example, the concentrations of gemfibrozil were between 165 and 899 ng/L for the Amiad filter feed and 140 and 855 ng/L for the MF permeate, which indicates that both Amiad filters and MF membrane system did not reject the any of the TOCs.

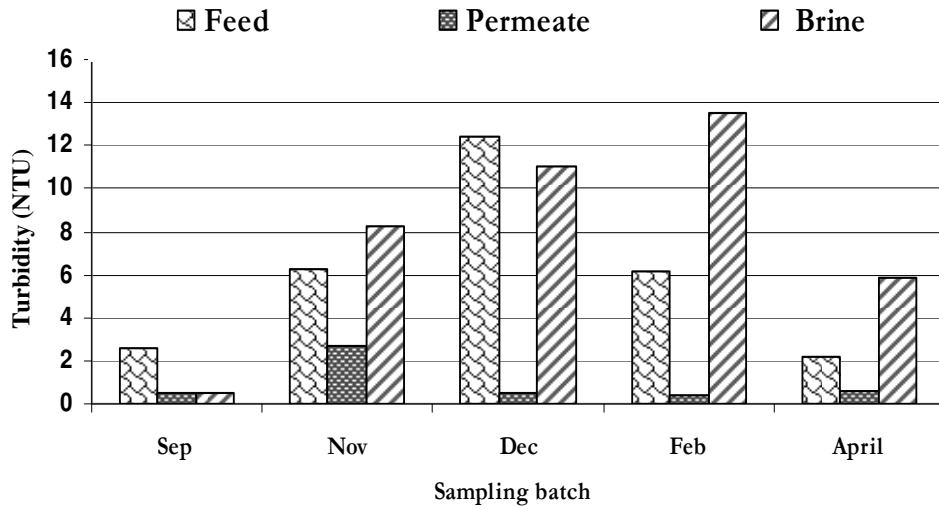
## **6.7 RO filtration process**

### **6.7.1 Physicochemical Characteristics**

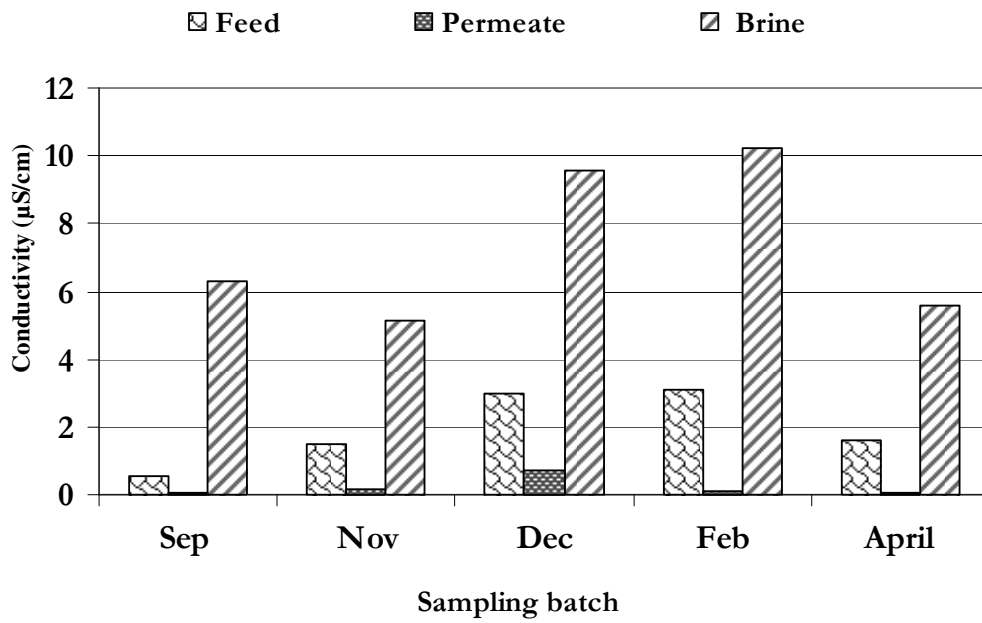
Measured values of conventional parameters for the RO feed (sample # 6), permeate (sample # 8) and brine (sample # 10), for the sampling batch of September, November, December 2005, February and April 2006 are presented in Figures 6-4 to 6-9. Corresponding average values of conventional parameters in the RO feed were turbidity 5.9 (2.2-12.4) NTU, conductivity 1.9 (0.6-3.1)  $\mu\text{S}/\text{cm}$ , pH 7.4 (7.3-7.5) unit, TOC 14.7 (5.6-36.3) mg/L and TN 4.0 (3.2-4.8) mg/L (see Figures 6-4 to 6-9).

The removal efficiency of the conventional parameters was determined by the calculation of the rejection efficiency using Equation 6-2. On average, the rejection efficiency of the RO was 80%, 90%, 87%, 91% and 82% for turbidity, conductivity, UV absorbance, NPOC and TN, respectively (Figures 6-4 to 6-9). In general, these results showed the superior efficiency in reducing values of all conventional parameters to less than 1 mg/L for TN and TOC, less than 1  $\mu\text{S}/\text{cm}$  and 1 NTU for conductivity and turbidity, respectively.

According to Matilainen et al. (2007), there is no single parameter that can give a complete picture about the water quality. For example, UV adsorption – as a detection method- does not detect small aliphatic compounds due to a lack of conjugated double bonds, and thus are not quantitated by a UV 245 nm measurement.



**Figure 6-4: Concentrations of turbidity (NTU) in RO feed, permeate and brine**



**Figure 6-5: Concentrations of conductivity (µS/cm) in feed, permeate and brine**

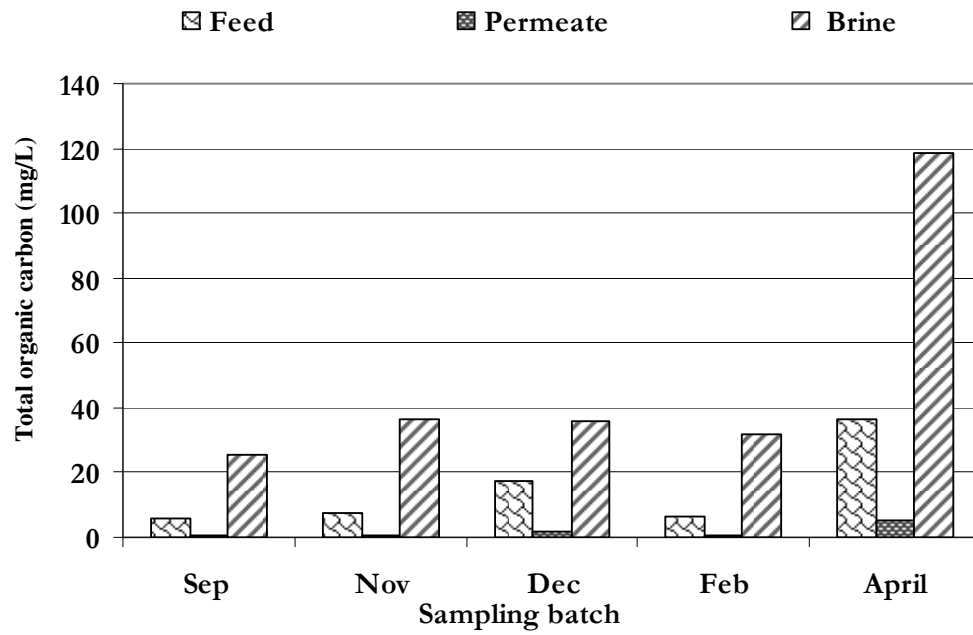


Figure 6-6: Concentrations of total organic carbon (mg/L) in feed, permeate and brine.

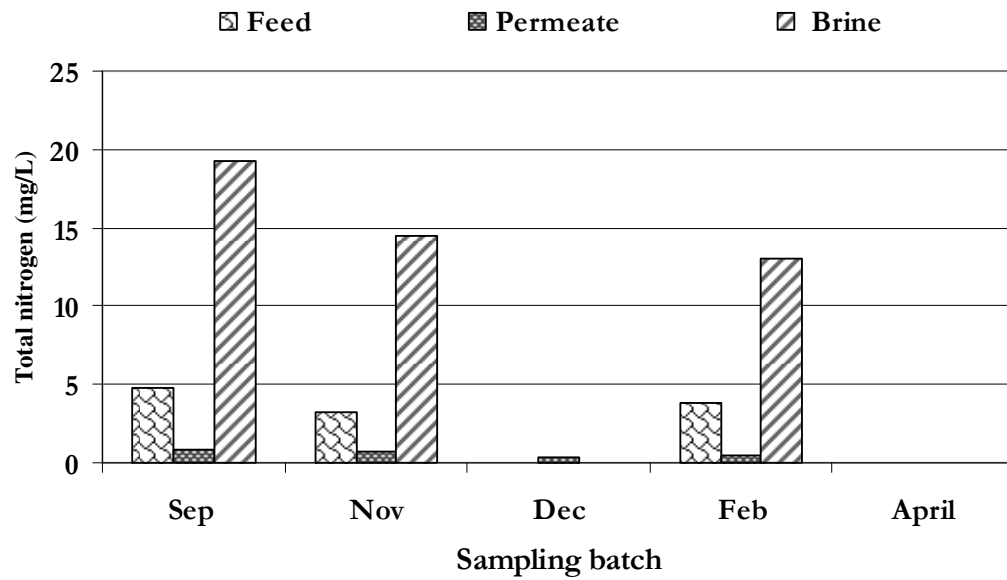


Figure 6-7: Concentrations of total nitrogen (mg/L) in RO feed, permeate and brine.

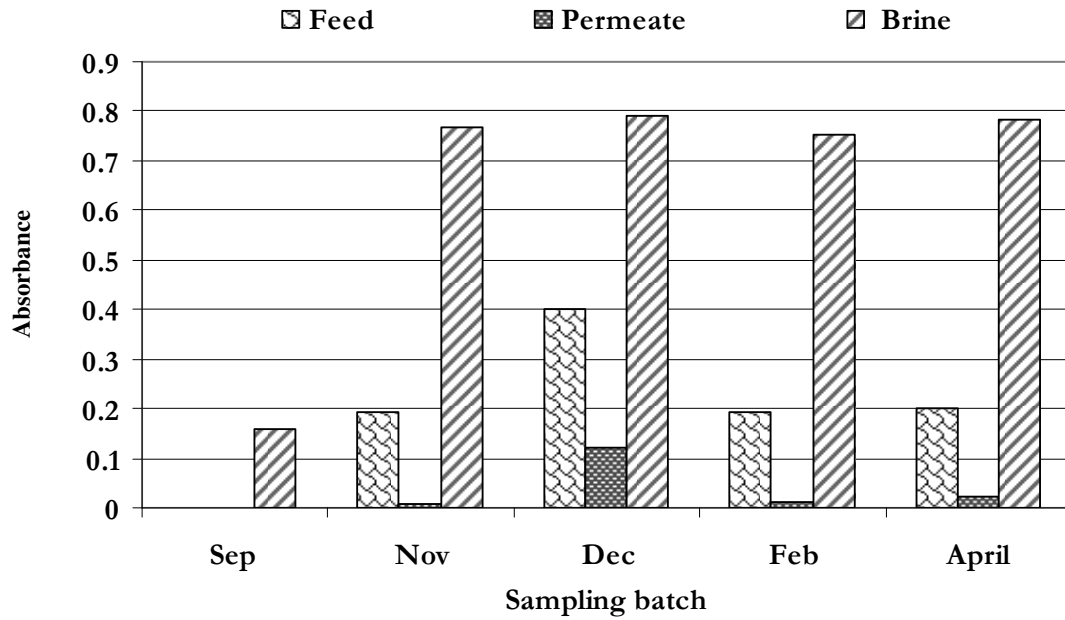


Figure 6-8: Measurement of absorbance (245 nm) in feed, permeate and brine

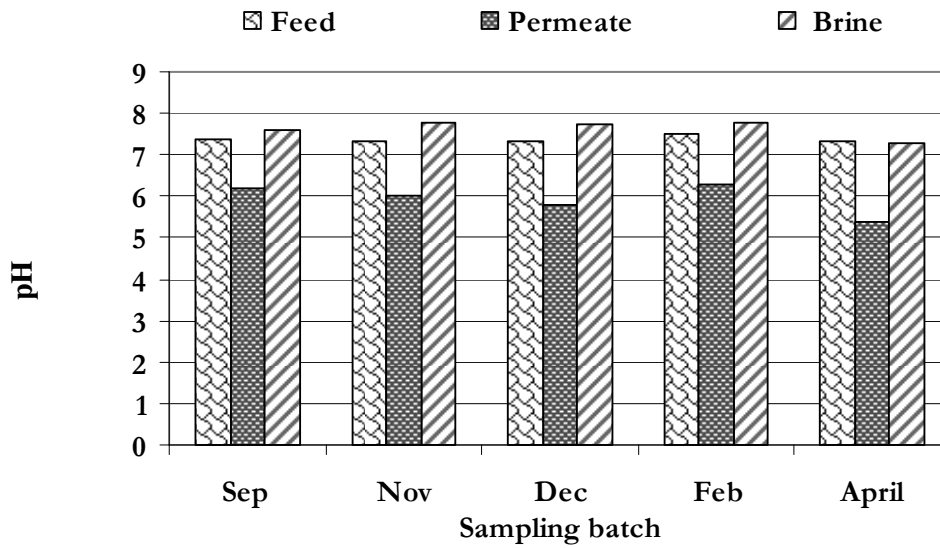


Figure 6-9: Measurement of pH (unit) for RO feed, permeate and brine



Previous studies have investigated the efficiency of RO compared to other types of membranes such as (NF), and low pressure reverse osmosis (LPRO). These investigations indicated the great advantage of using RO in producing a high quality of recycled water. In general, the rejection results of the RO membrane represent greatly reduced pollutants in the permeate. Lopez-Ramirez et al, (2006) found that the drinking water standards were widely exceeded by the reclaimed wastewater for the RO membrane with multi barriers approach. Furthermore, indicator micro-organisms were absent from the RO permeate, which would allow safe reuse of water, such as irrigation of raw vegetables.

In this study, there was no clear relationship between the content of organic carbon and nitrogen in influencing the distribution of TOCs in the RO streams. This might be due to the complexity of RO feed in treatment plants and the difference between field experiments compared to bench scale experiments where synthetic water was used by other researchers. Katsoyiannis (2005) found that organic pollutants favoured advective transport in the dissolved phase of the treated effluent.

### **6.7.2 Inorganic Constituent Removal**

Not surprisingly, the RO membrane rejected most of the cations and anions on an average of 97% and 78%, respectively (Table 6-4). The rejection of various cations either monovalent or multivalent (i.e.  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$ ,  $\text{K}^+$  and  $\text{Si}^{2+}$ ) was steady with the highest value of 98% for calcium and magnesium. Furthermore, the rejection of anions was similar to cations except for boron and fluoride. The rejection of boron was very poor (29%) leaving a maximum concentration of 0.16 ppm in the permeate and 0.40 ppm in the brine. Conversely, in spite of, moderate rejection of fluoride by the RO membrane (66%), fluoride was not detected in the permeate (Table 6-4).

### **6.7.3 Trace Organic Compounds**

In wastewater treatment plants, TOCs may be completely or partially degraded, which takes place mostly in the activated biological sludge process. These PhACs and EDCs vary in their degradation in various wastewater treatment processes. The remaining TOCs are passed into the more advanced technologies such as membrane systems.

**Table 6-4: Metals composition of the RO, brine and permeate**

Composition	Average concentrations <sup>(1)</sup>			Conc. Factor (CF)	Ave. Rejection	STD
	Feed	Permeate	Brine			
<u>CATIONS</u>						
calcium (mg/L)	35.0	ND <sup>(2)</sup>	148.0	4.3	> 0.98	0.01
magnesium (mg/L)	35.6	ND	156.0	4.5	>0.98	0.02
sodium (mg/L)	314.0	12.7	1320.0	4.3	0.96	0.01
potassium (mg/L)	23.0	1.1	103.8	4.7	0.95	0.01
silica (mg/L)	8.8	0.3	34.0	3.9	0.97	0.01
Σ of Cations (me/L)	416.4	13.6	1761.8	21.6	0.97	0.01
<u>ANIONS</u>						
bicarbonate (mg/L)	162.0	10.8	646.0	4.0	0.93	0.02
barium (mg/L)	0.05	ND	0.05	2.4	>0.78	0.16
boron as B (mg/L)	0.23	0.16	0.40	1.8	0.29	0.08
chloride (mg/L)	518.0	16.5	1674.0	3.5	0.97	0.01
sulphate (mg/L)	130.8	ND	466.0	3.6	>0.99	0.00
fluoride (mg/L)	0.21	0.07	0.79	3.8	0.66	0.26
Σ of Anions	811.3	27.5	2787.2	17.2	0.97	0.01
<u>HEAVY METALS</u>						
iron (mg/L)	0.08	0.01	0.28	3.6	0.90	0.04
manganese (mg/L)	0.11	ND	0.5	4.2	>0.98	3.43

(1) Average based on detected concentrations in 5 samples through the season (2) :ND: not detected, so that the rejection was calculated based on the detection limit as a value

The mass balance analysis of TOCs in the RO membrane was conducted at the three water streams: feed, permeate and brine. Most of these compounds were found at detectable concentrations in the three streams. The separation behaviour of organic chemicals is important to their fate in the RO system.

