

Occurrence of pharmaceutically active and non-steroidal estrogenic compounds in three different wastewater recycling schemes in Australia

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Abstract

Due to its more and more limited availability, clean water is now recognized as a valuable resource and this has changed the way wastewater is viewed. Once seen as a problem to be dealt with it is now a potential auxiliary source of water, thanks to recent advances in water treatment technology, particularly tertiary treatment for water recycling. The discovery that natural and synthetic chemicals, in the form of excreted hormones and pharmaceuticals, as well as a vast array of compounds with domestic and industrial applications, can enter the environment via wastewater treatment plants and cause a wide variety of toxic effects, suggests the need for improvement of wastewater treatment. Very low concentrations of organic contaminants are reportedly hazardous to the environment. Three Australian wastewater recycling schemes, two of which employ reverse osmosis (RO) technology, the other applying ozonation and biological activated carbon filtration (BAC), have been studied for their ability to remove trace organic contaminants including eleven pharmaceutically active compounds and two non-steroidal estrogenic compounds. Contaminant concentrations were determined using a sensitive analytical method comprising solid phase extraction, derivatization and GC MS with selected ion monitoring. In raw wastewater, concentrations of analgesics and non-steroidal anti-inflammatory medications were comparable to those found in wastewaters around the world. Remarkably, removal efficiencies for the three schemes were superior to literature values. RO was responsible for the greatest proportion of contaminant removal. The ability of the RO and microfiltration membranes to brine (concentrate) many of the compounds was demonstrated and highlights the need for continued research into monitoring wastewater treatment processes, improved water recycling schemes and ultimately, safer water and a cleaner environment.

Key words: Wastewater recycling, Trace organic removal, brine and concentrate, reverse osmosis, ozonation, biological active carbon filtration

1 Introduction

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. Hence there is a growing momentum favoring reuse of wastewater as well as a strong resistance to current disposal methods that have been seen as both environmentally damaging and a waste of potentially valuable resources (Beder, 1989).

However, some major wastewater treatment plants in Australia are still discharging primary effluents. In recent years, increasing pollution in the receiving waters and more stringent effluent limitations for discharges to sensitive zones have been the driving forces in implementing new treatment techniques. Targeted parameters - in addition to grit and suspended solids - are chemical oxygen demand (COD), biochemical oxygen demand (BOD), pH, total suspended solids (TSS), nutrients (nitrogen and phosphorus), cations, anions, heavy metals and priority pollutants. This new approach for wastewater management has greatly affected the concept of wastewater recycling and the quality of water produced may be suitable for a range of reuse applications. Work is in progress to determine tailored guidelines for different water reuse applications.

The number of organic compounds that have been synthesized since the turn of the century now exceeds a half million, and some 10,000 new compounds are added each year. As a result, many of these compounds are now also found in the wastewater from most municipalities and communities. Different classes of trace contaminants have been detected such as surfactants (Birkett and Lester, 2003, Paxéus, 1996), polycyclic aromatic hydrocarbons (PAHs) (Blanchard *et al.*, 2001, Blanchard *et al.*, 2004, Paxéus, 1996, Pham and Proulx, 1997), polychlorinated biphenyls (PCBs) (Blanchard *et al.*, 2001, Blanchard *et al.*, 2004, Paxéus *et al.*, 1992, Pham and Proulx, 1997), persistent organic compounds (Katsoyiannis and Samara, 2004), phthalates (Fromme *et al.*, 2002, Paxéus, 1996), non-steroidal estrogenic compounds (nSECs) (Bendz *et al.*, 2005, Birkett and Lester, 2003, Bolz *et al.*, 2000, Clara *et al.*, 2005, Khan *et al.*, 2005, Korner *et al.*, 2000, Lee *et al.*, 2004, Paxéus, 1996, Price *et al.*, 2005, Sekela *et al.*, 1999) steroid hormones (Khan, 2002, Khan *et al.*, 2005, Price *et al.*, 2005), pharmaceutically active compounds (PhACs) (Bendz *et al.*, 2005, Blanchard *et al.*, 2004, Carballa *et al.*, 2004, Clara *et al.*, 2005, Granier *et al.*, 1988, Joss *et al.*, 2005, Khan, 2002, Koutsouba *et al.*, 2003, Lindqvist *et al.*, 2005, Loraine and Pettigrove, 2006, Macia' *et al.*, 2004, Pham and Proulx, 1997, Price *et al.*, 2005, Stumpf *et al.*, 1999, Ternes, 1998, Vieno *et al.*, 2005) and pesticides (Dewedar *et al.*, 1995, Katsoyiannis and Samara, 2004, Singh *et al.*, 2004, Van der Bruggen *et al.*, 1998).

Most pharmaceuticals (if not all) administered to humans and animals are partially excreted and discharged directly to the sewage system depending upon the physiochemical properties of the compounds. Investigations carried out in Austria, Brazil, Canada, Croatia, England, Germany, Greece, Italy, Spain, Switzerland, the Netherlands and the United States detected more than 80 pharmaceuticals and their metabolites in the aquatic environment at concentrations in the µg/L range or lower (Herberer, 2002). Reported compounds include pharmaceuticals with a wide range of applications: analgesics, anti-inflammatory compounds, beta-blocker, lipid regulators, antiepileptic, antibiotics, X-ray media contrast agents and contraceptive drugs (Herberer, 2002, Khan, 2002). Carballa *et al.* (Carballa *et al.*, 2004) have studied the presence of 13 pharmaceutical and personal care products (PPCPs) corresponding to different kinds of substances (artificial masks, pharmaceuticals and hormones) as an indicator of the presence of this type of pollution in the municipal wastewater generated by Galicia City (NW Spain). Eight compounds were detected in raw wastewater (galaxolide, tonalide, ibuprofen, naproxen, sulfamethoxazole and iopromide). All these compounds were present in the range of 0.6 to 6.6 µg/L.

The overall removal efficiencies within the sewage treatment plant (STP) of Galicia City were between 40 to 90% (Carballa *et al.*, 2004). The detection of PhACs has also been reported in ground water contaminated by landfill leachate or manufacturing residues. Rarely, PhACs have also been detected in drinking water samples (Herberer, 2002).

