



Assessment on groundwater contamination from a former hard chromium plating site in Iggesund

by

Isabell Alnehem

Supervisor: Ingrid Ericson Jogsten

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Summary

Before the persistent and toxicological properties of perfluoroalkyl and polyfluoroalkyl substances (PFASs) were known they were used worldwide. The thermal and chemical stability from the carbon-fluorine bond makes these substances desirable for industrial applications. One particular PFAS that have received much attention is perfluorooctanesulfonic acid (PFOS) which is included in the Stockholm convention. Analyses have detected PFASs, especially the ones with longer carbon chain, in the environment, wildlife and humans so replacements are being searched for. This study investigates groundwater around a former hard chromium plating site, which is one of the registered exceptions where PFOS still is used. Five different located sampling points were collected and analyzed from this site in Iggesund, which is in the northern parts of Sweden. The substances analyzed for were thirteen perfluorinated carboxylic acids (PFCAs: C4-C14, C16 and C18), five perfluorinated sulfonic acids (PFSAs: C4, C6, C8 and C10) and 6:2 fluorotelomer sulfonate (6:2 FTS). The 6:2 telomer substances is being used as a replacement for similar compounds with longer carbon chains, but are believed to undergo biotransformation to persistent alkyl acids like perfluorohexanoic acid (PFHxA) in the environment. Solid phase extraction was performed on 500 mL filtered groundwater with and the concentrated samples were analyzed on an Ultra Performance Liquid Chromatography (UPLC), tandem mass spectrometer. The glass microfiber filters used for filtrating the groundwater were analyzed for particle bound PFASs. Results from the water extraction analysis showed eight detected PFAS, with PFOS as the major contributor (72 - 9600 ng/L). The PFOS concentrations differs substantially between the five groundwater samples where the two sampling points located south of the facility, and closest to the actual hard chromium plating, were clearly higher than the other three. Two other substances detected in high concentration were perfluorobutanesulfonic acid (PFBS), 8-1550 ng/L, and perfluorohexanesulfonic acid (PFHS), 18-140 ng/L which can be produced as an impurity during the production of PFOS. PFCAs in all samples were detected in lower concentrations (1-25 ng/L).

Additional to the PFAS analysis, the groundwater was also measured for chromium since the carcinogenic hexavalent form is used in the chromic acid bath during hard chromium plating. In the same two samples that had the highest PFAS concentration, chromium was found in high concentration, 34900-44800 µg/L. These result indicates that the chromic acid baths is the source for the elevated concentrations found in the groundwater. If the facilities are left to deteriorate it will lead to continuously spreading of chromium and the highly water soluble PFASs downstream to Iggesundån which is of concern for the environment and water living organisms.

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1 Introduction

The risk with new exploitation of the land needs to be determined for the two facilities at a former hard chromium plating site in Iggesund, outside Hudiksvall in northern Sweden.

Golder Associates (Golder) is an environmental consultant company with the mission to investigate soil, water and other contaminated areas from former industries. Golder has the responsibility to establish what measures need to be taken with the buildings, investigate the concentrations in the water/soil and potential transport and risks exposures to the surrounding people and environment. Two main objectives for Golder are: [1]

- No risk for people that pass the property today or in the future.
- No risk for contamination spreading to water living organisms in Iggesundån which is a recipient from the facilities.

The hard chromium plating activities at Iggesund's industrial property started in the early 1940s as a part of the steel manufactory. Thirty years later, after several expansions, there were two different facilities called the upper facility (Sågfallet) and the lower facility (Sågbladet) on this site. The lower facility was closed later in the 1970s and the building torn down in the beginning of 2000. Now a power station has taken its place. For the upper facility activities continued until the company was declared bankrupt in 2009 and the facility was decontaminated. Today, this property stands empty and deteriorates. Chemicals such as lye, trichloroethylene and chromic acid were used during the active years [2].

Previous environmental studies (from winter 2013 until spring 2014) have been performed by Golder Associates, on the upper facility's water pipes and basement. The lower facility was not possible to examine because of the power station and the lines they had drawn all over the property. These chemical analyses revealed elevated levels of metals and organic pollutants in the groundwater due to the former activities. Among the highest concentrations detected were chromium and perfluorooctane sulfonic acid $C_8F_{17}SO_3H$ (PFOS). Another detected pollutant was perfluorooctanoic acid $C_7F_{15}COOH$ (PFOA) [2].

1.1 Aims and objectives

The aim of this present study is to determine today's situation on the contaminated groundwater from the former hard chromium plating site located in Iggesund.

Specific objectives are to:

- Measure the presence of perfluoroalkyl and polyfluoroalkyl substances (PFASs) on filtered groundwater with Ultra Performance Liquid Chromatography (UPLC), Xevo TQ-S tandem mass spectrometer after solid phase extraction with Oasis WAX cartridges.
- Measure the particle bound PFASs to compare the difference from dissolved PFASs.
- Measure the presence of chromium, by inductively coupled plasma mass spectrometry (ICP-MS) to see if there is remaining chromic acid that still contaminates the groundwater.

- Compare possible correlations between total PFASs concentration with chromium concentration to determine if they come from the same contaminated source.

2 Background and theory

Golder Associates performed environmental studies on the upper facility 2013-2014 and then again 2016, that displayed elevated levels of chromium and PFOS, Table 1, in the groundwater. These results were compared with the action levels given from the national food administration (National Food Administration) for drinking water. For total PFAS concentration the action level is 90 ng/L and for total chromium concentration it is 50 µg/L [3,4]. When concentrations exceeds the action level measures need to be taken. It should be emphasized that the groundwater within or around the property is not used for drinking water. The water from Iggesundån is used for hydropower. This action level is used for comparison and to minimize the risk of not including important compounds and underestimate the risk[1].

Table 1. Concentration of chromium, PFOS and PFOA in 5 different groundwater samples from the contaminated former hard chromium plating site Iggesund detected 2013-2014 and 2016. Action level in bold is added for comparison

Sample points →	GA006	GA008	GA009	GA010	GA012	Action level
2013: Cr (µg/l)	82100	53900	9.2	<0.5	<0.5	50
2016: Cr (µg/l)	34500	55300	5.87	0.637	1.75	
2014: PFOA (µg/l)	0.077	0.011	*	*	0.009	0.09
2016: PFOA (µg/l)	0.0133	0.0362	*	*	0.0118	
2014: PFOS (µg/l)	13	4.1	*	*	0.047	0.09
2016: PFOS (µg/l)	9.08	24.1	*	*	0.110	

* Was not included in this analysis

Chromium was measured on filtered groundwater and PFOS/PFOA on unfiltered groundwater.

Groundwater tubes were installed to collect the samples. When the water level was investigated between the tubes the flow direction was determined to go southeast from sample GA012 towards sample GA006 + GA008 + GA009 and further on to Iggesundån. Elevated concentrations were found in sample points south of the facility. Surface water and sediment from Iggesundån was also studied to obtain more data for the risk assessment. The investigation area consisted to some part of moraine, which was also found in the bottom of Iggesundån. Since it is a recipient from the industrial property the contaminated groundwater could possible spread the contamination when in contact with Iggesundån. Results showed higher concentrations downstream from the facility compared to upstream [2]. The high levels in Iggesund gave reason to proceed with a risk assessment considering human and environmental health [1].

The name fluorinated substances/chemicals is used for both inorganic and organic substances when at least one fluorine atom is included. Perfluoroalkyl substances is a subset of these chemicals where all the hydrogen atoms is replaced by fluorine on all carbons (except the functional group), which is present in the analogues alkanes, Figure 1. For polyfluoroalkyl

Perfluoroalkyl sulfonic/carboxylic acids (PFSA and PFCAs) are subgroups of PFASs with different functional groups. The two most reported in scientific literature are PFOS and PFOA due to their persistence and extensive occurrence [5]. Production of PFAS is via telomerization or electrochemical fluorination (ECF), two main synthesis processes that are used by major companies like 3M [12]. Industrial use and the release of PFAS is one of the sources that contributes to PFAS in the environment. Other contributions come from used and disposed consumer products with PFAS impurities. Indirect emission of PFAS comes from degraded polymers and precursor compounds [5].

The transport from the source through atmosphere and ocean currents is important to understand when investigating contamination. PFASs has been found widespread and in remote locations. It is believed that precursor compounds like polyfluoroalkylated sulfonamides and fluorotelomer alcohols, that are more volatile than their metabolites, are transported through air to metabolize or degrade (atmospheric oxidation) to PFOS and PFOA [13]. Measurements of the air have detected telomers on atmospheric particles [13]. The reports on these precursors in water are scarcer and needs sensitive methods due to the lower concentrations. It is believed that direct emission of PFCAs and PFSA during fluorochemical manufacturing processes is transported via oceanic currents [12]. In ocean water they are expected to be found as anions which makes them susceptible for oceanic transport since they are relatively water soluble [14].

Widespread use of chemicals such as PFAS is not always without consequences. These particular substances have gotten attention because of their persistence, toxic properties and bioaccumulation. PFOS is included as an annex B substance: restriction required in use, in the Stockholm convention on Persistent Organic Pollutants [7]. Detection of PFAS has been found in both humans and wildlife as well in the environment. PFOS was the first substance to display the global extent of the contamination in wildlife [15]. Soon after that study other PFASs, such as PFOA, were detected in human blood bought from companies that handle biological supplies [16]. PFSA and PFCAs binds to the protein in blood and accumulate primarily in the kidney and liver [17].

