

OCCURRENCE AND FATE OF PPCPs IN WASTEWATER TREATMENT PLANT OF NEW ZEALAND



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What Are They?

Pharmaceuticals and Personal Care products (PPCPs)

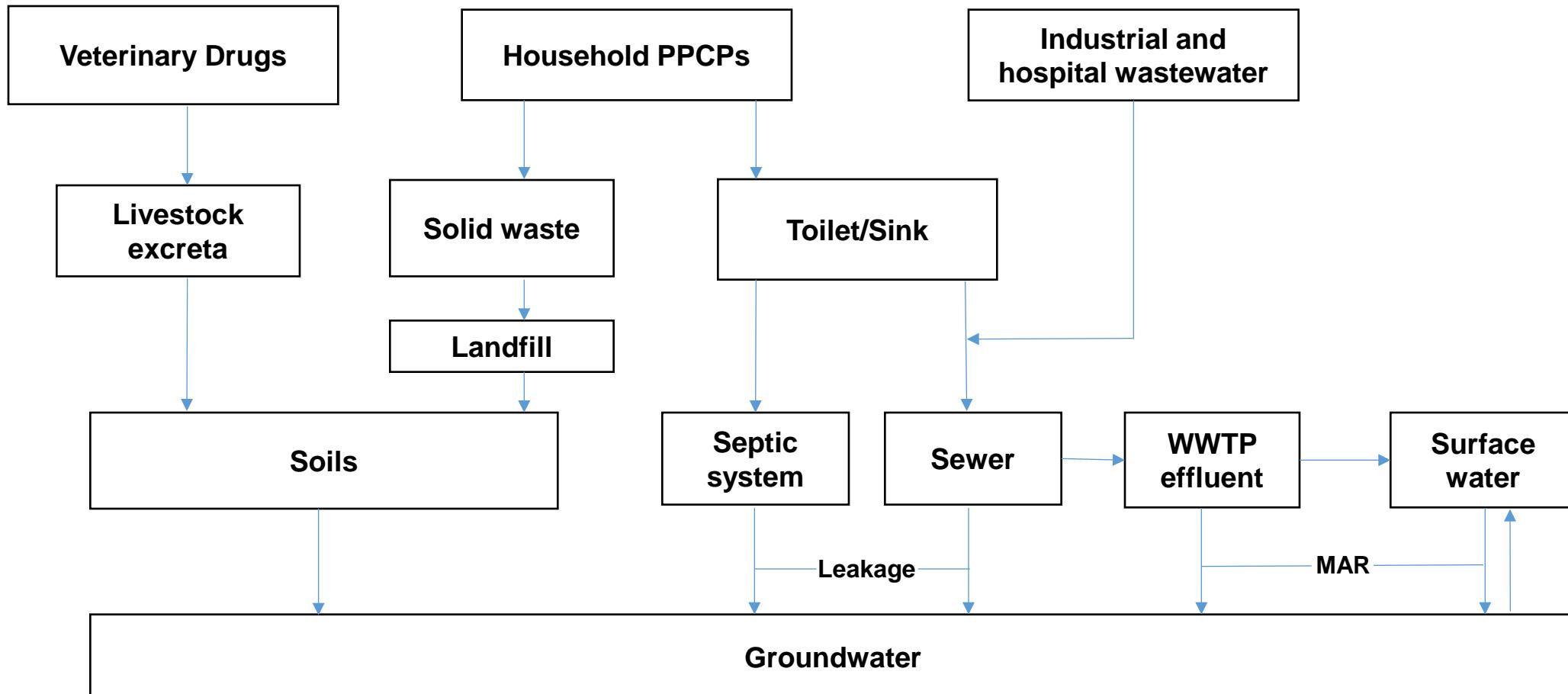
- They include any product used in personal healthcare, cosmetics, and medications, and contain a diverse collection of chemical compounds ranging from drugs, fragrances, lotions, and including the following but not limited to...



Personal care products

Introduction

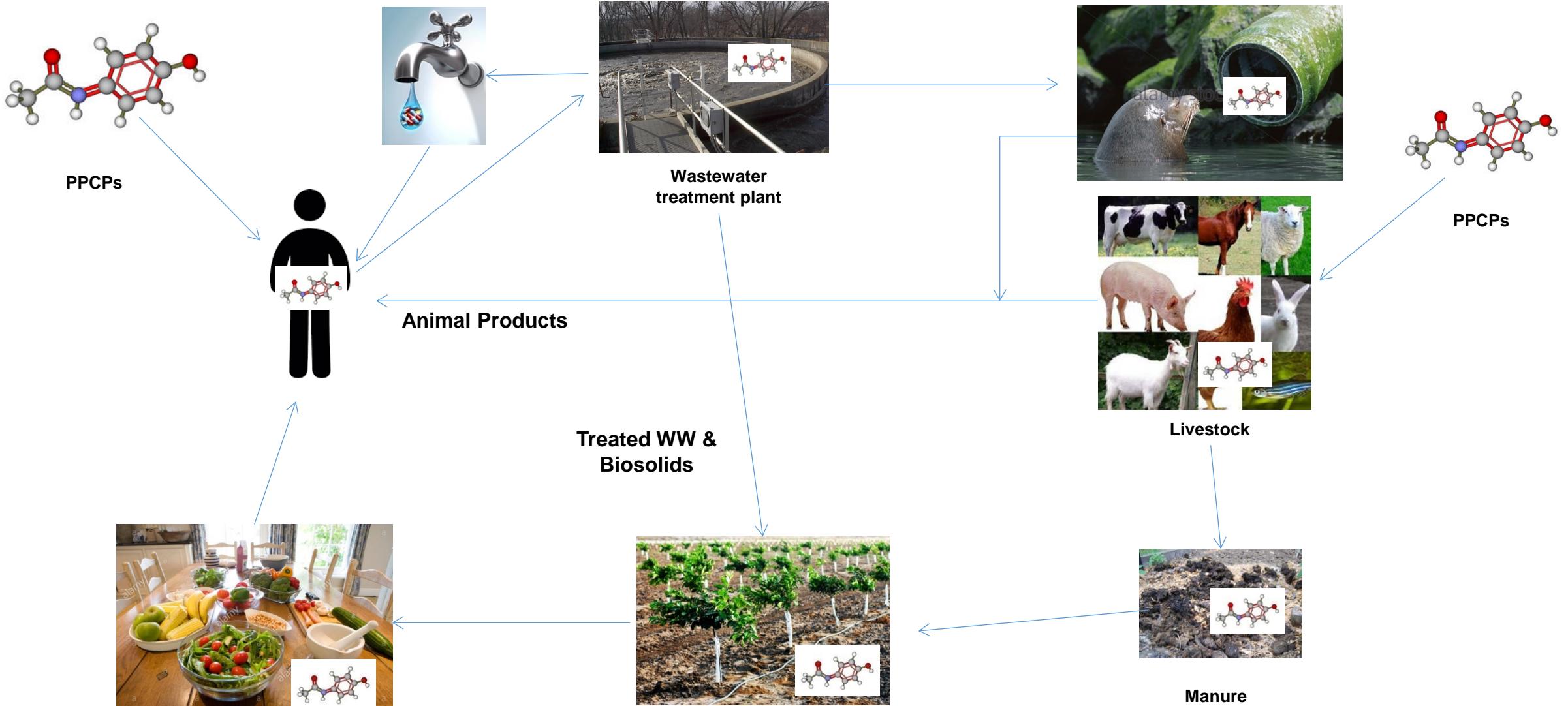
- The pharmaceutical and personal care products (PPCPs) enter into aquatic system through various pathways¹.



Sources and pathways for PPCPs entering groundwater (MAR: managed aquifer recharge)

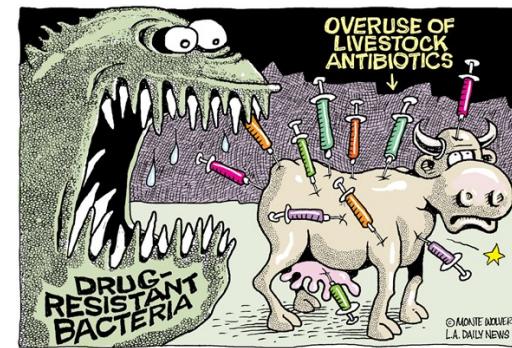
¹ Sui, Q., Cao, X., Lu, S., Zhao, W., Qiu, Z., & Yu, G. (2015). Occurrence, sources and fate of pharmaceuticals and personal care products in the groundwater: A review. *Emerging Contaminants*, 1(1), 14-24. <http://dx.doi.org/10.1016/j.emcon.2015.07.001>

Cyclic flow of PPCPs



Why so much of concern??

- The combination of diverse group of drugs at ng/L level can have adverse effect on human embryonic cell growth.¹
- Few drugs like metformin acts as an endocrine disruptor at environmental relevant concentrations and may give rise to intersex fish.²
- Potential for development of antibiotic resistant bacteria.³
- Rapid decline in population of vultures were observed in India and Pakistan due to diclofenac poisoning when they feed on carcasses of treated livestock.⁴



¹ Pomati, F., Castiglioni, S., Zuccato, E., Fanelli, R., Vigetti, D., Rossetti, C., & Calamari, D. (2006). Effects of a complex mixture of therapeutic drugs at environmental levels on human embryonic cells. *Environmental Science & Technology*, 40(7), 2442-2447.

² Niemuth, N. J., & Klaper, R. D. (2015). Emerging wastewater contaminant metformin causes intersex and reduced fecundity in fish. *Chemosphere*, 135, 38-45. doi: 10.1016/j.chemosphere.2015.03.060

³ Brown, K. D., Kulis, J., Thomson, B., Chapman, T. H., & Mawhinney, D. B. (2006). Occurrence of antibiotics in hospital, residential, and dairy effluent, municipal wastewater, and the Rio Grande in New Mexico. *Science of The Total Environment*, 366(2), 772-783. <http://dx.doi.org/10.1016/j.scitotenv.2005.10.007>

⁴ GREEN, R. E., NEWTON, I., SHULTZ, S., CUNNINGHAM, A. A., GILBERT, M., PAIN, D. J. and PRAKASH, V. (2004), Diclofenac poisoning as a cause of vulture population declines across the Indian subcontinent. *Journal of Applied Ecology*, 41: 793-800. doi:10.1111/j.0021-8901.2004.00954.x

Research Background

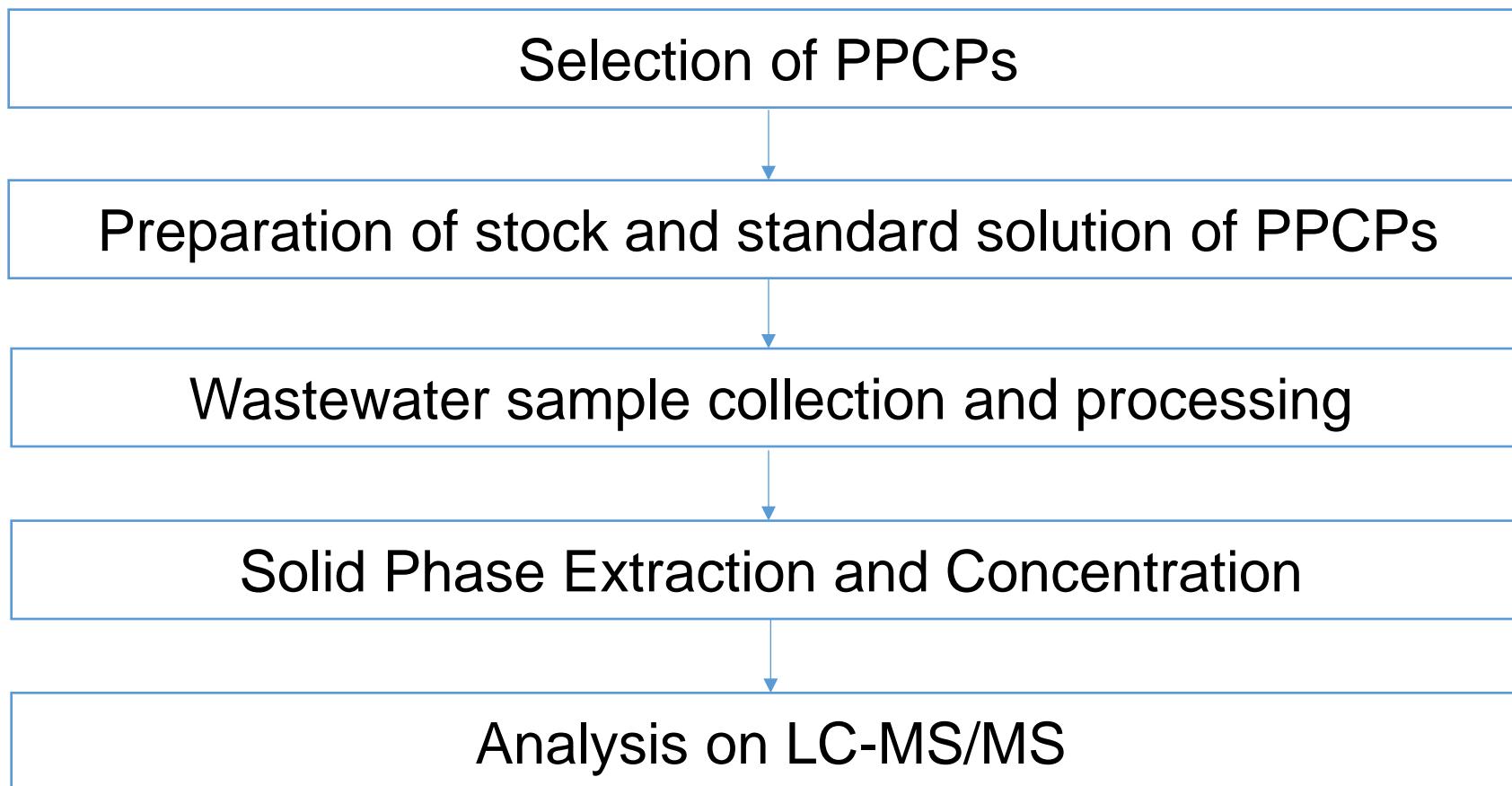
- The wastewater is considered as the major contributor towards total PPCPs in aquatic system¹.
- The PPCPs have been detected from ng/L to µg/L in surface and wastewater².
- These PPCPs being incompletely removed by conventional wastewater treatment plant can impose potential threat to ecosystem³.

