

Supporting Information

for

**Total organic halogen (TOX) in treated wastewaters: an optimized method and comparison
with target analysis**

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Table S1: SGS AXYS Method MLA-075 REV 09 VER 01. Target compounds for PCPPs analysis by LC-MS/MS and reporting limits (RL). This method is suitable for the determination of a suite of hormones and pharmaceutical and personal care compounds in biosolid, aqueous and POCIS samples. The analysis required extraction at two pH conditions. Basic extraction (*) at a pH of 10 and acidic extraction at a pH of 2. All aqueous samples were filtered and the aqueous portion was cleaned up by solid phase extraction before analysis by LC/ESI-MS/MS. Surrogate standards are added to all samples before extraction.

Name	RL (ng/L)	Name	RL (ng/L)
1,7-Dimethylxanthine	54.9	Hydrocodone*	1.12
4-Epianhydrochlortetracycline	75.6	Hydrocortisone	5.49
4-Epianhydrotetracycline	13.7	Ibuprofen	3.66
4-Epichlortetracycline	13.7	Isochlortetracycline	5.49
4-Epioxytetracycline	5.49	Lincomycin	2.74
4-Epitetracycline	5.49	Lomefloxacin	2.74
10-hydroxy-amitriptyline	0.194	Meprobamate	1.37
2-hydroxy-ibuprofen	5.85	Metformin*	0.281
Acetaminophen	13.7	Methylprednisolone	3.66
Albuterol*	0.281	Metoprolol	0.459
Alprazolam	0.274	Miconazole	1.37
Amitriptyline	0.274	Minocycline	54.9
Amlodipine	0.92	Naproxen	1.83
Amphetamine*	0.281	Norfloxacin	38.2
Anhydrochlortetracycline	48.7	Norfluoxetine	0.459
Anhydrotetracycline	13.7	Norgestimate	5.23
Atenolol*	0.281	Norverapamil	0.137
Atorvastatin*	1.12	Ofloxacin	1.37
Azithromycin	3.13	Ormetoprim	0.549
Benzoylcegonine	0.137	Oxacillin 1	2.74
Benzotropine	0.64	Oxolinic acid	4.48
Betamethasone	1.37	Oxycodone*	0.562
Bisphenol A	5.49	Oxytetracycline	5.49
Caffeine	13.7	Paroxetine	0.92
Carbadox	2.74	Penicillin G 1	2.77
Carbamazepine	1.37	Penicillin V	2.74
Cefotaxime	26.7	Prednisolone	3.66
Chlortetracycline	5.49	Prednisone	5.49
Cimetidine*	0.562	Promethazine	0.274
Ciprofloxacin	7.3	Propoxyphene	0.274

Clarithromycin	1.37	Propranolol	0.274
Clinafloxacin	9.97	Ranitidine*	0.562
Clonidine*	1.12	Roxithromycin	0.468
Cloxacillin 1	3.01	Sarafloxacin	13.7
Cocaine	0.137	Sertraline	0.274
Codeine*	1.12	Simvastatin	1.84
Cotinine*	0.281	Sulfachloropyridazine	1.37
DEET (N,N-diethyl-m-toluamide)			
0.274		Sulfadiazine	1.37
Dehydronifedipine	0.699	Sulfadimethoxine	0.376
Demeclocycline	13.7	Sulfamerazine	0.557
Desmethyldiltiazem	0.137	Sulfamethazine	2.47
Diazepam	0.459	Sulfamethizole	0.549
Digoxigenin	17.7	Sulfamethoxazole	2.39
Digoxin	5.49	Sulfanilamide	13.7
Diltiazem	0.534	Sulfathiazole	1.37
Diphenhydramine	0.549	Tetracycline	5.49
Doxycycline	5.49	Theophylline	5.49
Enalapril*	0.281	Thiabendazole	1.37
Enrofloxacin	2.74	Trenbolone	1.84
Erythromycin	2.1	Trenbolone acetate	0.274
Flumequine	1.37	Triamterene*	0.281
Fluocinonide	1.84	Triclocarban	0.366
Fluoxetine	1.37	Triclosan	5.49
Fluticasone propionate	1.84	Trimethoprim	1.37
Furosemide	3.66	Tylosin	5.49
Gemfibrozil	0.732	Valsartan	3.66
Glipizide	0.732	Verapamil	0.137
Glyburide	0.732	Virginiamycin M1	6.81
Hydrochlorothiazide	8.05	Warfarin	0.366