#### 6.7.3.1 Acidic pharmaceuticals

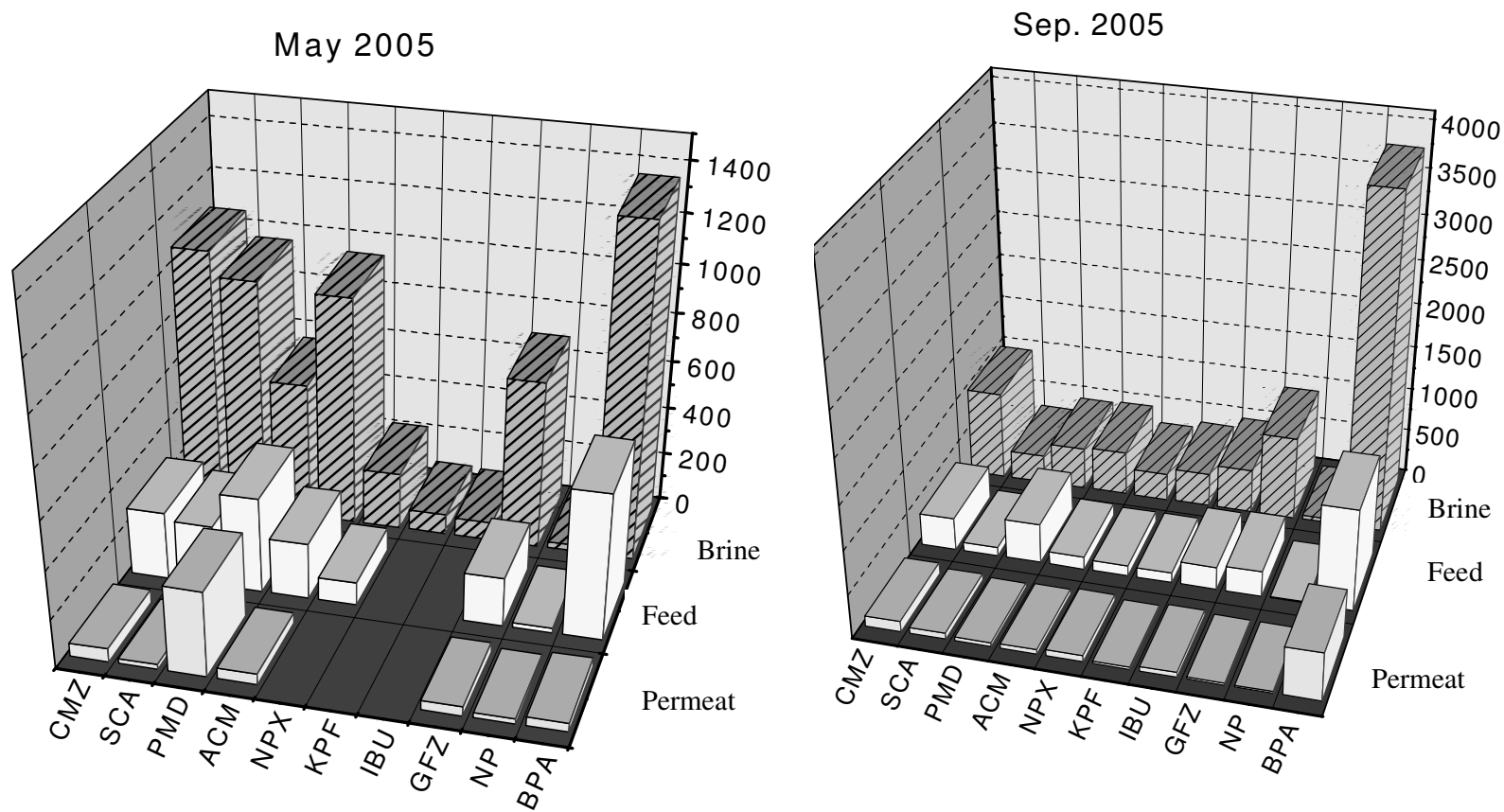
Various acidic pharmaceutical compounds were found in the feed that was derived from the WWTP (see Section 4.4.2). These variations were originally a result of annual fluctuations of compounds in raw wastewater in addition to other processes involved in wastewater treatment. Acetylsalicylic acid (ASA) is one of the most popular pain killers mainly sold as an over-the-counter drug. According to Heberer (2002a), ASA is easily degraded by decetylation into the

more active form salicylic acid plus two other metabolites. Residues of salicylic acid do not necessarily have to be derived from ASA. Other sources such as the use of salicylic acid as a keratolytic, dermatice or preservative of food or its natural formation are even more likely to be responsible for the occurrence of this compound in the aquatic environment (Heberer, 2002b).

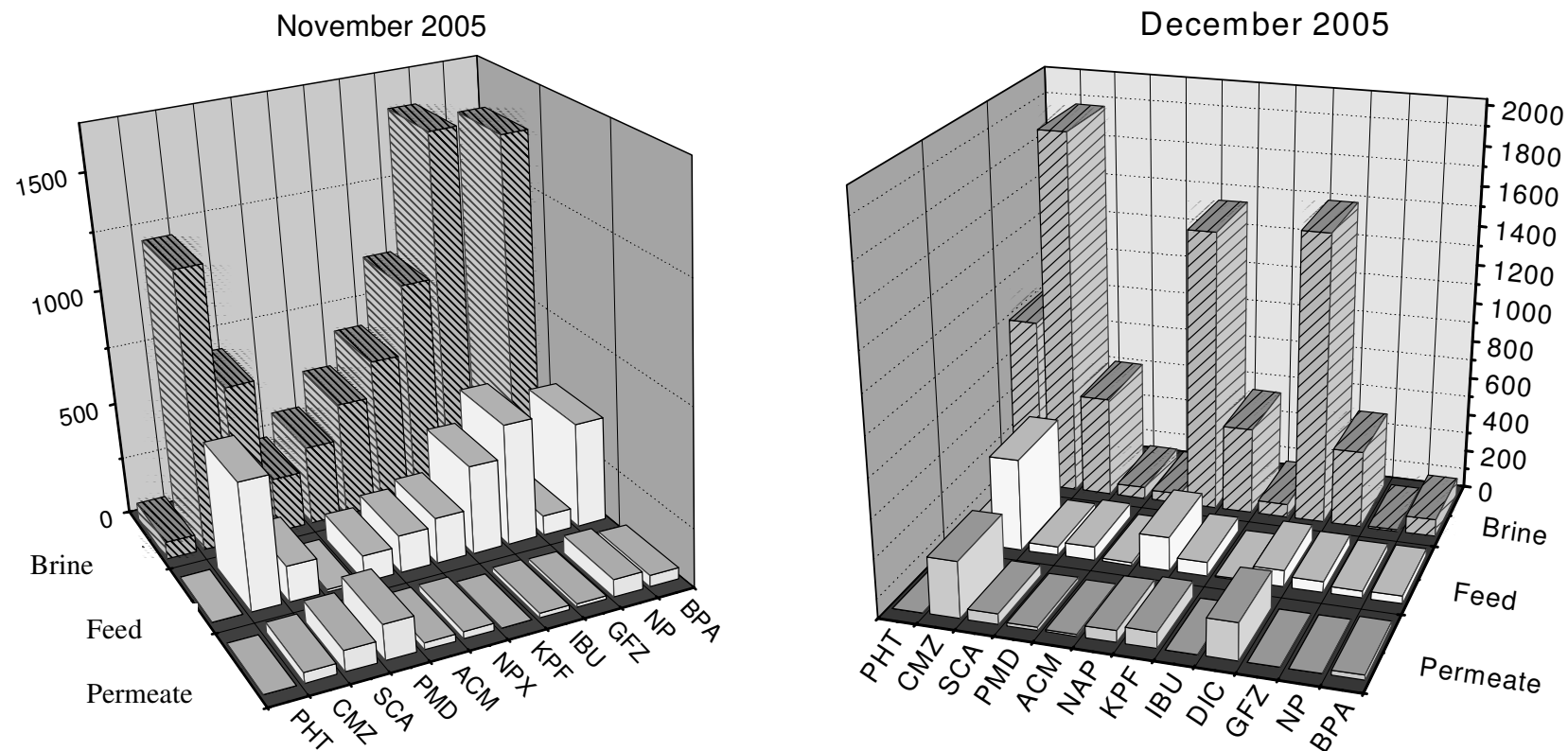
Clofibric acid and diclofenac were less frequently detected in the raw wastewater and in the feed as explained in Section 5. Therefore, the performance of RO against these compounds could not be evaluated in the current experiment. Heberer (2002b) has reported that diclofenac could efficiently be removed from surface water or municipal sewage effluents using membrane filtration. Other acidic compounds were detected in all feed samples as shown in Figures 6-10 to 6-13. These concentrations were up to 841 ng/l for gemfibrozil in feed, 190 ng/L for diclofenac in permeate and 2390 ng/L for gemfibrozil in brine.

**Table 6-5: General characteristics of trace organic compounds (Barcelo, 2007)**

*\* (Nghiem and Schäfer, 2006)*



**Figure 6-10: Concentration of trace organic compounds (ng/L) in RO feeds, permeate and brine for May and Sep 2005**



**Figure 6-11: Concentration of trace organic compounds (ng/L) in RO feeds, permeate and brine for Nov. and Dec. 2005**

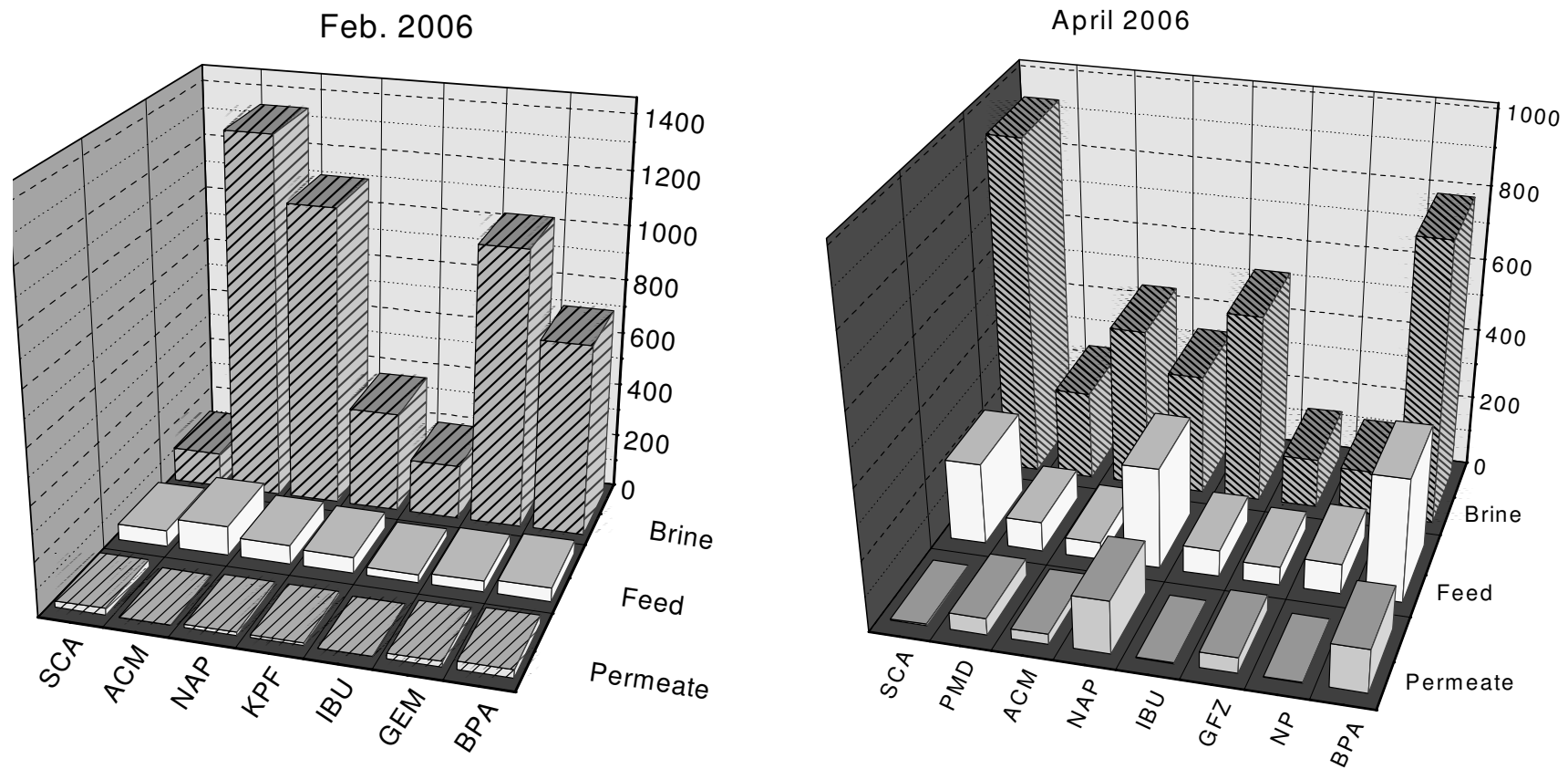
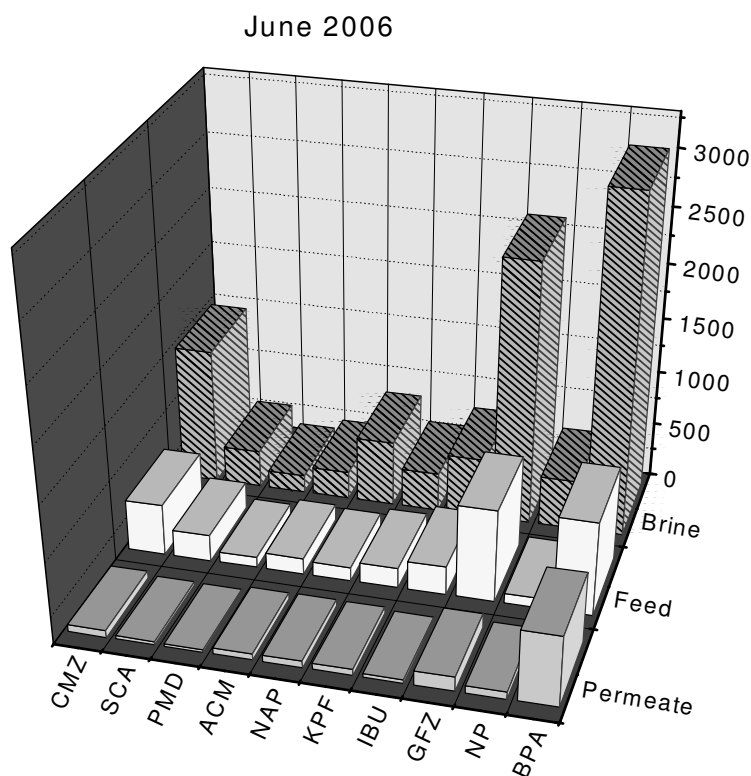


Figure 6-12: Concentration of trace organic compounds (ng/L) in RO feeds, permeate and brine for Feb. and April 2006



**Figure 6-13: Concentration of trace organic compounds (ng/L) in RO feeds, permeate and brine for June 2006**

The rejection efficiencies for acidic pharmaceuticals ranged between 30% and 100% (Figure 6-14). Notably, the mean rejection increased from 68% to 93% with increasing  $\log K_{OW}$  from 1.2 to 4.8 for salicylic acid, naproxen, ketoprofen, ibuprofen and gemfibrozil. It has been reported that the rejection of solute by NF/RO membranes is affected by a wide range of parameters such as feed pH, solute charge expressed through  $pK_a$ , molecular weight and geometry, polarity and hydrophobicity, as well as the membrane surface charge (Van der Bruggen et al., 1998; Van der Bruggen et al., 1999; Kiso et al., 2000; Kiso et al., 2001; Ozaki and Li, 2002; Kimura et al., 2003b; Kimura et al., 2004).

The  $\log K_{OW}$  value of the acidic pharmaceuticals were between 0.7 – 4.77 (Table 6-5). The plot of  $\log K_{OW}$  versus rejection efficiency shows a positive correlation between the  $\log K_{OW}$  and rejection efficiencies of acidic PhACS (Figure 6-15). The  $\log pK_a$  values ranged between 3.5-4.9 (see Table 6-5). The plot of  $pK_a$  versus rejection efficiencies also showed a positive correlation between the acidic PhACs and the rejection of the RO (Figure 6-16). Surprisingly, these results

were not in accord with the findings of Jjemba (2006) who could not correlate the solubility, log  $K_{OW}$  and  $pK_a$  with predicting the behaviour of PhACs concentrations in the environment.

