Polyfluorated alkyl substances contamination in a remote environment (Faroe Islands)

Auteur : Bâlon, Axel
Promoteur(s) : Joaquim-Justo, Celia
Faculté : Faculté des Sciences
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Department of Sciences and Environment Monitoring
Laboratory of Animal Ecology and Ecotoxicology

Umhvørvisstovan – Environment Agency

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Master thesis written by

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Aiming for the grade of

Master in Environmental Sciences and Management

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Table of content

List of possible abbreviations

IS	Internal standard
LoD	Limit of Detection
LoQ	Limit of Quantification
MeOH	Methanol
NH_4Ac	Ammonium acetate
PFAS	Poly/per fluoroalkyl substances[1]
PFC	Polyfluoro carbon
PP	Polypropylene
PP tubes	Polypropylene tubes
RS	Recovery standard
SPE	Solid Phase Extraction
TIC	Total ion current chromatogram
UPLC	Ultra Performance Liquid Chromatography
MS	Mass Specrometry
SPE	Solid Phase Extraction

List of figures

[1] A list of the analysed PFAS is available in Table 1 (page 5)

List of tables

List of graphs

INTRODUCTION

I. General presentation of the Faroe Islands and the Umhvørvisstovan

The subject of this master thesis was offered by the Umhvørvisstovan (Environment Agency in English), based in Argir, Faroe Islands.

Figure 1 View of Argir from Tórshavn - Personal Picture, 2015

The Faroe Islands (Føroyar in Faroese) is a country dependent from Denmark. It consists of 18 main islands (~1400 km²) and was inhabited by approximately 50 000 people in 2013 (Wikipédia, 2017).

Its remote location, as depicted in Figure 2, would let one think that it is not concerned by most common environmental issues one can meet in continental countries. Unfortunately, the truth is quite different: the marine and atmospheric currents bring some pollutants to the islands, potentially putting some of the flora and fauna at risk.

Figure 2 Location of the Faroe Islands -
(Umhvorvisstovan, n.d.)

The Umhvørvisstovan, founded in 2008, is part of the Ministry of Fisheries of the Faroe Islands. Among its tasks are the Faroese cadastre, country mapping, energy supply supervision, environment protection and research, etc (Umhvørvisstovan, n.d.).

Most of the lab work however was performed at the iNOVA Research Park, located in Tórshavn (see Figure 3). iNOVA is a place where different institutions (both public and private) can rent rooms and have access (on agreement) to different facilities such as:

(a) Chemistry and biology laboratories: available to the Umhvørvisstovan are a liquid chromatograph, an ultra performance liquid chromatograph coupled with a tandem mass spectrometer, benches, fume hoods, centrifuges and many other lab equipments.
The University of the Faroe Islands also has some PCR as well as other microbiological instruments.
(b) Offices and conference rooms.
(c) Human Performance and Health Laboratory.
(d) Food lab.

Figure 3 Location of the Umhvørvisstovan and iNOVA Research Park - (Umhvorvisstovan, n.d.), *modified to add scale and text*

II. Polyfluorinated alkylated substances (PFASs)

1. Background information

Polyfluoroalkyl and perfluoroalkyl substances, abbreviated as PFAS[2] in this master thesis, are manmade chemicals (Bossi, Dam, & Rigét, 2015) that have been produced and used for more than 60 years (Eriksson & Kärrman, 2015).

They are mainly used in industrial and commercial applications for impregnating products, due to their strong oil and water repellent properties (Eriksson, Kärrman, Rotander, Mikkelsen, & Dam, 2013), but also in fire fighting foams (Lee et al., 2008).

The fluorine-carbon bonds make PFAS very resistant to thermal and chemical attacks, which is very advantageous for their intended use, but also makes them highly persistent when released in the environment (Skaar, 2016).

Regulations on polyfluorinated alkylated substances are starting to be imposed. The first "regulation" concerned PFOS (perfluorooctanesulfonic acid, an eight-carbon chain with a R-SO_3H ending) and started in 2000 when the 3M Company announced a voluntary ban of their PFOS-based chemicals. The EU later regulated PFOS in EU Directive 2006/122/ECOF of the European Parliament. This directive is effective since 2008 (Bossi et al., 2015) and states that PFOS *"The Scientific Committee on Health and Environmental Risks* […] *concluded that PFOS fulfil the criteria for classification as very persistent, very bioaccumulative and toxic. PFOS also have a potential for long range environmental transport and have the potential to produce adverse effects and therefore fulfil the criteria for being considered as persistent organic pollutants (POPs) under the Stockholm Convention"* and restricts the use of PFOS-containing substances and processes, although tolerating "*Other minor uses of PFOS*". It also stated that "*Perfluorooctanoic acid*" (PFOA in this paper) "*and its salts are suspected to have a similar risk profile to PFOS*" and should be monitored.

Its overall objective is stated as "*to introduce harmonised provisions with regard to PFOS, thus preserving the internal market whilst ensuring a high level of protection of human health and the environment* […]" (European Parliament, 2006).

In 2006, the PFOA Stewardship Program (which includes several PFAS producers) initiated a voluntary phase-out from PFOA-based compounds, following the lead of the 3M Company (Eriksson & Kärrman, 2015; Skaar, 2016).

2. PFAS in the Faroe Islands

PFAS are still widely used in the industry for their surfactant properties, mostly in the textile industry (e.g. Goretex™). Another common use of those compounds is in fire prevention, especially against Class B fires[3] where the surfactant will coat the fuel, preventing its re-ignition (Fire Equipment Manufacturers' Association, 2017).

With their closest neighbours being over 300 km away and no local industry producing PFAS, one could think those compounds would not be found on the Islands. However, PFAS are nowadays ubiquitous in the aquatic environment.

The two major transport pathways of PFAS are long-range atmospheric transport (including oxidation of precursor compounds) and direct oceanic transport. (Skaar, 2016), (Butt, Berger, Bossi, & Tomy, 2010)

Direct oceanic transport is of little importance here, as the focus of this study is inland lakes. Atmospheric transport and subsequent wet and dry deposition on another hand are the main suspected sources of PFAS in Faroese lakes - at least in the isolated ones. With the high frequency of rainfall in the Faroe Islands - up to 300 raining days per year and from 800 to over 3000 mm per year, depending on the island and altitude (Cappelen, 2015) - the impact of rain on PFAS lakes' concentration might be important.

[2] The abbreviation PFC is sometimes used for PerFluoro Compounds, but will not be used in this master thesis, as it could lead to confusion with PolyFluoroCarbons.

[3] Class B fires are fires in flammable liquids (e.g. gasoline) and gases, but not cooking oils and grease (Fire Equipment Manufacturers' Association, 2017)

3. Analysed PFAS

This master thesis will focus on 18 frequently encountered compounds all listed in Table 1, with some of the main analytical parameters. Those 18 substances are the ones currently analysed in most environment monitoring campaigns in Scandinavia (information given by PhD Maria Dam), and are well-documented.

This list of "compounds under surveillance" will quite likely be extended in the coming years as the list of PFAS found in the environment is increasing with time despite the ban on the production of some of the most toxic of those substances.

It should also be mentioned that perfluorinated substances are persistent; their estimated half-life is usually between 2.3 to 3.8 years in humans (Eriksson & Kärrman, 2015), and new homologues are created frequently and see their usage increasing in some parts of the world (Eriksson & Kärrman, 2015).

Lastly, the degradation of longer-chain PFAS may sometimes lead to the formation of shorter-chain compounds (Eriksson & Kärrman, 2015), and some precursor compounds like fluorotelomer alcohols are not regulated yet and intensively used in some regions of the world (Bossi et al., 2015) (Eriksson et al., 2013).

High persistence and transport *via* oceanic and atmospheric currents are the reason why the levels of PFAS in the Arctic environment have been increasing since the 1970's (Eriksson et al., 2013), although the level of some compounds appear to have started decreasing (e.g. PFOS, quite likely due to its voluntary ban by the main producers in 2000) (Bossi et al., 2015).

4. Previous studies - Where does this study come from?

Either it was part of specific studies or part of a "Nordic Screening"[4], PFAS in the Faroe Islands have already been the subject of many studies.

In their paper named "*Perfluorinated alkyl substances (PFAS) in terrestrial environments in Greenland and Faroe Islands"*, (Bossi et al., 2015) found considerable differences among the concentrations of PFAS in trout (*Salmo trutta*) from two lakes of the Faroe Islands: PFOS (perfluorooctane sulfonyl) concentration in trout from Lake á Mýranar[5] was about twice as high as in trout from Sandur (the island). This difference turned out to match quite well the difference in the amount of rainfall from both places.

Since, to our knowledge, this has not yet been further investigated, we thought that it would be an interesting subject, fitting quite well with the academic objectives of this master thesis.

[4] Nordic screenings are pollutants monitoring campaigns that take place once in a while in most Nordic countries (Scandinavia, Greenland, Iceland)

[5] Lake "á Mýranar" is also called Lake "á Mýrunum"; this is specific to Faroese conjugation. In this master thesis, the name will almost always be shorten to "á Mýrunum"

Compound number	Abbreviation	Complete name	Parent ion m/z	Daughter ion m/z	Cone voltage (V)	Collision voltage (V)	Average RT (minutes)
1	PFBA169	Perfluorobutanoic acid	212.97	169.00	20	11	0.6
	ISPFBA169		216.97	172.00	20	11	
2	PFPeA219	Perfluoropentanoic acid	262.97	219.00	20	8	1.4
3	PFBuS80	Perfluorobutanoic sulfonate	298.90	79.96	20	26	1.7
	PFBus99		298.90	98.90	20	26	
4	PFHxA119	Perfluorohexanoic acid	312.97	118.95	20	26	2.4
	PFHxA269		312.97	269.00	20	9	
	ISPFHxA269		314.97	270.00	20	9	
5	PFHpA	Perfluoroheptanoic acid	362.97	168.97	20	16	3.1
	PFHpA		362.97	319.00	20	10	
6	PFHxS80	Perfluorohexanoic sulfonate	398.90	79.96	20	34	3.2
	PFHxS99		398.90	98.90	20	30	
	PFHxS119		398.90	119.01	20	28	
	ISPFHxS103		402.90	102.90	20	30	
	ISPFHxS120		402.90	119.01	20	28	
7	PFOA119	Perfluorooctanoic acid	412.97	118.93	20	30	3.7
	PFOA169		412.97	168.97	20	18	
	PFOA369		412.97	369.00	20	10	
	ISPFOA372		416.97	372.00	20	10	
	RSPFOA376		420.97	376.00	20	10	
8	PFNA219	Perfluorononanoic acid	462.99	219.00	20	18	4.2
	PFNA419		462.99	419.00	20	12	
	ISPFNA419		467.99	423.00	20	12	
9	PFOSA78	Perfluorooctane sulfonamide	497.90	78.00	82	30	4.9
	PFOSA169		497.90	168.96	82	28	
	ISPFOSA		505.90	77.80	82	30	
10	PFOS80	Perfluorooctanoic sulfonate	498.97	79.96	20	44	4.2
	PFOS99		498.97	98.96	20	38	
	PFOS130		498.97	130.00	20	45	
	PFOS169		498.97	169.03	20	34	

	ISPFOS99		502.97	98.96	20	38	
	RSPFOS99		506.97	98.96	20	38	
11	PFDA219	Perfluorodecanoic acid	512.97	219.00	20	18	4.6
	PFDA469		512.97	469.00	20	11	
	ISPFDA470		514.97	470.00	20	11	
12	PFUnDA269	Perfluoroundecanoic acid	562.97	268.99	20	18	4.9
	PFUnDA519		562.97	519.00	20	12	
	ISPFUnDA520		564.97	520.00	20	12	
13	PFDS80	Perfluorodecanoic sulfonate	598.97	79.96	20	58	4.9
	PFDS99		598.97	98.90	20	42	
14	PFDoDA169	Perfluorododecanoic acid	612.97	168.96	40	22	5.2
	PFDoDA569		612.97	569.00	34	14	
	ISPFDoDA570		614.97	570.00	34	14	
15	PFTrDA169	Perfluorotridecanoic acid	662.90	168.96	20	26	5.4
	PFTrDA619		662.90	619.00	20	14	
16	PFTDA169	Perfluorotetradecanoic acid	712.90	168.97	20	28	5.6
	PFTDA669		712.90	669.00	20	14	
17	PFHxDA169	Perfluorohexadecanoic acid	812.90	168.96	30	32	6.0
	PFHxDA769		812.90	769.00	30	15	
18	PFOcDA169	Perfluorooctadecanoic acid	912.90	168.96	36	36	6.2
	PFOcDA869		912.90	869.00	36	15	

Table 1 List of the 18 analysed compounds, the Internal Standards (with prefix IS) and Recovery Standards (with prefix RS) as well as some of the parameters used for their analysis
Data are from MS Method Input files, compounds' names are from (Bossi et al., 2015) **and** (Skaar, 2016)

METHODS

This master thesis consists in two main parts, with two linked objectives. The second one is partly dependent on the completion and conclusions drawn from the first one.

Briefly, the first objective is to analyse fish samples from previous years and observe the trend for PFAS concentration over the past few years.

The second objective is to check whether there is a relation between rainfalls and the concentration of PFAS in different lakes. This will be done by sampling 6 different lakes and comparing the results with some recent weather data.

The main limits that will be encountered are:

(a) Time: preparing the samples takes quite some time (see I.4 page 11 for more details). Planning on preparing and analysing too many samples would only lead to time shortage and not enough time for the analysis of results and writing of this paper;

(b) Technical/practical issues: all sampling will be performed by hand, which means time investment. Plus, some of the lab material is shared with other companies, which means possible delays during the preparation of the samples.

I. PFAS in fishes

1. PFAS time-trend in fishes

Arctic char samples from lake á Mýrunum are available from 2000 until 2014 (see Table 2 for more details) in the Environmental Specimen Bank.

Samples (consisting of arctic char muscle tissues taken on the right filet[6]) from every available year will be analysed so that we can observe the evolution of PFASs' concentration over time.

Those results will also be compared with some analyses performed at Orebro's University (Universitetet i Örebro) on fishes from 2011 and 2012 (Bossi et al., 2015)(Bossi et al., 2015).

2. Evolution of PFAS concentration in regard to rainfalls

The results previously obtained will be compared with historical meteorological data from the weather station of Høgareyn, which is located quite close to the lake where fishes are from.

The purpose of this is to see whether the concentration of PFAS in fishes is related to the precipitations. This has not been studied in the Faroe Islands.

3. Sample selection

3. i. Number of samples

Five fish samples will be analysed for each available year, all from male Arctic Chars (*Salvelinus Alpinus*). This number of samples will allow for the exclusion of some samples if something happens during the preparation or the analysis, while still having some results. In addition, a method blank will be prepared with every batch[7] to make sure the polypropylene tubes (later abbreviated as PP tubes) are not leaking any PFAS in the samples. Table 2 summarizes the characteristics of the selected samples. Note that the fishes from 2000 and 2010 could not be analysed as they were not found with the other samples.

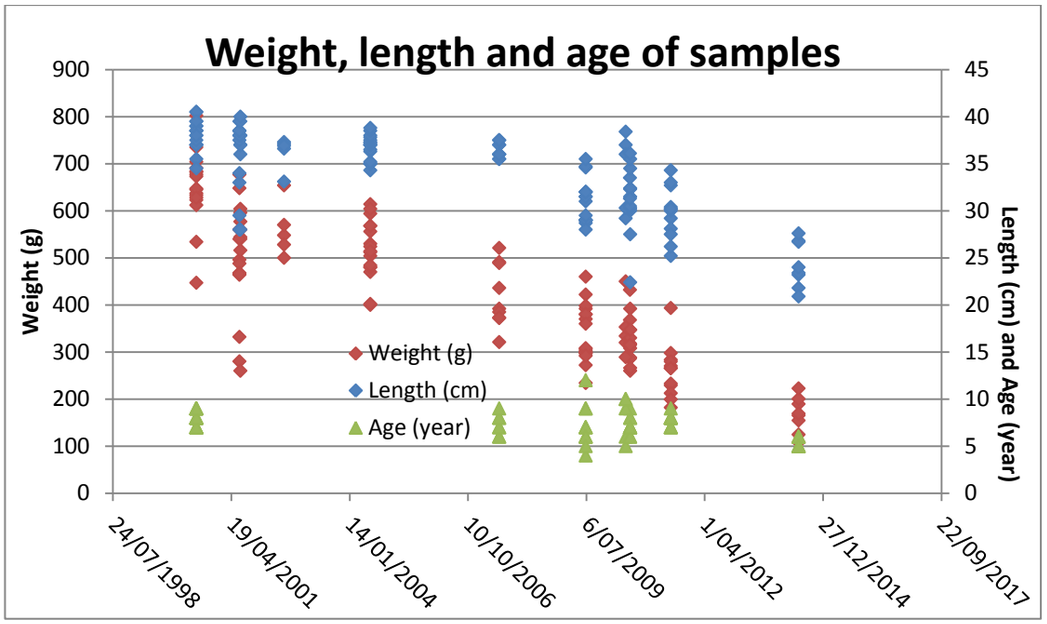
[6] Except for samples from 2002 where the left filet was used.