¹ Sui, Q., Cao, X., Lu, S., Zhao, W., Qiu, Z., & Yu, G. (2015). Occurrence, sources and fate of pharmaceuticals and personal care products in the groundwater: A review. *Emerging Contaminants*, 1(1), 14-24. <http://dx.doi.org/10.1016/j.emcon.2015.07.001>

² Cizmas, L., Sharma, V. K., Gray, C. M., & McDonald, T. J. (2015). Pharmaceuticals and personal care products in waters: occurrence, toxicity, and risk. *Environmental Chemistry Letters*, 13(4), 381-394. 10.1007/s10311-015-0524-4

³ Ebele, A. J., Abou-Elwafa Abdallah, M., & Harrad, S. Pharmaceuticals and personal care products (PPCPs) in the freshwater aquatic environment. *Emerging Contaminants* <http://dx.doi.org/10.1016/j.emcon.2016.12.004>

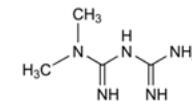
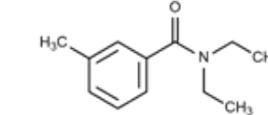
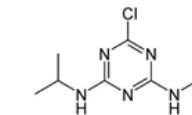
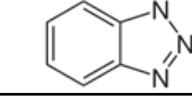
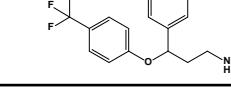
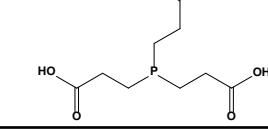
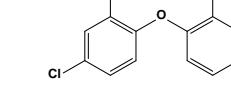
Research Methodology



PPCPs selected for the study

Category	Pharmaceutical	pK _a	Log K _{ow}	Molecular formula	Molecular structure
Analgesics/ Anti inflammatory	Acetaminophen	9.38	0.46	C ₈ H ₉ NO ₂	
	Diclofenac	4.15	4.51	C ₁₄ H ₁₁ Cl ₂ NO ₂	
	Naproxen	4.15	3.18	C ₁₄ H ₁₄ O ₃	
	Ibuprofen	4.91	3.97	C ₁₃ H ₁₈ O ₂	
Antibiotics	Clarithromycin	8.99	3.16	C ₃₈ H ₆₉ NO ₁₃	
	Roxithromycin	9.20	2.75	C ₄₁ H ₇₆ N ₂ O ₁₅	
	Trimethoprim	7.12	0.91	C ₁₄ H ₁₈ N ₄ O ₃	
	Sulfamethoxazole	5.70	0.89	C ₁₀ H ₁₁ N ₃ O ₃ S	
β blocker and lipid regulators	Atenolol	9.60	0.16	C ₁₄ H ₂₂ N ₂ O ₃	
	Metoprolol	9.60	1.88	C ₃₄ H ₅₆ N ₂ O ₁₀	
Antiepileptic	Carbamazepine	13.90	2.45	C ₁₅ H ₁₂ N ₂ O	
Psychoactive	Caffeine	10.40	-0.07	C ₈ H ₁₀ N ₄ O ₂	

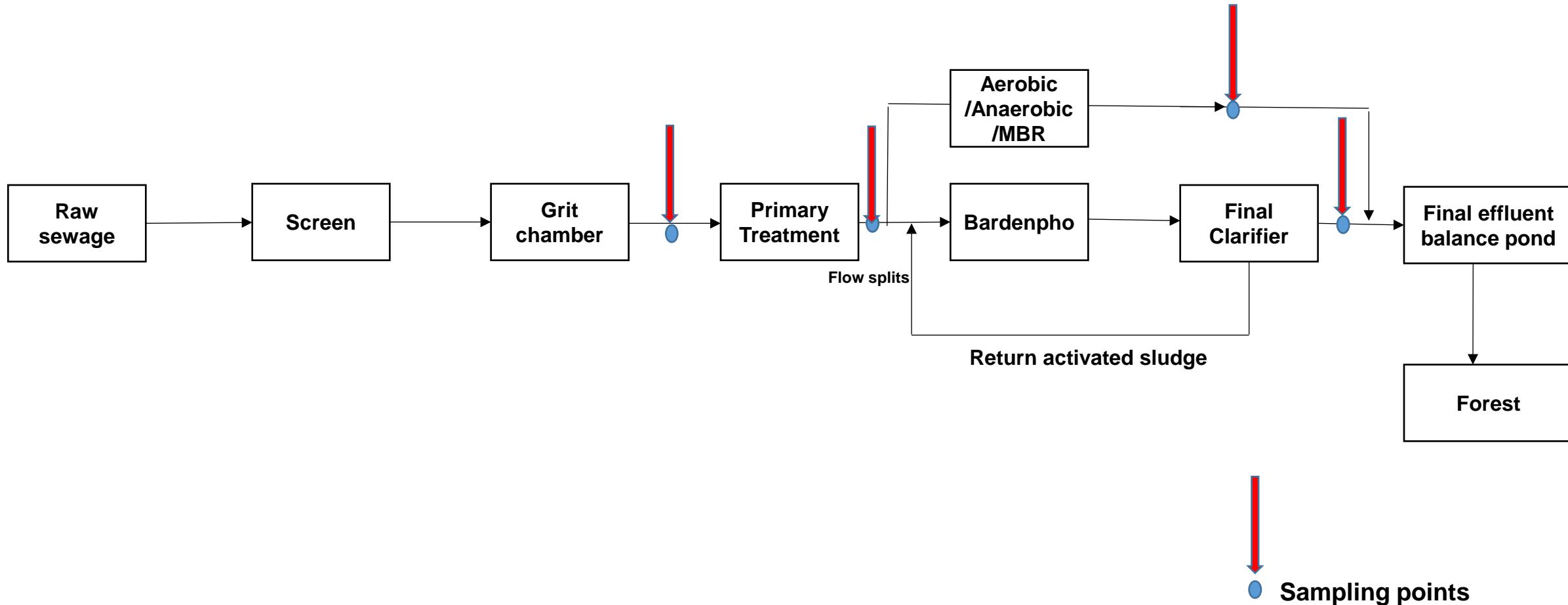
PPCPs selected for the study

Category	Pharmaceutical	pK _a	Log K _{ow}	Molecular formula	Molecular structure
Antidiabetic	Metformin	12.40	<-0.50	C ₄ H ₁₁ N ₅	
Insect repellent	N, N-Diethyl-meta-toluamide (DEET)	4.75	2.02	C ₁₂ H ₁₇ NO	
Herbicide	Atrazine	1.60	2.61	C ₈ H ₁₄ ClN ₅	
Corrosion inhibitor	Benzotriazole	8.37	1.44	C ₆ H ₅ N ₃	
Antidepressant	Fluoxetine	10.10	4.10	C ₁₇ H ₁₈ F ₃ NO	
Flame retardant	Tris (2-chloroethyl) phosphate (TCEP)	9.10	1.78	C ₆ H ₁₂ Cl ₃ O ₄ P	
Antimicrobial	Irgasan	7.90	4.70	C ₁₂ H ₇ Cl ₃ O ₂	

Wastewater sample collection and processing

- The samples were collected from a wastewater treatment plant of New Zealand.
- The raw and treated (at all stages) composite wastewater samples were collected in HDPE bottles pre-rinsed with DI water over 7 days.
- The pH was adjusted to 2.0 for all samples.
- The samples were then put in ice packs and transferred immediately to the lab and were filtered with 0.7 μ GF/F glass fibre filter to eliminate suspended particles.
- The samples were stored at 4 °C prior to solid phase extraction.

Overview of WWTP



Solid Phase Extraction and Concentration¹

Preconditioning of cartridge with methanol and milli Q water

Loading of wastewater sample on cartridge

Washing cartridge with milli Q water

Drying cartridge under vacuum for 30 min

Elution of analytes with 10 mL of methanol

Vacuum concentration down to 1 mL

¹ Kosma, C. I., Lambropoulou, D. A., & Albanis, T. A. (2014). Investigation of PPCPs in wastewater treatment plants in Greece: Occurrence, removal and environmental risk assessment. *Science of The Total Environment*, 466–467, 421-438. <http://dx.doi.org/10.1016/j.scitotenv.2013.07.044>

Matrix recovery

- The PPCP recoveries were calculated by matrix method by spiking the known concentration of PPCPs in to the wastewater prior to solid phase extraction.
- The recoveries of caffeine, metformin, naproxen, ibuprofen, trimethoprim and sulfamethoxazole were corrected by using the internal standards as surrogates.

S.No.	Internal standards	PPCPs
2	Sulfamethoxazole $^{13}\text{C}_6$ ¹	Sulfamethoxazole
3	Trimethoprim d ₉ ¹	Trimethoprim
4	Caffeine $^{13}\text{C}_3$ ¹	Caffeine
5	Metformin d ₆ ²	Metformin
6	Naproxen d ₃ ³	Naproxen

¹Elliott, S.M., and Erickson, M.L., 2014, Pharmaceutical compounds in shallow groundwater in non-agricultural areas of Minnesota—Study design, methods, and data, 2013: U.S. Geological Survey Data Series 878, 11 p., <http://dx.doi.org/10.3133/ds878>.

²Trautwein, C., Berset, J.-D., Wolschke, H., & Kümmerer, K. (2014). Occurrence of the antidiabetic drug Metformin and its ultimate transformation product Guanylurea in several compartments of the aquatic cycle. *Environment International*, 70, 203-212. <http://dx.doi.org/10.1016/j.envint.2014.05.008>

³Aminot, Y., Fuster, L., Pardon, P., Le Menach, K., & Budzinski, H. (2018). Suspended solids moderate the degradation and sorption of waste water-derived pharmaceuticals in estuarine waters. *Science of The Total Environment*, 612, 39-48. <http://dx.doi.org/10.1016/j.scitotenv.2017.08.162>

