Diurnal and Day to Day Variability in Micropollutant Concentrations in the Influent and Effluent at a Wastewater Treatment Plant in South East Queensland

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The Urban Water Security Research Alliance (UWSRA) is a $50 million partnership over five years between the Queensland Government, CSIRO's Water for a Healthy Country Flagship, Griffith University and The University of Queensland. The Alliance has been formed to address South East Queensland's emerging urban water issues with a focus on water security and recycling. The program will bring new research capacity to South East Queensland tailored to tackling existing and anticipated future issues to inform the implementation of the Water Strategy.

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FOREWORD

Water is fundamental to our quality of life, to economic growth and to the environment. With its booming economy and growing population, Australia's South East Queensland (SEQ) region faces increasing pressure on its water resources. These pressures are compounded by the impact of climate variability and accelerating climate change.

The Urban Water Security Research Alliance, through targeted, multidisciplinary research initiatives, has been formed to address the region's emerging urban water issues.

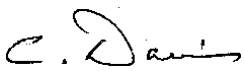
As the largest regionally focused urban water research program in Australia, the Alliance is focused on water security and recycling, but will align research where appropriate with other water research programs such as those of other SEQ water agencies, CSIRO's Water for a Healthy Country National Research Flagship, Water Quality Research Australia, eWater CRC and the Water Services Association of Australia (WSAA).

The Alliance is a partnership between the Queensland Government, CSIRO's Water for a Healthy Country National Research Flagship, The University of Queensland and Griffith University. It brings new research capacity to SEQ, tailored to tackling existing and anticipated future risks, assumptions and uncertainties facing water supply strategy. It is a $50 million partnership over five years.

Alliance research is examining fundamental issues necessary to deliver the region's water needs, including:

- ensuring the reliability and safety of recycled water systems.
- advising on infrastructure and technology for the recycling of wastewater and stormwater.
- building scientific knowledge into the management of health and safety risks in the water supply system.
- increasing community confidence in the future of water supply.

This report is part of a series summarising the output from the Urban Water Security Research Alliance. All reports and additional information about the Alliance can be found at http://www.urbanwateralliance.org.au/about.html.



Chris Davis
Chair, Urban Water Security Research Alliance

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Background

The release of micropollutants, such as pharmaceuticals, personal care products and hormones, is expected to vary not only from day to day due to their domestic and industrial use pattern, but also diurnally, due to daily life patterns. Therefore, as a follow up of the previous routine sampling program (July 2008), a campaign of intensive sampling was undertaken to assess the extent of variability associated with concentrations of selected micropollutants in influent and effluent samples.

Water samples were collected over a one-week period at Oxley Creek wastewater treatment plant (WWTP) from Wednesday 29th August until Tuesday 4th November 2008. Samples were collected on a daily basis at 9 am for seven days, while on Friday 31st August samples were collected every 2 h for a 24 h period. The concentrations of 11 pharmaceuticals and personal care products were monitored in collected water samples, including the cytotoxic surfactant benzalkonium chloride (BAC), the antiepileptic carbamazepine (CBZ) and the antidepressants fluoxetine (FLX), sertraline (SER) and venlafaxine (VEN). Some of these compounds have not been analysed in previous monitoring campaigns in the current project. In addition, the illicit drug methamphetamine (MAP) was included the suit of analyte as it may reflect a very different use pattern and therefore may serve as a good marker compound.

Key Findings

- Measured influent flow rates and water quality of both influent and effluent were reasonably stable over the seven day monitoring period. Also, the weather was stable over the monitoring period and no rain events occurred, with a subsequent hydraulic retention time (HRT) of approximately 33 h. Diurnally, there was a predictable peak (at 9 am), followed by a subsequent decline in flow rates until early the next morning before rising again to a mid-morning peak in the short term sampling.
- The variability in micropollutant concentrations was not consistent with the measured influent flow rates. While CBZ (a little sorbed pharmaceutical) followed the pattern of flow rate, another pharmaceutical compound diphenylamine (substantially sorbed) lagged behind the flow rate and its concentration peaked either late afternoon (5 pm) or in the early hours of the morning (3 am).
- All of the micropollutants analysed in this study were found to show the highest concentrations during the weekend instead of weekdays. Indeed the concentrations of several compounds (e.g. CBZ and VEN) were an order of magnitude lower during the week than during the weekend.
- The effluent concentrations of the compounds were largely influenced by the treatment efficiency for a given compound. For example, while CBZ and DPH were hardly removed during the treatment process, the BAC and MAP were almost completely (99%) removed during the treatment. However, due to very high concentrations of BAC in the influent (as high as 42,750 ng/L), its effluent concentrations were still greater than other micropollutants studied.
- The majority of other analytes were detected at low concentrations, generally at ng/L levels, particularly in the effluents. Based on relative concentrations in the influent and effluent, five of the analytes were likely to be readily removed during the treatment process, while the remainder had similar influent and effluent concentrations. The analytes which may have shown resistance to removal included CBZ, CHP, DPH, PCZ, SER and VEN. Although these findings were reflected in literature, a suitable Lagrangian sampling strategy would need to be implemented to properly determine removal rates.
- Given the Oxley treatment plant is mainly capturing domestic wastewater, the pattern seems to reflect: (i) household activities (e.g. washing) which tend to concentrate over the weekend; and (ii) more people being at home over the weekend rather than at office (located in the catchments of other treatment plant), as reflected in the pharmaceutical concentrations.

- The sampling in this study both over a short term (two-hourly sampling) and longer term (daily) period demonstrates that there is a considerable degree of variability in the concentrations of a number of pharmaceuticals and personal care products in influent and effluent samples at Oxley Creek WWTP.

Overall, this study demonstrates that a high degree of day to day as well as diurnal variability would be expected for micropollutants. However, this variability is likely to be influenced by factors such as use patterns in the community, as opposed to factors such as water flow inputs.

1. INTRODUCTION

Following on from a routine sampling program commencing in July 2008, water samples were collected over a one-week period at Oxley Creek WWTP from Wednesday 29th August until Tuesday 4th November 2008. Samples were collected from water streams both entering the WWTP (influent) and leaving the WWTP (effluent). A number of selected compounds, the majority of which were pharmaceuticals, were measured in Oxley Creek WWTP. Oxley Creek WWTP was selected based on it receiving wastewater from predominantly domestic sources. Influent is treated to a tertiary level through an activated sludge plant followed by UV disinfection. The hydraulic residence time under average dry weather conditions is around 33 h, with average water quality parameters of influent and effluent over the study period given in Table 1.

The aim of this study was to quantify the concentrations of analytes in both the influent and effluent water streams over a week and also over a 24 h period. The respective concentrations were then used to assess the variability of each analyte at particular periods of collection and whether this variability followed any distinct patterns.

Table 1: Water quality parameters of wastewater influent and effluent during Friday 31st August 2008 sampling campaign with mean ± standard deviation values for the fortnight 24th August to the 7th September 2008 given in parentheses.

Source	pH	ECa(µS/cm)	TSS[b](mg/L)	Total N[c](mg/L)	Total P[d] (mg/L)	COD[e] (mg/L)	BOD[f] (mg/L)
Influent	7.2 (7.3±0.1)	1600 (1567±153)	410 (420±46)	70 (67±3)	16 (14.7±1)	960 (905±68)	400 (347±50)
Effluent	7.8 (7.9±0.2)	1200 (1200±0)	5 (6.3±1.3)	2.1 (2.3±0.2)	2.3 (1.7±0.8)	38 (45±8)	2.5 (4±2.6)

[a] electrical conductivity; [b] total suspended solids; [c] nitrogen; [d] phosphorus; [e] chemical oxygen demand; [f] biological oxygen demand.

2. METHODS AND MATERIALS

2.1. Selected Analytes

The analytes selected for the monitoring campaign included pharmaceuticals representing a range of therapeutic classes, including antidepressants, antihistamines, an antiepileptic, an antibiotic and an antihypertensive. Also included were a household cleaner/disinfectant, a fungicide and an illicit stimulant. The selected analytes were as follows:

Compound	Compound class/use
Atenolol (ATL)	β-blocker
Benzalkonium Chloride (BAC)	Surfactant/disinfectant
Carbamazepine (CBZ)	Anti-epileptic
Chlorpheniramine (CHP)	Antihistamine
Diphenhydramine (DPH)	Antihistamine
Fluoxetine (FLX)	SSRI antidepressant
Methamphetamine (MAP)	Illicit stimulant
Propiconazole (PCZ)	Fungicide
Sertraline (SER)	SSRI antidepressant
Trimethoprim (TRM)	Antibiotic
Venlafaxine (VEN)	SSNRI antidepressant

Their respective analytical details are listed in Appendix A (Table 3).

2.2. Collection and Preparation of Samples for Analysis

Briefly, triplicate wastewater samples were collected from both influent and effluent streams mid-morning (9 am). Grab samples were collected in clean 1 L amber glass bottles, along with field blanks (1 L ultrapure water treated identically to samples to assess potential contamination). Samples were sent back to the laboratory in the dark at +4°C and loaded onto Waters HLB solid phase extraction (SPE) cartridges. SPE cartridges were then eluted for analysis of selected analytes using high pressure liquid chromatography combined with tandem mass spectrometry (LC-MS/MS).

Glass cleaning procedures, sample clean up and extraction methods are summarised in Appendix B and Appendix C.

2.3. Analysis by LC-MS/MS

For analysis by HPLC-MS/MS, a Finnigan TSQ Quantum Discovery Max (Thermo Electron Corporation) was used. HPLC separation was performed on an Alltech Alltima C_{18} 150 x 2.1 mm (3 µm particle size) column with a mobile phase flow rate of 0.2 mL/min. The mobile phase composition was 10 mM ammonium formate/0.1% formic acid (A) and acetonitrile (B) using the following gradient parameters: 90%-30% A (0-5 min), 0% A (6-15 min), 90% A (16-25 min). MS/MS analysis was undertaken using electrospray ionisation (ESI) in positive ionisation mode. Qualitative and quantitative analysis of compounds was based on retention time, multiple reaction monitoring (MRM) of two transition ions and the ratios between the transition ions.

2.4. Quantification of Analytes

A standard addition method was used for assessment of interference of analysis in the often substantial matrix of wastewater samples. For standard addition, samples were split into two 500 µL sub-samples and one of these samples was spiked with 50 µL 0.5 mg/L mixed standard solution. The other 500 µL sub-sample was spiked with 50 µL methanol. The response of the mixed standard-spiked solution was compared with that of a comparable spike in pure methanol and the effect of the matrix on the signal was given as:

$$\%ME = \left(\frac{C_{ss} - C_{ns}}{C_s}\right)x100$$

Where: %ME is percent effect of the matrix on the response of the analyte spiked to the sample (C_{ss}), corrected for in the unspiked sample (C_{ns}), relative to that in a Milli-Q water solution (C_s). The extent of the matrix effect was then factored into the measured response to give a final concentration.

3. RESULTS AND DISCUSSION

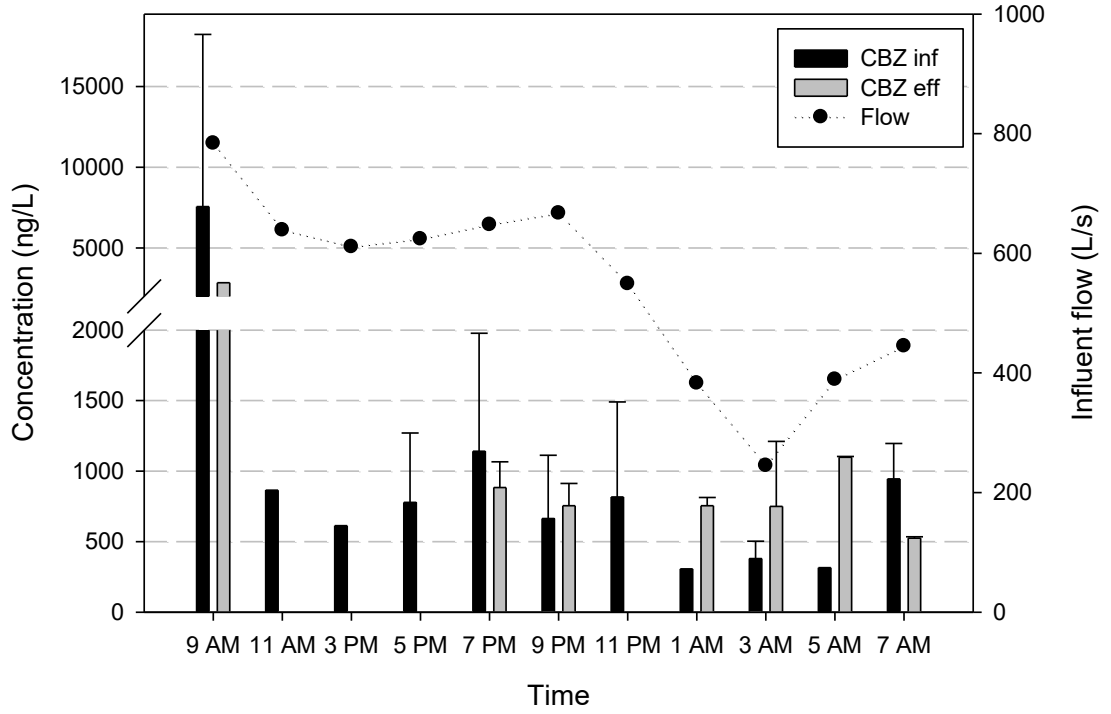
3.1 Diurnal Patterns in Influent and Effluent Concentrations of the Micropollutants

The measured concentrations in the collected wastewater influent and effluent during two-hourly sampling campaigns are summarised for each of the analytes in Appendix B (Figure 5). Some selected compounds with contrasting behaviours have been shown Figures 1 and 2. The pattern of influent flow (L/s) is also shown in the figures. Please note that for the Friday two-hourly sampling, no effluent data is available for the 11:00, 15:00 and 17:00 h samples.

The flow rates of wastewater entering this treatment plant showed that the peak rate of flow occurred at 9 am, whereas the lowest flow rate was noted in the early hours of the morning at 3 am. From 9 pm to 3 am, the flow rates decreased rapidly by a factor of more than 3, reflecting the pattern of domestic water use. However, the concentration of a micropollutant compound in the influent did not always follow the rate of flow. While carbamazepine (CBZ, a little sorbed pharmaceutical) followed the pattern of flow rate (Figure 1), diphenylamine (DPH, a substantially sorbed drug) lagged behind the flow rate and its concentration peaked either late afternoon (5 pm) or early hours of the morning (3 am).