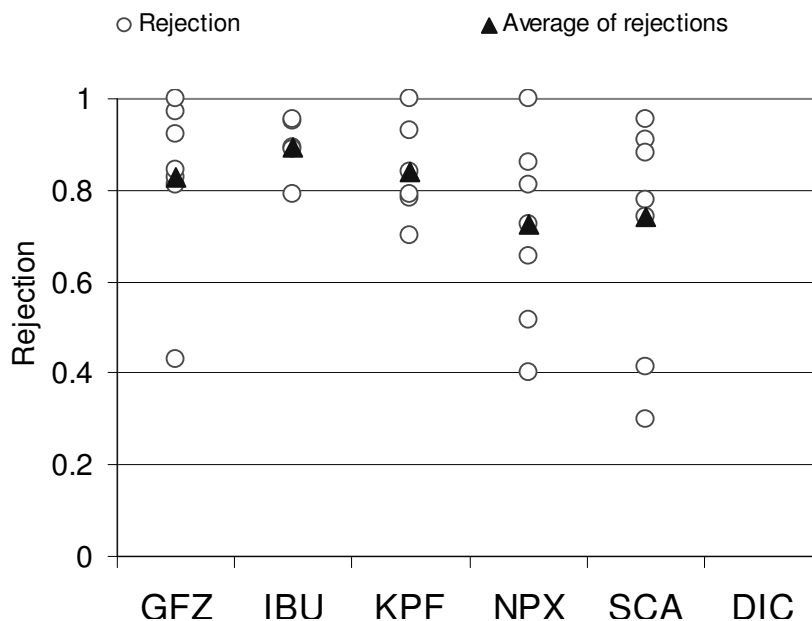


Figure 6-14: Rejection percentage of acidic pharmaceuticals

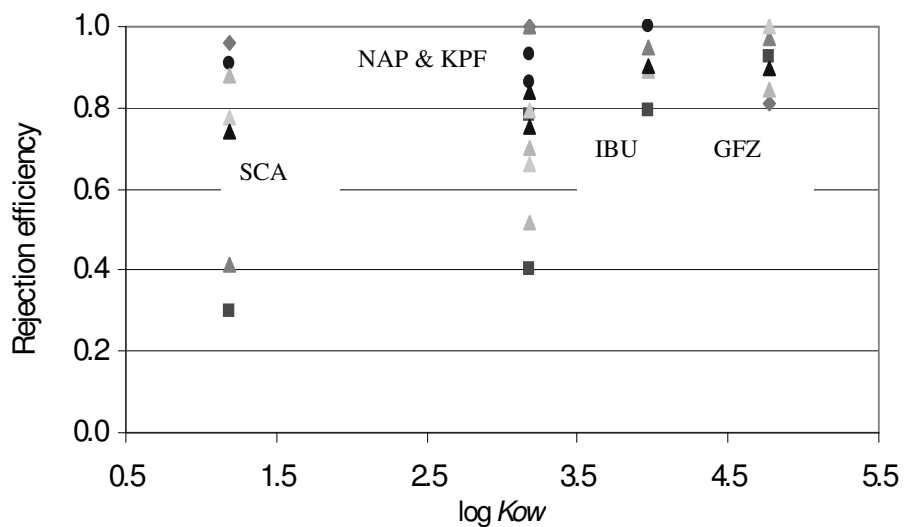
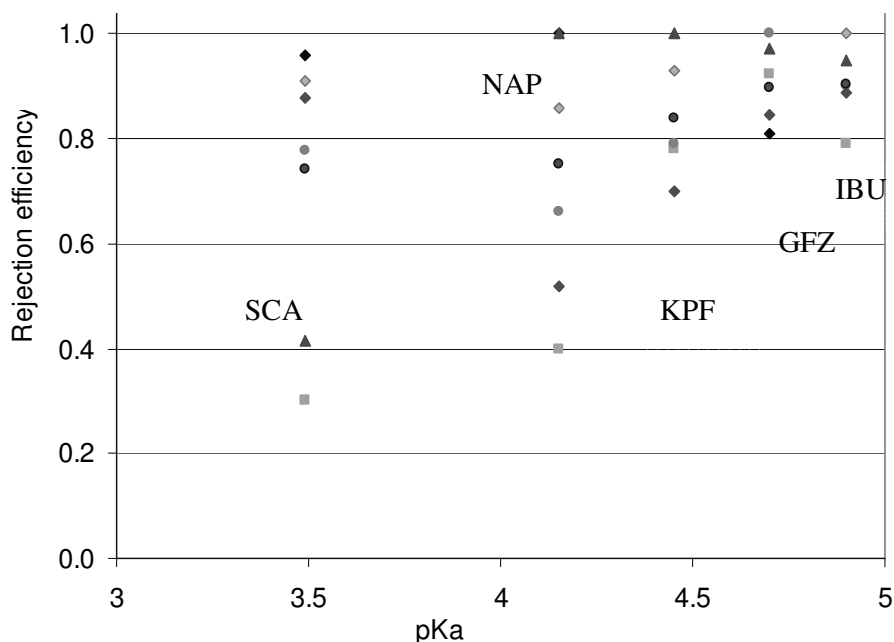


Figure 6-15: Plot of the octanol/water coefficient (log  $K_{OW}$ ) of the acidic pharmaceuticals against rejection efficiency





**Figure 6-16: Plot of the water dissociation coefficient (pKa) of the acidic pharmaceuticals against rejection efficiency.**

### 6.7.3.2 Neutral pharmaceuticals

The neutral pharmaceuticals, namely acetaminophen, carbamazepine, and primidone were found in all RO feeds, while phenytoin was found once. The average concentrations of these compounds found in the RO feed, permeate and brine were up to 550, 350 and 1380ng/L, respectively (see Figures 6-10 to 6-13). In general, rejection efficiencies of these compounds were from 63% to 100% with an average of 82% (Figure 6-17).

The solubility of compounds in this group varies, some are moderately soluble (11-100 mg/L, i.e, phenytoin and carbamazepine) and some are highly soluble ( $\geq 100$ mg/L, i.e, primidone and acetaminophen) (see Table 6-5). Log  $K_{OW}$  values of this group ranged between 0.46 and (see Table 6-5). The plot of log  $K_{OW}$  versus rejection efficiency showed a weak positive (Figure 6-18) as well as the pKa and the rejection efficiencies (Figure 6-19). However, the solubility, log  $K_{OW}$  and pKa did not correlate with the behaviour of these PhACS in the RO. Recent studies by Tolls (2001) indicated log  $K_{OW}$  may not be good indicator of the behaviour of pharmaceuticals in the environment.

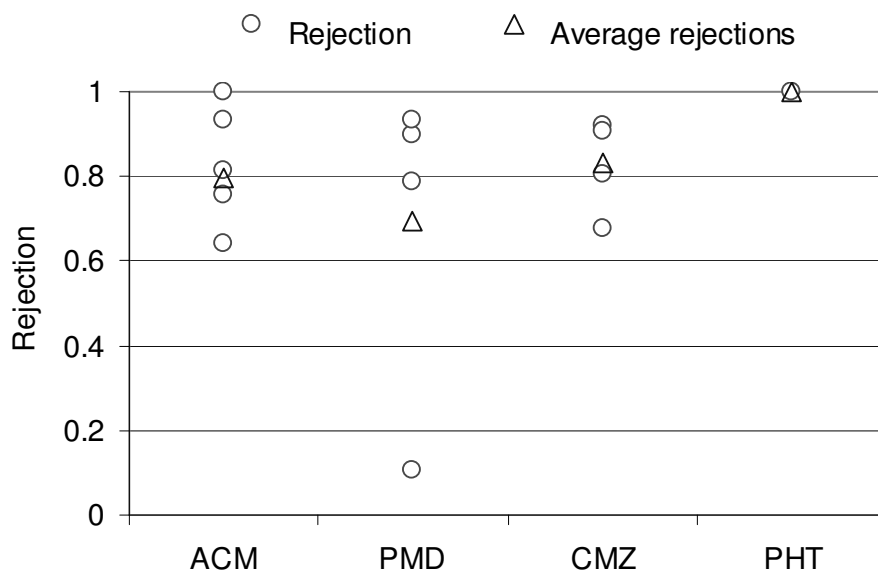


Figure 6-17: Rejection percentage of neutral pharmaceuticals

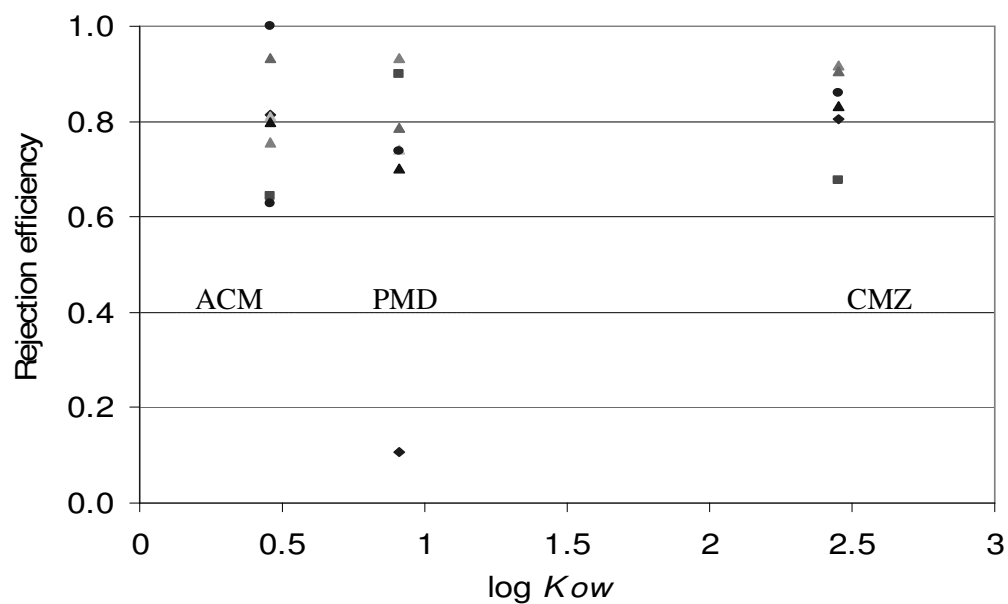
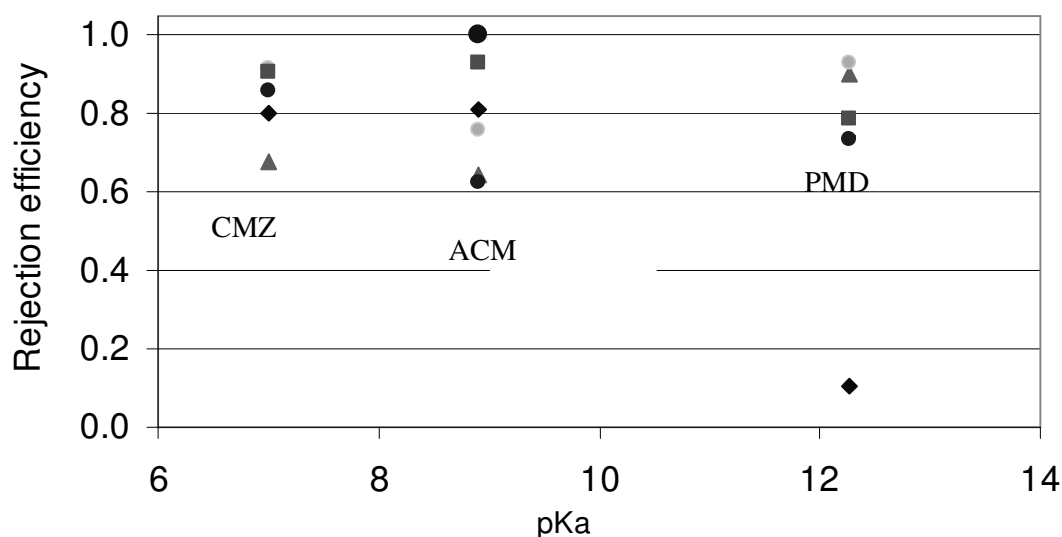


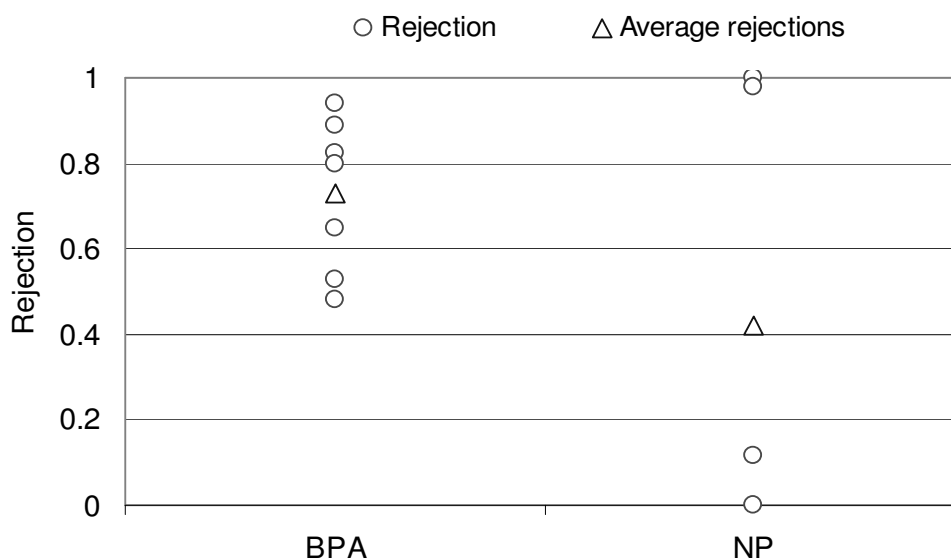
Figure 6-18: Plot of the octanol –water coefficient ( $K_{ow}$ ) of the neutral pharmaceuticals against rejection efficiency. (Note:  $R^2$  for the average values)



**Figure 6-19: Plot of the water dissociation coefficient (pKa) of the neutral pharmaceuticals against rejection efficiency.**

### 6.7.3.3 Endocrine disrupting compounds

The rejection of nonylphenol and bisphenol A varied greatly especially for NP. Rejection varied between 0 to 100% for nonylphenol and 53% to 100% for bisphenol A (see Figure 6-20). It is very difficult to associate the operating parameters with these rates of elimination because of such a broad range of rejection. Figures 6-10 to 6-13 illustrate the percentage removal. Once again, due to the wide range of variability and limitation of data, there was no potential to determine any relationship between the rejection and molecular weight or molecular size in this case study. Kimura et al., (2003b) identified a linear relationship between molecular weight of the non-charged compounds and rejection. However, in this study, such a clear relationship was not observed. Although physico-chemical characteristics of compounds tested in this study varied over a wide range, a relationship between any of these and rejection could not be described. Kiso et al (Kiso et al., 2000) reported a positive correlation between hydrophobicity of non-phenolic compounds ( $\log K_{OW}$ ) and their rejection by nanofiltration. Kimura et al. (2003b) found low concentration range of solutes was an indication of lower rejection efficiency.



**Figure 6-20: Rejection percentage of the endocrine disrupting compounds**

Rejection mechanisms by RO were investigated by many researchers (Ozaki and Li, 2002; Van der Bruggen et al., 2003b). Rejections may be influenced by dipole moment of compounds, hydrophobicity of compounds represented by  $K_{ow}$  and molecular size. As reported by Ozaki and Li (2002), it is difficult and complicated to elucidate the core mechanisms for the rejection of trace organic compounds by RO under actual conditions.

However, most studies on rejection mechanisms by RO were conducted on pilot scales using virgin membranes, high concentrations and using either base or synthetic water. These pilot scales were run under ideal conditions. Snyder and co-workers (2007) suggested that the compounds which breached RO under the full scale were not consistent, and no clear relationship between molecular structure and membrane could be established. Breaching of the RO could be the result of diffusion into and through the membrane, short-circuiting of the membrane or supporting media failure.

## 6.8 Product water

The concentrations of PhACs and EDCs were reduced as these compounds passed through the dual membrane systems in the water recycling plant. Clofibric acid, diclofenac and phenytoin were not detected in any product water samples. Other compounds (nonylphenol, gemfibrozil, ibuprofen, ketoprofen, naproxen, acetaminophen, primidone, salicylic acid and carbamazepine)

were detected in most product water samples with a maximum concentration of 120 ng/L (Table 6-6).

Bisphenol A (BPA) was detected in all product water samples with concentrations ranging from 20-464 ng/L. These concentrations are not surprising since BPA had the second highest concentration among the compounds found in the influent. The presence of BPA in the water product would be considered to have a potential impact on the environment and the final user pathway. Recent studies (Nakada et al., 2006; Roberts and Thomas, 2006; Gomez et al., 2007; Santos et al., 2007) have shown that levels of compounds found in the effluent of WWTP are often higher by more than one order of magnitude than the results obtained in this study. Therefore, it is most likely that the removal of PhACs and other compounds is more effective in the advanced treatment plant using RO systems than other conventional treatment plants (Snyder et al., 2007).

Recently, Snyder et al. (2007) have investigated the removal of a broad range of EDCs during drinking and wastewater treatment processes at bench, pilot and full scale. They found that RO membranes removed nearly all investigated compounds to levels less than method reporting limits (MDL) (1-10 ng/L). However, trace levels of some contaminants were still detectable (<MDL) in RO permeate (e.g., gemfibrozil and naproxen). It should be noted that the latter study was a snapshot and it does not give such a comprehensive picture as the work presented here.

