



# Australian

## Water Conservation and Reuse Research Program

Endocrine Disrupting Chemicals (EDCs) and  
Pharmaceuticals and Personal Care  
Products (PPCPs) in Reclaimed Water in  
Australia.

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# Endocrine Disrupting Chemicals (EDCs) and Pharmaceuticals and Personal Care Products (PPCPs) in Reclaimed Water in Australia.

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City of Mitcham SA

Queensland EPA

Albury City Council

Western Water

Beaudesert Shire Council

Wide Bay Water Corporation

Ipswich Water

Narrandera Shire Council

## Abbreviations used in the report

AOP	advanced oxidation process
APE	alkylphenol ethoxylate
AWCRRP	Australian Water Conservation and Reuse Research Program
BPA	bisphenol A
DDD	(1,1-dichloro-2,2-bis( <i>p</i> -chlorophenyl)ethane
DDE	(1,1-dichloro-2,2-bis( <i>p</i> -chlorophenyl)ethylene
DDT	(1,1,1-trichloro-2,2-bis( <i>p</i> -chlorophenyl)ethane
DES	diethylstilbestrol
DOC	dissolved organic carbon
E1	estrone
E2	17 $\beta$ -estradiol
EE2	17 $\alpha$ -ethynylestradiol
EDC	endocrine disrupting chemical
EU	European Union
GAC	granular activated carbon
NOM	natural organic matter
NP	nonylphenol
OP	octylphenol
PAC	powder activated carbon
PBB	polybrominated biphenyl
PBDE	polybrominated diphenyl ether
PCB	polychlorinated biphenyl
PPCP	pharmaceutical and personal care product
STP	sewage treatment plant
TBT	tributyltin
US EPA	US Environmental Protection Agency

## Table of Contents

Executive Summary.....	5
1. Introduction.....	8
2. EDCs and PPCPs in Reclaimed Water .....	10
2.1. What are EDCs?.....	10
2.1.1. <i>Endocrine system</i> .....	10
2.1.2. <i>Mechanisms of endocrine disruption</i> .....	11
2.2. What are PPCPs? .....	13
2.3. Occurrence of EDCs and PPCPs in Reclaimed Water.....	13
2.5. Environmental Fate of EDCs and PPCPs in Water Reuse Situations.....	16
3. Potential Impact of EDCs and PPCPs on Ecosystem and Human Health	18
3.1. An Overview of EDC and PPCP Effects on Organisms.....	18
3.1.1. <i>EDCs</i> .....	18
3.1.2. <i>PPCPs</i> .....	19
3.2. Potential Impact of EDCs and PPCPs on Ecosystem and Human Health Associated with Water Reuse.....	19
4. Potential Treatment Technologies in Removing or Reducing EDCs and PPCPs in Waste streams.....	21
4.1. Removal in Biological Wastewater Treatment.....	21
4.2. Removal by Adsorption to Solids Formed by Coagulant Addition.....	22
4.3. Removal by Activated Carbon.....	22
4.4. Removal by Conventional and Advanced Oxidation Processes.....	23
4.5. Removal by Direct Photolysis .....	24
4.6. Removal by Membrane Filtration.....	24
4.7. Summary of Removal Performance.....	25
5. Knowledge Gaps on EDCs and PPCPs in Reclaimed Water in Australia	26
References.....	28

## **Executive Summary**

This review on endocrine disrupting chemicals (EDCs) and pharmaceuticals and personal care products (PPCPs) associated with recycled water in Australia is a part of the Australian Water Conservation and Reuse Research Program (AWCRRP). Therefore, it needs to be read together with the other reviews under the program for an appreciation of the proper context of water reuse covered in the program.

The specific objectives of the review were: (i) to provide a summary of existing Australian and international research on EDCs and PPCPs that are likely to be present in reclaimed water; (ii) to summarize the data on presence of these contaminants in reclaimed water and their environmental fate relevant to water reuse situations; (iii) to provide an overview of potential effects and impacts of these organic contaminants in reclaimed water on ecosystem and human health; and (iv) to identify knowledge gaps and research needs on EDCs and PPCPs in reclaimed water in Australia.

### **Current State of Knowledge on EDCs and PPCPs**

EDCs and PPCPs are emerging environmental issues, which have attracted increasing attention internationally and generated some concerns among the scientific community, media and general public. In recent years, evidence has emerged showing that some chemicals (e.g. estradiol, nonylphenol, bisphenol A, PCBs and some pesticides) at certain concentrations can cause disruption to endocrine systems and can affect hormonal control of development in aquatic organisms and wildlife (Hayes et al., 2002; Damstra et al., 2002, Lintelmann et al., 2003). These chemicals are often described as endocrine disrupting chemicals (EDCs). Evidence on the effects of exposure to EDCs on wildlife is substantial, including some reports from Australia (e.g. Batty and Lim, 1999). Observed endocrine disruption effects include imposex of molluscs by organotin compounds; developmental abnormalities, demasculisation and feminisation of alligators in Florida by organochlorines; feminisation of fish by waste water effluent from sewage treatment plants and paper mills; hermaphroditism in frogs from pesticides (Damstra et al., 2002, Lintelmann et al., 2003). In contrast, while some published reports suggest endocrine disruption effects on human health such as decrease in semen quality and increase in cancer (testicular and breast cancer) rates, a causal relation between exposure to such chemicals and adverse health effects in humans has not been firmly established, except in isolated cases, for example, a synthetic hormone diethylstilbestrol (DES) has been shown to cause reproductive and developmental problems (Damstra et al. 2002).

PPCPs are a group of compounds which include pharmaceutical drugs, ingredients in cosmetics, food supplements, and other personal care products, as well as their respective metabolites and transformation products (Daughton and Ternes, 1999). Residues of PPCP have been detected in sewage effluent (Ternes, 1998; Khan and Ongerth, 2002) and in aquatic environments (Heberer, 2002a&b; Kolpin et al., 2002). Many of the PPCPs are designed to be biologically active and therefore the wide detection of these compounds in sewage effluents and in the environment has generated some concern about their potential impact on ecosystem and human health. Some reports have been published raising issues

such as the possible development of antibiotic-resistant bacteria upon exposure to untreated hospital and domestic sewage effluents (Andersen and Sandaa, 1994; Reinthaler et al., 2003), genotoxic effects of certain drugs (Hartmann et al., 1998), and endocrine disruption by therapeutically administered synthetic and natural hormones (Purdom et al., 1994). However, there are many unknowns concerning potential long-term subtle effects on non-target organisms.

### **Occurrence and Fate of EDCs and PPCPs in Reclaimed Water**

EDC and PPCP have been detected in treated wastewater effluents at concentrations ranging from ng/L to µg/L, possibly due to incomplete removal during sewage treatment. Commonly reported EDCs in reclaimed waters include estrogens (estradiol, and estrone), the contraceptive drug ethynylestradiol, and surfactant degradation products nonylphenols (NP) and octylphenol (OP) and their mono- and diethoxylates (NPE1 and NPE2). In effluents from treatment plants, hormones are generally detected at low (<10) ng/L concentrations, whereas the alkylphenols and their ethoxylates are found in the range of µg/L range. All of these compounds have shown estrogenic activities to varying degrees of potency, and can cause feminisation of male fish at elevated concentrations in aquatic environments (Purdom et al., 1994). However, the EDCs such as estradiol and nonylphenols have been found to be susceptible to biodegradation under aerobic conditions. In contrast, some other known and potential EDCs (e.g. PCBs, DDT and their metabolites) present at trace levels in effluent are much more persistent in the environment.