[7] A batch = samples for a specific year. No method blank was realised for fishes from year 2014.

Fish key	Date	Length	Weight	Sexe	Age
Sa-0074	5/07/2001	37	544	male	/
Sa-0077	5/07/2001	37	560	male	/
Sa-0081	27/06/2001	37.5	488	male	/
Sa-0082	5/07/2001	38	540	male	/
Sa-0086	5/07/2001	38	516	male	/
Sa-0122	9/07/2002	37.3	548	male	/
Sa-0127	9/07/2002	36.6	528	male	/
Sa-0128	9/07/2002	37.1	654	male	/
Sa-0132	9/07/2002	36.9	570	male	/
Sa-0123	9/07/2002	33.1	500	male	/
Sa-0099	7/07/2004	37	614	male	/
Sa-0101	7/07/2004	37	594	male	/
Sa-0102	7/07/2004	37.5	524	male	/
Sa-0105	7/07/2004	37.2	568	male	/
Sa-0116	7/07/2004	36.5	556	male	/
Sa-0176	1/07/2007	37	392	male	6.0
Sa-0180	1/07/2007	37.5	385	male	7.0
Sa-0183	1/07/2007	36	321	male	8.0
Sa-0184	1/07/2007	37	491	male	7.0
Sa-0185	1/07/2007	37.5	373	male	8.0
Sa-0195	1/07/2009	29	272	male	6.0
Sa-0196	1/07/2009	29	300	male	7.0
Sa-0201	1/07/2009	28.7	302	male	7.0
Sa-0202	1/07/2009	29.5	308	male	7.0
Sa-0203	1/07/2009	31	392	male	6.0
Sa-0256	20/06/2011	29.2	229	male	7.0
Sa-0258	20/06/2011	30	284	male	7.0
Sa-0263	20/06/2011	30.4	270	male	8.0
Sa-0266	20/06/2011	30.2	280	male	8.0
Sa-0274	20/06/2011	28.1	233	male	7.0
Sa-0332	4/06/2014	26.8	190	male	/
Sa-0336	4/06/2014	26.7	200	male	6.0
Sa-0338	4/06/2014	27.6	223	male	6.0
Sa-0345	4/06/2014	24	169	male	5.0

Table 2 List of the fish samples from á Mýrunum and their characteristics

The samples previously listed have been selected from a list of 315 samples according to their age. When the age was not available, they were sorted depending on their length (first criterion) and weight (second criterion). Graph 1 shows these three variables amongst the available fish samples. When selecting the samples according to the length, we tried to aim for values the most available amongst all year (that is, around 30-35 cm).



Graph 1 Weigth, length and age of available Arctic Char samples from Lake á Mýrunum - *Graph from MS Excel 2007*

3. ii. About the importance of the fishes' sex [8]

Since quite a large number of samples will be analysed, and since they spread over 14 years, it is important to make sure that all samples have the "same" behaviour toward PFAS. The sex of the fishes might be a source of different behaviour, due to phenomena such as maternal transfer of pollutants (as discussed in e.g. Weijs, L. et al. Maternal transfer of organohalogenated compounds in sharks and stingrays. Mar. Pollut. Bull. 92, (2015)).

This possibility - different behaviour depending on the fishes' sex - has been further studied based on some PCB (polychlorated biphenyl) data previously collected by the Umhvørvisstovan.

The - around - 200 fish samples were also Arctic Chars from Lake Á Mýrunum, collected between 1998 and 2014. They were analysed for the quantification of 16 different PCBs.

(a) Linear regressions using R

Linear regressions were made using the statistic software R in order to compare the PCB contamination between males and females over the year. An extract of the R code used is given in Figure 4 and the whole code is available in Annexe 8, page 36.

```
for (an in levels(annee)) {
selection <- tableau[which(tableau$Year == an),]
    plot(selection[,3],selection[,5],type="n",main = paste(names(tableau[5]), an), xlab =
selectionmale <- tableau[which(tableau$Sex == "male" & tableau$Year == an),]
selectionfemale <- tableau[which(tableau$Sex == "female" & tableau$Year == an),]

    # Linear regression, add PCB conc and reg lines to graphs
male <- lm(selectionmale[,5]~selectionmale[,3], selectionmale)
    points(selectionmale[,3],selectionmale[,5],col = "blue")
    lines(selectionmale[,3],male$fitted,col = "blue")

female <- lm(selectionfemale[,5]~selectionfemale[,3], selectionfemale)
    points(selectionfemale[,3],selectionfemale[,5],col = "red")
    lines(selectionfemale[,3],female$fitted,col = "red")
```

Figure 4 R code extract (the whole code is given in the Annexe 8).
The missing part after "xlab =" sets the labels on the graphs.

The following graphs showed that the fish's sex might have a slight influence on the PCB contamination as some regression lines diverge from males to females, as can be seen in Figure 5.

[8] All software and package used are listed in References 0
List of software used page 33

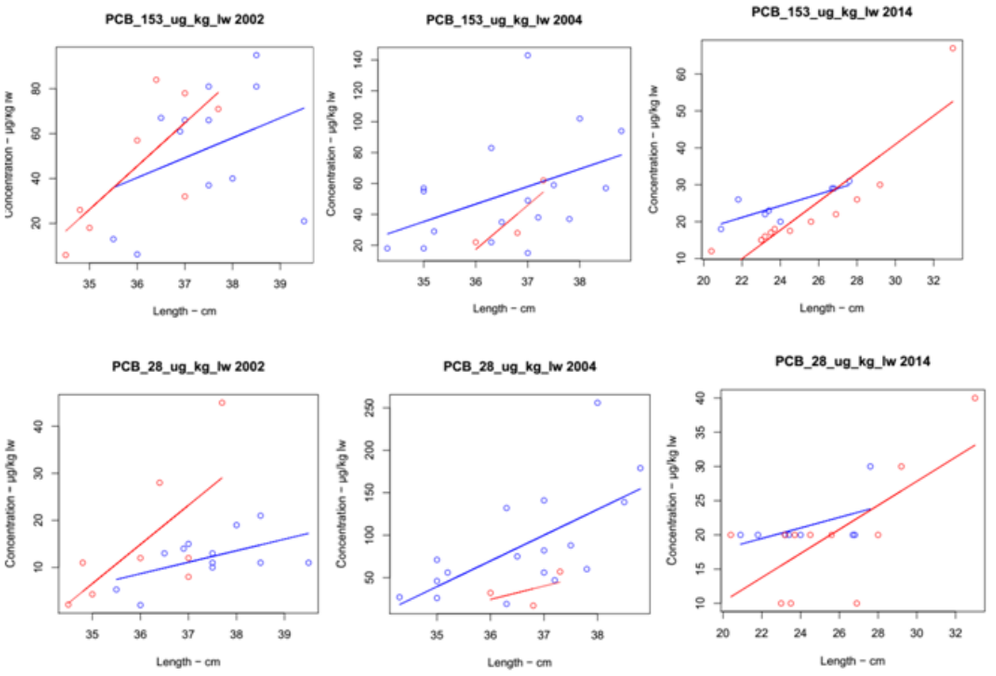


**Figure 5 Linear regressions for PCB 153 and 28, years 2002, 2004 and 2014.
The blue lines and dots are for Males and the red lines and dots are for Females.
The regression lines diverge from males to females.**

However, it is not always the case and often both regression lines are quite similar, as depicted in Figure 6.

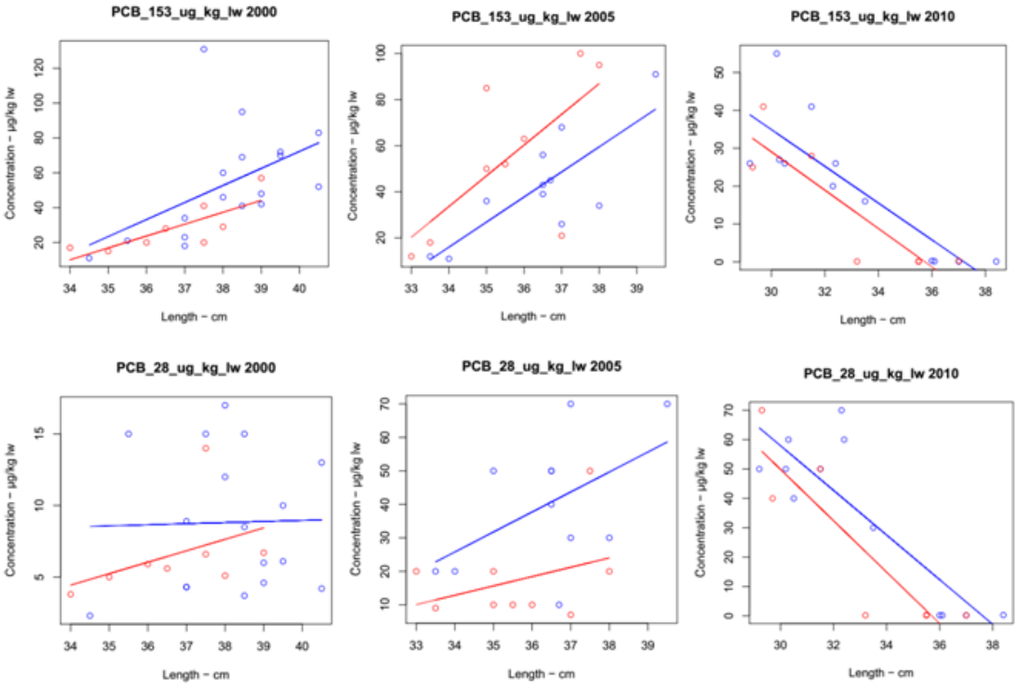


**Figure 6 Linear regressions for PCB 153, years 2000, 2005 and 2010 and PCB 28 (same years).
The blue lines and dots are for Males and the red lines and dots are for Females.**

As there were more male samples available than female samples and just to be sure to avoid any additional source of uncertainty, all of the analyses were performed on male samples.

3. iii. R code validation

The R code was validated by comparison of the regression's curve (lines) equation with regression's curve equations obtained using Microsoft Excel 2006 software.

PCBs 28 and 153 were chosen for validation as advised by Pr. Célia Joaquim-Justo so that we would have two different chlorination levels (PCB 28 has 3 chlorines on positions 2,4,4' while PCB 153 has 6 chlorines on positions 2,2',4,4',5,5') inducing possible different behaviours in the fishes.

As it can be seen in the table given in Annexe 12, page 38, the regression coefficients are similar with both programs (note: exclude the differences due to rounding the numbers), which means that the R codes should be correct.

4. Sample preparation

The samples were usually taken from the right filet and were kept in plastic bags (which might result in some contamination), sometimes wrapped in aluminium foil. Due to the relatively small volume of some of the samples, it was decided not to "peel" the parts of the sample that were in contact with the plastic bag.

Samples from 2002 were cut directly from the left filet of the fishes as the right one had already been used. All samples are from the ESB (Environmental Specimen Bank) and were kept frozen until prepared (-25°C).

The following sample-preparation procedure is based on (Eriksson et al., 2013) and (Kallenborn, Berger, & Järnberg, 2004) as well as some documents comparing procedures followed at Orebro and iNOVA, given by PhD. Dam.

(a) Take ~5g of fish muscle, homogenize and weight out precisely ~1 g
(b) Spike sample with internal standard (10 µl of 200 ng/ml standards)
(c) Extraction:
(d) Add 4 ml acetonitrile, vortex for 30 seconds, ultrasonicate for 15 min, and shake for 15 min. Centrifuge at ~ 9000 *g* for 30 min. Extract supernatant.
(e) Repeat 2x and combine the extracts (total ~8 ml)
(f) Evaporate under gentle N_2 stream to 2 ml
(g) Sample clean-up (3x)
(h) Add 1 ml n-hexane, shake for 30s, discard upper phase
(i) Centrifuge at ~9000 *g* for 30 min
(j) Filter into pre-prepped vials (50 mg ENVI-carbon + 100 µl glacial acetic acid)
(k) Add recovery standards[9]
(l) Evaporate to dryness
(m) Add 0.2 ml methanol and 0.3 ml 2 mM ammonium acetate
(n) Centrifuge at 9000 *g* for 30 min before analysing
(o) Run blanks, standards and samples

The whole preparation requires 2 to 3 days, with the evaporation taking most of the time.

The standards are PFAS compounds with ^{13}C (isotope 13 of carbon); the behaviour of the standards during the preparation and separation will therefore be the same as that of their corresponding analyte.

[9] The Recovery Standard should be added at the very last step, but this is the standard procedure already in use at the Umhvørvisstovan so we decided to follow it as it is.

II. From the rain to the lake

Rainfalls in the Faroe Islands can greatly vary from a place to another, depending mostly on the altitude, ranging from ~850 mm/year in Mykines Fyr to over 3000 mm/year in the northern islands. Some places might receive up to 4000 mm/year according to estimates. (Cappelen, 2015)

During a previous study, (Bossi et al., 2015) noticed that the concentration of PFAS in some fishes would vary greatly depending on its original location. After further investigation, it appeared that the rainfalls in those two places also differed by a factor two, and that maybe the concentration of PFAS follow the average rainfall in the area. To our current knowledge, this phenomenon has not yet been studied in the Faroe Islands.

In a study from 2013 by Taniyasu et al., the evolution of PFAS content over time in a single rain event in Japan was discussed. The results showed that PFAS content of rain is not the same in every millimetre, but they did not investigate the relation with PFAS contamination of freshwater reservoirs. (Taniyasu et al., 2013).

The idea of this project is therefore to gather some freshwater lake samples from different appropriate sampling sites, analyse them for PFAS and compare the results with recent meteorological data. The aim of the study is to see whether there is a correlation between the amount of rainfall and the concentration of PFAS in the lakes.

1. Sampling

1. i. Methodology

The procedure is based on the one used by the University of Örebro in Sweden (Kärrman, n.d.) and on work from (Taniyasu et al., 2013), (Eriksson et al., 2013), (Skaar, 2016), (Waters corporation, n.d.) and (Lee et al., 2008).

The bottles were washed with Milli-Q water, then HPLC-MS grade pure water and lastly with HPLC-MS grade methanol.

While sampling, fluorinated materials should be avoided, whether it is clothing or lab material. The bottles are filled with the sample and emptied to rinse them, before taking a new sample, which is kept. All bottles must be properly labelled (site and date of sampling, sample number or field blank number).

Field blanks are bottles cleaned with methanol, rinsed with Milli-Q water and then filled with Milli-Q water in the lab. During the sampling, they are opened and the water is let in contact with the ambient air for a short while before being closed. No field blank has been done due to a lack of container, but a method blank was done.

The internal standard should be added as soon as possible, and the samples are stored in a fridge at +4°C before being treated.

1. ii. Sampling sites

The lakes to be analysed have to be located close to and approximately at the same altitude as a weather station. The selected lakes are listed here-under. Table 3 summarizes the sampling sites, dates, sampler, sample volume and date when the internal standard was added.

Sampling site	Date	Sampler	IS added	Sample ID	Preparation	Volume (ml)
Hoydalsvegur A	30/04/2017	Kári M	1/05/2017	Tor A	2/05 - 04/05/17	1000
Hoydalsvegur B	30/04/2017	Kári M	1/05/2017	Tor B	2/05 - 04/05/17	1000
Sørvágsvatn	29/04/2017	Maria D	1/05/2017	Sor	2/05 - 04/05/17	1000
Lítluvatn (Sandoy)	29/04/2017	Maria D	1/05/2017	Lit	2/05 - 04/05/17	920
Á Mýrunum	30/04/2017	Maria D	1/05/2017	Myr	03/05 - 04/05/17	990
Villingadalsvatn	2/05/2017	Maria D	2/05/2017	Vil	03/05 - 04/05/17	990
Kollafjørður	30/04/2017	Kári M	1/05/2017	Kol	03/05 - 04/05/17	1000
Reiðskarð	2/05/2017	Maria D	2/05/2017	Reið	03/05 - 04/05/17	1000
Reinmúlalag	4/05/2017	Axel	4/05/2017	Rein		990
Havnadal	4/05/2017	Axel	4/05/2017	Hav		1000
Havnadal	4/05/2017	Axel	4/05/2017	Hav blk		990

blank						
Sørvágsvatn blank	3/05/2017	Maria D	3/05/2017	Sor blk		1000

Table 3 List of water samples.
Note that samples from Hoydalsvegur and Kollafjørður are from "hot springs", not from lakes.

Two hot springs (Hoydalsvegur and Kollafjørður) were added to the seven lakes in order to check whether PFAS contamination reaches ground water. Figure 7 shows all locations on a general map; more precise pictures are available in the annexes (Annexe 1 page 32 to Annexe 7 page 35).