**Table 6-6: Concentrations of PhACs and EDCs (ng/L) in the recycled water**

Compounds <sup>a</sup>	NP	BPA	GFZ	CLB	ACM	SCA	PHT	PMD	CMZ	NPX	KPF	IBU	DCF
Months													
May	20	44	25	ND	23	16	ND	42	35	ND	ND	ND	ND
Sep	15	464	28	ND	40	60	ND	49	80	35	20	30	ND
Nov	60	30	ND	ND	27	70	ND	7	50	24	ND	18	ND
Dec	ND <sup>b</sup>	20	ND	ND	ND	30	ND	ND	20	39	10	50	ND
Feb	ND	300	ND	ND	ND	30	ND	ND	ND	ND	ND	55	ND
Apr	ND	121	50	ND	20	20	ND	40	ND	50	ND	50	ND
Jun	54	450	120	ND	44	20	ND	29	35	55	44	20	ND
Average	21	204	32	ND	22	35	ND	24	31	29	11	32	ND

a):Compounds: Nonylphenol (**NP**), Bisphenol A (**BPA**), Gemfibrozil (**GFZ**), Clofibric acid (**CLA**), Acetaminophen (**ACM**), Salicylic acid (**SCA**), Phenytoin (**PHT**), Primidone (**PMD**), Carbamazepine (**CMZ**), Naproxen (**NPX**), Ketoprofen (**KPF**), Ibuprofen (**IBU**) and Diclofenac (**DCF**);

(b):ND: not deteted c):Mean of positive detection

## **6.9 Summary**

Wastewater effluent contains significant amounts of organic and inorganic compounds as a result of incomplete removal by wastewater treatment processes. The objective of this chapter was to investigate the fate of trace organic and inorganic compounds by dual membrane processes through the water recycling plant at Luggage Point Water Reclamation Plant (LPWRP). Samples were collected from the feed, permeate and backwash/brine of both microfiltration and reverse osmosis membrane systems throughout the year of May 2005 to June 2006.

Microfiltration was found to reject particulate and colloidal material to provide an essential pre-treatment for the RO. Reverse osmosis was found to be capable of significant rejection of most target compounds, with an average of 78% to 97% for metals, 68% to 100% for acidic pharmaceuticals and 63% to 100% for neutral pharmaceuticals. Furthermore, there were large variations among the removal of endocrine disrupting chemicals by the reverse osmosis membrane systems. For example, nonylphenol rejection ranged between zero and 100%, and due to this variation no further conclusion was drawn for ECDs removal by RO systems. No strong relationship between the rejection of trace organic compounds and their physico-chemical properties was observed for the LPWRP.

# Chapter

## 7 Conclusions and Recommendations

---

### 7.1 Introduction

The growing trend in water reclamation and reuse in the world is to consider water reuse practice as an essential component of integrated water resource management. The development of water reclamation and reuse in many countries is closely related to water scarcity, water pollution control measures and obtaining alternative water resources. The drought that afflicted much of Australia in 2002-2006 resulted in water restrictions being imposed in major cities of Australia including Sydney, Melbourne, Canberra, Perth and Brisbane for prohibiting use of garden sprinklers and irrigation of lawns. Similar restrictions apply in most agricultural irrigation areas which use 65% of Australian's water resources.

Over 500 municipal wastewater treatment plants now engaging in the water reclamation of at least part of their treated effluent. In the USA, the proportion of reclaimed and reuse was 7.4% of the total volume of wastewater generated, and is growing at 2025, with growing of 15% per year. In some Australian capitals, this proportion remains relatively low, however, there has been some increase in the past few years up to 19% in 2004.

The development of membrane technologies has provided practical means of achieving high removals with reasonable cost and reliability. In wastewater reclamation, the use of MF or UF membrane plants as a pretreatment stage for the NF or RO systems, represent the industry standard to produce a high quality of product water.



The overall objectives of this research project were to evaluate the performance of water reclamation plants and to investigate the seasonal variation and fate of trace organic and inorganic compounds in a number of wastewater schemes. Furthermore, the project aimed to evaluate the efficiency of wastewater treatments and water recycling processes in removal of trace pollutants and to estimate the mass balance of trace organic pollutants in MF and RO membrane systems.

A comprehensive review of the current literature provided an indication of the concentrations of organic pollutants that have been identified in sewage around the world and hence, an indication of what might be expected in Australian situation. The critical survey revealed that the great majority of the literature regarding pollutants in sewage has focused on the fate of these pollutants in wastewater treatment processes. To the author's knowledge, this project is the first to investigate the fate of pollutants in a water recycling plant implementing a dual membrane system and the first to examine the mass balance of membrane systems on a large scale, rather than bench top experiments or a pilot plant.

Analytical methods were developed and optimized in this project to provide a technique capable of the efficient analysis of targeted compounds in wastewater matrices. The developed methods involved filtration, SPE, derivatization and GC MS analysis. Limits of detection for the trace organic compounds ranged between 1 and 50 ng/L. Percentage of recovery ranged between 70% and 92% for all target compounds.

The current monitoring required of recycling schemes by providers is minimal. The majority of monitoring parameters are the quality parameters specified by EPA licenses. However, most current wastewater discharge and reuse guidelines are limited to bulk parameters. Specific organic contaminants are to date not regulated in Australia and monitoring is hence neither economic nor encouraged with any incentives. Research and development support for companies and monitoring of the performance of the key contaminants will provide greater insight for the operator in terms of the ability to remove trace organic compounds and assist in development of increased regulation for recycled water.

The purpose of this chapter is to review our findings regarding the performance of main water recycling streams including raw wastewater, secondary effluent, product water, backwash and concentrate. Accordingly, the results of this research are divided according to these progressive water recycling streams.

## 7.2 Raw Wastewater

The results of raw wastewater analysis showed that the target trace organic compounds, including eleven pharmaceutically active compounds and two endocrine disrupting compounds, were found in wastewater treatment plants. However, their concentrations varied from one treatment plant to another, depending on many factors including the size of population and the age profile of people serviced by the wastewater treatment plants, as well as the discharge of local industries into the stream of sewage plant. These two factors determine the mass of pollutants entering the future water resources (collection system). Furthermore, the types of pollutant varied depending on seasonal temperature variations, the occurrence of certain diseases associated with them (i.e., flu and cold) and precipitation values.

Generally, the concentration of pharmaceuticals in the raw wastewater was lower than reported elsewhere around the world which might indicate a lower consumption of drug compared to other countries. Furthermore, the highest detectable concentrations of drugs in wastewater was found to be over –the- counter pain relief medication.

The contribution of local industry and small business to the pollution of wastewater was seen by the amount of bisphenol A and nonylphenol in the wastewater as quantified for the case study of Luggage Point Water Reclamation Plants (LPWRP).

Fully investigation of the micropollutants fate in wastewater treatment plants was impossible due to both time constraints and the fact that little systematic relationships were found between the removal of organic contaminants and water treatment processes. It was not possible to pursue studies of the mechanisms of removal for the treatment plants under investigation

## 7.3 Secondary effluent

It is clear that the effluent will have a better quality regarding the organic and nitrogen contents due to the efficiency of new technologies implemented such as activated sludge processes in the wastewater treatment plants. As far as suitability of the secondary effluent, with particular reference to suspended solids, the levels are much lower (93%) than the untreated concentrations. Furthermore, a slightly marginal change in the total dissolved solids (12%) occurred during secondary wastewater treatment.

Despite the high removal of heavy metals and trace organic compounds (>70%) by primary wastewater treatments, their remaining concentrations suggest the necessity of further treatment to produce high quality water. The fate of organic and inorganic pollutants in the sewage sludge should be considered when the sludge is disposed on agricultural land as the total metal loading of the raw wastewater will end up in the sludge.

## 7.4 Product water

The removal efficiency for conventional parameters (e.g., organic carbon, nitrogen, UV, turbidity and conductivity) by state-of-the-art wastewater treatment plants / water recycling plants was excellent. The resulting product water showed parameters of less than 1 unit measurements (mg/L for TN and TOC, mhos/cm<sup>3</sup> for conductivity and NTU for turbidity) that could be used for various applications as non-potable water. These findings indicated that the drinking water standards were exceeded by the reclaimed wastewater for the RO membrane with a multi barrier approach. Furthermore, the RO permeate did not show the presence of any microorganisms (i.e., *E coli* or, viruses) as been reported in many studies, indicating their complete rejection. These results allow the reuse of water in a safe way such as irrigation of raw vegetables.

The rejection efficiency for trace organic compounds was excellent compared to other studies as a result of implementing dual MF/ RO membrane systems as employed in the case study plants including Water Reclamation and Management Scheme (WRAMS) and LPWRP. The concentration of all analytes decreased on average by one order of magnitude during primary and secondary treatments. These concentrations were reduced by another order of magnitude by the RO system in the water recycling plant resulting in concentrations of most trace organic compounds in the product water of less than 0.1 µg/L with the exception of bisphenol A (BPA). BPA was detected in all water product samples with concentrations ranging from 20 to 464 ng/L. These concentrations were not surprising since BPA had the second highest concentration among the compounds found in the influent. The presence of BPA in the product water would be considered to have a potential impact on the environment and the final user.

On the other hand, the concentrations of the PhACs that were detected in recycled water in this study do not currently have established drinking-water standards or health advisories. Therefore, the potential health consequences associated with exposure through drinking water/recycling

water are not known. These concentrations were far below doses used in therapy. For example, the maximum possible intake of gemfibrozil in product water in a life time (assuming an intake of 2 L per day for 70 years) was 1.7 mg, where as a single therapeutic dose is generally 100mg or greater. Nevertheless, the PhACs are designed to be ingested, others such as endocrine disrupting compounds (EDCs) (i.e., NP and BPA) are not designed for human consumption. The human health consequence of chronic ingestion of these compounds is even less well understood than the PhACs.

## 7.5 Backwash

With membrane processes there was an obvious production of waste streams such as the MF backwash water with high suspended solids (high turbidity) and organic contents (high TOC, TN and absorbance measurements). There was no significant difference in the concentrations of trace organic compounds in the MF feed, MF permeate and MF backwash, which indicates that MF did not contribute to the removal of trace organic compounds. Backwash water, as a side stream of the MF filtration, would not contribute to any further hazards as long as no residuals from any chemicals added for scaling, biological fouling control or any other processes throughout the wastewater treatment plant were present.

## 7.6 Concentrate

The RO concentrate is significantly different to the backwash because the RO retentate contains concentrated salts which increase conductivity. Furthermore, the RO membrane serves as a large reservoir for organic matter (i.e., high organic carbon, TN and absorbance measurements) as well as trace organic compounds such as PhACs and EDCs due to the adsorption of contaminants on membranes and their likely release in the brine. The concentrations of trace organic compounds reached  $\mu\text{g/L}$  levels. The concentration factor for the detected compounds ranged between one and five for all detected trace compounds. With regard to the metals content of the brine (anions, cations and heavy metals), the RO membrane concentrates these metals by a factor between three and five, resulting in an approximate of 0.5% (w/v) of total content of the rejected brine.

Despite the fact that concentrations of trace organic compounds in the brine were one order of magnitude greater than in the feed, these concentrations were generally lower than the concentrations in the raw wastewater by one order of magnitude. However, the disposal of the brine still poses a pollution issue as was the case for raw wastewater.

## 7.7 Suggestions for further studies:

Interest in wastewater reclamation and reuse has increased considerably over the past decade by implementation of membrane –based treatments. However, there is a need for further development for removal of low level (ng/L) of trace organic compounds (i.e., BPA and NP), which were detected in the recycled water.

Further research can usefully be conducted to address the uncertain issues and questions associated with toxicology of endocrine disrupting compounds in reclaimed water. Research has shown that significant amounts of drugs are released from sewage treatment plants as well as reclaimed water to the environment. Therefore, there is a risk that humans might be exposed to drugs through water drawn from contaminated supplies. Although this risk is small, the increasing demands on water supplies will probably lead to greater incidences of indirect and direct water-reuse situations. Nevertheless, drinking two litres of the “tainted” water everyday for a life time would not cumulatively deliver the equivalent of a single prescribed dose of any of the compounds present. The information does not completely rule out the long-term effects that might go unnoticed, and it is of course impossible to prove that the risk of any pollutant is negligible.

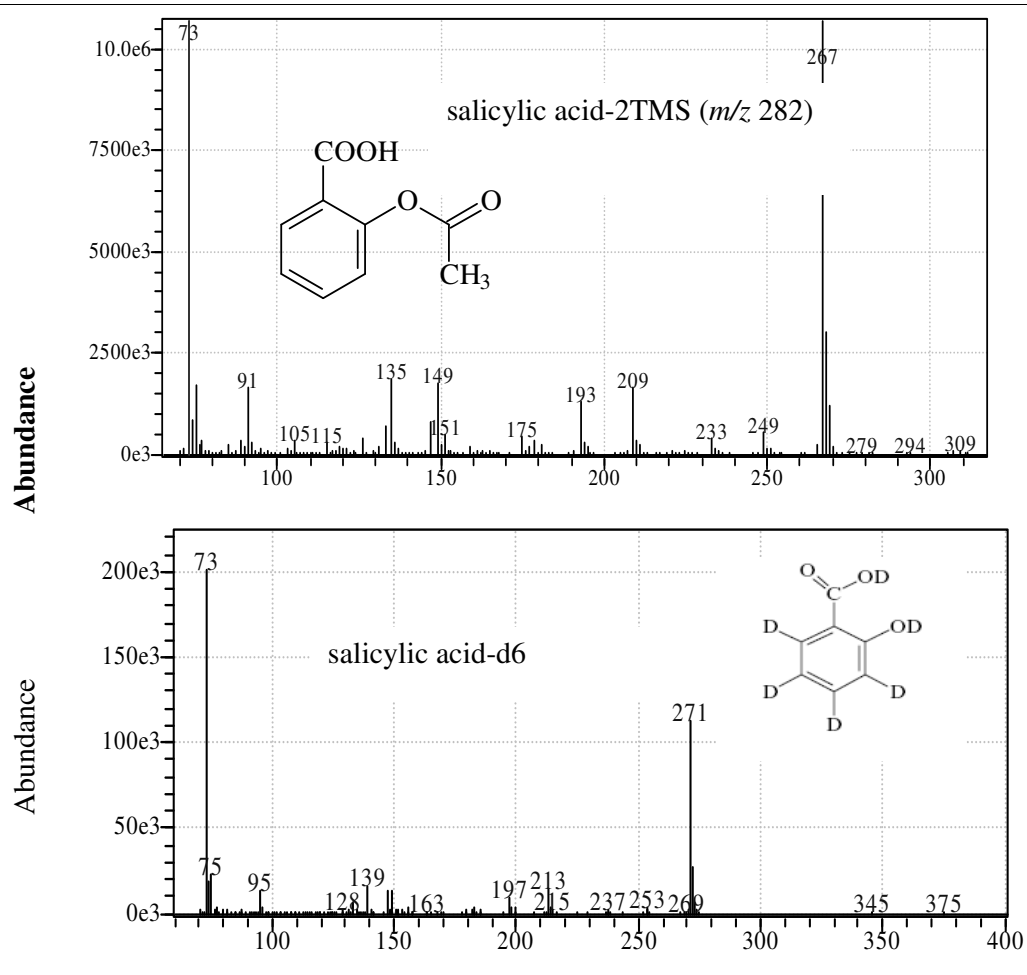
The current research has focused predominantly on the analysis of parent compounds. Many of the compound metabolites are also biologically active compounds and may be excreted at much higher rates than the parent compounds. Degradation products of pharmaceutical residues are a further potential source of persistent biologically active contaminants. Efforts should be undertaken to identify important metabolites and degradation products.

