PNNL-28216

Pacific Northwest
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Analysis of Perfluorinated, Pharmaceutical, Personal Care Compounds and Heavy Metals in Waste Water Sludge using GC-MS/MS and Multicollector ICP-MS

November 2018

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U.S. DEPARTMENT OF ENERGY

Prepared for the U.S. Department of Energy
under Contract DE-AC05-76RL01830

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Summary

A set of GC-MS/MS analytical methods was developed to detect and quantify PFCs and PPCPs in five wastewater sludge samples obtained from the Great Lakes Water Authority and in four dry sludge samples after they were HTL treated. Multicollector ICP-MS was used to analyze the heavy metals in the samples. Methylene chloride was used to extract the compounds from sludge samples. For non-GC-able compounds, derivatization was performed before analysis. IBCF was used for derivatizing PPCPs and PFCs.

Due to the nature of the samples, the presence of rich organic elements not only complicated the analytical work, but also affected the accuracy of measurements, because of interferences. Nevertheless, a set of PPCPs and PFCs was detected and quantified in the sludge samples in concentrations comparable to those reported in the literature.

Acknowledgments

This work was funded by Bioenergy Technologies Office of the U.S. Department of Energy's Office of Energy Efficiency and Renewable Energy. The authors of this report thank Justin M. Billing and Richard T. Hallen of the Hydrothermal Liquefaction Treatment (HTL) Program team for providing the samples and supporting this work.

Acronyms and Abbreviations

ADHD	Attention-Deficit Hyperactivity Disorder
EPA	U.S. Environmental Protection Agency
GC	gas chromatography
HTL	Hydrothermal Liquefaction Treatment
IBCF	isobutyl chloroformate
ICP-MS	inductively coupled plasma mass spectrometry
LC	liquid chromatography
LC-MS/MS	liquid chromatography with tandem mass spectrometry
MRM	multiple reactions monitoring
MS	mass spectrometry
MSTFA	N-Methyl-N-(trimethylsilyl) trifluoroacetamide
MW	molecular weight
NA	not available
PFC	perfluorinated chemical
PFCA	perfluorinated carboxylic acid
PFOA	perfluorooctanoic acid
PFOS	perfluorooctane sulfonate
PNNL	Pacific Northwest National Laboratory
PPCP	pharmaceutical and personal care product
SIM	selected ion morning
TMS	trimethylsilyl

Contents

Figures

Tables

1.0 Introduction

Wastewater treatment plant biosolids/sludge can potentially be converted into useful fuel. In recent years, research into wastewater sludge, which can be used as feedstock for fuel conversion, has intensified (Halling-Sorensen et al. 1998; Mottaleb et al. 2015). The Hydrothermal Liquefaction Treatment (HTL) Program team at Pacific Northwest National Laboratory (PNNL) is evaluating the feasibility of this conversion, using wastewater sludge from various cities. In municipal waste, different classes of residual contaminates can potentially remain in the sludge after wastewater treatment. The presence and concentrations of these contaminants need to be determined to ascertain the proper methods of handling of the sludge. The focus of the work reported here was to assess the presence and determine the concentrations of residual pharmaceutical and personal care compounds (PPCPs) and perfluorinated compounds (PFCs) in the waste stream before and after HTL processing.

The ensuing sections of this report present a processing overview, including a review of PFC and PPCP problems, followed by testing materials and methods, results, and conclusions.

2.0 Processing Overview

Samples before and after HTL processing are described below, followed by a brief discussion of the problems associated with PFCs and PPCPs.

2.1 Samples before HTL Processing

Five sludge samples were received from Detroit. About 100 g of each sample (see Table 1 for sample descriptions) was obtained for the PPCPs and PFCs extraction and analysis (Figure 1). . Samples GLWA P-1, GLWA P-2, GLWA P+S-1, and GLWA P+S-2 represent four streams from the Great Lakes Water Authority, either Primary (P) (i.e., the settled solids from the first round of clarifying ponds) or Primary (P) + Secondary (S) (i.e., the dewatered aerobic bacterial biomass from the aeration ponds, known as secondary treatment).

Figure 1. Sludge samples used for PPCP and PFC extraction.

Table 1. Descriptions of the five sludge samples before HTL processing.

Sample No.	Sample ID	Matrix	Approx. Mass, g	Sample Date	Descriptions of Samples Received at PNNL
S-1	Detroit 50/50	Wet Sludge	~100	October 4, 2016	WW-06: This is a 50:50 blend of primary and secondary sludge solids that was specially prepared by GLWA for the test.
S-2	GLWA P-1	Wet Sludge	~100	November 30, 2016	This is dewatered primary sludge from GLWA.
S-3	GLWA P+S-1	Wet Sludge	~100	December 9, 2016	This is dewatered primary and secondary sludge blended together at the current (typical) operating ratio of the plant.
S-4	GLWA P-2	Wet Sludge	~100	November 30, 2016	Duplicate of GLWA P-1.
S-5	GLWA P+S-2	Wet Sludge	~100	December 9, 2016	Duplicate of GLWA P+S-1.

To determine the presence of the compounds and to quantify their concentrations, extraction and derivatization procedures and analytical gas chromatography/mass spectrometry (GC/MS) methods were developed for detecting PPCPs and PFCs.

Additionally, all four samples were screened for the presence of heavy metals using the Multicollector inductively coupled plasma mass spectrometry (ICP-MS) method.

2.2 Samples after HTL Processing

Table 2. Descriptions of four sludge samples used in this research.

Sample No.	Sample ID	Form	Approx. Mass, g	Sample Date	Descriptions of Samples Received at PNNL
S-1	WW-07 Tote Aqueous Product	Liquid	150	July 11, 2017	HTL aqueous phase from Detroit 50:50 sludge.
S-2	WW-07 Filterwash	Solid	50	July12, 2017	Solids recovered from the filter housing after the run. Dried to constant mass.
S-3	WW-07 BD 1-4	Solid	50	July 11, 2017	Solids collected during the first four filter blowdowns during the run. Precipitated solids are periodically removed during sludge processing. The wet sample is dried to constant mass.
S-4	WW-07 BD 5-8	Solid	50	July 11, 2017	Solids collected during the last four filter blowdowns during the run.

2.3 Review of PFC and PPCP Problems

Among emerging contaminants in our environment, PFCs and PPCPs have recently attracted more and more attention, because they are considered to be a cause of a variety of health problems. PFCs are associated with reduced female fertility and sperm quality, reduced birth weight, Attention-Deficit Hyperactivity Disorder (ADHD), increased total and non-HDL (high-density lipoprotein; i.e., bad) cholesterol levels, and changes in thyroid hormone levels (Webster 2010). Likewise, many PPCPs are

endocrine disruptors, which at certain doses can interfere with endocrine (hormone) systems, causing cancerous tumors, birth defects, and other developmental disorders.

Perfluorinated Compounds PFCs such as perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS) have been used in a wide range of industrial and consumer products for many decades. PFCs, including PFOS and PFOA, have increasingly attracted concern in recent years because of their global distribution, persistence, strong bioaccumulation, and potential toxicity. These chemicals form a new class of recalcitrant pollutants. PFCs have been produced and used for more than 50 years (Giesy and Kannan 2002). They are commonly applied as surfactants for metal planting, vinyl polymerization, fire-fighting foams, gasoline, and water repellents for leather and paper (Giesy and Kannan 2002; Sinclair and Kannan 2006; Prevedouros et al, 2006).

Because of U.S. Environmental Protection Agency (EPA) regulations and the frequency of PFCs being detected in the environment and being reported in research literature (e.g., Sepulvado et al. 2011; Higgins et al. 2005; Sinclair et al, 2006), the PFCs listed in Table 3 were selected as the target compounds for the purposes of our analysis.