The main believed exposure pathways for humans are through the diet. Another significant source is contaminated drinking water [18]. For over 1.5 billion people worldwide groundwater are their main drinking water source [19]. For European countries it is common that around 65 % of their drinking water is from groundwater supplies, which applies to Sweden. [20]. Studies have revealed that film forming foams are one of the main contributor of PFASs in groundwater [21]. It is the "long-chain" PFASs (PFCAs: carbon length of ≥ 7 PFSA: carbon length of ≥ 6) [22] that is of specific interest for the global regulatory community. This is because of their more bioaccumulative nature compared to the "short-chain" PFASs [5].

The Swedish National Food Administration has highlighted eleven PFAS, recently updated from seven, which should be analyzed for in drinking water (table 2).

Table 2. Name, abbreviation and structural formula of 11 highlighted PFAS from the Swedish National Food Administration

Perfluorobutanesulfonic acid	(PFBS)	C ₄ F ₉ SO ₃ H
Perfluorohexanesulfonic acid	(PFH _x S)	C ₆ F ₁₃ SO ₃ H
Perfluorooctanesulfonic acid	(PFOS)	C₈F₁₇SO₃H
Fluorotelomersulfonic acid	(6:2 FTS)	C ₆ F ₁₃ CH ₂ CH ₂ SO ₃ H
Perfluorobutanoic acid	(PFBA)	C ₃ F ₇ CO ₂ H
Perfluoropentanoic acid	(PFPeA)	C ₄ F ₉ CO ₂ H
Perfluorohexanoic acid	(PFH _x A)	C ₅ F ₁₁ CO ₂ H
Perfluoroheptanoic acid	(PFHpA)	C ₆ F ₁₃ CO ₂ H
Perfluorooctanoic acid	(PFOA)	C₇F₁₅CO₂H
Perfluorononanoic acid	(PFNA)	C ₈ F ₁₇ CO ₂ H
Perfluorodecanoic acid	(PFDA)	C ₉ F ₁₉ CO ₂ H

There are no legally binding limit values for PFAS, but drinking water should not contain levels that could be harmful for people's health. The action level in Sweden of total PFAS concentration is therefore 90 ng/L. Health limit for when the water should be avoided to drink or even used for cooking is based on the total daily intake and set to 900 ng/L [3]. The European environmental quality standard (EQS) for PFOS is 0.65 ng/L [23] but background levels in the Swedish environment has been detected between 0.2 - 4 ng/L [24].

A voluntary phase out of production of PFOS and similar compounds started in 2000 by major global manufacturer in Europe and United States due to concerns for the environment and the potential toxicological impact. Alternative PFASs have been developed as replacement in certain cases [5]. An increase in the use of the shorter chained fluorinated compounds has been seen as a result of this [9].

3 Method

Five groundwater samples were collected after the installation of polyethylene plastic groundwater tubes around the property in Iggesund. The sampling points was selected in places where the chemicals had been handled. The sampling plan is presented in Figure 3 and was mostly from 2-3 meter below the surface. Sample GA010 is the only sampling point placed inside the building. The compounds were analyzed for in both dissolved form and bound to particles. Groundwater was chosen to be analyzed since it is a major path for pollutants to spread.



Figure 3. Sampling plan from Iggesund hard chromium plating site with the sampling points indicated by red circles. The waters flow direction is shown with blue arrows.

3.1 Groundwater samples

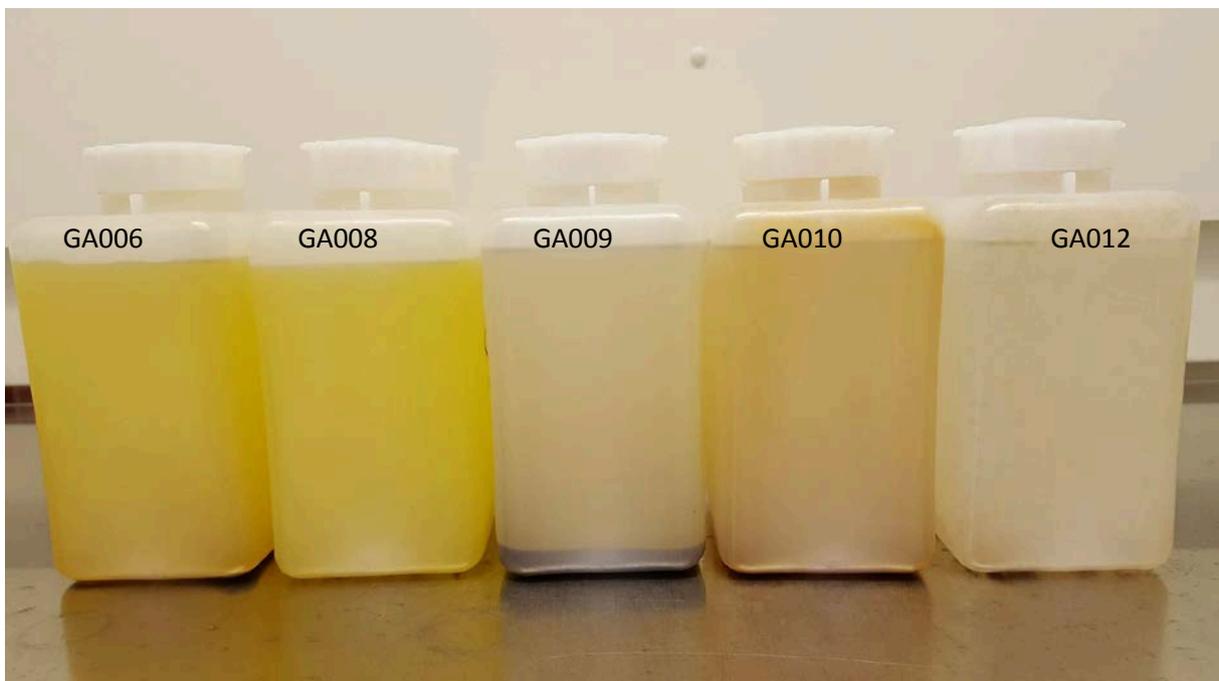


Figure 4. The five groundwater samples from Iggesund

The samples were collected from the groundwater tubes with a peristaltic pump in April 2016. Samples were stored in 2 L polyethylene containers, Figure 4, and kept in the refrigerator (4°C) until analysis. In heavily contaminated areas south of site the groundwater had turned yellow from the chromium contamination. Samples north and east of the facility was slightly

grayish in color whilst the sample collected inside the facility had a reddish tone. One of the sample, GA009, had a lot of solid material in the bottom.

The samples pH was measured in June 2016, and was found mainly neutral, between 6.15 and 6.58.

3.2 Direct injection

The PFASs measured in this study are presented in Appendix 5. Only linear PFOS is measured among the PFOS isomers. A direct injection on the UPLC-MS/MS was performed on 100 µl unfiltered groundwater samples with 50:50 2 mM NH₄Ac in methanol/water as a "preliminary screening". In the run a blank with MilliQ and a standard with 1000 pg calibration standard (CS) was included. For every sample 1000 pg internal standard (IS) and recovery standard (RS) was added. The content of IS, RS and CS is presented in Appendix 6. Using labeled standards will minimize the error due to sample loss from the extraction steps or during the injection. CS is a quantification mix of ¹²C reference substances. RS is added before injection in UPLC and is used as an injection spike to compensate for differences in volume. IS is added before treatment even though direct injection has no treatment just for the simplicity of calculating concentrations in the same way as the other analysis.

When using the mixture of 50:50 2 mM NH₄Ac in methanol/water it was seen that the first eluting compound (PFBA) had a split chromatographic peak (in both standard and sample). In the following analysis a mixture of 30:70 2mM NH₄Ac in methanol/water was used. No PFBA was detected in the direct injection or the other analysis.

3.3 Sample pre-treatment

The groundwater samples were filtrated through 1.0 µm pore size glass microfiber filters, (GF/B Whatman), with the help of an applied vacuum. When all groundwater was filtrated the sample container was rinsed with a small amount of methanol to make sure all PFASs had released from the walls. The dissolved PFASs will go through the filter but the compounds bound to particles will stay in the filter, as seen in Appendix 2, so the filter was saved in aluminum foil and kept in the refrigerator for further analysis.

For inorganic analysis the groundwater samples were diluted ten times with distilled water and filtrated through a 0.20 µm nylon syringe filter.

3.4 Solid phase extraction

The solid phase extraction performed was based on the ISO International Standard 25101 water method [25]. A working schedule for the extraction analysis is presented in Appendix 1. In contrast to the ISO method, the Iggesund samples were filtered before extraction. The result thus represent the dissolved compounds which is often more mobile. Another reason was to get 500 mL through without clogging the cartridge.

After the filtration all water samples were added 2000 pg IS of PFASs. Spiked MilliQ water, used as quality control (QC) samples for the method, was added 2000 pg native standard.

Since the QC samples are extracted the same way as the groundwater sample they are used to assess the accuracy and reliability of the method.