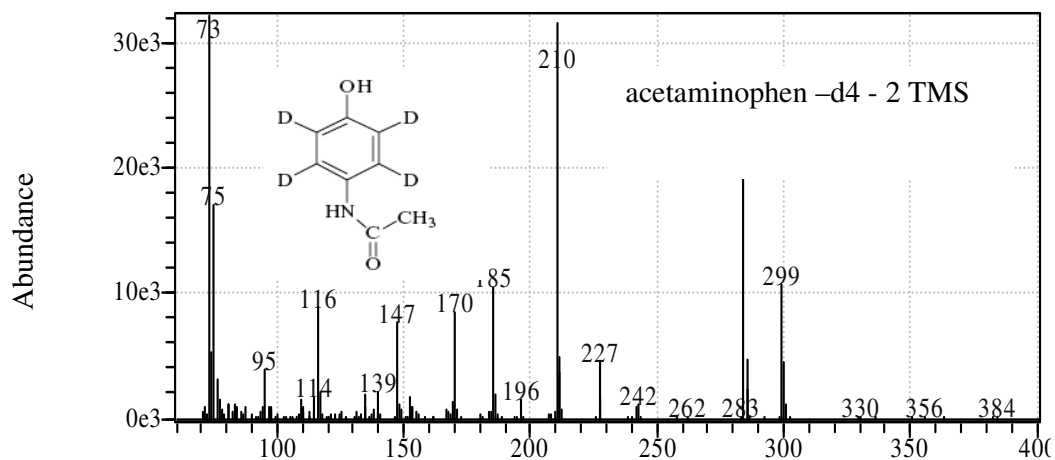
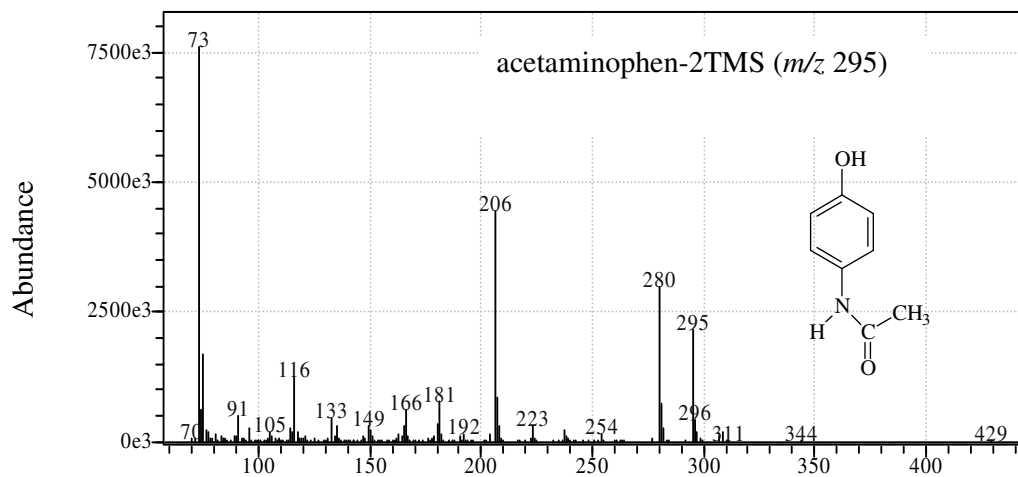
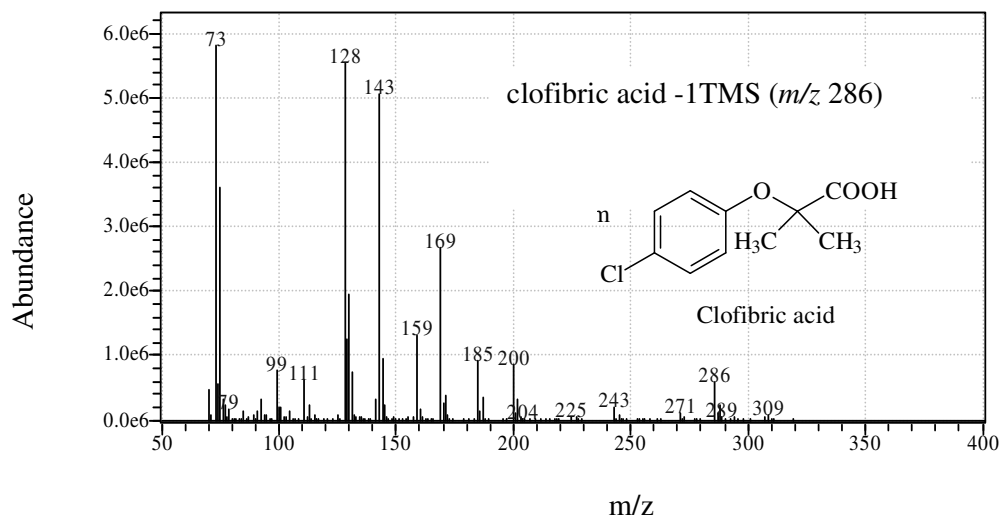
The current developed procedure for determination of pharmaceuticals and endocrine disrupting compounds are generally laborious, time- consuming and include usage of a relatively large sample. There is an urgent need for a more comprehensive method for the extraction and analysis of a wide variety of organic compounds, which offers low detection limits, reproducibility, robust and completely automation.

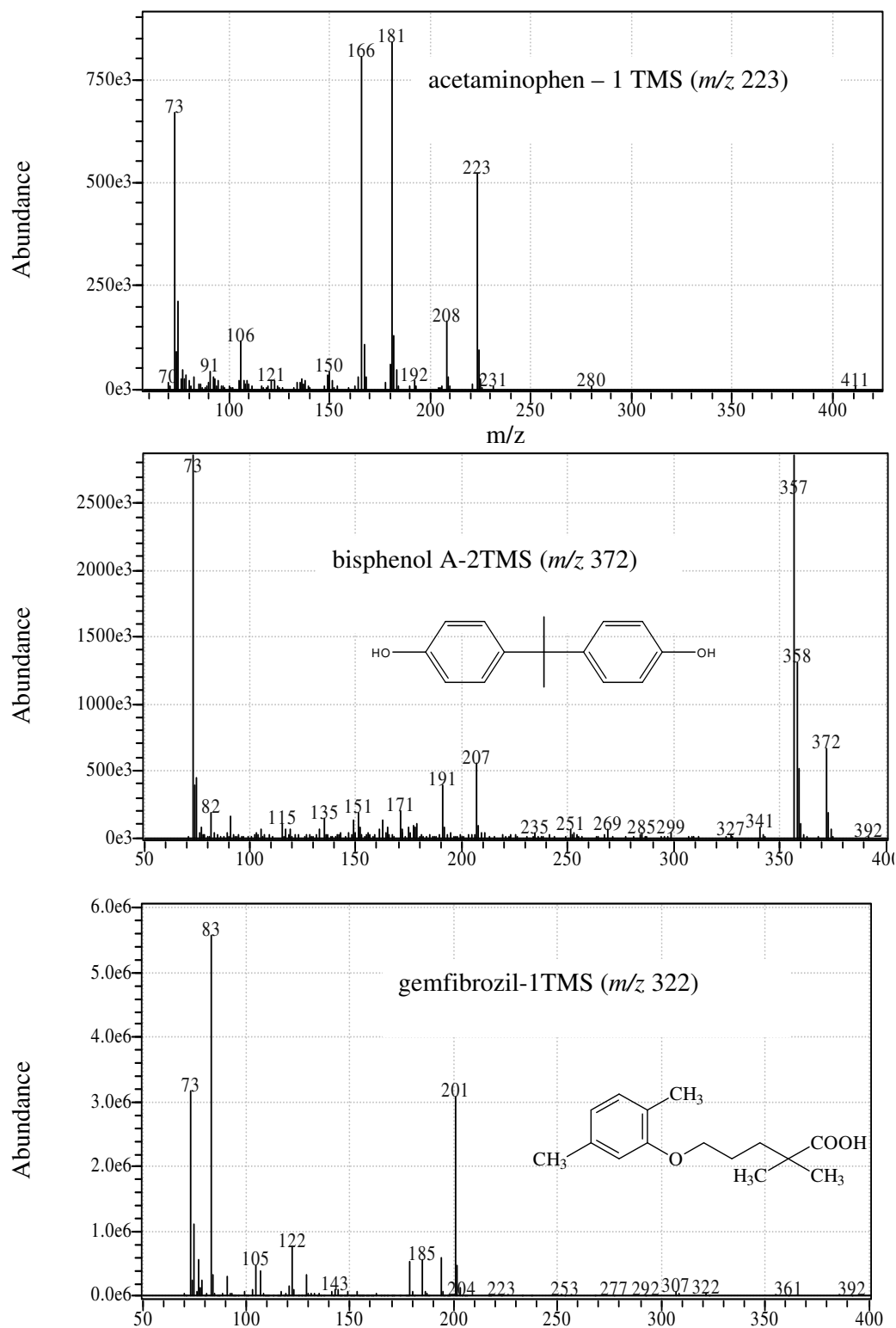
The current study has focused on the removal of organic microcontaminants in the wastewater through activated sludge and membrane technology. Further studies could usefully be conducted to investigate the capabilities of natural systems (e.g. lagoons or wetlands, etc) in reducing the concentrations of organic microcontaminants.

# 8 Appendices

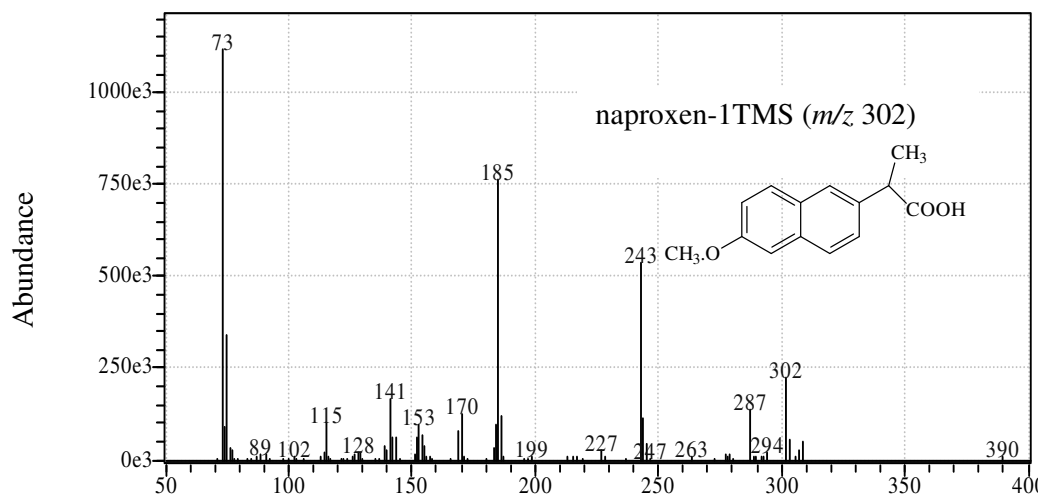
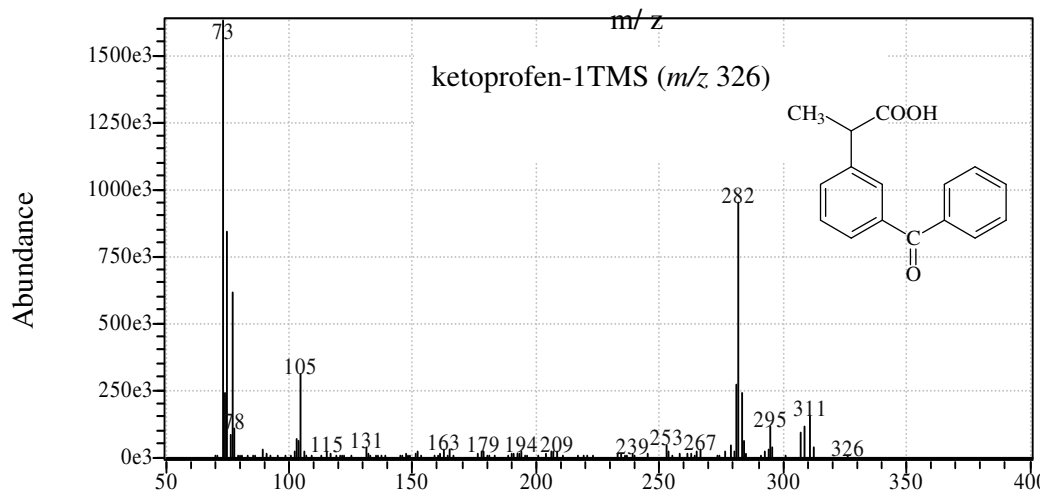
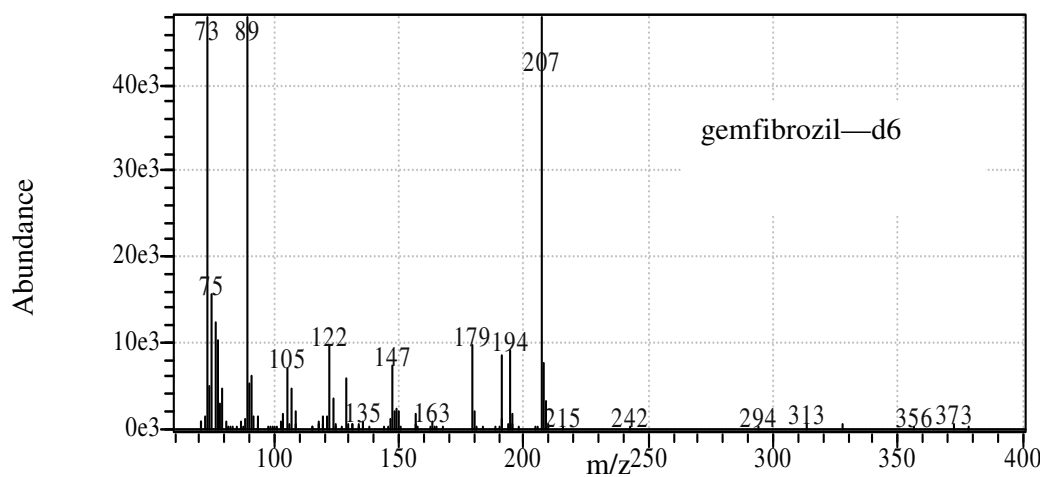
**Appendix 8-1: Electron impact mass spectra of potential analytes and deuterated standards.**