Table 3. Target PFC compounds for analysis.

Compound Name	Abbreviation or the Name Commonly Used	CAS No.	Formula	MW
Sulfluramid	BFOSA	4151-50-2	$C_{10}H_6F_{17}NO_2S$	527.20
1H,1H,2H,2H-Perfluoro-1-octanol	Perfluorooctanol	647-42-7	$CF_3(CF_2)_5CH_2CH_2OH$	364.10
1H,1H,2H,2H-Perfluoro-1-decanol	Perfluorodecanol	678-39-7	$CF_3(CF_2)_7CH_2CH_2OH$	464.12
Perfluorooctanoic acid	PFOA	335-67-1	$CF_3(CF_2)_6COOH$	414.07
1H,1H,2H,2H-Perfluorododecan-1-ol (97%)	Perfluorododecanol	865-86-1	$C_{12}H_5F_{21}O$	564.13
Perfluoro-octanesulphonamide	PFOSA	754-91-6	$C_8H_2F_{17}NO_2S$	499.14
N-Methyl perfluoro-octanesulfonamide	MeFOSA	31506-32-8	$C_9H_4F_{17}NO_2S$	513.17
Heptafluorobutyric acid	PFBA	375-22-4	$CF_3CF_2CF_2COOH$	214.04
Perfluoropentanoic acid (97%)	PFPeA	2706-90-3	$CF_3(CF_2)_3COOH$	264.05
Perfluoroundecanoic acid (95%)	PFUA	2058-94-8	$CF_3(CF_2)_9CO_2H$	564.09
PerfluoroHeptanoic acid (99%)	PFHpA	375-85-9	$CF_3(CF_2)_5CO_2H$	364.06
Perfluorodecanoic acid (98%)	PFDeA	335-76-2	$CF_3(CF_2)_8CO_2H$	514.08
Perfluorononanoic acid (97%)	PFNA	375-95-1	$CF_3(CF_2)_7COOH$	464.08
Tricosafluorododecanoic acid (95%)	PFDoA	307-55-1	$CF_3(CF_2)_{10}CO_2H$	614.10
Nonafluorobutane-1-sulfonic acid (97%)	PFBuS	375-73-5	$CF_3(CF_2)_3SO_3H$	300.10

Compound Name	Abbreviation or the Name Commonly Used	CAS No.	Formula	MW
N-Ethyl-N-(2-hydroxyethyl)perfluoro-octylsulfonamide	BFOSE	1691-99-2	$C_{12}H_{10}F_{17}NO_3S$	517.26
N-(2-Hydroxyethyl)-N-methylperfluoro-octanesulfonamide	MeFOSE	24448-09-7	$C_{11}H_8F_{17}NO_3S$	557.22

2.4 Pharmaceutical and Personal Care Compounds

More than 3000 pharmaceuticals are being used in the world now, and the number is increasing all the time (Halling-Sorensen et al. 1998). Eighty percent of them pass through the human body unaltered and enter the environment (Halling-Sorensen et al. 1998; Mottaleb et al. 2015). They all affect living organisms and their metabolites might have more dangerous effects (Togola and Budzinski 2007). To some degree, the same can be said about personal care products, many of which contain biologically active substances, especially hormones.

Based on a literature search, the PPCP compounds listed in Table 3 were selected as the target compounds for analysis in this study.

Table 4. Target PPCP compounds for analysis.

– Compound Name	– CAS No.	– Formula	– MW	– Class
– 17-alpha-Ethynylestradiol	– 57-63-6	– C20H24O2	– 296.40	– Hormone
– 17-beta-Estradiol	– 50-28-2	– C18H24O2	– 272.38	– Hormone
– 4-para-Nonylphenol	– 84852-15-3	– C15H24O	– 220.35	– Steroid
– 4-tert-Octylphenol	– 140-66-9	– C14H22O	– 206.32	– Other drugs
– Acetaminophen	– 103-90-2	– C8H9NO2	– 151.16	– Other drugs
– Bisphenol A	– 80-05-7	– C15H16O2	– 228.29	– Hormone-like
– Caffeine	– 58-08-2	– C8H10N4O2	– 194.19	– Other drugs
– Carbamazepine	– 298-46-4	– C15H12N2O	– 236.27	– Other drugs
– Ciprofloxacin HCL	– 86393-32-0	– C17H18FN3O3·HCl	– 385.82	– Antibiotics
– Diclofenac sodium salt	– 15307-79-6	– C14H10Cl2NNaO2	– 318.13	– Other drugs
– Erythromycin USP	– 114-07-8	– C37H67NO13	– 733.9	– Antibiotics
– Estrone	– 53-16-7	– C18H22O2	– 270.37	– Hormone
– Fluoxetine HCl	– 56296-78-7	– C17H18F3NO·HCl	– 345.79	– Other drugs
– Gemfibrozil	– 25812-30-0	– C15H22O3	– 250.3	– Other drugs
– Ibuprofen	– 15687-27-1	– C13H18O2	– 206.28	– Other drugs
– Naproxen	– 22204-53-1	– CH3OC10H6CH(CH3)CO2H	– 230.26	– Other drugs
– Ofloxacin	– 82419-36-1	– C18H20FN3O4	– 361.37	– Other drugs
– Primidone	– 125-33-7	– C12H14N2O2	– 218.25	– Other drugs
– Progestrone	– 57-83-0	– C21H30O2	– 314.46	– Hormone
– Sulfamethoxazole	– 723-46-6	– C10H11N3O3S	– 253.28	– Antibiotics
– Testosterone	– 58-22-0	– C19H28O2	– 288.42	– Hormone

– Compound Name	– CAS No.	– Formula	– MW	– Class
– Triclosan	– 3380-34-5	– C12H7Cl3O2	– 289.54	– Antibiotics
– Trimethoprim	– 738-70-5	– C14H18N4O3	– 290.32	– Antibiotics

3.0 Materials and Methods

Sample extraction, the preparation of standards and samples, derivatization of each for PPCPs and PFCs, and the associated analytical methods, sample preparation and analysis methods are described in the following sections.

3.1 Sample Extraction

Methylene chloride (CH_2Cl_2)—one of the most common extractants used to extract a wide majority of semi-volatile compounds— was used to extract PFCs and PPCPs from the sludge during this study. For the sludge samples, 5 g of sludge was extracted using 20 mL of CH_2Cl_2 in a 40mL glass vial for 48 hours. During the extraction, the mixture of sludge with extractant was mixed by a rotational mixer. The extraction systems were then centrifuged to separate the extractant from the sample. The extractant from each sample was then transferred to a vial for further processing and analysis (Figure 2).

Figure 2. Sludge extracting vials after centrifugation (left) and vials with separated extractant (right).

3.2 Standard and Sample Preparation

PPCP standards at 200 ppm concentration were ordered from Restek Corporation (Bellefonte, PA). PFCs were ordered from Aldrich (Milwaukee, WI, USA), Apollo Scientific (Cheshire, UK), and Synquest laboratories (Alachua, FL, USA). PFC compounds were dissolved in acetonitrile. The PPCP and PFC standards were diluted using CH_2Cl_2 to prepare sets of standards used for GC-MS/MS calibration. The extractant CH_2Cl_2 was used for analysis with no further processing. Blank samples were run before and after the calibration and after every sample in order to avoid cross-contamination. Internal standards for the EPA 8270 method were added to each standard, sample, and blank.

3.3 Standard and Sample Derivatization

3.3.1 PPCP Derivatization

Derivatization of the following three PPCP compounds was conducted to achieve better identification and quantification.