Non-steroidal estrogenic compounds (nSECs), of which bisphenol A (BPA) is one of the most predominant examples and is manufactured in large quantities with over 90% being used in the plastic 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. Formme *et al.*, (2002) found low concentrations of BPA in surface water (0.0005 to 0.41 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).

Bergeron (1999) has reported the estrogenic activity of BPA, with potency orders of magnitude less than 17β-estradiol. Chen *et al.*, (Chen *et al.*, 2002) determined that other bisphenols used in industrial applications are also weakly estrogenic.

Nonylphenol ethoxylates (NPHEO) are a group of nonionic surfactants which are used in household and industrial applications. Under anaerobic conditions, biodegradation of nonylphenol ethoxylates yields the more toxic 4-substituted monoalkylphenol (4-nonylphenol, NP) (Sekela *et al.*, 1999). The estrogenic potencies of NP and its ethoxylates (NPEO) are in order of magnitude five to six times lower than 17-βestradiol. Levels of NPEO and NP in the United Kingdom range from <0.02 to 53 µg/L in surface water and from < 0.02 to 300 µg/L in effluent concentrations from sewage treatment plants (STW) (Birkett and Lester, 2003).

To place abundance of those compounds into perspective; Paxéus *et al.*, (1992) found that the major organic components in the influent to wastewater treatment plants were long chain fatty acids and their esters mainly from soap, edible oils and fat. The second largest group were the washing and cleaning related products consisting of ethers of polyethylene glycol (PEG) and polypropylene glycol (PPG), alkylphenols and alkylphenol ethoxylates (APEOs) which originated from detergents (Eriksson *et al.*, 2002, Paxéus, 1996, Paxéus and Schröder, 1996).

The primary objective of this study is to investigate the occurrence of nSECs and PhACs throughout wastewater recycling schemes. Acetaminophen, carbamazepin, clofibric acid, diclofenac sodium, gemfibrozil, ibuprofen, ketoprofen, naproxen, primidone, phenytoin and salicylic acid represent PhACs. BPA and NP represent nSECs. These compounds were selected based on previous detection in wastewater combined with anticipated health and environmental effects or bioaccumulation potential. This paper provides information that can be used for further research, in guiding regulatory providers and in designing further treatment schemes and monitoring programs. The results of this study will indicate the benefit of the technology implemented in wastewater recycling schemes.

2 Wastewater Recycling Schemes

2.1 Gerringong Gerroa Sewage Scheme (GGSS)

Owned by Sydney Water and operated by General Water Australia, the Gerringong Gerroa Sewerage 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 and receives domestic discharges. 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 (Boake, 2006, Sydney Water, 2005). A minimum of 80% of treated wastewater is used by adjacent dairy farmers for pasture production that currently irrigates 70 hectares (Radcliffe, 2004).

The GGSS consists of screens, a biological reactor, clarifier, sand filtration, ozonation, biological activated carbon (BAC), microfiltration (MF), UV disinfection and chlorination (see Figure 1). Samples were taken in December 2005.

2.2 Water Reclamation and Management Scheme (WRAMS)

The Water Reclamation and Management Scheme (WRAMS) 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 2.2ML/day and can treat up to 7ML/day (Chapman, 2006).

WRAMS consists of screen, grit removal, an activated sludge process, UV disinfection, microfiltration (MF), reverse osmosis (RO) and chlorination (see Figure 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 is only used as for storm water treatment which is supplied via a brickpit. Sewage is treated by MF only as no salt removal is intended. Samples were taken in May 2005.

2.3 Luggage Point Water Reclamation Plant (LPWRP)

Brisbane Water has ten sewage treatment plants (STPs), from which it discharges 285 ML/day into the environment (adjacent to the environmentally sensitive Moreton Bay), 2 ML/day are used on golf courses and more than 10 ML/day are recycled through LPWRP. 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 BP refinery (four km away) as cooling tower make up, boiler feed water and other process uses. LPWRP returns the rejects (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 consists of automatically backwashing 300 µm screens, microfiltration (MF) and reverse osmosis (RO) (see Figure 3). All wastewater is treated by RO in this case. Additional chemical treatment is used to adjust water pH and chlorination. Samples were taken in September 2005.

3 Materials and Methods

3.1 Chemicals

Standards of carbamazepine, clofibric acid, ibuprofen, ketoprofen, diclofenac sodium, naproxen, primidone, gemfibrozil, bisphenol A, 4-nonylphenol, salicylic acid, acetaminophen and phenytoin were all purchased from Sigma-Aldrich, Australia. Carbamazepine-d10, 2-hydroxybenzoic acid-d6, gemfibrozil-d6, (+/-)-ibuprofen-d3, 5,5, phenytoin-d10, and 4-n-nonylphenol 2,3,5,6-d6,O,D were purchased from Scientific Technology, Australia.

3.2 Sampling and sample preparation

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 Figure 1 to Figure 3. All samples were collected in 2.5 L amber glass bottles, transferred overnight and processed immediately.

Upon receipt in the laboratory each sample was filtered using three different filters, GF/D (2.7 µm) and GF/F (0.7 µm) Whatman filters and 0.48 µm Nylon filter membrane (Alltech, Australia). Filtered samples were kept in the amber bottle overnight at 4 °C and sample enrichment was carried out the next day. Before sample enrichment, water samples of one liter were allowed to reach room temperature and the pH was adjusted to pH 2-3 to enhance trapping of the acidic compounds on the solid phase extraction (SPE) sorbent. Finally, the wastewater samples were spiked with a mixture of

the deuterated internal standards for analyte quantitation. MilliQ water (1 L) was also spiked with a standard mixture of the investigated compounds to confirm recovery of analytes.

For solid phase extraction (SPE), 60mg Water Oasis HLB sorbent cartridges (Waters, Australia) were used. SPE was performed using a 24 fold extraction manifold (Supelco Visiprep 24). The SPE cartridges were conditioned sequentially with 5 mL methyl tetra butyl ether (MTBE), 5mL methanol and 5 mL MilliQ water. Extraction of the 1L sample was carried out under vacuum at a flow rate of approximately 15 mL/min. After sample loading the cartridge was washed with 3 mL 5% methanol in water (v/v). In order to eliminate the presence of water from the eluate, a column of anhydrous sodium sulfate was prepared and fitted under the SPE column before the elution procedure started. The SPE columns were eluted with 5 mL 10% methanol in MTBE (v/v). The elution volume was then evaporated to dryness at 39 °C under a stream of nitrogen.

