PPCPS' REMOVAL IN A WASTEWATER TREATMENT PLANT OF NEW ZEALAND

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ABSTRACT

In this study, the occurrence and removal efficiency of 19 selected pharmaceuticals and Personal care products (PPCPs) was investigated in an urban wastewater treatment plant of New Zealand to evaluate the removal efficiency of the treatment plant which relies on membrane bioreactor (MBR) and Bardenpho process for wastewater treatment. This is the first comprehensive study in New Zealand that reveals the occurrence and removal of PPCPs in a wastewater treatment plant. The 24-hours composite samples were first acidified and filtered and then stored at 4 ºC before analysis. The solid phase extraction followed by vacuum concentration was used for concentrating trace amount of PPCPs present in wastewater. The samples were analyzed by a triple quadrupole tandem mass spectrometer (LC-MS/MS) in both positive and negative electrospray ionization (ESI) mode. The reverse phase amide HPLC column was used to separate the analytes.Results showed that all of the monitored PPCPs were detected in influent and more than 80% were present in wastewater final effluent. Acetaminophen, caffeine, and metformin were the most frequently detected compounds in the influent and were present in the range of 6,000- 40,000 ng/L. The wastewater treatment facility was unable to remove most of the PPCPs efficiently. The removal efficiency was more than 99% for acetaminophen, caffeine, and ibuprofen while it was significantly low (<50%) for trimethoprim, benzotriazole, and TCEP. This study revealed that MBR and Bardenpho processes are not adequate to efficiently remove most of the monitored PPCPs. It highlights the need for further tertiary treatment to improve the overall removal efficiency of the PPCPs from wastewater.

KEYWORDS

PPCPs, Wastewater, MBR, Bardenpho, Removal Efficiency, Emerging Contaminants, New Zealand wastewater treatment plant, Pharmaceuticals

PRESENTER PROFILE

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1 INTRODUCTION

The study of occurrence and fate of pharmaceuticals and personal care products (PPCPs) in aquatic system is one of the most widely researched areas since last decade. The wastewater effluent is considered as one of the major source (Al-Odaini, Zakaria et al. 2010). PPCPs remain ecologically active even at trace concentration in the aquatic system and can cause toxicity to aquatic organisms (Crane, Watts et al. 2006, Fent, Weston et al. 2006, Santos, Aparicio et al. 2007, Kwon and Rodriguez 2014). The fate of PPCPs in the environment is depicted in Figure 1.

