Pharmaceuticals and Personal Care Products (PPCPs) in Higgins Lake

Submitted by

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Summary

Six surface water samples from the Higgins Lake were analyzed in Dr. Hui Li's laboratory at Michigan State University. The water sample and site information are summarized in Table 1. PPCPs in water samples were extracted and analyzed based on the EPA method 1694. The experimental procedure is described below. We targeted the total of thirty PPCPs (listed in Table 2) in the analysis, with the limit of detection (LOD) as low as 1 ng/L levels for many analytes. The analytical results showed that nineteen PPCPs were detected in the six surface water samples. These PPCPs were amoxicillin, ampicillin, clindamycin, chlortetracycline, demeclocycline, doxycycline, erythromycin, lincomycin, minocycline, oxytetracycline, sulfadiazine, sulfamethoxazole, trimethoprim, carbamazepine, lamotrigine, caffein, 3-methylxanthine, 7-methylxanthine, paraxanthine, 1,7-dimethyluric acid, 1,3,7-trimethyluric acid. Notably, two tetracycline-family members minocycline (127-333 ng/L) and demeclocycline (5.4-13 ng/L) are the two most abundant antibiotics in the water samples.

Experimental Procedure

Sample Preparation

Six water samples were received, and stored in 1-L amber glass bottles at 4 ℃ before processing the samples within one week. All samples were first filtered through 0.7 μm GF/F

membrane before the extraction. The filtrate was stored in a pre-weighed glass bottle. The bottle weights with and without the filtrate was used to estimate the weight (volume) of the sample. Two 1.0 L of reagent water served as the method blank and acid operation procedure reference (OPR) samples. All water samples were adjusted to pH value 2.0 ± 0.5 using 6 M HCl solution. Native PPCPs (Table 2) was spiked into the OPR sample, and isotope-labeled internal standards into all water samples. Na_2EDTA (500 mg) was added to each of the acid fraction samples to prevent the potential complexation of PPCPs with metals.

Table 1. Sample name and collection sites

Sample number	Site
1	Kennedy beach
2	Cut river bridge
3	Samoset beach park
4	W. Higgin Lake DNR
5	N. Higgin Park beach
6	Gerrishtwp Park

SPE Extraction

Waters Oasis HLB cartridges were preconditioned with 5.0 mL of methanol/acetone (v/v =1:1), 15 mL of methanol and 6.0 mL of reagent water (pH ~ 2). The filtrated water samples were loaded to the HLB cartridges at a flow rate of 2 to 5 mL/min. After the samples passed through the cartridge, 10-mL aliquot of reagent water was used to wash the SPE cartridge. After the cartridge was nearly dry, the cartridge was eluted with 6.0 mL of methanol, followed by 6.0 mL of methanol/acetone (v/v = 1:1).

Concentration and Analysis

The elutes from SPE cartridges were concentrated to nearly dry using a gentle stream of nitrogen in a water bath held at about 50 ^{0}C. The samples were the reconstituted to the final volume of 4.0 mL with methanol. A certain volume of the samples (979 μL) was taken to a HPLC vial into which 10 μL of injection internal standards and 10 μL of 1% formic acid were spiked prior to LC-MS/MS analysis.

Quantification of PPCPs

All samples were analyzed by a Shimadzu high-performance liquid chromatography coupled to a SCIEX 4500 tandem Qtrap quadrupole mass spectrometer under sMRM mode. PPCP concentration was quantified using the isotope dilution method. Six to seven calibration standards were prepared with all native compounds and isotope-labelled PPCPs.

Results

The measured concentration of PPCPs in the water samples collected in Higgins Lake are summarized in Table 2. The PPCP concentration was all below than 1 μg/L. Some samples contained relatively high concentration at ng/L levels. Chlortetracycline concentration ranged between 3.7 and 14 ng/L, demeclocycline between 11 and 32 ng/L, doxycycline between 8.0 and 13 ng/L, erythromycin between 7.0 and 27 ng/L, minocycline between 127 and 333 ng/L, and caffeine between 7.4 and 10 ng/L.

Table 2. PPCP concentration (ng/L) measured in the water samples collected from Higgins Lake

Sample / Analyte	Kennedy beach	Cut river bridge	Samoset beach park	W. Higgin Lake DNR	N. Higgin Park beach	Gerrishtwp Park
Amoxicillin	2.0	< MQL[a]	1.4	1.5	1.2	3.4
Carbadox	< MQL	< MQL	< MQL	5.7	< MQL	< MQL
Ampicillin	< MQL	< MQL	0.3	0.3	< MQL	0.7
Chlortetracycline	3.9	6.3	14	6.0	3.7	5.6
Ciprofloxacin	< MQL	< MQL	< MQL	< MQL	< MQL	< MQL
Clindamycin	0.1	0.1	0.1	0.1	0.1	0.2
Demeclocycline	32	< MQL	< MQL	14	16	11
Doxycycline	13	< MQL	8.7	9.6	< MQL	8.0
Erythromycin	< MQL	10	27	< MQL	7.0	7.0
Lincomycin	0.1	0.5	0.1	0.7	0.1	0.1
Minocycline	265	144	194	333	127	329
Ofloxacin	< MQL	< MQL	< MQL	< MQL	< MQL	< MQL
Oxytetracycline	6.0	< MQL	6.4	4.3	< MQL	6.4
Sulfadiazine	< MQL	0.4	< MQL	< MQL	< MQL	0.5
Sulfamerazine	0.8	< MQL	2.1	< MQL	< MQL	< MQL
Sulfamethoxazole	2.1	2.6	4.3	1.7	< MQL	< MQL

Trimethoprim	1.7	1.2	0.9	1.2	2.8	3.5
Carbamazepine	< MQL	1.3	<MQL	< MQL	< MQL	< MQL
Lamotrigine	0.6	0.6	3.0	0.9	0.8	1.2
Diphenhydramine	< MQL	< MQL	< MQL	< MQL	< MQL	< MQL
Acetaminophen	< MQL	< MQL	< MQL	< MQL	< MQL	< MQL
Caffein	9.0	10	10	9.1	9.5	7.4
3-Methylxanthine	< MQL	1.5	0.8	< MQL	< MQL	< MQL
7-Methylxanthine	2.1	0.0	2.7	1.9	< MQL	< MQL
Theobromine	< MQL	< MQL	7.2	< MQL	< MQL	< MQL
Theophylline	< MQL	1.6	< MQL	0.9	< MQL	1.2
Paraxanthine	1.1	2.0	1.2	0.7	0.6	2.0
1,7-Dimethyluric Acid	1.3	1.1	< MQL	2.8	< MQL	1.1
1,3,7-Trimethyluric Acid	4.7	2.5	8.1	6.6	2.3	7.6
Xanthine	< MQL	< MQL	< MQL	< MQL	< MQL	< MQL

[a] MQL: method quantification level.