To determine PhACs and nSECs concentrations, a derivatization step was necessary. The extract residues were dissolved in 300 µL of acetonitrile and then derivatized by adding 100 µL of BSTFA and TMCS (99:1). The analytes were allowed to react for 1h at 70 °C. Finally, 100 µL of fluazifop standards were added to each vial before injection as an instrument internal standard to confirm injection of each sample onto the GC column.

3.3 Identification and quantification of compounds

A Shimadzu-GC 17A gas chromatograph was used, equipped with an auto-injector model AOC-20i, mass detector model QP5000, Phenomenex Zebron ZB-5 column and Split / Splitless injector. The oven temperature program was 100 °C (0 min); 30 °C/min.; 150 °C (4 min); 3 °C /min; 195 °C (0 min.); 1 °C/min; 205 °C (5 min); 30 °C/min; 250 °C (3 min). The injection temperature was held at 270 °C. Helium was used as a carrier gas (flow rate 1 mL/min) and the interface temperature was held at 270 °C. For identification of each analyte, three compound specific ions were recorded in the SIM mode. Analytes were identified positively in case identical retention time and mass ratios similar to the mass ratio retrieved through calibration were obtained.

Deuterated standards were used as internal standard for quantitation of PhACs and nSECs (1ng/L). Calibration curves for PhACs and nSECs were found to be linear within the 5.0 to 0.1 ng/µL range. Minimum detection limits (MDLs) were 0.01µg/L for all analytes.

3.4 Determination of the concentration factor in reverse osmosis

The concentration factor is a ratio of the concentration of a component in the brine compared to the influent (feed), which depends on the recovery of water and retention of individual compounds. Retention is dependant on many factors such as the chemical characteristics of compounds, membrane characteristics, water matrix and adsorption interactions between compounds and membrane (Van der Bruggen *et al.*, 2003). The membrane recovery (r) and retention (or rejection) (Ret) are defined in equations (1) and (2), respectively.

$$r = \frac{Q_p}{Q_f} \quad (1)$$

$$\text{Ret} = 1 - \frac{C_p}{C_f} \quad (2)$$

The flow and mass balances are defined in equations (3) and (4).

$$Q_f = Q_p + Q_c \quad (3)$$

$$C_f Q_f = C_p Q_p + C_c Q_c \quad (4)$$

Where: Q_p , Q_f and Q_c are the permeate, feed and brine flow (L/h), respectively. Likewise, C_p , C_f and C_c are the permeate, feed and brine concentration (mg/L).

Combining the mass and flow balance in equations (3) and (4) with retention in equation (2) and recovery in equation (1) yields the concentration of solutes in the RO brine.

$$C_c = C_f \left[\frac{1 - (1 - \text{Re}_j) r}{1 - r} \right] \quad (5)$$

Dividing the concentration of solutes in the brine from equation (5) by the concentration of solute in the feed results in the concentration factor shown in equation (6)

$$F = \frac{C_c}{C_f} \quad (6)$$

3.5 Determination of other Chemical Parameters

Each sample collected from GGSS and LPWRP was characterized chemically by measuring pH, conductivity, absorbance at 245 nm, turbidity, total organic carbon (TOC, measured as non purgeable carbon (NPOC)) and total nitrogen (TN) in the laboratory.

TOC and TN were measured using Shimadzu model TOC- Vcsh equipped with the total nitrogen analyzer TNM-1. Other parameters such as pH, turbidity, absorbance and conductivity were determined using standard laboratory equipment.

Total solids (TS), total suspended solids (TSS), chemical oxygen demand (COD) and nutrient contents for the influent and effluents were provided by the scheme authorities as required.

4 Results and Discussion

The abundance of trace contaminants in water recycling schemes is of interest for a number of reasons. Firstly, the concentration in the product water has to date attracted the most attention due to the need for safety of the water, particularly if it is intended for human contact or even consumption (Higgins *et al.*, 2002). However, low contaminant concentrations resulting from advanced technology, such as ozonation and reverse osmosis, combined with low consumption of water, means that this is unlikely to be a problem, with the exception of failures such as the desorption of adsorbed contaminants (Nghiem and Schäfer, 2006). Secondly, skin contact and occupational health and safety of workers may be of concern. Little work is available on the human health risks of handling contaminants in recycled wastewater. This study aims to provide important data in terms of concentrations to be expected in different process streams.

Thirdly, and probably most crucially, discharge of partially treated wastewater, backwash waters and brines inland or into sensitive marine environments is a major concern. Further, this environmental health hazard may translate into a human health risk if compounds are accumulated or concentrated in seafood. In this research the concentration of compounds in process streams including microfiltration backwash water and reverse osmosis brines will be reported.

4.1 Physicochemical Characteristics

The physicochemical characteristics provided by the scheme operators for the influent and effluent streams reveal which parameters are parts of the continuous plant monitoring process (see Table 2). Results and monitored parameters vary between schemes. The most important learning from these results is that currently monitoring of recycling schemes is minimal. 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 (Higgins *et al.*, 2002). 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 enforced. 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. It should be noted here that the RO permeate and brine data has been analyzed on request for this research. In terms of organic content (COD) and total dissolved solids (TDS), RO is the superior treatment as expected from previous research.

To understand performance of the scheme in more detail, a small number of analyses were carried out in the laboratory. These parameters are pH, conductivity, turbidity, total organic carbon (TOC), absorbance at 245 nm and total nitrogen (see Figure 4). pH was observed to fluctuate between pH 6 and 9.

In GGSS, the trend of water quality is generally increasing during treatment. A dramatic decrease in turbidity, conductivity, absorbance, total nitrogen and organic carbon occurred after clarification and a significant further drop in turbidity occurred after BAC, however, beyond this treatment no further decrease in values for any of those parameters was detected (Figure 4).

In LPWRP the trend is also one of increased water quality. All parameter values dropped post activated sludge and further reductions were found for all parameters except absorbance after RO (Figure 4). The final water quality was superior with regards to organic carbon and conductivity which was evident from COD and TDS. Unfortunately, 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).