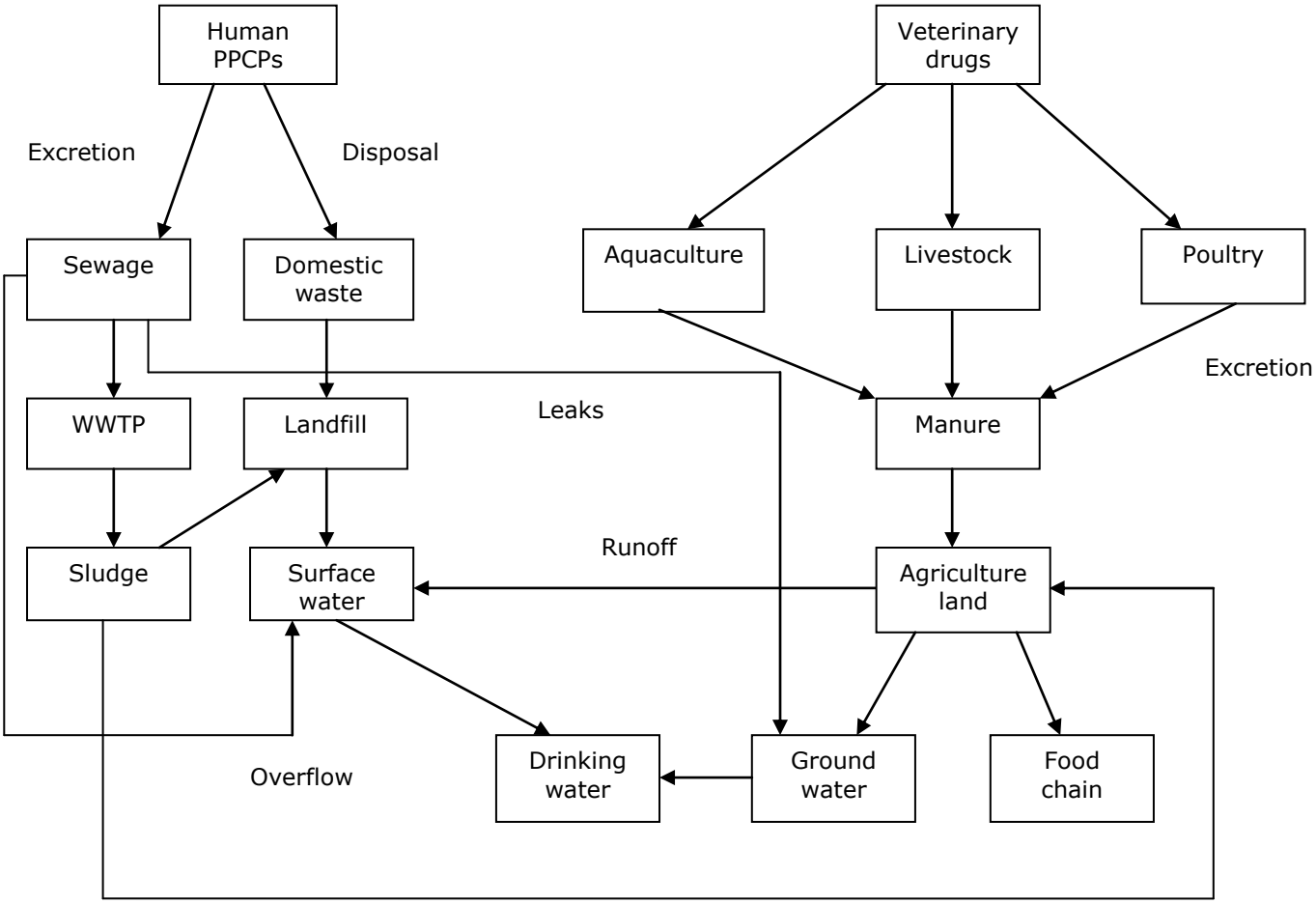


Figure 1. Sources and fate of environmental pollutants (Adapted from (Ebele, Abou-Elwafa Abdallah et al. 2017))

The research reports on the occurrence of PPCPs in wastewater effluents of North America and Europe are on rise since past 10 years (Lishman, Smyth et al. 2006). However, there is no report on the presence of these pharmaceuticals including endocrine disrupting chemicals (EDCs) and personal care products in New Zealand wastewater effluent and drinking water. The scientific community has shown that conventional wastewater treatment processes are not very effective in removing emerging contaminants, including PPCPs and EDCs (Behera, Kim et al. 2011, Padhye, Yao et al. 2014), that leads to their presence in rivers, lakes (Comoretto and Chiron 2005, Zhang, Zhang et al. 2007, Wu, Huang et al. 2014) and groundwater (Kreuzinger, Clara et al. 2004, Sui, Cao et al. 2015).

The present study focuses on studying the occurrence and removal of pharmaceuticals and personal care products in the wastewater treatment plant in one of the major cities of New Zealand.

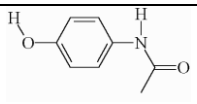
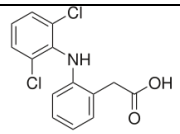
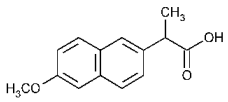
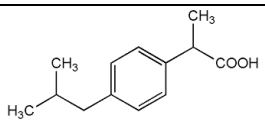
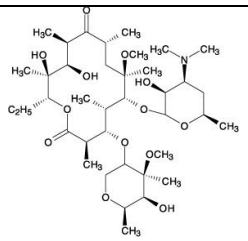
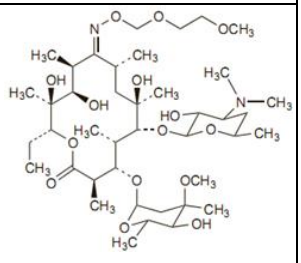
2 DISCUSSION