The effluent concentrations of the compounds were largely influenced by the treatment efficiency for a given compound. For example, while CBZ and DPH were hardly removed during the treatment process, benzalkonium chloride (BAC) and methamphetamine (MAP) were completely removed during the treatment (Figure 2). Therefore, despite BAC being present in very high concentrations in the influent (as high as 42,750 ng/L), its effluent concentrations were less than 1% of that found in the influent. Despite its 99% removal in treatment process, its concentration in the effluent was still among the highest of the micropollutants analysed in this study (Table 2).

Other pharmaceutical compounds such as fluoxetine (FLX), trimethoprim (TRM) and sertraline (SER) were moderately removed during the treatment process. It was interesting to note that venlafaxine (VEN) and the fungicide propiconazole (PCZ) showed higher concentrations in the effluent than in the influent (Figure 6). The reasons are unclear.



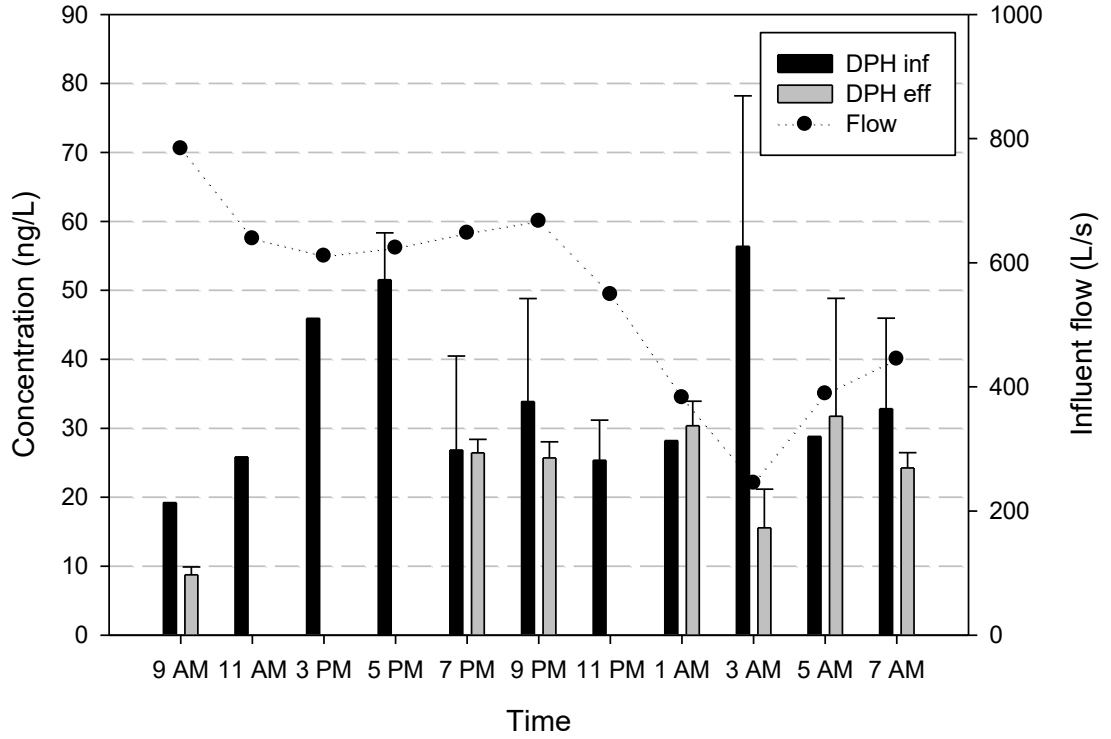


Figure 1: Concentrations of carbamazepine (CBZ) and diphenhydramine (DPH) in influent and effluent and influent flow rates during the two-hourly sampling on Friday 31st August. Note both compounds show little removal during the treatment process.

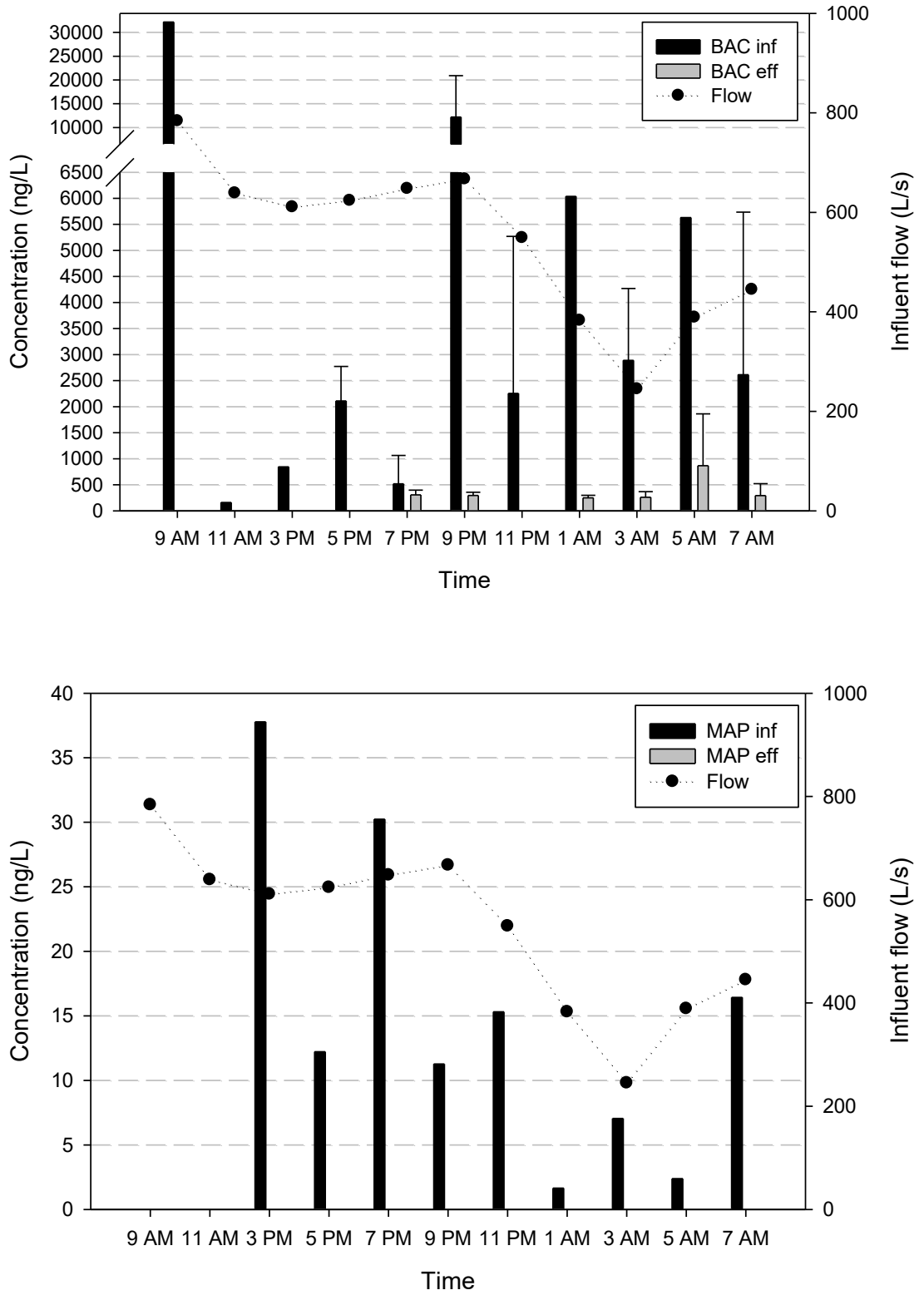


Figure 2: Concentrations of benzalkonium chloride (BAC) and methamphetamine (MAP) in influent and effluent and influent flow rates during the two-hourly sampling on Friday 31st August. Note both compounds are effectively removed during the treatment process.

3.2 Day to Day Variations in Micropollutants Concentrations

The measured concentrations in the collected wastewater influent and effluent during the week-long sampling campaign are summarised for each of the analytes in Appendix B (Figure 6). Data on some selected compounds have been shown in Figures 3 and 4. Please note that no data on influent on Monday or Tuesday; and effluent on Wednesday is available for the daily sampling.

Firstly, there was little variation in the flow rate when samples were taken at the same time during the week (Figures 3, 4 and 6). Secondly, all of the micropollutants analysed in this study were found to show the highest concentrations during the weekend instead of weekdays (Figure 6, Appendix B). Let us take the example of two pharmaceutical compounds CBZ and venlafaxine (VEN), the daily concentration data of which is presented in Figure 3. The concentrations of both compounds were found to be much higher from Friday to Sunday than during the week. Unfortunately, the influent data for Monday and Tuesday were not available. However, looking at the effluent data (both compounds being fairly persistent through the treatment process), one can conclude that concentrations of both of these compounds were an order of magnitude lower during the week than during the weekend.

The variation in daily concentrations of BAC over the study period is presented in Figure 4. This compound was found to be present in very high concentrations but is very effectively removed in the treatment process (99% removal). The concentrations on Friday to Sunday were also much higher than during the week. There was a gradual increase in concentration in the influent as the week progressed, but the highest concentration was noted on Saturday. BAC is the anticorrosion agent used in equipment such as washing machines and dishwashers. Given the Oxley WWTP is mainly capturing domestic wastewater, the pattern seems to reflect: (i) household activities (e.g. washing) which tend to concentrate over the weekend; and (ii) more people being at home over the weekend rather than at the office (often located in the catchments of another treatment plant e.g. Luggage Point), as reflected in the pharmaceutical concentrations.

The illicit drug methamphetamine (MAP) was included in the suite of analytes as its use pattern is clearly more concentrated over the weekend than during the weekdays. The data presented in Figure 4 clearly reflected the pattern expected. The drug in the influent or effluent was only detectable over Saturday and Sunday, the highest being on the Sunday. In the effluent, it reached the detection level only on Sunday, because the drug is removed well in the treatment plant (as can be seen from Figure 2) and any traces that entered on Monday would be efficiently removed. There was no data for influents available for Monday.

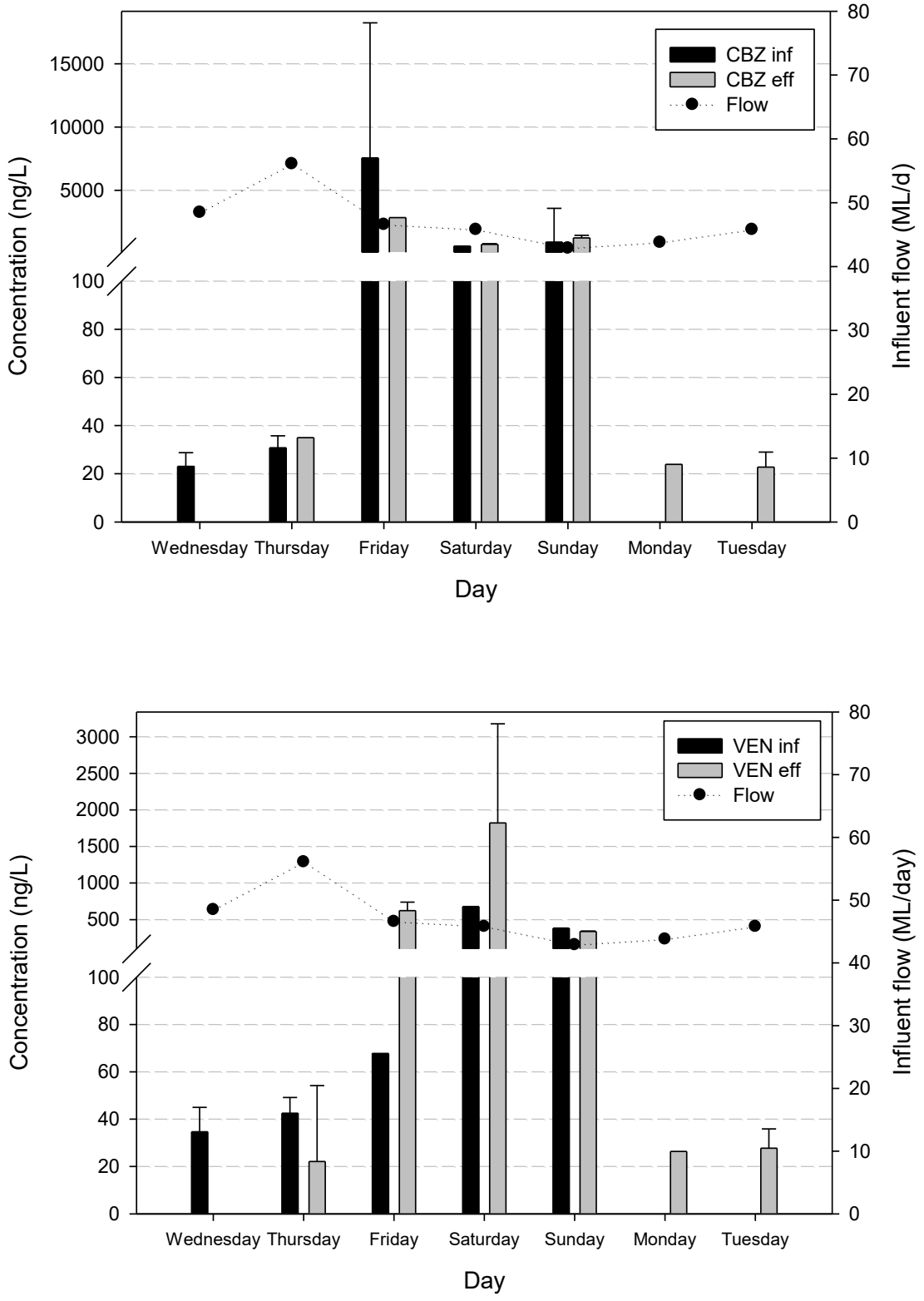


Figure 3: Concentrations of carbamazepine and venlafaxine in influent and effluent and influent flow rates during the daily sampling from Wednesday 29th August until Tuesday 4th September.