Table S2: SGS AXYS Method MLA-096 REV.01 VER. 07. Target compounds for HFRs analysis by GC-(ECNI)-MS and reporting limits (RL). This method describes the analysis of selected chlorinated and brominated flame retardants in aqueous samples. The samples are spiked with a suite of isotopically labeled quantification standards and liquid-liquid extracted with dichloromethane. The extracts are cleaned up by liquid-liquid extraction with 1:1 acetonitrile:water at three pHs (pH=10, pH=7 and 2). Influent samples are further cleaned up using gel permeation chromatography if necessary. The resulting extracts are dried over anhydrous sodium sulfate, reduced and analyzed by gas chromatography electron capture negative ion mass spectrometry (GC-(ECNI)-MS).

Name	RL (ng/L)	Name	RL (ng/L)
Dechlorane	0.0732	Total TBECH	0.699
DP Anti	0.152	HBB	0.0123
DP Syn	0.107	PBBZ	0.0526
Dec 602	0.0197	1,2,4,5-TBB	0.0701
Dec 603	0.0161	1,2,4-TriBB	0.588
Dec 604	0.29	1,2-DiBB	0.123
HCDBCO	0.0798	1,4-DiBB	0.232
ATE	0.0831	PBT	0.0405
BATE	0.264	PBEB	0.0299
DPTE	0.687	PBBB	0.383
BTBPE	0.682	pTBX	1.62
BEHTBP	0.377	TBCT	0.0426
EHTBB	0.381		

Table S3: SGS AXYS Method MLA-098 REV.01 VER.03. Target compounds for OPFRs analysis by LC-MS/MS and reporting limits (RL). This method describes the analysis of organophosphate flame retardants (OPFRs) in whole aqueous samples containing up to 1% solids. Samples are spiked with isotopically labelled surrogate standards and liquid-liquid extracted with dichloromethane. The resulting extract is cleaned up by solid phase extraction on an aminopropyl cartridge and by column chromatography using a silica chromatographic column. The final extract is spiked with recovery standard and analyzed by liquid chromatography and tandem mass spectrometry (LC-MS/MS). Typical reporting limits are in the range of 0.1 - 5 ng/L for a 0.5 L aqueous samples. For influent and effluent samples reporting limits are in the range of 5 - 250 ng/L for 0.1 L sample sizes. For TBP and TBEP quantification limits are elevated by laboratory background levels.

Name	RL (ng/L)	Name	RL (ng/L)
TEP	0.202	TDBPP	6.07
TCEP	2.02	TBP	0.202
TPrP	0.202	TBEP	40.6
TCPP	1.01	TCrP*	0.404
V6	1.01	EHDPP	10.1
TDCPP	10.1	TEHP	0.404
TPP	1.01		

Table S4: SGS AXYS Method MLA-110 REV.02 VER. 11. Target compounds for PFAS analysis by LC-MS/MS and reporting limits (RL). This method describes the analysis of per- and polyfluoroalkyl substances (PFAS) in aqueous, solid, biosolid, tissue, blood/serum and AFFF product samples and solvent extracts, determined as the total of linear and branched isomers. After spiking with isotopically labeled surrogate standards samples are extracted and cleaned up by solid phase extraction using weak anion exchange cartridges. The extracts are then analyzed by liquid chromatography/mass spectrometry (LC-MS/MS). Extract samples don't undergo solid phase extraction. The samples are spiked with surrogate and recovery standards and analyzed by LC-MS/MS. Final sample concentrations are determined by isotope dilution/internal standard quantification.