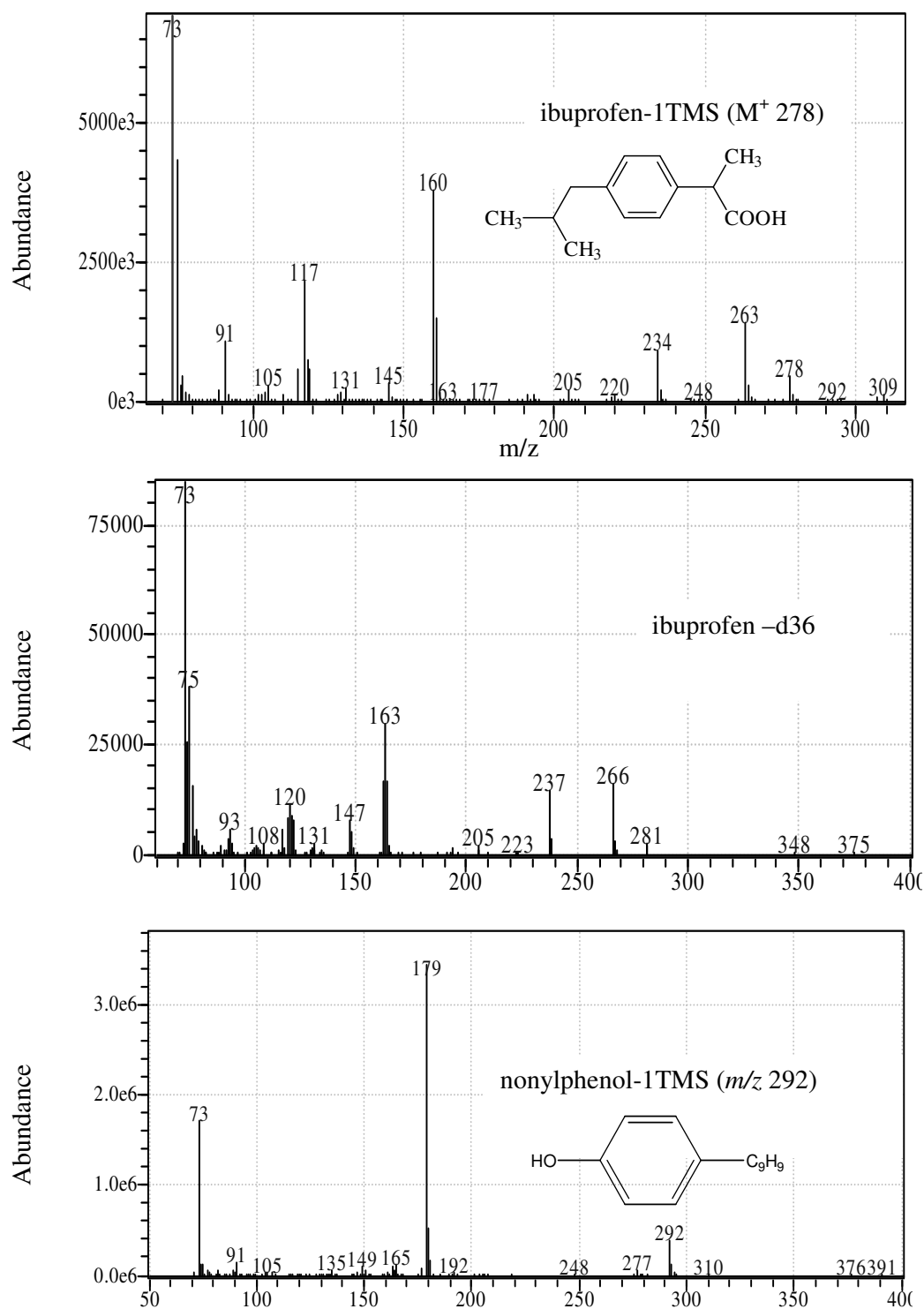


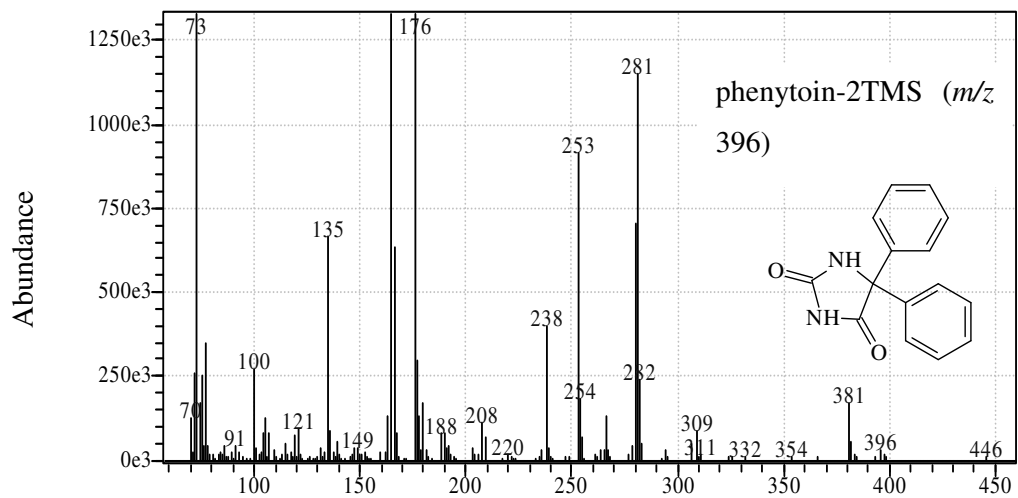
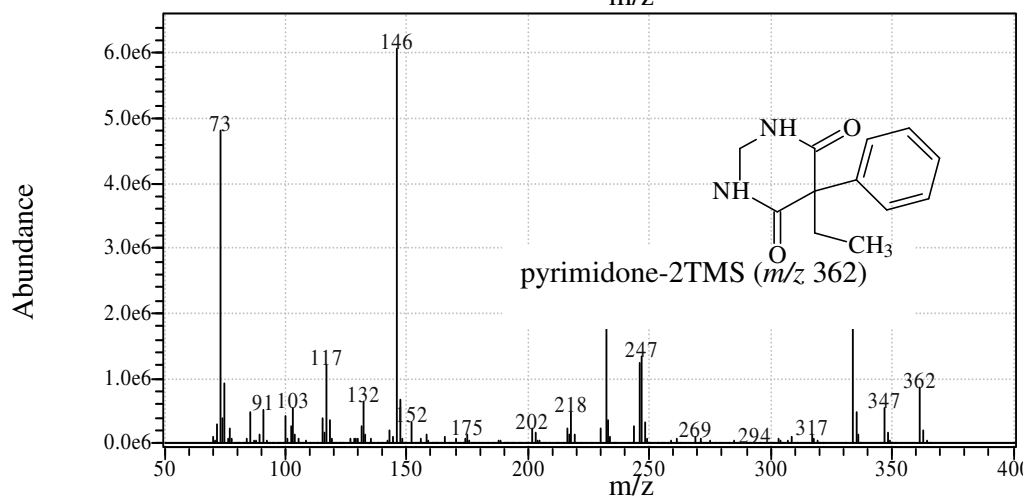
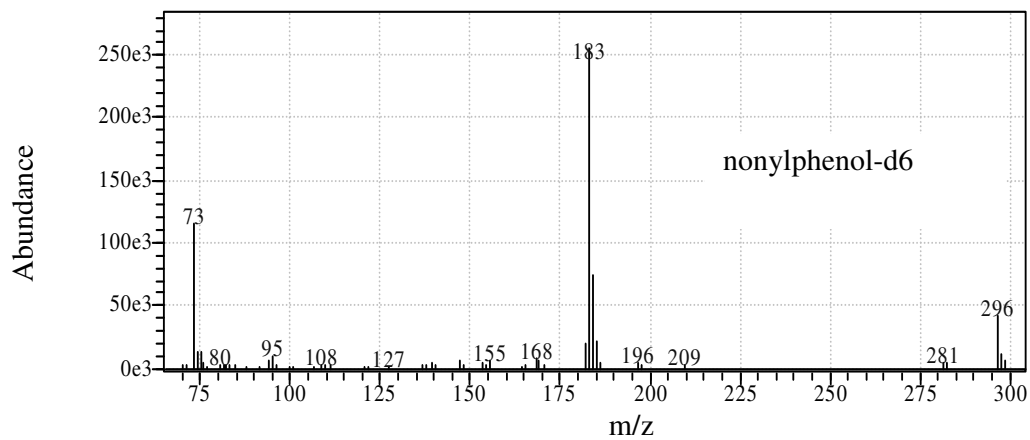




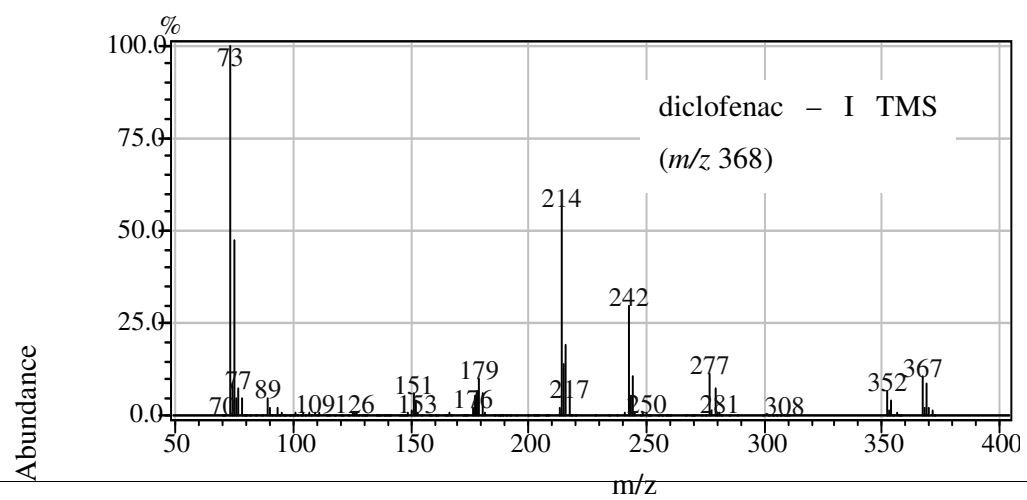












**Appendix 8-2: Sampling locations for the three schemes**

<b>Sample no.</b>	<b>Sample location and for GGSS</b>
1	Raw Influent
2	Post Clarifier
3	Post sand filter
4	Post ozonation
5	Post BAC
6	Post CMF
7	Post UV
8	Product water Post storage and chlorination

<b>Sample no.</b>	<b>Sample location for WRAMS</b>	<b>Sample no.</b>	<b>Sample location for WRAMS</b>
1	Raw Influent	4	MF Permeate
2	Second Effluent	5	RO Concentrate
3	MF back flush	6	RO Permeate

<b>Sample no.</b>	<b>Sample location for LPWRP</b>
1	Raw Sewage Influent
2	Effluent Feed for MF & RO Plant ( Prior to ammonia & chlorine addition)
3	Effluent Feed for MF & RO Plant ( Post to ammonia & chlorine addition)
4	MF Feed (between amaid perfiltration & MF Racks)
5	MF filtrate prior to chemical condition of RO feed
6	MF filtrate post to chemical condition of RO feed
7	RO Permeate Prior to Chemical Conditioning ( Caustic & Chlorine)
8	RO Permeate Post to Chemical Conditioning ( Caustic & Chlorine)
9	RO Concentrate
10	Product water
11	MF Backwash

**Appendix 8-3: Various methods used for the Wastewater characterization.**

<b>Method</b>	<b>Method Source</b>
Chemical Oxygen Demand (COD) (1.610B)	Method number 5220 D, Closed Reflux Colorimetric Method. "Standard Methods for the Examination of Water and Wastewater, "21st Edition, 2005.
Alkalinity (SAS 1-5.012)	Method Detection Limit (MDL) 5 mg/L Method No. 2320B Titration Method, "Standard Methods for the Examination of Water and Wastewater", 21st Edition, AWWA APHA WEF, 2005 This method has been developed in-house with reference to Method 3120 - Metals by Plasma Emission Spectroscopy, Standard Methods for the Examination of Water and Wastewater 21st Edition and USEPA Method 200.7 Rev 4.4, Determination of Metals and Trace Elements in Water and Wastes by Inductively Coupled Plasma-Atomic Emission Spectroscopy.
Analysis of Metallic Elements (ICP-OES)(5.304)	Elements and their MDL (mg/L): Aluminium (0.005), Arsenic (0.005), Barium (0.005), Boron (0.010), Cadmium (0.001), Calcium (0.2), Chromium (0.002), Cobalt (0.005), Copper (0.001), Iron (0.002), Magnesium (0.2), Manganese (0.001), Molybdenum (0.01), Nickel (0.002), Lead (0.005), Potassium (0.5), Selenium (0.01), Silicon (0.05), Sodium (0.5), Sulphur (1) and Zinc (0.005). Method 4500- F C. Ion-Selective Electrode Method. Standard Methods for the Examination of Water and Wastewater 21st Edition, 2005.
Determination of Fluoride (1.620)	MDL(0.01mg/L) Method 4500-H+B Electrometric Method. "Standard Methods for the Examination of Water and Waste Water" APHA, AWWA, WEF Approved by Standard committee, 2000
pH (1/5.002)	Method no: 5310B "High-Temperature Combustion-Infrared Method" "Standard Methods for the Examination of Water and Wastewater" approved by Standards Committee 2000.
Total Organic Carbon (TOC) (1.603)	MDL(0.5mg/L) Lachat QuikChem Methods Manual, Method 31-107-04-1-B, 10-115-01-1-S, incorporating:
Total Nitrogen and Total Phosphorus (FIA.013, FIA.011B)	Grasshoff, K. Methods of Seawater Analysis, verlag chemie, Second Edition, 1976. Zimmerman, Carl. F. and Keefe, Carolyn W., EPA Method 353.4, Determination of Nitrate + Nitrite in Estuarine and Coastal Waters by Automated Colorimetric Analysis in An Interim Manual of Methods for the Determination of Nutrients in Estuarine and Coastal Waters., Revision 1.1, June 1991. D'Elia, C.F., Sterdler, P.A. and Corwin, N. Determination of Total Nitrogen in Aqueous Samples using Persulfate Digestion Limnol.

	Oceanorg., 22 p. 760-764.
	Ebina, J., Tsutsui, T., and Shirai, T., Simultaneous Determination of Total Nitrogen and Total Phosphorus in Water using Peroxodisulfate Oxidation, Water Res. Vol. 17, No. 12, pp. 1721-1726, 1983
	The method is applicable over the range 0.01-4 mg/L P and 0.01-5 mg/L N. QuikChem Method 10-117-07-1-A
Chloride By Flow Injection Analysis (FIA.109)	Method 4500Cl <sup>-</sup> G “Mercuric Thiocyanate Flow Injection Analysis” from “Standard Methods for the Examination of Water and Wastewater” 20 <sup>th</sup> Edition 1998.
	The applicable range is 3.0 to 200.0 mg Cl <sup>-</sup> /L. Lachat QuikChem Methods Manual, Method 31-107-06-1-A, 31-107-04-1A, 31-115-01-3B.
Ammonia, Nitrogen and Orthophosphorus (FIA.008, FIA.010, FIA.011A)	MDL: Ammonia N and Oxidized nitrogen, 0.05mg/L  Orthophosphorus 0.02mg/L

#### Appendix 8-4: Plant overview

Description	Value / type
Daily flow for WWT	150ML / day
Recycled plant product Flow	14 ML/day
Reject Flows for recycled Plant	2.8 ML/day (equivalent to 17%of inflow)

#### Appendix 8-5: Technical details of the MF membrane

Description	Value / type
Pore size:	0.1µm
Flow mode	Cross flow
No. of units	6
No. of modules in each unit	66
Recovery	97%
Feed pressure (kPa)	142
Filtrate pressure (kPa)	73
Trans membrane pressure (TMP) (kPa)	69
TMP (daily) (kPa)	77 - 88
Feed temperature (° C)	30
Filtrate Turbidity (NTU)	7.33
Filtrate conductivity (µS/cm)	1617



**Appendix 8-6: Chemical dosing rate for MF and RO systems**

	<b>Chemical</b>	<b>Dose and conditions</b>
MF feed	Sodium hypochlorite	2.0 mg/L
	Sodium hypochlorite (Reverse filtration)	15mg/L
	Ammonia	Ratio to MF chlorine 1:4
RO feed	Sodium hypochlorite	PID controlled , Redox 160mV, total chlorine < 1 mg/L
	Hypersperse MDC150 (Antiscalant)	3.2 mg/L
RO permeate	Sodium metabisulphate	PID controlled , Redox 160mV
	Sodium hypochlorite	0.2 mg/L
	Sodium hydroxide	PID controlled , approximately 0.45 mg/L to make pH 6.5 – 7.2
Product water	Sodium hypochlorite	PID controlled , pH 6.5 – 7.2, free chlorine 0.3 – 0.5 mg/L

**Appendix 8-7: Membrane cleaning protocol for MF and RO systems**

<b>Membrane</b>	<b>Process</b>	<b>Note</b>
MF	Reverse filtration	Every first 20 minutes
	Reverse filtration plus air scrub and shaking off	Every second 20 minutes
	Clean in place (CIP) using NaOH/NaOCl and citric acid solutions	Monthly bases
RO	RO flushing	
	Clean in place (CIP)HCl, NaOH, EDTA & BDNAP biocide	Every 6 months

**Appendix 8-8: Technical details of the RO unit**

<b>Description</b>	<b>Type / Value</b>
Membrane	Filmtech BW 30 – 365-FR (fouling resistant RO (DOW)
Composite	Polyamida thin film
Salt rejection	99-99.5%
No. of units	6
No. of membranes per units	186
RO modules	Flat sheet, 8 inch vessels
Feed pressure stage 1, 2 & 3 (kPa)	1112, 997 & 752
Feed temperature ( <sup>0</sup> C)	31
Permeate pressure (stage 1, 2 & 3) (kPa)	533, 251 & 78
Delta pressure (stage 1, 2 & 3) (kPa)	114, 245 & 173
Daily flow (stage 1, 2 & 3) (kL)	627, 280 & 149
Recovery (stage 1, 2 & 3) (%)	44, 35 & 34
Combined recovery (%)	76%
Conductivity for permeate (μS/cm)	45.3
Turbidity for permeate (NTU)	0.021

**Appendix 8-9: RO membrane sheet fact**

# 9 References

---

- Adams, C., Wang, Y., Loftin, K., Meyer, M., 2002. Removal of antibiotics from surface and distilled water in conventional water treatment processes. *Journal of Environmental Engineering-ASCE* 128, 253-260.
- Ahel, M., Giger, W., Koch, M., 1994. Behaviour of alkylphenol polyethoxylate surfactants in the aquatic environment. Occurrence and transformation in sewage treatment. *Water Research* 28, 1131-1142.
- Aherne, G., Hardcastle, A., Nield, A., 1990. Cytotoxic drugs and the aquatic environment: Estimation of bleomycin in river and water samples. *Journal of Pharmacy and Pharmacology* 42, 741-742.
- Ahrer, W., Buchberger, W., 2001. Combination of Aqueous and Non-Aqueous Capillary Electrophoresis with Electrospray Mass Spectrometry for the Determination of Drug Residues in Water. *Monatshefte für Chemie / Chemical Monthly* 132, 329.
- Alcock, R.E., Sweetman, A., Jones, K.C., 1999. Assessment of organic contaminant fate in waste water treatment plants I: Selected compounds and physicochemical properties. *Chemosphere* 38, 2247-2262.
- Al-rifai, J., Gabelish, C., Schafer, A., 2007. Occurrence of pharmaceutically active and non-steroidal estrogenic compounds in three different wastewater recycling schemes in Australia. *Chemosphere* 69: 803-815
- Andersen, J., Schluter, L., Aertebjerg, G., 2006. Coastal eutrophication: recent developments in definitions and implications for monitoring strategies. *Journal of Plankton Research* 28, 7, 621-628.
- APHA, 2005. Standards Methods for the examination of water and wastewater American Public Health Association Washington, DC. 21st edition.

## REFERENCES

- Barcelo, D., 2007. Comprehensive Analytical Chemistry. Elsevier, Amsterdam, The Netherlands.
- Bellona, C., Drewes, J.E., Xu, P., Amy, G., 2004. Factors affecting the rejection of organic solutes during NF/RO treatment - a literature review. *Water Research* 38, 2795-2809.
- Bendz, D., Paxeus, N.A., Ginn, T.R., Loge, F.J., 2005. Occurrence and fate of pharmaceutically active compounds in the environment, a case study: Hoje River in Sweden. *Journal of Hazardous Material* 122, 195-204.
- Bergeron, R., Thompson, T., Leonard, L., Pluta, L., Gaido, K., 1999. Estrogenicity of bisphenol A in a human endometrial carcinoma cell line. *Molecular Cell Endocrinology* 150, 179-187
- Birkett, J.W., Lester, J.N., 2003. Endocrine disrupters in wastewater and sludge treatment processes. Lewis United States.
- Bixio, D., Thoeye, C., Wintgens, T., Ravazzini, A., Miska, V., Muston, M., Chikurel, H., Aharoni, A., Joksimovic, D., Melin, T., 2008. Water reclamation and reuse: implementation and management issues. *Desalination* 218, 13-23.
- Biziuk, M., Przyjazny, A., Czerwinski, J., Wierowski, M., 1996. Occurrence and determination of pesticides in natural and treated waters. *Journal of Chromatography A* 754, 103-123.
- Blanchard, M., Teil, M., Ollivon, D., Legenti, L., Chevreuil, M., 2001. Origin and distribution of polyaromatic hydrocarbons and polychlorobiphenyls in urban effluents of wastewater treatment plants of the Paris area. *Water Research* 35, 3679- 3687
- Blanchard, M., Teil, M., Ollivon, D., Legenti, L., Chevreuil, M., 2004. Polycyclic aromatic hydrocarbons and polychlorobiphenyls in wastewater and sewage sludge from Paris area (France). *Environmental Research* 95, 184- 197.
- Boake, M.J., 2006. Recycled water - case study: Gerringong Gerroa. *Desalination* 188, 89-96.
- Bolz, U., Korner, W., Hagenmaier, H., 2000. Development and validation of a GC/MS method for determination of phenolic xenoestrogens in aquatic samples. *Chemosphere* 40, 929-935.