The cartridges used in the extraction, Oasis WAX reversed-phase/weak anion exchange (6 cc, 150 mg, Waters, Milford, USA), can chromatographically separate different compounds and remove interferences when adding solvents with different ion strengths, pH or polarity. Separating the target analytes from interfering substances will better prepare the sample for the UPLC analysis. Conditioning the cartridges with 4 mL HPLC-grade methanol (Fisher Scientific, Ottawa, Canada) will activate the sorbent packing before the sample is loaded to ensure interaction. Then 4 mL MilliQ water will maximize retention. The samples are loaded on the cartridges with an applied vacuum, using a pump, to get a continuous flow of 1-2 drops/second, see Appendix 3. When all samples were loaded the cartridge was washed with 4 mL of 25 mM Sodium-acetate buffer pH 4 (E. Merck, Darmstadt, Germany) to elute co-retaining interferences. The cartridges was then dried using the vacuum pump before it was again washed with 4 mL methanol to elute neutral compounds. Elution of the compounds was done with 4 mL of the alkaline solution 2% NH₄OH in methanol to change the WAX structure which disrupts the interactions and allows collection of the anions. Evaporation of the eluate was done under nitrogen gas (appendix 4) to 0.5 mL. This was filtrated with 0.2-µm nylon filters to LC vials with 2000 pg RS PFAS and evaporated down to 0.2 mL. Lastly, 0.3 mL of 2 mM NH₄Ac in H₂O was added to the final extracts and left a final volume of 0.5 mL.

For quantification a standard (Appendix 6) of 2000 pg was prepared to the same final volume as the sample extracts (170 µL MeOH and 300 µL 2mM NH₄Ac in H₂O with 10 µL IS PFAS, 10 µL 12C CS and 10 µl RS PFAS.) Thanks to the standard it is possible to compare retention times with our samples and identify compounds. The amount of each compounds in the groundwater samples were calculated in TargetLynx by a calibration standard using the amount and area of the standard.

Formulas used for the quantification of PFASs:

$RRF = ((A_{IS}) / (A_{CS})) * \text{amount analyte added to standard sample}$

RRF = relative response factor

A_{IS} = Area Internal ¹³C standard, in standard sample

A_{CS} = Area Analyte ¹²C congener, in standard sample

$C_{SA} = ((A_S) / (A_{ISS})) * (RRF / \text{amount of sample})$

C_{SA} = amount of analyte in sample

A_S = area analyte ¹²C congener in sample

A_{ISS} = area internal ¹³C standard in sample

$\text{Recovery} = ((A_{ISS} / A_{RSS}) / ((A_{IS} / A_{RS}))$

A_{RSS} = Area recovery ¹³C standard in sample

A_{RS} = Area recovery ¹³C standard, in standard sample

3.4.1 Method validation

Before the extraction and analysis of the groundwater samples a method validation was performed using two blanks with MilliQ and two spiked MilliQ water samples. During this validation, two of the samples, GA006 and GA012, were also included. Since the two samples were extracted again in the actual run these results were used as quality control to test the repeatability. For the validation a volume of 200 mL water was used, except for GA012 where 500 mL was used. In the actual extraction of samples 500 mL was used for all samples.

3.5 Particle bound PFAS

The GF filters used before the SPE were saved and dried at 40°C to constant weight. Extraction of the filters was done with the organic solvent methanol, 2000 pg IS was added and filters were ultrasonicated for 2 x 30 minutes. The methanol extract was evaporated down to 0.5 mL and then filtrated with 0.2-µm nylon filters and mixed with 2000 pg RS PFAS in LC vials before evaporated again down to 0.2 mL. Methanol is volatile and therefore a favorable solvent to use when evaporating a larger volume. Some of the samples would not evaporate to this volume, probably due to some water or impurities left in the filter, but the final volume for each sample was adjusted to 0.5 mL with 2 mM NH₄Ac in H₂O. A Standard was prepared the same way as previously described.

3.6 Inorganic analysis

The groundwater samples was analyzed using ion chromatography to measure the concentrations of anions and cations after being diluted ten times and filtrated. After an overview image of the ion distribution further analysis for chromium measurements was performed due to the use of chromic acid during Iggesunds active years and its carcinogenic properties. The sensitive detector ICP-MS is a powerful tool for elemental detection.

4 Instrumental analysis and quality assurance

The analysis of PFASs was done on an Ultra Performance Liquid Chromatography (UPLC), Xevo TQ-S electro spray ionization mass spectrometer with applied negative voltage (Waters Corporation, Milford, USA). By using multiple reaction monitoring (MRM) with two mass filtering stages, low detection limits of ions of interest is possible compared to measuring all fragment ions in full scan ms/ms. The linearity is regularly checked every three months with a calibration curve run including 0.02, 0.2, 0.4, 1, 2, 4, 10, 20, 40, 80 ng/mL calibration standards. Temperature of the column was 50° for direct injection but was increased to 60° for the extraction and filter analysis. Flow rate was set to 0.3 mL/min and injection volume to 10 µL. Mobile phase used were 30:70 2mM ammonium acetate in methanol/water. For each compound two product ions were monitored which is presented in Appendix 5. For quantification the most abundant one was used and the second most abundant was used for qualification. PFBA and PFPeA were the only compounds with only one obtained product ion.

Only internal standard recoveries between 50-120 % is acceptable, but recoveries between 20-50% and 120-150% are still reported with remarks. The internal standards used were

PFCAs, ¹³C-labeled PFCAs (C4, C6, C8-C12), and ¹³C or ¹⁸O-labeled PFSA (C6, C8), also presented in Appendix 6. A blank MilliQ water and a spiked MilliQ water were treated and analyzed the same way as the groundwater samples for every analysis. Since the blank only consist of water, which is the solvent that the compounds is dissolved in, it should have zero to small amounts of the analytes of interest. The spiked water is used to state the accuracy and reliability for the method. Recoveries for the spiked water internal standard were between 71-89 %. The SPE was not spiked with as high concentrations that was detected in the samples, so it is possible that not all substances was adsorbed to the SPE. Two groundwater samples, GA006 and GA012 were extracted twice to determine if the method gives repeatable results. Methanol instrumental blank injections were included in every run to check the instrument for contaminations that can disturb the results.

Method detection limit (MDL) was calculated for each compound by multiplying the signal in the procedural blank times three. For the extraction more than one blank was used so an average was calculated and multiplied with three. The two transition product ions concentrations were compared to determine that they did not differ more than 15 %. If the compounds concentration was higher than the MDL but the product ions concentrations differed more than 15% it was reported with a remark.

5 Results

PFAS was detected in all 5 groundwater samples. From the 19 compounds analyzed for, eight were found in the water extraction analysis, three PFSA and five PFCAs (Figure 5A and B). Total PFAS concentrations in the water extraction analysis ranged between 141 - 11300 ng/L with PFOS in elevated levels (Figure 6). All eight compounds were detected in every sample but in widely different concentrations. Sample GA008 and GA006 showed the highest concentrations. Lowest concentrations occurred in sample GA012.

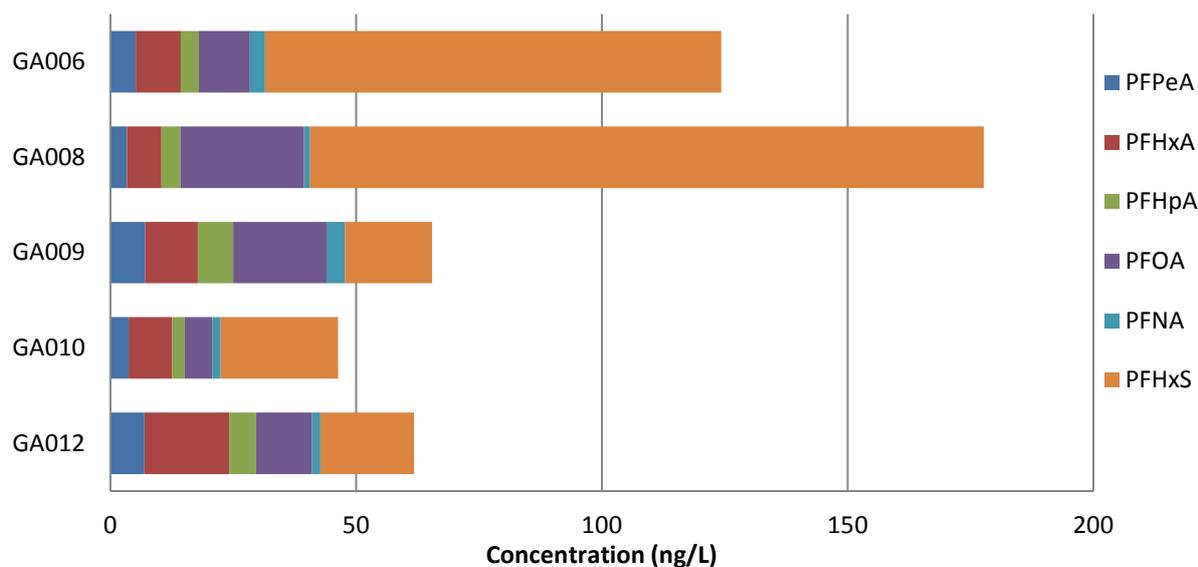


Figure 5A. Distribution of 8 detected PFAS (PFOS and PFBS shown in figure 5B) from extraction of groundwater samples from Iggesund's hard chromium site. Note: qualification ion for PFHxA is not within the 15% certainty for samples GA006, GA008 and GA010