4.2 Trace Contaminants in Raw Wastewaters

The raw wastewater results for the GGSS samples show surprisingly little in the way of PhACs, compromising low concentrations of ibuprofen (0.7 µg/L), ketoprofen (0.2 µg/L) and gemfibrozil (0.05 µg/L) only (see Figure 5). These results may be explained by the small population (4000) and the possible dilution of domestic sewage with other waste streams entering the system. The presence of ibuprofen and ketoprofen (non-steroidal anti-inflammatory) and gemfibrozil (blood lipid regulator) could reflect the older population living in the Gerringong and Gerroa area.

The results in the LPWRP and WRAMS show a high concentration of four different compounds namely salicylic acid (38.8 and 9.0 µg/L), acetaminophen (8.1 and 23.3 µg/L), ibuprofen (10.3 and 2.8 µg/L), and naproxen (7.8 and 3.1 µg/L), respectively (Figure 5). The first two compounds are analgesics and the second are from the non steroidal anti-inflammatory group. 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, but more specifically, salicylic acid (38.5 µg/L) and naproxen (7.8 µg/L) are found at the highest published concentrations. 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 (Table 1). Bisphenol A was detected at high concentrations in the LPWRP, where local industry may have contributed, compared to the other two schemes.

Compounds not detected in the raw wastewater may have been present at concentrations lower than the detection limit.

4.3 Trace Organics Removal in Microfiltration (MF)

The contaminant concentrations in the influent, effluent and back flush reject of the MF for LPWRP and WRAMS show that the MF did not contribute to the removal of these compounds (Figure 5). Concentrations were at or below the detection limits in the influent, effluent and backwash water. These results agree with another study where only partial reduction in pharmaceuticals concentrations was demonstrated (Khan *et al.*, 2004). 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 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 the most effective treatment in removing the PhACs and nSECs even at influent concentrations below detection limits. RO brines may contain the highest concentrations if compounds are retained. These results agree with studies of other contaminated waters (Adams *et al.*, 2002, Drewes *et al.*, 2002, Heberer *et al.*, 2002, Khan *et al.*, 2004). RO membranes may further serve as a large reservoir for the PhACs and nSECs and their release is likely in the brine or during membrane cleaning processes. 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). Results of RO for WRAMS are inconclusive. It should be noted here that the RO was not fully operational during this sampling exercise and that when operation is resumed confirmatory data will be obtained. It should be noted here however, that trace organics from municipal effluents are not targeted in this scheme as municipal effluent is treated only with MF, not RO.

4.5 Concentration of Trace Organics in Reverse Osmosis (RO)

In light of the interest in the RO brine concentrations, the likely concentration factor of trace contaminants in the reverse osmosis process has been calculated. Figure 6 shows concentration factor as a function of recovery and retention. A water recycling plant RO is usually operated at a recovery between 80 to 95% and the retention of trace organics varies from 0 to 100%. Retention is dependant on many factors such as the chemical characteristics of compounds, membrane characteristics, water matrix and adsorption interactions between compounds and the membrane (Agenson *et al.*, 2003).

A maximum concentration factor of 40 times can hence be expected if a compound is fully retained and system recovery is high. A comparison between the mathematical model and actual results showed that diclofenac, naproxen, ketoprofen, carbamazepine & phenytoin have a concentration factor 10-20 while primidone, acetaminophen and bisphenol A have a concentration factor 3-9. While results are in the right order of magnitude, losses are likely to occur on the membranes, in sample analysis and incomplete retention (where levels are below the detection limit but volumes are high).

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 previous reports by Ternes (1998) that diclofenac, ibuprofen, indometacine, naproxen, ketoprofen and phenazone were present in more than 50% of the investigated STP discharge and the 90 percentile concentration of diclofenac and ibuprofen 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).

The removal efficiencies of PhACs and nSECs in the three schemes were determined by comparing the results of the raw wastewater and the recycled water. The removal rates of these compounds during passage through the different processes were higher than 90% for all compounds except for ketoprofen (80%). Despite the high concentrations in the raw wastewater, their removal was high in the treatment processes. In this study, the removal efficiencies are superior to literature values. 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 (Heberer *et al.*, 2002, Lindqvist *et al.*, 2005, Soulet *et al.*, 2002, Stumpf *et al.*, 1999, Ternes, 1998). The main reasons for variation are reported to be different treatment processes and variation in the functioning of the process (Soulet *et al.*, 2002, Tixier *et al.*, 2003). The hybrid processes ozonation and BAC as well as the MF and RO to treat municipal wastewater is applying the most advanced technology available. The water quality

produced is excellent and potentially too good for irrigation. The use of MF for water recycling produces a product of clearly lower quality.

These results indicate no doubt the effectiveness of advanced and more recently implemented technology in the different schemes such as ozonation, biological activated carbon, membranes and UV disinfection in the removal of trace contaminants. These results comply 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 this elimination of these compounds, which could be abiotic degradation induced by solar irradiation, biotransformation, physical sequestration or a combination of these, remains to be elucidated (Bendz *et al.*, 2005, Sekela *et al.*, 1999).

5 Conclusions

Three wastewater treatment plants have been analyzed for the presence of eleven pharmaceuticals and two non-steroidal estrogenic compounds, most of which have been detected in the influent of the three studied schemes. Some compounds were detected in other process streams such as MF backflush or RO brine which is indicative of an effective retention process but also demonstrates the creation of a new disposal problem. While the data is preliminary and requires confirmation with a longer term study, the presence of many trace organic compounds at substantial concentrations has been confirmed. Further work is required to determine the human and environmental health effects of those compounds in comparison with other exposure routes such as food residues.

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Figure Captions

Figure 1 Schematic of the Gerringong Gerroa Sewerage Scheme (GGSS) and sampling points used for this study.

Figure 2 Schematic of the Water Reclamation and Management Scheme (WRAMS) and sampling points used for this study.

Figure 3 Schematic of the Luggage Point Water Reclamation Plant (LPWRP) and sampling points used for this study.

Figure 4 Wastewater characteristics total organic carbon (TOC, measured as non purgeable organic carbon (NPOC)), turbidity, total nitrogen (TN), absorbance and conductivity of samples collected from GGSS (A) and LPWRP (B).

Figure 5 Concentrations of PhACs and nSECs in GGSS (A), WRAMS (B) and LPWRP (C).