- Bowen, W.R., Welfoot, J.S., Williams, P.M., 2002. Linearized transport model for nanofiltration: Development and assessment. *AIChE Journal* 48, 760-773.
- Brisbane Water, 2002. Luggage Point Water Reclamation Plant: Basic Operation. Brisbane Water Training Centre, Brisbane, Australia.
- Buser, H.R., Poiger, T., Muller, M.D., 1999. Occurrence and Environmental Behavior of the Chiral Pharmaceutical Drug Ibuprofen in Surface Waters and in Wastewater. *Environmental Science and Technology* 33, 2529-2535.
- Buzier, R., Tusseau-Vuillemin, M.-H., dit Meriadec, C.M., Rousselot, O., Mouchel, J.-M., 2006. Trace metal speciation and fluxes within a major French wastewater treatment plant: Impact of the successive treatments stages. *Chemosphere* 65, 2419-2426.
- Cai, Q.-Y., Mo, C.-H., Wu, Q.-T., Zeng, Q.-Y., Katsoyiannis, A., 2007. Concentration and speciation of heavy metals in six different sewage sludge-composts. *Journal of Hazardous Materials* 147, 1063-1072.
- Carballa, M., Omil, F., Lema, J.M., Llompart, M., Garcia-Jares, C., Rodriguez, I., Gomez, M., Ternes, T., 2004. Behaviour of pharmaceuticals, cosmetics and hormones in a sewage treatment plant. *Water Research* 38, 2918-2926.
- Chapman, H., 2006. WRAMS, sustainable water recycling. *Desalination* 188, 105-111.
- Chipasa, K.B., 2003. Accumulation and fate of selected heavy metals in a biological wastewater treatment system. *Waste Management* 23, 135-143.
- Clara, M., Scharf, S., Scheffknecht, C., Gans, O., 2007. Occurrence of selected surfactants in untreated and treated sewage. *Water Research* 41, 4339-4348.
- Clara, M., Strenn, B., Gans, O., Martinez, E., Kreuzinger, N., Kroiss, H., 2005. Removal of selected pharmaceuticals, fragrances and endocrine disrupting compounds in membrane bioreactor and conventional wastewater treatment plant. *Water Research* 39, 4797-4807.
- COM (2006), Proposal for a Directive of the European Parliament and of the Council on Environmental Quality Standards in the Field of water policy and amending Directive

2006/60/EC. Brussels 17.7.2006.  
<[http://eur.europ.eu/lexUriServ/site/en/com/2006/com2006\\_0397en01.pdf](http://eur.europ.eu/lexUriServ/site/en/com/2006/com2006_0397en01.pdf)>

Cooper, P.F., Downing, A.L., 1998. J. Chem. Inst. Water Environmental Management 12, 303-313.

Couper, J.M., Leise, E.M., 1996. Serotonin Injections Induce Metamorphosis in Larvae of the Gastropod Mollusc *Ilyanassa obsoleta*. Biollogical Bulletin 191, 178-186.

Daughton, C.G., Ternes, T.A., 1999. Pharmaceuticals and personal care products in the environment: Agents of subtle change? Environmental Health Perspectives 107, 907-938.

Deborde, M., Rabouan, S., Duguet, J.P., Legube, B., 2005. Kinetics of Aqueous Ozone-Induced Oxidation of Some Endocrine Disruptors. Environmental Science and Technology 39, 6086-6092.

Department of Health and Aging, 2005. Australian Statistics on Medicines 2003. Commonwealth of Australia

Drewes, J., Heberer, T., Redderson, K., 2002. Fate of pharmaceuticals during indirect potable reuse. Water Science and Technology 46, 73-80.

Drewes, J.E., 2007. Removal of pharmceuticals in wastewater and drinking water treatments. In: Petrovic, M., Barcelo, D. (Eds.). Comprehensive Analytical Chemistry: fate and removal of pharmaceuticals in the water cycle. Elsevier, Amesterdam, The Netherlands.

Duarte, H.A., Carvalho, S., Paniag, E.B., Simas, A.M., 1999. Journal of Pharmaceutical Science 88, 111.

Eichenberger, B., Chen, K., 1982. Origin and nature of selected inorganic constituents in natural waters. Academic Press, New York.

Ferrari, B., Paxeus, N., Giudice, R.L., Pollio, A., Garric, J., 2003. Ecotoxicological impact of pharmaceuticals found in treated wastewaters: study of carbamazepine, clofibric acid, and diclofenac. Ecotoxicology and Environmental Safety 55, 359-370.

- Ferrer, I., Thurman, E.M., 2003. Liquid chromatography/time-of-flight/mass spectrometry (LC/TOF/MS) for the analysis of emerging contaminants. *Trac-Trends in Analytical Chemistry* 22, 750-756.
- Fong, P.P., Huminski, P.T., D'Urso, L.M., 1998. Induction and potentiation of parturition in fingernail clams (*Sphaerium striatinum*) by selective serotonin re-uptake inhibitors (SSRIs). *The Journal of Experimental Zoology* 280, 260-264.
- Fromme, H., Kuchler, T., Otto, T., Pilz, K., Müller, J., Wenzel, A., 2002. Occurrence of phthalates and bisphenol A and F in the environment. *Water Res* 36, 1429-1438.
- Fuentes, A., Llorens, M., Saez, J., Isabel Aguilar, M., Ortuno, J.F., Meseguer, V.F., Comparative study of six different sludges by sequential speciation of heavy metals. *Bioresource Technology* In Press, Corrected Proof, 1072.
- Gagne, F., Blaise, C., Andre, C., 2006. Occurrence of pharmaceutical products in a municipal effluent and toxicity to rainbow trout (*Oncorhynchus mykiss*) hepatocytes. *Ecotoxicology and Environmental Safety* 64, 329-336.
- Garrison, A.W., Pope, J.D., Allen, F.R. (Eds.), 1976. GC/MS analysis of organic compounds in domestic wastewaters. Ann Arbor Science Publishers Inc, Ann Arbor, 517-556.
- Golet, E.M., Alder, A.C., Giger, W., 2002. Environmental Exposure and Risk Assessment of Fluoroquinolone Antibacterial Agents in Wastewater and River Water of the Glatt Valley Watershed, Switzerland. *Environmental Science and Technology* 36, 3645-3651.
- Gomez, M.J., Martinez Bueno, M.J., Lacorte, S., Fernandez-Alba, A.R., Aguera, A., 2007. Pilot survey monitoring pharmaceuticals and related compounds in a sewage treatment plant located on the Mediterranean coast. *Chemosphere* 66, 993-1002.
- Gonzalez-Barreiro, C., Lores, M., Casais, M.C., Cela, R., 2003. Simultaneous determination of neutral and acidic pharmaceuticals in wastewater by high-performance liquid chromatography-post-column photochemically induced fluorimetry. *Journal of Chromatography A* 993, 29-37.



## REFERENCES

- Granier, L., Chesterikoff, A., Chevreuil, M., Létolle, R., 1988. Essai de bilan des polychlorobiphényles (PCB) à la station d'épuration de l'agglomération parisienne (Abstract). Academic Science Paris Series II 306 1175-1178
- Granier, L., Chevreuil, M., Carru, A.M., Letolle, R., 1990. Urban runoff pollution by organochlorines (polychlorinated biphenyls and Lindane) and heavy metals (lead, zinc and chromium). Chemosphere 21, 1101-1108.
- Gros, M., Petrovic, M., Barcelo, D., 2006. Development of a multi-residue analytical methodology based on liquid chromatography-tandem mass spectrometry (LC-MS/MS) for screening and trace level determination of pharmaceuticals in surface and wastewaters. Talanta 70, 678-691.
- Halket, J.M., Zaikin, V.G., 2003. Derivatization in mass spectrometry - 1. Silylation. European Journal of Mass Spectrometry 9, 1-21.
- Halling-Sorensen, B., Nielsen, S.N., Lanzky, P.F., Ingerslev, F., Luthoft, H.C.H., Jorgensen, S.E., 1998. Occurrence, fate and effects of pharmaceutical substances in the environment - A review. Chemosphere 36, 357-394.
- Hansen, P.D., Dizer, H., Hock, B., Marx, A., Sherry, J., McMaster, M., Blaise, C., 1998. Vitellogenin - a biomarker for endocrine disruptors. TrAC Trends in Analytical Chemistry 17, 448-451.
- Heberer, T., 2002a. Occurrence, fate and removal of pharmaceutical residues in aquatic environment: a review of recent research data. Toxicology Letters 131, 5-17.
- Heberer, T., 2002b. Tracking persistent pharmaceutical residues from municipal sewage to drinking water. Journal of Hydrology 266, 175-189.
- Heberer, T., 2007. Removal of pharmaceuticals during drinking water production. In: Petrovic, M., Barcelo, D. (Eds.). Comprehensive Analytical Chemistry: Analysis, fate and removal of pharmaceuticals in the water cycle. Elsevier, Amsterdam, The Netherlands, pp. 475-514.

- Heberer, T., Feldmann, D., Redderson, K., Altmann, H.J., Zimmermann, T., 2002. Production of drinking water from highly contaminated surface waters: removal of organic, inorganic and microbial contaminants applying mobile membrane filtration units. . *Acta Hydrochim Hydrob* 30, 24-33.
- Hennion, M.C., Cau-Dit-Coumes, C., Pichon, V., 1998. Trace analysis of polar organic pollutants in aqueous samples: Tools for the rapid prediction and optimisation of the solid-phase extraction parameters. *Journal of Chromatography A* 823, 147-161.
- Hignite, C., Azarnoff, D.L., 1977. Drugs and drug metabolites as environmental contaminants: Chlorophenoxyisobutyrate and salicylic acid in sewage water effluent. *Life Sciences* 20, 337-341.
- Hirsch, R., Ternes, T.A., Bobeldijk, I., Weck, R., 2001. Determination of environmentally relevant compounds using fast GC/TOF-MS. *Chimia* 55, 19-22.
- Huber, M.M., Gobel, A., Joss, A., Hermann, N., Löffler, D., McArdell, C.S., Ried, A., Siegrist, H., Ternes, T.A., von Gunten, U., 2005a. Oxidation of pharmaceuticals during ozonation of municipal wastewater effluents: A pilot study. *Environmental Science & Technology* 39, 4290-4299.
- Huber, M.M., Korhonen, S., Ternes, T.A., von Gunten, U., 2005b. Oxidation of pharmaceuticals during water treatment with chlorine dioxide. *Water Res.* 39, 3607-3617.
- Jjemba, P.K., 2006. Excretion and ecotoxicity of pharmaceutical and personal care products in the environment. *Ecotoxicology and Environmental Safety* 63, 113-130.
- Jobling, S., Nolan, M., Tyler, C.R., Brighty, G., Sumpter, J.P., 1998. Widespread Sexual Disruption in Wild Fish. *Environmental Science Technology* 32, 2498-2506.
- Jobling, S., Sumpter, J.P., 1993. Detergent components in sewage effluent are weakly oestrogenic to fish: An in vitro study using rainbow trout (*Oncorhynchus mykiss*) hepatocytes. *Aquatic Toxicology* 27, 361-372.
- Johnson, A.C., Sumpter, J.P., 2001. Removal of Endocrine-Disrupting Chemicals in Activated Sludge Treatment Works. *Environmental Science and Technology* 35, 4697-4703.

## REFERENCES

- Jones, O.A.H., Voulvoulis, N., Lester, J.N., 2007. Ecotoxicity of pharmaceuticals. In: Petrovic, M., Barcelo, D. (Eds.). *Comprehensive Analytical Chemistry: fate and removal of pharmaceuticals in the water cycle*. Elsevier, Amsterdam, The Netherlands.
- Joss, A., Keller, E., Alder, A.C., Gobel, A., McArdell, C.S., Ternes, T., Siegrist, H., 2005. Removal of pharmaceuticals and fragrances in biological wastewater treatment. *Water Research* 39, 3139-3152.
- Karvelas, M., Katsoyiannis, A., Samara, A., 2003. Occurrence and fate of heavy metals in the wastewater treatment process. *Chemosphere* 53, 1201- 1210.
- Kasim, N.A., Whitehouse, M., Ramachandran, C., Bermejo, M., Lennernas, H., Hussain, A.S., Junginger, H.E., Stavchansky, S.A., Midha, K.K., Shah, V.P., Amidon, G.L., 2004. Molecular Properties of WHO Essential Drugs and Provisional Biopharmaceutical Classification. *Molecular Pharmaceutics* 1, 85-96.
- Katsoyiannis, A., Samara, C., 2004. Persistent organic pollutants (POPs) in the sewage treatment plant of Thessaloniki, Northern Greece: occurrence and removal. . *Water Research* 38, 2685-2698.
- Katsoyiannis, A., Samara, C., 2005. Persistent organic pollutants (POPs) in the conventional activated sludge treatment process: fate and mass balance. *Environmental Research* 97, 245-257.
- Khan, S., 2002. Occurrence, Behaviours and Fate of Pharmaceutical Residues in Sewage Treatment. School of Civil and Environmental Engineering, (PhD thesis). The University of New South Wales, Sydney, Australia.
- Khan, S., Wintgens, T., Sherman, P., Zaricky, J., Schäfer, A.I., 2005. Individual and combined treatment modules for water recycling. *Environmental Progress* 24, 383-391.
- Kim, S.D., Cho, J., Kim, I.S., Vanderford, B.J., Snyder, S.A., 2007. Occurrence and removal of pharmaceuticals and endocrine disruptors in South Korean surface, drinking, and waste waters. *Water Research* 41, 1013-1021.

- Kimura, K., Amy, G., Drewes, J., Watanabe, Y., 2003a. Adsorption of hydrophobic compounds onto NF/RO membranes: an artifact leading to overestimation of rejection. *Journal of Membrane Science* 221, 89-101.
- Kimura, K., Amy, G., Drewes, J.E., Heberer, T., Kim, T.-U., Watanabe, Y., 2003b. Rejection of organic micropollutants (disinfection by-products, endocrine disrupting compounds, and pharmaceutically active compounds) by NF/RO membranes. *Journal of Membrane Science* 227, 113-121.
- Kimura, K., Toshima, S., Amy, G., Watanabe, Y., 2004. Rejection of neutral endocrine disrupting compounds (EDCs) and pharmaceutical active compounds (PhACs) by RO membranes. *Journal of Membrane Science* 245, 71-78.
- Kiso, Y., Kon, T., Kitao, T., Nishimura, K., 2001. Rejection properties of alkyl phthalates with nanofiltration membranes. *Journal of Membrane Science* 182, 205.
- Kiso, Y., Nishimura, Y., Kitao, T., Nishimura, K., 2000. Rejection properties of non-phenylic pesticides with nanofiltration membranes. *Journal of Membrane Science* 171, 229-237.
- Kolpin, D.W., Skopec, M., Meyer, M.T., Furlong, E.T., Zaugg, S.D., 2004. Urban contribution of pharmaceuticals and other organic wastewater contaminants to streams during differing flow conditions. *Science of The Total Environment*. 328, 119-130.
- Korner, W., Bolz, U., Sumuth, W., Hiller, G., Schuller, W., Hanf, V., Hagenmaier, H., 2000. Input/output balance of estrogenic active compounds in a major municipal sewage plant in Germany. *Chemosphere* 40, 1131-1142.
- Kosjek, T., Heath, E., Krbavcic, A., 2005. Determination of non-steroidal anti-inflammatory drug (NSAIDs) residues in water samples. *Environment International* 31, 679-.
- Koutsouba, V., Heberer, T., Fuhrmann, B., Schmidt-Baumler, K., Tsipi, D., Hiskia, A., 2003. Determination of polar pharmaceuticals in sewage water of Greece by gas chromatography-mass spectrometry. *Chemosphere* 51, 69-75.
- Lange, R., Dietrich, D., 2002. Environmental risk assessment of pharmaceutical drug substances-  
-conceptual considerations. *Toxicology Letters* 131, 97-104.