Wastewater Quality Characterization

The wastewater was analysed within 24 hours for general parameters like

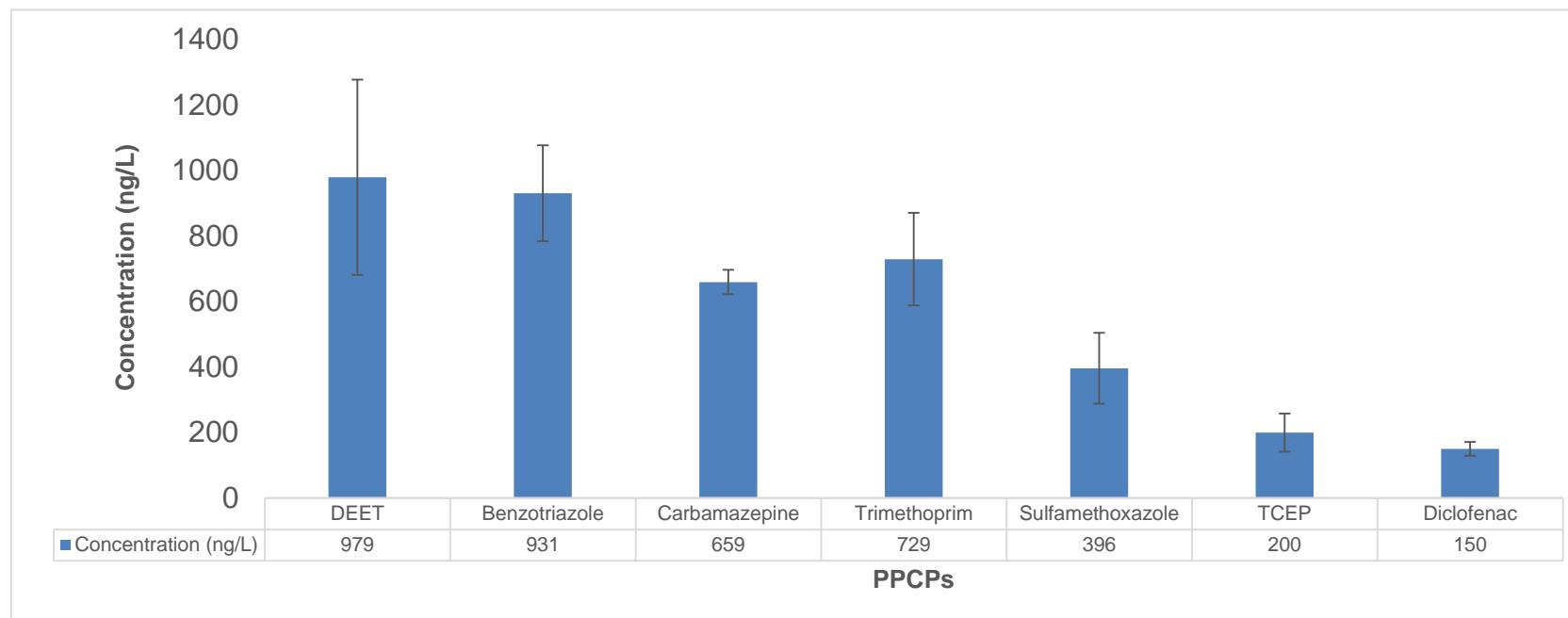
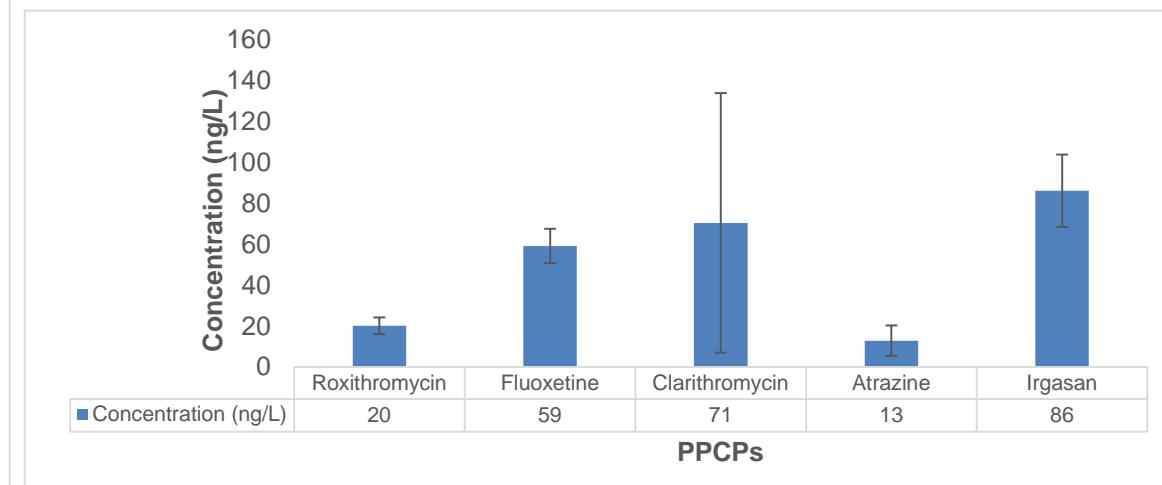
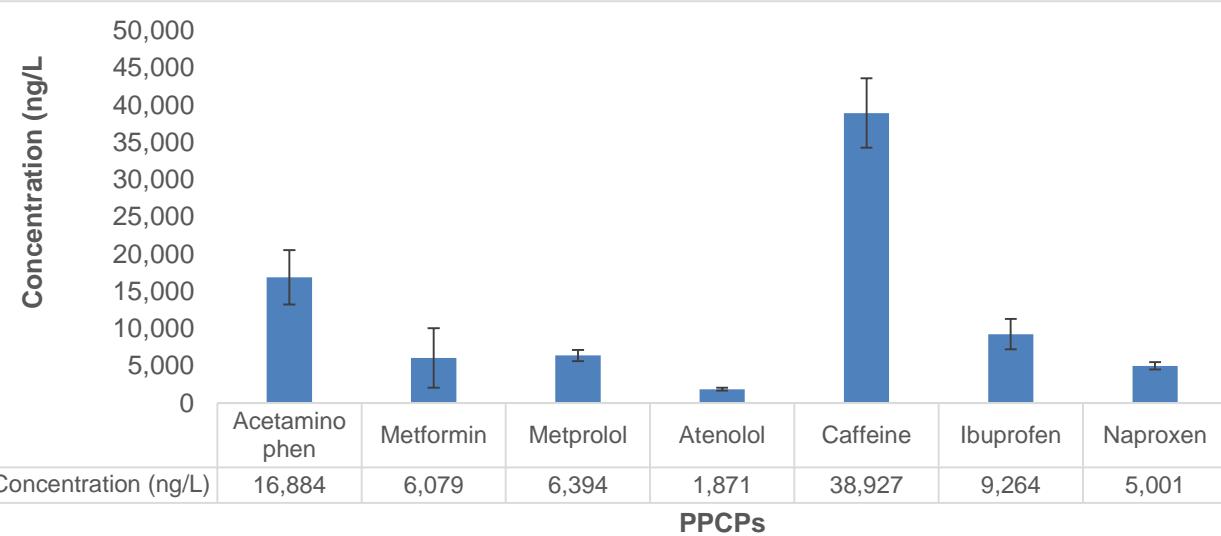
- pH
- Alkalinity
- Carbonaceous Biochemical Oxygen Demand (CBOD)
- Chemical Oxygen Demand (COD)
- Dissolved Reactive Phosphorus (DRP)
- Nitrogen (Ammoniacal Nitrogen + Nitrite Nitrogen + Total Kjeldahl Nitrogen+ Total Oxidised Nitrogen)
- Total Phosphorus
- Turbidity
- Suspended solids

Results and Discussion

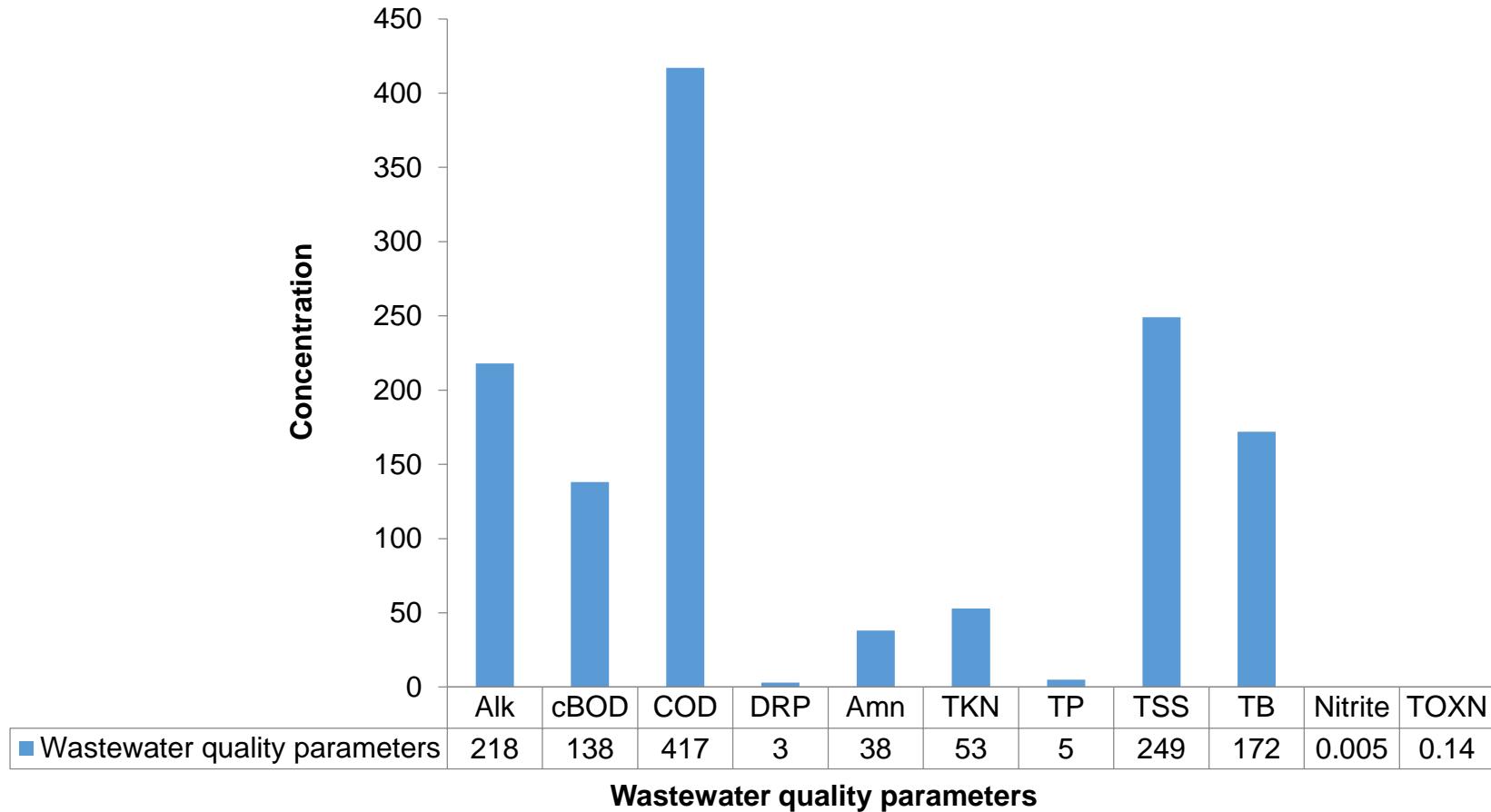
Matrix Recovery

Pharmaceuticals	Matrix Recovery (%)			
	Influent	Primary Effluent	MBR	Bardenpho
Trimethoprim	19-28	22	42	40
Sulfamethoxazole	30-70	44	69	72
Roxithromycin	9-17	12	26	20
Carbamazepine	37-56	45	53	53
Metformin	0.1-1	0.1	0.1	0.1
Fluoxetine	14-22	18	33	33
Clarithromycin	7-15	10	25	18
Metoprolol	21-61	19	62	70
TCEP	26-40	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

Average influent PPCPs concentration over a week



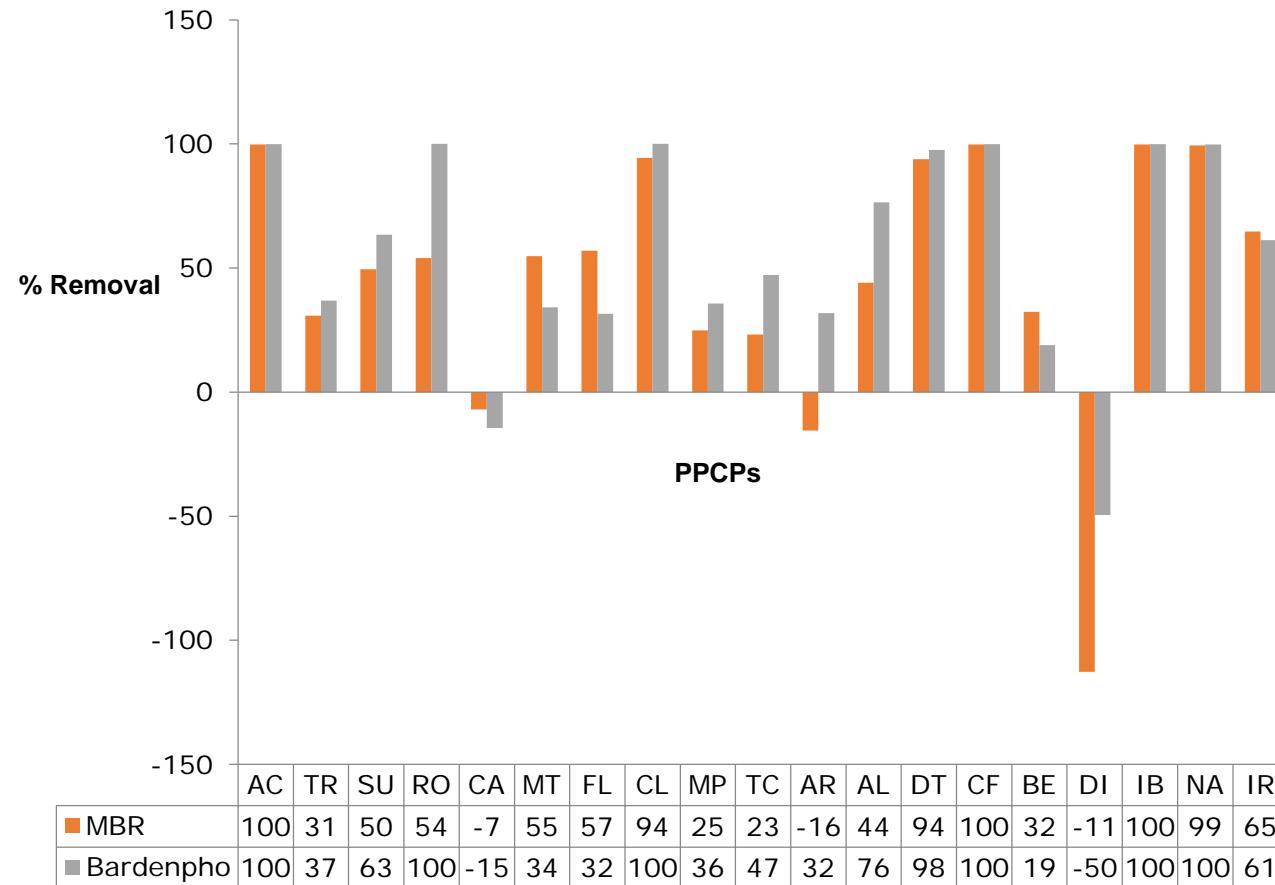
Average influent concentration of wastewater quality parameters