- Gemfibrozil (25812-30-0)
- Naproxen (22204-53-1)
- Ibuprofen (15687-27-1).

All three compounds were analyzed directly using GC/MS, but the results were inconsistent and depended too much on the condition of the instrument. Occasional derivatization of these compounds sometimes happens during the analyses.

In our first study (Zhong et al. 2016), the procedure of derivatizing non-GC-able compounds to Trimethylsilyl (TMS) esters was used, and is described in details by Shareef et al. (2006). N-Methyl-N-(trimethylsilyl) trifluoroacetamide (MSTFA) (Sigma-Aldrich, Inc.) was used as the derivatizing agent. This method was also used in this study. The derivatizing process included the following steps:

1. Mix 0.2 mL of MSTFA with 0.2 mL of CH_2Cl_2.
2. Add 20 mg of a compound to be derivatized.
3. Mix and place the mixture in an oven set at 60°C for 30 min.

3.3.2 PFC Derivatization

We used a modified derivatization procedure based on the Perfluorinated Carboxylic Acid (PFCA) derivatization method reported by Dufkova et al. (2012). We consider the modified procedure more reliable and less dependable on the derivatization condition and purity of the compounds involved. The PFCA standards were derivatized in 2.0 mL glass vials with 16 µL of pyridine, 32 µL of isobutyl alcohol, and 40 µL of isobutyl chloroformate (IBCF) to 720 µL of the appropriately diluted acetonitrile solution of the PFCA mixture, bringing the overall volume of the reaction mixture to 800 µL. The mixture was stirred for 20 s in an ultrasonic bath, then maintained quiet for 8 min, after which 800 µL of hexane were added to the mixture, and the isobutyl esters formed were extracted by shaking for 1 min. The upper hexane layer was collected in vials for GC-MS/MS analysis. Other derivatization techniques reported in the literature (e.g., Alzaga R et al. 2004) use the derivatization agent thionyl chloride ($SOCl_2$).

3.4 Analytical Methods for PPCPs and PFCs

Some PFCs and PPCPs cannot be analyzed using GC/MS. For these compounds, liquid chromatography with tandem mass spectrometry (LC-MS/MS) is used for the analysis. Nevertheless, many PFC and PPCP compounds can be analyzed by GC-MS, either directly or after their proper derivatization to esters. The GC-MS technique might have some advantages, because of the higher resolution of GC columns compared to LC columns.

A GC-MS/MS system (Agilent 7000C) (Figure 3) was used for the analysis. The scan mode was used to identify compounds by their mass spectra and to determine the retention times of the compounds in the samples. The selected ion morning (SIM) method was then used to measure a set of compounds. Multiple reactions monitoring (MRM) was applied to determine the concentrations of the compounds that were hard to determine using the SIM method. Each of the methods is described more detail, as follows.

- **Scan method.** The scan method is the least sensitive, but the most informative method. Most of the compounds can be identified by their mass spectra even if we do not have the standard for those compounds. In the scan method, MS produces the mass spectra of each compound. The most intensive ions in the mass spectra are used to create the SIM method or MRM method.
- **SIM method.** In this method, GC/MS registers only the characteristic ions for certain compounds whose retention times were previously determined during the standards run. In many applications, this method is sufficient for most of the compounds and has a sensitivity 100 to 1000 times higher than the scan method. In this work, the samples were highly loaded with organic materials, which produced significant interferences. In general, the compound with smaller MWs and shorter retention times (e.g., 4-tert-octylphenol) were more reliably quantified. The compounds with higher MWs in the second half of the chromatogram had more interferences, so the MRM method was used to determine the concentrations of those compounds.
- **MRM method.** In this method, the first mass spectrometer selects characteristic ions for certain compounds and the second mass spectrometer registers only the fragment ions for the selected characteristic ions after they are broken down in the collision cell, which is located between the two mass spectrometers. This makes the MRM method more selective than the SIM method, but the samples are so complex that we have observed some interferences even in MRM method. The ions selected by the first mass spectrometer are called parent ions, and the ions coming out from the collision cell are called product ions. Different energies in the collision cell are applied during the optimization runs, and the most efficient values are used during the analytical runs.

Figure 3. GC-MS/MS system used for analysis.

3.5 Sample Preparation for Elemental Analyses

For the preparation of heavy metals by MC-ICP-MS, aliquots of the wastewater sludge samples were transferred into quartz crucibles and heated in a muffle furnace for 8 hours at 110°C, resulting in a weight loss of approximately 75%. The dried samples were heated for another 9 hours at 425°C, resulting in an

additional weight loss of 15%. The dried samples were transferred into 50 mL Teflon vials and digested for 20 hours at 85°C with 4 mL of 1:1 concentrated nitric acid and concentrated hydrofluoric acid. After heating the digestates to approximately 0.5 mL, 2.5 mL of concentrated hydrochloric acid was added to the vials. The samples were digested for 28 hours, then heated to dryness. The residue was digested with 1 mL of concentrated hydrochloric acid and 4 mL of concentrated nitric acid for 30 min. Deionized water was added to a 20 mL volume and the sample solution was digested for 12 hours. All acids were Fisher Optima grade.

3.6 Analytical Method for Elemental Analyses

Elemental analyses were done on the Multicollector ICP-MS NU Plasma HR using the previously reported method (Mitroshkov et.al. 2015, 2016). In the elemental analysis, only the central Faraday cup (Ax) was used. In this mode, the system quickly jumps from one isotopic peak of a certain element to the isotopic peak of another element. The scan rate was 1000 msec/amu and the dwell time was 2 sec. Unlike in isotopic analyses, where the MS has the ability to find precisely the center of the peak, the accurate centering of every peak every time is unattainable. Therefore, it is important to accurately calibrate the mass scale. For this purpose, two different standards were used:

- The internal standard contains eight elements: Bi, Ho, In, Lu, Rh, Sc, Tb, Y (High Purity Standards, SC, USA); in order to cover the low side of mass scale Li and Be were also added to this standard; U was added for the higher end of the mass scale
- ICP-MS standard contains 68 elements (High Purity Standards, SC, USA).

The internal standard provides an 11-point calibration, followed by the ICP-MS standard, which provides a 66-point calibration.

4.0 Results

4.1 Results for PFCs for the Samples before HTL Processing

So far, the reported data on PFCs in sludge are very limited, but some available data are in the same range of concentrations as ours. For Higgins et al. (2005), the concentration of PFCs in domestic sludge ranged from 5 to 152 ng/g (0.005 to 0.152 mg/kg) for total perfluoro-carboxylates and 55 to 3370 ng/g (0.055 to 3.37 mg/kg) for total perfluoroalkyl sulfonyl-based chemicals. In our investigation, the sulfonyl-based chemicals were in the range of 6 to 253 ng/g (0.006 to 0.253 mg/kg) and for total perfluorocarboxylates and perfluorinated alcohols our data were in the range of 5 to 2526 ng/g (0.005 to 2.53 mg/kg) (Table 4).

The choice of extractant for this kind of analytical work is very important, but has not been investigated sufficiently. Higgins et al. (2005) used a mixture of methanol and acetic acid. In addition to using CH_2Cl_2 as the extractant, we have used methanol. Methanol extraction extracted a smaller amount of PFCs than CH_2Cl_2 extraction. Because our purpose was to investigate a big group of different compounds that had very different properties, the choice of one of the most universal extractants— CH_2Cl_2—was appropriate.

We investigated matrix spiked sludge and aqueous products in order to determine the efficiency of the extraction. When using the matrix spike approach the question that always remains is how adequately do the results of the matrix spike experiments represent the extraction from real samples. The problem is that, due to possible complexation of PFCs in the sludge, the extraction of the sludge and the extraction of the spiked samples might differ.