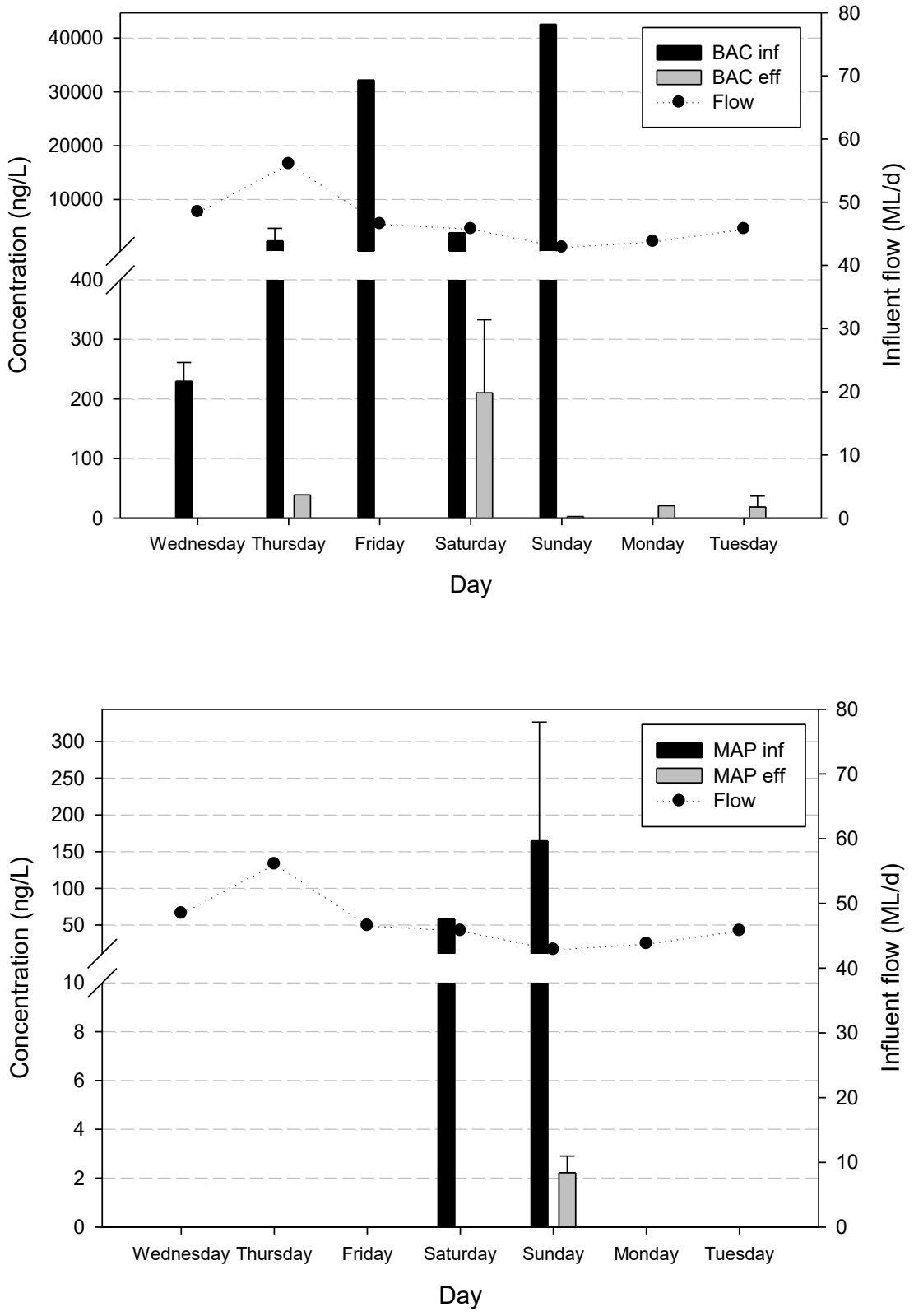


Figure 4: Concentrations of benzalkonium chloride and methamphetamine in influent and effluent and influent flow rates during the daily sampling from Wednesday 29th August until Tuesday 4th September.

3.3 Comparison with Concentrations Reported in the Literature

The data ranges are also summarised in Table 2, with comparisons of concentrations ranges found in the literature. In general, the values determined in the influent and effluent samples are within the ranges expected from other studies. For chlorpheniramine (CHP), there were no published studies available for comparison using the search terms "aquatic", "wastewater", "influent", "effluent", "sewer" and "environment" in ISI Web of Knowledge. In the case of DPH, there were few studies available for comparison, although the effluent concentrations measured in this study were lower than those determined in the literature (Table 2).

The concentrations for some analytes were at the higher end or greater than those found in the literature values, such as for CBZ, propiconazole (PCZ), sertraline (SER), trimethoprim (TRM) and VEN. The majority of the studies accessed in literature were conducted in the Northern Hemisphere, which is likely to account for the discrepancies between the values detected in the present study. This is particularly important when considering the respective use patterns of pharmaceuticals from country to country. For example, the most commonly used antidepressant taken in Canada in 2006 was VEN, which had a daily consumption approximately four times greater than SER and nearly seven times greater than fluoxetine (FLX) (Lajeunesse *et al.*, 2008). In contrast, of these antidepressants, SER was the most commonly prescribed in Australia in 2006, with a dosing level less than double that of VEN and nearly three times greater than FLX (CoA, 2009).

The highest concentrations determined in the influent was found for BAC, with a maximum value of 42 570 ng/L, although this was not as high as values found in the literature (Table 2). The influent concentrations were in marked contrast to the effluent concentrations, which, except for one sample, were all less than 1 µg/L and generally in the low to mid-ng/L range. This suggests that almost complete removal of BAC during the treatment process occurred during the sampling campaign. A high removal capacity of WWTPs with respect to BAC is also anticipated from other studies (Clara *et al*., 2007; Martinez-Carballo *et al*., 2007).

MAP was also apparently effectively removed during the treatment process, with only one effluent sample containing a measurable concentration which was close to its LOQ (Figures 1 and 2 and Table3). High removal rates of MAP were also previously determined in NE Spain (Huerta-Fontela *et al*., 2008). Atenolol (ATL), FLX and TRM also had markedly lower concentrations in the effluent relative to the influent, suggesting effective removal during passage through the WWTP.

In contrast, similar concentrations in influent and effluents were noted for CBZ, CHP, DPH, PCZ, SER and VEN, which suggests less effective removal of these compounds occurred during the sampling period. The low removal rates of CBZ during treatment in WWTPs have been well documented previously (Gros *et al*., 2006; Metcalfe *et al*., 2003; Miao *et al*., 2005; Nakada *et al*., 2007; Vieno *et al*., 2007; Zhang and Geißen, 2010) and this also is reflected in the current study. Relatively low removal efficiencies have also been demonstrated prior to the present study for PCZ (Kahle *et al*., 2008), SER (Lajeunesse *et al*., 2008; Vasskog *et al*., 2008) and VEN (Lajeunesse *et al*., 2008), while this information was not found for CHP and DPH.

Table 2: Summary of concentration ranges detected during sampling along with comparative literature values.

Analyte	Concentration Range Influent (ng/L)	Concentration Range Effluent (ng/L)	Literature Range (ng/L)	Reference
Atenolol (ATL)	<LOQ[a]-161	<LOQ-37	<LOQ-740 (I[b]); <LOQ-1150 (E[c]) 840-2800 (I)	Gros *et al.* (2006) Radjenovic *et al.* (2009)
Benzalkonium Chloride (BAC)	229-42570	<LOQ-865	7200-170000 (I); 140-2100 (E) 14000-170000 (I); 34-500 (E)	Martinez-Carballo *et al.* (2007) Clara *et al.* (2007)
Carbamazepine (CBZ)	23-7560	22-2843	<LOQ-950 (I); <LOQ-630 (E) 356 (I); 251 (E) 2300 (I); 1900 (E)	Gros *et al.* (2006) Miao *et al.* (2005) Metcalfe *et al.* (2003)
Chlorpheniramine (CHP)	<LOQ-37	<LOQ-63	na[d]	-
Diphenhydramine (DPH)	<LOQ-56	<LOQ-32	589±16 (E)	Bartelt-Hunt *et al.* (2009)
Fluoxetine (FLX)	<LOQ-76	<LOQ-27	50-70 (E) 3.5 (I)-3 (E) 120-2300 (I)	Schultz and Furlong (2008) Lajeunesse *et al.* (2008) Radjenovic *et al.* (2009)
Methamphetamine (MAP)	<LOQ-165	<LOQ-2	350±78 (E) 3-277 (I); 3-90 (E)	Bartelt-Hunt *et al.* (2009) Huerta-Fontela *et al.* (2008)
Propiconazole (PCZ)	15-11576	<LOQ-3482	4-27 (I); 5-40 (E) 173-239 (I); 12-143 (E)	Kahle *et al.* (2008) Van de Steene and Lambert (2008)
Sertraline (SER)	4-376	<LOQ-331	20 (I); 4-15 (E) 6 (I)-6 (E) 60-80 (E)	Vasskog *et al.* (2008) Lajeunesse *et al.* (2008) Schultz and Furlong (2008)
Trimethoprim (TRM)	7-1061	<LOQ-288	340-930 (I); 50-70 (E) <LOQ-496 (I); <LOQ-174 (E)	Watkinson *et al.* (2007) Choi *et al.* (2008)
Venlafaxine (VEN)	35-2371	<LOQ-2147	196±25 (I); 176±13 (E) 1200-2200 (E)	Lajeunesse *et al.* (2008) Schultz and Furlong (2008)

a limit of quantification (see Table 3); b Influent (I); c Effluent (E); d not available.

It should be noted, however, that the sampling undertaken was not based on a Lagrangian approach, where the respective packets of water entering the plant were followed to the outfall for sampling based on the hydraulic behaviour within the WWTP. Therefore, levels of removal are approximations only and a more comprehensive analysis would involve consideration of the hourly changes in inflows to the WWTP and the influence it has on the time taken to reach the outfall.

Another point worth considering is the use of grab sampling techniques, particularly with respect to the collection of the inherently variable influent. Collection of samples at two-hourly intervals could lead to incorrect assumptions based on the potential for high variability of inputs, which could also be reflected (although to a lesser extent) in the effluent samples (Ort *et al.*, 2010a; Ort *et al.*, 2010b). For example, inputs of anthropogenic gadolinium into a WWTP measured in two-minute grab samples over a four-hour period showed that a peak in concentration occurred over a 20 min. period (Ort *et al.*, 2010a).

When considering the concentrations of analytes, or even analyte loading when influent flow rates are taken into account (data not shown), it can be seen there was a high degree of variability in the values for respective analytes. Therefore, while the sampling methodology in this study may not give a good representation of actual removal rates, it supports the notion that variability in concentrations of contaminants is reflected in the variability of inputs to the WWTP. Another study assessing the daily concentrations in influent and effluent for a number of stimulants over a week also demonstrated variability in concentrations (Huerta-Fontela *et al*., 2008). Composite 24 h samples were used to measure concentrations for this particular study, which found high variability in concentrations of nicotine, amphetamine and methylenedioxymethamphetamine (MDMA). Also, concentrations of these three compounds were found to peak on the weekends. In the present study, this was also found to be the case for MAP, which could reflect its more prevalent use on the weekend (Figure 2). However, a similar pattern was also noted for all the other analytes, which is not so easily accounted for by their expected use patterns.

For the two-hourly sampling, the influent flow rate peaked at 784 L/s at 9 am and declined to 245 L/s at 3 am the next day before increasing again. This represents an approximate difference of three times between the highest and lowest flows over this period. The influence of flows on the overall loading of pharmaceuticals in wastewater is therefore probably not as important as other factors independent of flow, such as usage within the population. For example, the concentration of BAC in influent ranged from 160 ng/L to in two hours (Figure 2), which cannot be explained by differences in flow rate. Also, the patterns in variability in concentrations was not consistent amongst the analytes. This suggests that there were other factors that influenced the measured concentrations, apart from levels of inputs from sources. For example, influent concentrations of BAC peaked at 9 am (32 µg/L)before dropping markedly in the next four samples (0.16-2.1 µg/L) before rising again at 9 pm to 12.2 µg/L (Figure 2). BAC is a surfactant commonly used as a dual-purpose disinfectant and its inputs may be reflected better by use patterns as a cleaning agent rather than peak morning flows of inputs.

4. CONCLUSIONS

The sampling in this study both over a short term (two-hourly sampling) and longer-term (daily) period demonstrates that there is a considerable degree of variability in the concentrations of a number of pharmaceuticals and personal care products in influent and effluent samples at Oxley Creek WWTP.

There was also a predictable peak (at 9 am), followed by a subsequent decline in flow rates until early the next morning before rising again to a mid-morning peak in the short term sampling. The flow rates at a given time everyday during the week were reasonably stable over the sampling week.

The variability in micropollutant concentrations was not consistent with the measured influent flow rates. While CBZ (a little sorbed pharmaceutical) followed the pattern of flow rate, diphenylamine (another substantially sorbed pharmaceutical compound) lagged behind the flow rate and its concentration peaked either late afternoon (5 pm) or in the early hours of the morning (3 am).

The effluent concentrations of the compounds were largely influenced by the treatment efficiency for a given compound. For example, while CBZ and DPH were hardly removed during the treatment process, BAC and MAP were almost completely (99%) removed during the treatment. However, due to very high concentrations of BAC in the influent (as high as 42,750 ng/L), its effluent concentrations were still greater than other micropollutants studied.

All of the micropollutants analysed in this study were found to show the highest concentrations during the weekend instead of weekdays. Indeed, the concentrations of several compounds (e.g. CBZ and VEN) were an order of magnitude lower during the week than during the weekend. Given the Oxley treatment plant is mainly capturing the domestic wastewater, the pattern seems to reflect the household activities which tend to dominate over the weekend (e.g. clothes washing) and more people being at home over the weekend rather than at the office (usually located in the catchments of another wastewater treatment plant).

The majority of other analytes were detected at low concentrations, generally at ng/L, particularly in the effluents. Based on relative concentrations in the influent and effluent, five of the analytes were likely to be readily removed during the treatment process, while the remainder had similar influent and effluent concentrations. The analytes which may have shown resistance to removal included CBZ, CHP, DPH, PCZ, SER and VEN. Although these findings were reflected in literature, a suitable Lagrangian sampling strategy would need to be implemented to properly determine removal rates.

The findings from this study demonstrate that monitoring of micropollutants within influent or effluent streams should either be undertaken as an intensive short-term sampling campaign or as an integrative sampling approach. This would then allow better decision-making pertaining to treatment options within the treatment plant (with respect to influents) or assessment of ecological risks posed by contaminant levels (with respect to effluents).