Note:-All units are in mg/L except turbidity, expressed as NTU

Alk	cBOD5	COD	DRP	Amn	TKN	TOXN	TP	TSS	TB
Alkalinity	5 days Carbonaceous Biochemical Oxygen Demand	Chemical Oxygen Demand	Dissolved Reactive Phosphorus	Ammonia	Total Kjeldahl Nitrogen	Total Oxidised Nitrogen	Total Phosphorus	Total Suspended Solid	Turbidity

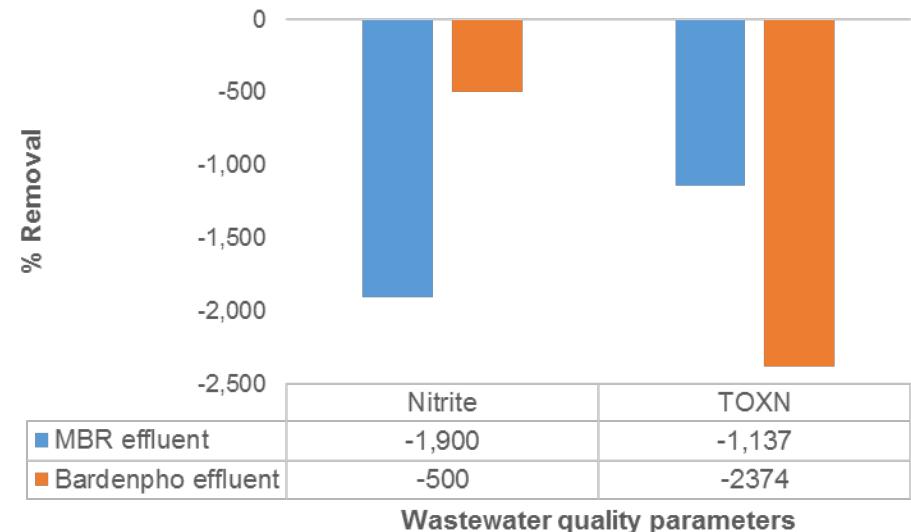
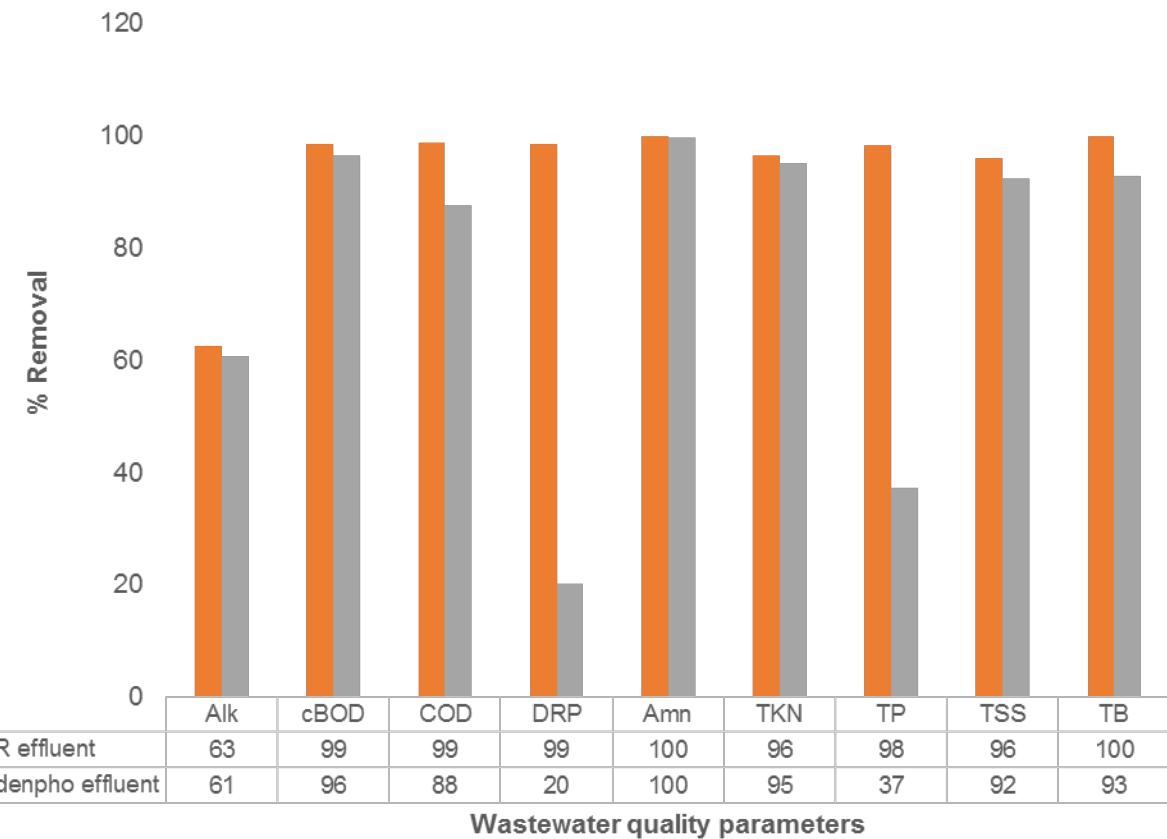
PPCPs Removal efficiency



AC	TR	SU	RO	CA	MT	FL	CL	MP	TC
Acetaminophen	Trimethoprim	Sulfamethoxazole	Roxithromycin	Carbamazepine	Metformin	Fluoxetine	Clarithromycin	Metoprolol	TCEP

AR	AL	DT	CF	BE	DI	IB	NA	IR
Atrazine	Atenolol	DEET	Caffeine	Benzotriazole	Diclofenac	Ibuprofen	Naproxen	Irgasan

Removal of Wastewater Quality Parameters



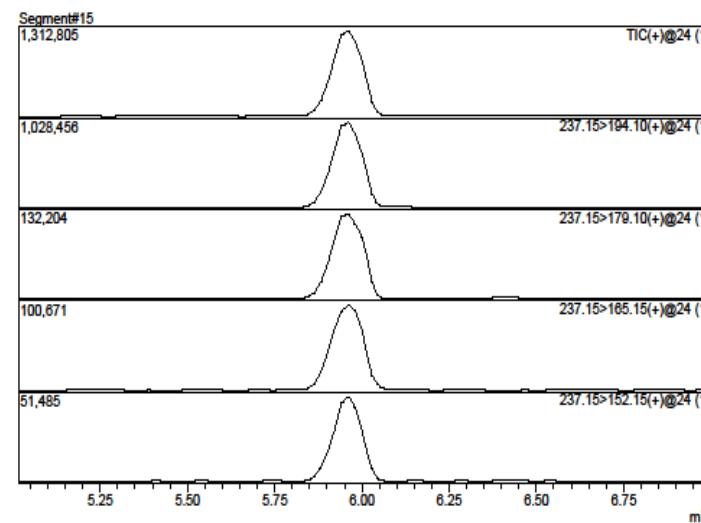
Alk	cBOD5	COD	DRP	Amn	TKN	TOXN	TP	TSS	TB
Alkalinity	5 days Carbonaceous Biochemical Oxygen Demand	Chemical Oxygen Demand	Dissolved Reactive Phosphorus	Ammonia	Total Kjeldahl Nitrogen	Total Oxidised Nitrogen	Total Phosphorus	Total Suspended Solid	Turbidity

Conclusion

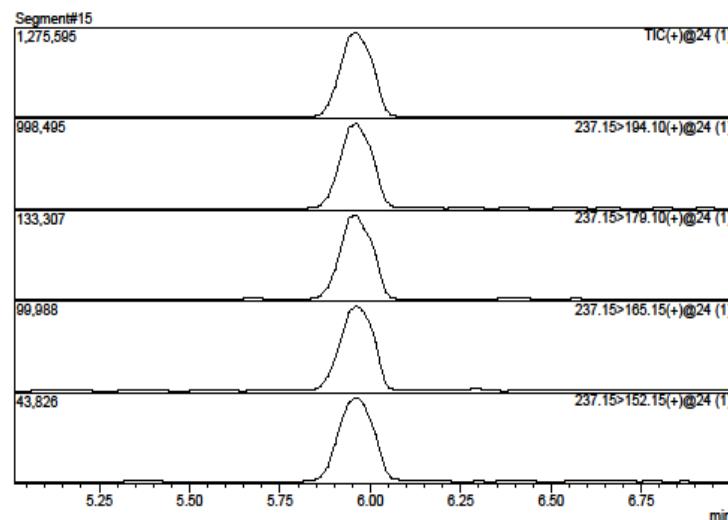
- All of the monitored PPCPs were detected in influent and more than 80% were traced in effluent by LC-MS/MS.
- The total influent load of PPCPs in a week was found to be around 89 ppb where as the total effluent load was around 11 ppb.
- Acetaminophen and caffeine were the most frequently detected compounds in the influent.
- The wastewater treatment facility was unable to remove most of the PPCPs efficiently.
- The removal efficiency was high for acetaminophen, caffeine and ibuprofen while it was significantly low for trimethoprim, benzotriazole and TCEP.
- This research highlights need for advanced oxidation processes to improve the overall removal efficiency of the PPCPs from wastewater.