For matrix spike experiments, only the PFCs, which can be directly analyzed using the GC/MS method without derivatization, were used. They represent a different kind of PFCs.

A known amount of PFC compounds was added to a known amount of WW-07 Tote Aqueous Product and WW-07 BD 1-4 solid samples (see Table 4 fora description of the recovery of PFCs by CH_2Cl_2 extraction). The spiked concentrations were 2 mg/L in the aqueous sample and 8 mg/kg in the solid sample. The spiked samples were then extracted to analyze the PPCP concentrations using the sample processing procedures and analytical methods developed for PFC compounds analysis. The sample spiking and extraction details were as follows:

- Matrix spike for WW-07 Tote aqueous product – 2.0 mL of 50 ppm PFC stock solution was added to 50 mL of WW-07 Tote liquid. The final concentration was 2.0 mg/L.
- Matrix spike for WW-07 BD 1-4 solid – Water was first added to 5 g of the dry solid to moisturize the sample. 0.8 mL of 50 ppm PFC compound stock solution was then added to the mixture. The final concentration was 8 mg/kg (dry).
- Extraction –20 mL of CH_2Cl_2 was added to 5 g of PFC spiked solid; and 10 mL of CH_2Cl_2 was added to a 50 mL spiked aqueous sample. Assuming all the PFCs were extracted, the concentrations of the PPCP compounds would be 2 ppm in the extractant from solid extraction and 10 ppm from the aqueous phase extraction.

Table 5. The recovery of PFCs by methylene chloride extraction.

Substance	WW-07 Aq. Product, Recovery %	WW-07 BD 1-4 Solid , Recovery %
Sulfluramid (BFOSA)	112.2	120.9
1H,1H,2H,2H-Perfluoro-1-octanol	95.1	112.4
1H,1H,2H,2H-Perfluoro-1-decanol	79.2	128.5
1H,1H,2H,2H-Perfluorododecan-1-ol	102.6	119.0
N-Methyl perfluoro-octanesulfonamide (MeFOSA)	71.8	77.6
Perfluoro-octanesulphonamide (PFOSA)	111.5	125.4

In our previous and current research, we have analyzed PPCPs using the SIM and MRM methods. The data obtained by the MRM method are more reliable, because of the significantly higher selectivity of the MRM method compared to the SIM method. Nevertheless, we did not analyze PFCs using the SIM method, because the spectra of PFCs are not very different from many other fluorinated compounds, which are present in the sludge and have too many similar ions (e.g., m/z=69,131,219, etc.).

The presence of other fluorinated compounds, which was not included in the scope of our research, would have made the analyses in SIM mode unreliable due to many interferences.

Table 6. The results for PFCs analyses by MRM method in sludge samples. Direct GC/MS/MS analyses without the derivatization. Conc. units: - µg/g (mg/kg)

				Conc. in Wet Sludge (mg/kg)		
Sample No.	Sample ID	Sample (g)	CH_2Cl_2 (mL)	BFOSA-Sulfuramid	MeFOSA	Perfluorodecanol
Sam-1	Detroit 50/50	5.06	20.00	0.2395	0.2525	1.4264

Sample No.	Sample ID	Sample (g)	CH_2Cl_2 (mL)	Conc. in Wet Sludge (mg/kg)		
				BFOSA-Sulfuramid	MeFOSA	Perfluorodecanol
Sam-2	GLWA P-1	5.06	20.00	0.0166	0.0179	0.2485
Sam-3	GLWA P+S-1	5.02	20.00	0.0129	0.0089	0.1585
Sam-4	GLWA P-2	5.05	20.73	0.0077	0.0080	0.2046
Sam-5	GLWA P+S-2	5.00	20.88	0.0058	0.0057	0.1524
Sam-1	Detroit 50/50	5.06	20.00	2.5317	0.3282	0.1701
Sam-2	GLWA P-1	5.06	20.00	0.6756	0.1145	0.0078
Sam-3	GLWA P+S-1	5.02	20.00	0.4907	0.0681	0.0125
Sam-4	GLWA P-2	5.05	20.73	0.5146	0.1088	0.0146
Sam-5	GLWA P+S-2	5.00	20.88	0.4460	0.0766	0.0131

Table 6. The results for PFCs analyses by MRM method in sludge samples. The compounds were derivatized before the GC/MS/MS analyses. Conc. units: - µg/g (mg/kg)

Sample No.	Sample ID	Sample (g)	CH_2Cl_2 (mL)	Conc. in Wet Sludge (mg/kg)		
				Heptafluorobutyric Acid	Perfluorodecanoic Acid	Perfluoroheptanoic Acid
Sam-1	Detroit 50/50	5.06	20.00	0.0296	<0.002	0.0587
Sam-2	GLWA P-1	5.06	20.00	0.0290	<0.002	0.0533
Sam-3	GLWA P+S-1	5.02	20.00	<0.002	<0.002	0.0087
Sam-4	GLWA P-2	5.05	20.73	0.0154	<0.002	0.0470
Sam-5	GLWA P+S-2	5.00	20.88	0.0138	<0.002	0.0486
Sam-1	Detroit 50/50	5.06	20.00	0.5917	0.0468	0.0129
Sam-2	GLWA P-1	5.06	20.00	0.6424	0.0180	0.0078
Sam-3	GLWA P+S-1	5.02	20.00	0.1721	0.0035	0.0010
Sam-4	GLWA P-2	5.05	20.73	0.6383	0.0098	0.0055
Sam-5	GLWA P+S-2	5.00	20.88	0.6453	0.0112	0.0060

Sample No.	Sample ID	Sample (g)	CH_2Cl_2 (mL)	Conc. in Wet Sludge (mg/kg)	
				Perfluoroundecanoic Acid	Tricosafluorododecanoic Acid
Sam-1	Detroit 50/50	5.06	20.00	0.2234	0.1088
Sam-2	GLWA P-1	5.06	20.00	0.1749	0.0584
Sam-3	GLWA P+S-1	5.02	20.00	0.1387	0.0161
Sam-4	GLWA P-2	5.05	20.73	0.1589	0.0322
Sam-5	GLWA P+S-2	5.00	20.88	0.1559	0.0280

4.1.1 Results for PFCs for the Samples after HTL Processing

Table 7. The results for PFCs analyses by MRM method in solid sludge samples after HTL treatment. Direct GC/MS/MS analyses without the derivatization. Conc. units: - µg/g (mg/kg)

				Conc. in aq. Product and Solids (mg/kg)		
Sample No.	Sample ID	Sample (g)	CH_2Cl_2 (mL)	BFOSA-Sulfuramid	MeFOSA	Perfluorodecanol
Sam-1	WW-07 aq. product	100	10.00	<0.004	<0.004	<0.004
Sam-2	WW-07 Filter wash	5.00	20.00	<0.004	<0.004	<0.004
Sam-3	WW-07 BD 1-4	5.01	20.00	<0.004	<0.004	<0.004
Sam-4	WW-07 BD 5-8	5.06	20.73	<0.004	0.0041	<0.004

Sample No.	Sample ID	Sample (g)	CH_2Cl_2 (mL)	Conc. in aq. Product and Solids (mg/kg)		
				Perfluorododecanol	Perfluorooctanol	PFOSA
Sam-1	WW-07 aq. product	100	10.00	<0.004	<0.004	<0.004
Sam-2	WW-07 Filter wash	5.00	20.00	0.0043	<0.004	<0.004
Sam-3	WW-07 BD 1-4	5.01	20.00	<0.004	<0.004	<0.004
Sam-4	WW-07 BD 5-8	5.06	20.73	0.0041	<0.004	<0.004