Various PPCPs have been detected in wastewater, including antibiotics, nonsteroidal anti-inflammatory drugs, beta-blockers, antiepileptics and disinfectants such as triclosan, and many others (e.g. Ternes, 1998; Khan and Ongerth, 2002). Wastewater reuse on agricultural land may result in such compounds being transferred to the soil environment, yet little is known about their fate in these environments. Many drugs are very polar and, as a result, highly mobile in the environment; therefore they could leach into groundwater (as demonstrated by Berlin groundwater contamination by clofibric acid (Heberer and Stan, 1997)). In general, the fate of EDCs and PPCPs depends not only on the physiochemical properties of the individual compound but also on the nature of the receiving environment (pH, redox condition, etc).

### **Potential Impact of EDCs and PPCPs Associated with Water Reuse**

The studies reported in Australian and international literature have shown adverse impacts due to the exposure of aquatic organisms to EDCs, but no cause and effect relation has been established for human health. The critical factor that will determine the risk of adverse impacts on terrestrial and aquatic organisms through water reuse in Australian environments is the degree to which they are exposed to any EDCs present. The highest potential risk exists for the situation where untreated effluent is directly discharged into the aquatic environment (there are some cases in Australia) where receptor organisms may be directly exposed to these compounds. Indeed, in the literature, most reports of endocrine disruption relate to direct exposure in aquatic

environments, either due to spills of EDCs or direct discharge of effluent with low dilution in the receiving environment. Application of reclaimed water on land may lead to rapid breakdown of degradable organic compounds but potentially also to accumulation of persistent organic compounds depending on loadings, soil and environmental conditions. Release of compounds to surface water and leaching of mobile compounds to groundwater may potentially occur, but not to the same degree as would be expected in the case of direct discharge or injection. Contamination or uptake by plants on lands irrigated with wastewater is possible and exposure via food to toxicants can occur but so far there is little information in the literature enabling clear understanding of these pathways. In any case, it must be recognized that the land application of recycled water provides greater opportunities for attenuation of EDCs and PPCPs in the soil environment as compared to direct discharge of wastewater effluent in riverine or marine environments. It is difficult to properly assess the potential risks due to EDCs and PPCPs without sufficient data on their transformation, fate and exposure. However, due to the low concentrations of EDCs and PPCPs reported in treated wastewater, the risks to human and ecosystem health are expected to be low, especially for the case where reclaimed water is used for irrigation on agricultural land.

### **Knowledge Gaps and Future Priorities**

The major knowledge gap in relation to assessment of potential risks associated with EDCs relates to the lack of information on potential exposure to these compounds through reuse of water under Australian environmental conditions. The exposure is dependent on several factors including type of water reuse, the nature of EDCs present and their concentration in any reclaimed water. Some of the factors that will determine the levels of EDCs in Australian wastewaters include the source of reclaimed water (urban, industrial, rural), efficiency of the treatment process, the fate and behaviour of EDCs under the climatic conditions in various parts of Australia (tropical versus temperate), dilution and other factors. These factors are expected to vary from site to site.

Recognizing the need for a sound assessment of risks and impacts of EDCs in reclaimed water in Australian environment, the following are identified as future priorities.

- (1) Identify important scenarios of water reuse in Australia, based on the nature of application, environmental conditions, receptor environments etc.
- (2) Identify priority EDCs and PPCPs and establish their residue levels in reclaimed water under the selected scenario. Development and validation of sensitive and robust analytical methods (including chemical and biological) for EDCs and PPCPs is an essential prerequisite to this.
- (3) Quantify the fate of EDCs and PPCPs in wastewater treatment plants and in the identified receiving environment;
- (4) Carry out a risk assessment using the existing hazard data from international literature together with scenario-specific Australian data on potential exposure to EDCs and PPCPs.
- (5) Identify management options available (including improved treatment) to minimise the risks under scenarios with significant potential risk.

## 1. Introduction

Due to the scarcity of fresh water resources, effluents from wastewater treatment plants as well as stormwater have increasingly been reclaimed and reused around the world. In some arid and semi-arid regions, in particular, reclaimed water has been recognized as a valuable resource (Asano and Levine, 1996), especially for non-potable use such as irrigating crops. However, depending on the nature of application of reclaimed water (Table 1), there is considerable public concern about potential risks associated with pathogens, inorganic and organic contaminants to the environment and human health (Abdulraheem, 1989; Gallegos et al., 1999). A wide range of organic contaminants may be present in wastewater and the environment receiving it (Daughton and Ternes, 1999; EU 2001; Kolpin et al. 2002). These include PAHs, PCBs, pesticides, detergent residues (alkylphenols), plasticisers (DEHP), linear alkylbenzene sulfonates (LASs), natural and synthetic estrogens, poly brominated diphenyl ethers (PDBEs), disinfection byproducts and others. Some of these chemicals have the potential to disrupt the normal function(s) of endocrine systems in organisms and thus causing health effects on wildlife and humans (Damstra et al. 2002). These chemicals are commonly referred to as endocrine disrupting chemicals (EDCs). Large amounts of pharmaceuticals and personal care products (PPCPs) are in common use for treatment and personal care of humans and animals, which may end up in wastewater effluents and surface water (Daughton and Ternes, 1999; Heberer 2002a&b). Some PPCPs have endocrine disrupting effects (e.g. contraceptive ingredient ethinylestradiol), but have varying modes of action and effects on non-target organisms.

Indeed, EDCs and PPCPs are some of the compounds of emerging environmental concerns in relation to water reuse. The issue of EDC in Australia has been discussed in the context of effluent reuse (Lim et al., 2000), ecosystem health (Ying and Kookana, 2002; Kookana et al. 2003; Chapman and Moore, 2003) and human health impact through drinking water (Falconer et al., 2003; Moore and Chapman, 2003). On PPCPs, however, relatively little information is available in Australia, except the work by Khan (2002). Internationally, several reviews have been carried out in recent years on EDCs and PPCPs (e.g. Damstra et al. 2002; Lintelmann et al. 2003; Heberer 2002a&b). Recently, Global Water Research Coalition (GWRC 2003) has published several reports on EDCs in relation to their sources, occurrences in water, methods of their measurement, knowledge gaps and priorities.

Owing to increasing reuse of reclaimed water, we reviewed current knowledge on the issue of EDCs and PPCPs, their occurrence and fate, as well as their potential impact on the ecosystem health associated with water reuse on land. The organic contaminants other than EDCs and PPCPS in wastewater are not covered in this review and readers are referred to other reviews in literature (e.g. EU 2001 and reviews cited therein; Birkett and Lester, 2003).

The specific objectives of the study were:

- (i) to provide a summary of existing Australian and International research on EDCs and PPCPs that are likely to be present in reclaimed water;
- (ii) to summarize the data on the presence of these contaminants in reclaimed water and their environment fate relevant to the water reuse situations;
- (iii) to review potential effects and impact of these organic contaminants in reclaimed water on ecosystem and human health; and
- (iv) to identify knowledge gaps and research needs on EDCs and PPCPs in reclaimed water in Australia.

Table 1. Water reuse application for wastewater and potential concerns related to each application (after Birkett and Lester 2003).