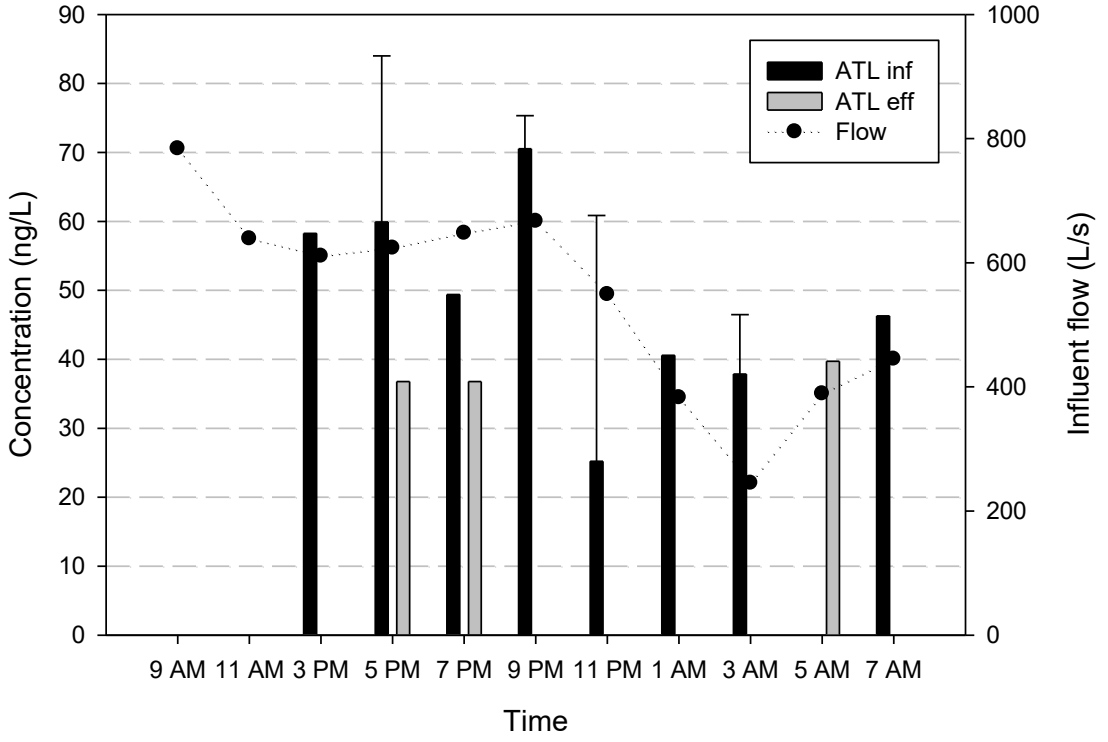
APPENDIX A: PREPARATION OF SAMPLING CONTAINERS

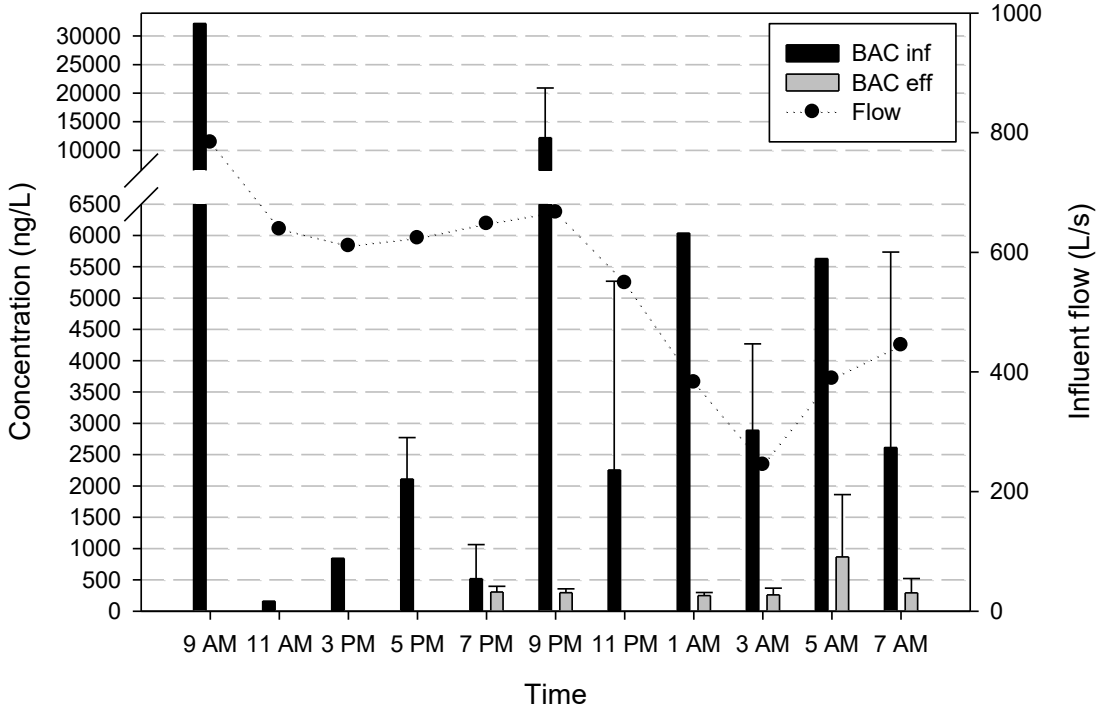
Table 3: Summary of method parameters for target analytes.

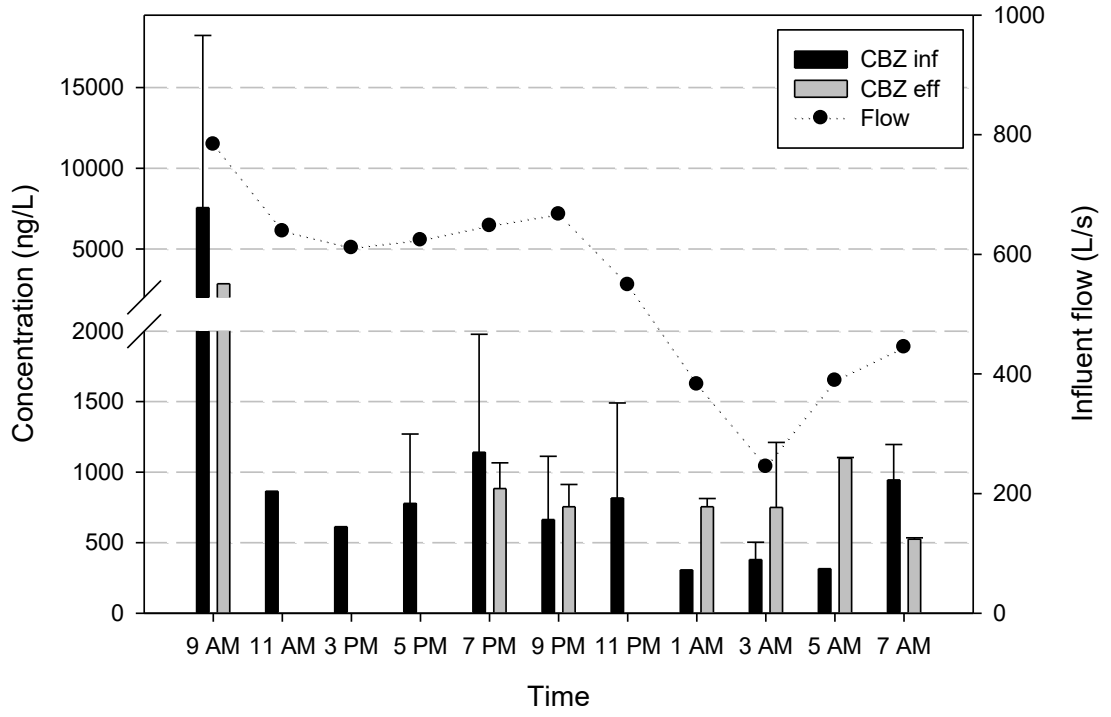
Compound	Compound Class/Use	Analytical Method Parameters			
		Method	Recovery[a]	MS Target ions[b]	LOQ[c]
Atenolol (ATL)	β-blocker	LC-MS/MS	71±16	136[M+H]$^+$→91,119	1 – 100 ng/L
Benzalkonium Chloride (BAC)	Surfactant/disinfectant	LC-MS/MS	44±6	304[M+H]$^+$→91,212	1 – 100 ng/L
Carbamazepine (CBZ)	Anti-epileptic	LC-MS/MS	103±5	237[M+H]$^+$→193,194	1 – 100 ng/L
Chlorpheniramine (CHP)	Antihistamine	LC-MS/MS	100±13	275[M+H]$^+$→230	1 – 100 ng/L
Diphenhydramine (DPH)	Antihistamine	LC-MS/MS	118±8	256[M+H]$^+$→167	1 – 100 ng/L
Fluoxetine (FLX)	SSRI antidepressant	LC-MS/MS	75±11	310[M+H]$^+$→44,148	1 – 100 ng/L
Methamphetamine (MAP)	Illicit stimulant	LC-MS/MS	80±12	150[M+H]$^+$→91,119	1 – 100 ng/L
Propiconazole (PCZ)	Fungicide	LC-MS/MS	102±12	342[M+H]$^+$→69,159	1 – 100 ng/L
Sertraline (SER)	SSRI antidepressant	LC-MS/MS	75±14	306[M+H]$^+$→159,275	1 – 100 ng/L
Trimethoprim (TRM)	Antibiotic	LC-MS/MS	95.2±6	291[M+H]$^+$→230,261	1 – 100 ng/L
Venlafaxine (VEN)	SSNRI antidepressant	LC-MS/MS	107±4	278[M+H]$^+$→58,260	1 – 100 ng/L

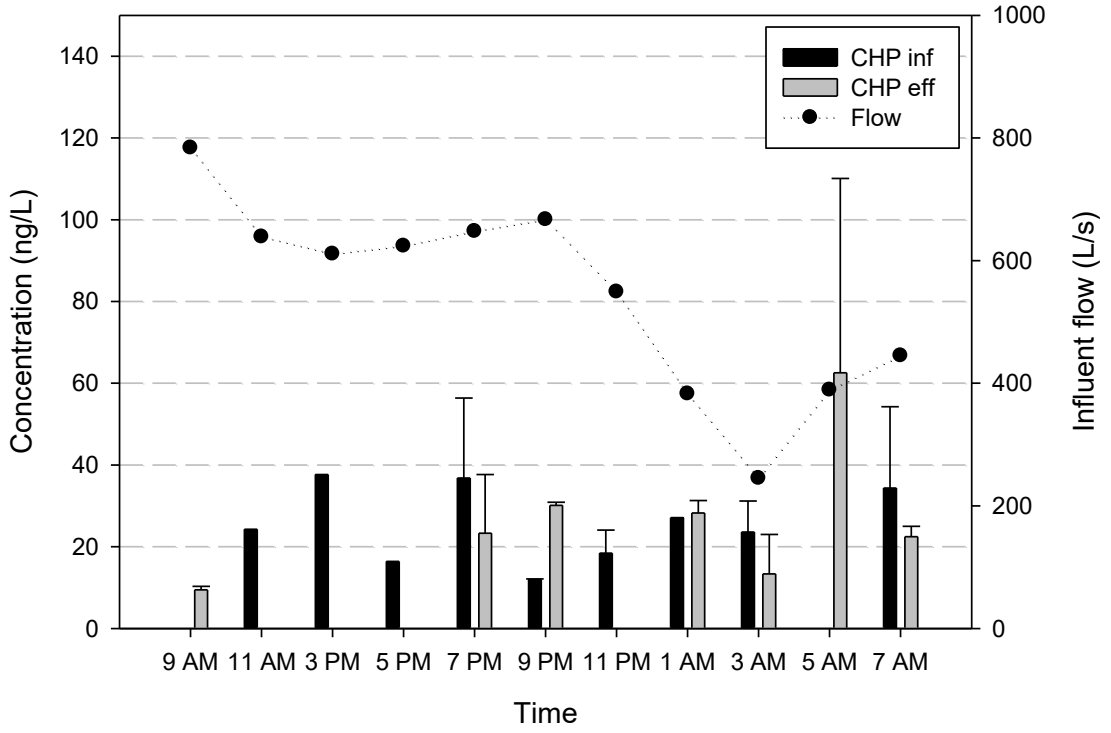
[a] Mean recovery from SPE cartridges from 6 matrix-spiked samples
[b] Ions used in LC-MS/MS MRM method, with each ion pair having an expected relative ratio
[c] limit of quantification based on SPE recovery/pre-concentration and instrumental limits of quantification

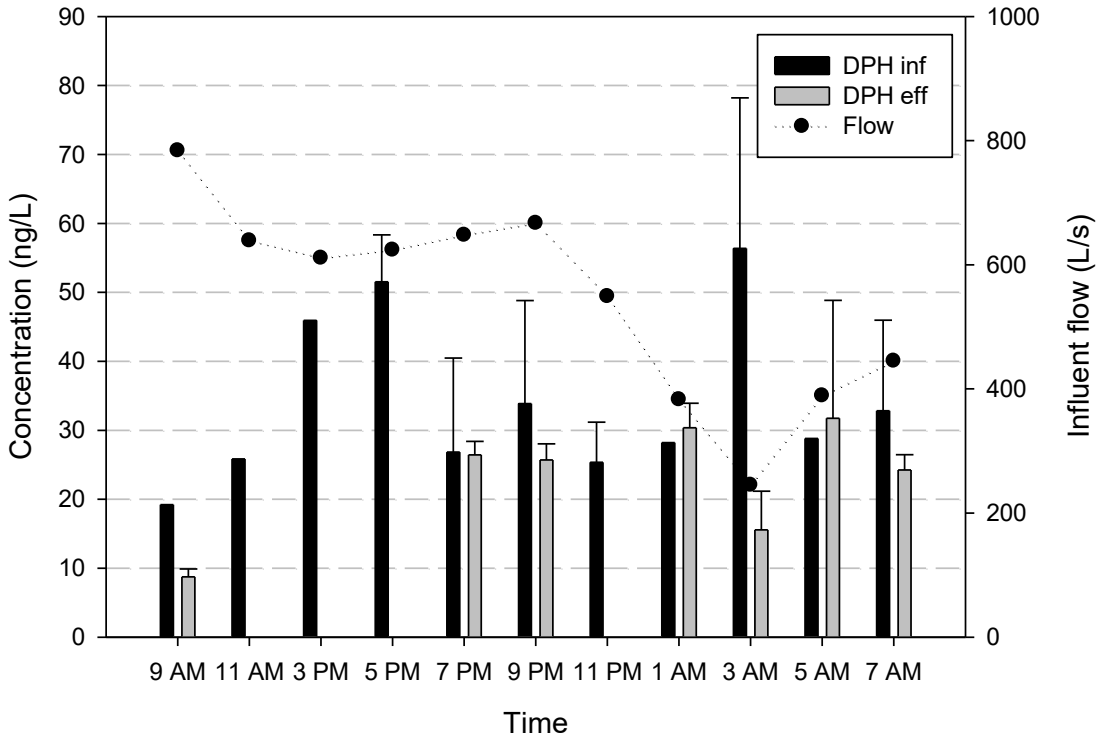
APPENDIX B: THE DIURONAL PATTERN OF CONCENTRATIONS OF ALL THE 11 MICROPOLLUTANTS