Figure 6 Effect of recovery and retention on the concentration of compounds in the RO brine.

Figure 1

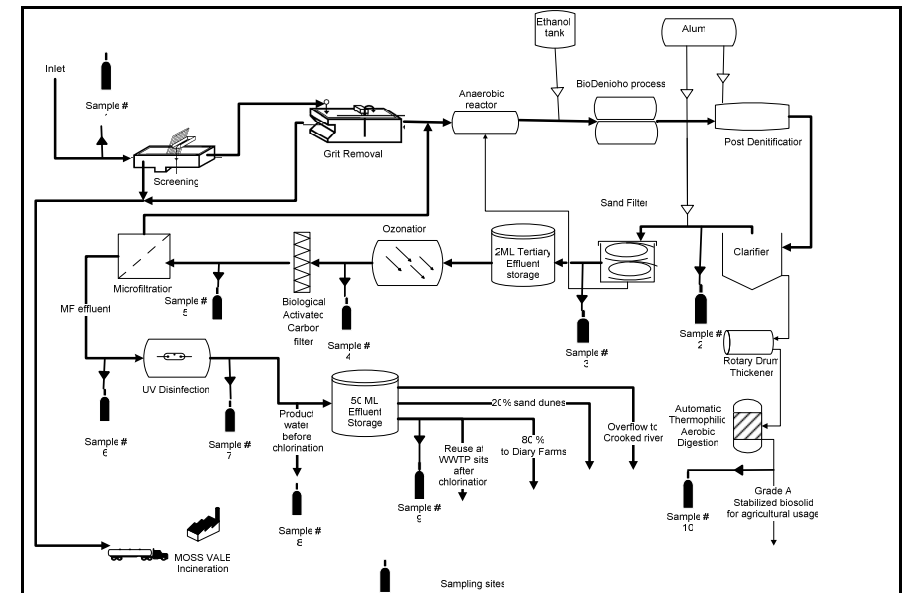


Figure 2