Thank You

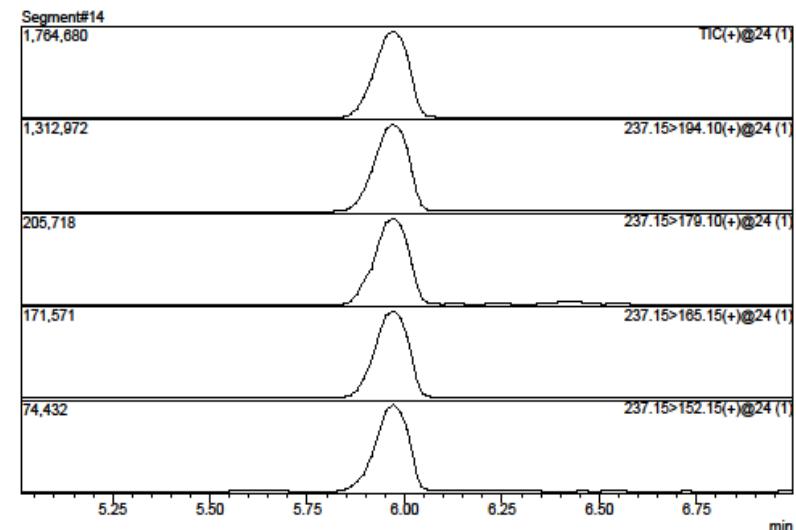
Chromatograms of Carbamazepine



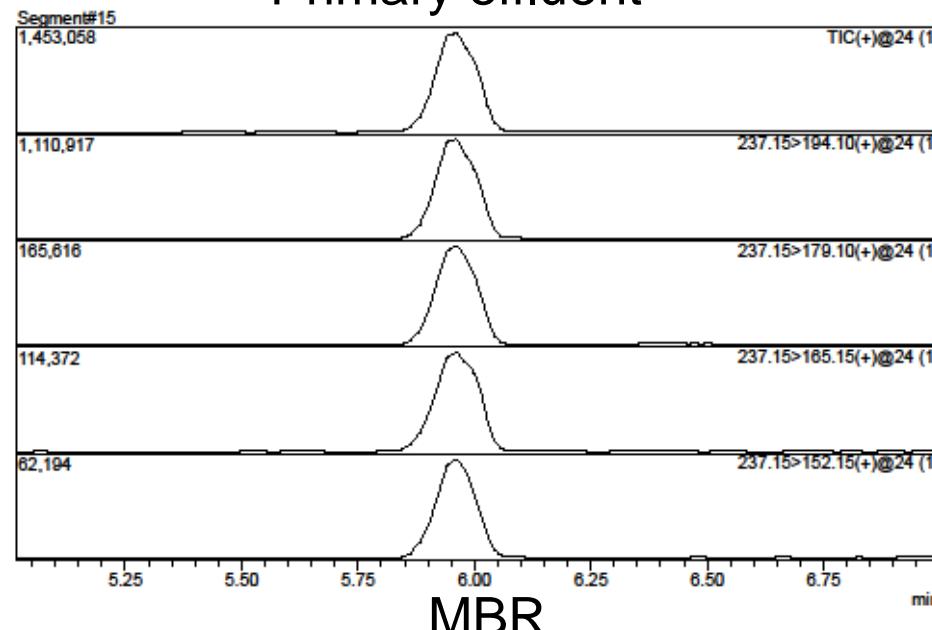
Influent



Primary effluent



Bardenpho

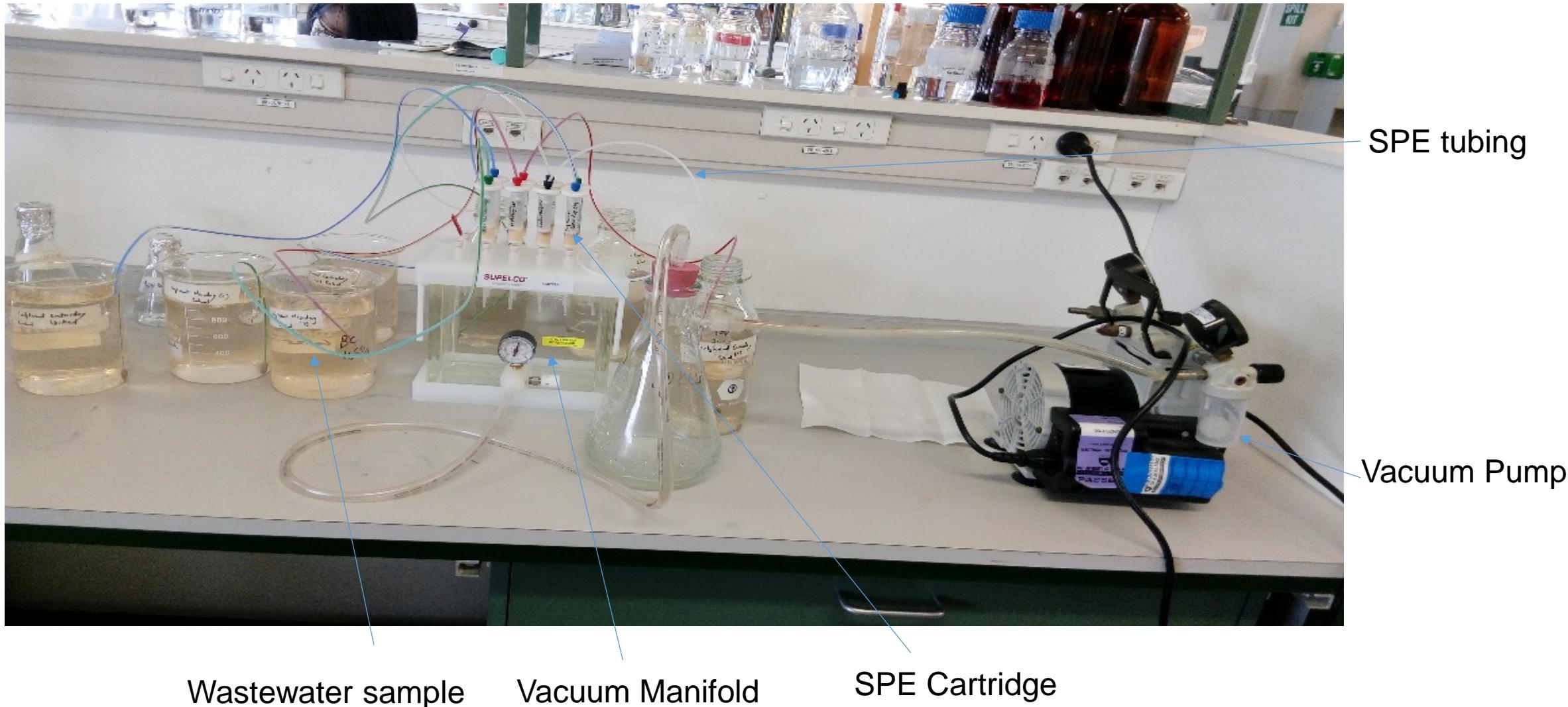


MBR

Concentration of PPCPs (Influent + Effluent)

Compound	Median Influent Concentration (ng/L)	Primary Effluent (ng/L)	MBR (ng/L)	Bardenpho (ng/L)
Acetaminophen	16,884 ± 3637.92	13,200	36.50	14.80
Trimethoprim	729.28 ± 141.46	1240	505	460
Sulfamethoxazole	396.42 ± 107.89	455	200	145
Roxithromycin	20.20 ± 4	8.40	9.30	Not detected
Carbamazepine	659.29 ± 37.02	730	705.50	755
Metformin	6,079.30 ± 3992	20,000	2,750	4000
Fluoxetine	59.21 ± 8.39	68	25.50	40.5
Clarithromycin	70.50 ± 63.50	Not detected	4	Not detected
Metoprolol	6,394.30 ± 768.87	11,725	4,805	4110
TCEP	199.92 ± 57.88	340	153.50	105.5
Atrazine	12.90 ± 7.43	26	14.90	8.80
Atenolol	1,870.57 ± 190	2109	1,047	441
DEET	979.28 ± 297.99	815	60.5	24
Caffeine	38,927 ± 4646.59	50,650	58.6	22
Benzotriazole	930.71 ± 146.16	1,390	630	755
Diclofenac	150.43 ± 20.97	210	320	225
Ibuprofen	9,264.29 ± 2030.61	7,800	24	3.5
Naproxen	5,000.7 ± 497.67	5,310	29	13.5
Irgasan	86.28 ± 17.68	145	30.50	33.50
Total	88714.58	116221.40	11408.80	11157.10

Solid Phase Extraction (SPE) set up



LC Parameters

- The reverse phase amide HPLC column (10 cm x 2.1 mm) was used to separate analytes.

Positive Electrospray Ionization (ESI) mode		Mobile Phase	
Time (min)	Gradient	A	B
0.01	5% B	0.1% Formic acid	Acetonitrile with 0.1% Formic acid
3.0	20% B		
4.0	45% B		
6.1	65% B		
7.0	100% B		
7.45	5% B		
10.0	Stop		

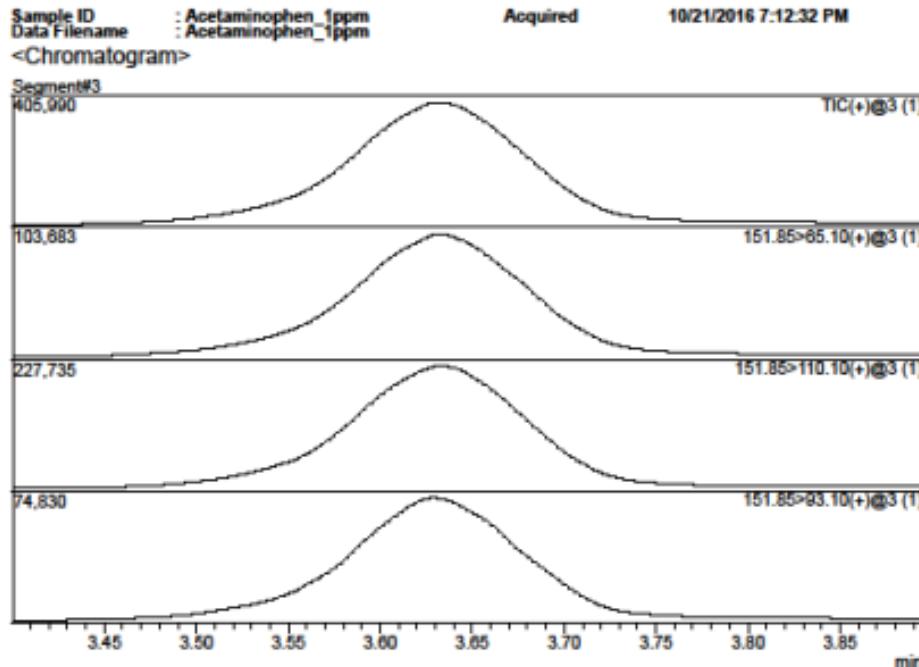
Negative Electrospray Ionization (ESI) mode		Mobile Phase	
Time (min)	Gradient	A	B
0.01	20% B	Milli Q water + 5 mM Ammonium acetate	90% Acetonitrile + 5 mM Ammonium acetate
4.5	96% B		
5.0	100% B		
6.4	20% B		
8.0	Stop		

MS Acquisition Details

PPCPs	Molecular weights	Precursor ion	Product ion		Collision Energy	Quantifier to qualifier ratio	Retention time	ESI polarity
			Quantifier ion	Qualifier ion				
Acetaminophen	151.16	151.85	110.10	65.10	-17,-23	42.85	3.607	+
Trimethoprim	290.32	291.10	230.10	123.10	-23,-24	87.12	4.153	+
Sulfamethoxazole	253.28	253.90	156	92.10	-16,-28	89.25	5.581	+
Roxithromycin	837.04	837.40	158.15	679.4	-36,-23	52.19	5.443	+
Carbamazepine	236.27	237.15	194.10	179.10	-19,-35	16.48	5.959	+
Metformin	129.16	130.25	71.10	60.05	-22,-15	96.97	0.508	+
Fluoxetine	309.3	309.95	44.15	148.10	-13,-9	9.82	5.466	+
Clarithromycin	747.95	748.40	158.10	590.40	-28,-20	29.61	5.410	+
Metoprolol	267.36	268	116.10	74.10	-20,-23	77.40	4.611	+
TCEP	285.48	287.10	224.85	125	-12,-17	95.02	6.235	+
Atrazine	215.68	216.25	174.10	104	-17,-29	32.36	6.60	+
Atenolol	266.33	267.10	145	190.1	-15,-20	85.72	1.275	+
DEET	191.27	192.10	119	91.10	-18,-31	67.94	6.473	+
Caffeine	194.19	195.10	138.10	110	-19,-23	27.70	4.374	+
Benzotriazole	119.12	120.25	65.15	39.05	-22,-37	32.14	5.157	+
Diclofenac	296.14	294	250.15	214.1	12,22	3.42	3.125	-
Ibuprofen	206.29	205.10	161.30	----	10	NA	3.423	-
Naproxen	230.26	229.05	185.25	170	9,16	96.89	2.379	-
Irgasan	289.54	286.90	35.05	37	10,10	36.36	6.329	-
Bisphenol A	228.29	226.90	212.20	133.0	19,24	20.72	4.585	-

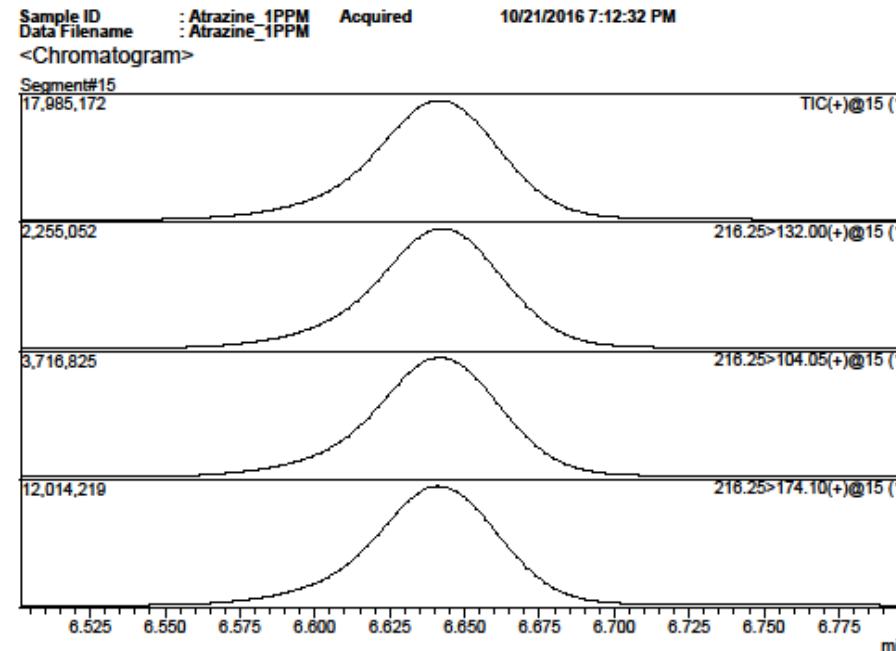
MS Chromatograms of PPCPs

==== Shimadzu LabSolutions Data Report ====



MS chromatogram of Acetaminophen

==== Shimadzu LabSolutions Data Report ====



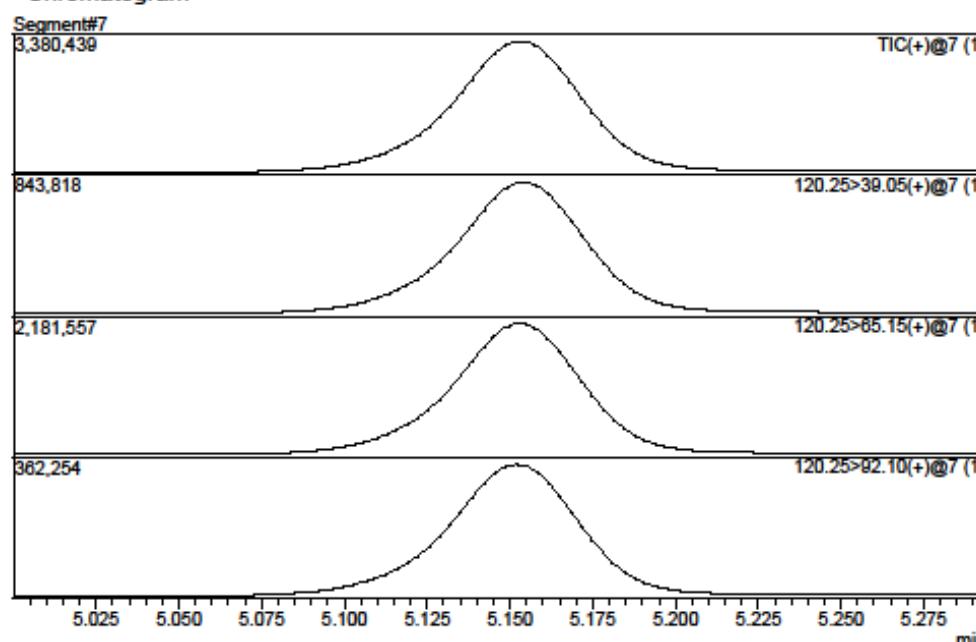
MS chromatogram of Atrazine

==== Shimadzu LabSolutions Data Report ====

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Data Filename : Benzotriazole_1ppm