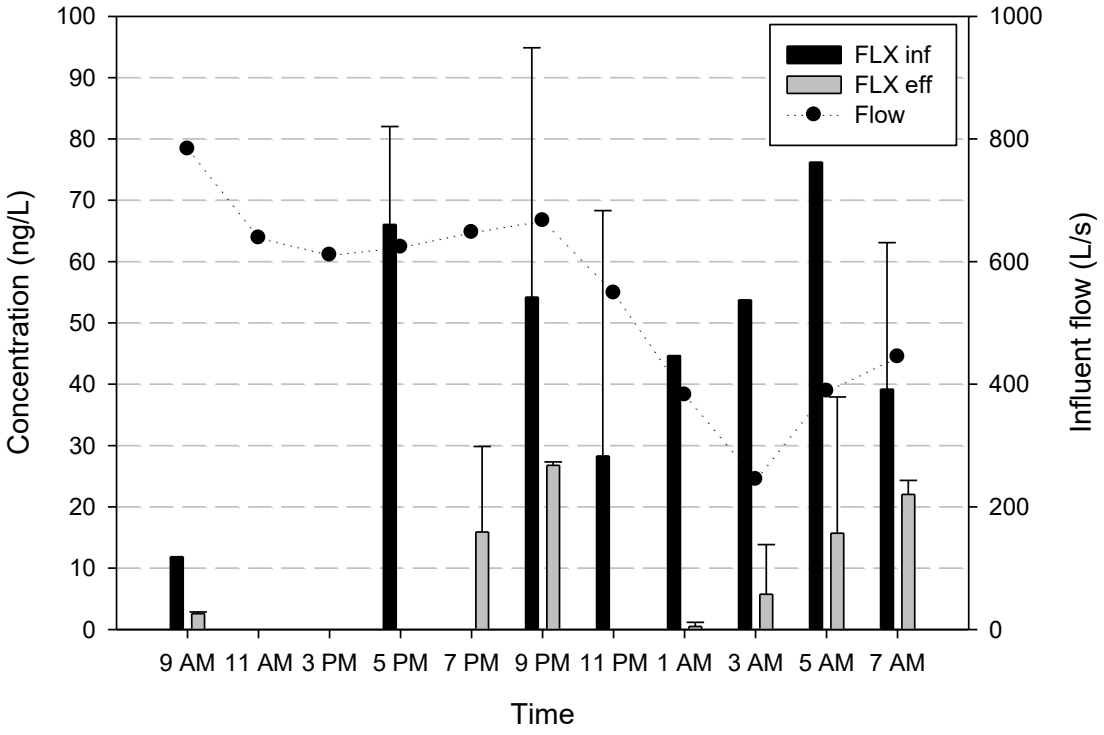


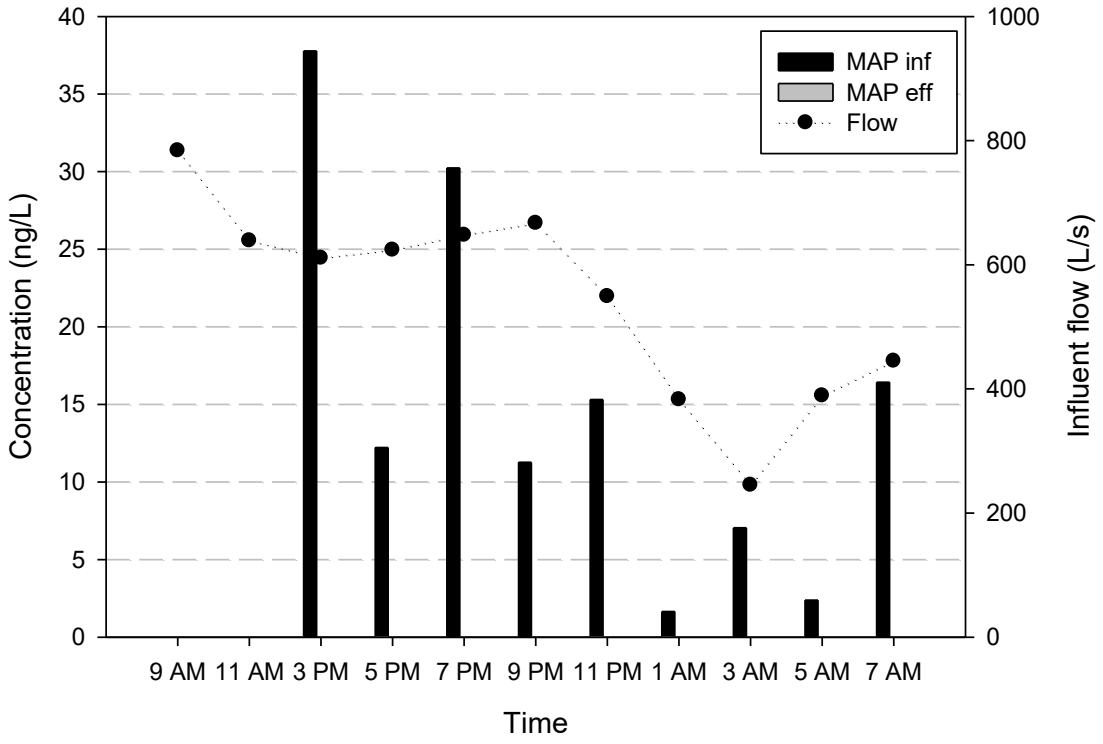


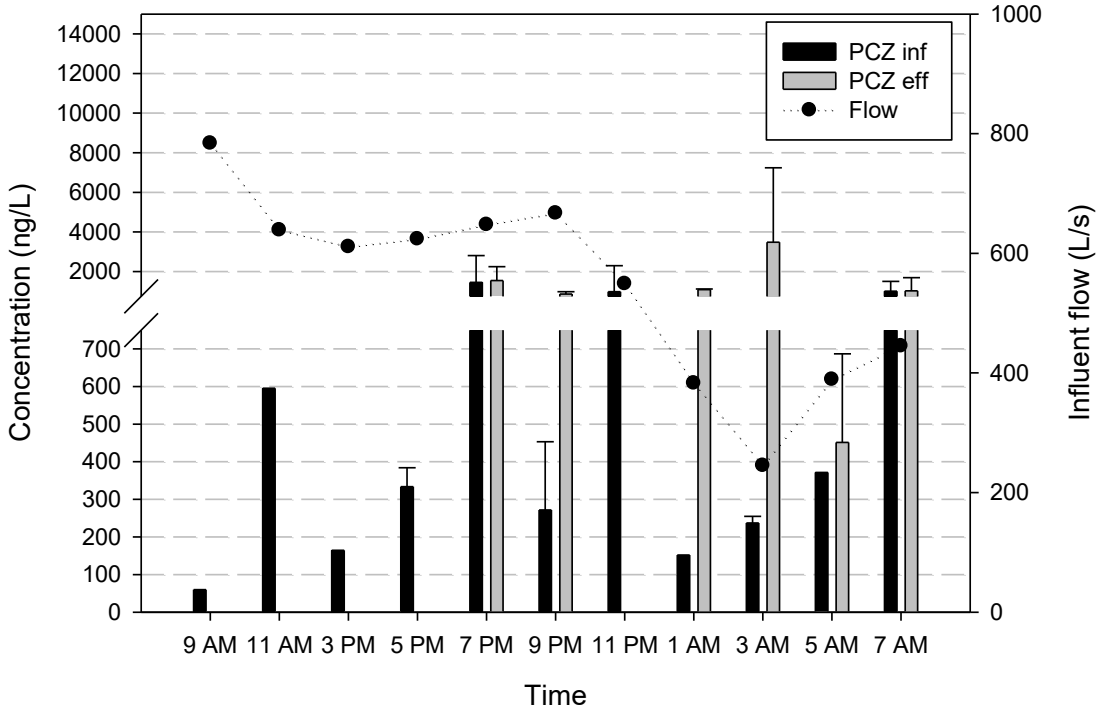

CBZ inf
CBZ eff
Flow
Concentration (ng/L)
Influent flow (L/s)
Time
9 AM
11 AM
3 PM
5 PM
7 PM
9 PM
11 PM
1 AM
3 AM
5 AM
7 AM

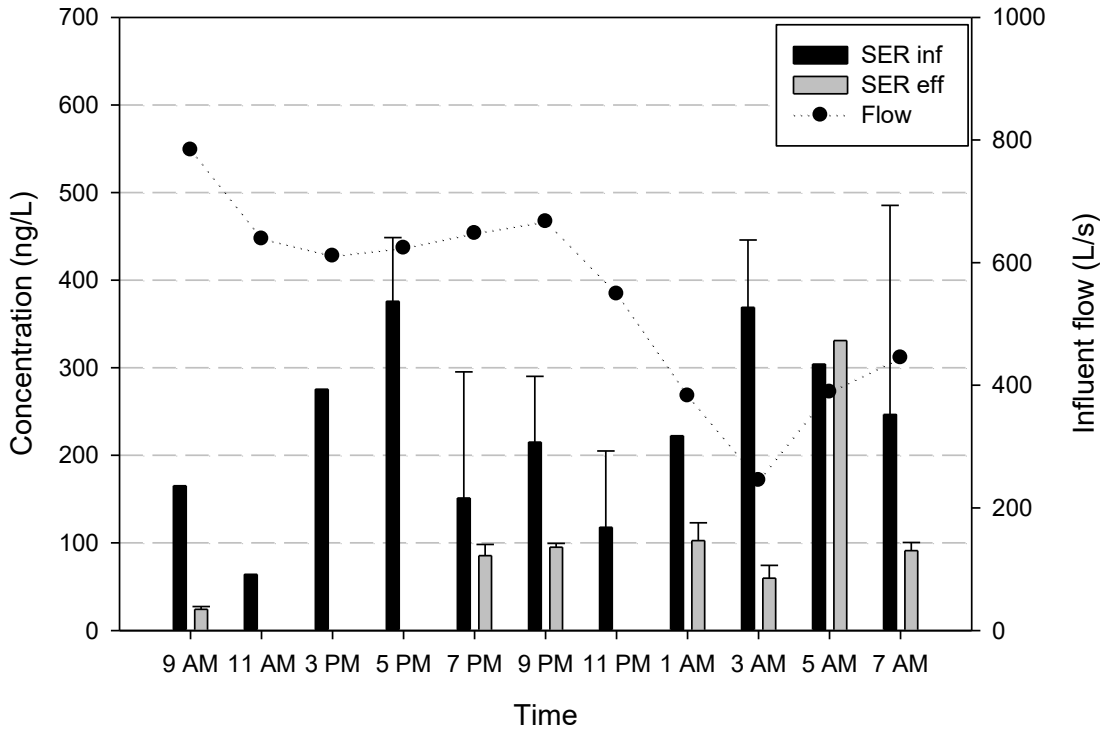

CHP inf
CHP eff
Flow
Concentration (ng/L)
Influent flow (L/s)
Time
9 AM
11 AM
3 PM
5 PM
7 PM
9 PM
11 PM
1 AM
3 AM
5 AM
7 AM

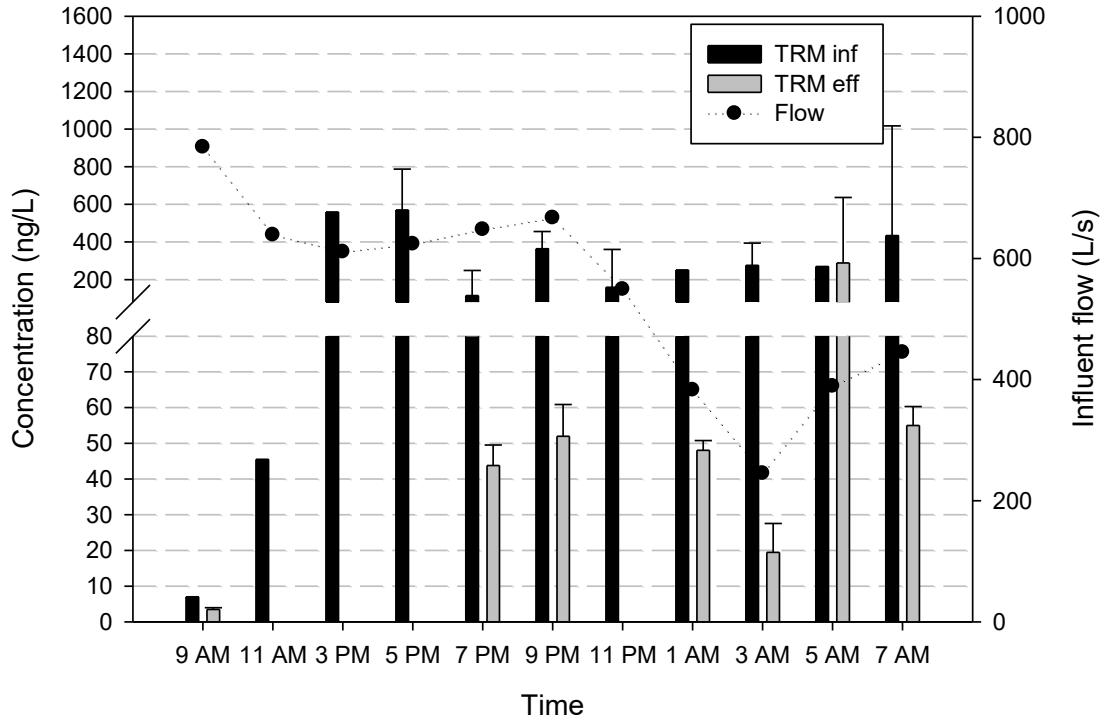

DPH inf
DPH eff
Flow
Concentration (ng/L)
Influent flow (L/s)
0
10
20
30
40
50
60
70
80
90
0
200
400
600
800
1000
9 AM
11 AM
3 PM
5 PM
7 PM
9 PM
11 PM
1 AM
3 AM
5 AM
7 AM
Time


FLX inf
FLX eff
Flow
Concentration (ng/L)
Influent flow (L/s)
0
10
20
30
40
50
60
70
80
90
100
0
200
400
600
800
1000
9 AM
11 AM
3 PM
5 PM
7 PM
9 PM
11 PM
1 AM
3 AM
5 AM
7 AM
Time


MAP inf
MAP eff
Flow
Concentration (ng/L)
Influent flow (L/s)
Time
9 AM
11 AM
3 PM
5 PM
7 PM
9 PM
11 PM
1 AM
3 AM
5 AM
7 AM


PCZ inf
PCZ eff
Flow
Concentration (ng/L)
Influent flow (L/s)
Time
9 AM
11 AM
3 PM
5 PM
7 PM
9 PM
11 PM
1 AM
3 AM
5 AM
7 AM