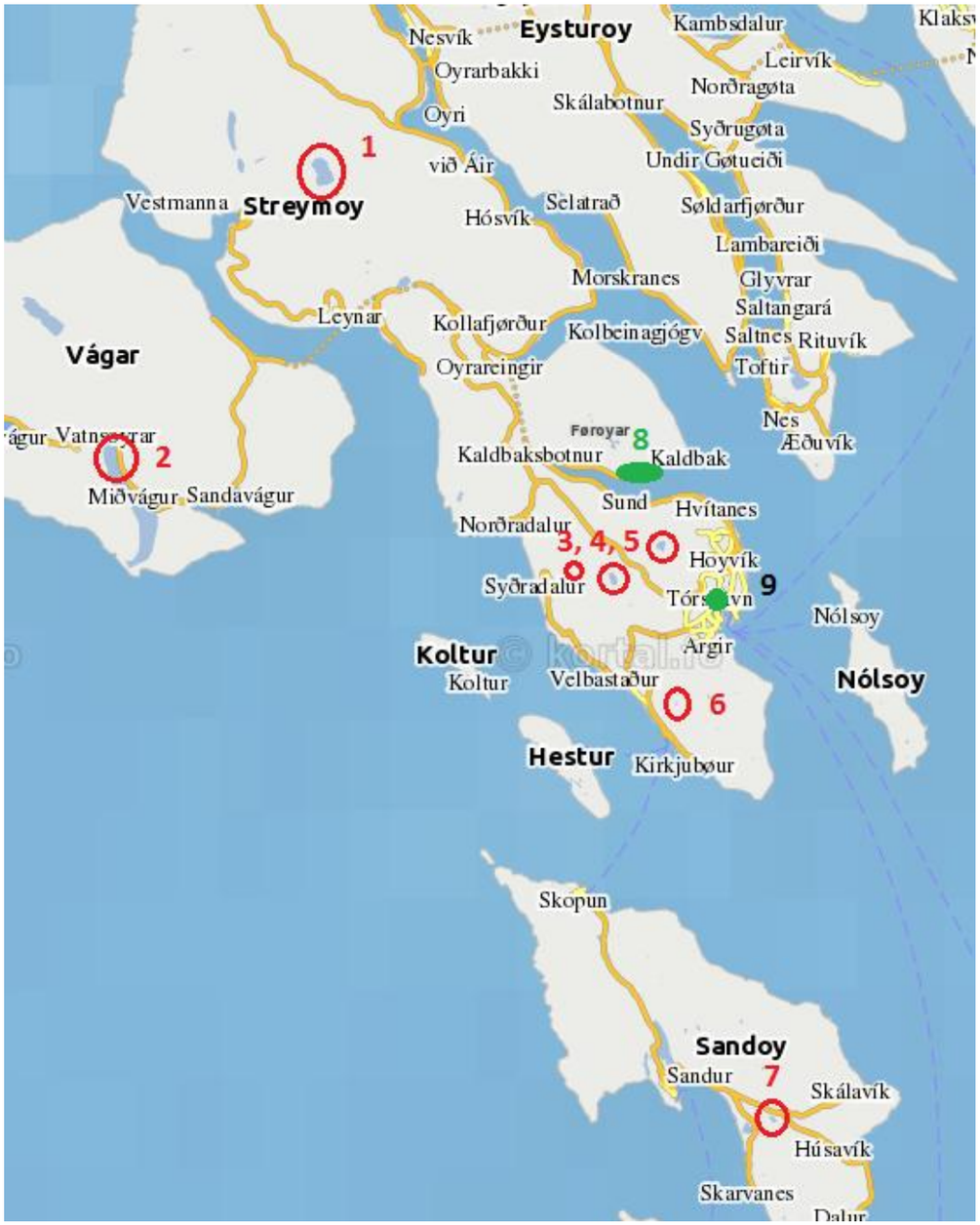


Figure 7 Map showing all sampled lakes (in red) and the two hot springs (in green)
Lakes: 1) Lake Á Mýrunum 2) Sørvagsvatn 3) Reiðskarð 4) Havnadal
5) Villingadelsvatn 6) Reynsmúli 7) Lítluvatn
Hot springs: 8) Kollafjørður 9) Hoydalsvegur
Picture from Kortal.fo (Umhvorvisstovan, n.d.)**, edited**

(a) Á Mýrunum, Streymoy: as the fish samples analysed for the first part are from this lake, it seems quite obvious that it has to be analysed for PFAS. There is a weather station close by, in Høgareyn.
(b) Sørvágsvatn (also called Leitisvatn (Dam & Hoydal, 2007)[10]), in Vágar: two weather stations are available relatively close: the one from the airport of Vágar, and one near Vatnsoyrar.
Despite being close to a village and to the airport (which means there might be direct anthropogenic contamination), water from this lake is used for drinking water (Dam & Hoydal, 2007).
(c) Villingadelsvatn, Streymoy: water from this lake is used as drinking water in Tórshavn, where there is a weather station
(d) Havnadal, Streymoy: water from this lake is used as drinking water in Tórshavn, where there is a weather station
(e) Reiðskarð, Streymoy: according to PhD Dam, this place should be free from direct anthropogenic contamination; it would be interesting to see whether any difference can be noticed from the two previous lakes. Accessible by a ~20 min walk from the road
(f) Reynsmúli, Streymoy: a weather station in Velbastaðhális should have available data. The lake is accessible by a ~20 min walk from the road.
(g) Lítluvatn, Sandoy: while a bit further away (~8 km), the weather station of Brekkuni Stóra is almost at the same altitude as the lake; there should therefore not be much difference in the rainfalls
(h) Kollafjørður: one of the two hot springs added to the list. The origins of the water are not yet known (explained by PhD. Maria Dam), and the reason for analysing a sample from this source is to know whether PFAS contamination can reach underground waters.
(i) Hoydalsvegur: the second hot spring added to the sample list.

2. Weather data

The meteorological data for Høgareyn weather station (Lake á Mýrunum) are from Landversk, an institution owning 26 weather stations spread across the Faroe Islands (Landversk byggír land, 2016).

The initial plan was to gather data from year 2000 to 2014, but data were available only for the 2006 to 2014 period, with some gaps in it. The data that were used are:

(a) "rain" column: marked as "0" when there is no rain and marked "1" when it is raining
(b) "rainint" column: rain intensity, given in mm/h
(c) The date

The initial files were either .xls files or .txt files; they were formatted and treated using R (references for R and all additional packages are available in the "List of software used", page 31.

As some files were messed up (the data were sometimes not in the right column), it was necessary to make sure that the right data were extracted. This was done by making sure that the "rain intensity" column was corresponding to the "rain" column - that is, when the "rain" column was marked as "0", the "rain intensity" column should be "0" too.

Due to the data being quite old and not exactly reliable (according to the supplier Landversk), some "margin of error" was tolerated about the "rain" to "rain intensity" relation, and the average of the "rain intensity" was used as a second criterion. As the rain intensity data (in mm/h) were sometimes offset with the atmospheric pressure (in hPa), a criteria of an average of over 100 could be used to differentiate which data was in the column (the average atmospheric pressure being over 990 hPa).

The complete code is given in Figure 8; it created datasets per year.

[10] The spelling "Sörvagsvatn has been seen too.

```r
setwd("C:/Users/Axel/Desktop/Ecole/ULg2/Mémoire/study plan/Meteo data/Hog")
require("stringr")

donnees2010 <- data.frame(Date.and.time = as.character(), rainint = as.numeric())

for (x in 1:12) {
      nom <- paste("2010",str_pad(x,2, pad = "0"), ".txt", sep = "")
      mesdonnees = read.table(nom,sep = "\t", header = TRUE, stringsAsFactors = FALSE,dec = ",")
      while(mesdonnees[nrow(mesdonnees),1] == "") {mesdonnees <- mesdonnees[-nrow(mesdonnees),]}

      long <- nrow(mesdonnees) - 3
      mesdonnees <- subset(mesdonnees[1:long,])

      c <- colnames(mesdonnees)
      ifelse("rainint" %in% c == TRUE, "cond" <- 1,"cond" <- 2)

      # if cond = 2: no column "Rainint" -> NA
      if (cond == 2) {donnees2010 <- rbind(donnees2010, data.frame(Date = mesdonnees$Date.and.time, rainint = NA))}

      # if cond = 1: column "Rainint" -> check its value (columns are sometimes mixed up...)
      if (cond == 1) {
            a <- 0
            for (i in 1:nrow(mesdonnees)) {
              ifelse(mesdonnees$rain[i] == 0 && mesdonnees$rainint[i] != 0,a <- a +1, a <- a)
            }
            # if "rainint" = 0 when "rain" = 0 -> probably the good column
            if (a == 0) {
              donnees2010 <- rbind(donnees2010, data.frame(Date = mesdonnees$Date.and.time, rainint = mesdonnees$rainint))
            }
            # if "rainint" =/= 0 when "rain" = 0 -> check rainint average (few rain may not be detected when low intensity
            if (a != 0 && mean(as.numeric(na.omit(mesdonnees$rainint))) < 100) {
              donnees2010 <- rbind(donnees2010, data.frame(Date = mesdonnees$Date.and.time, rainint = mesdonnees$rainint))
            } else {
              donnees2010 <- rbind(donnees2010, data.frame(Date = mesdonnees$Date.and.time, rainint = mesdonnees[,11]))
            }
      }
}
# Default: col.names = TRUE, append = FALSE (it'll overwrite any previous table, no confirmation required !!!)
write.table(donnees2010,"donnees2010.txt", sep = "\t",row.names = FALSE)
```

Figure 8 R code used to extract the data from the .txt files from Landversk - *personal document*

The data were then processed using a second code, given in Figure 9. This code requires additional packages (listed in the References) and will calculate the total precipitations per month.

Two datasets were created with all the results: one for the 2010-2014 period, with reasonable results, and one for the 2006-2009 period, whose results make no sense (see II.2. i for further details).

In both cases it turned out necessary to exclude some results, as they were obviously absurd. Data exclusion is a sensible subject and many would say that all results should be kept, but in this specific case it was made clear by the supplier (Landversk) that all data should not be blindly trusted because of its lack of precision: "[…] *because it is not an exact measurement"* (Sølvi Sjurðarson, Programmer and Technician at Landsverk). It was therefore decided that the final results - that is, the total precipitation per month - should be sorted. A criterion of "above the average plus two times the standard deviation" or "below the average minus two times the standard deviation" was used for sorting (lines 18 to 24 in the code from Figure 9).

```r
setwd("C:/Users/Axel/Desktop/Ecole/ULg2/Mémoire/study plan/Meteo data/Hog")
mesdonnees = read.table("donnees2006.txt",sep = "\t", header = TRUE, stringsAsFactors = FALSE)
names(mesdonnees) <- c("time","value")
require('dplyr')
require('xts')
require('lubridate')
mesdonnees <- mesdonnees %>% distinct(time, .keep_all = TRUE)

xtsdata <- xts(mesdonnees$value, order.by = as.POSIXct(mesdonnees$time, tz = "GMT", format = "%d-%m-%Y %H:%M"))

mon_avg <- apply.monthly(xtsdata,mean)
mon_tot <- mon_avg

for (i in 1:length(mon_avg)) {
  mon_tot[i,] <- round(mon_avg[i,] * 24 * days_in_month(mon_avg[i,]),1)
}

avg <- mean(mon_tot)
std <- sd(mon_tot)
for (i in 1:length(mon_tot)) {
  if (mon_tot[i,] > (avg + 2*std) | mon_tot[i,] < (avg - 2*std)) {
    mon_tot[i,] <- NA
  }
}

write.zoo(mon_tot, "monthly totals 2006.txt", sep = "\t", index.name = "Date")
```

Figure 9 R code used to calculate the total precipitations per month - *personal document*

2. i. Excluding the data for the 2006-2009 period

The data for the 2006-2009 period yielded some nonsense results; the calculated total precipitations over a month would often exceed 2000 mm, and the total precipitations per year would reach over 15000 mm. According to J. Cappelen, the highest precipitations in the Faroe Islands can reach up to 4000 mm per year (Cappelen, 2015) ; the results obtained from the Landversk data give some totals exceeding that number by a factor 4.

The data were treated the same way as those for the 2010-2014 period; an error in the code can therefore be excluded. The most reasonable explanation is that the initial dataset has some errors. Rain intensities over 100 mm/h (corresponding to extreme rainfalls according to (Météo-France, n.d.)) seem to be quite frequent, and numbers as high as 170 mm/h appear in the data.

As can be seen in Table 4, the monthly precipitations almost correspond to the expected precipitations over a year in the Faroe Islands, with values as high as 2500 mm over a month.

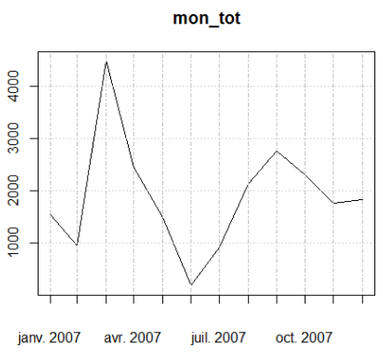
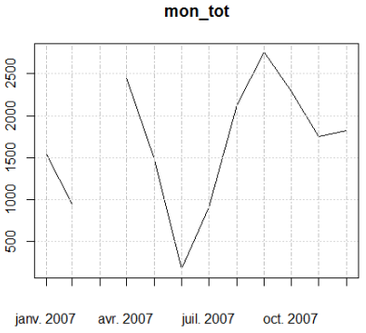
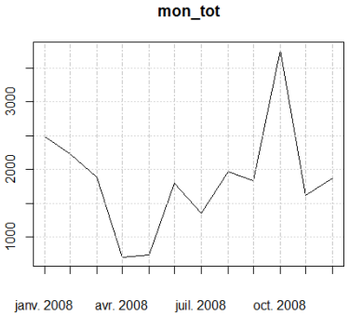
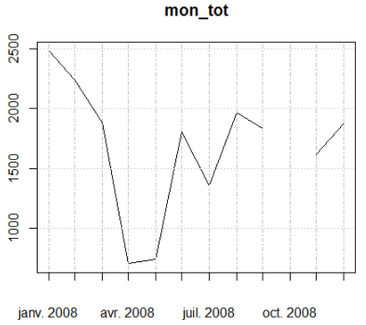
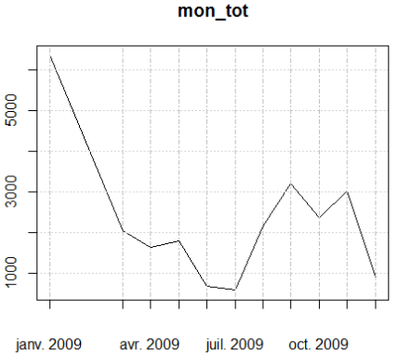
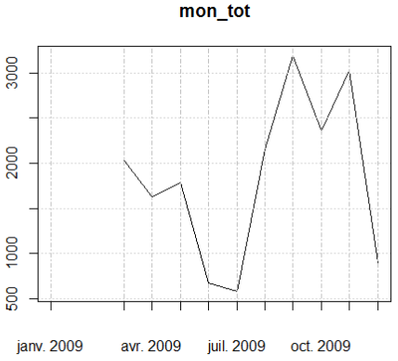
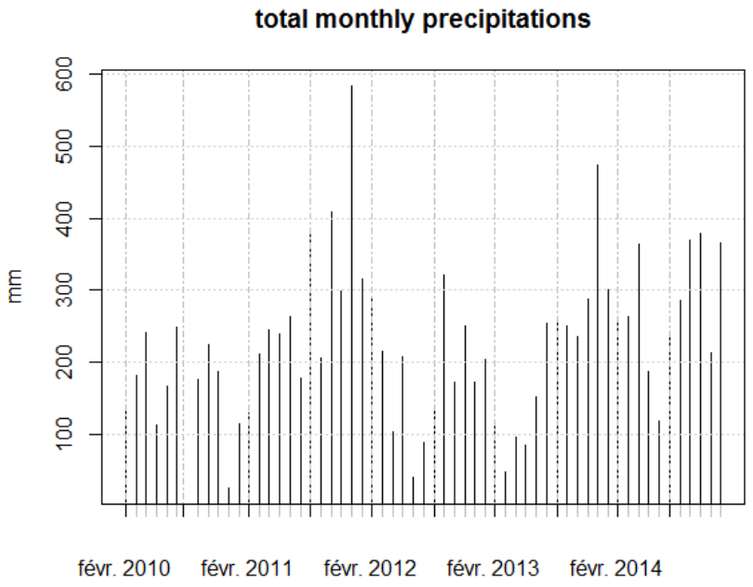
No exclusion	Excluding if > μ+2sd or < μ+2sd
	
	
	

Table 4 Graphs obtained for the monthly total precipitations over the 2006-2009 period
Y axes are in mm - *personal documents, designed using R and R studio*

For this reason, the data for this period won't be exploited any further.

2. ii. Monthly total precipitations for the 2010-2014 period

As shown by Graph 2, the dataset for the 2010-2014 period yielded much "better" results that can be exploited later on.



Graph 2 Total monthly precipitations (in mm) for the 2010-2014 period - *personal document, designed using R and R studio*

Further manipulations on those data will be detailed in the Results part of this paper.

3. Water samples preparation

The following procedure is based on some previous analyses done here at the Umhvørvisstovan (Eriksson et al., 2013), modified according to some recommended procedures from Waters Inc. (Waters corporation, n.d.)