Acquired 10/21/2016 7:12:32 PM

<Chromatogram>



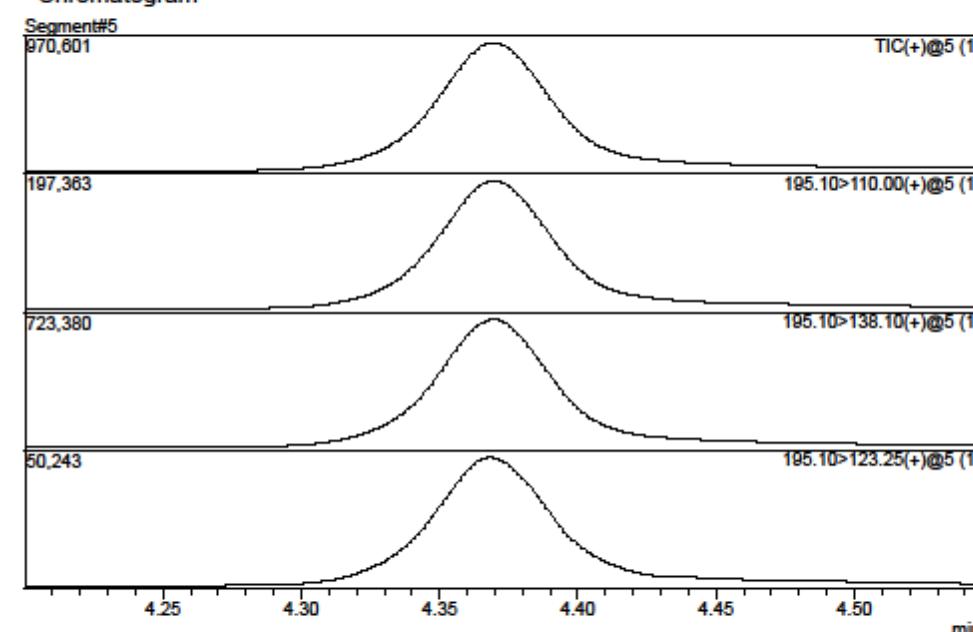
MS chromatogram of Benzotriazole

==== Shimadzu LabSolutions Data Report ====

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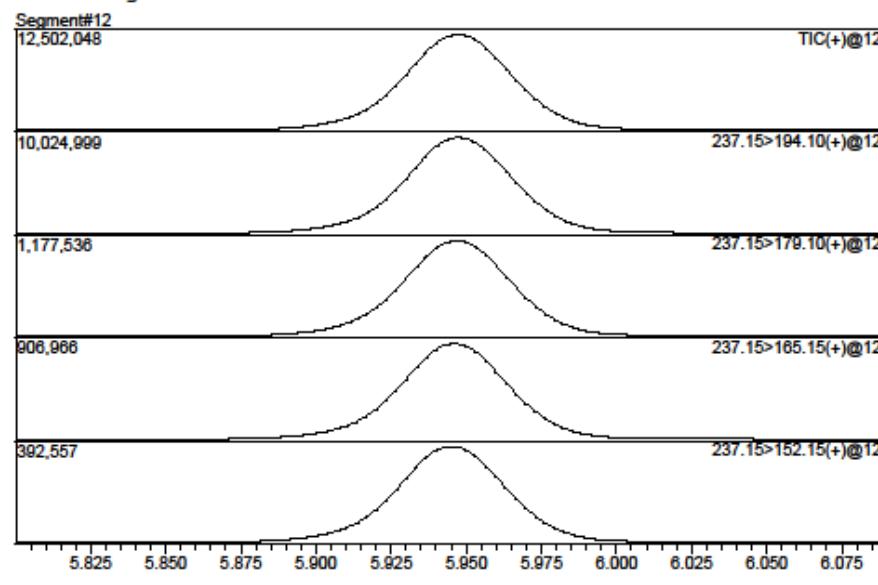


MS chromatogram of Caffeine

==== Shimadzu LabSolutions Data Report ====

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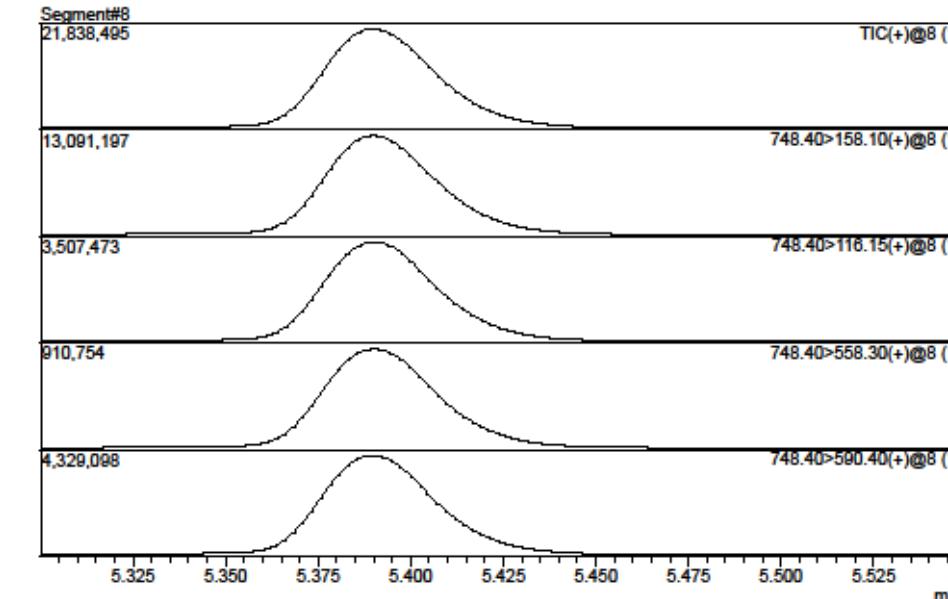


MS chromatogram of Carbamazepine

==== Shimadzu LabSolutions Data Report ====

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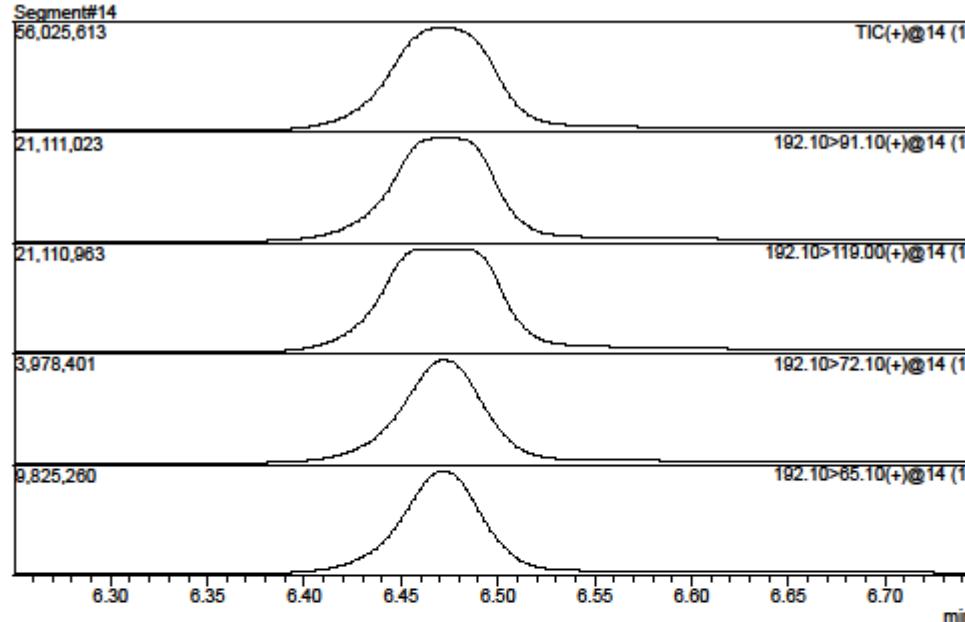


MS chromatogram of Clarithromycin

==== Shimadzu LabSolutions Data Report ====

Sample ID : DEET_1PPM Acquired 10/21/2016 7:12:32 PM
Data Filename : DEET_1PPM

<Chromatogram>

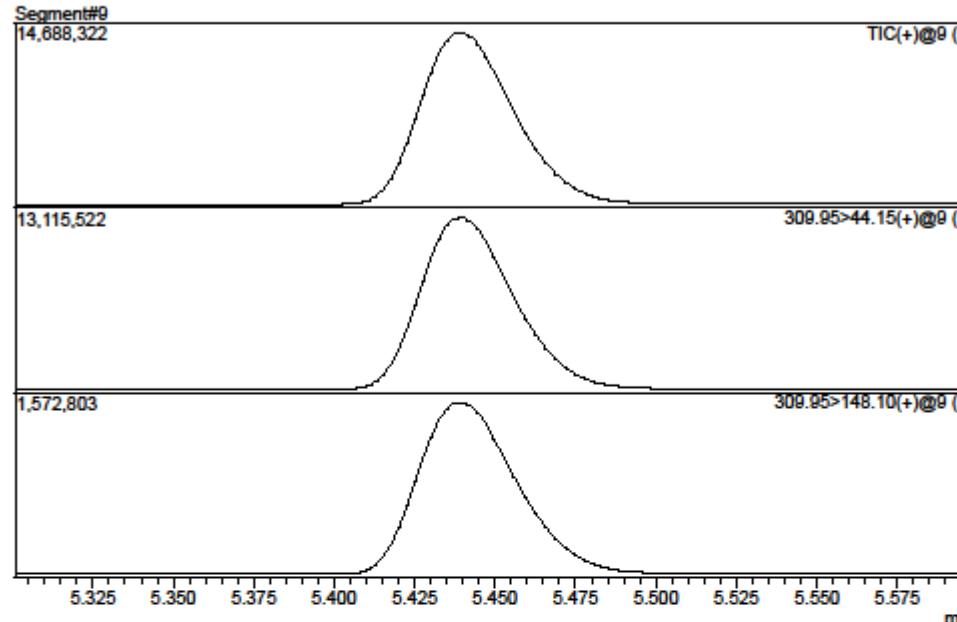


MS chromatogram of DEET

==== Shimadzu LabSolutions Data Report ====

Sample ID : Fluoxetine_1ppm Acquired 10/21/2016 7:12:32 PM
Data Filename : Fluoxetine_1ppm

<Chromatogram>

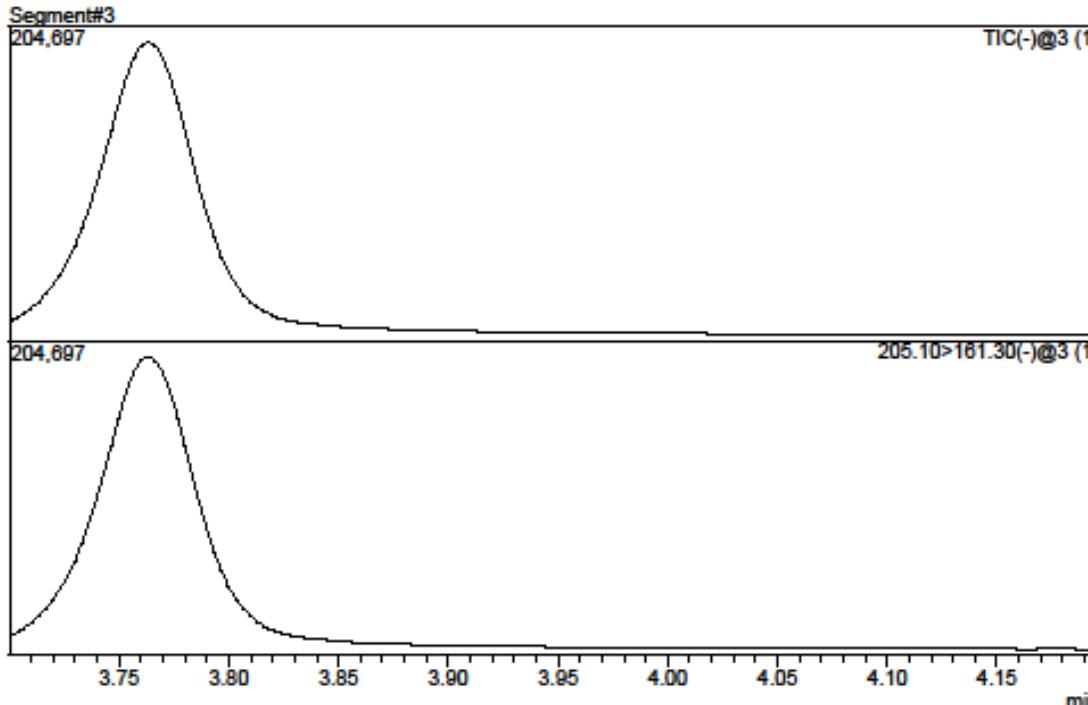


MS chromatogram of Fluoxetine

==== Shimadzu LabSolutions Data Report ====

Sample ID :Ibuprofen_1ppm Acquired 10/22/2016 1:36:52 PM
Data Filename :Ibuprofen_1ppm