Water reuse application		Potential concerns for reusing wastewater					
		Negative Public perception	Toxicity to Aquatic Biota	Eutrophication	Pathogens	Heavy metals	Toxic organic compounds
<b>Potable</b>	Pipe to pipe	✓			✓	✓	✓
	Groundwater recharge,	✓			✓	✓	✓
	Surface water discharge,	✓	✓	✓	✓	✓	✓
<b>Non Potable</b>	Groundwater recharge,				✓	✓	✓
<b>Agricultural use</b>	Crop Irrigation,	✓			✓	✓	✓
<b>Industrial use</b>	Cooling, Washing, Construction, Stack scrubbing,						
<b>Recreational</b>	Landscape irrigation,	✓			✓	✓	✓
	Boating and fishing,	✓	✓	✓	✓	✓	✓
	Bathing,	✓	✓	✓	✓	✓	✓
<b>Urban use</b>	Fire protection,				✓		✓
	Toilet flushing,				✓		
	Air conditioning, Street/car washing,				✓	✓	✓

## 2. EDCs and PPCPs in Reclaimed Water

In this section, we provide some background information on EDCs and PPCPs, followed by discussions on their occurrence in reclaimed water and their fate in the environment associated with water reuse.

### 2.1. What are EDCs?

An endocrine disrupting chemical has been defined, by the Organization of Economic and Cooperative Development (OECD), as “an exogenous substance or mixture that alters the function(s) of the endocrine systems and consequently causes adverse health effects in an intact organism, or its progeny or (sub) populations” (Lister and Van Der Kraak, 2001).

From reports in literature, a wide range of chemicals have been found or suspected to be capable of disrupting the endocrine systems (Table 2). The list of EDCs include:

- pesticides (e.g. DDT, vinclozolin, TBT, atrazine),
- persistent organochlorines and organohalogens (e.g. PCBs, dioxins, furans, brominated fire retardants),
- alkyl phenols (e.g. nonylphenol and octylphenol),
- heavy metals (e.g. cadmium, lead, mercury),
- phytoestrogens (e.g. isoflavoids, lignans,  $\beta$ -sitosterol), and
- synthetic and natural hormones (e.g.  $\beta$ -estradiol, ethynylestradiol).

A list of EDCs, as compiled by Ying and Kookana (2002) from different sources is provided in Table 2. Many of these compounds have little in common structurally or in terms of their chemical properties, but evoke agonist (similar) or antagonist responses, possibly through comparable mechanisms of action.

It is pertinent to describe the endocrine system briefly here, before discussing the mechanisms of endocrine disruption.

#### 2.1.1. Endocrine system

An endocrine system is found in nearly all animals, including mammals, non-mammalian vertebrates (e.g. fish, amphibians, reptiles and birds) and invertebrates (e.g. snails, lobsters, insects and other species). Along with the nervous system, the endocrine system is one of the two communication systems that regulate all responses and functions of the body.

The endocrine system consists of endocrine glands (ductless glands that discharge hormones directly into blood stream) and the hormones they produce, thus guiding the development, growth, reproduction and other bodily functions in humans and animals.

The major endocrine glands of the body include the pituitary, thyroid, parathyroid, adrenals, pancreas, pineal gland and gonads (ovaries in females and testes in males).

Hormones are the biochemicals that act as chemical messengers and interact with specific receptors in cells to trigger responses and prompt normal biological functions. Hormones generally fall into four main categories: (1) amino acid derivatives, (2) proteins, (3) steroids and (4) eicosanoids (Lister and van der Kraak, 2001). The unifying nature of hormone action is the presence of receptors on target cells, which bind a specific hormone with high affinity and stereo-specificity. Steroid and thyroid hormones act by entering target cells and stimulating specific genes. All other hormones bind to receptors on the cell surface and activate second-messenger molecules within the target cells. The body has hundreds of different kinds of receptors; each one is designed to receive a particular kind of chemical signal. The hormone and its receptor have a 'lock-and-key' relationship. The binding of the hormone with the receptor triggers the production of particular proteins that 'turn on' the biological activity associated with the hormone.

Subtle effects on the endocrine system can result in changes in growth, development or behaviour that can affect the organism itself, or the next generation (Guillette et al., 1996; vom Saal et al., 1997; Palanza et al., 1999). Hormones play a crucial role in the proper development of the growing fetus. Embryos and fetuses are especially sensitive at particular times to low doses of endocrine disruptors (Guillette et al., 1996; vom Saal et al., 1997; Palanza et al., 1999). Substances that have no effect in an adult can impact the developing embryo. The timing of exposure may be more important than the dose. The ultimate effects of endocrine disruption might not be seen until later in life or even until the next generation (Colborn et al., 1996; US EPA, 1997).

### *2.1.2. Mechanisms of endocrine disruption*

There are several ways that chemicals can interfere with the endocrine system (Sonnenschein and Soto, 1998). They can mimic or block natural hormones, alter hormonal levels and thus affect the functions controlled by hormones. Less direct effects involve alteration of the body's ability to produce hormones, interference with the ways hormones travel through the body and changes in numbers of receptors. Regardless of the situation, having too much or too little of the hormones the endocrine system needs may cause it to function inappropriately.

EDCs can cause endocrine disruption through a range of mechanisms by acting as:

- (1) environmental estrogens, e.g. methoxychlor, bisphenol A;
- (2) environmental antiestrogens, e.g. dioxin, endosulfan;
- (3) environmental antiandrogens, e.g. vinclozolin, DDE,
- (4) toxicants that reduce steroid hormone levels, e.g. fenarimol, endosulfan;
- (5) toxicants that affect reproduction primarily through effects on the central nervous system, e.g. dithiocarbamate; and
- (6) others (e.g. altering thyroid hormone levels, aromatase activity).

Table 2. List of suspected/known endocrine disrupting chemicals (EDCs) compiled from literature by Ying and Kookana (2002).

Classification	Endocrine disrupting chemicals	
Pesticides	2,4-D Atrazine Benomyl Carbaryl Cypermethrin Chlordane ( $\gamma$ -HCH) DDT and its metabolites Dicofol Dieldrin/Aldrin Endosulfan Endrin Heptachlor Hexachlorobenzene (HCB) Iprodione	Kepone (Chlordecone) Lindane Malathion Mancozeb Methomyl Methoxychlor Mirex Parathion Pentachlorophenol Permethrin Simazine Toxaphene Trifluralin Vinclozolin
Organohalogens	Dioxins and furans PCBs	PBBs and PBDEs 2,4-Dichlorophenol
Alkylphenols	Nonylphenols Octylphenols Pentaphenols	Nonylphenol ethoxylates Octylphenol ethoxylates Butylphenols
Heavy metals	Cadmium Lead	Mercury Arsenic
Organotins	Tributyltin (TBT)	Triphenyltin (TPhT)
Phthalates	Di-ethylhexyl phthalate Butyl benzyl phthalate Di-n-butyl phthalate Di-n-pentyl phthalate	Di-hexyl phthalate Di-propyl phthalate Dicyclohexyl phthalate Diethyl phthalate
Natural Hormones	17 $\beta$ -Estradiol Estrone	Estriol Testosterone
Pharmaceuticals	Ethinylestradiol Mestranol	Tamoxifen Diethylstilbestrol (DES)
Phytoestrogens	Isoflavonoids Coumestans Lignans	Zearalenone $\beta$ -sitosterol
Phenols	Bisphenol A	Bisphenol F
Aromatic hydrocarbons	Benzo(a)pyrene Benz(a)anthracene Benzo(b/h)fluoranthene 6-hydroxy-chrysene	Anthracene Pyrene Phenanthrene n-Butyl benzene

## 2.2. What are PPCPs?

Pharmaceuticals and personal care products (PPCPs) include a large number of chemical contaminants that can originate from human usage and excretion, veterinary applications of a variety of products, such as prescription/non-prescription medications, and fungicides and disinfectants used for industrial, domestic, agricultural and livestock practices (Daughton and Ternes, 1999). PPCPs and their metabolites are continually introduced into the aquatic environment and are prevalent at detectable concentrations (Kolpin et al., 2002), which can affect water quality and potentially impact drinking water supplies, and ecosystem and human health (Roefler et al., 2000; Trussell, 2001; Heberer, 2002b).