(a) Spike an appropriate sample volume (~1000 ml) with internal standard (10 µl at 20 ng/ml)
(b) Condition the cartridges with 5 ml methanol, rinse with 10 ml deionised water
(c) Load the sample ~5 ml/min
(d) Dry the cartridge under vacuum for ~30s
(e) Elute with 4 ml of methanol, rinse the bottles with ~4 ml methanol and elute the rinsing solution through the cartridge
(f) Evaporate the eluted solutions under gentle N_2 stream to an appropriate volume (~0.500 ml)
(g) Transfer 300 µl of the methanol eluant to a UPLC vial, add 900 µl of deionised water and Recovery Standards
(h) Run blanks, standards and samples

The cartridges used are Oasis HLB Plus LP cartridges from Waters (225 mg solvent, 60 µm particle size). PFAS being slightly non-polar (the longer the carbon chain the more non polar the compound), it is not necessary to use really non-polar solvents such as hexane as long as the flow is low enough.

Since the sample volume were large (approximately one litre), it turned out necessary to filter the sample before forcing it through the SPE cartridges to avoid clogging. This was done using fibreglass filters, placed inside a cut reservoir, placed at the entrance of the tubing (see scheme in Figure 10). The fibreglass filter was soaked in methanol during the elution.

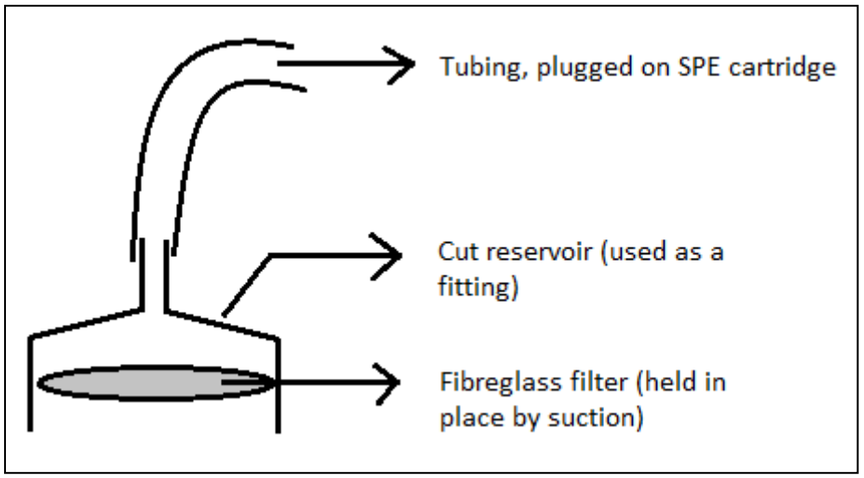


Figure 10 Filtering system used before the SPE cartridges - *personal document, drawn using MS Paint*

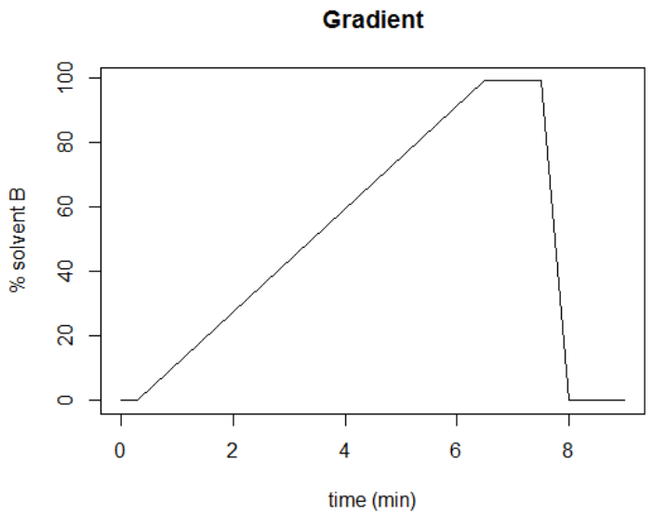
Despite filtering the sample, some SPE cartridges got clogged and part of the sample could not be forced through. This is not a problem for the quantification as the internal standard was already added.

III. LC/MS-MS analysis

1. Instruments

The instruments used are an Acquity UPLC and a XEVO TQ-S tandem mass spectrometer.

The mobile phases used are 2 mM ammonium acetate in 30% methanol/water as solvent A and 2 mM ammonium acetate in methanol as solvent B. The gradient is represented by Graph 3 here-under.



Graph 3 UPLC gradient; solvent B is 2mM ammonium acetate in methanol - *personal document, designed using R and R studio*

The approximate expected retention times for each compound are listed in Table 1 (page 6); they were adjusted before every batch run based on either a low concentration standard run or a high concentration standard run.

2. Quantification

The quantification of the analytes is done using Masslynx software from Waters Corporation.

The calibration curve was realised by Ms Andrea Midjord on the 10th of January 2017. Due to the bad results yielded by the analyses (either the peaks were too low, the wrong one was selected due to slight retention time variation or there was no peak at all - suspected reasons explained in III.3 here-under), most peaks had to be manually adjusted when possible. Blank substraction was automated by Masslynx, although it was necessary to review some of the blank chromatograms too (and sometimes remove the blank as the internal standard was simply not detected in the run).

The final results for the fish samples (the water samples could not be analysed) are generally quite bad, with many compounds being either not detected at all or detected but below the limit of quantification (abbreviated LoQ further in this paper). Reasons for saying this are (summarized): the solvent pump had failures, meaning that the analyte flow was uncertain. The retention time could therefore vary randomly (hence the no-detection of standards). This plus the high variation from the calibration curve let me think the analyses should not be trusted, although the few results obtained look coherent. More details on those technical issues are given in the next point.

3. Encountered issues

Before anything, it should be mentioned that pressure problems (drops or ripples) had been happening for the past couple of months (earliest mention in the logbook: 22nd February 2017) and were supposedly solved after flushing the system with 100% methanol to get rid of some bacteria that could have clogged the system. Unusual amounts of air bubbles could also be noticed in the purging system. I also mentioned the fact that no stream could be observed in the desolvation chamber of the MS (Figure 11), indicating a severe failure in the system.

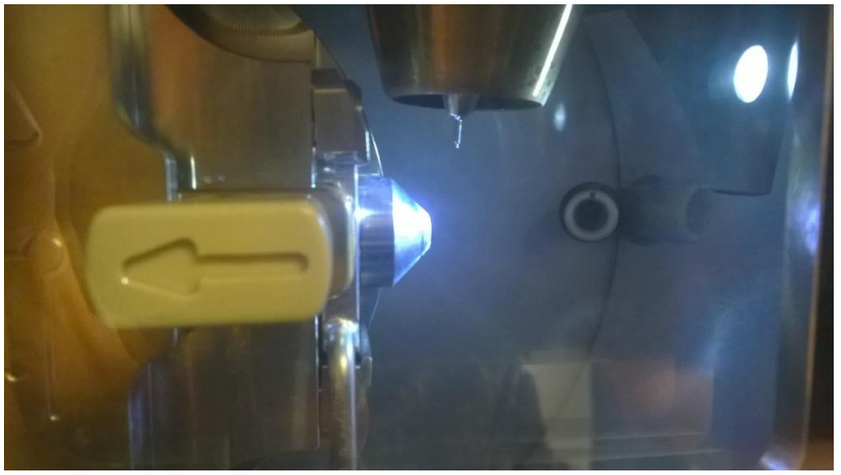


Figure 11 Desolvation chamber of the mass spectrometer. When the instrument is operating, a fine stream should be observed coming from the capillary and directed towards the ionisation chamber - *personal picture*

While doing the fish samples analyses, I noticed that some of the samples showed no peak in the chromatograms. Since we had no certainty that all samples should be contaminated (understand: should contain PFAS), I did not investigate the issue much further and kept going with the samples preparation. Another issue was the presence of carry-overs in the solvent and blank runs for the three long-chain compounds

While doing the test-run for the retention times for the second batch (run on the 7th of April 2017), the low concentration standard showed no peak. I therefore used a high concentration standard to check the retention times, which worked. The low concentration standard did show some peaks in the chromatograms after running the high concentration standard. The pressure took quite a long time before stabilizing (about 10 minutes) but I considered this normal as the instrument should be left to run with a fixed flow for half an hour before being operational.

When looking at the results, I noticed that the “no peak phenomenon” did not occur for “some compounds in some samples”, but was usually a whole sample showing no peak at all. I concluded that “something had happened during the run” and that I would have to redo some of the analyses, again without investing the issue much further.

When doing the test run for the 3rd batch (on the 21st of April 2017), the pressure took an even longer time before stabilizing, and showed some unexpected drops and rises. Letting the system run a constant flow (0.450 ml/min, 50-50 for both solvents - 2 mM 30% NH_4Ac in 30% methanol/, 2 mM NH_4Ac $_{(MeOH)}$) for about an hour seemed to get the system back in order.

Again, compounds 1 to 15 in the low concentration standard could not be detected during the test-runs. The high concentration standard could be detected, and the retention times were coherent with the previous runs. However, this time I could not get anything to show up on the chromatograms for the low concentration standard, even after preparing a new one again and increasing the concentration (from 0.08 pg/g to over 0.20 pg/g).

It is at this point (around April 24th) that I finally made the relation between the pressure's weird behaviour and all other problems (undetected standards, blank chromatograms for the samples). A change in pressure indicates that the solvent flow is varying; the gradient is therefore not respected and the retention time is affected. Proper quantification cannot be done in such circumstances.

While looking at the so-far collected data, it turned out that the results were far worse than expected; in every batch of five samples, at least two samples showed absolutely nothing in the TIC (total ion current chromatogram). When trying to do the quantification, the deviation of the standard (quality control) (compared to the calibration curve) was really high (deviation values as high as > 30% were observed quite often, sometimes reaching >80% deviation).

Below are the results of those analyses. All values and concentrations obtained should be handled carefully and should not be trusted. The integration of the peak was manually corrected for many samples and compounds and due to the poor quality of the analyses might be completely wrong. Many compounds were also excluded as their results simply made no sense, without statistical justification (e.g. blanks showing 15000 pg/g of analytes).

RESULTS

I. Fish sample analyses

1. General comments

After manually editing all peaks in the chromatograms, it was possible to get results for some samples but only for some compounds. Those results are summarized in Table 6. Examples of what is considered as an "acceptable graph" are shown by Figure 12 and Figure 13. An example of "unacceptable chromatogram" is given by Figure 14. In the later, the intensity in the 3rd graph is about 10^3; it should be much higher since this is the internal standard (usually around 10^6), this means that the internal standard was not detected.

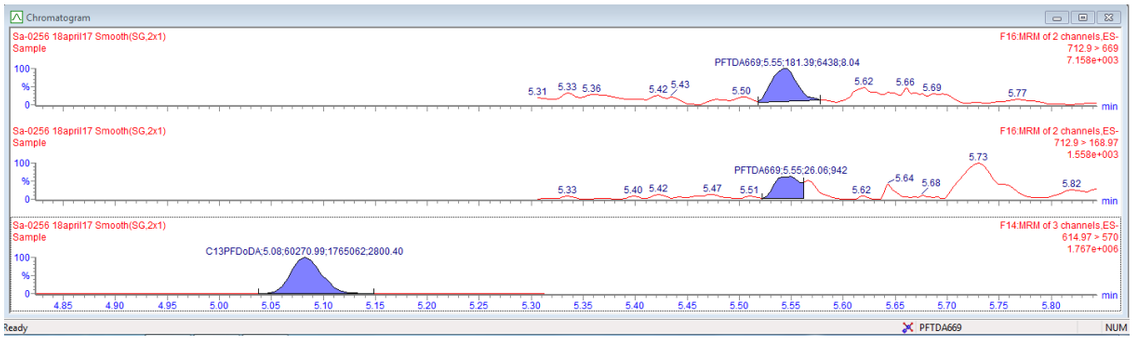


Figure 12 Chromatogram for compound PFTDA, sample Sa-0256 - *personal document, from TargetLynx*

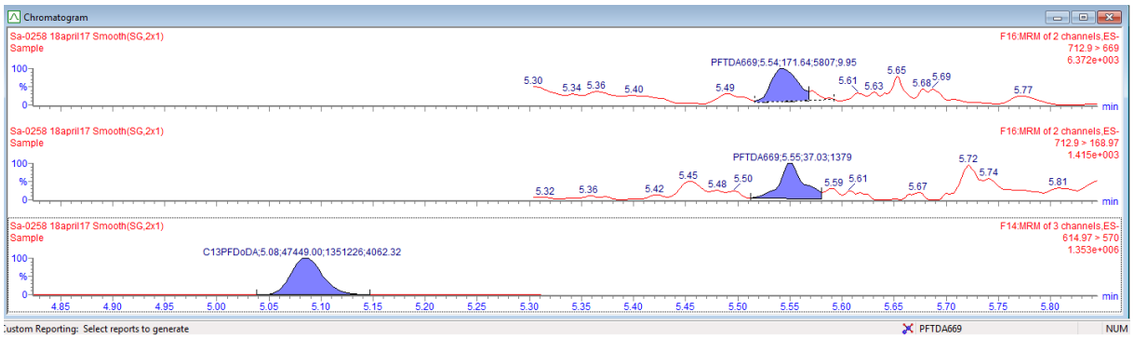


Figure 13 Chromatogram for compound PFTDA, sample Sa-0258 - *personal document, from TargetLynx*

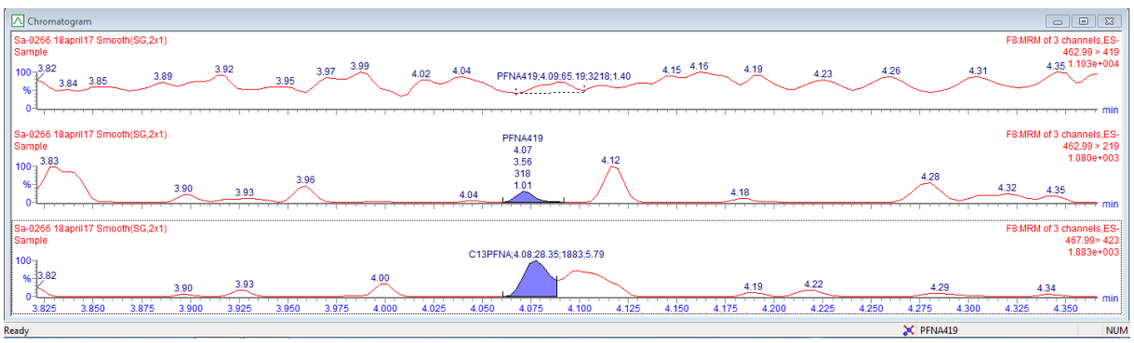


Figure 14 Chromatogram for compound PFNA, sample Sa-0266 - *personal document, from TargetLynx*

The deviation of the calibration standards run with the samples related to the calibration curve is, as previously said, overall too high with values as high as 80% deviation. This was not really taken into account while doing the quantification as it would have meant that most of the remaining results should have been excluded.

The recovery rate criterion however was kept: results with recovery rates below 20% or above 150% were excluded. While not accepted in some laboratories, results with recovery rates between 20-50% or 120-150% were kept (they are written with a “w” in Table 6).

A complete table with all recovery rates and LoQ averages per compound and per run is available in Annexe 16, page 41.

2. PFAS Time trend in fishes

An attempt at realising time trends of PFAS concentrations in arctic chars from lake Á Mýrunum was made, based on the data previously discussed in I.1 and .0. . Again, all results obtained in this part should be handled carefully as they are based on unreliable results.

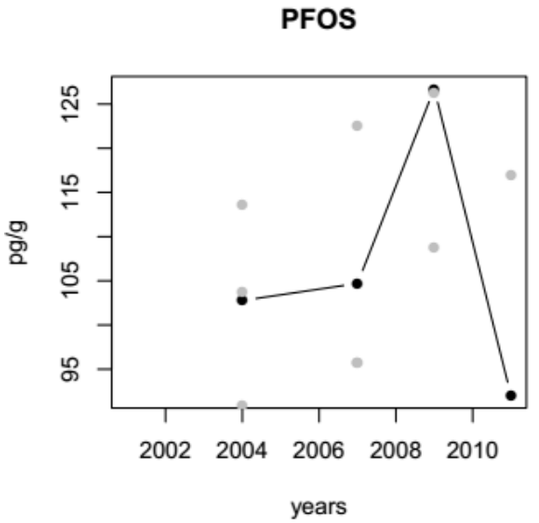
Compounds for which results were available for less than three years will not be discussed; making a time trend based on two datasets is not reliable. Concerned PFAS are: PFBuS, PFHxS, PFBA, PFPeA, PFHxA and PFHpA. All graphs are still available in the Annexe 15, page 40.