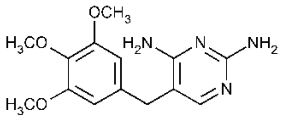
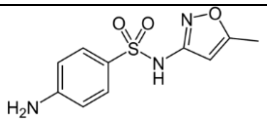
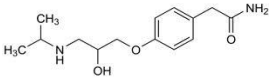
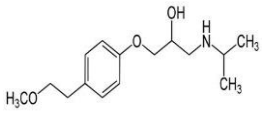
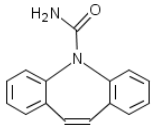
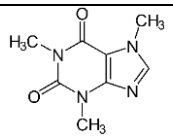
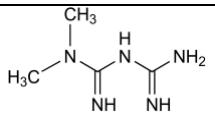
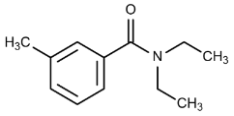
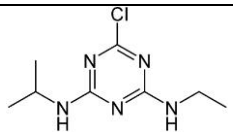
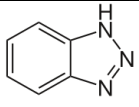
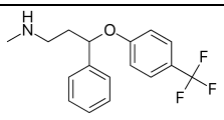
2.1 MATERIALS AND METHOD

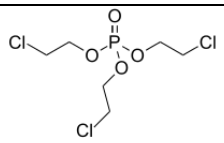
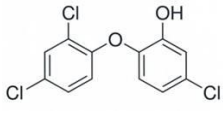
2.1.1 CHEMICALS

The pharmaceutical standards of analytical grade were purchased from Sigma Aldrich, New Zealand. The organic solvents such as methanol and acetonitrile of LC-MS grade were purchased from Thermofisher, New Zealand. The mobile phase additives such as formic acid and ammonium acetate were purchased from Sigma Aldrich, New Zealand. Oasis HLB (500 mg, 6 cc) cartridges were purchased from Waters Corporation (USA). The Stock of 1,000 mg/L solutions of each PPCP was prepared in methanol and stored at – 18 °C prior to use. Table 1 lists the PPCPs selected for the study.

Table 1 List of PPCPs

CLASS	PHARMACEUTICAL	MOLECULAR FORMULA	MOLECULAR STRUCTURE
ANALGESICS/ ANTI INFLAMMATORY	ACETAMINOPHEN	$C_8H_9NO_2$	
	DICLOFENAC	$C_{14}H_{11}CL_2NO_2$	
	NAPROXEN	$C_{14}H_{14}O_3$	
	IBUPROFEN	$C_{13}H_{18}O_2$	
ANTIBIOTICS	CLARITHROMYCIN	$C_{38}H_{69}NO_{13}$	
	ROXITHROMYCIN	$C_{41}H_{76}N_2O_{15}$	

	TRIMETHOPRIM	$C_{14}H_{18}N_4O_3$	
	SULFAMETHOXAZOLE	$C_{10}H_{11}N_3O_3S$	
β BLOCKER AND LIPID REGULATORS	ATENOLOL	$C_{14}H_{22}N_2O_3$	
	METOPROLOL	$C_{34}H_{56}N_2O_{10}$	
ANTIEPILEPTIC	CARBAMAZEPINE	$C_{15}H_{12}N_2O$	
PSYCHOACTIVE	CAFFEINE	$C_8H_{10}N_4O_2$	
ANTIDIABETIC	METFORMIN	$C_4H_{11}N_5$	
INSECT REPELLANT	DEET	$C_{12}H_{17}NO$	
HERBICIDE	ATRAZINE	$C_8H_{14}CLN_5$	
CORROSION INHIBITOR	BENZOTRIAZOLE	$C_6H_5N_3$	
ANTIDEPRESSANT	FLUOXETINE	$C_{17}H_{18}F_3NO$	

FLAME RETARDANT	TCEP	$C_6H_{12}CL_3O_4P$	
ANTIMICROBIAL	IRGASAN	$C_{12}H_7CL_3O_2$	

2.1.2. SAMPLING LOCATION AND SAMPLE COLLECTION

The samples were collected from a wastewater treatment plant (WWTP)_of a major city in New Zealand. The WWTP has a capacity to treat 20-25 MLD (million liters per day) of wastewater. Most of wastewater is generated by domestic use. The wastewater treatment plant uses 5-stage Bardenpho process and Membrane Bioreactor (MBR) as final treatment unit before final discharge. The treated effluent from the plant is used for irrigation purpose. The influent and treated (primary treatment, Bardenpho and MBR) composite wastewater samples were collected in HDPE bottles over a week.