SER inf
SER eff
Flow
Concentration (ng/L)
Influent flow (L/s)
Time
9 AM
11 AM
3 PM
5 PM
7 PM
9 PM
11 PM
1 AM
3 AM
5 AM
7 AM


TRM inf
TRM eff
Flow
Concentration (ng/L)
Influent flow (L/s)
Time
9 AM
11 AM
3 PM
5 PM
7 PM
9 PM
11 PM
1 AM
3 AM
5 AM
7 AM

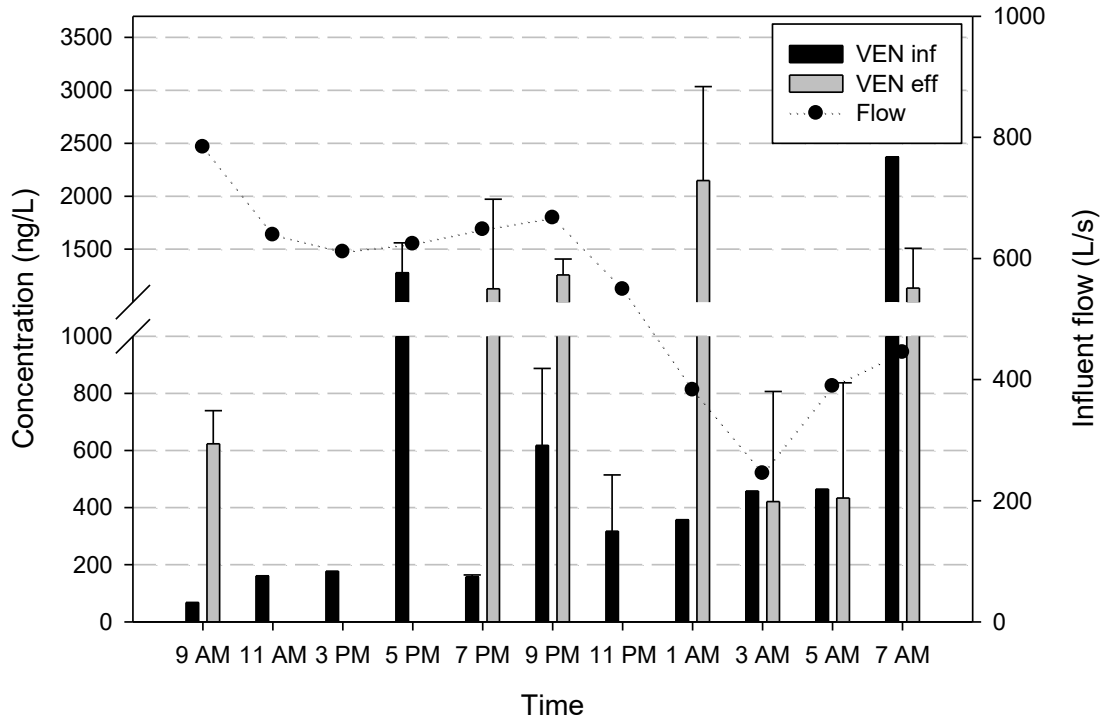
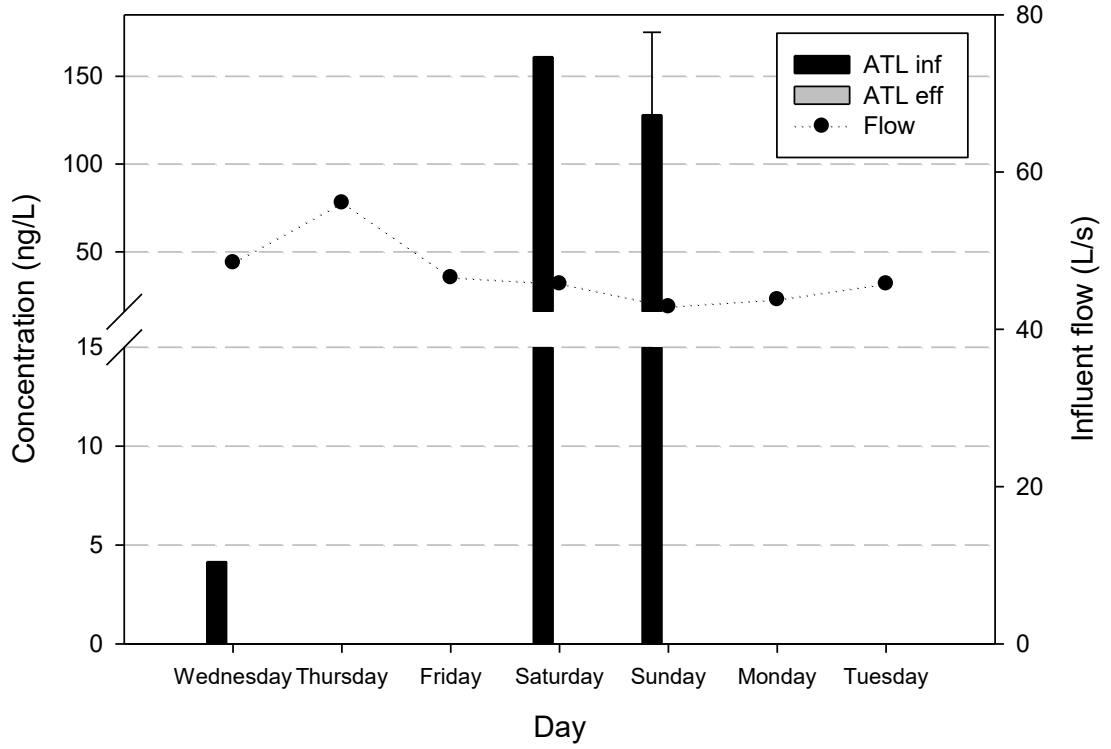
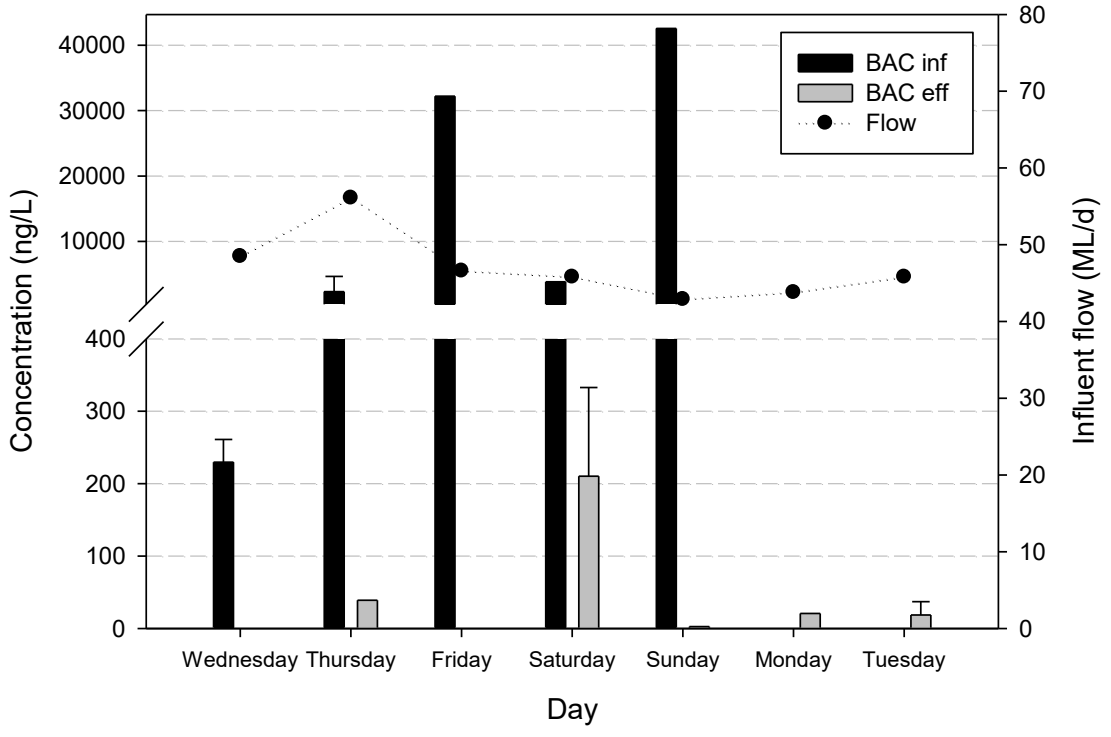
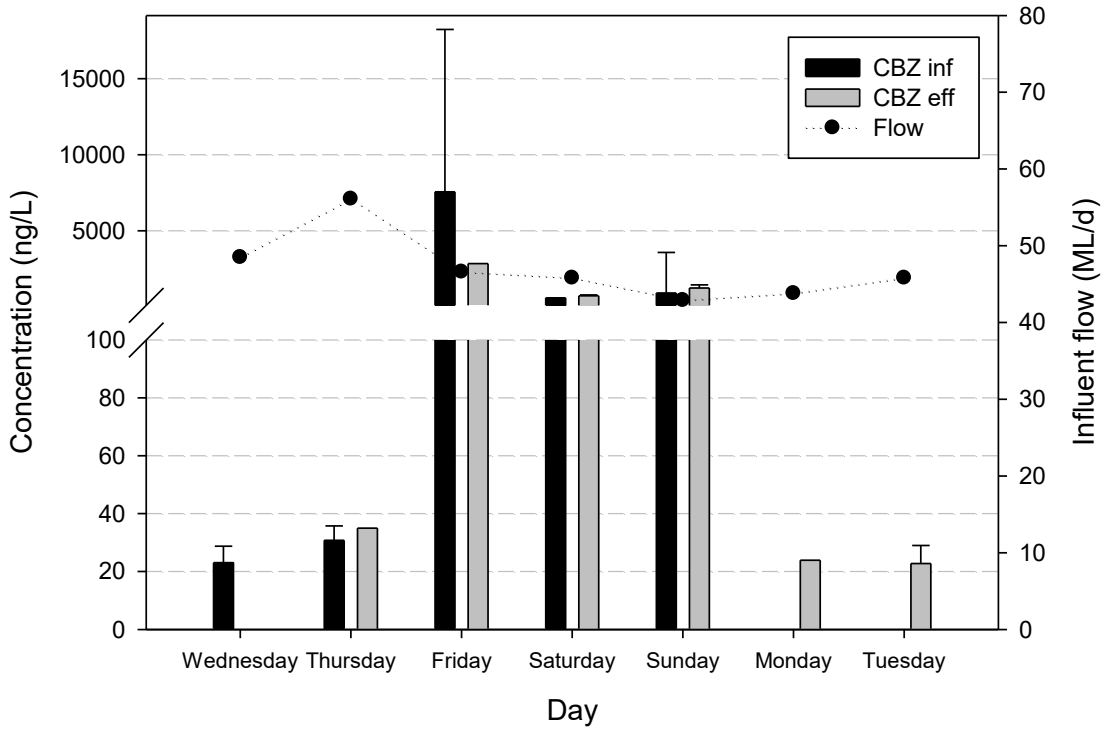
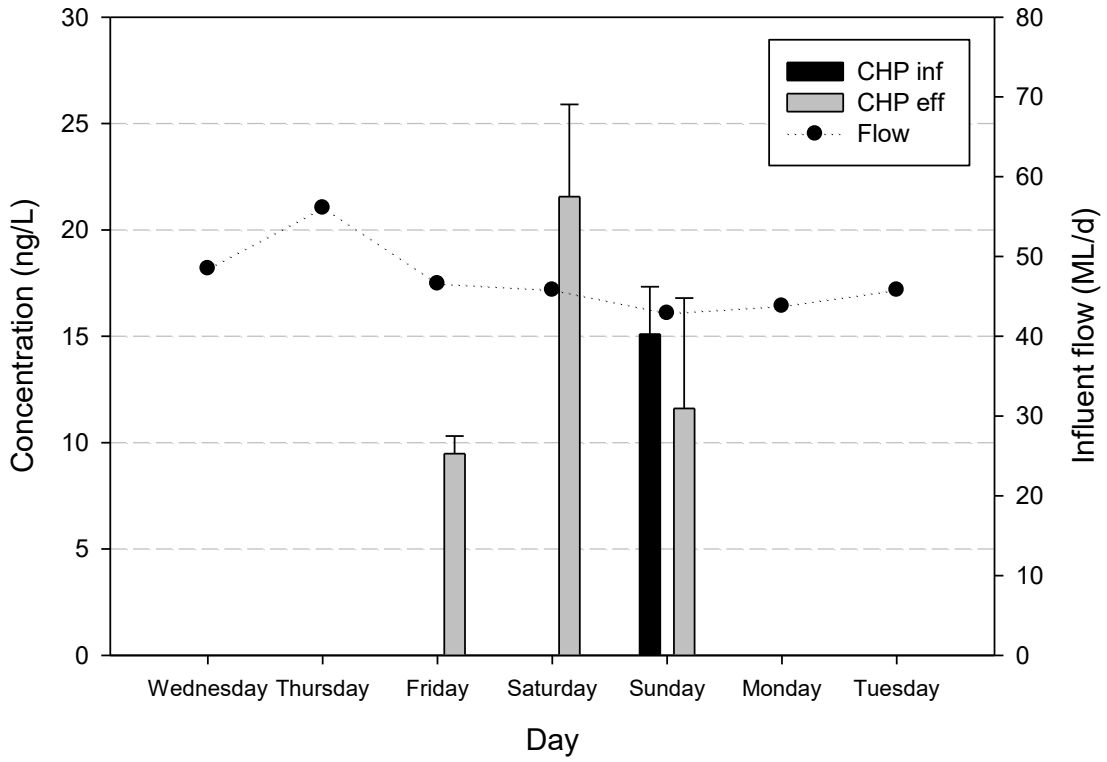


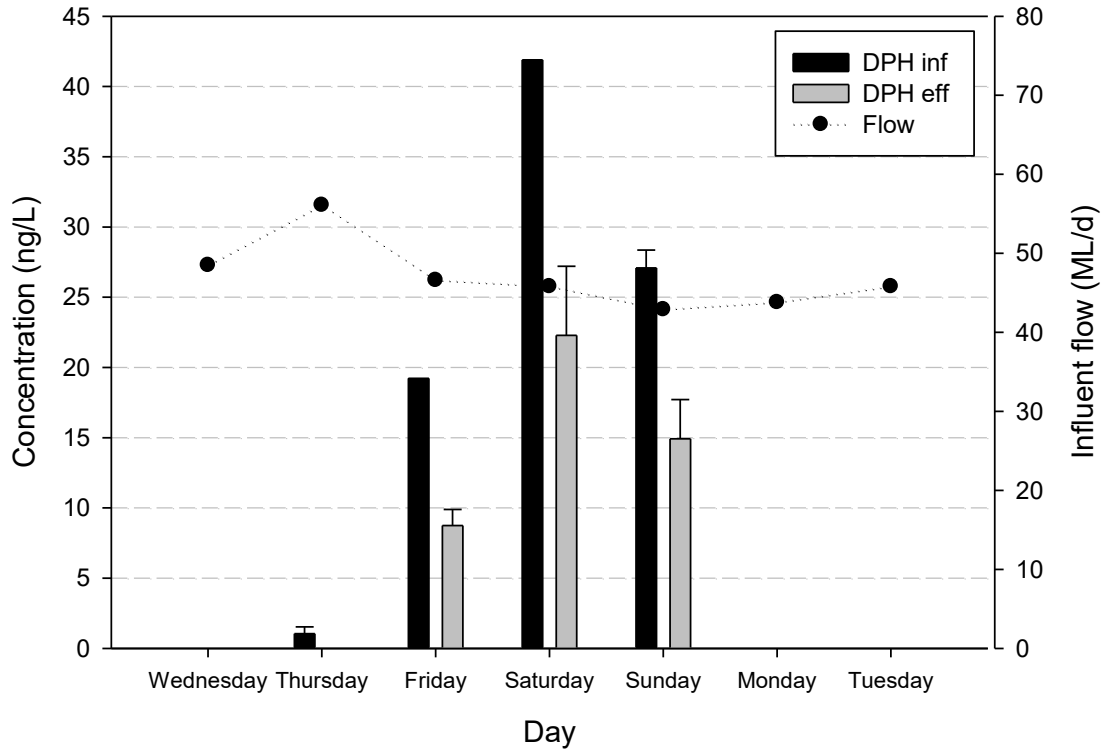
Figure 5: Concentrations of selected analytes in influent and effluent and influent flow rates during the two hourly sampling on Friday 31st August. For the identity of the compound please refer to the abbreviations used in Table 2.