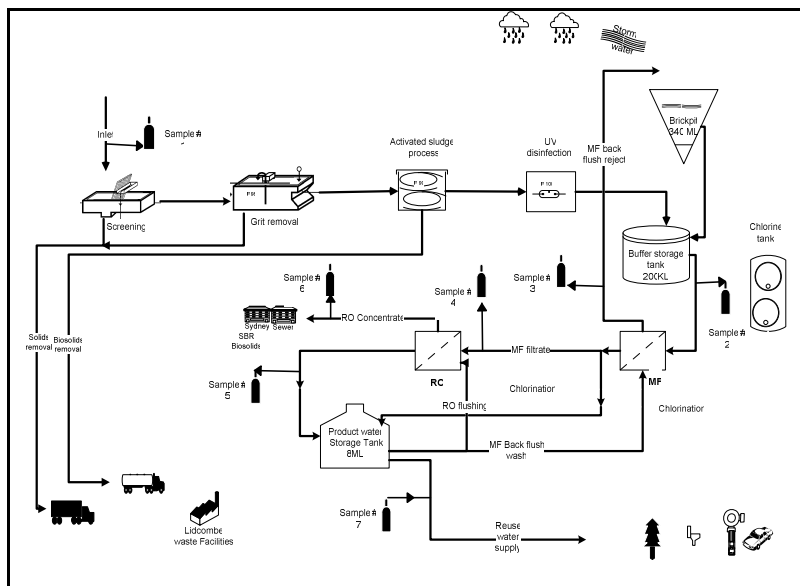


Figure 3

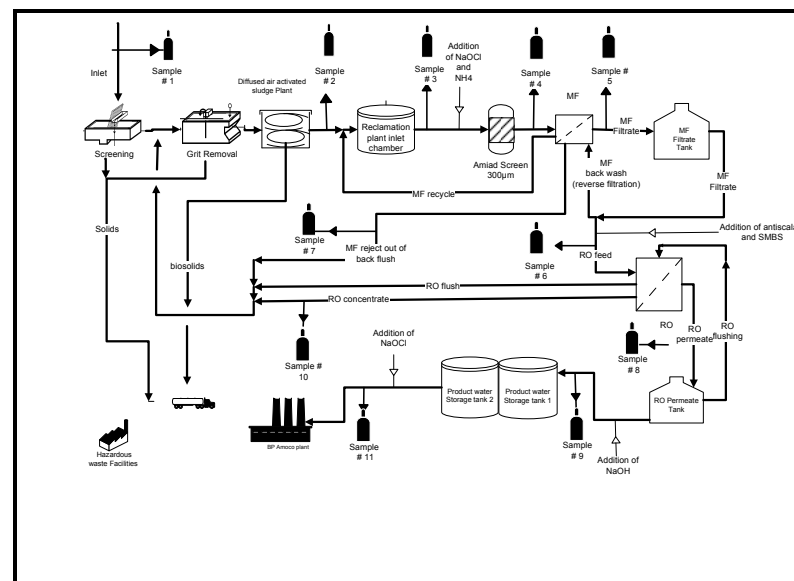


Figure 4

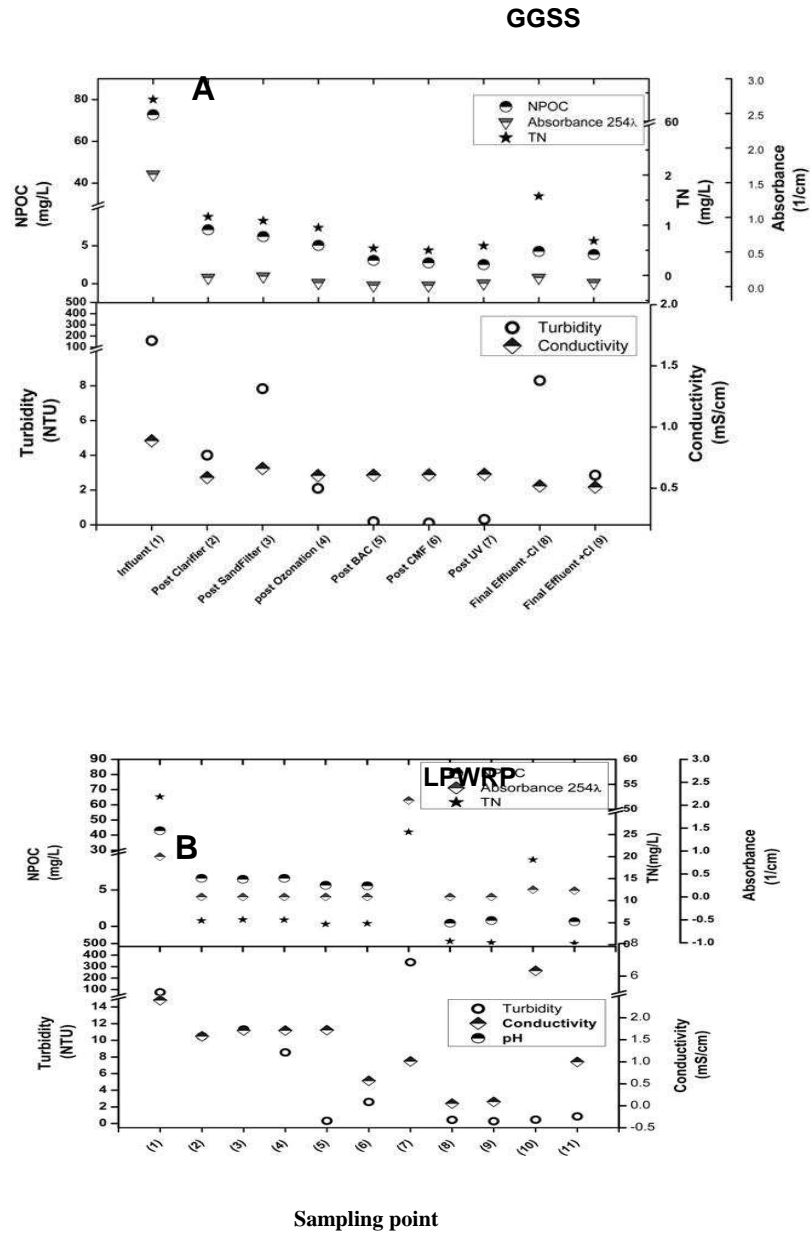
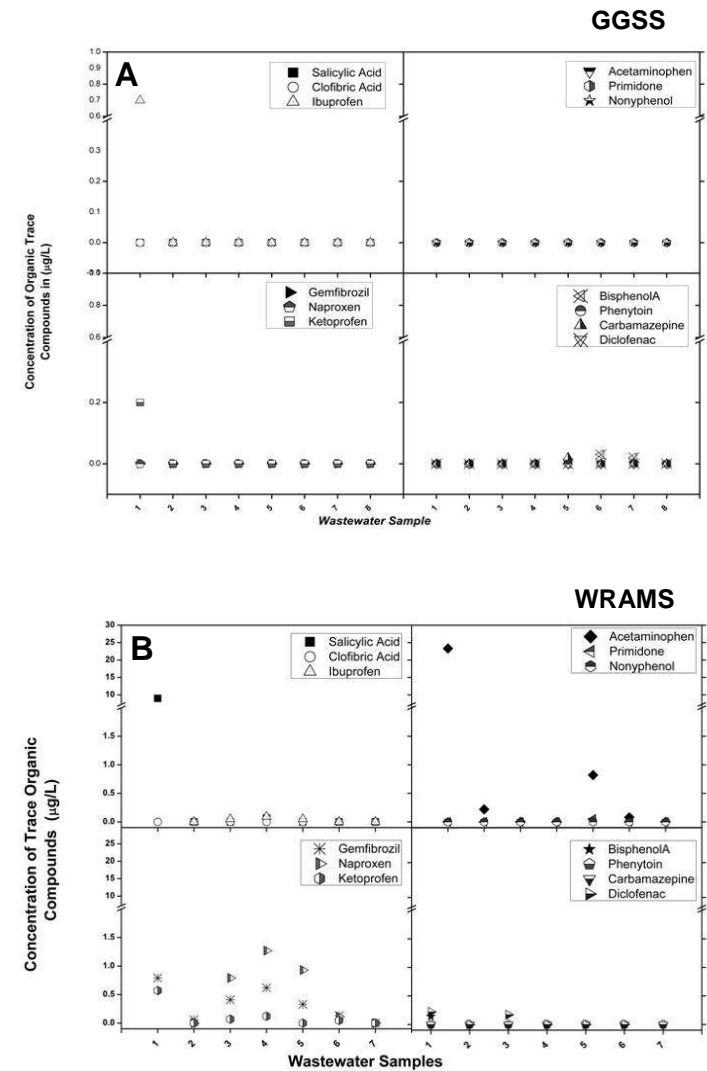