The main sources of contaminant PPCPs are sewage effluents, hospital waste, and animal waste. Effluents from sewage treatment plants contain a variety of PPCPs such as clofibric acid, naproxen, ibuprofen, caffeine, triclosan and antibiotics, which are not completely removed during treatment (Ternes, 1998; Boyd et al., 2003). The PPCPs that have been reported in the aquatic environment are: analgesics and anti-inflammatory drugs, antibiotics/bacteriostatics (antibacterial drugs), antiepileptic drugs, beta-blockers, blood lipid regulators, cytostatic drugs, oral contraceptives (17 $\alpha$ -ethinylestradiol and mestranol) and others (Heberer, 2002a; Daughton and Ternes, 1999).

The long-term effects of continuous, low-level exposure to PPCPs and their metabolites are not well understood (Daughton and Ternes, 1999). This is a matter of concern since pharmaceuticals are designed to be biologically active, and may affect non-target organisms. Furthermore, there is evidence for the development of antibiotic-resistant bacteria upon exposure to untreated hospital and domestic sewage effluents (Andersen and Sandaa, 1994; Reinthaler et al., 2003), for genotoxic effects of certain drugs (Hartmann et al., 1998), and for endocrine disruption by therapeutically administered synthetic and natural hormones (Purdom et al., 1994).

## 2.3. Occurrence of EDCs and PPCPs in Reclaimed Water

There are cocktails of organic compounds in recycled water, including disinfection byproducts formed by chlorination during treatment, and refractory synthetic organic compounds added to sewage by households, hospitals and industries, and not removed by the wastewater treatment processes (Drewes and Jekel, 1998). Among these compounds, many of them could be classified as known or potential EDCs, which include pesticides, organohalogenes, phthalates, surfactant degradation products, hormones (naturally excreted by animals and humans, or synthesized as drugs) and some PPCPs. The levels of these organic compounds in reclaimed water depend on the input and treatment technology used in wastewater treatment plants.

In Australia, there is little published data on the levels of EDCs and PPCPs in wastewater effluents; most of the available monitoring data are on heavy metals, pesticides and organic compounds of industrial origin. There are very few published data on emerging

contaminants such as hormones, alkylphenols and PPCPs in Australia. Consequently, we mainly discuss data of these compounds from overseas studies. However, the levels of EDCs and PPCPs in the effluents from Australian wastewater treatment plants may or may not be similar to those found overseas. The ambient environmental conditions during the treatment process may have a significant effect on the levels of these compounds in treated wastewater. For example, in a comparative study on a Brazilian and a German sewage treatment plant (STP), Ternes et al. (1999a, b) observed significant difference in hormone removal rates between the two STPs and suspected higher temperature in Brazilian STP may have been responsible for higher removal rates.

Some EDCs such as nonylphenols, octylphenols and estrogens, and pharmaceuticals have been widely identified and reported in wastewater effluents overseas (e.g. Daughton and Ternes, 1999; Nasu et al., 2001; Rudel et al., 1998; Tabata et al., 2001; Kuch and Ballschmitter, 2001). The levels are in the range of parts per trillion (ng/L) to parts per billion ( $\mu\text{g/L}$ ) for most EDCs and PPCPs in treated wastewater effluents (tables 3, 4 and 5). Concentrations of metabolites of alkylphenol ethoxylates (APE) including nonylphenols (NP) and octylphenols (OP) in treated wastewater effluents have been found to range from  $<0.1 \mu\text{g/L}$  to  $369 \mu\text{g/L}$  in the US; between  $6 \mu\text{g/L}$  and  $343 \mu\text{g/L}$  in Spain, and up to  $330 \mu\text{g/L}$  in the UK. Estrogenic steroids have been detected in effluents of sewage treatment plants in different countries at concentrations ranging up to  $70 \text{ ng/L}$  for estrone (E1),  $64 \text{ ng/L}$  for  $17\beta$ -estradiol (E2),  $18 \text{ ng/L}$  for estriol (E3) and  $42 \text{ ng/L}$  for ethynylestradiol (EE2), respectively. Ternes (1998) reported detection of diclofenac, indometacin, ibuprofen, naproxen, ketoprofen and phenazone with concentrations more than  $1 \mu\text{g/L}$  in STP effluents. The concentration of diagnostic contrast media such as iopamidol and iopromide were found as high as  $15 \mu\text{g/L}$  in STP effluents due to their high usage (Ternes and Hirsch, 2000).

Table 3. Concentration of alkylphenols and their ethoxylates in effluents of sewage treatment plants (STPs) (Ying et al., 2002b).

Location	Sample numbers	Concentration ( $\mu\text{g/L}$ ) *				
		NP	NPE1	NPE2	NPE3	OP
Canada	8	0.8-15.1 (1.9)				0.12-1.7 (0.69)
UK	16	<0.2-5.4 (0.5)				
Switzerland	2	5-11	30-65	47-77		
Spain	3	6-343				
Japan	10	0.08-1.24	0.21-2.96			0.02-0.48
USA	6	0.18-15.9 (1.52)			8.77-78.8 (46.2) <sup>δ</sup>	
	1	16	5.5	0.8		0.15
	6	0.171-37 (1.02)			<LOD-332 (9.3) <sup>δ</sup>	<LOD-0.673 (0.072)
Germany	16	<LOD-0.77 (0.111)				<LOD-0.073 (0.014)
Italy	12	0.7-4 (1.8)			2-27 (10) <sup>δ</sup>	

\* Concentration range and median in parentheses. LOD = limit of detection. NP = nonylphenols; OP = 4-t-octylphenol; NPE1, NPE2, NPE3 = nonylphenol mono-, di-, tri-ethoxylates.

<sup>δ</sup>Concentration of total NPE.

Table 4. Concentration of hormones in effluents of STPs (Ying et al., 2002a).

Location	Concentration (ng/L)*			
	Estrone (E1)	17 $\beta$ -Estradiol (E2)	Estriol (E3)	Ethinylestradiol (EE2)
Italy	2.5-82.1 (9.3)	0.44-3.3 (1.0)	0.43-18 (1.3)	<LOD-1.7 (0.45)
Netherlands	<0.4-47 (4.5)	<0.1-5.0 (<LOD) <sup>a</sup>	-	<0.2-7.5 (<LOD)
Germany	<LOD-70 (9)	<LOD-3 (<LOD)	-	<LOD-15 (1)
Canada	<LOD-48 (3)	<LOD-64 (6)	-	<LOD-42 (9)
UK	1.4-76 (9.9)	2.7-48 (6.9)	-	<LOD-7 (<LOD)
Japan	-	3.2-55 (14) <sup>b</sup>	-	-
	-	<LOD-43 (13) <sup>c</sup>	-	-
		0.3-30 (14) <sup>d</sup>		
USA	-	0.477-3.66 (0.9)	-	<LOD-0.759 (0.248)
Germany	<0.1-18 (1.5)	<0.15-5.2 (0.4)	-	<0.10-8.9 (0.7)

\* Concentration range and median in parentheses.

<sup>a</sup> LOD = limit of detection. <sup>b</sup> summer sampling. <sup>c</sup> autumn sampling. <sup>d</sup> winter sampling.