				Conc. in Wet Sludge (mg/kg)		
Sample No.	Sample ID	Sample (g)	CH_2Cl_2 (mL)	Heptafluorobutyric Acid	Perfluorodecanoic Acid	Perfluoroheptanoic Acid
Sam-1	WW-07 aq. product	100	10.00	<0.0001	<0.0001	<0.0001
Sam-2	WW-07 Filter wash	5.00	20.00	<0.004	<0.004	<0.004
Sam-3	WW-07 BD 1-4	5.01	20.00	<0.004	<0.004	<0.004
Sam-4	WW-07 BD 5-8	5.06	20.73	<0.004	<0.004	<0.004

				Conc. in Wet Sludge (mg/kg)		
Sample No.	Sample ID	Sample (g)	CH_2Cl_2 (mL)	Perfluorononanoic Acid	Perfluorooctanoic Acid	Perfluoropentanoic Acid
Sam-1	WW-07 aq. product	100	10.00	0.0007	<0.0001	<0.0001
Sam-2	WW-07 Filter wash	5.00	20.00	<0.004	<0.004	<0.004
Sam-3	WW-07 BD 1-4	5.01	20.00	<0.004	<0.004	<0.004
Sam-4	WW-07 BD 5-8	5.06	20.73	<0.004	<0.004	<0.004

				Conc. in Wet Sludge (mg/kg)	
Sample No.	Sample ID	sample (g)	CH_2Cl_2 (mL)	Perfluoroundecanoic Acid	Tricosafluorododecanoic Acid
Sam-1	WW-07 aq. product	100	10.00	0.0001	<0.0001
Sam-2	WW-07 Filter wash	5.00	20.00	<0.004	<0.004
Sam-3	WW-07 BD 1-4	5.01	20.00	<0.004	<0.004
Sam-4	WW-07 BD 5-8	5.06	20.73	<0.004	<0.004

Sample ID	Conc. in Wet Sludge (mg/kg)

Sample No.		Sample (g)	CH_2Cl_2 (mL)	N-Ethyl-N-(2-hydroxyethyl)perfluoro-octylsulfonamide	N-(2-Hydroxyethyl)-N-methylperfluoro-octanesulfonamide
Sam-1	WW-07 aq. product	100	10.00	0.0001	<0.0001
Sam-2	WW-07 Filter wash	5.00	20.00	<0.004	<0.004
Sam-3	WW-07 BD 1-4	5.01	20.00	<0.004	<0.004
Sam-4	WW-07 BD 5-8	5.06	20.73	<0.004	<0.004

4.2 Results for PPCPs

4.2.1 Matrix Spikes Test for PPCPs

In the matrix spike tests for the HTL Sludge Analysis project, a known amount of PPCP compounds was added to a known amount of WW-07 Tote Aqueous Product and WW-07 BD 1-4 solid samples (see Table 7 for the sample description). The spiked concentrations were 2 mg/L in the aqueous sample and 4 mg/kg in the solid sample. The aqueous and solid samples were set to react with spiked PPCPs for 4 days. The spiked samples were then extracted for PPCPs using CH_2Cl_2 for 2 days. The extracts were analyzed for PPCP concentrations using the sample processing procedures and analytical methods developed for the PPCP compounds analysis. The sample spiking and extraction details were as follows.

- Matrix spike for WW-07 Tote aqueous product – 0.5 mL of 200 ppm PPCP stock solution was added to 50 mL of WW-07 Tote liquid. The final concentration was 2 mg/L.
- Matrix spike for WW-07 BD 1-4 solid – 1 mL of deionized water was first added to 5 g of the dry solid to moisturize the sample. 0.1 mL of 200 ppm PPCP stock solutions was then added to the solid. The final concentration was 4 mg/kg (dry).
- Extraction –20 mL of CH_2Cl_2 was added to the 5 g PPCP-spiked solid, and10 mL of CH_2Cl_2 to the 50 mL spiked aqueous sample. Assuming all the PPCPs are extracted, the concentrations of the PPCP compounds in the extractant should be 1 ppm from solid extraction and 10 ppm from the aqueous phase extraction.

Table 8. The recovery of PPCPs by methylene chloride extraction.

– Compounds	– WW-07 BD 1-4 Solid, Recovery %	– WW-07 Aq. Product, Recovery %
– Acetaminophen	– 88.1	– 68.4
– Bisphenol A	– 83.9	– 110.0
– Caffeine	– 89.8	– 76.6
– Carbamazepine	– 81.3	– 97.2
– Estradiol	– 61.6	– 75.7
– Estrone	– 108.9	– 92.8
– Ethynylestradiol	– 86.7	– 75.4
– Gemfibrozil	– 82.7	– 95.2
– Ibuprofen	– 94.1	– 97.9
– Octylphenol	– 82.8	– 166.2
– Primidone	– 254.9	– 73.2
– Progestrone	– 103.3	– 59.4
– Testosterone	– 98.3	– 60.5

– Compounds	– WW-07 BD 1-4 Solid, Recovery %	– WW-07 Aq. Product, Recovery %
– Triclosan	– 91.1	– 89.1

The somewhat excessive recovery values obtained for Octylphenol and Primidone. These values were likely caused by different reasons. Octylphenol appears to be very ubiquitous, so occasional contamination is possible. It is possible that Primidone, as observed for a few other compounds, exhibits different responses in the standard and in the samples. Certain compound are very sensitive to contamination in the injector, and can be absorbed or even derivatized at the contaminated surfaces. The presence of many organic compounds in complex samples like these, “screen” these analyzed compounds from contact with contaminated surfaces. As a result, these kinds of compounds exhibit higher responses in the samples than in the standards.

Overall, the concentrations of PPCPs determined in this round of research were significantly lower than in the previous study (Zhong et al. 2016). We also found that the derivatization method using IBCF, as used in this research, works more reliably than the TMS method used in our previous research. Both isobutyl and methyl esters of derivatized compounds were observed.

In Table 8 through Table 14, the comparative results for PPCPs analysis using the SIM and MRM methods are reported. The comparison of SIM and MRM results is important, because it gives additional confirmation of and improves the reliability of the results. Also, the feasibility of the SIM method for such complex samples is tested.

Table 9. The results for PPCP analyses before HTL treatment. Concentrations are given for wet sludge (mg/kg). Red text indicates false positive.

	4-tert-octylphenol	Acetaminophen	Bisphenol A	Carbamazepine	Diclofenac
SIM					
Sam-1	1.234	0.468	4.806	<0.040	0.343
Sam-2	1.133	0.383	2.275	<0.040	0.233
Sam-3	0.530	0.285	3.312	<0.040	<0.040
Sam-4	1.050	0.235	2.201	<0.040	<0.040
Sam-5	0.651	0.351	4.748	<0.040	<0.040
MRM					
Sam-1	1.203	<0.040	4.476	0.058	0.254
Sam-2	1.162	<0.040	2.941	0.019	0.164
Sam-3	0.546	<0.040	3.261	0.017	0.044
Sam-4	1.109	<0.040	2.751	0.022	0.030
Sam-5	0.683	<0.040	4.418	0.051	0.028

In Table 8, one can see that there is very good agreement for 4-tert-octylphenol, Bisphenol A, and Diclofenac. Carbamazepine in SIM mode has too many interferences and was not reliably detected. Acetaminophen is the example of false positive in SIM method; it was not detected using the MRM method.

Table 10. The results for PPCP analyses before HTP treatment. Concentrations are given for wet sludge (mg/kg). Red text indicates false positive.