Figure 5



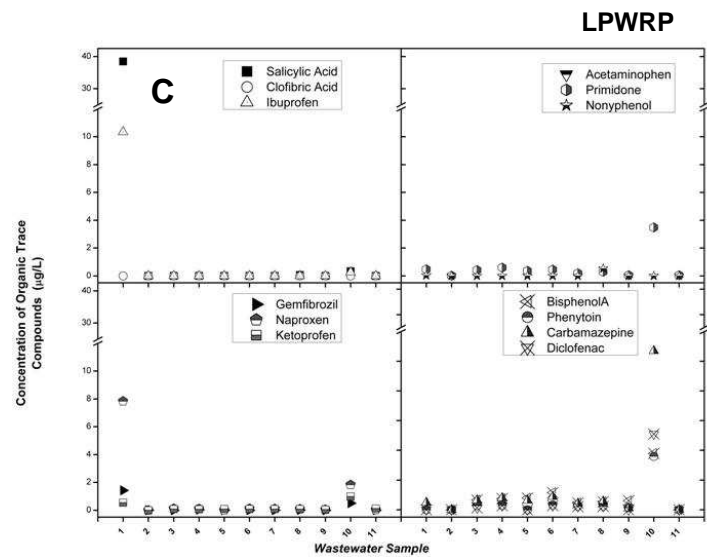


Figure 6

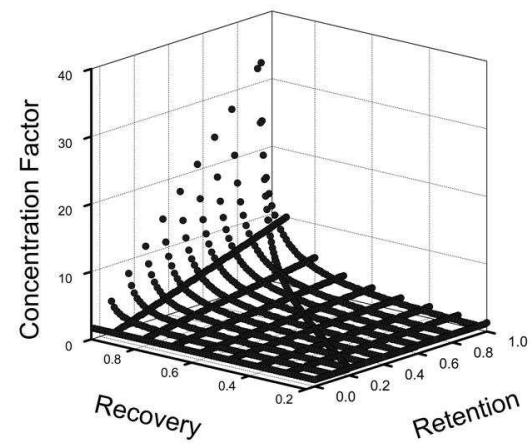


Table 1 Pharmaceutically Active Compounds (PhACs) and reported levels in the literature (* Degradation products, ⁽¹⁾ (Pham and Proulx, 1997), ⁽²⁾ (Blanchard *et al.*, 2004), ⁽³⁾ (Granier *et al.*, 1988), ⁽⁴⁾ (Price *et al.*, 2005), ⁽⁵⁾ (Khan, 2002), ⁽⁶⁾ (Carballa *et al.*, 2004), ⁽⁷⁾ (Paxéus, 1996), ⁽⁸⁾ (Buser *et al.*, 1999), ⁽⁹⁾ (Soulet *et al.*, 2002), ⁽¹⁰⁾ (Lee *et al.*, 2004), ⁽¹¹⁾ (Ternes, 1998), ⁽¹²⁾ (Koutsouba *et al.*, 2003), ⁽¹³⁾ (Clara *et al.*, 2005), ⁽¹⁴⁾ (Joss *et al.*, 2005), ⁽¹⁵⁾ (Stumpf *et al.*, 1999), ⁽¹⁶⁾ (Macia' *et al.*, 2004), ⁽¹⁷⁾ (Heberer *et al.*, 1995), ⁽¹⁸⁾ (Bolz *et al.*, 2000), ⁽¹⁹⁾ (Korner *et al.*, 2000), ⁽²⁰⁾ (Sekela *et al.*, 1999), ⁽²¹⁾ (Dewedar *et al.*, 1995), ⁽²²⁾ (Vieno *et al.*, 2005), ⁽²³⁾ (Benz *et al.*, 2005), ⁽²⁴⁾ (Lindqvist *et al.*, 2005), ⁽²⁵⁾ (Loraine and Pettigrove, 2006)

PhACs	Reported concentrations in wastewater (µg/L)
Analgesics and anti-inflammatory compounds	
Acetaminophen (Paracetamol)	10 ⁽¹⁾ , 26 ⁽¹⁾ , 148.1 ⁽²⁾ , 291.9 ⁽³⁾ , 2.52-7.83 ⁽⁴⁾
Acetylsalicylic acid (ASA)(Aspirin)	0.22 ⁽¹⁾ , 54 ⁽¹⁾ , 0.34 ⁽¹⁾ , 13 ⁽¹⁾ , 3.2 ⁽⁵⁾ , 11.39-14.93 ⁽⁵⁾ 8.88 ⁽²⁾ , 16.08 ⁽³⁾ , 54 ⁽¹¹⁾
Ortho-hydroxyhippuric acid*	6.8 ⁽¹⁾
Gentisic acid*	4.6 ⁽¹⁾
Phenazone	0.069-0.37 ⁽⁵⁾
Propyphenazone	0.010 ⁽⁵⁾ , 0.01-0.2 ⁽¹²⁾ ,
Non-steroidal anti-inflammatory compounds	
Diclofenac	3.02 ⁽¹⁾ , 0.035-0.560 ⁽⁵⁾ , 0.28-2.24 ⁽⁵⁾ , 0.05-5.63 ⁽⁴⁾ , 0.09-4.11 ⁽¹³⁾ , 0.01-0.56 ⁽¹²⁾ , 1.0 ⁽¹⁴⁾ , 0.8 ⁽¹⁵⁾ , 0.16 ⁽²³⁾ , <0.5-0.5 ⁽²⁴⁾ , 100-510 ⁽⁹⁾
Ibuprofen	2.31 ⁽²⁾ , 3.58 ⁽³⁾ , 5.7 ⁽⁶⁾ , 0.37-2.84 ⁽⁴⁾ , 1.2-2.68 ⁽¹³⁾ 1.1 ⁽¹⁴⁾ , 0.3 ⁽¹⁵⁾ , 23.4 ⁽²²⁾ , 0.49 ⁽²³⁾ , 10-19.7 ⁽²⁴⁾ , 0.99-3.3 ⁽⁸⁾ , 108-990 ⁽⁹⁾ , 3.23-25.8 ⁽²⁵⁾
Ketoprofen	0.13 ⁽²⁾ , 0.36-0.61 ⁽⁴⁾ , 0.5 ⁽¹⁵⁾ , 2.9 ⁽²²⁾ , 0.49 ⁽²³⁾ , 1-3 ⁽²⁴⁾ 80-270 ⁽²⁶⁾
Naproxen	3.84 ⁽²⁾ , 3.01 ⁽³⁾ , 5.7 ⁽⁶⁾ , 0.37-1.7 ⁽⁴⁾ , 1.0 ⁽¹⁴⁾ , 0.6 ⁽¹⁵⁾ , 0.51 ⁽¹⁶⁾ , 8.6 ⁽²²⁾ , 3.65 ⁽²³⁾ , 3-8 ⁽²⁴⁾ , 23.21 ⁽²⁵⁾
Mefenamic	190-1900 ⁽⁹⁾
Antibiotics/Bacteriostatics	
Penicillin G	<0.025 ⁽⁵⁾
Penicillin V	<0.035 ⁽⁵⁾
Sulfamethoxazole	0.58 ⁽⁶⁾ , 0.02 ⁽²³⁾ ,
Trimetoprim	0.11-0.37 ⁽⁵⁾
Anti-epileptics (Anti-convulsants)	
Carbamazepine	0.21-0.91 ⁽⁵⁾ , 0.26 ⁽²⁾ , 0.10 ⁽³⁾ , 0.01 ⁽⁴⁾ , 0.325-1.85 ⁽¹³⁾ 0.9 ⁽¹⁴⁾ , 1.68 ⁽²³⁾ ,
Primidone	< 0.10 ⁽⁴⁾
Atenolol	0.03 ⁽²³⁾ ,
Metoprolol	0.16 ⁽²³⁾ ,
Propranolol	0.05 ⁽²³⁾ ,
Beta-blockers (anti-drenergics)	
Clofibrac acid*	0.47-1.48 ⁽⁵⁾ , < 0.10 ⁽⁴⁾ , 1.0 ⁽¹⁵⁾ , 1.2 ⁽¹⁷⁾ , 10-170 ⁽⁹⁾
Gemfibrozil	1.50 ⁽²⁾ , 3.00 ⁽³⁾ , 0.12-1.0 ⁽⁴⁾ , 0.3 ⁽¹⁵⁾ , 0.71 ⁽²³⁾ ,
Bezafibrate	3.32 ⁽⁵⁾ , 1.55-7.60 ⁽¹³⁾ , 1.2 ⁽¹⁵⁾ , 2.2 ⁽²²⁾ , <0.5-0.1 ⁽²⁴⁾ ,
Contrast media	
Iodinated Xray	130 ⁽¹⁾
Diatrizoate	3.3 ⁽⁵⁾