Table 5. Concentrations of selected PPCPs in effluents of STPs.

Compound name	Concentration ( $\mu\text{g/L}$ )	Reference
Benzafibrate	0.02-0.07	Miao et al., 2002
	<0.25-4.6	Ternes, 1998
Clofibric acid	<LOD-0.51	Heberer et al., 2001
	<LOD-2	Garrison et al., 1976
	0.25-4.55	Stan & Heberer, 1997
Diclofenac	0.01-0.56	Heberer et al., 2001
	0.03-0.07	Miao et al., 2002
Ibuprofen	<0.005-0.01	Miao et al., 2002
	<0.05-1.43	Gans et al., 2002
	0.002-0.081	Buser et al., 1999
Naproxen	0.22 $\pm$ 0.15	Khan, 2002
	0.02-0.30	Miao et al., 2002
	<LOD-0.12	Heberer et al., 2001
	>0.05-0.52	Ternes, 1998
Metoprolol	0.35 $\pm$ 0.12	Khan, 2002
	>0.025-2.2	Hirsch et al., 1996; Ternes, 1998
Carbamazepine	0.28-1.11	Gans et al., 2002
	>0.05-6.3	Ternes, 1998
Triclosan	0.01-0.02	Boyd et al., 2003
	0.2-2.7	McAvoy et al., 2002

## 2.5. Environmental Fate of EDCs and PPCPs in Water Reuse Situations

The risk of EDCs and PPCPs to humans and the environment is strongly influenced by their fate and behavior in the environment. Given the wide range of EDCs and PPCPs that may be present in reclaimed water, their fate in the environment is expected to vary greatly with the nature of compound in question. For example,  $17\beta$ -estradiol is generally found at ng/L levels in the environment, it has low persistence in water and soil (less than a week) and has moderate affinity for sorption on organic carbon ( $K_{oc}$ ) and mobility in the environment (Ying et al., 2002a). In contrast, endosulfan is usually detected at  $\mu\text{g/L}$  level, shows much longer persistence in water and soil (an average half-life of 50 days) and has much higher  $K_{oc}$  and low mobility with water. The high value of  $K_{oc}$ , representing greater sorption affinity for organic carbon, indicates greater potential of the compound to be associated with sewage sludge rather than wastewater. NP has been reported to rapidly dissipate in soils with an estimated half-life ranging from 4.5 days to 16.7 days (Topp and Starratt, 2000). Indicative environmental fate parameters of some EDCs are presented in Table 6.

Enormous quantities of PPCPs are prescribed by humans to treat various diseases and used in personal care. Khan and Ongerth (2004) reported the amounts of the top ten pharmaceutical drugs used in Australia range from 10 to 296 tonnes per annum and there are at least 50 drugs with use greater than 1.8 tonnes per annum. A fraction of the drugs end up in WWTPs and because of incomplete removal in the treatment plants many of these drugs or their metabolites have been detected in treated wastewater (e.g. Richardson and Bowron, 1985; Singer et al., 2002). Khan and Ongerth (2004) used a conceptual model for predicting the fate (including aerobic biodegradation) of the top 50

pharmaceutical drugs in Australia, and found a wide variation in residual concentrations and half-lives in STPs. They predicted that 27 of the pharmaceuticals and 2 metabolites can be expected to be present in raw sewage at a concentration of 1 µg/L or greater.

Many drugs have very high water solubilities and thus are mobile in the environment. In 1992, the drug metabolite clofibric acid, was first found in Berlin groundwater samples and in groundwater samples collected from former sewage irrigation fields near Berlin (Stan and Linkerhagner, 1992; Heberer, 2002b). Polar chemicals in reclaimed water used for irrigation, could leach into groundwater as demonstrated in Berlin.

The environmental fate and behavior of EDCs and PPCPs may vary greatly with temperature and the matrix in which they are present and as a result, their breakdown rates and persistence are different in environmental compartments such as water, soil and air. Even the rate of removal of EDCs during treatment in the sewage treatment plant has been found to depend on several factors including the chemical nature of the compound, the treatment technology and climatic conditions (Schäfer et al. 2002). Movement of organic contaminants in soil also is closely related to soil characteristics such as soil organic matter, clay contents and pH. Therefore, in order to assess the fate and behavior of these organic contaminants in reclaimed water, we need to understand not only the chemical structure and properties, but also the environmental conditions such as climate and soil physiochemical properties.

Table 6. Some indicative parameters for the environmental fate and behaviour of EDCs (estimated or compiled from various sources in the literature) (Kookana et al., 2003).

Parameter	17 β-estradiol	β-sitosterol	bisphenol A	4-nonyl-phenol	endosulfan
Potency (relative to estradiol)	1	1/220,000	1/15,000	1/5000	1/5,000,000
Environmental concentration reported (µg/L)	<0.010	20-50	< 1	0.2-200	<5
Mobility (Koc, L/kg)	<5000	unknown	<1000	60000	10000
Half-life	<week	unknown	<month	days	months
Bioconcentration factor	2000	unknown	200	10,000	5000

### **3. Potential Impact of EDCs and PPCPs on Ecosystem and Human Health**

In this chapter, we provide an overview of the reported effects of EDCs and PPCPs on organisms in general, followed by a discussion on potential impacts of these compounds on ecosystems and human health in situations associated with water reuse.

#### **3.1. An Overview of EDC and PPCP Effects on Organisms**

##### *3.1.1. EDCs*

Hormone-like effects of chemicals have been observed for decades in fish, wildlife and humans, at levels of exposure that in many cases exceed the normal environmental concentrations (Colborn et al, 1993; Guillette et al., 1994; Kavlock et al., 1996; Jobling et al., 1998; Sonnenschein and Soto, 1998, Damstra et al., 2002). In recent years, considerably greater evidence has been accumulated showing that some chemicals (e.g. estradiols, nonylphenol, bisphenol A, PCBs and some pesticides) at certain concentrations can cause disruption to endocrine systems that control development in aquatic organisms and wildlife (Hayes et al., 2002; Damstra et al., 2002).

Damstra et al. (2002) reported that “there is sufficient evidence to conclude that adverse endocrine-mediated effects have occurred in some wildlife species”. These include imposex of molluscs by organotin compounds (Alzieu, 2000; Gibbs et al., 1990; Horiguchi et al., 1994); developmental abnormalities, demasculisation and feminisation of alligators in Florida by organochlorines (Guillette et al., 1994 and 2000); feminisation of fish by waste water effluent from sewage treatment plants and paper mills (Jobling et al., 1998; Bortone et al., 1989); hermaphroditism in frogs from pesticides such as atrazine (Hayes et al. 2002).

There are reports that human testicular and breast cancer rates have increased during the last four decades, especially in developed countries (Brown et al., 1986; Hakulinen et al., 1986; Adami et al., 1994; Feuer, 1995; Moller, 1993; Ries et al., 1991; Wolff et al., 1993). However, except in a few cases (e.g. DES), a causal relation between exposure to chemicals and adverse health effect in humans has not been firmly established.

In Australia, the endocrine disruption effects reported so far is listed below. However, it is noteworthy that these reports do not relate to wastewater reuse. The observed effects include:

- abnormal reproductive and developmental functions in offspring of women who took DES and thalidomide (Colborn et al., 1996),
- imposex of marine molluscs in harbours caused by TBT in antifouling paints (Daly and Fabris, 1993; Kohn and Almasi, 1993; Burt and Ebell, 1995),
- reduced gonopodium size of male mosquito fish (*Gambusia a. holbrooki*) exposed to sewage effluent in NSW (Batty and Lim, 1999),

- decreased fertility of sheep in WA caused by phytoestrogen in pasture grasses (Bennetts et al., 1946; Adams, 1998) and
- decreased breeding success of the peregrine falcon in South Australia being associated with high organochlorine residues (Falkenberg et al., 1994).