	Estradiol	Estrone	Ethynylestradiol	Fluoxetine	Gemfibrozil
SIM					
Sam-1	0.581	0.721	1.618	3.378	<0.040
Sam-2	0.499	0.299	1.366	2.514	<0.040
Sam-3	0.298	0.276	1.185	2.605	<0.040
Sam-4	0.547	0.355	1.444	2.329	<0.040
Sam-5	0.266	0.290	1.328	2.475	<0.040
MRM					
Sam-1	0.484	0.784	0.074	2.264	7.208
Sam-2	0.164	0.274	<0.040	1.793	5.043
Sam-3	0.065	0.146	<0.040	1.344	6.740
Sam-4	0.060	0.129	<0.040	1.380	4.761
Sam-5	0.052	0.088	<0.040	1.315	5.417

As seen in Table 9, for Estradiol, Estrone, and Fluoxetine, there is reasonably close agreement between the SIM and MRM results, although, due to more significant interferences, there are mostly higher concentrations for SIM results. For Ethynylestradiol, we have false positive results. There are no data in SIM mode for Gemfibrozil, because of high-level interferences. Later (see below), the derivatization results confirmed that Gemfibrozil is present in the samples at a detectable level.

Table 11. The results for PPCP analyses before HTP treatment. Concentrations are given for wet sludge (mg/kg).

	Ibuprofen	Naproxen	Primidone	Progestrone	Testosterone
SIM					
Sam-1	2.046	<0.040	<0.040	<0.040	<0.020
Sam-2	1.361	<0.040	<0.040	<0.040	<0.020
Sam-3	0.689	<0.040	<0.040	<0.040	<0.020
Sam-4	1.059	<0.040	<0.040	<0.040	<0.020
Sam-5	0.835	<0.040	<0.040	<0.040	<0.020
MRM					
Sam-1	1.707	<0.040	<0.020	0.024	<0.020
Sam-2	1.185	<0.040	<0.020	0.021	<0.020
Sam-3	0.496	<0.040	<0.020	<0.020	<0.020
Sam-4	0.949	<0.040	<0.020	<0.020	<0.020
Sam-5	0.592	<0.040	<0.020	<0.020	<0.020

As shown in Table 10, there is good agreement between SIM and MRM data for Ibuprofen. Everything else is very low or undetected. The SIM results are a bit higher, which is understandable, because MRM method provides higher selectivity than the SIM method and the influence of interferences is smaller in the MRM method.

Table 12. The results for PPCP analyses before HTP treatment. Concentrations are given for wet sludge (mg/kg).

	Triclosan	Trimephoprim	Caffeine
SIM			
Sam-1	6.460	<0.080	0.238
Sam-2	4.015	<0.080	0.242
Sam-3	3.383	<0.080	0.133
Sam-4	3.859	<0.080	0.219
Sam-5	4.272	<0.080	0.152

These compounds were analyzed only in SIM mode, because in previous research found that they were in high concentrations, well separated chorographically, and had very distinct mass spectra. Therefore, there was no need for applying the more complicated, although more selective, MRM method for these compounds. In future research, the MRM method will be developed for detecting these compounds, too, because they can be present in lower concentrations in different samples.

Table 13. The results for Ibuprofen, Naproxen, and Gemfibrozil in derivatized samples analyses. Concentrations are given for wet sludge (mg/kg).

	Gemfibrozil by Isobutyl Ester	Ibuprofen by Isobutyl Ester	Naproxen by Isobutyl Ester
SIM			
Sam-1	NA	2.479	NA
Sam-2	NA	1.710	NA
Sam-3	NA	1.685	NA
Sam-4	NA	1.851	NA
Sam-5	NA	1.883	NA

NA = the data are not available.

So far, the derivatized samples have been analyzed only in SIM mode. We plan to develop the MRM method during the next step of our research. For Ibuprofen there is good agreement between the SIM and MRM data for non-derivatized sample analyses, although for derivatized sample analysis the values are somewhat higher. We suppose that some Ibuprofen isobutyl ester might be present in the sample even before the derivatization. This suggests that TMS derivatization method we used in previous research might be still preferable, even though it is less reliable than the IBCF derivatization method. The presence of isobutyl esters in the samples before derivatization appears to be more likely than the presence of TMS esters.

For the data that are not available (NA), the characteristic ions for Gemfibrozil and Naproxen esters are registered at corresponding RT, but the results are inconclusive because of the high level of interferences, and to indicate the detection level is not possible.

4.2.2 Results for PPCP after Treatment

The analyses of pre-treatment samples reported here have demonstrated that the MRM method is superior to the SIM method, so the analysis of post-treatment samples was done using only the MRM method.

Table 14. The MRM results for the non-derivatized samples after HTL treatment. Concentrations are given for dry sludge in mg/kg, for aqueous phase in mg/L.

	4-tert-octylphenol	Acetaminophen	Bis-phenol A	Carbamazepine	Diclofenac
Sam-1	<0.001	<0.001	<0.001	<0.001	0.222
Sam-2	0.455	<0.04	<0.02	<0.04	0.575
Sam-3	3.531	<0.04	<0.02	<0.04	1.733
Sam-4	2.976	<0.04	<0.02	<0.04	1.396

	Estradiol	Estrone	Ethynylestradiol	Fluoxetine	Gemifibrozil
Sam-1	<0.001	<0.001	<0.001	<0.001	<0.001
Sam-2	<0.002	<0.02	<0.02	<0.04	<0.02
Sam-3	<0.002	<0.02	<0.02	<0.04	<0.02
Sam-4	<0.002	<0.02	<0.02	<0.04	<0.02

	Ibuprofen	Primidone	Progesterone	Testosterone
Sam-1	<0.001	<0.001	<0.001	<0.001
Sam-2	<0.04	<0.02	<0.04	<0.04
Sam-3	<0.04	<0.02	<0.04	<0.04
Sam-4	<0.04	<0.02	<0.04	<0.04

	Triclosan	Trimephoprim	Caffeine
Sam-1	0.01	<0.04	0.028
Sam-2	0.113	<0.04	<0.02
Sam-3	<0.02	<0.04	<0.02
Sam-4	<0.02	<0.04	<0.02

Table 15. The results for Ibuprofen, Naproxen, and Gemfibrozil in derivatized samples analyses after HTL treatment. Concentrations are given for wet sludge (mg/kg).

MRM.

	Gemfibrozil by Isobutyl ester	Ibuprofen by Isobutyl Ester	Naproxen by Isobutyl ester
Sam-1	<0.001	0.202	<0.001
Sam-2	<0.04	<0.02	<0.02
Sam-3	<0.04	4.175	<0.02
Sam-4	<0.04	1.774	<0.02

4.3 Results for Elemental Analyses.

For elemental analyses, the concentrations are given for wet sludge (ng/g) (Table 15 and Table 16). Negative values for a few elements mean that the registered values for these elements were below the values recorded in the Preparation Blanks.

Table 16. The results of elemental analyses: element concentrations in wet sludge before HTL treatment (ng/g).