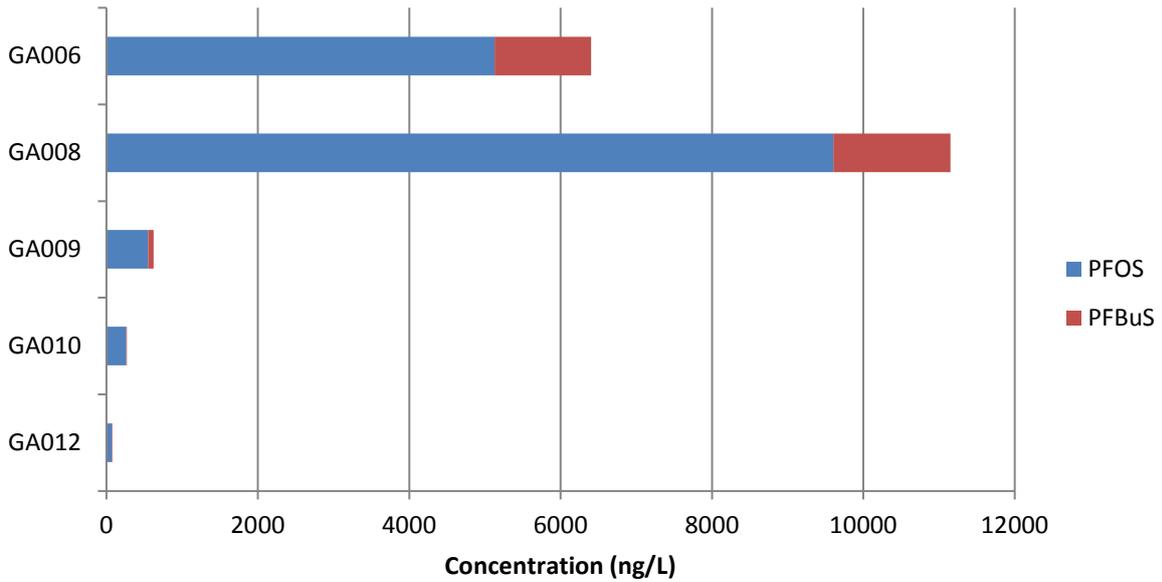


Figure 5B. Detected PFOS and PFBuS from extraction of groundwater samples from Iggesund's hard chromium site.

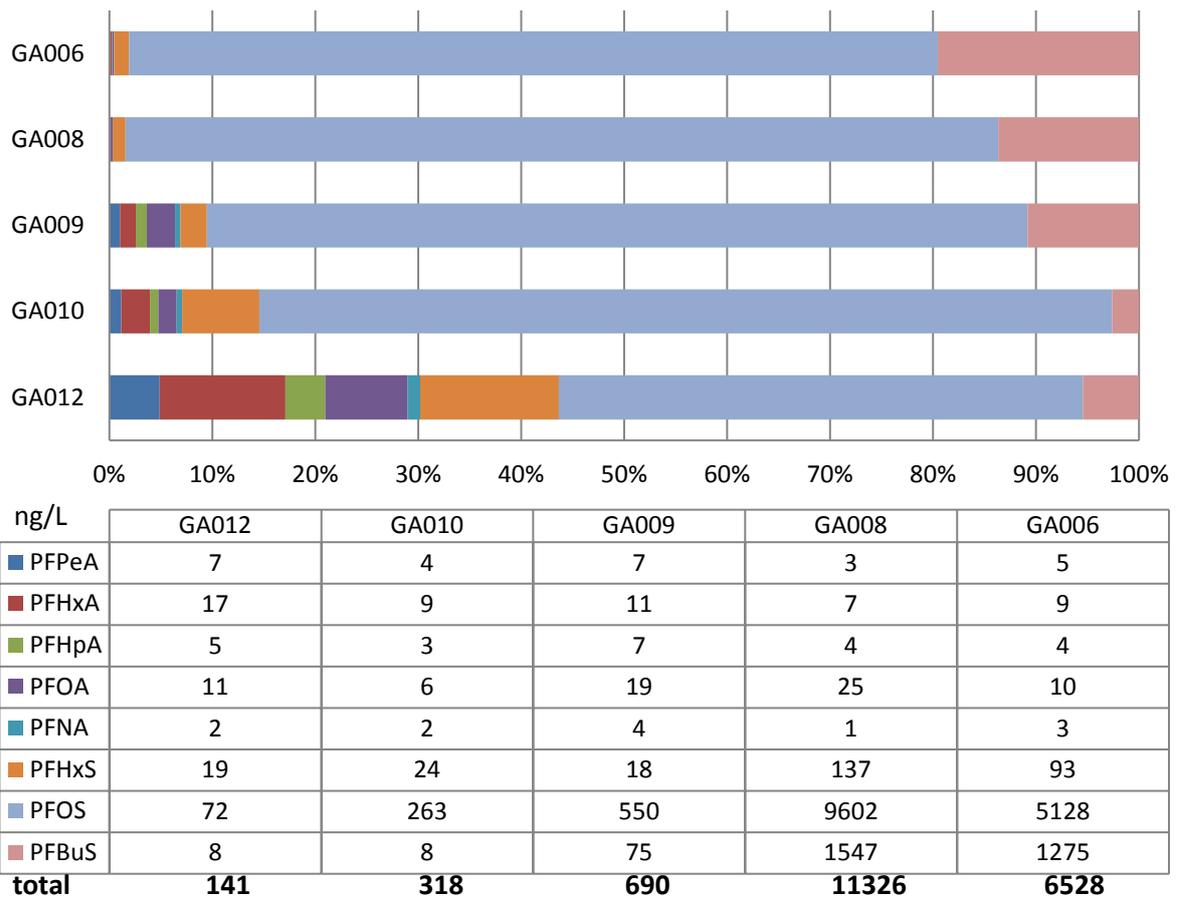


Figure 6. Relative abundance and concentrations (ng/L) of the 8 detected PFAS in groundwater from Iggesund's hard chromium site.

Three perfluoroalkyl sulfonic acid (PFSAs) and five perfluoroalkyl carboxylic acids (PFCAs) were detected. Samples GA006, GA008 and GA009 had such high concentrations that the chromatogram was oversaturated and the samples needed to be diluted 100 times.

The concentration differed from 4 - 21% for seven of the eight detected compounds between method validation result (1) in Figure 7) and the actual run results (2) in Figure 7). PFOS with its high concentration showed the largest difference, 41 % between sample GA012 and 85% for sample GA006 with the qualification ion within the 15% certainty. The IS recovery for PFOS was 85% (GA006) and 71% (GA012) so the high difference between concentration obtained cannot be explained by differences in extraction efficiency. That the samples were diluted could result in more tentative results.

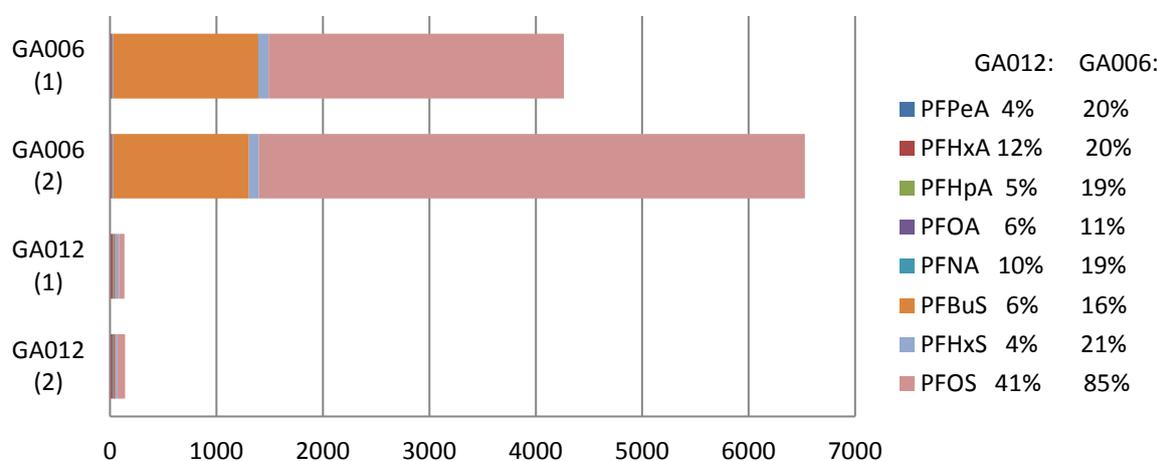


Figure 7. Comparing the results of GA006 and GA012 that was extracted twice in the method validation.

Only the three PFSAs were detected in the direct analysis (Figure 8). The compounds are found in higher concentration in the direct injection, which is to be expected since the unfiltered direct injection shows total concentration. The filtered water extraction analysis only shows the compounds dissolved in water.

Only linear PFOS is measured but in the chromatogram other isomers could be seen (Figure 9). This will lead to an underestimation of the total PFOS concentration.