<Chromatogram>

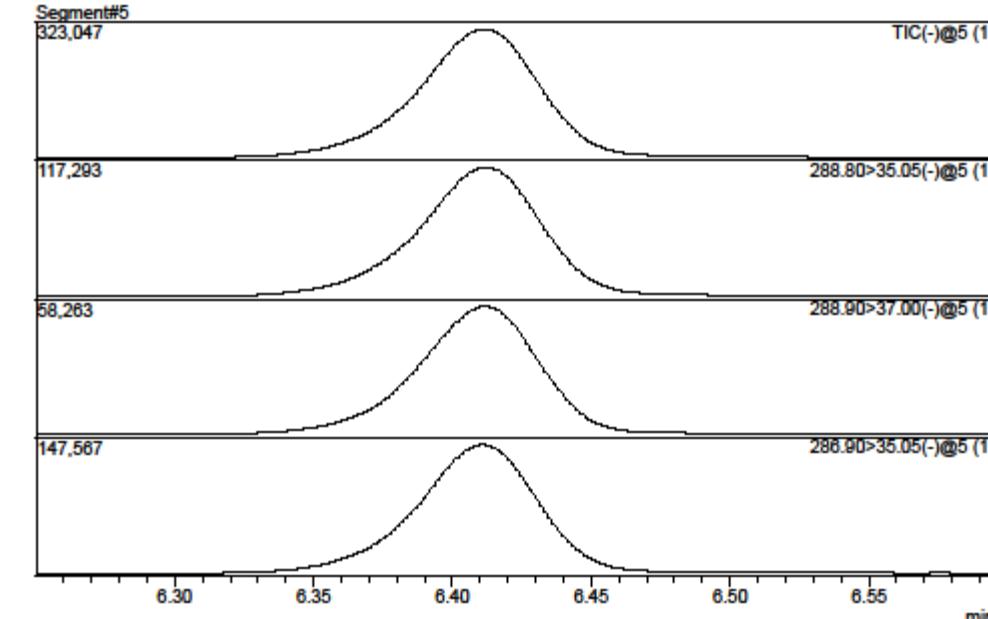


MS chromatogram of Ibuprofen

==== Shimadzu LabSolutions Data Report ====

Sample ID :Irgasan_1ppm Acquired 10/22/2016 1:36:52 PM
Data Filename :Irgasan_1ppm

<Chromatogram>

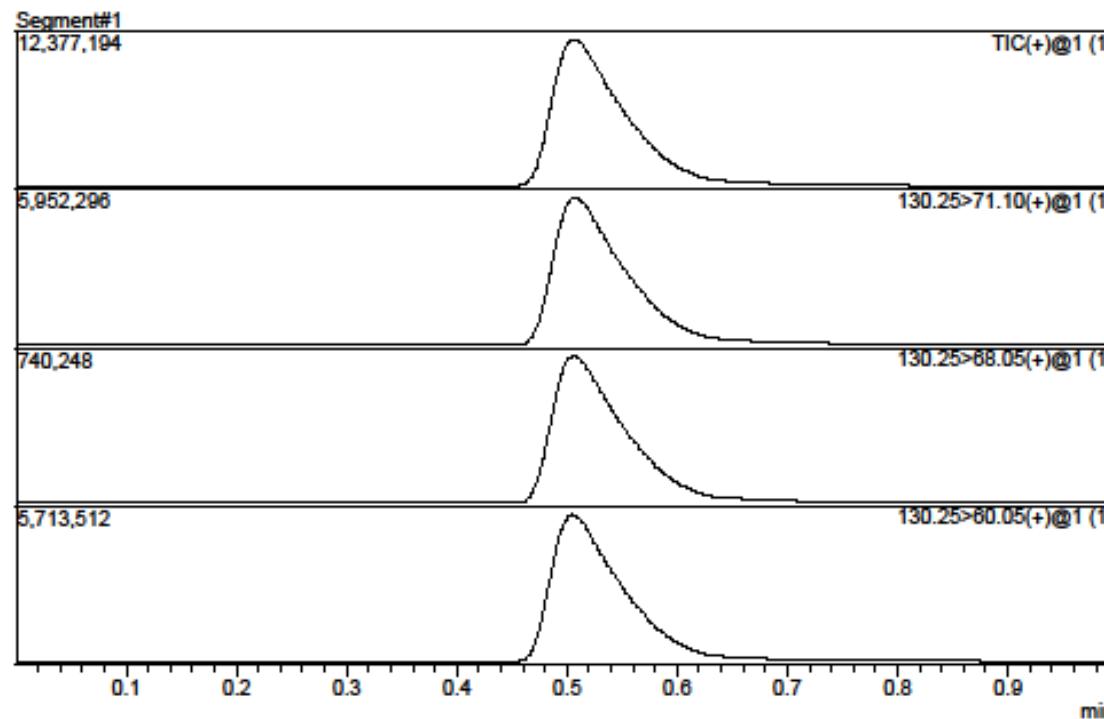


MS chromatogram of Irgasan

==== Shimadzu LabSolutions Data Report ====

Sample ID : Metformin_1ppm Acquired 10/21/2016 7:12:32 PM
Data Filename : Metformin_1ppm

<Chromatogram>

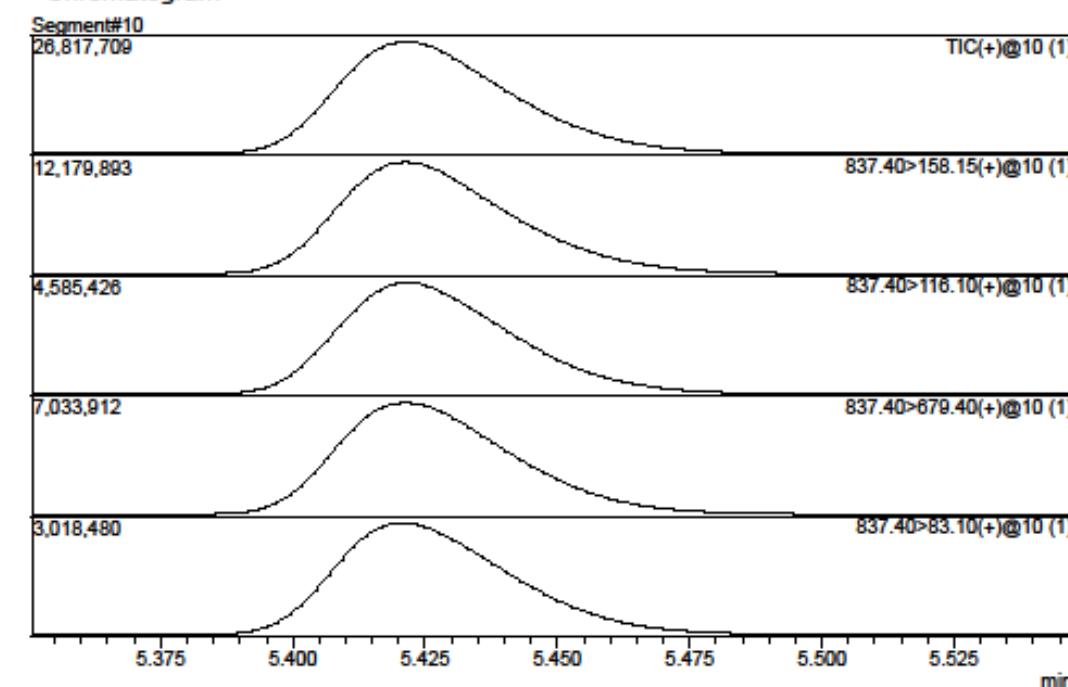


MS chromatogram of Metformin

==== Shimadzu LabSolutions Data Report ====

Sample ID : Roxithromycin_1ppm Acquired 10/21/2016 7:12:32 PM
Data Filename : Roxithromycin_1ppm