In summary, endocrine disruption is a complex field of study and the majority of scientific community believe that, while laboratory evidence demonstrates that some chemicals behave as endocrine disrupters and can potentially cause adverse health impact in wildlife and humans, more research is needed to establish cause and effect relationship for endocrine disruption effects (Birkett, 2003). Nevertheless, GWRC (2003) concluded that since the EDCs are present in influent and effluent from treatment plants, use of untreated surface water as drinking water (e.g. urban areas of developing countries), is not without risk.

### *3.1.2. PPCPs*

PPCPs include many classes of drugs such as hormone steroids, antibiotics, blood lipid regulators, nonopioid analgesics/nonsteroidal anti-inflammatory drugs, beta-blockers/ $\beta_2$ -sympathomimetics, antidepressants, antiepileptics, antineoplastics, impotence drugs, tranquilizers, and retinoids, and many personal care products such as fragrances, preservatives and disinfectants (Daughton and Ternes, 1999; Khan, 2002). It is clear that these PPCPs have different modes of action, toxicity and effects on nontarget organisms. There are some reports on the effects of PPCPs on non target organisms. They include hormonal disruption by steroid drugs (Purdum et al., 1994), bacterial resistance to antibiotics and antimicrobials (Reinthal et al., 2003), genotoxicity of fluoroquinolones (Hartmann et al., 1998), physiological responses from antidepressants such as inducing spawning of bivalves by serotonin (Fong, 1998), and toxicity of amino nitro musk transformation products to aquatic organisms (Behechti et al., 1998).

## **3.2. Potential Impact of EDCs and PPCPs on Ecosystem and Human Health Associated with Water Reuse**

The critical factor that will determine the risk of adverse impact through water reuse in the Australian environment is the degree of exposure of terrestrial or aquatic organisms to EDCs and PPCPs. While there is evidence in the literature of potential endocrine disruption effects of chemicals on aquatic life, there is a clear lack of data on exposure that precludes any meaningful assessment of risk. Only broad qualitative assessment can be made considering various scenarios of potential water reuse.

The worst case of risk (if any) exists in the scenario where untreated effluent is directly discharged into the aquatic environment, where receptor organisms have direct exposure to these compounds or the water is used for drinking purposes. Indeed, in literature, most reports on endocrine disruption relates to direct exposure in the aquatic environment, either due to spill of EDCs or direct discharge of effluent with low potential dilution in

the receiving environment. Aquifer storage of reclaimed water for subsequent recovery would also lead to some degree of attenuation of EDCs during storage, depending upon the residence time, the aquifer characteristics (aerobic, anaerobic, carbon and nutrient status) and type of compounds (Ying et al. 2003). The eventual level of exposure and risk will be determined by the end use of recovered water.

Among the various reuse applications (Table 1), industrial, urban and agricultural use will have lower risk than direct discharge of untreated effluent into the aquatic environment. Land application can lead to rapid breakdown of organic compounds but some persistent organic compounds may accumulate, depending on loadings, soil and environmental conditions. The release of compounds from soils to surface waters and the leaching of mobile compounds into groundwater may occur, but not to the same degree as from direct discharge or injection. Contamination or uptake by plants on lands irrigated with wastewater is possible and exposure via food to toxicants can potentially occur but there is little information in the literature to clearly understand these pathways. In any case, it needs to be recognized that land application of recycled water provides greater opportunities for attenuation of EDCs and PPCPs in the soil environment as compared to direct discharge of wastewater effluent into riverine or marine environments. While it is difficult to assess the potential risks due to EDCs and PPCPs without sufficient data on their fate and exposure, accepting the low levels of EDCs and PPCPs reported to be present in treated wastewater, the risks to the environment and humans are expected to be low, especially where reclaimed water is used for irrigation of agricultural land.

While there are several potential routes for human exposure to organics in reclaimed water, (including: plant uptake and consumption, airborne dust and vapors, and drinking of surface and ground water) no direct cause-effect relationship has been found so far between any exposure of EDCs and PPCPs in reclaimed water and human health. A review by the World Health Organisation (WHO) has concluded that low-level environmental exposure to EDCs has not yet been demonstrated to cause harm to human health (Damstra et al., 2002). GWRC (2003) concluded that uptake of EDCs by humans from treated drinking water is relatively low in comparison to other sources such as food. It has been reported that despite low concentrations of organics in reclaimed wastewater, some of the EDCs (e.g. phthalates) can be bioconcentrated by plants (e.g. Yin et al., 2003) irrigated with the wastewater. Of course, some chemicals may also be metabolized by plants. The concentrations of EDCs and PPCPs in reclaimed water are many orders of magnitude lower than the concentrations likely to cause detectable health impacts in humans (Falconer et al. 2003) and therefore indirect human exposure to these chemicals is also expected to be minimal (Moore and Chapman, 2003). However, as pointed out by Daughton and Ternes (1999), although acute toxicity is lacking, subtle effects of PPCPs might be the major concern. Clearly, there are aspects that need to be better understood before any meaningful inferences can be drawn to quantify the effects of PPCPs on the environment.

## **4. Potential Treatment Technologies in Removing or Reducing EDCs and PPCPs in Waste streams**

EDCs and PPCPs present in waste streams intended for reuse may potentially be removed by a variety of conventional and developing technologies including biological wastewater treatment, adsorption on porous media (including deep bed filters and subsurface aquifer material), coagulant and/activated carbon addition, oxidation (including advanced oxidation) processes, UV degradation and membrane separation. It should be recognized however that EDCs and PPCPs possess a wide range of chemical properties and the ease of removal by any specific technology may vary greatly depending upon the particular properties. Indeed, as shown by Stumpf et al. (1999), the removal rates of some polar drugs during passage through a Brazilian STP varied from 12 to 90%.

### **4.1. Removal in Biological Wastewater Treatment**

The extent of removal of EDCs in activated sludge sewage treatment has been reviewed by Johnson and Sumpter (2001) with emphasis given to the fate of alkylphenol polyethoxylates (APEs) and steroid estrogens. As indicated earlier, while APEs such as nonylphenol polyethoxylates (NPEs) could represent a significant fraction (up to 10%) of the DOC (dissolved organic carbon) entering sewage treatment plants, these compounds are successfully eliminated in an activated sludge environment by biodegradation. However, troublesome breakdown products such as nonylphenol (NP) and shorter chain ethoxylates including hydrophilic carboxylated species are now recognized to form. While the carboxylated species would be expected to remain in solution (and have been shown to be relatively resistant to further biodegradation), compounds such as NP are hydrophobic ( $\log K_{ow} = 4.5$ ) and will preferentially distribute to the solid phase. Sludges are normally treated by anaerobic digestion but NP appears to persist under these conditions. Steroid estrogens have been observed to be removed in the activated sludge process to an extent reasonably consistent with their hydrophobicity. Thus,  $17\alpha$ -ethinylestradiol (EE2), with a  $\log K_{ow}$  of around 4, is reasonably hydrophobic and has been found to exhibit, on average, 85% removal from the aqueous phase of activated sludge. This compound is not easily biodegraded so most of this removal presumably involves adsorption to the organic-rich solid phase. Similar removal rates have been reported for estradiol (E2) ( $\log K_{ow} = 3.1$ ) but estrone (E1), with a similar  $\log K_{ow}$ , exhibits variable and, at times, low removal rates. The variability in E1 removal rates may be related to the fact that it is reasonably biodegradable. Sumpter and Johnson (2001) concluded that while an increase in hydraulic retention time within the conventional activated sludge process should increase the extent of removal of these compounds, alternative technologies that remove these “microorganic contaminants” more effectively are likely to be required.