	Li	Be	Na	Mg	Al	Si	P	K
GLWA P-1	3.40E+03	2.17E+02	1.18E+06	2.60E+06	5.32E+06	1.36E+07	4.25E+06	2.55E+06
GLWA P-2	3.76E+03	1.46E+02	6.38E+05	2.41E+06	3.55E+06	1.18E+07	3.89E+06	2.22E+06
GLWA P+S-1	1.93E+03	9.28E+01	7.11E+05	2.68E+06	1.18E+06	5.28E+07	4.29E+06	2.46E+06
GLWA P+S-2	1.47E+03	7.46E+01	4.50E+05	1.21E+06	2.85E+06	3.06E+06	4.64E+06	1.14E+06
	K	**Ca**	**Sc**	**Ti**	**V**	**Cr**	**Mn**	**Fe**
GLWA P-1	2.55E+06	1.03E+06	8.57E+02	5.73E+05	1.83E+04	3.54E+04	6.07E+04	8.10E+06
GLWA P-2	2.22E+06	1.00E+06	7.18E+02	5.45E+05	1.77E+04	3.60E+04	6.09E+04	8.34E+06
GLWA P+S-1	2.46E+06	7.38E+05	4.00E+02	3.70E+05	8.99E+03	2.90E+04	4.62E+04	7.91E+06
GLWA P+S-2	1.14E+06	5.85E+05	2.94E+02	2.93E+05	7.00E+03	2.24E+04	3.56E+04	6.24E+06
	Co	**Ni**	**Cu**	**Zn**	**Ga**	**Ge**	**As**	**Se**
GLWA P-1	4.41E+03	2.00E+04	5.41E+04	2.33E+05	1.25E+04	1.85E+02	1.56E+03	1.77E+03
GLWA P-2	6.89E+03	2.04E+04	6.21E+04	2.11E+05	1.04E+04	4.84E+02	1.58E+03	1.97E+03
GLWA P+S-1	4.24E+03	1.65E+04	6.48E+04	2.32E+05	1.28E+04	2.65E+02	1.26E+03	1.99E+03
GLWA P+S-2	3.26E+03	1.28E+04	5.24E+04	1.80E+05	1.12E+04	9.56E+01	1.07E+03	1.58E+03
	Rb	**Sr**	**Y**	**Zr**	**Nb**	**Mo**	**Ru**	**Rh**
GLWA P-1	7.67E+03	3.04E+04	1.22E+03	1.83E+04	8.85E+02	3.00E+03	2.49E+01	7.48E+00
GLWA P-2	8.01E+03	3.21E+04	1.20E+03	2.65E+04	9.98E+02	3.15E+03	3.18E+01	1.25E+01
GLWA P+S-1	3.92E+03	2.84E+04	7.65E+02	1.98E+04	5.70E+02	2.59E+03	2.11E+01	8.86E+00
GLWA P+S-2	3.08E+03	2.18E+04	5.85E+02	1.56E+04	4.71E+02	2.03E+03	1.18E+01	7.52E+00

	Pd	Ag	Cd	In	Sn	Sb	Te	Cs
GLWA P-1	2.46E+01	5.30E+02	8.70E+02	3.94E+01	9.00E+03	5.47E+02	6.30E+03	3.68E+02

GLWA P-2	4.27E+01	5.72E+02	7.68E+02	4.32E+01	1.06E+04	5.44E+02	7.52E+03	3.74E+02
GLWA P+S-1	1.37E+02	6.37E+02	5.51E+02	4.50E+01	1.23E+04	4.02E+02	8.66E+03	1.94E+02
GLWA P+S-2	1.91E+01	5.32E+02	4.10E+02	3.43E+01	9.87E+03	3.29E+02	6.92E+03	1.47E+02
	Ba	**La**	**Ce**	**Pr**	**Nd**	**Sm**	**Eu**	**Gd**
GLWA P-1	8.77E+04	2.78E+03	5.19E+03	5.06E+02	1.72E+03	3.08E+02	9.13E+01	3.20E+03
GLWA P-2	9.93E+04	2.45E+03	5.43E+03	4.95E+02	1.67E+03	2.94E+02	1.47E+02	1.03E+04
GLWA P+S-1	8.01E+04	1.31E+03	2.68E+03	2.52E+02	8.51E+02	1.56E+02	5.29E+01	2.34E+03
GLWA P+S-2	5.90E+04	1.03E+03	2.08E+03	2.01E+02	6.75E+02	1.23E+02	4.21E+01	1.80E+03
	Tb	**Dy**	**Ho**	**Er**	**Tm**	**Yb**	**Lu**	**Hf**
GLWA P-1	3.56E+01	2.02E+02	4.00E+01	1.18E+02	1.85E+01	1.22E+02	1.73E+01	4.32E+02
GLWA P-2	3.55E+01	1.96E+02	3.99E+01	1.12E+02	1.61E+01	1.11E+02	1.57E+01	5.49E+02
GLWA P+S-1	2.15E+01	1.06E+02	2.13E+01	6.27E+01	8.31E+00	5.76E+01	8.38E+00	4.11E+02
GLWA P+S-2	1.57E+01	8.05E+01	1.64E+01	4.83E+01	6.34E+00	4.60E+01	6.56E+00	3.34E+02
	Ta	**W**	**Re**	**Os**	**Ir**	**Pt**	**Au**	**Tl**
GLWA P-1	6.16E+01	1.82E+03	2.26E+01	-1.29E+02	-1.05E+00	1.26E+01	5.21E+01	1.50E+01
GLWA P-2	7.54E+01	1.83E+03	2.18E+01	-2.39E+01	7.98E-02	3.93E+00	4.14E+01	2.15E+01
GLWA P+S-1	3.74E+01	1.82E+03	4.66E+00	-4.40E+01	2.29E-01	6.67E-01	3.68E+01	1.41E+01
GLWA P+S-2	3.05E+01	1.68E+03	4.51E+01	-4.83E+01	-5.69E-01	-2.10E-01	3.57E+01	1.06E+01
	Pb	**Bi**	**Th**	**U**				
GLWA P-1	1.19E+04	9.95E+03	5.53E+02	9.19E+02				
GLWA P-2	1.19E+04	7.08E+03	5.32E+02	9.64E+02				
GLWA P+S-1	6.90E+03	4.95E+03	2.72E+02	6.82E+02				
GLWA P+S-2	5.71E+03	4.21E+03	2.21E+02	5.60E+02				

Table 17. The results of elemental analyses: element concentrations in wet sludge after HTL treatment (ng/g).

Sample	Li	Be	Na	Mg	Al	P	K	Ca
WW-07 BD_1-4	2.38E+04	1.01E+03	2.79E+06	1.64E+07	3.70E+07	4.93E+07	1.22E+07	1.03E+07
WW-07 BD_5-8	2.24E+04	1.07E+03	2.67E+06	1.99E+07	4.55E+07	4.81E+07	1.39E+07	1.14E+07
WW-07 Filter wash	1.99E+04	1.37E+03	2.27E+06	1.99E+07	4.42E+07	4.72E+07	1.16E+07	1.29E+07
WW-07 HTL Aq. Prod.	1.44E+02	-8.84E-03	5.60E+04	4.25E+02	2.94E+02	2.87E+03	1.32E+05	6.08E+01
Sample	**Sc**	**Ti**	**V**	**Cr**	**Mn**	**Fe**	**Co**	**Ni**
WW-07 BD_1-4	4.76E+03	4.29E+06	1.04E+05	1.56E+06	5.89E+05	9.13E+07	1.00E+05	7.72E+05
WW-07 BD_5-8	5.38E+03	4.72E+06	1.17E+05	1.64E+06	6.35E+05	9.88E+07	1.05E+05	7.51E+05