<Chromatogram>



MS chromatogram of Roxithromycin

==== Shimadzu LabSolutions Data Report ====

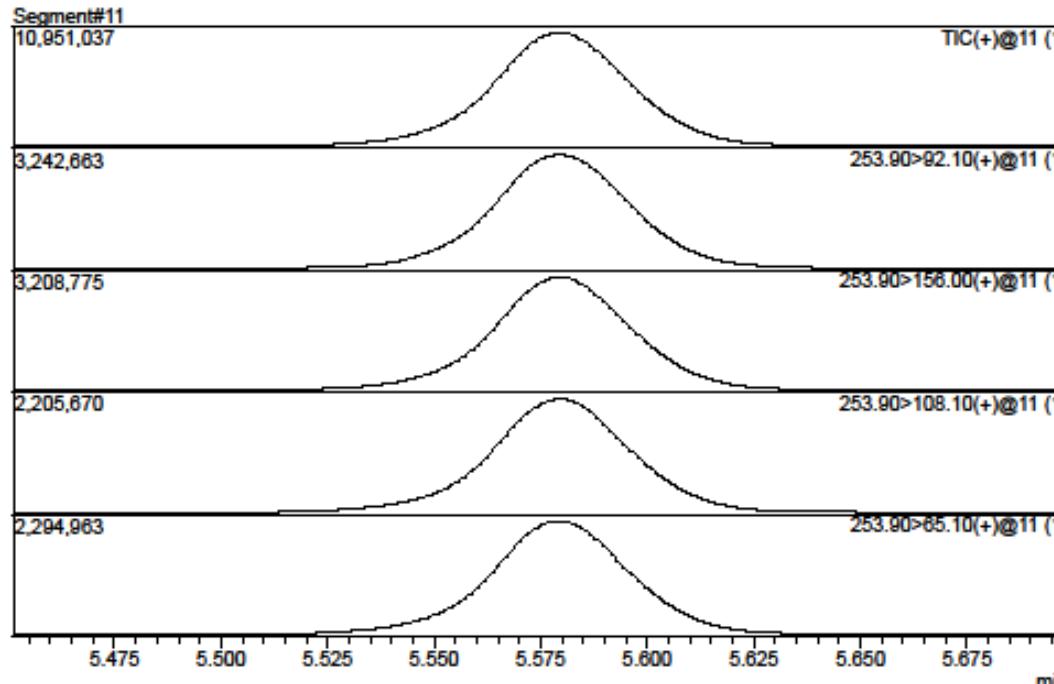
Sample ID
Data Filename

: Sulfamethoxazole_1ppm
: Sulfamethoxazole_1ppm

Acquired

10/21/2016 7:12:32 PM

<Chromatogram>



MS chromatogram of Sulfamethoxazole

==== Shimadzu LabSolutions Data Report ====

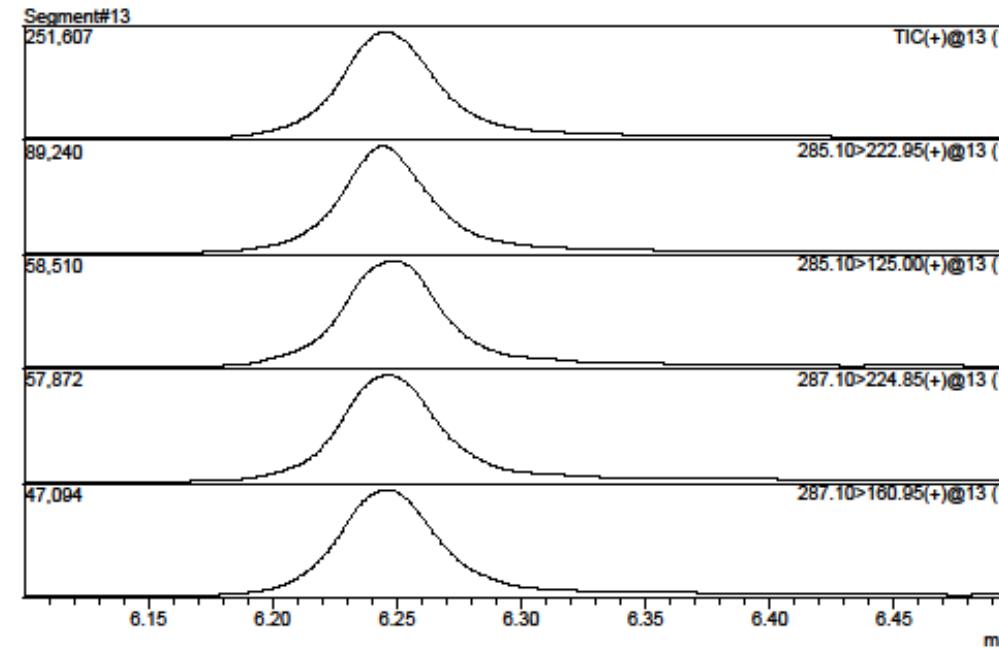
Sample ID
Data Filename

: TCEP_1PPM
: TCEP_1PPM

Acquired

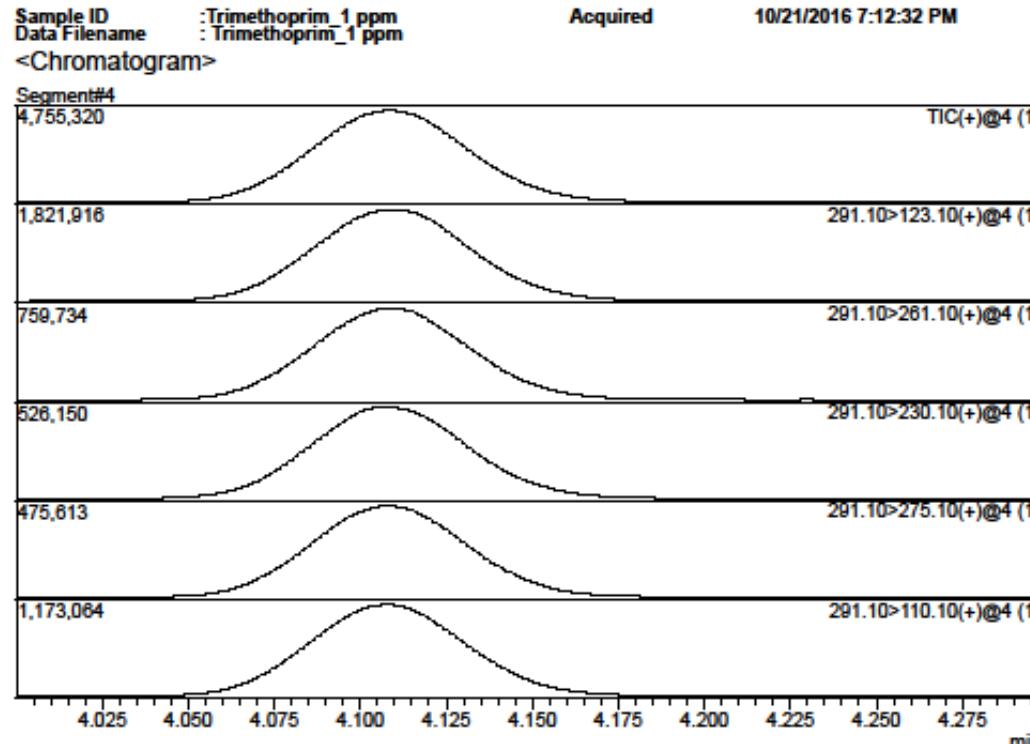
10/21/2016 7:12:32 PM

<Chromatogram>



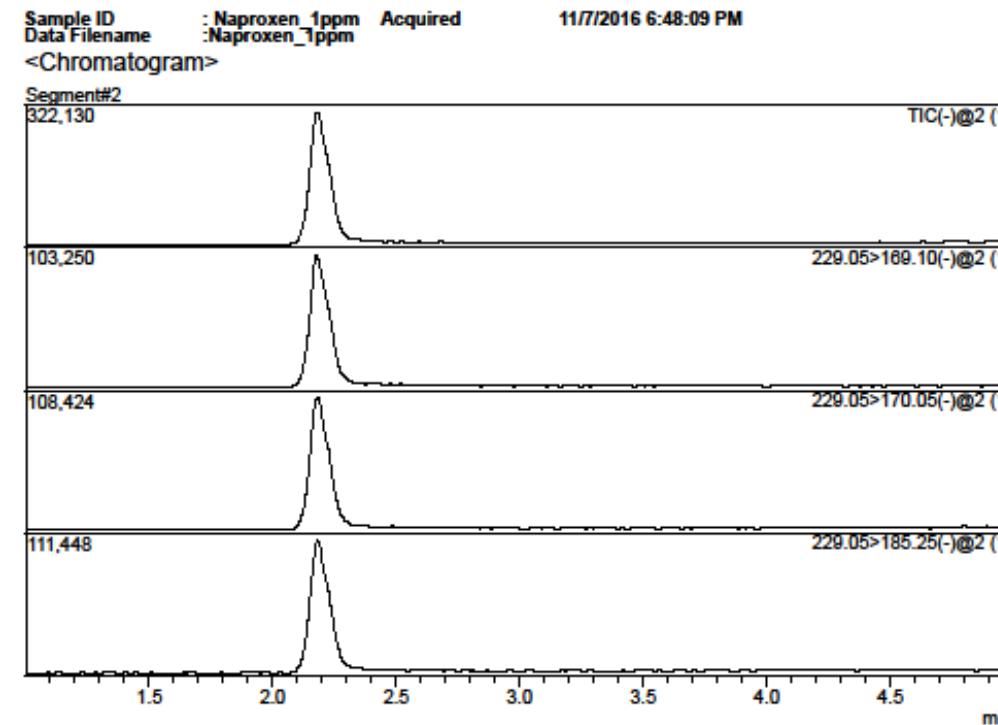
MS chromatogram of TCEP

==== Shimadzu LabSolutions Data Report ====



MS chromatogram of Trimethoprim

==== Shimadzu LabSolutions Data Report ====

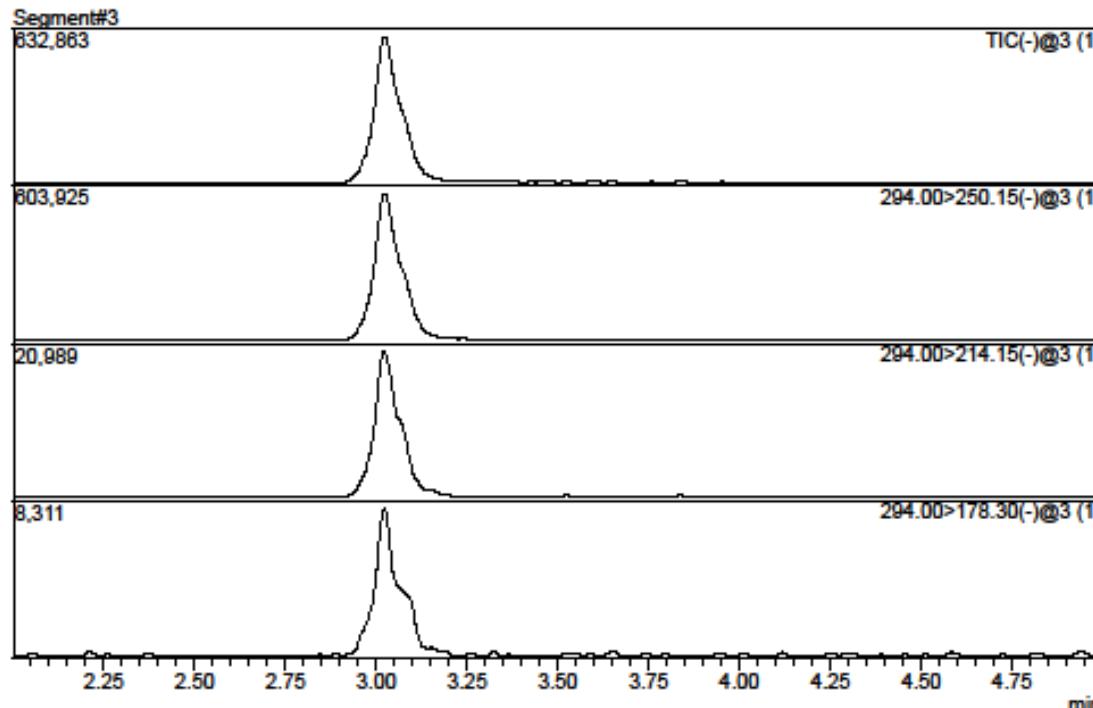


MS chromatogram of Naproxen

==== Shimadzu LabSolutions Data Report ====

Sample ID : Diclofenac_1ppm Acquired
Data Filename : Diclofenac_1ppm 11/7/2016 6:48:09 PM

<Chromatogram>

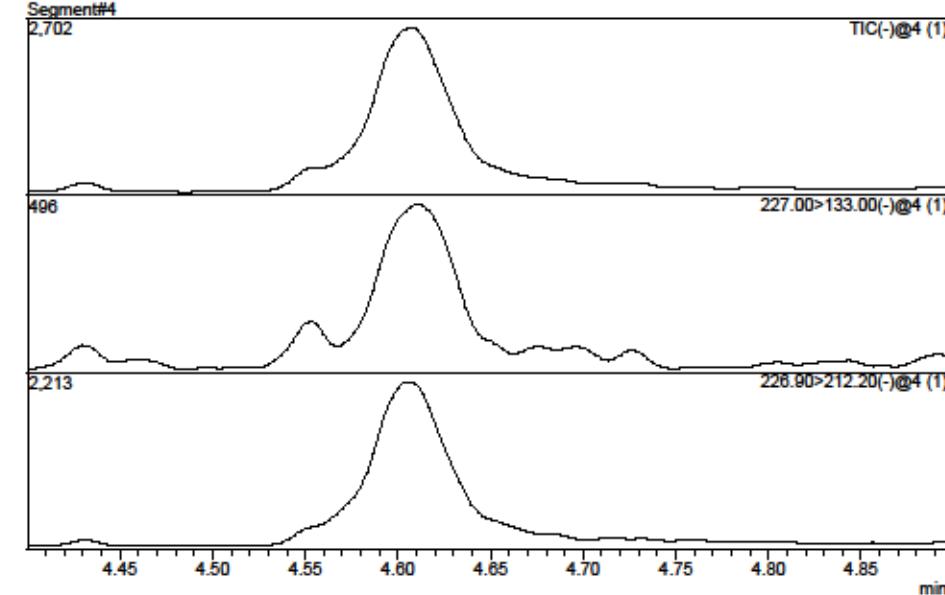


MS chromatogram of Diclofenac

==== Shimadzu LabSolutions Data Report ====

Sample ID : Bisphenol A_1PPM Acquired
Data Filename : Bisphenol A_1PPM 10/22/2016 1:36:52 PM

<Chromatogram>



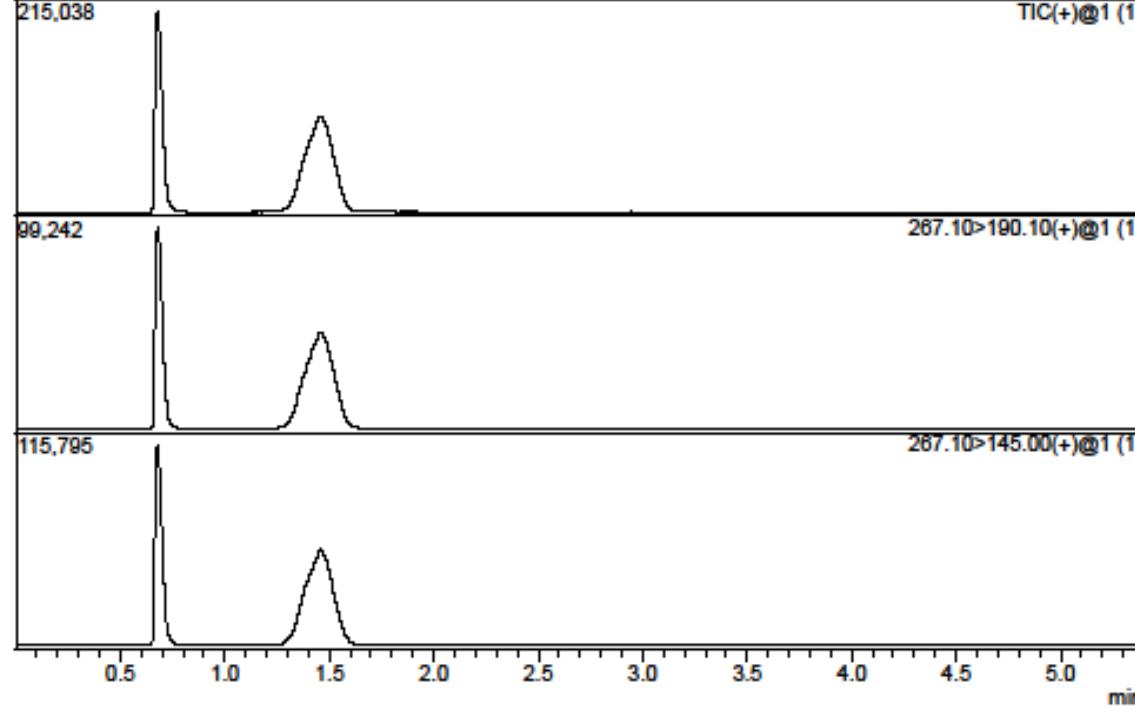
MS chromatogram of Bisphenol A

===== Shimadzu LabSolutions Data Report =====

Sample ID : 1_Atenolol
Data Filename : 1_Atenolol.lcd Acquired 11/27/2016 2:09:33 PM

<Chromatogram>

Segment#1



MS chromatogram of Atenolol