## 4.2. Removal by Adsorption to Solids Formed by Coagulant Addition

Metal salts such as aluminum sulfate and ferric chloride are commonly added in both water treatment and wastewater treatment to aid treatment. These salts hydrolyze and nucleate forming precipitates of the metal oxyhydroxides which both adsorb dissolved contaminants and induce removal of contaminant particles (such as clays and particulate organic matter) by increasing collision frequency. Natural organic matter (including bacterial exudates), which is negatively charged over most of the pH range of interest as a result of the deprotonation of acidic functional groups, adsorbs readily to oxyhydroxide surface groups, especially at neutral to acidic pHs where the oxyhydroxides exhibit a positive surface charge. Trace organics, even if charged, will be unlikely to compete with the bulk organic matter for these surface groups though they may be removed to some extent if the “background” organic content is not too high. Thus, approximately 25% of the NPEs in ground waters (which are generally relatively low in organics) have been reported to be removed during coagulation with alum (Fielding et al., 1998). Hydrophobic trace organic compounds exhibiting log  $K_{ow}$ 's of 3 or greater (such as bisphenol A, E2, EE2, octylphenol and PAHs) may partition to some extent to any organic coatings on the particles produced on coagulant addition but the more hydrophilic (negatively charged) entities would be expected to exhibit little affinity for organically coated oxide surfaces.

## 4.3. Removal by Activated Carbon

Activated carbon can be used to remove many different pesticides, pharmaceuticals and estrogenic compounds from aqueous streams. Hydrophobic interactions are the dominant mechanism for removal of most organic compounds in activated carbon adsorption systems though ion exchange interactions can result in removal of polar solutes (Snyder et al., 2003a&b; Crittenden et al., 1999). As a result of the hydrophobic interactions, activated carbon efficiently removes most nonpolar organic compounds (i.e. those compounds with log  $K_{ow} > 2$ ). The ability of activated carbon to remove more polar compounds will depend on the strength of the polar interactions though prediction of the strength of these interactions is difficult (Snyder et al., 2003b).

The presence of natural organic matter (NOM) or wastewater organics (such as bacterial exudates) may lower the extent of trace contaminant removal by activated carbon as a result of competition for surface sites (Wu and Pendleton, 2001) and/or pore blocking. Thus, Adams et al. (2002) found that the presence of 10.7 mg/L NOM decreased the removal of seven antibiotics spiked into river water by 10 to 20% (from 50 to >99%). Even more dramatic competitive effects were found by Chang et al. (2004) in comparative studies of estrone removal from secondary effluent compared to buffer solutions containing only estrone (at the same concentrations as in the effluent) though the differences were reduced at high PAC (powder activated carbon) doses.

The rate of adsorption of the trace contaminant to the activated carbon and the contact time provided will be important determinants of extent of contaminant removal. In PAC

systems, one to three hours contact time is normally provided prior to removal of the PAC by settling/filtration compared to contact times of typically less than 30 minutes in GAC (granular activated carbon) where the effluent is passed through a packed bed. The rate of adsorption of contaminants to the activated carbon will be determined by the nature of the activated carbon used (the smaller the size, the more rapid will be the uptake kinetics), by the presence of competing solutes and, at least in GAC where systems may operate for some months, by how long the GAC has been in operation since more strongly adsorbable constituents can displace previously adsorbed compounds.

#### **4.4. Removal by Conventional and Advanced Oxidation Processes**

A range of oxidants including chlorine, chloramines, chlorine dioxide and ozone are used in water and wastewater treatment for disinfection purposes. These oxidants may also induce the transformation of organic compounds present in the aqueous streams to which they are applied. Chlorine is widely used in Australia, and when added to water forms HCl and the weak acid, hypochlorous acid (HOCl), which dissociates to the hypochlorite anion ( $\text{OCl}^-$ ) at higher pH ( $\text{pK}_a = 7.5$ ). Both hypochlorous acid and hypochlorite anion are strong oxidants, with HOCl recognized to be the more facile oxidant of the two. HOCl/ $\text{OCl}^-$  would be expected to react with the phenolic groupings in EDC/PPCP compounds with addition of chlorine to the ring and possibly, subsequent ring cleavage. The chlorine-induced transformation of various EDC/PPCPs has been reported (Huang et al., 2001; Sedlak and Pinkston, 2001; Gould and Richards, 1984) with recent studies by Pinkston and Sedlak (2004) showing a substantial influence of ring substituents on reaction rate. These workers also investigated the rates of reaction of a range of pharmaceuticals and model compounds with combined chlorine and found these to be substantially slower than with an equivalent dose of free chlorine.

Chlorine dioxide ( $\text{ClO}_2$ ) is a relatively stable free radical which is applied either as an oxidant or a disinfectant in wastewater and drinking water treatment processes. Its use is attractive, in part, because of its apparent lower tendency to produce chlorinated byproducts than chlorine. While there have been no reports of investigations of the reactivity of  $\text{ClO}_2$  with EDC/PPCP compounds specifically, chlorine dioxide is recognized to react selectively with phenols. Hoigne and Bader (1994) have investigated the reaction of chlorine dioxide with a wide range of phenols. Since it is the phenoxide anion which reacts rapidly (up to  $10^6$  times as quickly as the non-dissociated species), the apparent total reaction rate constant increases for most types of phenols by a factor of 10 per pH increment over most of the pH range of interest in water treatment.

Ozone is a powerful oxidant and can oxidize substrates either directly or by producing hydroxyl radicals that then react with other entities (organic compounds, bicarbonate anions, bromide, etc). The two pathways compete for oxidizable substrates. Although the activation barrier for the direct oxidation of organics by aqueous ozone is much larger than that for oxidation by hydroxyl radicals, the concentration of molecular ozone is much larger than that of the radicals. Because the production of hydroxyl radicals is facilitated at high pH, the hydroxyl radical-mediated oxidation pathways tend to

dominate under those conditions, while direct oxidation with molecular ozone dominates under acidic conditions. In some processes referred to as advanced oxidation processes (AOPs), the formation of hydroxyl radicals from ozone is enhanced by exposure of the solution to UV light, addition of hydrogen peroxide, or other measures. While EDC/PPCPs would be expected to be prone to attack by hydroxyl radicals (and to react at diffusion controlled rates), a wide range of reactivities would be expected in direct attack by ozone. If these trace organic compounds are present in a matrix of natural organic matter or bacterial exudates, the “bulk” organics would be expected to be attacked in preference to the trace species though longer lived peroxy radicals generated by hydroxyl radical attack on the bulk material may be effective in inducing degradation of the trace contaminants. Ozone and AOPs in general would be expected to be particularly effective in degrading EDC/PPCPs in low DOC matrices such as groundwaters or tertiary treated effluents. While laboratory and field reports are far from extensive, a pilot plant study on ozonation and UV-disinfection effects has shown elimination of the steroidal hormone, estrone from a municipal sewage treatment plant effluent (Ternes et al., 2003). By applying an ozone dose as low as 5 mg/L over a contact time of 18 min, estrone was reduced from a mean concentration of 15 ng/L to less than the quantifiable limit of 3 ng/L. Ozonation processes have also shown promise for the efficient removal of EE2 (Huber et al., 2003).