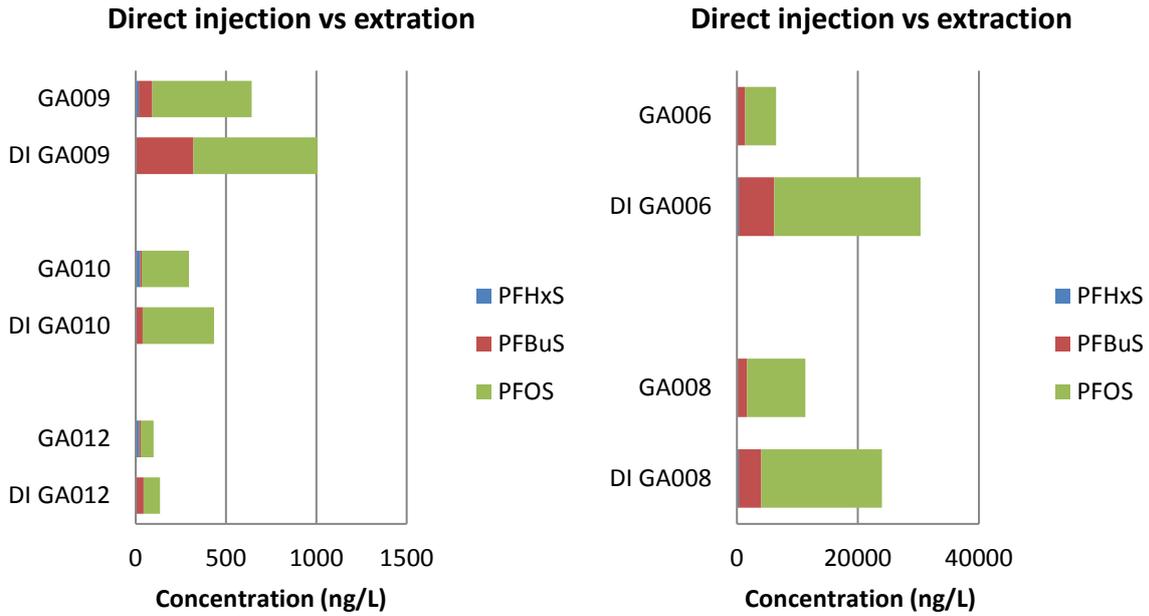


Figure 8. Comparing direct injection with extraction of the groundwater samples.

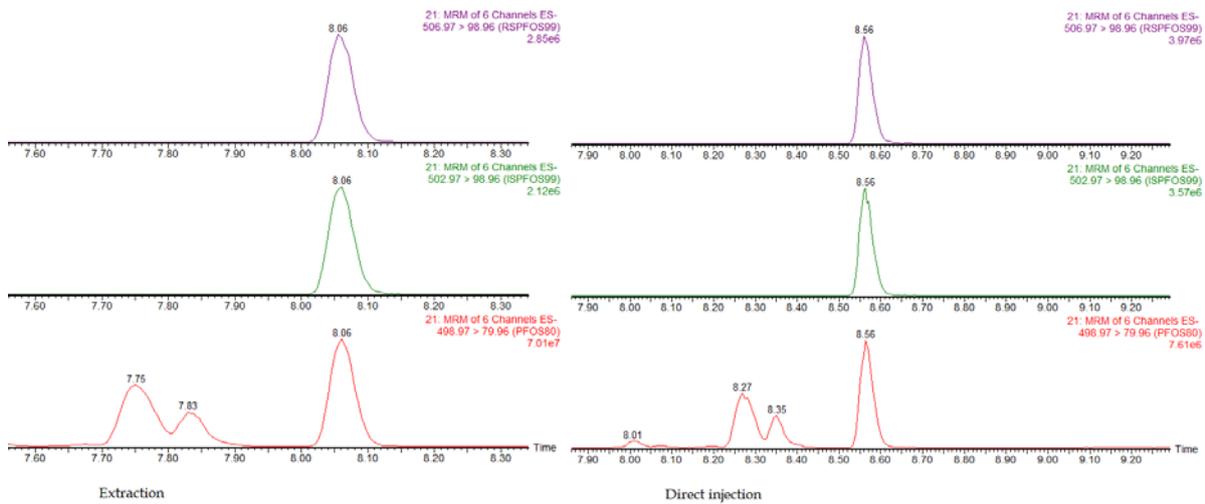


Figure 9. Chromatogram of PFOS, RS PFOS and IS PFOS for extraction (left) and direct injection (right). Only linear PFOS (the large peak) is measured. The smaller peaks are isomers of PFOS and are not measured in this report.

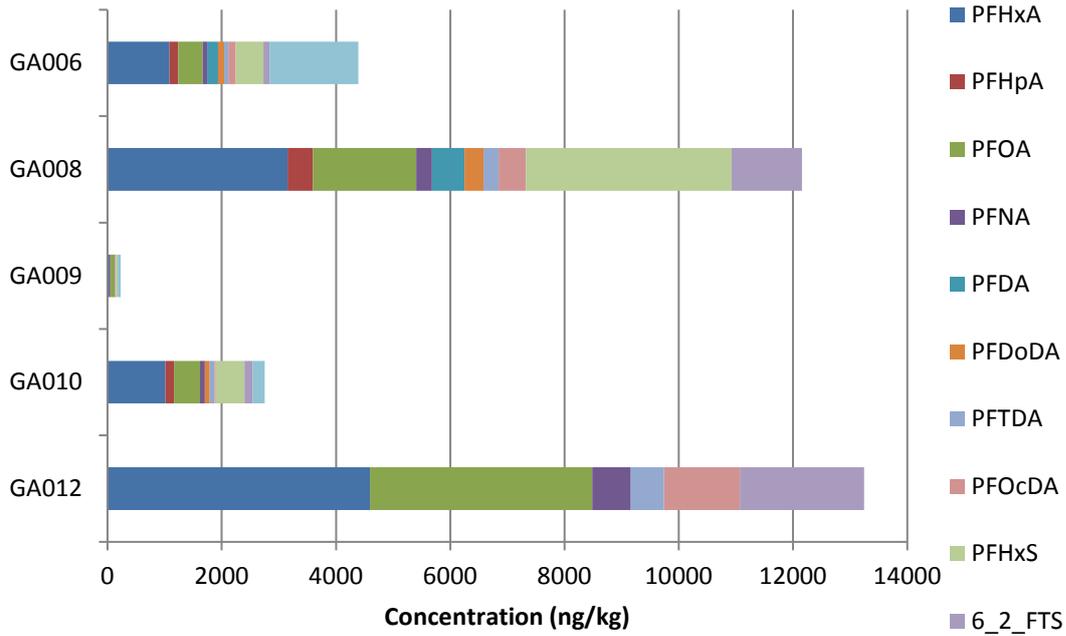


Figure 10A. Distribution of 12 detected PFAS (PFOS and PFBuS are shown in figure 10B) in groundwater from filter analysis. Note: qualification ion was not within the 15% certainty limit (ranged from 16 to 76 %) for:- PFHxA: GA006, GA008, GA009 and GA012. PFHpA: GA006, GA008, GA009 and GA010. PFNA: GA008. PFDA: GA008. PFDoDA: GA006. PFTDA: GA006, GA008 and GA012. PFOcDA: GA009. 6:2-FTS: GA008.

Particles in ground water was measured by analysis of the filters. The same compounds were detected as for the water samples with addition of four PFCAs of longer carbon length and 6:2-FTS (Figures 10A, 10B, 11). Sample GA009 had a lot of sediment in the container which resulted in its filter weighing almost 20 times more than the other filters and resulted in lower concentration/kg. Sample GA008 was in such high concentrations that the chromatogram was oversaturated and the sample needed to be diluted 100 times.

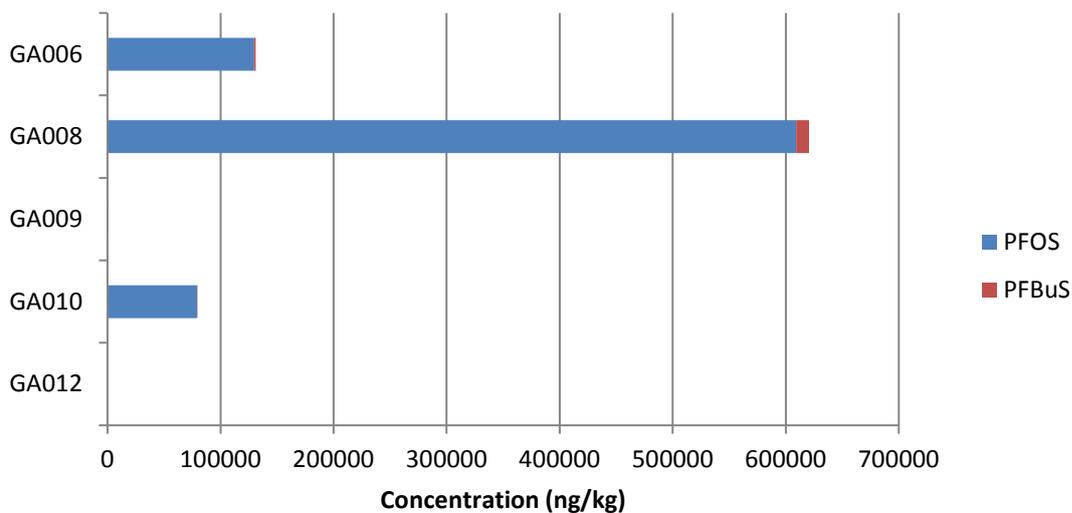


Figure 10B. Detected PFOS and PFBuS in particles from filtrated groundwater.