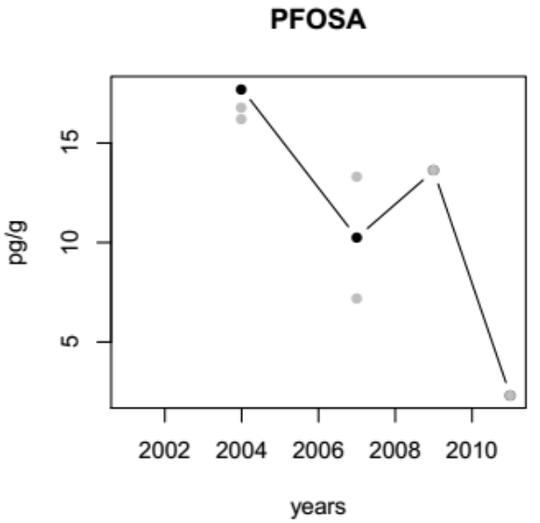
2. i. Overview of the time-trends per compound

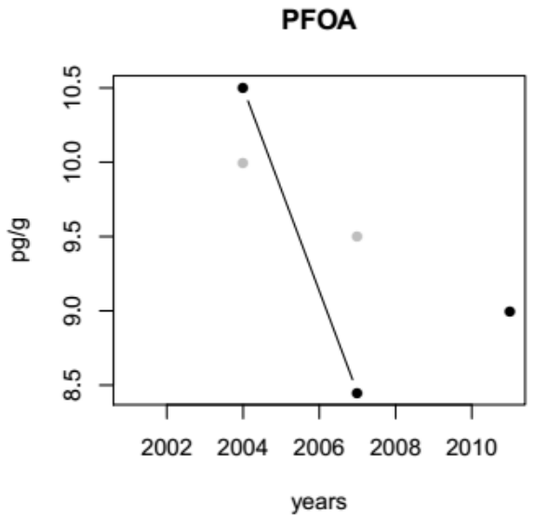
The following graphs show the evolution of PFAS concentration over the years. Black dots are the average of the results, black lines are joining the means (no line between the dots means that no data were obtained for the intermediary year(s)), and grey dots are all the data collected in this project.

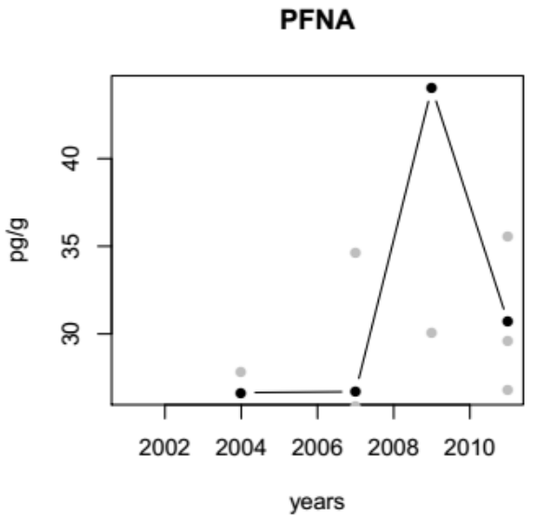
Boxplots would have shown the results more clearly but the low number of data would have made them “not so representative” (I concluded that showing the average and real concentration values on the same plot was, in this case, clearer than boxplots).

Analyses were performed for years 2001, 2004, 2007, 2009 and 2011. Analyses were also planned for years 2000, 2002, 2010 and 2014 but could not be done due to the technical issues previously discussed.

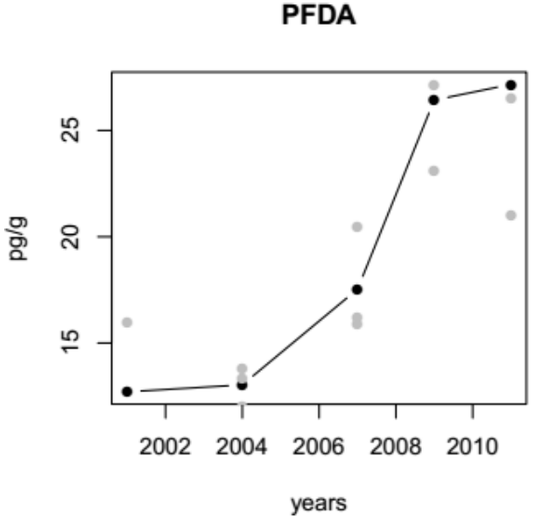


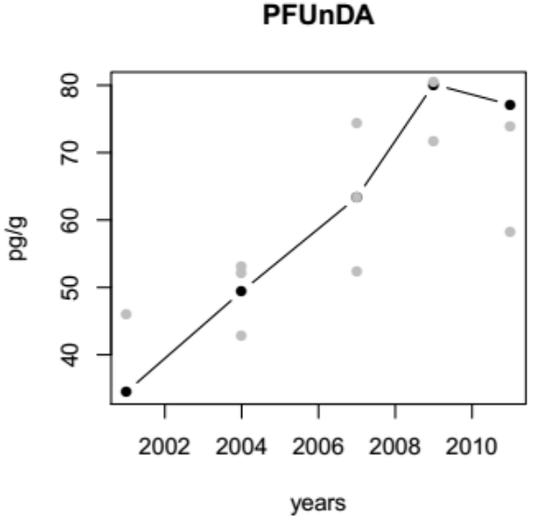


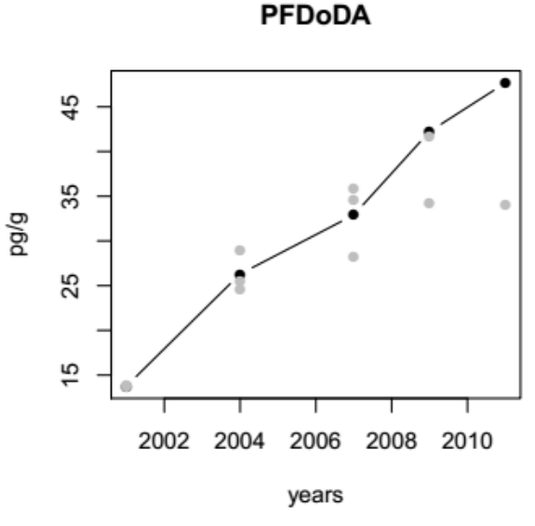


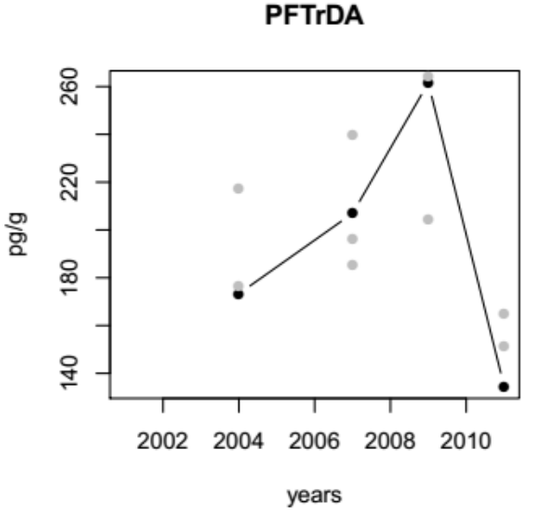


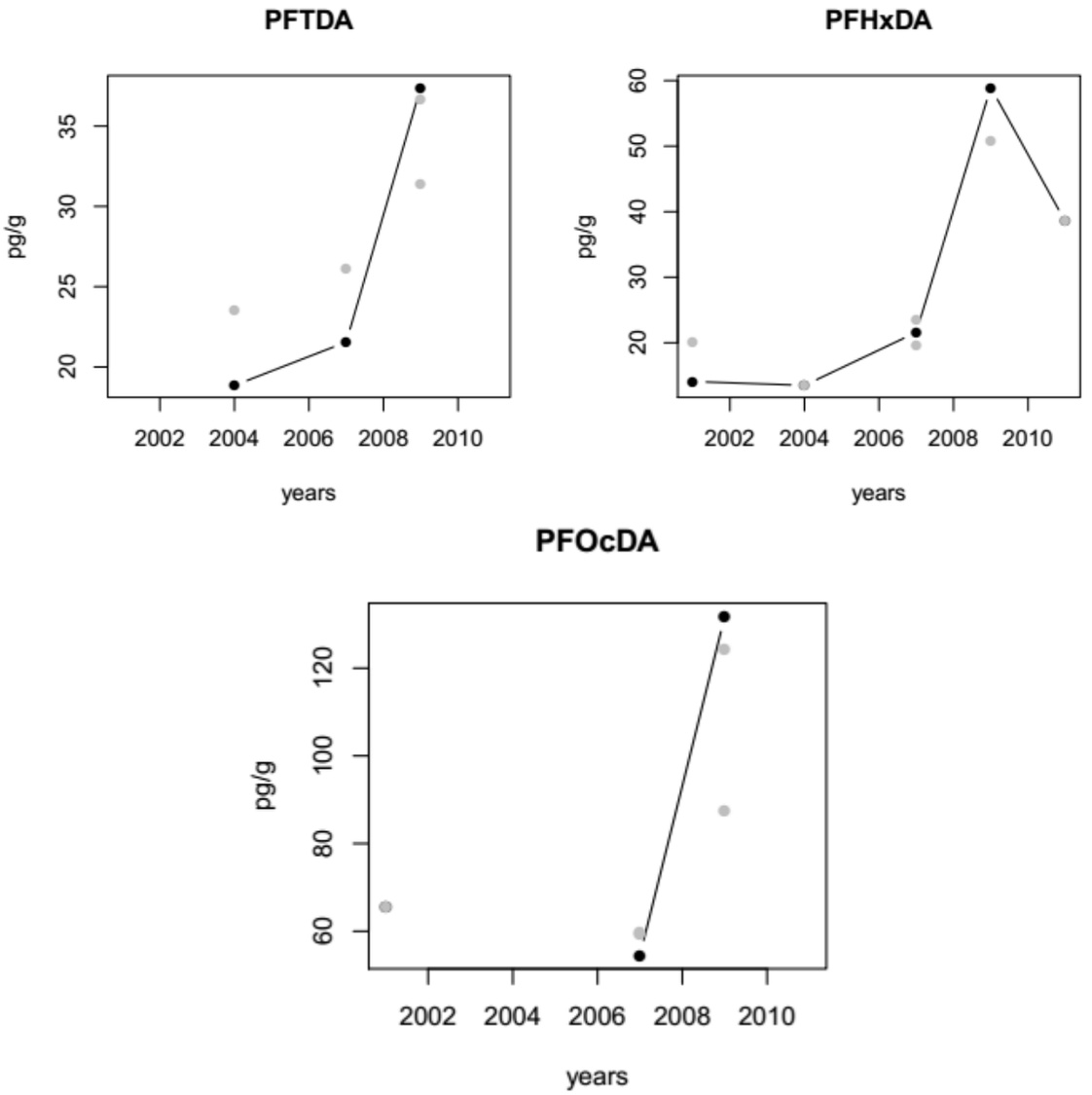
In the PFOA graph above, the black dots from 2007 and 2011 are not linked as no data could be collected for 2009.











Graphs 4 Evolution of different PFAS over the years - *personal documents, designed using R and R studio*

Only one value was collected for PFOcDA in 2001.

Except for PFOA and PFOSA, an increase in the concentrations can be observed until 2009. The concentrations then usually seem to decrease between 2009 and 2011. PFDoDA and PFDA are two exceptions, although in the case of PFDA the increase for the 2009-2011 period is significantly less important than for the previous years.

It is quite surprising to see that PFOS concentration keeps increasing untill 2009 (from 102.77 pg/g in 2004 to 126.73 pg/g in 2009) despite its voluntary ban initiated by the 3M Company in 2000 (Bossi et al., 2015; Eriksson & Kärrman, 2015; Skaar, 2016). However, official regulations took action only in 2008 (EU Directive 2006/122/ECOF of the European Parliament). This plus the existence of precursor compounds (among which PFOSA) may explain why PFOS's concentration kept increasing until 2009. It would be interesting to do analyses on samples from 2010 to see what happened in-between, and samples from 2014 to see at what rate PFOS concentration would decrease in fishes living in a remote environment.

2. ii. Unconsidered parameters

Although the size of the fish was taken into account while selecting the samples, there is still some difference between the size of fishes over the years: fishes from 2007 and before were between 33.1 cm and 39.0 cm, with an average of 36.9 cm, while fishes from 2009 and later are much smaller (between 26.7 cm and 31.0 cm, with an average of 29.1 cm). The difference is quite clear from 2007 to 2009. However, fishes were about the same age in both period (7 years old when fished).

It is hard to tell whether this reduction in size is linked to the contamination of the population with PFAS or whether it is due to an external factor we aren't aware about. Examples of those factors could be food shortage or intraspecific competition (members of a same specie compete for limited ressources)[11].

3. Comparing the results with Bossi et al. 2014

In their paper, Bossi et al. analysed liver samples, while muscle samples were analysed in this paper.

Muscle tissues were chosen for analyses in this project because they are more representative of long-term expositions, while liver tissues are more suitable for recent exposition since it is the entrance to the body. Since the objective in this paper was to establish a time trend of PFAS in fishes from a same lake, it made more sense to do the analyses on muscle tissues. Plus, doing the analyses on muscle tissues let us avoid quantifying lipids.

The samples are in both cases Arctic chars, fished in 2011 and 2012. A difference of a factor 10 (approximately) appears for every compound, with my results showing the lower concentrations, as can be seen in Table 5.

Compound	Bossi et al. 2014	Present paper	Factor
	pg/g	pg/g	
PFOS	750.00	92.00	8.15
PFNA	280.00	30.67	9.13
PFDA	200.00	30.03	6.66
PFUnA	630.00	77.10	8.17
PFDoA	510.00	47.67	10.70
PFTrA	1570.00	134.60	11.66
PFTeA	1730.00	< LoQ (15.5)	N.A.

Table 5 Arctic char samples from 2011 analyses' results - *personnal document from* (Bossi et al., 2015)
LoQ for PFTeA was determined as 15.5 pg/g in the analyses

Since the analyses were not performed on the same tissues and taking all the problems that happened into account, it is hard to compare those numbers; data from liver samples from other similar fishes (ideally living in similar conditions) would allow verifying those results.

Still, the results are for the most part quite coherent; PFTrA is present in highest concentration, PFOS and PFUnA are present in lower concentration than PFTrA but higher than PFNA, PFDA and PFDoA.

The exact factor between the results ranges between 6.66 for PFDA and 11.66 for PFTrA. PFOS and PFUnA have really close factors (respectively 8.15 and 8.17) and quite similar concentrations, while PFNA and PFDA have really close concentrations (in my results) but different factors (respectively 9.13 and 6.66).

PFTeA is an exception; despite being detected in relatively high concentration in liver tissues by Bossi et al. in 2014, it turned out being detected in concentrations below the limits of quantification for this compound, which is 15.5 pg/g. That is over a hundred times lower than in 2014. However, the chromatograms for this specific compound looked correct in all three samples (Sa-056, Sa-058 and Sa-063) but the deviation of the high concentration standard related to the calibration curve was really high (79.6%). Despite such high deviation, the "concentration" of the analyte is still very low, so maybe PFTeA does not accumulate in muscle tissues? I would suggest redoing the analyses with fully operational instruments before drawing conclusions.

[11] Interspecific competition is less likely as the lake is isolated; it is quite unlikely that a new specie would emerge, although it is possible that another specie would see a large increase in population size. The abrupt difference between 2007 and 2009 is quite surprising thought.