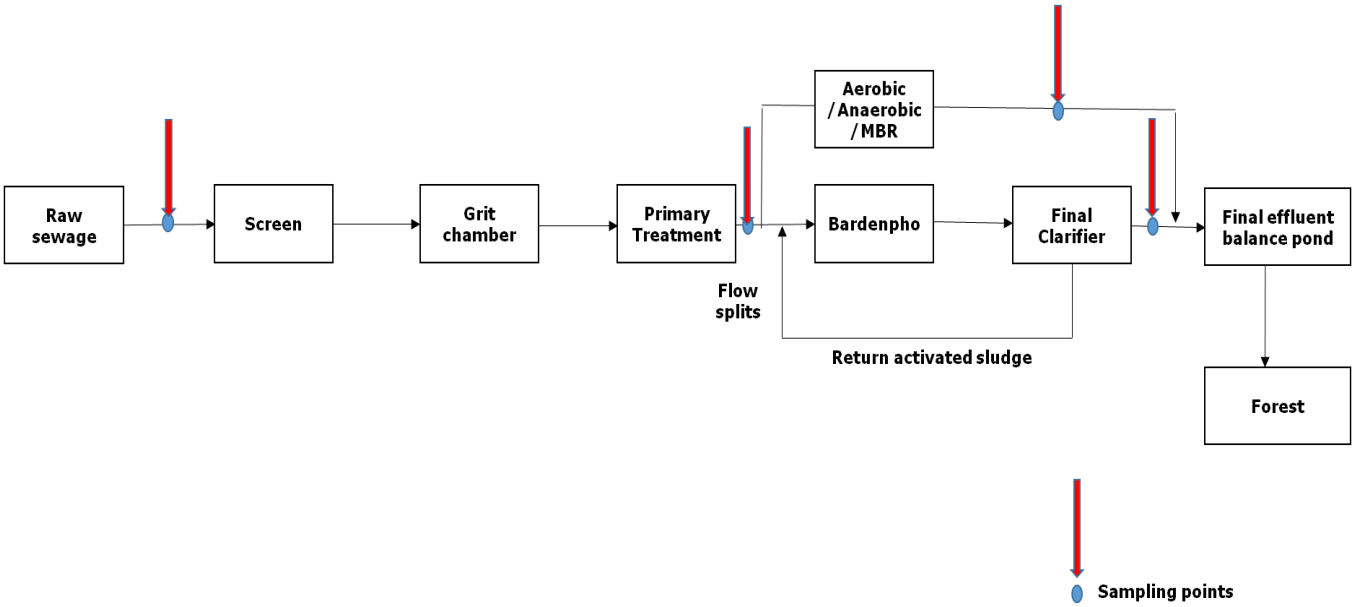


FIGURE 2. PROCESS DIAGRAM OF AN URBAN WWTP OF NEW ZEALAND

2.1.2. WASTEWATER QUALITY CHARACTERIZATION

The wastewater was analyzed within 24 hours for general parameters like pH, alkalinity, carbonaceous Biochemical Oxygen Demand (cBOD), Chemical Oxygen Demand (COD), Dissolved Reactive Phosphorus (DRP), nitrogen (ammonia nitrogen + nitrite nitrogen +

total Kjeldahl nitrogen+ total oxidised nitrogen), Total phosphorus, Turbidity and Suspended solids.

2.1.3. SAMPLE PROCESSING

The pH was adjusted to 2 for all samples. The samples were then put in ice packs and transferred immediately to the lab and were filtered with 0.7 µm glass fibre filter to eliminate suspended particles. The samples were stored at 4 °C prior to solid phase extraction. The solid phase extraction (SPE) was carried out for 1,000 mL of samples from each stage of treatment using oasis HLB (500 mg, 6 cc) cartridge following the steps detailed in (Kosma, Lambropoulou et al. 2014). The analytes were eluted with 10 ml (2 x 5 ml) of methanol at flow rate of 1 drop/second. The 10 ml extracts were transferred to vacuum concentrator to concentrate down 10 ml to 1 ml ensuring minimum analyte loss.

2.1.4. LC-MS/MS ANALYSIS

The analysis was conducted on Shimadzu 8040 triple quadrupole LC-MS/MS. The reverse phase amide HPLC column (10 cm x 2.1 mm, 3 µm) was used to separate analytes. The analysis was done in both positive and negative electro spray ionization (ESI) mode. The mobile phase A was milliQ water with 0.1% formic acid for positive mode and milliQ water with 5 mM ammonium acetate for negative mode. The mobile phase B was acetonitrile with 0.1% formic acid for positive mode and acetonitrile with 5 mM ammonium acetate for negative mode. The LC gradient for positive mode of ESI started with 5% B at 0.01 min and maintained for 1.5 min, increased to 20% B at 3 min, 45% B at 4 min and 65% B at 6.1 min and 100 % B at 7 min, decreased to 5% B at 7.45 min followed by post time of 1.45 min. The LC gradient for negative ESI mode started with 20% B at 0.01 min, increased to 96% B at 4.5 min and 100 % B at 5 min and maintained for 1.3 minutes followed by decrease to 20% B at 6.4 min and post time of 1.5 min. The MS acquisition was done in MRM mode.