## REFERENCES

- Larsen, T.A., Lienert, J., Joss, A., Siegrist, H., 2004. How to avoid pharmaceuticals in the aquatic environment. *Journal of Biotechnology* 113, 295-304.
- Lee, H.B., Peart, T.E., Chan, J., Gris, G., 2004. Occurrence of endocrine-disrupting chemicals in sewage and sludge samples in Toronto, Canada. *Water Quality Research Journal of Canada* 39, 57-63.
- Leslie, G., Marshall, T., Law, I., Don, L., 2002. Delivery and Performance of the Luggage Point Water Reclamation Project. Brisbane Water, Brisbane, Australia.
- Lester, J. N., 1987. Heavy metals in wastewater and sludge treatment processes. Vol II: Treatment and disposal. CRC Press. Inc. Boca Raton, Florida, pp 15-40.
- Lester, J.N., Harrison, R.M., Perry, R., 1979. The balance of heavy metals through a sewage treatment works I. Lead, cadmium and copper. *The Science of The Total Environment* 12, 13-23.
- Lindqvist, N., Tuhkanen, T., Kronberg, L., 2005. Occurrence of acidic pharmaceuticals in raw and treated sewages and in receiving waters. *Water Research* 39, 2219-2228.
- Liu, R., Zhou, J.L., Wilding, A., 2004. Simultaneous determination of endocrine disrupting phenolic compounds and steroids in water by solid-phase extraction-gas chromatography-mass spectrometry. *Journal of Chromatography A* 1022, 179-189.
- Löffler, D., Rombke, J., Meller, M., Ternes, T.A., 2005. Environmental fate of pharmaceuticals in water/sediment systems. *Environmental Science & Technology* 39, 5209-5218.
- Lopez-Ramirez, J.A., Oviedo, M.D.C., Alonso, J.M.Q., 2006. Comparative studies of reverse osmosis membranes for wastewater reclamation. *Desalination* 191, 137-142.
- Loraine, G.A., Pettigrove, M.E., 2006. Seasonal variations in concentrations of pharmaceuticals and personal care products in drinking water and reclaimed wastewater in Southern California. *Environmental Science & Technology* 40, 687-695.
- Macia', A., Borrull, F., Calull, M., Aguilar, C., 2004. Determination of some acidic drugs in surface and sewage treatment plant waters by capillary electrophoresis-electrospray ionization-mass spectrometry. *Electrophoresis* 25, 3441-3449.

- Matilainen, A., Vieno, N., Tuhkanen, T., 2007. Efficiency of the activated carbon filtration in the natural organic matter removal. *Environment International* In Press, Corrected Proof.
- Metcalf & Eddy, I., 2003. *Wastewater engineering: Treatment and Reuse*. McGraw-Hill, Inc., Singapore.
- Tchobanoglous, G., Burton, F., Leverenz, H. and Tsuchihashi, R., 2007. *Water Reuse*. McGraw-Hill, Inc., Singapore.
- Metcalf, C.D., Koenig, B.G., Bennie, D.T., Servos, M., Ternes, T.A., Hirsch, R., 2003. Occurrence of neutral and acidic drugs in the effluents of Canadian sewage treatment plants. *Environmental Toxicology and Chemistry* 22, 2872-2880.
- Moeder, M., Schrader, S., Winkler, M., Popp, P., 2000. Solid-phase microextraction-gas chromatography-mass spectrometry of biologically active substances in water samples. *Journal of Chromatography A* 873, 95-102.
- Moffat, A.C., 1986. *Clarke's Isolation and Identification of Drugs in pharmaceuticals, body fluids and postmortem material*, London, UK.
- Nakada, N., Shinohara, H., Murata, A., Kiri, K., Managaki, S., Sato, N., Takada, H., 2007. Removal of selected pharmaceuticals and personal care products (PPCPs) and endocrine-disrupting chemicals (EDCs) during sand filtration and ozonation at a municipal sewage treatment plant. *Water Research* 41, 4373-4382.
- Nakada, N., Tanishima, T., Shinohara, H., Kiri, K., Takada, H., 2006. Pharmaceutical chemicals and endocrine disrupters in municipal wastewater in Tokyo and their removal during activated sludge treatment. *Water Research* 40, 3297-3303.
- Nghiem, L.D., Schäfer, A.I., 2006. Critical risk points of NF/RO membrane filtration processes in water recycling applications. *Desalination* 187, 303-312.
- Nghiem, L.D., Schäfer, A.I., Melimelech, M., 2004. Removal of Natural Hormones by Nanofiltration Membranes: Measuring, Modeling and Mechanisms. *Environmental Science and Technology* 38, 1888-1896.

## REFERENCES

- Nielsen, J.S., Hrudey, S.E., 1983. Metal loading and removal at a municipal activated sludge plant. *Water Research* 17, 1041-1052.
- Noble, R and Alexander Stern, S. "1995" *Membrane separations technology: principle and applications*, Elsevier
- Orhon, D., Ates, E., Sozen, S., Cokger, E., 1997. Characterization and COD Fractination of Domestic Wastewaters. *Environmental Pollution* 95,191-207.
- Otaki, M., Yano, K., Ohgaki, S., 1998. Virus removal in membrane separation process. *Water Science and Technology* 37, 10:107-116.
- Ozaki, H., Li, H., 2002. Rejection of organic compounds by ultra-low pressure reverse osmosis membrane. *Water Research* 36, 123-130.
- Paxéus, N., 1996. Organic pollutants in the effluents of large wastewater treatment plants in Sweden. *Water Research* 30, 1115-1125.
- Paxéus, N., Robinson, P., Balmér, P., 1992. Study of organic pollutants in municipal wastewater in Goteborg, Sweden. . *Water Science and Technology* 25 249-256. .
- Pham, T., Proulx, S., 1997. PCBs and PAHs in the Montreal urban community (Quebec, Canada) wastewater treatment plant and in the effluent plume in the St Lawrence River. *Water Research* 31, 1887-1896.
- Pichon, V., 2000. Solid-phase extraction for multiresidue analysis of organic contaminants in water. *Journal of Chromatography A* 885, 195.
- Pinkston, K.E., Sedlak, D.L., 2004. Transformation of Aromatic Ether- and Amine-Containing Pharmaceuticals during Chlorine Disinfection. *Environmental Science and Technology* 38, 4019-4025.
- Quintana, J.B., Carpinteiro, J., Rodriguez, I., Lorenzo, R.A., Carro, A.M., Cela, R., 2004. Determination of natural and synthetic estrogens in water by gas chromatography with mass spectrometric detection. *Journal of Chromatography A* 1024, 177.

- Radcliffe, J., 2003. Water- The Australian Dilemma. In: Radcliffe, J. (Ed.). WATER - The Australian Dilemma. Australian Academy of Technological Science and Engineering.
- Radcliffe, J., 2004. Water recycling in Australia. Australian Academy of Technological Science and Engineering, Victoria, Australia.
- Richardson, M.L., Bowron, J.M., 1985. The fate of pharmaceuticals in the aquatic environment. J. Pharm. Pharmacol. 37, 1-12.
- Roberts, P.H., Thomas, K.V., 2006. The occurrence of selected pharmaceuticals in wastewater effluent and surface waters of the lower Tyne catchment. Science of Total Environment 356, 143-153.
- Santarsiero, A., Veschetti, E., Donati, G., Ottaviani, M., 1998. Heavy Metal Distribution in Wastewater from a Treatment Plant. Microchemical Journal 59, 219-227.
- Santos, J.L., Aparicio, I., Alonso, E., 2007. Occurrence and risk assessment of pharmaceutically active compounds in wastewater treatment plants. A case study: Seville city (Spain). Environment International 33, 596-601.
- Schäfer, A.I., Nghiem, L.D., Waite, T.D., 2003. Removal of the natural hormone estrone from aqueous solutions using nanofiltration and reverse osmosis. Environmental Science and Technology 37, 182-188.
- Schäfer, A. and Wintgens, T., 2002 Membrane Technology: Course Manual 2002, Centre for Water and Waste technology, UNSW, Australia
- Schwarzenbach, R.P., Gschwend, P.M., Imboden, D.M., 2003. Environmental Organic Chemistry. Wiley-Interscience.
- Seghezzo, L., Zeeman, G., Van Lier, J., Hamelers, H., Lettinga, G., 1998. A review : The anaerobic treatment of sewage in the UASB and EGSB reactors. Bioresource Technology 65, 175- 190.
- Seiler, J.P., 2002. Pharmacodynamic activity of drugs and ecotoxicology--can the two be connected? Toxicology Letters 131, 105-113.



## REFERENCES

- Sekela, M., Brewer, R., Moyle, G., Tuominen, T., 1999. Occurrence of an environmental estrogen (4-nonylphenol) in sewage treatment plant effluent and the aquatic receiving environment. *Water Science and Technology* 39, 2170-2220.
- Sharp, J.H., Beauregard, A.Y., Burdige, D., Cauwet, G., Curless, S.E., Lauck, R., Nagel, K., Ogawa, H., Parker, A.E., Primm, O., 2004. A direct instrument comparison for measurement of total dissolved nitrogen in seawater. *Marine Chemistry* 84, 181-1993.
- Simpson, G., 2006. Personal Communication. Process Operations Engineer Production Branch, Brisbane Water, QLD, Australia. Email: poe3bw@brisbane.qld.gov.au
- Singh, K., Mohan, D., Sarita, S., Dalwani, R., 2004. Impact assessment of treated/untreated wastewater toxicants discharged by sewage treatment plants on health, agricultural and on environmental quality in the wastewater disposal area. *Chemosphere* 55, 227- 255.
- Snyder, S.A., Adham, S., Redding, A.M., Cannon, F.S., DeCarolis, J., Oppenheimer, J., Wert, E.C., Yoon, Y., 2007. Role of membranes and activated carbon in the removal of endocrine disruptors and pharmaceuticals. *Desalination* 202, 156-181.
- Snyder, S.A., Leising, J., Westerhoff, P., Yoon, Y., Mash, H., Vanderford, B., 2004. Biological and physical attenuation of endocrine disruptors and pharmaceuticals: Implications for water reuse. *Ground Water Monitoring and Remediation* 24, 108-118.
- Snyder, S.A., Westerhoff, P., Yoon, Y., Sedlak, D.L., 2003. Pharmaceuticals, personal care products, and endocrine disruptors in water: Implications for the water industry. *Environmental Engineering Science* 20, 449-469.
- Soliman, M.A., Pedersen, J.A., Suffet, I.H., 2004. Rapid gas chromatography-mass spectrometry screening method for human pharmaceuticals, hormones, antioxidants and plasticizers in water. *Journal of Chromatography A* 1029, 223-237.
- Sörme, L., Lagerkvist, R., 2002. Sources of heavy metals in urban wastewater in Stockholm. *Science of The Total Environment* 298, 131-145.
- Soulet, B., Tauxe, A., Tarradellas, J., 2002. Analysis of acidic drugs in Swiss wastewaters. *International Journal of Environment and Analytical Chemistry* 82, 659-667.

- Spengler, P., Korner, W., Metzger, J.W., 2001. Substances with estrogenic activity in effluents of sewage treatment plants in southwestern Germany. 1. Chemical analysis. *Environmental Toxicology and Chemistry* 20, 2133-2141.
- Staples, C.A., Dome, P.B., Klecka, G.M., Oblock, S.T., Harris, L.R., 1998. A review of the environmental fate, effects, and exposures of bisphenol A. *Chemosphere* 36, 2149-2173.
- Stumpf, M., Ternes, T.A., Wilken, R.-D., Silvana Vianna, R., Baumann, W., 1999. Polar drug residues in sewage and natural waters in the state of Rio de Janeiro, Brazil. *Science of The Total Environment* 225, 135-141.
- Tanghe, T., Devriese, G., Verstraete, W., 1998. Nonylphenol degradation in lab scale activated sludge units is temperature dependant. *Water Research* 32, 2889-2896.
- Taxe-Wuersch, A., De Alencastro, L.F., Grandjean, D., Tarradellas, J., 2005. Occurrence of several acidic drugs in sewage treatment plants in Switzerland and risk assessment. *Water Research* 39, 1761-1772.
- Tebbutt, T., 1992. Principles of water quality control. Pergamon Press, Oxford.
- Ternes, T., Bonerz, M., Schmidt, T., 2001. Determination of neutral pharmaceuticals in wastewater and rivers by liquid chromatography-electrospray tandem mass spectrometry. *Journal of Chromatography A* 938, 175-185.
- Ternes, T.A., 1998. Occurrence of drugs in German sewage treatment plants and rivers. *Water Research* 32, 3245-3260.
- Ternes, T.A., Herrmann, N., Bonerz, M., Knacker, T., Siegrist, H., Joss, A., 2004. A rapid method to measure the solid-water distribution coefficient (K<sub>d</sub>) for pharmaceuticals and musk fragrances in sewage sludge. *Water Research* 38, 4075-4084.
- Ternes, T.A., Meisenheimer, M., McDowell, D., Sacher, F., Brauch, H.J., Gulde, B.H., Preuss, G., Wilme, U., Seibert, N.Z., 2002. Removal of pharmaceuticals during drinking water treatment. *Environmental Science & Technology* 36, 3855-3863.

## REFERENCES

- Ternes, T.A., Stuber, J., Herrmann, N., McDowell, D., Ried, A., Kampmann, M., Teiser, B., 2003. Ozonation: a tool for removal of pharmaceuticals, contrast media and musk fragrances from wastewater? *Water Research* 37, 1976-1982.
- Ternes, T.A., Stumpf, M., Mueller, J., Haberer, K., Wilken, R.D., Servos, M., 1999. Behaviour and occurrence of estrogens in municipal sewage treatment plants -- I. Investigations in Germany, Canada and Brazil. *Science of The Total Environment* 225, 81-92.
- Thomas, P.M., Foster, G.D., 2005. Tracking acidic pharmaceuticals, caffeine, and triclosan through the wastewater treatment process. *Environmental Toxicological Chemistry* 24, 25-30.
- Tixier, C., Singer, H.P., Oellers, S., Muller, S.R., 2003. Occurrence and fate of carbamazepine, clofibric acid, diclofenac, ibuprofen, ketoprofen, and naproxen in surface waters. *Environmental Science and Technology* 37, 1061-1068.
- Tolls, J., 2001. Sorption of Veterinary Pharmaceuticals in Soils: A Review. *Environmental Science and Technology* 35, 3397-3406.
- U.S. Environmental Protection Agency, 2002. Ground water & Drinking Water: list of Drinking Water Contaminants & MCLs. U.S. Environmental Protection Agency.
- United States Pharmacopeia, 2000. Drug Information for the Health Care Professional. Micromedex, Englewood, USA.
- Van der Bruggen, B., Lejon, L., Vandecasteele, C., 2003a. Reuse, treatment and discharge of the concentrate of pressure-driven membrane processes. *Environmental Science & Technology* 37, 3733-3738.
- Van der Bruggen, B., Schaep, J., Maes, W., Wilms, D., Vandecasteele, C., 1998. Nanofiltration as a treatment method for the removal of pesticides from ground waters. *Desalination* 117, 139-152.
- Van der Bruggen, B., Schaep, J., Wilms, D., Vandecasteele, C., 1999. Influence of molecular size, polarity and charge on the retention of organic molecules by nanofiltration. *Journal of Membrane Science* 156, 29.

- Van der Bruggen, B., Vandecasteele, C., 2002. Modeling of the retention of uncharged molecules with nanofiltration membranes. *Water Res* 36, 1360-1368.
- Van der Bruggen, B., Vandecasteele, C., Van Gestel, T., Doyen, W., Leysen, R., 2003b. A Review of Pressure-Driven Membrane Processes in Wastewater Treatment and Drinking Water Production. *Environmental Progress* 22, 46-56.
- Vanderford, B.J., Pearson, R.A., Rexing, D.J., Snyder, S.A., 2003. Analysis of endocrine disruptors, pharmaceuticals, and personal care products in water using liquid chromatography/tandem mass spectrometry. *Analytical Chemistry* 75, 6265 - 6274.
- Vieno, N., Tuhkanen, T., Kronberg, L., 2005. Seasonal variation in the occurrence of pharmaceuticals in the effluents from a sewage treatment plant and in the recipient water. *Environmental Science & Technology* 39, 8220-8226.
- von Gunten, U., 2003. Ozonation of drinking water: Part I. Oxidation kinetics and product formation. *Water Research* 37, 1443-1467.
- Webb, S.F., 2001. A data-based perspective on the environmental risk assessment of human pharmaceuticals 1 -Collation of available ecotoxicity data. Springer, Berlin, 175-201.
- Weigel, S., Bester, K., Huhnerfuss, H., 2001. New method for rapid solid-phase extraction of large-volume water samples and its application to non-target screening of North Sea water for organic contaminants by gas chromatography-mass spectrometry. *Journal of Chromatography A* 912, 151.
- Westerhoff, P., Yoon, Y., Snyder, S., Wert, E., 2005. Fate of endocrine-disruptor, pharmaceutical, and personal care product chemicals during simulated drinking water treatment processes. *Environmental Science and Technology* 39, 6649-6663.
- White, R., Jobling, S., Hoare, S.A., Sumpter, J.P., Parker, M.G., 1994. Environmentally persistent alkylphenolic compounds are estrogenic. *Endocrinology* 135, 175-182.
- Williams, M.E., Hestekin, J.A., Smothers, C.N., Bhattacharyya, D., 1999. Separation of Organic Pollutants by Reverse Osmosis and Nanofiltration Membranes: Mathematical Models and Experimental Verification. *Ind. Eng. Chem. Res.* 38, 3683-3695.

## REFERENCES

- Wilson, B.A., Smith, V.H., deNoyelles, F., Larive, C.K., 2003. Effects of Three Pharmaceutical and Personal Care Products on Natural Freshwater Algal Assemblages. *Environmental Science and Technology* 37, 1713-1719.
- Xu, P., Drewes, J.E., Bellona, C., Amy, G., 2005. Rejection of Emerging Organic Micropollutants in Nanofiltration-Reverse Osmosis Membrane Applications. *Water Environment Research* 77, 40-48.
- Zafra, A., del Olmo, M., Suarez, B., Hontoria, E., Navalon, A., Vilchez, J.L., 2003. Gas chromatographic-mass spectrometric method for the determination of bisphenol A and its chlorinated derivatives in urban wastewater. *Water Research* 37, 735-747.