Injection ID	Sample	PFBuS	PFHxS	PFOS	PFDS	PFOSA	PFBA	PFPeA	PFHxA	PFHpA
		pg/g	pg/g	pg/g	pg/g	pg/g	pg/g	pg/g	pg/g	pg/g
Sa-0074 31mar17	07-2001	n.d.	n.d.	#NOM?	n.d.	#N/A	n.d.	n.d.	n.d.	n.d.
Sa-0077 31mar17	07-2001	n.d.	n.d.	#NOM?	n.d.	#N/A	n.d.	n.d.	n.d.	n.d.
Sa-0081 31mar17	06-2001	n.d.	n.d.	#NOM?	n.d.	#N/A	n.d.	n.d.	n.d.	n.d.
Sa-0082 31mar17	07-2001	n.d.	n.d.	<LOQ*	n.d.	#N/A	n.d.	n.d.	n.d.	n.d.
Sa-0086 31mar17	07-2001	n.d.	n.d.	<LOQ*	n.d.	#N/A	n.d.	n.d.	n.d.	n.d.
Sa-0256 18april17	06-2011	n.d.	2.3	78.4	<LOQ*	<LOQ^{+}	#NOM?	n.d.	#NOM?	<LOQ*
Sa-0258 18april17	06-2011	n.d.	4.5	80.7	<LOQ*	2.3^{+}	#NOM?	n.d.	<LOQ*	<LOQ
Sa-0263 18april17	06-2011	n.d.	6.0	116.9	<LOQ*	<LOQw	#NOM?	n.d.	#NOM?	3.9
Sa-0099 20april17	07-2004	n.d.	<LOQ*	113.7	<LOQ*	20.2^{+}	#NOM?	n.d.	#NOM?	<LOQ
Sa-010-B 20april17	07-2004	n.d.	<LOQ	90.9w	<LOQ*w	16.8^{+}	#NOM?	n.d.	#NOM?	<LOQ*w
Sa-0105 20april17	07-2004	n.d.	<LOQ	103.7	<LOQ*	16.2^{+}	#NOM?	n.d.	#NOM?	<LOQ*
Sa-0195 04april17	07-2009	35.8*	n.d.	126.3	n.d.	13.6^{+}	823.5	<LOQ	2408.6*	<LOQ*
Sa-0196 04april17	07-2009	80.5*	n.d.	145.1	n.d.	<LOQ^{+}	1243.2w	886.2q	7863.2*w	<LOQw
Sa-0201 04april17	07-2009	40.8*	n.d.	108.8	n.d.	<LOQ^{+}	1047.8	435.6	2889.2*	<LOQ*
Sa-0176 06april17	07-2007	39.8*	n.d.	95.8	n.d.	<LOQw	478.0	33.8	491.2*	<LOQ*
Sa-0180 06april17	07-2007	91.3*	n.d.	95.8	n.d.	7.2w	352.8	113.6	706.0	<LOQ*
Sa-0183 06april17	07-2007	27.4*w	n.d.	122.5	n.d.	13.3w	237.5	23.1	340.0	<LOQ

Legend :	"w" : Recovery between 20-50 or 120-150; not always accepted
	"$^{+}$" : Recovery too low (<20% or >150%)
	"*" : Not confirmed by qualifier ion
	n.d. : Not detected

Injection ID	Date	PFOA	PFNA	PFDA	PFUnDA	PFDoDA	PFTrDA	PFTDA	PFHxDA	PFOcDA
		pg/g	pg/g	pg/g	pg/g	pg/g	pg/g	pg/g	pg/g	pg/g
Sa-0074 31mar17	07-2001	n.d.	#NOM?	10.7	30.8	13.7w	#NOM?	<LOQ*w	8.2w	65.7w
Sa-0077 31mar17	07-2001	n.d.	#NOM?	16.0w	46.1^{+}	<LOQ*$^{+}$	<LOQ*$^{+}$	<LOQ*$^{+}$	<LOQ*$^{+}$	<LOQ*$^{+}$
Sa-0081 31mar17	06-2001	n.d.	#NOM?	11.4	26.6w	13.8w	#NOM?	6.3w	20.0*w	<LOQw
Sa-0082 31mar17	07-2001	n.d.	<LOQ*$^{+}$	<LOQ^{+}	<LOQ*$^{+}$	<LOQ*$^{+}$	<LOQ*$^{+}$	<LOQ*$^{+}$	<LOQ*$^{+}$	<LOQ*$^{+}$
Sa-0086 31mar17	07-2001	n.d.	<LOQ*$^{+}$	<LOQ^{+}	<LOQ*$^{+}$	<LOQ*$^{+}$	<LOQ*$^{+}$	<LOQ*$^{+}$	<LOQ*$^{+}$	<LOQ*$^{+}$
Sa-0256 18april17	06-2011	6.5	26.8	26.5w	73.9w	51.3^{+}	151.5^{+}	<LOQ^{+}	38.5*$^{+}$	<LOQ^{+}
Sa-0258 18april17	06-2011	6.4*	35.6w	34.0w	99.2w	57.6^{+}	164.8^{+}	<LOQ^{+}	<LOQ^{+}	<LOQ*$^{+}$
Sa-0263 18april17	06-2011	14.1*	29.6	21.0w	58.2w	34.1^{+}	87.5^{+}	<LOQ^{+}	<LOQ*$^{+}$	<LOQ*$^{+}$
Sa-0099 20april17	07-2004	<LOQ*	27.8w	13.8w	42.9w	24.5^{+}	217.3^{+}	23.5*$^{+}$	<LOQ^{+}	<LOQ^{+}
Sa-010-B 20april17	07-2004	11.0*w	25.5w	12.0w	52.2w	25.5^{+}	126.4^{+}	<LOQ*$^{+}$	<LOQ*$^{+}$	<LOQ*$^{+}$
Sa-0105 20april17	07-2004	10.0*	<LOQ*w	13.3w	53.1w	28.9w	176.2w	14.2w	13.5*w	<LOQ*w
Sa-0195 04april17	07-2009	<LOQ*	49.1	27.1w	88.1w	50.8^{+}	264.1^{+}	36.7^{+}	67.1^{+}	183.2^{+}
Sa-0196 04april17	07-2009	<LOQ*	52.9	29.1	80.6w	41.6w	315.8w	44.1*w	<LOQw	124.4w
Sa-0201 04april17	07-2009	<LOQ*	30.1	23.1	71.7w	34.3^{+}	204.7^{+}	31.4^{+}	50.8*$^{+}$	87.6^{+}
Sa-0176 06april17	07-2007	7.4*	19.6*	16.2	52.3	28.3w	196.2w	<LOQw	19.7*w	44.8w
Sa-0180 06april17	07-2007	<LOQ*	25.9	15.9	63.5w	34.5^{+}	185.1^{+}	17.0^{+}	<LOQ^{+}	59.6^{+}
Sa-0183 06april17	07-2007	9.5*	34.6	20.5	74.3w	35.9^{+}	239.5^{+}	26.1^{+}	23.5*$^{+}$	59.2^{+}

Table 6 Fish analyses results - *personal document*

n.d. stands for Not Detected, #NOM? and #N/A mean that the Excel calculation sheet is fault

II. Analyses/Interpretations that could not be done

1. PFAS time trend related to precipitations

Unfortunately, most PFAS data collected are from 2007, 2009 and sometimes 2011, while the exploitable weather data are for the 2010-2014 period.

1. i. What would have been done with correct datasets

The "absolute" concentrations (i.e. the values measured in fishes) would probably not allow for easy observations and it is quite likely that it would have been more efficient to work on integrated values (i.e. the evolution from year x to year x+1).

The same thing would have been done with the weather data, so that it would be easy to see which year was the rainiest one.

Comparing those integrated values might have allowed seeing whether a rainier year would lead to a larger increase in PFAS concentration in the samples or not.

However, the observed general trends (see Graphs 4) tend to make me think it would probably not have been very concluding, as the concentrations are usually decreasing after 2011.

2. Lake water samples

Again, those samples could not be analysed due to technical issues (the LC pump should be changed in late June only).

Had they been analysed, it would have been interested to see whether the lakes from rainier areas tend to show higher PFAS concentrations or whether those two factors are not related in any way.

Of course, having samples for only one year, no exact conclusion would have been drawn, but those results could potentially have lead to further studies?

CONCLUSION

Keeping in mind that this is based on somewhat unreliable results, this project showed that the concentrations of most of the 18 analysed PFAS in a population of Arctic Chars from a remote lake in the Faroe Islands kept increasing until around 2009 before generally decreasing in 2011. Two exceptions are PFDA and PFTDA; their respective concentration keeps increasing in 2011, thought much less than in 2009.

Unfortunately, due to technical issues detailed in this paper, all of the analyses could not be performed. Therefore, it was not possible to link PFAS concentration in either fish samples or in lake water samples with meteorological data.

If this project was to be continued, I would suggest redoing all of the fish analyses as they were not performed in ideal conditions. It might be a good idea to verify the calibration curve, as it was done taking all peak tails into account.

Comparing the general PFAS trend in the arctic chars with similar specie in a similar environment would help confirming the results. PFAS behaviour in both species would have to be identical as some species will degrade some compounds in different ways than some other species.

However, I would not recommend working on the precipitation-concentration relations in Lake Á Mýrunum; the lack of meteorological data would make it too clunky to draw any conclusion. Gathering lake water samples over the years from the different lakes selected in this project and observing the PFAS contamination's evolution would probably turn out more conclusive.

This master project taught me to search for relations between different phenomena that, at first sight, appear not to be related (e.g. precipitations with contamination in a lake) and to think about possible external factors.

It also forced me to try and learn things by myself; R and R Studio turned out being really practical programs and when looking back at some of the work performed for this project I realise I would have saved a lot of time if working with R instead of Excel and Visual Basic. Nonetheless, R and R Studio still have their limits and I found that the most effective was to mix R/R Studio and Excel and exploit their respective strengths, rather than sticking to one program.

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ANNEXES

1. More precise maps of the sampling sites

Annexe 1 Á Mýrunum - (Umhvorvisstovan, n.d.)

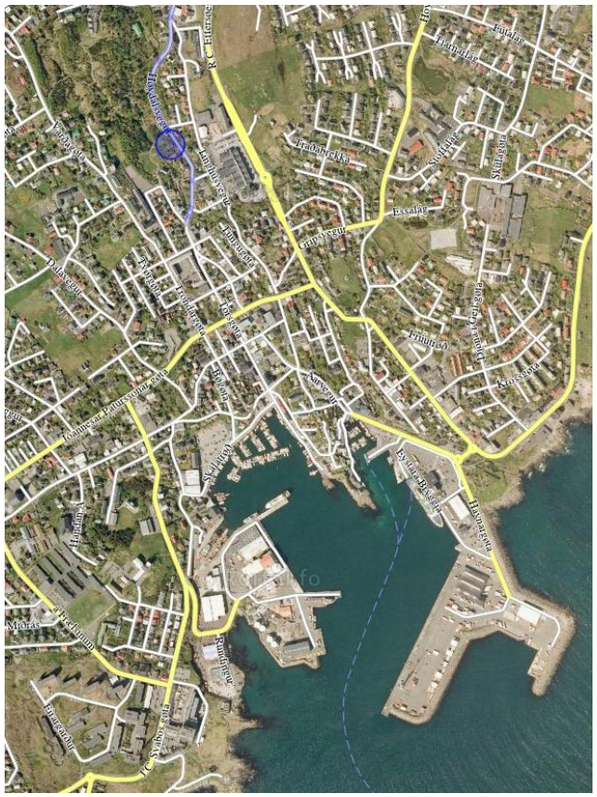
Annexe 2 Sørvagsvatn - (Umhvorvisstovan, n.d.)

Annexe 3 From left to right: Reiðskarð, Havnadal and Villingadelsvatn - (Umhvorvisstovan, n.d.)

Annexe 4 Reynsmúli - (Umhvorvisstovan, n.d.)

Annexe 5 Lítluvatn - (Umhvorvisstovan, n.d.)

Annexe 6 Kollafjørður - (Umhvorvisstovan, n.d.)



Annexe 7 Hoydalsvegur - (Umhvorvisstovan, n.d.)

2. R codes

All codes were adjusted with the correct file names and paths; some fields are variable and may not be corresponding from one code to another in those Annexes.

```r
# Set database path
repIN <- setwd("C:/Users/Axel/Desktop/Ecole/ULg2/Mémoire/Importance sexe C")
mesdonnees = read.csv("PCB_SA.csv",sep = ",", header = FALSE, stringsAsFactors = FALSE)

# Save graphs in pdf file
pdf("graphs Arctic chars.pdf",5,5)

a <- nrow(mesdonnees)
for (ligne in c(1:a)) {

# Set csv path: x = csv name / y = csv path
x = mesdonnees[,1]
y = mesdonnees[,2]

repIN <- setwd(y[ligne])
tableau = read.csv(x[ligne],sep = ",", header = TRUE, stringsAsFactors = TRUE)

    # Select data depending on year and sex
    annee <- factor(tableau$Year)

            #save Coefficients in a .txt file
            nomPCB <- x[ligne]
            nom <- substr(nomPCB, nchar(nomPCB)-6,nchar(nomPCB)-4)
            nomfichier <- paste("coefficients ", nom, ".txt", sep = "")
            cat("annee", "\t", "Intercept", "\t", "Slope", "\n", file = "nomfichier.txt", sep = "")

    for (an in levels(annee)) {
    selection <- tableau[which(tableau$Year == an),]
        plot(selection[,3],selection[,5],type="n",main = paste(names(tableau[5]), an), xlab = "Length - cm",
             ylab = "Concentration - µg/kg lw")
    selectionmale <- tableau[which(tableau$Sex == "male" & tableau$Year == an),]
    selectionfemale <- tableau[which(tableau$Sex == "female" & tableau$Year == an),]

        # Linear regression, add PCB conc and reg lines to graphs
    male <- lm(selectionmale[,5]~selectionmale[,3], selectionmale)
        points(selectionmale[,3],selectionmale[,5],col = "blue")
        lines(selectionmale[,3],male$fitted,col = "blue")

    female <- lm(selectionfemale[,5]~selectionfemale[,3], selectionfemale)
        points(selectionfemale[,3],selectionfemale[,5],col = "red")
        lines(selectionfemale[,3],female$fitted,col = "red")

cat(an, "\t", male$coefficients[1], "\t",male$coefficients[2], "\n", "\t", female$coefficients[1], "\t",
    female$coefficients[2], "\n", file = nomfichier, append = "TRUE",sep = "")
    }
}
dev.off()
```

47:10 (Top Level)

Annexe 8 R code used to trace the linear regressions to observe the possible impact of fishes' sex on contamination
- personal document

```r
setwd("C:/Users/Axel/Desktop/Ecole/ULg2/Mémoire/Results/Quantif")
data = read.csv("quantif.csv", sep = ";", dec = ".", header = T,stringsAsFactors = F)
avg <- data[1:5,-1]
avg <- avg[,-5]

alldata <- data[10:26,-6]

pdf("time trends.pdf")
par(mfrow = c(2,2))

for (i in 3:19){
plot(x = avg$Date,y = avg[,i], type = "b", main = colnames(avg[i]),xlab = "years",ylab = "pg/g",pch = 16)
points(x = alldata$Date, y = alldata[,i],pch = 16, col = "grey")
}

dev.off
```

Annexe 9 R code used to obtain the time-trend plots with the PFAS results from Annexe 14
- personal document

```r
setwd("C:/Users/Axel/Desktop/Ecole/ULg2/Mémoire/study plan/Meteo data/Hog")
require("stringr")

donnees2010 <- data.frame(Date.and.time = as.character(), rainint = as.numeric())

for (x in 1:12) {
      nom <- paste("2010",str_pad(x,2, pad = "0"), ".txt", sep = "")
      mesdonnees = read.table(nom,sep = "\t", header = TRUE, stringsAsFactors = FALSE,dec = ",")
      while(mesdonnees[nrow(mesdonnees),1] == "") {mesdonnees <- mesdonnees[-nrow(mesdonnees),]}

      long <- nrow(mesdonnees) - 3
      mesdonnees <- subset(mesdonnees[1:long,])

      c <- colnames(mesdonnees)
      ifelse("rainint" %in% c == TRUE, "cond" <- 1,"cond" <- 2)

      # if cond = 2: no column "Rainint" -> NA
      if (cond == 2) {donnees2010 <- rbind(donnees2010, data.frame(Date = mesdonnees$Date.and.time, rainint = NA))}

      # if cond = 1: column "Rainint" -> check its value (columns are sometimes mixed up...)
      if (cond == 1) {
            a <- 0
            for (i in 1:nrow(mesdonnees)) {
              ifelse(mesdonnees$rain[i] == 0 && mesdonnees$rainint[i] != 0,a <- a +1, a <- a)
            }
            # if "rainint" = 0 when "rain" = 0 -> probably the good column
            if (a == 0) {
              donnees2010 <- rbind(donnees2010, data.frame(Date = mesdonnees$Date.and.time, rainint = mesdonnees$rainint))
            }
            # if "rainint" =/= 0 when "rain" = 0 -> check rainint average (rain may not be detected when low intensity)
            if (a != 0 && mean(as.numeric(na.omit(mesdonnees$rainint))) < 100) {
              donnees2010 <- rbind(donnees2010, data.frame(Date = mesdonnees$Date.and.time, rainint = mesdonnees$rainint))
            } else {
              donnees2010 <- rbind(donnees2010, data.frame(Date = mesdonnees$Date.and.time, rainint = mesdonnees[,11]))
            }
      }
}
# Default: col.names = TRUE, append = FALSE (it'll overwrite any previous table, no confirmation required !!!)
write.table(donnees2010,"donnees2010.txt", sep = "\t",row.names = FALSE)
```

39:73 (Top Level)

Annexe 10 R code used to sort out the meteorological data from the .csv and .txt files from Landversk - *personal document*

```r
setwd("C:/Users/Axel/Desktop/Ecole/ULg2/Mémoire/study plan/Meteo data/Hog")
mesdonnees = read.table("donnees2006.txt",sep = "\t", header = TRUE, stringsAsFactors = FALSE)
names(mesdonnees) <- c("time","value")
require('dplyr')
require('xts')
require('lubridate')
mesdonnees <- mesdonnees %>% distinct(time, .keep_all = TRUE)

xtsdata <- xts(mesdonnees$value, order.by = as.POSIXct(mesdonnees$time, tz = "GMT", format = "%d-%m-%Y %H:%M"))

mon_avg <- apply.monthly(xtsdata,mean)
mon_tot <- mon_avg

for (i in 1:length(mon_avg)) {
  mon_tot[i,] <- round(mon_avg[i,] * 24 * days_in_month(mon_avg[i,]),1)
}

avg <- mean(mon_tot)
std <- sd(mon_tot)
for (i in 1:length(mon_tot)) {
  if (mon_tot[i,] > (avg + 2*std) | mon_tot[i,] < (avg - 2*std)) {
    mon_tot[i,] <- NA
  }
}

write.zoo(mon_tot, "monthly totals 2006.txt", sep = "\t", index.name = "Date")

r2006 = read.table("monthly totals 2006.txt",sep = "\t", header = TRUE, stringsAsFactors = FALSE)
names(r2006) <- c("time","value")
r2007 = read.table("monthly totals 2007.txt",sep = "\t", header = TRUE, stringsAsFactors = FALSE)
names(r2007) <- c("time","value")
r2008 = read.table("monthly totals 2008.txt",sep = "\t", header = TRUE, stringsAsFactors = FALSE)
names(r2008) <- c("time","value")
r2009 = read.table("monthly totals 2009.txt",sep = "\t", header = TRUE, stringsAsFactors = FALSE)
names(r2009) <- c("time","value")

r2006_2009 <- rbind(r2006, r2007, r2008, r2009)
xtsdata <- xts(r2006_2009$value, order.by = as.POSIXct(substr(r2006_2009$time,1,10), tz = "GMT", format = "%Y-%m-%d"))
write.zoo(xtsdata, "monthly totals 2006-2009.txt", sep = "\t", index.name = "Date")
```