Name	RL (ng/L)	Name	RL (ng/L)
PFBA	1.47	6:2 FTS	1.33
PFPeA	0.737	8:2 FTS	1.47
PFHxA	0.368	3:3 FTCA	1.47
PFHpA	0.368	5:3 FTCA	9.21
PFOA	0.368	7:3 FTCA	9.21
PFNA	0.368	PFOSA	0.368
PFDA	0.368	N-MeFOSA	0.424
PFUnA	0.368	N-EtFOSA	0.921
PFDoA	0.368	N-MeFOSAA	0.368
PFTTrDA	0.368	N-EtFOSAA	0.368
PFTeDA	0.368	N-MeFOSE	3.68
PFBS	0.368	N-EtFOSE	2.76
PFPeS	0.37	HFPO-DA	1.4
PFHxS	0.368	ADONA	1.47
PFHpS	0.368	NFDHA	0.737
PFOS	0.368	PFMPA	0.737
PFNS	0.368	PFMBA	0.368
PFDS	0.368	9Cl-PF3ONS	1.48
PFDoS	0.368	11Cl-PF3OUdS	1.48
4:2 FTS	1.47	PFEESA	0.368

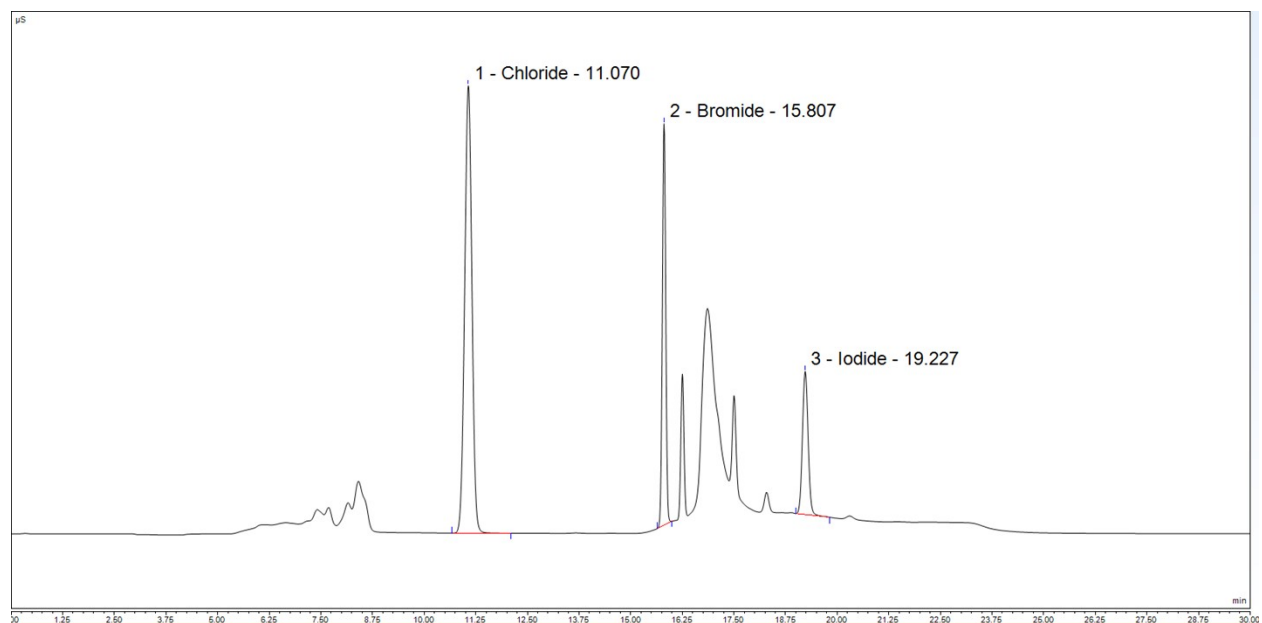


Figure S1: Ion chromatogram of 100 $\mu\text{g/L}$ analytical standard of chloride, bromide, and iodide in absorption solution (20 μM ammonium hydroxide + 0.003% hydrogen peroxide in ultrapure water). A Dionex AS20 analytical column was used with a flow rate of 0.25 mL/min.