WW-07 Filter wash	6.22E+03	5.00E+06	1.28E+05	1.70E+06	6.95E+05	1.02E+08	1.28E+05	8.31E+05
WW-07 HTL Aq. Prod.	5.87E-02	1.05E+02	1.08E+00	2.71E+00	8.99E-01	1.21E+02	3.29E-01	1.75E+00
Sample	**Cu**	**Zn**	**Ga**	**Ge**	**As**	**Se**	**Rb**	**Sr**
WW-07 BD_1-4	9.33E+05	3.03E+06	1.42E+05	1.18E+04	6.73E+03	3.19E+04	5.04E+04	4.29E+05
WW-07 BD_5-8	9.66E+05	3.15E+06	1.36E+05	8.90E+03	4.66E+03	2.86E+04	5.41E+04	4.14E+05
WW-07 Filter wash	9.95E+05	3.24E+06	1.56E+05	7.08E+03	3.18E+03	3.40E+04	5.84E+04	4.75E+05
WW-07 HTL Aq. Prod.	1.20E+01	2.36E+00	2.51E+01	8.04E+00	8.29E+01	4.01E-01	1.00E+02	1.59E+01
Sample	**Y**	**Zr**	**Nb**	**Mo**	**Ru**	**Rh**	**Pd**	**Ag**
WW-07 BD_1-4	9.40E+03	2.54E+05	7.77E+03	5.08E+04	2.28E+02	6.26E+01	4.76E+02	7.37E+03
WW-07 BD_5-8	1.04E+04	2.72E+05	8.58E+03	5.91E+04	1.13E+02	5.13E+01	3.94E+02	8.38E+03
WW-07 Filter wash	1.21E+04	3.00E+05	1.01E+04	5.42E+04	8.06E+01	8.11E+01	6.38E+02	9.94E+03
WW-07 HTL Aq. Prod.	1.00E-01	1.97E+00	1.00E-01	1.11E+01	9.47E-02	6.17E-03	9.81E-02	3.29E-02
Sample	**Cd**	**In**	**Sn**	**Sb**	**Te**	**Cs**	**Ba**	**La**
WW-07 BD_1-4	8.00E+03	4.89E+02	1.19E+05	3.57E+03	8.35E+04	2.64E+03	9.66E+05	1.85E+04
WW-07 BD_5-8	8.53E+03	5.92E+02	1.28E+05	3.67E+03	8.99E+04	2.80E+03	1.07E+06	2.12E+04
WW-07 Filter wash	8.86E+03	5.04E+02	1.28E+05	1.66E+03	8.95E+04	2.82E+03	1.11E+06	2.43E+04
WW-07 HTL Aq. Prod.	1.39E-02	1.90E-02	3.45E+00	1.75E+01	2.44E+00	9.33E+00	3.99E+02	6.00E-02
Sample	**Ce**	**Pr**	**Nd**	**Sm**	**Eu**	**Gd**	**Tb**	**Dy**
WW-07 BD_1-4	3.57E+04	3.36E+03	1.11E+04	1.97E+03	7.88E+02	4.78E+04	2.59E+02	1.44E+03
WW-07 BD_5-8	4.17E+04	3.80E+03	1.24E+04	2.19E+03	8.04E+02	4.32E+04	2.82E+02	1.53E+03
WW-07 Filter wash	4.77E+04	4.39E+03	1.44E+04	2.54E+03	1.01E+03	6.10E+04	3.37E+02	1.81E+03
WW-07 HTL Aq. Prod.	1.95E-01	9.20E-03	1.16E-02	2.42E-03	2.06E-02	2.18E+00	-5.53E-04	2.60E-03
Sample	**Ho**	**Er**	**Tm**	**Yb**	**Lu**	**Hf**	**Ta**	**W**
WW-07 BD_1-4	2.61E+02	7.77E+02	1.07E+02	7.02E+02	1.02E+02	4.97E+03	7.84E+02	9.96E+04
WW-07 BD_5-8	2.97E+02	8.85E+02	1.21E+02	8.08E+02	1.20E+02	5.65E+03	9.86E+02	1.10E+05
WW-07 Filter wash	3.61E+02	1.06E+03	1.53E+02	9.91E+02	1.52E+02	6.16E+03	1.02E+03	1.05E+05
WW-07 HTL Aq. Prod.	1.93E-02	7.39E-03	4.53E-04	4.03E-03	-3.86E-04	4.20E-02	3.18E-02	3.09E+01
Sample	**Re**	**Os**	**Ir**	**Pt**	**Au**	**Tl**	**Pb**	**Bi**
WW-07 BD_1-4	3.04E+02	3.08E+01	7.27E+00	1.17E+02	1.80E+03	5.17E+02	1.01E+05	4.11E+04
WW-07 BD_5-8	3.76E+02	5.43E+01	1.83E+01	1.13E+02	1.10E+03	6.50E+02	1.27E+05	5.26E+04
WW-07 Filter wash	5.14E+03	2.36E+01	4.46E+01	1.18E+02	1.29E+03	6.60E+02	1.19E+05	4.78E+04
WW-07 HTL Aq. Prod.	1.29E-01	-3.51E-03	3.98E-02	4.57E-02	7.49E-01	7.09E-01	6.36E-01	1.03E-01
Sample	**Th**	**U**						
WW-07 BD_1-4	3.15E+03	1.23E+04						
WW-07 BD_5-8	3.75E+03	1.59E+04						
WW-07 Filter wash	4.29E+03	1.42E+04						
WW-07 HTL Aq. Prod.	6.68E-03	4.07E-02						

5.0 Conclusion

For all the PFC and PPCP compounds, except Perfluorononanoic acid and caffeine, the concentrations in sludge Sample-1 were significantly higher than in the other four samples; while in sludge Samples-2, 3, 4, and 5 there was no trend in concentrations change. The PPCP with the highest concentration was Bisphenol A, a plasticizer also identified as an endocrine disruptor that had a concentration in the range of 2.2-4.8 ppm. The compound 4-tert-octylphenol was detected in the concentration range of 0.5–1.2 ppm; also an endocrine disruptor, it is used to manufacture alkylphenol ethoxylates, which are anionic surfactants used in detergents.

The PFC with the highest concentration of 2.5 ppm was Perfluorododecanol. The higher concentrations in Sample-1 most likely are due to this sludge having undergone different processing steps than the other four samples.

To date, no occupational exposure limits have been identified for the PPCP and PFC compounds and no concentration limits have been set for sludge disposal. However, these compounds are getting increased attention because wastewater sludges are sources of air contamination (Ahrens et al. 2011) and groundwater pollution (Sepulvado et al. 2011). Regulations are expected to establish the associated occupational exposure limits.

The analysis of the samples after they were HTL processed demonstrates that the process removes most of the hazardous compounds from the sludge. The results of the analysis show that practically all analyzed PFCs were destroyed in the sludge during the HTL treatment process.

Most of the PPCPs were also destroyed, but some, such as Ibuprofen, Diclofenac, and 4-Tert-octylphenol, were detected after the treatment. It is somewhat challenging to compare the results for these most persistent contaminants before and after treatment, because these were different sources and the samples we've received after the treatment were dry and the samples received before the treatment were wet. Considering that liquid sludge samples contain an average of 80% water, the results for dry sludge were adjusted for moisture content. The before and after treatment concentrations are presented in Table 17 for comparison. It appears that although some reduction in concentrations takes place, the concentrations of these most stable compounds are generally in the same range.

Table 18. Comparison of the before and after treatment concentrations. Concentrations are given for wet sludge (mg/kg).

	4-tert-octylphenol	Ibuprofen	Diclofenac
Before Treatment.			
Sam-1	1.234	2.479	0.343
Sam-2	1.133	1.710	0.233
Sam-3	0.530	1.685	<0.040
Sam-4	1.050	1.851	<0.040
Sam-5	0.651	1.883	<0.040
After Treatment			
Sam-1	<0.001	0.04	0.044
Sam-2	0.091	<0.004	0.115
Sam-3	0.706	1.036	0.347

Sam-4	0.595	0.355	0.279

6.0 References

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