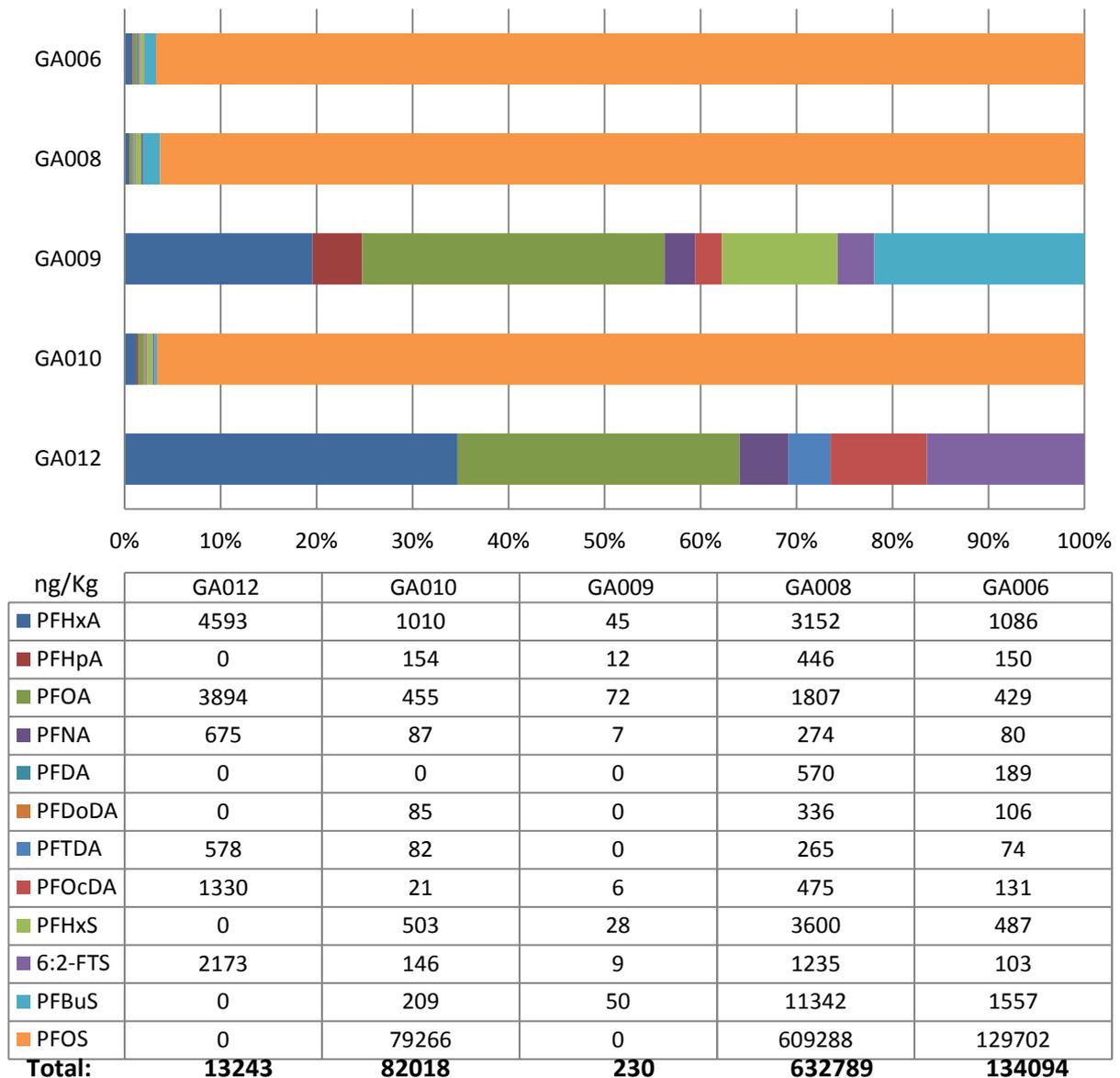


Figure 11. Relative abundance and concentration of the 12 detected PFAS in particles from filtered groundwater.

The concentration of PFAS on filters were also expressed as the concentration of the entire water sample as can be seen in Table 3. The amount ng detected from the extracted filter was divided by the volume (1,250 L) of the filtered groundwater. The low concentrations in Table 3 shows that PFASs mostly is dissolved in water. When adding the dissolved and particle bound PFASs it should be the total concentration as measured with direct injection, but that is not the result here. This could be due to not rinsing the sample container thoroughly enough with methanol and thus missing some amounts.

Table 3. Concentration of PFASs extracted from filter in total volume (1,250 L) water filtered.

ng/L	GA012	GA010	GA009	GA008	GA006
PFHxA	0.25	0.35	0.24	0.50	0.38
PFHpA	0.05	0.05	0.06	0.07	0.05
PFOA	0.22	0.16	0.38	0.29	0.15
PFNA	0.04	0.03	0.04	0.04	0.03
PFDA	0.06	0.05	0.03	0.09	0.07
PFDoDA	0.03	0.03	0.02	0.05	0.04
PFTDA	0.03	0.03	0.02	0.04	0.03
PFOcDA	0.07	0.01	0.03	0.08	0.05
PFBuS	0.04	0.07	0.27	1.80	0.54
PFHxS	0.15	0.17	0.15	0.57	0.17
PFOS	21.56	27.46	15.81	199.98	45.04
6:2-FTS	0.12	0.05	0.05	0.20	0.04

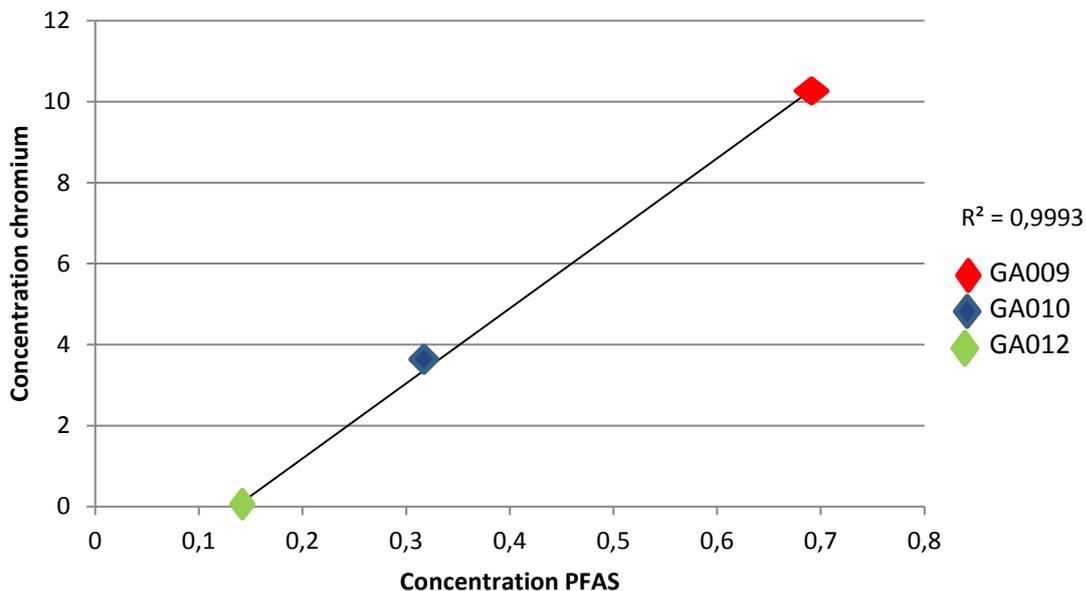


Figure 12. Correlation analysis between chromium and PFASs concentration ($\mu\text{g/L}$) from water extraction.

The R^2 value of =0,99 indicates a positive correlation between chromium and total PFASs concentration (Figure 12) and thus indicates possible contamination from same source. GA006 and GA008 shows the same correlation but is not displayed since they were in such high concentration (34800 and 44700 $\mu\text{g/L}$) and would steer the whole trend line. Figure 12 shows that the correlation is occurring for the lower concentrations as well.

Recoveries for the internal standards in the reported compounds were between 50 - 120 % for all of the analysis.

6 Discussion

A total of 19 PFAS were analyzed in this report which included 5 perfluoroalkyl sulfonic acids and 13 perfluoroalkyl carboxylic acids along with 6:2-FTS (presented in Appendix 5). For the water extraction analysis five PFCAs and three PFSAs were detected. All detected compounds are among the 11 PFAS on the Swedish national food administration (Livsmedelverkets) risk management list. The total PFAS concentration for the five groundwater samples ranged between 141-11300 ng/L. There is a great variation between the results and the highest concentrations were found in sample GA006 (6530 ng/L) and sample GA008 (11300 ng/L). These were the two samples that were collected south of the facility and had a yellow color. GA006 and GA008 has similar PFAS distribution pattern which indicates contamination from the same source. What separates the samples is that GA008 has higher concentration of PFOS.