PhACs	Reported concentrations in wastewater (µg/L)
Iopamidol	4.3 ⁽⁵⁾
Iopromide	7.5 ⁽⁵⁾ , 6.6 ⁽⁶⁾ , 0.026-3.84 ⁽¹³⁾ , 1.1 ⁽¹⁴⁾ ,
Iomeprol	1.6 ⁽⁵⁾
Ioxithalamic acid	0.17 ⁽⁵⁾
Iothalamic acid	0.18 ⁽⁵⁾
Cytostatics (antineoplastic agents)	
Ifosfamide	0.029 ⁽⁵⁾
Cyclophosphamide	0.143 ⁽⁵⁾
Oral Contraception	
Diethylstilbestrol	0.043 ⁽⁵⁾
Calcium-channel blocking agents	
Verapamil	0.050-0.068 ⁽⁵⁾
Others	
Metadone	0.28 ⁽³⁾ , 0.06 ⁽²⁾
Phenytoin	0.29 ⁽³⁾ , 0.18 ⁽²⁾
Morphin	1.39 ⁽³⁾ , 0.52 ⁽²⁾
Musk Fragrance	
Galaxolide	3.4 ⁽⁶⁾ , 0.83-4.44 ⁽¹³⁾ , 1.0 ⁽¹⁴⁾ , 0.79 ⁽²³⁾ ,
Tonalide	1.7 ⁽⁶⁾ , 0.21-1.10 ⁽¹³⁾ , 0.7 ⁽¹⁴⁾ ,
nESCs	
Bisphenol A	< 0.03- 0.34 ⁽⁴⁾ , 0.16-28.1 ⁽¹⁰⁾ , 0.72-2.38 ⁽¹³⁾ , ., 3.01 ⁽¹⁹⁾ ,
Nonylphenol	0.5-3 ⁽⁷⁾ , < 0.10-0.17 ⁽⁴⁾ , 28-16.7 ⁽¹⁰⁾ , 1.28-4.03 ⁽¹³⁾ , 2.1-2.45 ⁽¹⁹⁾ , 2.9 ⁽²⁰⁾ , 1.14 ⁽²³⁾ ,
Nonylphenol ethoxylate NPEO ¹ & NPEO ²	0.5-17 ⁽⁷⁾ , 31-868 ⁽¹⁰⁾ , 0.60-7.30 ⁽¹³⁾ ,
Octylphenol	1 ⁽⁷⁾ , 1.05 ⁽¹⁰⁾ , 0.44-0.68 ⁽¹³⁾ , 0.27 ⁽¹⁸⁾ , 0.18-0.32 ⁽¹⁹⁾ ,
Octylphenol ethoxylate OPEO ¹ & OPEO ²	2 ⁽⁷⁾ , 0.04-0.66 ⁽¹³⁾ ,
Octanoic acid, hexadecyl ester	5-28 ⁽⁷⁾
Octanoic acid, octadecyl ester	2-5 ⁽⁷⁾
Ethylene glycol monoleate	42 ⁽⁷⁾

Table 2 Characteristics of raw wastewater and product water of the three schemes

Characteristics	Schemes	GGSS		WRAMS		LPWRP	
		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 CaCO₃	mg/L	241	n.m.	n.m.	n.m.	n.m.	n.m.
Conductivity at 25 °C	µS/cm	n.m.	564.	n.m.	431	2398	n.m.
Turbidity	NTU	n.m.	n.m.	n.m.	0.11	n.m.	n.m.
Solid Content							
Total Suspended Solids	mg/L	248	2	200	< 2	261.5	n.m.
Total Dissolved Solids	mg/L	n.m.	311	350	n.m.	n.m.	n.m.
Organic Content							
Biochemical Oxygen Demand (BOD5)	mg/L	235	2	200	5	257.8	n.m.
Chemical Oxygen Demand (COD)	mg/L	525	10	470	57	583.3	n.m.
Nutrients							
Nitrogen							
Total Nitrogen	mg/L	53.5	0.79	40	5.7	n.m.	0.40
Ammonia as N	mg/L	41.5	0.01	30	2.9	36.5	<0.004
Oxidized Nitrogen	mg/L	0.01	n.m.	9.7	n.m.	n.m.	n.m.
Nitrate as N	mg/L	n.m.	n.m.	0.05	n.m.	n.m.	n.m.
Nitrite as N	mg/L	n.m.	n.m.	0.27	n.m.	n.m.	n.m.
Phosphorus							
Total Phosphorus	mg/L	10.8	0.017	7.00	0.84	10.57	<0.010
Anions & cations							
Aluminum	mg/L	n.m.	0.13	n.m.	n.m.	0.50	<0.005
Calcium	mg/L	n.m.	98.5	n.m.	n.m.	45.2	n.m.
Chlorine (free residual)	mg/L	n.m.	n.m.	n.m.	0.15	n.m.	8.5
Fluoride		n.m.	n.m.	n.m.	n.m.	n.m.	< 0.01
Magnesium	mg/L	n.m.	18	n.m.	n.m.	46.4	n.m.
Potassium	mg/L	n.m.	85.8	n.m.	n.m.	30.5	n.m.
Sodium	mg/L	n.m.	368	n.m.	n.m.	393.7	n.m.
Sulphides		n.m.	n.m.	n.m.	n.m.	6.8	n.m.
Microorganisms							
Faecal Coliforms (MF)	CFU/100mL	n.m.	0	n.m.	0	n.m.	n.m.

(n.m.: not measured)