2.2. RESULTS AND DISCUSSION

2.2.1. WASTEWATER QUALITY CHARACTERIZATION

The general wastewater quality parameters were analyzed by wastewater treatment facility within 24 hours of the sample collection and results are shown in Table 2. The pH of influent and effluent were found to be around 7.2 and 7.3, respectively. The alkalinity removal ranged between 80-85% by both Bardenpho and MBR treatment units. The chemical oxygen demand (COD), carbonaceous COD, dissolved reactive phosphorus (DRP) and total phosphorus removal was found to be more than 98% by MBR. The wastewater treatment plant was able to remove total suspended solid (TSS) and turbidity by more than 90%. The ammonia and total Kjeldahl nitrogen (TKN) removal was also found to be more than 90%. However, the removal efficiency for total oxidized nitrogen (TOXN) was found to be negative by both MBR and Bardenpho, which could be due to low rate of denitrification in the system.

Table 2. General wastewater quality

Parameters	Influent	Primary effluent	MBR	Bardenpho

Alkalinity (mg/L)	218.04	237.5	81.7	85.8
$CBOD_5$[1] (mg/L)	137.57	95	2	5
COD[2] (mg/L)	417.14	360	<6	52
DRP[3] (mg/L)	3.46	3.75	0.05	2.76
NH_4 (mg/L)	37.55	36.35	0.05	0.14
Nitrite (mg/L)	<0.01	<0.01	0.1	0.03
pH	7.32	7.37	7.0	7.21
TKN[4] (mg/L)	52.79	52.41	1.86	2.64
TOXN[5] (mg/L)	0.135	0.01	1.67	3.34
Total Phosphorus (mg/L)	5.49	6.01	0.09	3.45
TSS[6] (mg/L)	249	126	10	19
Turbidity (NTU)	172.42	124	0.2	12.4

1. Carbonaceous Biological Oxygen Demand
2. Chemical Oxygen Demand
3. Dissolved Reactive Phosphorus
4. Total Kjeldahl Nitrogen
5. Total Oxidised Nitrogen (Nitrite+ Nitrate)
6. Total Suspended Solid

2.2.2. MATRIX RECOVERY

The matrix recovery was found to be very low (<2%) for metformin. The low recovery of metformin (<1%) was also reported by (Petrie, Youdan et al. 2016). The range of recoveries for PPCPs in different wastewater matrices is shown in Table 3. The matrix recovery of atenolol was found to be in the range of 9-15% in influent samples and 17-23% in effluent, which is comparable to the recoveries (~7% in influent and 27±4 % in effluent) reported by (Mohapatra, Huang et al. 2016). The recoveries of acetaminophen, sulfamethoxazole, carbamazepine and caffeine in this study was found to be significantly higher than recoveries obtained by (Mohapatra, Huang et al. 2016) using matrix method. The recovery of benzotriazole was found to be in the range of 12-36% for both influent and effluent matrices, which is significant lower than the recovery (>90%) obtained by (Asimakopoulos, Ajibola et al. 2013). The reason of low recoveries could be either due to weak interaction between analytes and cartridge sorbent or inefficient elution of the analytes with the organic solvent.

Table 3. Matrix Recovery

PHARMACEUTICALS	MATRIX RECOVERY (%)			
	INFLUENT	PRIMARY EFFLUENT	MBR	BARDENPHO
ACETAMINOPHEN	44-110	110	30	31
TRIMETHOPRIM	19-28	22	42	4
SULFAMETHOXAZOLE	30-60	44	69	72
ROXITHROMYCIN	9-17	12	26	20
CARBAMAZEPINE	37-57	45	53	53
METFORMIN	<1-1	<1	<1	<1
FLUOXETINE	14-22	18	32	33
CLARITHROMYCIN	7-15	10	25	18
METOPROLOL	21-61	20	62	70
TCEP	21-40	34	40	34
ATRAZINE	35-61	47	66	62
ATENOLOL	9-15	12	17	23
DEET	25-51	37	63	66
CAFFEINE	36-68	36	61	48
BENZOTRIAZOLE	12-26	14	35	36
DICLOFENAC	40-81	61	93	97
IBUPROFEN	47-113	113	48	113
NAPROXEN	>100	>100	>100	>100
IRGASAN	65-93	82	72	87