#### **4.5. Removal by Direct Photolysis**

Direct exposure to sunlight has been found to be effective in EDC degradation in some instances with almost complete degradation within 100 hours (Gray and Sedlak, 2003). In natural systems however, effective removal may be limited by the rapid attenuation of the sunlight as a result of adsorption by other chromophores such as natural organic matter and light scattering by any particles present in the water column. UV irradiation in the presence of catalysts such as semiconducting  $\text{TiO}_2$  has been shown to reduce degradation times for estradiol to about 3 hours (Nakashima et al., 2002, Ohko et al., 2002). As found for algal toxins, degradation would be expected to be particularly effective under conditions where adsorption to the  $\text{TiO}_2$  surface occurs (Feitz and Waite, 2003) though at higher pH, long-lived peroxy radicals generated by hydroxyl radical attack on natural organic matter (if present) may lead to some degradation of trace contaminants.

#### **4.6. Removal by Membrane Filtration**

Most organic EDC/PPCPs range from 150 to 500 Daltons and thus removal from liquid streams may be undertaken by size exclusion using nanofiltration or reverse osmosis membranes. In view of the low molecular weight of most EDC/PPCPs, it is not surprising that loose nanofiltration membranes have been found to achieve only minor removal of EDCs, while tight nanofiltration achieve moderate to good removal (Schafer et al., 2003, Snyder et al., 2003a). Reverse osmosis will give almost complete removal from solution (Huang and Sedlak, 2001).

It should be noted that with membrane processes, highly effective removal may be initially observed but, in some instances, be misleading as a result of extensive adsorption of such trace contaminants on the membrane itself (Chang et al., 2003).

#### 4.7. Summary of Removal Performance

A summary of the removal performance of a variety of unit processes for a wide range of EDCs and PPCPs is presented in Table 6.

Table 6. Unit processes and operations used for EDCs and PPCPs removal and estimation of the extent of removal by individual processes (after Snyder et al., 2003b).

Group	Classification	AC	BAC	O <sub>3</sub> /AOPs	UV	Cl <sub>2</sub> /ClO <sub>2</sub>	Coagulation/ flocculation	Softening/ metal oxides	NF	RO	Degradation {B/P/AS} <sup>a</sup>
EDCs	Pesticides	E	E	L-E	E	P-E	P	G	G	E	E {P}
	Industrial chemicals	E	E	F-G	E	P	P-L	P-L	E	E	G-E {B}
	Steroids	E	E	E	E	E	P	P-L	G	E	L-E {B}
	Metals	G	G	P	P	P	F-G	F-G	G	E	P {B}, E {AS}
	Inorganics	P-L	F	P	P	P	P	G	G	E	P-L
	Organometallics	G-E	G-E	L-E	F-G	P-F	P-L	P-L	G-E	E	L-E
PhACs	Antibiotics	F-G	E	L-E	F-G	P-G	P-L	P-L	E	E	E {B} G-E {P}
	Antidepressants	G-E	G-E	L-E	F-G	P-F	P-L	P-L	G-E	E	G-E
	Anti-inflammatory	E	G-E	E	E	P-F	P	P-L	G-E	E	E {B}
	Lipid regulators	E	E	E	F-G	P-F	P	P-L	G-E	E	P {B}
	X-ray contrast media	G-E	G-E	L-E	F-G	P-F	P-L	P-L	G-E	E	E {B and P}
	Psychiatric control	G-E	G-E	L-E	F-G	P-F	P-L	P-L	G-E	E	G-E
PCPs	Synthetic musks	G-E	G-E	L-E	E	P-F	P-L	P-L	G-E	E	E {B}
	Sunscreens	G-E	G-E	L-E	F-G	P-F	P-L	P-L	G-E	E	G-E
	Antimicrobials	G-E	G-E	L-E	F-G	P-F	P-L	P-L	G-E	E	F {P}
	Surfactants/detergents	E	E	F-G	F-G	P	P-L	P-L	E	E	L-E {B}

<sup>a</sup>B, biodegradation; P, photodegradation (solar); AS, activated sludge; E, excellent (>90%); G, good (70–90%); F, fair (40–70%); L, low (20–40%); P, poor (<20%).

## **5. Knowledge Gaps on EDCs and PPCPs in Reclaimed Water in Australia**

Some guidelines and manuals have been developed in regard to reclaimed wastewater for irrigation (Chang et al., 1996; Marecos do Monte et al., 1996; US EPA, 1992). Most of the irrigation water quality criteria including Australian ones focus on parameters of nutrients, inorganic compounds and pathogens (Chang et al., 1996). This does not adequately address the possible risks to the environment and human health posed by many trace organic pollutants like EDCs and PPCPs in reclaimed wastewater.

Undoubtedly, the scientific evidence and the community concern about the potential adverse impact of EDCs and PPCPs in the environment are growing rapidly, both overseas and in Australia. Despite the fact that currently there are no regulatory or policy guidelines in Australia, many governmental and private agencies are taking proactive measures to deal with EDCs and PPCPs. There is a need to better understand the potential risks that may arise from the exposure to the EDCs and PPCPs present in reclaimed wastewater in Australia.

Research needs to be considered from the standpoint of understanding the risks of the EDCs and PPCPs to environmental health, since the endocrine disruption effects of chemicals on wildlife is more clearly demonstrated (Damstra et al 2002). This is not to say that concerns about potential human health impact of EDCs and PPCPs are unfounded but are inherently more complex and difficult to deal with.

Risk is a result of a process where the potential hazard (EDCs and PPCPs in this case) could lead to an adverse effect on the receptor (the target or non target organism). This could be only possible if there is sufficient exposure of the receptor to the source of threat (hazard). Considering the above, we place the research priorities in the context of ability to carry out a proper risk assessment as the next key step forward.

Currently, the clear missing information needed for risk assessment is adequate data on exposures in the Australian environment. Generally, the overseas data suggest that the levels of EDCs and PPCPs can vary from ng/L to µg/L. However, as GWRC (2003) concluded, the data reported is limited and may not reflect the overall situation concerning the levels of occurrence and exposure.

The exposure is dependent on several factors including the type of water reuse, the nature of EDCs and PPCPs and their concentration when present in reclaimed water in Australia. Some of the factors that will determine the levels of EDCs and PPCPs in Australian wastewater include, the source of reclaimed water (urban, industrial, rural), efficiency of treatment process, the fate and behaviour of EDCs and PPCPs under the climatic conditions in various parts of Australia (tropical versus temperate), dilution and other factors. These factors are expected to vary from site to site.

Since it is imperative to make a sound assessment of risks and impacts of EDCs and PPCPs in reclaimed water in Australian environment, the following are identified as the priorities for future.

- (1) Identify important scenarios of water reuse in Australia, based on the nature of application, environmental conditions, receptor environments etc. Identify the exposure routes and receptor organisms to be protected under these scenarios.
- (2) Establish the levels of priority EDCs and PPCPs in reclaimed water under the selected scenario. Development and validation of sensitive and robust analytical methods (including chemical and biological) for identification and quantification of EDCs and PPCPs is an essential prerequisite to this.
- (3) Quantify the fate of EDCs and PPCPs in wastewater treatment plants and in the receiving environment (under a range of environmental conditions – tropical versus temperate);
- (4) Carry out a risk assessment using the existing hazard data from literature together with scenario-specific Australian data on potential exposure to EDCs and PPCPs.
- (5) Identify management options available (including improved treatment) to minimise the risks under scenarios with significant potential risk.

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