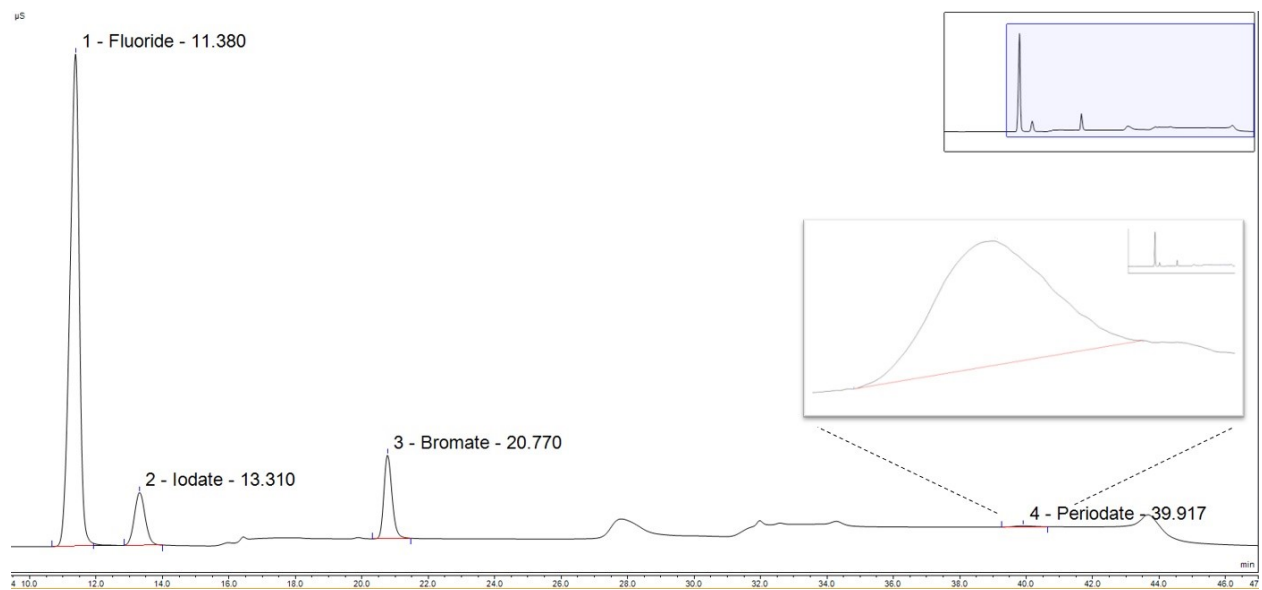


Figure S2: Ion chromatogram of 500 $\mu\text{g/L}$ analytical standard of fluoride, iodate, bromate, and periodate in ultrapure water. A Dionex AS15 analytical column was used with a flow rate of 0.3 mL/min.

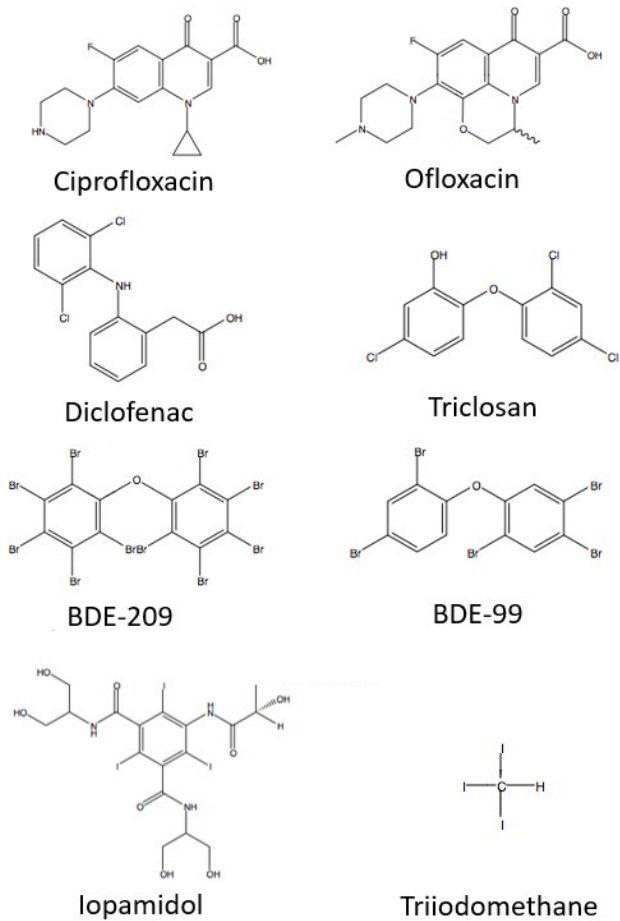


Figure S3. Structures and names of emerging contaminants that were used for percent recovery experiments.