2.2.3. OCCURRENCE AND FATE OF PPCPS

All of the monitored PPCPs were detected in influent and more than 80% were traced in effluent by LC-MS/MS. Acetaminophen, caffeine, and metformin were the most frequently detected compounds in the influent in the range of 6,000-40,000 ng/L. The total monitored PPCP load over a week in the influent was found to be approximately 96,000 ng/L (~96 µg/L) which is lower than the monitored PPCPs concentration (130-160 µg/L)

in influent of the U.S. wastewater treatment plant (Mohapatra, Huang et al. 2016). The wastewater treatment facility was unable to remove most of the PPCPs efficiently. The total concentration of PPCPs in the effluent was found to be in the range of 7,000-7,500 ng/L (~7-7.5 µg/L), which is comparable to the U.S. counterpart (3-4 µg/L) (Mohapatra, Huang et al. 2016).

The removal efficiency was found to be more than 99% for acetaminophen, caffeine, ibuprofen and naproxen. Similar removal efficiencies were observed for acetaminophen, ibuprofen and naproxen after MBR process by (Radjenovic, Petrovic et al. 2007). The removal efficiency was less than 50% for trimethoprim, benzotriazole and TCEP. The removal efficiency was found to be negative for diclofenac and carbamazepine similar to the findings of (Kosma, Lambropoulou et al. 2014), which could be due to the deconjugation of conjugated metabolites during the treatment. The influent and effluent concentration of carbamazepine ranged between 600-900 ng/L, similar to the results of (Clara, Strenn et al. 2004) after MBR and conventional activated sludge treatment. The removal efficiencies of fluoxetine, atenolol, trimethoprim and sulfamethoxazole was falling in the range of values obtained by (Radjenović, Petrović et al. 2009) after MBR and activated sludge treatment. However, the metprolol and DEET removal efficiency was found to be higher (>90%) compared to the results of study done by (Radjenović, Petrović et al. 2009, Behera, Kim et al. 2011, Wijekoon, McDonald et al. 2015), wherein they report less than 50% rate of removal. The removal efficiency of triclosan was found to be 70% which is similar to the finding of (Wijekoon, McDonald et al. 2015).

Table 4 shows the average concentration of PPCPs after each treatment stage.

Table 4. Average concentration of PPCPs

Compound	Median Influent Concentration (ng/L)	Primary Effluent (ng/L)	MBR (ng/L)	Bardenpho (ng/L)
Acetaminophen	16,600	13,000	31	16
Trimethoprim	729	1,240	505	460
Sulfamethoxazole	396	455	200	145
Roxithromycin	73	ND	9	ND
Carbamazepine	658	730	705	755
Metformin	6,508	20,000	2,750	4,000
Fluoxetine	59	68	25	40
Clarithromycin	71	ND*	4	4
Metoprolol	6,350	117	481	411
TCEP	200	340	154	106
Atrazine	26	26	15	9
Atenolol	1,871	2,109	1,047	441
DEET	979	815	60	24
Caffeine	38,162	50,650	59	22
Benzotriazole	931	1,390	630	755
Diclofenac	170	210	320	255
Ibuprofen	17,746	7800	24	4
Naproxen	4,400	5,310	29	14
Triclosan	100	145	30	30
Average	**96,029**	**1,04,405**	**7,078**	**7,491**

*Non-detectable

3 CONCLUSIONS

This is the first study in New Zealand that reveals the efficiency of wastewater treatment plant in treating the emerging contaminants. The research findings suggest that current treatment operation is not efficient in complete removal of most of the monitored PPCPs. The total PPCPs concentration in influent of a wastewater treatment plant of New Zealand was found to be lower than the total PPCP load in influent of a wastewater treatment plant of the U.S. However, the total PPCPs concentration in effluent was found to be comparable to the total PPCP load in final discharge of a wastewater treatment plant of the U.S. The total PPCP removal efficiency of MBR was found to be comparable to Bardenpho. This study highlights the need of advanced oxidation process in order to enhance the performance of the wastewater treatment plant.

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