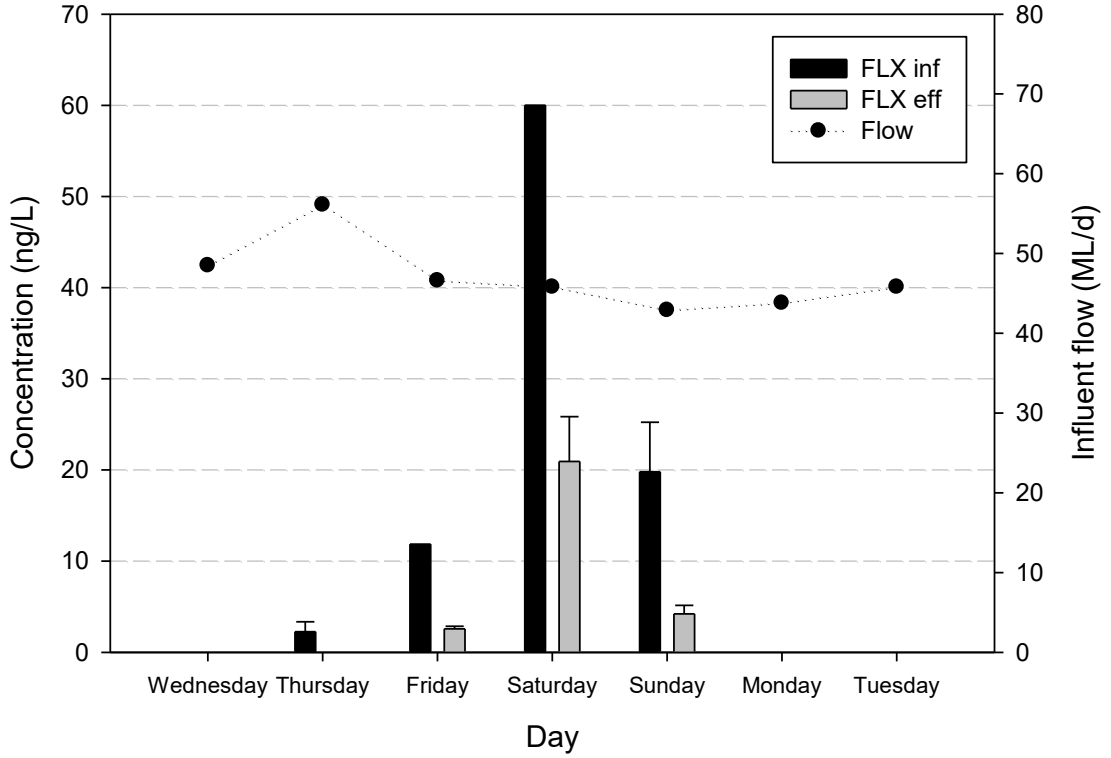

ATL inf
ATL eff
Flow
Concentration (ng/L)
Influent flow (L/s)
150
100
50
15
10
5
0
80
60
40
20
0
Wednesday
Thursday
Friday
Saturday
Sunday
Monday
Tuesday
Day

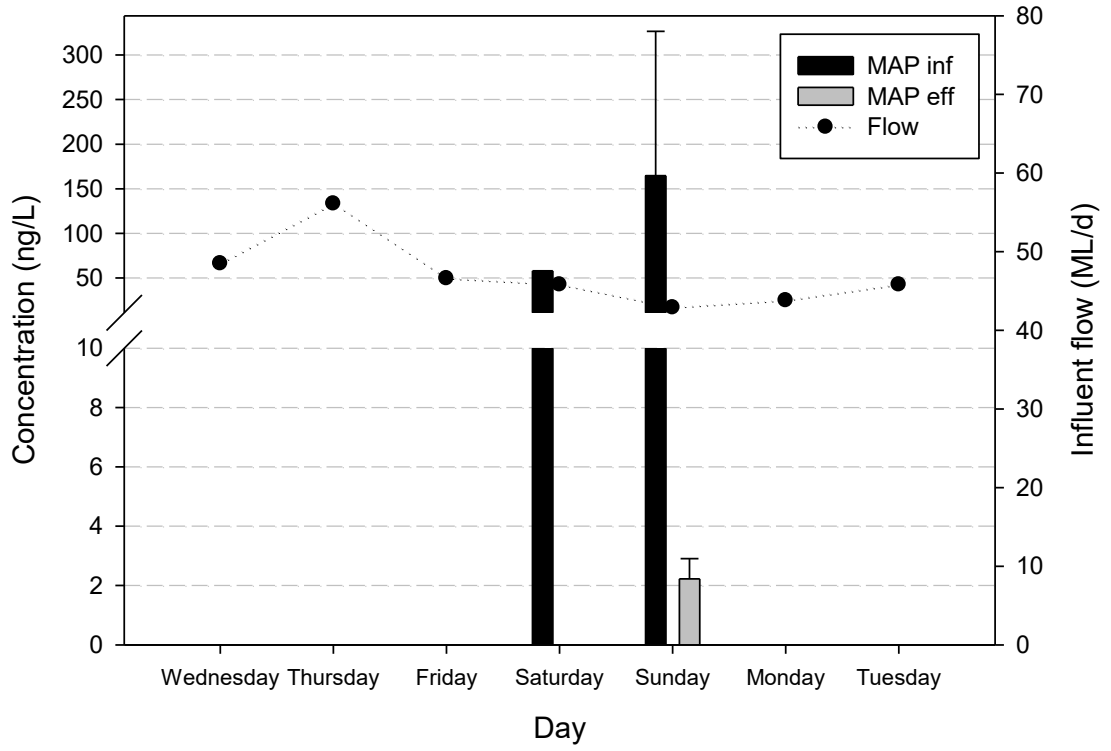

BAC inf
BAC eff
Flow
Concentration (ng/L)
Influent flow (ML/d)
40000
30000
20000
10000
400
300
200
100
0
80
70
60
50
40
30
20
10
0
Wednesday
Thursday
Friday
Saturday
Sunday
Monday
Tuesday
Day

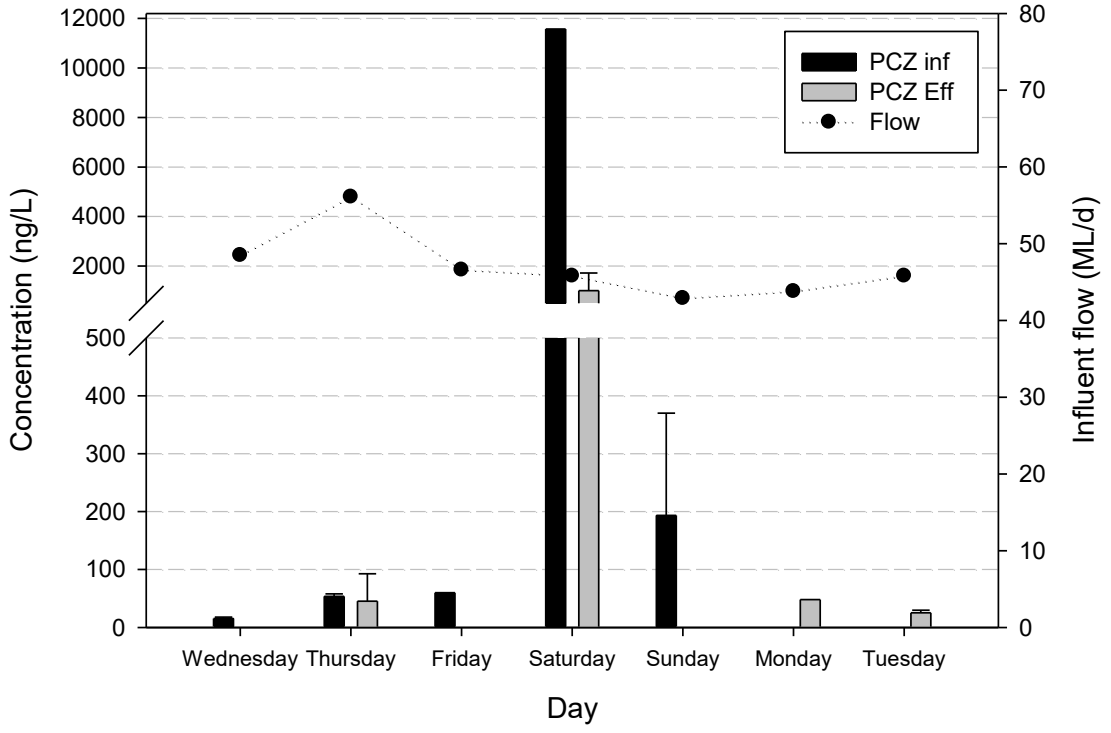

CBZ inf
CBZ eff
Flow
Concentration (ng/L)
Influent flow (ML/d)
15000
10000
5000
100
80
60
40
20
0
80
70
60
50
40
30
20
10
0
Wednesday
Thursday
Friday
Saturday
Sunday
Monday
Tuesday
Day

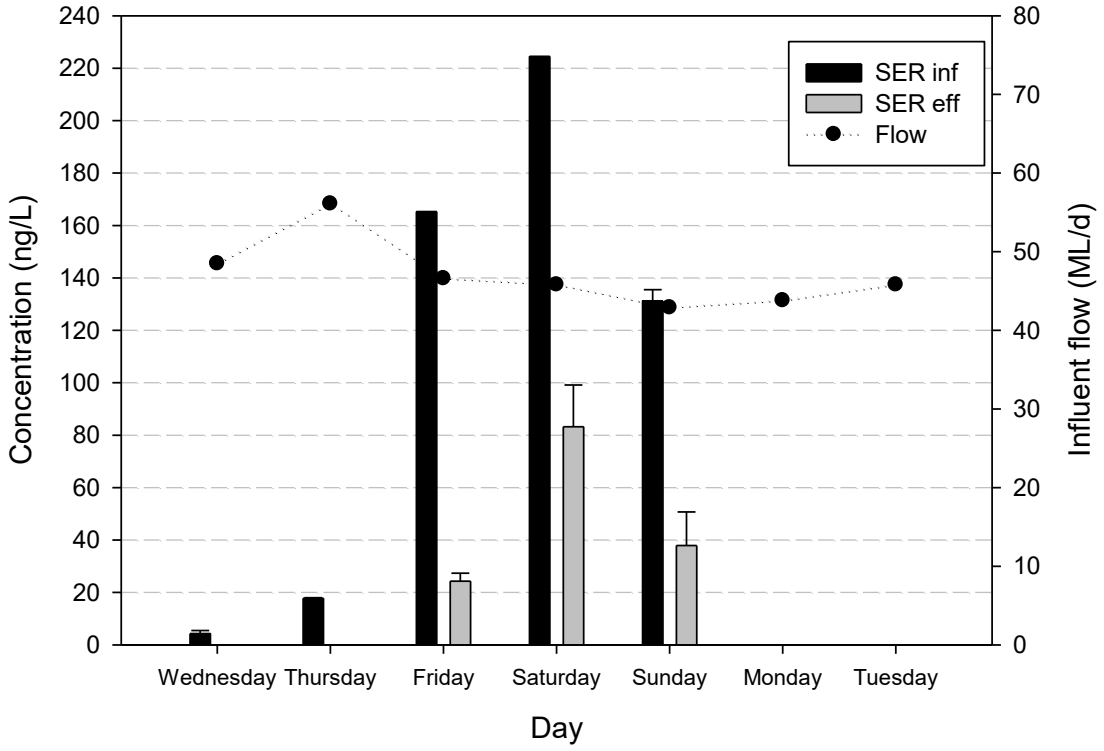

CHP inf
CHP eff
Flow
Concentration (ng/L)
Influent flow (ML/d)
30
25
20
15
10
5
0
80
70
60
50
40
30
20
10
0
Wednesday
Thursday
Friday
Saturday
Sunday
Monday
Tuesday
Day