39:84 (Top Level)

Annexe 11 R codes for plotting the precipitations, based on the .txt file obtained from Annexe 10's code. The second part of this code (after line 26) was used to gather data for the 2006-2009 period - *personal document*

3. R code validation - Importance of fishes' sex

PCB 153					
Year		Intercept	Slope	R regression equation	Excel regression equation
2000	Males	-319.062	9.784	y = 9.784x - 319.062	y = 9.784x - 319.06
	Females	-221.970	6.824	y = 6.8237x - 221.9703	y = 6.8237x - 221.97
2001	Males	23.000	NA		
	Females	-655.722	19.124	y = 19.1242x - 655.7223	
2002	Males	-278.892	8.868	y = 8.8681x - 278.8917	y = 8.8681x - 278.89
	Females	-649.496	19.306	y = 19.3061x - 649.4963	y = 19.306x - 649.5
2004	Males	-362.559	11.367	y = 11.3665x - 362.5592	y = 11.366x - 362.56
	Females	-1012.457	28.605	y = 28.6047x - 1012.457	
2005	Males	-353.898	10.879	y = 10.8793x - 353.8978	y = 10.879x - 353.9
	Females	-419.760	13.335	y = 13.3349x - 419.7601	y = 13.335x - 419.76
2007	Males	-159.278	5.944	y = 5.9444x - 159.2778	y = 5.9444x - 159.28
	Females	-334.158	10.363	y = 10.3628x - 334.1581	
2009	Males	20.839	-0.246	y = -0.2458x + 20.8386	y = -0.2458x + 20.839
	Females	-11.179	0.929	y = 0.9293x - 11.1786	y = 0.9293x - 11.18
2010	Males	180.664	-4.857	y = -4.8574x + 180.6637	y = -4.8574x + 180.66
	Females	181.122	-5.068	y = -5.0684x + 181.1221	y = -5.0684x + 181.12
2012	Males	-460.001	22.595	y = 22.5947x - 460.001	y = 22.595x - 460
	Females	-60.624	5.583	y = 5.5827x - 60.6239	y = 5.5827x - 60.624
2014	Males	-13.442	1.572	y = 1.5717x - 13.4422	y = 1.5717x - 13.442
	Females	-75.274	3.874	y = 3.8737x - 75.274	y = 3.8737x - 75.274
PCB 28					
Year		Intercept	Slope		
2000	Males	5.894	0.077	y = 0.0767x + 5.8943	y = 0.0767x + 5.8943
	Females	-22.750	0.800	y = 0.7997x - 22.7504	y = 0.7997x - 22.75
2001	Males	5.900	NA		
	Females	-98.022	2.889	y = 2.889x - 98.0217	y = 2.889x - 98.022
2002	Males	-79.533	2.450	y = 2.4498x - 79.5333	y = 2.4498x - 79.533
	Females	-284.857	8.326	y = 8.3261x - 284.857	y = 8.3261x - 284.86
2004	Males	-1021.662	30.315	y = 30.3153x - 1021.662	y = 30.315x - 1021.7
	Females	-540.771	15.698	y = 15.6977x - 540.7713	
2005	Males	-177.269	5.972	y = 5.9719x - 177.2693	y = 5.9719x - 177.27
	Females	-81.887	2.786	y = 2.7862x - 81.8872	y = 2.7862x - 81.887
2007	Males	-160.000	5.000	y = 5x - 160	y = 5x - 160
	Females	-114.186	3.721	y = 3.7209x - 114.186	
2009	Males	142.476	-3.513	y = -3.5126x + 142.476	y = -3.5126x + 142.48
	Females	129.402	-3.136	y = -3.1356x + 129.4019	y = -3.1356x + 129.4
2010	Males	285.991	-7.602	y = -7.6019x + 285.9914	y = -7.6019x + 285.99
	Females	312.318	-8.748	y = -8.7479x + 312.3183	y = -8.7479x + 312.32
2012	Males	-215.010	11.946	y = 11.9465x - 215.0099	y = 11.946x - 215.01
	Females	67.040	1.755	y = 1.7547x + 67.0402	y = 1.7547x + 67.04
2014	Males	2.523	0.771	y = 0.7707x + 2.5228	y = 0.7707x + 2.5228
	Females	-24.937	1.759	y = 1.7591x - 24.9369	y = 1.7591x - 24.937

Annexe 12 Regression coefficients for PCBs 153 and 28 from R and MS Excel 2007

4. Some data

monthly totals 2006-2009.txt | monthly totals 2010-2014.txt

1	2006-03-31	NA
2	2006-04-28	NA
3	2006-05-30	NA
4	2006-07-31	NA
5	2006-08-31	NA
6	2006-09-30	NA
7	2006-10-31	NA
8	2006-11-30	3055
9	2006-12-31	1793.6
10	2007-02-28	946.1
11	2007-03-31	NA
12	2007-04-30	2447.3
13	2007-05-31	1478.4
14	2007-06-30	173.1
15	2007-07-31	912.4
16	2007-08-31	2122.5
17	2007-09-30	2752.8
18	2007-10-30	2290.9
19	2007-11-30	1754.3
20	2007-12-31	1821.3
21	2008-02-29	2239.4
22	2008-03-31	1886.2
23	2008-04-30	698.7
24	2008-05-31	738.2
25	2008-06-30	1804.2
26	2008-07-31	1356.8
27	2008-08-31	1967.8
28	2008-09-30	1834.1
29	2008-10-31	NA
30	2008-11-30	1613.2
31	2008-12-31	1873.3
32	2009-03-31	2029.7
33	2009-04-30	1626.9
34	2009-05-31	1778.4
35	2009-06-30	668.6
36	2009-07-31	575.1
37	2009-08-31	2155.1
38	2009-09-30	3188.2
39	2009-10-31	2355.7
40	2009-11-30	3023.7
41	2009-12-31	895.6
42		

monthly totals 2006-2009.txt | monthly totals 2010-2014.txt

1	2010-01-31	148.5
2	2010-02-28	132.8
3	2010-03-31	181
4	2010-04-30	241.6
5	2010-05-31	112.5
6	2010-06-30	165.9
7	2010-07-28	247.6
8	2010-08-17	NA
9	2010-09-30	176.8
10	2010-10-31	224.6
11	2010-11-30	187.1
12	2010-12-31	26
13	2011-01-31	114.6
14	2011-02-28	129
15	2011-03-31	210.5
16	2011-04-30	245.1
17	2011-05-31	239.3
18	2011-06-30	264
19	2011-07-31	177.8
20	2011-08-31	383.1
21	2011-09-30	205.7
22	2011-10-31	408
23	2011-11-30	299.6
24	2011-12-31	582.9
25	2012-01-31	315.2
26	2012-02-29	287.3
27	2012-03-31	215
28	2012-04-30	103.9
29	2012-05-31	206.9
30	2012-06-30	41
31	2012-07-31	88.7
32	2012-08-31	136.4
33	2012-09-30	320.1
34	2012-10-31	171.4
35	2012-11-30	249.7
36	2012-12-31	172.7
37	2013-01-31	204.1
38	2013-02-28	111.6
39	2013-03-31	46.7
40	2013-04-30	95.7
41	2013-05-31	84
42	2013-06-30	151

Annexe 13 Meteorological data; monthly totals for the 2006-2009 and 2010-2014 periods - *personal document*

	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P	Q	R	S	T
1	Injection ID	Date	PFBuS	PFHxS	PFOS	PFDS	PFOSA	PFBA	PFPeA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnDA	PFDoDA	PFTrDA	PFTDA	PFHxDA	PFOcDA
2	average	2001												12.7	34.5	13.75			14.1	65.7
3	average	2004			102.77		17.73					10.5	26.65	13.03	49.4	26.3	173.3	18.85	13.5	
4	average	2007	52.83		104.7		10.25	356.1	56.83	512.4		8.45	26.7	17.53	63.37	32.9	206.93	21.55	21.6	54.53
5	average	2009	52.37		126.73		13.6	1038.17	660.9	4387			44.03	26.43	80.13	42.23	261.53	37.4	58.95	131.73
6	average	2011		4.27	92		2.3				3.9	9	30.67	27.17	77.1	47.67	134.6		38.5	
7																				
8																				
9																				
10																				
11	Sa-0074 3	2001												10.7	30.8	13.7			8.2	65.7
12	Sa-008131	2001												11.4	26.6	13.8		6.3w	20	
13	Sa-0077 3	2001												16	46.1					
14	Sa-0082 3	2001																		
15	Sa-0086 3	2001																		
16	Sa-0093 2	2004			113.7		20.2						27.8	13.8	42.9	24.5	217.3	23.5		
17	Sa-010-B 2	2004			90.9		16.8					11	25.5	12	52.2	25.5	126.4			
18	Sa-0105 2	2004			103.7		16.2					10		13.3	53.1	28.9	176.2	14.2	13.5	
19	Sa-0176 0	2007	39.8		95.8			478	33.8	491.2		7.4	19.6	16.2	52.3	28.3	196.2		19.7	44.8
20	Sa-0180 0	2007	31.3		95.8		7.2	352.8	113.6	706			25.9	15.9	63.5	34.5	185.1	17		59.6
21	Sa-0183 0	2007	27.4		122.5		13.3	237.5	23.1	340		9.5	34.6	20.5	74.3	35.9	239.5	26.1	23.5	59.2
22	Sa-0195 0	2009	35.8		126.3		13.6	823.5		2408.6			49.1	27.1	88.1	50.8	264.1	36.7	67.1	183.2
23	Sa-0196 0	2009	80.5		145.1			1243.2	886.2	7863.2			52.9	29.1	80.6	41.6	315.8	44.1		124.4
24	Sa-020104	2009	40.8		108.8			1047.8	435.6	2889.2			30.1	23.1	71.7	34.3	204.7	31.4	50.8	87.6
25	Sa-0256 1	2011		2.3	78.4							6.5	26.8	26.5	73.9	51.3	151.5		38.5	
26	Sa-0258 1	2011		4.5	80.7		2.3					6.4	35.6	34	93.2	57.6	164.8			
27	Sa-0263 1	2011		6	116.9						3.9	14.1	29.6	21	58.2	34.1	87.5			

Annexe 14 MS Excel .csv document with all quantification results - *personal document*

	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P	Q	R	S	T
1			PFBuS	PFHxS	PFOS	PFDS	PFOSA	PFBA	PFPeA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnDA	PFDoDA	PFTrDA	PFTDA	PFHxDA	PFOcDA
2	Injection ID	Date	pg/g	pg/g	pg/g	pg/g	pg/g	pg/g	pg/g	pg/g	pg/g	pg/g	pg/g	pg/g	pg/g	pg/g	pg/g	pg/g	pg/g	pg/g
3																				
4	Sa-0074 31mar17	07-2001	n.d.	n.d.	#NOM?	n.d.	#N/A	n.d.	n.d.	n.d.	n.d.	n.d.	#NOM?	10.7	30.8	13.7w	#NOM?	<LOQ*w	8.2w	65.7w
5	Sa-0081 31mar17	06-2001	n.d.	n.d.	#NOM?	n.d.	#N/A	n.d.	n.d.	n.d.	n.d.	n.d.	#NOM?	11.4	26.6w	13.8w	#NOM?	6.3w	20.0*w	<LOQw
6	Sa-0077 31mar17	07-2001	n.d.	n.d.	#NOM?	n.d.	#N/A	n.d.	n.d.	n.d.	n.d.	n.d.	#NOM?	16.0w	46.1*	<LOQ**	<LOQ**	<LOQ**	<LOQ**	<LOQ**
7	Sa-0082 31mar17	07-2001	n.d.	n.d.	<LOQ*	n.d.	#N/A	n.d.	n.d.	n.d.	n.d.	n.d.	<LOQ**	<LOQ*	<LOQ**	<LOQ**	<LOQ**	<LOQ**	<LOQ**	<LOQ**
8	Sa-0086 31mar17	07-2001	n.d.	n.d.	<LOQ*	n.d.	#N/A	n.d.	n.d.	n.d.	n.d.	n.d.	<LOQ**	<LOQ*	<LOQ**	<LOQ**	<LOQ**	<LOQ**	<LOQ**	<LOQ**
9																				
10	Sa-0099 20april17	07-2004	n.d.	<LOQ*	113.7	<LOQ*	20.2*	#NOM?	n.d.	#NOM?	<LOQ	<LOQ*	27.8w	13.8w	42.9w	24.5*	217.3*	23.5**	<LOQ*	<LOQ*
11	Sa-010-B 20april17	07-2004	n.d.	<LOQ	90.9w	<LOQ*w	16.8*	#NOM?	n.d.	#NOM?	<LOQ*w	11.0*w	25.5w	12.0w	52.2w	25.5*	126.4*	<LOQ**	<LOQ**	<LOQ**
12	Sa-0105 20april17	07-2004	n.d.	<LOQ	103.7	<LOQ*	16.2*	#NOM?	n.d.	#NOM?	<LOQ*	10.0*	<LOQ*w	13.3w	53.1w	28.9w	176.2w	14.2w	13.5*w	<LOQ*w
13																				
14	Sa-0176 06april17	07-2007	39.8*	n.d.	95.8	n.d.	<LOQw	478.0	33.8	491.2*	<LOQ*	7.4*	19.6*	16.2	52.3	28.3w	196.2w	<LOQw	19.7*w	44.8w
15	Sa-0180 06april17	07-2007	91.3*	n.d.	95.8	n.d.	7.2w	352.8	113.6	706.0	<LOQ*	<LOQ*	25.9	15.9	63.5w	34.5*	185.1*	17.0*	<LOQ*	59.6*
16	Sa-0183 06april17	07-2007	27.4*w	n.d.	122.5	n.d.	13.3w	237.5	23.1	340.0	<LOQ	9.5*	34.6	20.5	74.3w	35.9*	239.5*	26.1*	23.5**	59.2*
17																				
18	Sa-0195 04april17	07-2009	35.8*	n.d.	126.3	n.d.	13.6*	823.5	<LOQ	2408.6*	<LOQ*	<LOQ*	49.1	27.1w	88.1w	50.8*	264.1*	36.7*	67.1*	183.2*
19	Sa-0196 04april17	07-2009	80.5*	n.d.	145.1	n.d.	<LOQ*	1243.2w	886.2q	7863.2*w	<LOQw	<LOQ*	52.9	29.1	80.6w	41.6w	315.8w	44.1*w	<LOQw	124.4w
20	Sa-0201 04april17	07-2009	40.8*	n.d.	108.8	n.d.	<LOQ*	1047.8	435.6	2889.2*	<LOQ*	<LOQ*	30.1	23.1	71.7w	34.3*	204.7*	31.4*	50.8**	87.6*
21																				
22	Sa-0256 18april17	06-2011	n.d.	2.3	78.4	<LOQ*	<LOQ*	#NOM?	n.d.	#NOM?	<LOQ*	6.5	26.8	26.5w	73.9w	51.3*	151.5*	<LOQ*	38.5**	<LOQ*
23	Sa-0258 18april17	06-2011	n.d.	4.5	80.7	<LOQ*	2.3*	#NOM?	n.d.	<LOQ*	<LOQ	6.4*	35.6w	34.0w	99.2w	57.6*	164.8*	<LOQ*	<LOQ*	<LOQ**
24	Sa-0263 18april17	06-2011	n.d.	6.0	116.9	<LOQ*	<LOQw	#NOM?	n.d.	#NOM?	3.9	14.1*	29.6	21.0w	58.2w	34.1*	87.5*	<LOQ*	<LOQ**	<LOQ**

Summary:

Mark:	Meaning:	Used in further calculations?
n.a.	Not analyzes	No
n.d.	No peak detected	No
<LOQ	Below LOQ	No
<LOQ"	Below LOQ" calculated as: blank conc. × 3 × Std Dev	No
*	Not confirmed by qualifier ion	No
+	Recovery too low (< 20 %) or too high (> 150 %)	No
‡ (is "w" in the spreadsheet)	Recovery reliable, between 20 – 50 % or 120 – 150 %	Yes