The total concentration in every sample is higher than the action levels stated by National Food Administration, below 90 ng/L, to keep people from harm. The compound with most contribution, PFOS, will alone exceed the action level in 4 out of 5 samples with its relative abundance between 50-85 % of the total concentration. Only linear PFOS is measured but in the chromatogram other isomers could be seen. In environmental samples, as groundwater, branched and linear isomers of PFOS often occurs as a mixture [26]. Total PFOS concentration is therefore higher than reported in this study. When comparing Golder's result detected 2013-2014 and 2016 the PFOS concentration had decreased in sample GA006 from 13000 ng/L to 9080 ng/L but increased in sample GA008 from 4100 ng/L to 24100 ng/L. The chromium concentration followed the same pattern, decrease for sample GA006 from 82100 µg/L to 34500 µg/L and increase for sample GA008 from 53900 µg/L to 55300 µg/L. Golder analyzed PFOS on unfiltered groundwater samples and therefore got higher concentration than this study, GA006 5130 ng/L and GA008 9600 ng/L but it is still possible to see the increase in sample GA008 which means that the contamination is still actively spreading.

Without the elevated PFOS concentration contribution to the total concentration, sample GA012 and GA010 would be below the 90 ng/L action level since the other PFASs are in such low concentrations, ranging from 2-24 ng/L. The other three samples - GA009, GA008 and GA006 have besides PFOS elevated concentrations of PFBuS (75-1500 ng/L) and PFHxS, (18-137 ng/L). The concentration of PFOA in the samples, 6-25 ng/L, is the highest of all PFCAs but still in no alarming amount.

Sample GA012 is noticeable with its lower PFAS concentration (141 ng/L) compared to the others, which is mostly due to lower PFOS concentration than the other samples. When Golder investigated the flow direction they stated it to go towards southeast where sample GA006, GA008 and GA009 is located. Sample GA008 and GA006 with the highest concentrations were collected right below the facility. Sample GA009 having a lower concentration than GA006 and GA008 was collected further east of the facility. Sample GA010 which have even lower concentration than GA009 was collected inside the building as

seen in the sampling plan. In similarity with Golders previously studies, sample southeast and below the building (GA006, GA008 and GA009) have the highest concentrations and samples north of the building (GA012) have lower concentrations.

The knowledge of PFASs from industrial use and emission is insufficient [22]. Since many of the fluorinated substances is very potent in their actions they are only needed in low concentrations to get desired effect. Manufactures does not need to report amounts less than 100 tons per year [9]. Chemical Agency has stated some known applications where PFOS is a registered exception and in hard metal plating it is allowed as a mist suppressant to improve the working environment due to the use of carcinogenic hexavalent chromium.[9] The law demands use of best possible technique so for hard chromium plating that means usage of PFOS in closed systems. But still around 20% is released to the environment during the process from drainage [27] which is a problem since receiving waters can be contaminated from the chromium plating wastewater that still can contain PFOS concentrations up to 44100 ng/L [28]. The surface treatment bath management also needs clarification since PFOS remains in the solution after the process and are reused before discarded as hazardous waste [9]. Naturvårdsverket together with Chemical Agency will by the end of 2017 clarify the monitoring of the PFOS allowed exceptions [22]. The PFOS in Iggesunds groundwater is most likely to come from the plating baths. The high PFBuS concentrations is probably from the same source but there are not as good records over this compound as there is for PFOS. It is known that PFBuS has been announced as a substitute compounds for PFOS due to its similar structure but less accumulating nature [29]. Shorter chained PFASs can also be produced as an impurity during the ECF production of PFOS [5].

AFFF is the major source of PFAS to the Swedish environment and gives high point releases to groundwater [22]. The production of AFFF agents containing PFOS or degraded into PFOS was voluntary stopped in 2002 by 3M and existing stocks was allowed to be used until 2011 in the EU [30]. Now AFFF is mostly based on the shorter chained 6:2-FTS which have PFHxA as decomposition product [9]. Previous analysis of several foams on the Swedish market have also detected PFHpA and shorter chained PFCAs [31]. The PFASs concentrations in the groundwater from Iggesunds hard chromium plating site is not as elevated as the detected concentrations (26 000 - 33 000 ng/L) from Landvetter airport where AFFF has been used [32].

Particle bound PFASs:

The filter used for separating the dissolved compounds from the compounds bound to particles were also extracted and analyzed to only get the compounds bound to particles. Sample GA009 contained much particles as seen in Figure 2, therefore the concentration is so low in the filter extraction analysis. Most of the particles were scraped off but the filter still weighted almost 20 times more than the other filters. In the filter extraction analysis four more PFCAs compounds were detected with longer carbon chain, C10, C12, C14 and C18. Compounds with longer chain length will not solve in water as good as compounds with shorter chain so the filter extraction analysis will detect the longer carbon length PFAS. Also detected was 6:2-FTS which AFFFs now days mostly is based on. Occurrence of telomer sulfonates may point towards degradations of even larger telomer substances [31]. PFOS is

still the compound of highest concentration in sample GA010, GA008 and GA006 but the shorter chained PFCA (C6-C8) is dominating sample GA012 and GA009. Sample GA012 also displays elevated concentrations of 6:2-FTS but no PFSA. This sample point is clearly different from the others and could be contaminated by the use of AFFF, which the other sample point also may be but results is shaded by the high concentration from the chromium baths. When looking at the distribution pattern from the filter extraction analysis it looks like sample GA006, GA008 and GA010 has similar pattern which indicates pollution from the same source. GA010 is collected from inside the building and GA006 and GA008 is collected right below so this could be a possibility since pollutants travel with the groundwater. There were more uncertainty with the result from this analysis compared to the water extraction analysis. The 15% comparison between the quantification ion and qualification ion concentration is to know with certainty that it really is the compound detected and not a molecule with similar fragmentation that passed through the first quadrupole in the MS/MS. But the risk of this possibility is quite minimal.

In the direct injection (DI) only three compounds were detected. PFOS and PFBuS was detected in every sample but PFHxS were just found in GA006 and GA008 as presented in table 4.

Table 4. Concentrations (ng/L) of selected PFASs in water samples using direct injection on UPLC-MS/MS

	DI GA008	GA008	DI GA006	GA006		
PFHxS	310	137	312	93		
PFBuS	3736	1547	5838	1275		
PFOS	19920	9602	24201	5128		
	DI GA012	GA012	DI GA010	GA010	DI GA009	GA009
PFHxS	0	19	0	24	0	18
PFBuS	44	8	39	8	320	75
PFOS	91	72	394	263	685	550

The direct injection can be used as a preliminary screening for contaminated samples only. Some of the PFASs that were found in the water extraction and not detected during the direct injection, like PFOA that was measured at 25 ng/L and were detected just below the method detection limit in the direct injection. With more replicate perhaps some more compounds would be seen. The total PFAS concentration increased for all samples since direct injection will show both compounds bound to particles and compounds dissolved in water. It would be time efficient to be able to only do direct injection but this study does not support that other than as a screening approach.

PFAS is widely spread and can be transported over long ranges, where wet and dry atmospheric deposition is one of the causes for PFAS occurrence in ground water [33]. That can make it difficult to identify the source. When dealing with contaminated sites, considerations has to be made on how much previous properties contributed to the contamination because historical storage in soil and water can affect the result. In this Iggesund case where a lot of different hard chromium plating business has worked it was decided that every company had to pay depending on how many years they were active [2]. Actions needed to reduce PFAS concentrations in the environment are firstly to minimize the

emission from industries like hard chromium plating and also the use of PFAS in products. To replace or purify contaminated drinking water costs money and the ground may in some cases never be possible to build on again [22]. Pump & treat means that the groundwater is pumped to a purification plant where it is treated with example chemical reduction/oxidation to less hazardous compounds before placing it back. For PFOS contamination, activated carbon is a tested decontamination method [34]. Statens Geotekniska Institut (SGI) has the mission during 2016 - 2019 to research new techniques for treating PFAS contaminated groundwater and soil [22].

Visual inspection on Figure 2 suggest contamination of chromium due to the yellow color in sample GA006 and GA008. From the inorganic analysis elevated concentrations of chromium is detected in sample GA006, 34900 ($\mu\text{g/L}$) and GA008, 44800 ($\mu\text{g/L}$) which is the same samples were the PFAS concentration is the highest. For the three other samples with lower concentrations (0-10 $\mu\text{g/L}$) the R^2 value is 0,99 when comparing chromium concentration with total PFAS concentration, which indicates a positive correlation and indicates contamination from the same source, the chromic acid baths and PFOS as mist suppressant. This study only measured groundwater, but Golder have measured more sample points including sediment, soil and surface water around the property which gives more understanding of the contaminated situation and its mobility. The high levels gave reason to proceed with a risk assessment considering humans and environmental health which stated that the groundwater within or around the property is not used for drinking. As long as the site in Iggesund is continued to be used for industrial applications it will not cause a risk for people's health. Since there is no plans for using the water for drinking water in the future either it is not valuable of protection. The focus is to make sure the groundwater doesn't spread the contamination. It is an industrial site so high biological activity is not desirable. If the remaining buildings is left to deteriorate high contamination will spread to the surrounding environment and can continue to do so possibly for a long time since it is not known how much chromic acid liquid there is left in or under the building. This will have a negative impact on water living organisms which is one of the goals Golder have set and therefore a risk reduction is motivated. [1]

7 Conclusions

Of the five groundwater samples analyzed, sample GA006 and GA008 had the highest concentration of both total PFASs and chromium. These samples are located south below the facility where the flow direction has been stated to go by Golder and indicates transport with the groundwater. Pollutants spreading with the groundwater is a well known problem since so many people have groundwater as their main drinking source. PFOS alone exceed Livsmedelverkets action levels of PFAS with its elevated concentrations in four of the samples. Only sample GA012 north of the facility, which has the lowest concentration, is below. PFOS is a registered exception and used as a mist suppressant to reduce the emission from chromic acid baths. Despite requirements of usage in closed systems around 20% still reaches the environment through wastewaters which is most probably the case for Iggesund. Sample GA006 and GA008 also detected high concentrations of PFBuS followed by PFHxS which likely is produced under the ECF production of PFOS. The risk reduction stated by

Golder is that measures needs to be taken with the facility that now just stands to deteriorate which will continue to spread the contamination which is showed with the increased concentrations in sample GA008 from 2014 to 2016.