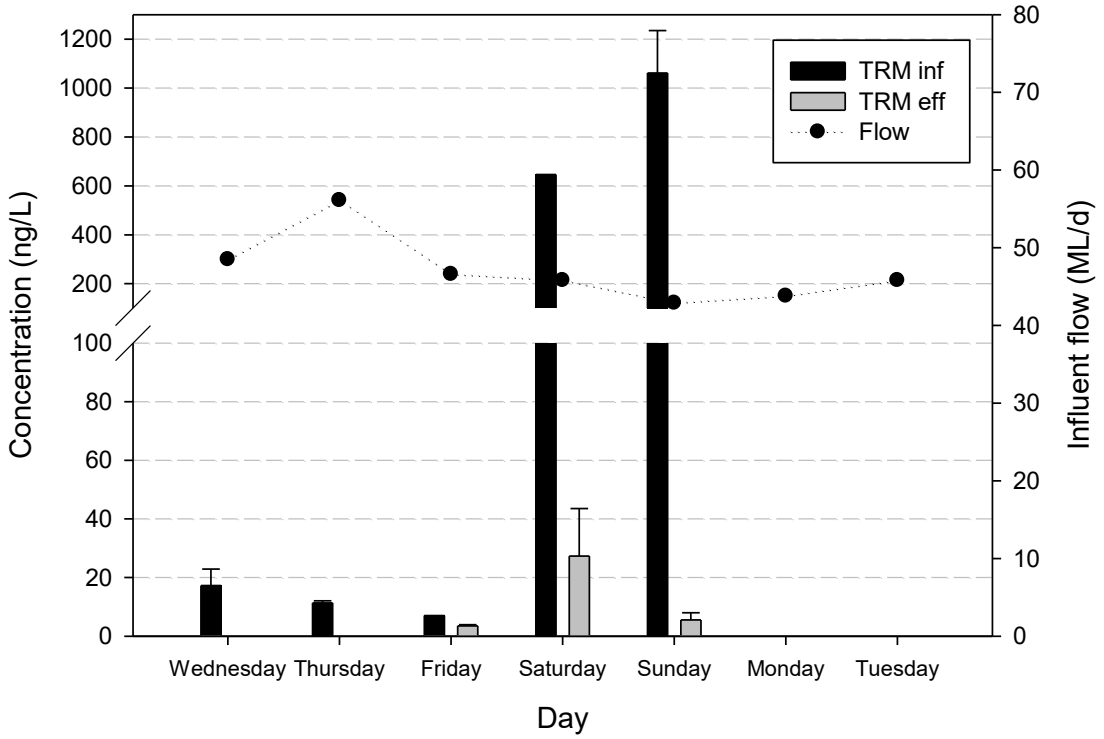

DPH inf
DPH eff
Flow
Concentration (ng/L)
Influent flow (ML/d)
0
5
10
15
20
25
30
35
40
45
0
10
20
30
40
50
60
70
80
Wednesday
Thursday
Friday
Saturday
Sunday
Monday
Tuesday
Day


FLX inf
FLX eff
Flow
Concentration (ng/L)
Influent flow (ML/d)
0
10
20
30
40
50
60
70
0
10
20
30
40
50
60
70
80
Wednesday
Thursday
Friday
Saturday
Sunday
Monday
Tuesday
Day


MAP inf
MAP eff
Flow
Concentration (ng/L)
Influent flow (ML/d)
300
250
200
150
100
50
10
8
6
4
2
0
80
70
60
50
40
30
20
10
0
Wednesday
Thursday
Friday
Saturday
Sunday
Monday
Tuesday
Day


PCZ inf
PCZ Eff
Flow
Concentration (ng/L)
Influent flow (ML/d)
12000
10000
8000
6000
4000
2000
500
400
300
200
100
0
80
70
60
50
40
30
20
10
0
Wednesday
Thursday
Friday
Saturday
Sunday
Monday
Tuesday
Day


SER inf
SER eff
Flow
Concentration (ng/L)
Influent flow (ML/d)
Wednesday
Thursday
Friday
Saturday
Sunday
Monday
Tuesday
Day


TRM inf
TRM eff
Flow
Concentration (ng/L)
Influent flow (ML/d)
Wednesday
Thursday
Friday
Saturday
Sunday
Monday
Tuesday
Day

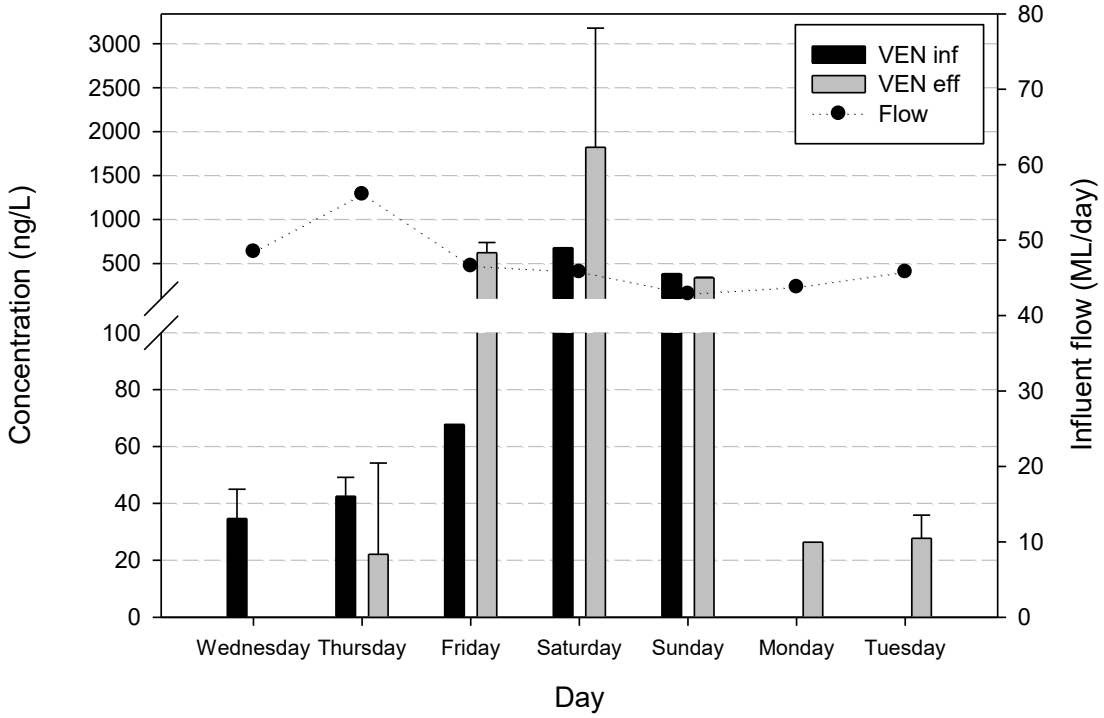


Figure 6: Concentrations of selected analytes in influent (inf) and effluent (eff) and influent flow rates during the daily sampling from Wednesday 29th August until Tuesday 4th September. For the identity of the compound please refer to the abbreviations used in Table 2, above.

APPENDIX C: PREPARATION OF SAMPLING CONTAINERS

Bottles used for sampling were thoroughly prepared prior to collection of samples. An overview of this procedure is as follows:

Soak each bottle and cap in a Pyroneg detergent solution for 16 hours

Decant half of the detergent solution in each bottle.

Shake vigorously for a minute and decant.

Rinse off any soap residue in the bottle using tap water.

Fill each bottle with ¼ full of deionised water.

Shake vigorously and decant.

Repeat deionised water rinse > 3 times.

Fill each bottle with ¼ full of Milli-Q water.

Shake vigorously and decant.

Repeat Milli-Q water rinse 3 times.

Rinse each bottle (1 L) and cap with 25 mL (each time) of HPLC grade acetone 3 times; inverting bottle to ensure mixing.

Rinse each bottle and cap with 25 mL (each time) of HPLC grade methanol 3 times.

Bake glassware at 350°C

Store bottles firmly capped

APPENDIX D: COLLECTION AND PREPARATION OF SAMPLES FOR ANALYSIS

Immediately following collection 1 L samples were spiked with 0.5 mL concentrated H_2SO_4 to reduce the pH to less than 2 and inhibit microbial activity. Samples were then immediately placed at 4°C in the dark for transport to the laboratory. Prior to loading onto SPE cartridges all samples were first filtered through a GF/A (1.2 μm pore size) followed by a GF/F (0.7 μm pore size) glass fibre filter.

SPE cartridges were pre-conditioned by adding 5 mL methanol followed by 5 mL Milli-Q water. Samples were then transferred to the SPE cartridges via PTFE tubes at a rate of <15 mL/min. Following completion of transfer of samples, SPE cartridges were dried for at least 10 min and then washed with 2 x 5 mL 5% methanol solution. SPE cartridges were then dried again under vacuum and stored in sealed plastic bags at -18°C in the dark until elution.

SPE cartridges were placed on a manifold and eluted into clean borosilicate glass tubes. SPE cartridges were eluted with 2 x 3 mL methanol followed by 2x3 mL dichloromethane. Eluate was then evaporated under N_2 at 40°C and blown gently until dry. Samples were then reconstituted with 1 mL methanol, vortexed for 20 s until they were homogenised then placed in amber 2 mL HPLC vials and stored in the dark at -18°C until analysis.

GLOSSARY

ATL	Atenolol
BAC	Benzalkonium chloride
CBZ	Carbamazepine
CHP	Chlorpheniramine
COT	Cotinine
DPH	Diphenhydramine
DNA	Deoxyribonucleic acid
EDC	Endocrine disrupting chemical
FLX	Fluoxetine
GC-MS	Gas chromatography combined with mass spectrometry
GC-MS/MS	Gas chromatography combined with tandem mass spectrometry
HRT	Hydraulic retention time
LC-MS/MS	Liquid chromatography combined with tandem mass spectrometry
LLOQ	Lower limit of quantification
LOQ	Limit of quantification
MAP	Methamphetamine
MDMA	Methylenedioxymethamphetamine
MRM	Multiple reaction monitoring
PCZ	Propiconazole
PPPC	Pharmaceutical and personal care product
SEQ	South East Queensland
SER	Sertraline
SIM	Selected ion monitoring
SNRI	Serotonin-norepinephrine re-uptake inhibitor
SPE	Solid phase extraction
STP	Sewage treatment plant
TRM	Trimethoprim
ULOQ	Upper limit of quantification
UV	Ultraviolet
VEN	Venlafaxine
WWTP	Wastewater treatment plant

REFERENCES

Bartelt-Hunt SL, Snow DD, Damon T, Shockley J and Hoagland K (2009). The occurrence of illicit and therapeutic pharmaceuticals in wastewater effluent and surface waters in Nebraska. Environmental Pollution 157, 786-791.

Choi K, Kim Y, Park J, Park CK, Kim MY, Kim HS and Kim P (2008). Seasonal variations of several pharmaceutical residues in surface water and sewage treatment plants of Han River, Korea. Science of the Total Environment 405, 120-128.

Clara M, Scharf S, Scheffknecht C and Gans O (2007). Occurrence of selected surfactants in untreated and treated sewage. Water Research 41, 4339-4348.

CoA (2009) 'Australian Statistics on Medicines (2008). Department of Health and Ageing, Australian Government, Commonwealth of Australia, Canberra.

Gros M, Petrovic M and Barcelo D (2006). Development of a multi-residue analytical methodology based on liquid chromatography-tandem mass spectrometry (LC-MS/MS) for screening and trace level determination of pharmaceuticals in surface and wastewaters. Talanta 70, 678-690.

Huerta-Fontela M, Galceran MT, Martin-Alonso J and Ventura F (2008). Occurrence of psychoactive stimulatory drugs in wastewaters in north-eastern Spain. Science of the Total Environment 397, 31-40.

Kahle M, Buerge IJ, Hauser A, Muller MD and Poiger T (2008). Azole fungicides: Occurrence and fate in wastewater and surface waters. Environmental Science & Technology 42, 7193-7200.

Lajeunesse A, Gagnon C and Sauve S (2008). Determination of basic antidepressants and their n-desmethyl metabolites in raw sewage and wastewater using solid-phase extraction and liquid chromatography - Tandem mass spectrometry. Analytical Chemistry 80, 5325-5333.

Martinez-Carballo E, Sitka A, Gonzalez-Barreiro C, Kreuzinger N, Furhacker M, Scharf S and Gans O (2007). Determination of selected quaternary ammonium compounds by liquid chromatography with mass spectrometry. Part I. Application to surface, waste and indirect discharge water samples in Austria. Environmental Pollution 145, 489-496.

Metcalfe CD, Koenig BG, Bennie DT, Servos M, Ternes TA and Hirsch R (2003). Occurrence of neutral and acidic drugs in the effluents of Canadian sewage treatment plants. Environmental Toxicology and Chemistry 22, 2872-80.

Miao XS, Yang JJ and Metcalfe CD (2005). Carbamazepine and its metabolites in wastewater and in biosolids in a municipal wastewater treatment plant. Environmental Science & Technology 39, 7469-7475.

Nakada N, Shinohara H, Murata A, Kiri K, Managaki S, Sato N and Takada H (2007). Removal of selected pharmaceuticals and personal care products (PPCPs) and endocrine-disrupting chemicals (EDCs) during sand filtration and ozonation at a municipal sewage treatment plant. Water Research 41, 4373-4382.

Ort C, Lawrence MG, Reungoat J and Mueller JF (2010a). Sampling for PPCPs in Wastewater Systems: Comparison of Different Sampling Modes and Optimization Strategies. Environmental Science & Technology 44, 6289-6296.

Ort C, Lawrence MG, Rieckermann J and Joss A (2010b). Sampling for Pharmaceuticals and Personal Care Products (PPCPs) and Illicit Drugs in Wastewater Systems: Are Your Conclusions Valid? A Critical Review. Environmental Science & Technology 44, 6024-6035.

Radjenovic J, Petrovic M and Barceló D (2009). Fate and distribution of pharmaceuticals in wastewater and sewage sludge of the conventional activated sludge (CAS) and advanced membrane bioreactor (MBR) treatment. Water Research 43, 831-841.

Schultz MM and Furlong ET (2008). Trace analysis of antidepressant pharmaceuticals and their select degradates in aquatic matrixes by LC/ESI/MS/MS. Analytical Chemistry 80, 1756-1762.

Van de Steene JC and Lambert WE (2008). Validation of a solid-phase extraction and liquid chromatography-electrospray tandem mass spectrometric method for the determination of nine basic pharmaceuticals in wastewater and surface water samples. Journal of Chromatography, A 1182, 153-160.

Vasskog T, Anderssen T, Pedersen-Bjergaard S, Kallenborn R and Jensen E (2008). Occurrence of selective serotonin reuptake inhibitors in sewage and receiving waters at Spitsbergen and in Norway. Journal of Chromatography A 1185, 194-205.

Vieno N, Tuhkanen T and Kronberg L (2007). Elimination of pharmaceuticals in sewage treatment plants in Finland. Water Research 41, 1001-1012.

Watkinson AJ, Murby EJ and Costanzo SD (2007) Removal of antibiotics in conventional and advanced wastewater treatment: Implications for environmental discharge and wastewater recycling. Water Research 41, 4164-4176.

Zhang Y and Geißen S-U (2010). Prediction of carbamazepine in sewage treatment plant effluents and its implications for control strategies of pharmaceutical aquatic contamination. Chemosphere 80, 1345-1352.

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