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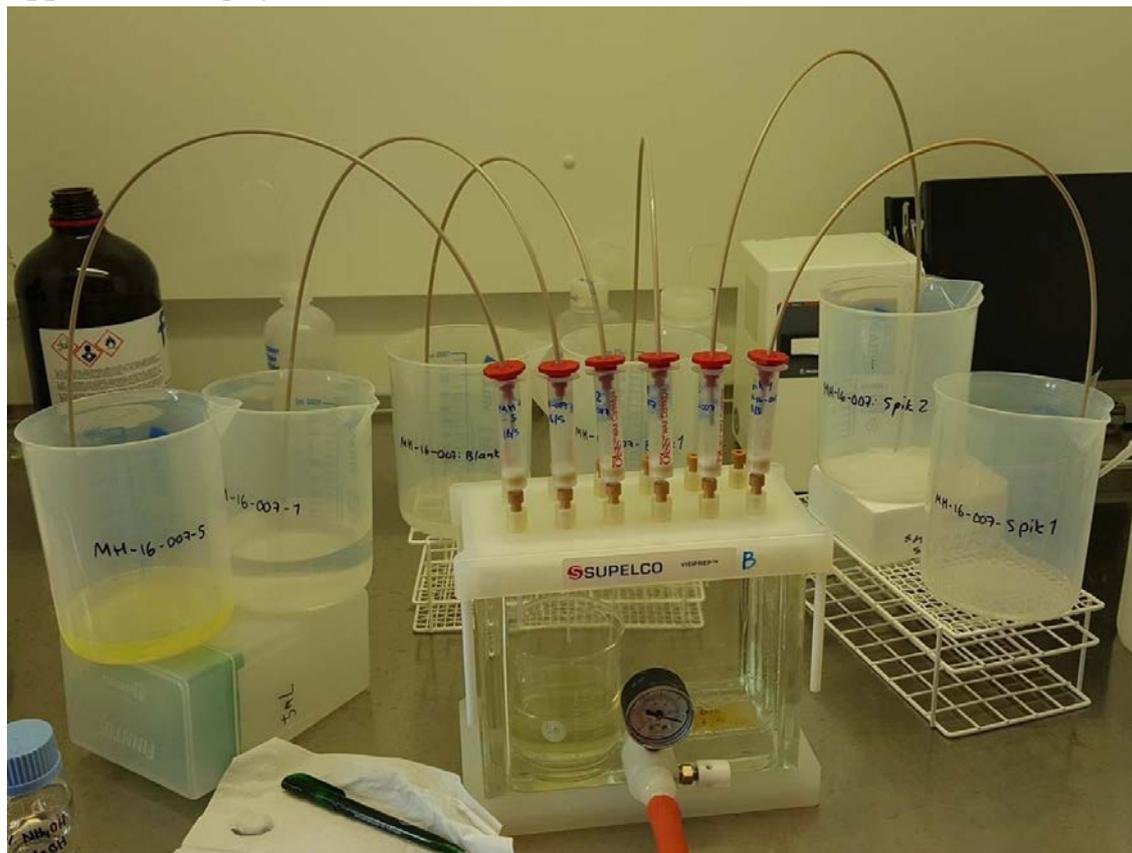
Appendix 1 Working schedule for PFAS-extraction on WAX-SPE of water samples

	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P
1	Arbetschema	20160518														
2	PFAS-extraktion på WAX-SPE	MH-16-007														
3	Prov	Std 1	Blank 1	Blank 2	Spik 1	Spik 2	Prov 1	Prov 2								
4	ISO 25101															
5	Water 200-1000 mL															
6	pre-wash MeOH (2% NH4OH in MeOH)															
7																
8	Filtration glass microfiber filter (GF/B)															
9	Save for particulate extraction															
10																
11	Spike															
12	IS PFAS 10 ul															
13	12C CS 1 10 ul to Spike samples															
14																
15	Oasis WAX (6cc/150 mg)															
16	Condition															
17	4 ml MeOH															
18	4 ml water															
19																
20	Load samples, vacuum, 1 drop/sec															
21																
22	Wash cartridges															
23	4 ml 25 mM Na-acetat buffer pH 4															
24																
25	Dry cartridges (vacuum/centrifuge)															
26																
27	Wash															
28	4 ml MeOH (discard)															
29	4 ml 2 % NH4OH i MeOH															
30																
31	Evaporate and filter (clean 0.2 um)															
32	Clean filters with 2% NH4OH in MeOH															
33																
34	RS to LC vials 10 ul															
35	Adjust volume to 500 ul															
36	200 ul + 300 ul mobile phase															

Appendix 2 Filtration setup and the filter after filtration.



Appendix 3 Setup of SPE



Appendix 4 Evaporation under nitrogen gas



Appendix 5 19 PFAS analyzed for in UPLC/MS/MS, name, abbreviation, transition and what internal standard used. Transition ion for quantification in bold.

Name	Abbreviation	Transition (m/z)	Internal Standard
Perfluorobutanesulfonic acid	(PFBS)	298.9 > 98.9 298.9 > 79.96	O18PFHxS
Perfluorohexanesulfonic acid	(PFHxS)	398.9 > 98.9 398.9 > 79.96 398.9 > 119.01	O18PFHxS
Perfluorooctanesulfonamide	(PFOSA)	497.9 > 168.96 497.9 > 78	C13PFOSA
Perfluorooctanesulfonic acid	(PFOS)	498.97 > 98.96 498.97 > 79.96 498.97 > 169.03	C13PFOS
Perfluorodecanesulfonic acid	(PFDS)	598.97 > 79.96 598.97 > 98.9	C13PFOS
Fluorotelomersulfonic acid	(6:2 FTS)	427 > 81 427 > 407	C136:2FTS
Perfluorobutanoic acid	(PFBA)	212.97 > 169	C13PFBA
Perfluoropentanoic acid	(PFPeA)	262.97 > 219	C13PFHxA
Perfluorohexanoic acid	(PFHxA)	312.97 > 118.95 312.97 > 269	C13PFHxA
Perfluoroheptanoic acid	(PFHpA)	362.97 > 168.97 362.97 > 319	C13PFHxA
Perfluorooctanoic acid	(PFOA)	412.97 > 168.97 412.97 > 369	C13PFOA
Perfluorononanoic acid	(PFNA)	462.99 > 419 462.99 > 219	C13PFNA
Perfluorodecanoic acid	(PFDA)	512.97 > 219 512.97 > 469	C13PFDA
Perfluoroundecanoic acid	(PFUnDA)	562.97 > 268.99 562.97 > 519	C13PFUnDA
Perfluorododecanoic acid	(PFDoDA)	612.97 > 569 612.97 > 168.96	C13PFDoDA
perfluorotridecanoic acid	(PFTrDA)	662.9 > 619 662.9 > 168.96	C13PFDoDA
perfluorotetradecanoic acid	(PFTDA)	712.9 > 669 712.9 > 168.97	C13PFDoDA
Perfluorohexadecanoic acid	(PFHxDA)	812.9 > 769 812.9 > 168.96	C13PFDoDA
perfluorooctanoicdecanoic acid	(PFOcDA)	912.9 > 869 912.9 > 168.96	C13PFDoDA

Appendix 6 Transition ion for internal standard and recovery standard.

Internal Standard¹	Transition (m/z)	Recovery Standard²
C136:2FTS	429 > 409	C13PFOS
C13PFOS	502.97 > 98.96	C13PFOS
C13PFHxS	402.9 > 102.9	C13PFHxS
C13PFBA	216.97 > 172	C13PFBA
C13PFHxA	314.97 > 270	C13PFOA
C13PFOA	416.97 > 372	C13PFOA
C13PFNA	467.99 > 423	C13PFNA
C13PFDA	514.97 > 470	C13PFDA
C13PFOSA	505.9 > 77.8	C13PFUnDA
C13PFUnDA	564.97 > 520	C13PFUnDA
C13PFDoDA	614.97 > 570	C13PFUnDA
Recovery Standard	Transition (m/z)	
C13PFBA	215.97 > 172	-
C13PFHxS99	401.9 > 98.9	-
C13PFOS	506.97 > 98.96	-
C13PFNA	471.99 > 427	-
C13PFDA	518.97 > 474	-
C13PFUnDA	569.97 > 525	-
C13PFOA	506.97 > 98.96	-

¹ Internal standard added before extraction

² Recovery standard added before UPLC/MS/MS, but after extraction.