Annexe 15 All PFAS quantifications, with annotations and legend

V	W	X	Y	Z	AA	AB	AC	AD	AE	AF	AG	AH	AI
		C13PFHxS	C13PFOS	ISPFOSA	C13PFBA	C13PFHxA	C13PFOA	C13PFNA	C13PFDA	C13PFUnDA	C13PFDoDA	C13M8PFOA	C13M8PFOS
Injection ID	Date	%Rec	%Rec	%Rec	%Rec	%Rec	%Rec	%Rec	%Rec	%Rec	%Rec	%Rec	%Rec
Sa-0074 31m	07-2001	185.4	120.8	#N/A	131.1	116.7	125.1	79	83.6	69.3	41.1	27.5	38.4
Sa-0081 31m	06-2001	126.4	75.9	#N/A	71.3	79.2	79.1	44.4	24.6	8.3	0	47.5	73.9
Sa-0077 31m	07-2001	132.8	89.7	#N/A	73.7	80.2	76.6	65.9	58.2	45.2	20.5	50.2	94.6
Sa-0082 31m	07-2001	31.4	50.1	#N/A	1805.2	634	133.2	3361.1	1272.3	4798.3	7586.7	0	0
Sa-0086 31m	07-2001	31.4	50.1	#N/A	1805.2	634	133.2	3361.1	1272.3	4798.3	7586.7	0	0
Sa-0099 20a	07-2004	82.1	57.5	18.3	56.8	61.1	60.1	56	44.1	29	11.5	56.2	90.9
Sa-010-B 20a	07-2004	79.8	52.7	17.8	50.5	55.9	53.3	48.5	37.2	23.4	9.2	52.8	89
Sa-0105 20a	07-2004	86.9	62.6	20.4	60.3	65.4	61.8	61.3	49.3	33.8	13.9	60	91.2
Sa-0176 06a	07-2007	76.5	54	7	45.8	51.7	55.2	36.8	40.1	27.2	17.7	51.7	50.8
Sa-0180 06a	07-2007	51.5	40.5	13.6	39.8	39.7	41	33.9	32.7	27.3	14.8	65.7	81
Sa-0183 06a	07-2007	78	60.8	14.3	48.6	53.6	51.2	33.3	38.2	39.5	27.9	58.2	73.1
Sa-0195 04a	07-2009	84.8	55.6	9.5	53	58.5	54.5	52.3	40	26	13.7	50.6	62.4
Sa-0196 04a	07-2009	80.8	59.4	6.2	42.1	49.9	58.4	50.5	55.1	37.5	23.7	49	42.7
Sa-0201 04a	07-2009	114.3	72.2	12.8	55.9	67.4	73	60.3	50.9	28.2	18.5	49.2	61.9
Sa-0256 18a	06-2011	83.6	67.4	20.8	60.7	62.5	67.5	63.7	63.1	55.6	30.3	67.5	86.3
Sa-0258 18a	06-2011	98	65	25.9	52.3	68.3	67.3	59.3	54.4	37.6	19.3	50.4	63.6
Sa-0263 18a	06-2011	135.2	86.6	25	84.6	91.7	82.7	83.4	66.1	41.4	17.9	49.3	71.5

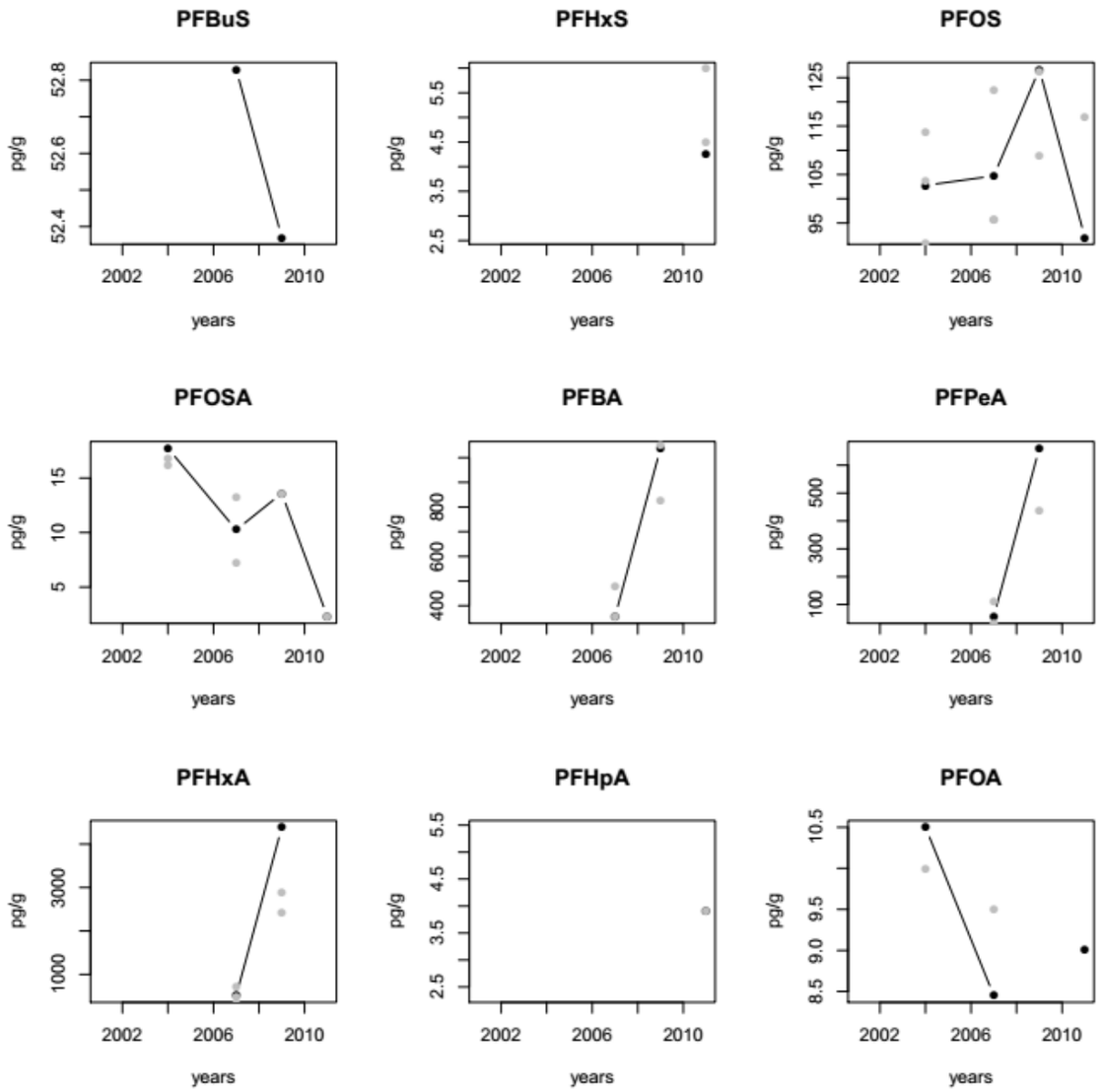
Annexe 16 Recovery rates for all performed analyses - *personal document*

AK	AL	AM	AN	AO	AP	AQ	AR	AS	AT	AU	AV	AW	AX	AY	AZ	BA	BB	BC	BD
		PFBuS	PFHxS	PFOS	PFDS	#N/A	PFBA	PFPeA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnDA	PFDoDA	PFTrDA	PFTDA	PFHxDA	PFOcDA
		LOQ/g	LOQ/g	LOQ/g	LOQ/g	#N/A	LOQ/g	LOQ/g	LOQ/g	LOQ/g	LOQ/g	LOQ/g	LOQ/g	LOQ/g	LOQ/g	LOQ/g	LOQ/g	LOQ/g	LOQ/g
2001	mean	n.d.	n.d.	#NOM?	n.d.	#N/A	n.d.	n.d.	n.d.	n.d.	n.d.	#NOM?	1.3	1.7	18754.9	#NOM?	23261	2.7	17.5
	median	n.d.	n.d.	#NOM?	n.d.	#N/A	n.d.	n.d.	n.d.	n.d.	n.d.	#NOM?	1.2	0	4.7	#NOM?	30336.3	0	0
	min	n.d.	n.d.	#NOM?	n.d.	#N/A	n.d.	n.d.	n.d.	n.d.	n.d.	#NOM?	0	0	0	#NOM?	6	0	0
	max			#NOM?		#N/A						#NOM?	3.6	8.4	46883.2	#NOM?	55619.9	7.4	59.5
	stdev			#NOM?		#N/A						#NOM?	#NOM?	#NOM?	#NOM?	#NOM?	#NOM?	#NOM?	#NOM?
	%RSD	n.d.	n.d.	#NOM?	n.d.	#N/A	n.d.	n.d.	n.d.	n.d.	n.d.	#NOM?	#NOM?	#NOM?	#NOM?	#NOM?	#NOM?	#NOM?	#NOM?
2004-2011	mean	n.d.	9.4	18.6	7.4	7.7	#NOM?	n.d.	#NOM?	14.9	6	14	3.8	2.9	10.8	7.5	15.5	30.5	51.7
	median	n.d.	4.9	10.4	7.3	6.6	#NOM?	n.d.	#NOM?	7.7	4	10.6	3.6	3	7.9	7.2	15.9	29.6	54.1
	min	n.d.	0.3	4.3	0	1.4	#NOM?	n.d.	#NOM?	2.4	1.8	4.4	2.6	0.9	3.7	4.3	10.3	9.6	15.7
	max		33.6	42	14	17.8	#NOM?		#NOM?	42.3	16.9	27.6	6.3	4.3	21.6	11.4	20.3	55.8	88.4
	stdev		#NOM?	#NOM?	#NOM?	#NOM?	#NOM?		#NOM?	#NOM?	#NOM?	#NOM?	#NOM?	#NOM?	#NOM?	#NOM?	#NOM?	#NOM?	#NOM?
	%RSD	n.d.	#NOM?	#NOM?	#NOM?	#NOM?	#NOM?	n.d.	#NOM?	#NOM?	#NOM?	#NOM?	#NOM?	#NOM?	#NOM?	#NOM?	#NOM?	#NOM?	#NOM?
2007-2009	mean	15.3	n.d.	14.4	n.d.	9.8	18.9	47.9	13.5	23.2	9.2	10.7	4.2	2.4	9.1	6.9	16.2	29.5	32.4
	median	10.5	n.d.	14.2	n.d.	7.4	0.9	30.8	0	16.6	8.5	8.9	3.4	1.7	7.3	6.8	13.9	12.9	33.5
	min	5.6	n.d.	8	n.d.	2.2	0.8	19.7	0	5.5	1	3.9	1.7	0	4.6	3.5	10.9	0	7.2
	max	37.8		21.1		21.2	109	150.1	80.7	74.1	26.2	21.9	8	7.1	18.8	9.4	24.1	78.4	54.3
	stdev	#NOM?		#NOM?		#NOM?	#NOM?	#NOM?	#NOM?	#NOM?	#NOM?	#NOM?	#NOM?	#NOM?	#NOM?	#NOM?	#NOM?	#NOM?	#NOM?
	%RSD	#NOM?	n.d.	#NOM?	n.d.	#NOM?	#NOM?	#NOM?	#NOM?	#NOM?	#NOM?	#NOM?	#NOM?	#NOM?	#NOM?	#NOM?	#NOM?	#NOM?	#NOM?

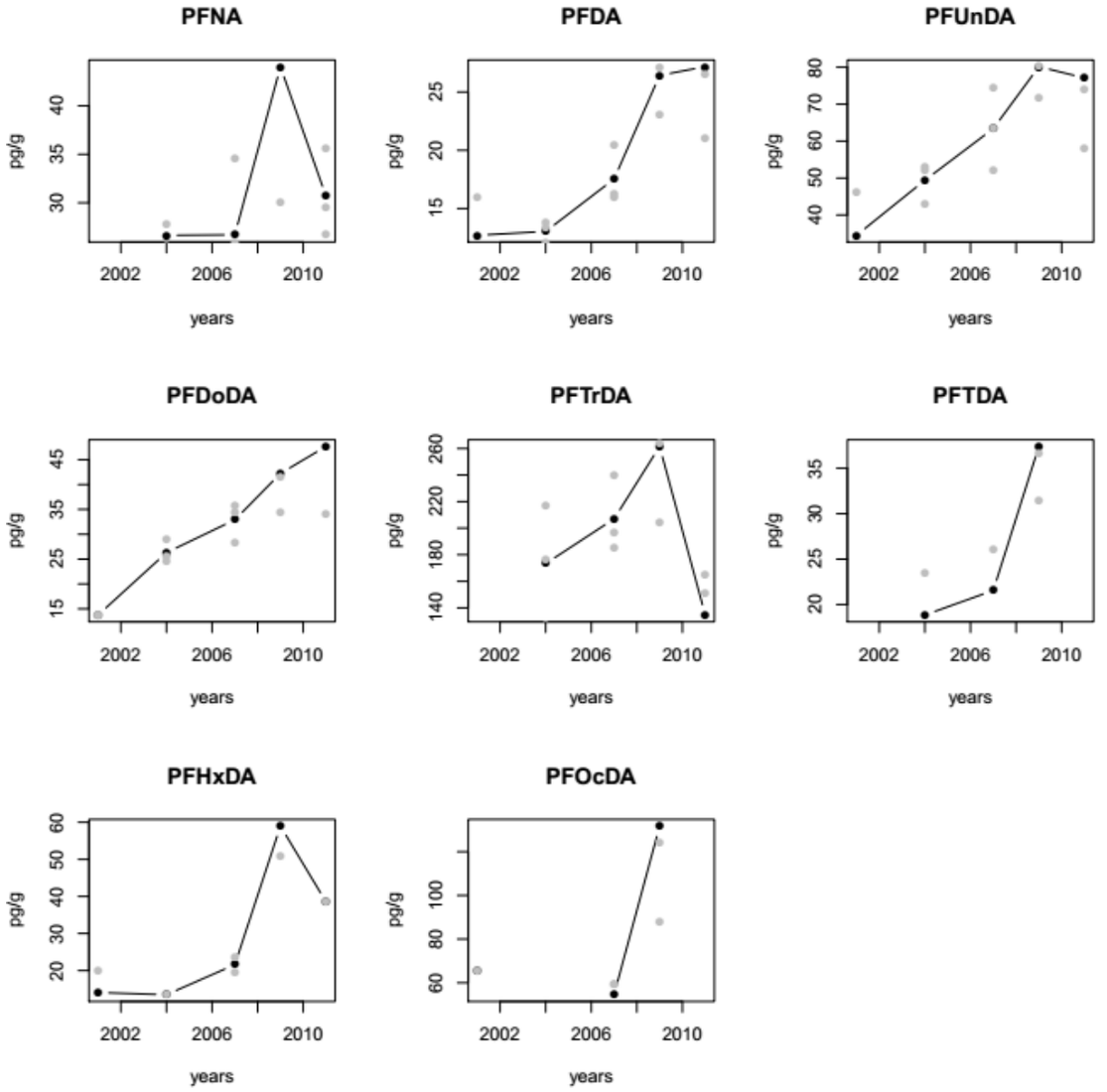
Annexe 17 Limits of quantification for every sample batch run- *personal document*

5. All PFAS time-trend graphs

Includes compounds for which only two years yielded results



Annexe 18 All PFAS time-trends plotted, including compounds with results for only 1 or 2 years
- personal document, realised in R Studio



Annexe 19 (continues Annexe 18) All PFAS time-trends plotted, including compounds with results for only 1 or 2 years
- personal document, realised in R Studio

ABSTRACT

Despite the increasing number of regulations on the production and uses of polyfluorinated substances, those persistent compounds are nowadays ubiquitous in marine environments, even in remote places such as the Faroe Islands.

This master thesis aimed to establish a time trend of 18 different PFAS in a population of Arctic chars (*Salvelinus Alpinus*) from Lake á Mýrunum from 2000 until 2014. This small lake is located on the island of Streymoy and is isolated from direct anthropogenic contamination.

The fish samples (right filet muscle) were prepared specifically for this purpose and analysed using an Ultra Performance Liquid Chromatograph and a tandem mass spectrometer.

The results would then be put in relation with meteorological data from Landversk, as atmospheric transport and wet depositions are suspected to be the main source of PFAS in the Faroe Islands, especially in places as isolated as Lake á Mýrunum. This would have allowed seeing whether the evolution of PFAS contamination in fishes seems to follow the precipitations.

Since precipitations in the Faroe Islands vary greatly from a place to another, nine lake were sampled. Those samples werre prepared using Solid Phase Extraction and would have been analysed for PFAS contamination in the water. The results would have been related to meteorological data to see whether lake water contamination is directly dependent of rain.

Due to technical issues (a pump from the UPLC failed), no lake water samples were analysed, and most of the fish sample analyses failed.

The conclusions, based on unreliable results, are that PFAS's concentration in fishes tend to increase until 2009 before starting to decrease in 2011. The meteo data turned out being unexploitable for the 2006-2009 period and the data from before 2006 could not be retrieved. The few results of the fish analyses could therefore not be related to the meteorological data.

Key words: polyfluorated alkyl substances (PFAS), wet depositions, PFOS/PFOSA, remote environment, Ultra Performance Liquid Chroamtography (UPLC), Mass Spectrometry (MS), Solid Phase Extraction (SPE)

RÉSUMÉ

Malgré les récentes régulations sur la production et l'utilisation de substances polyfluorées, ces composés persistants sont de nos jours ubiquitaires dans les milieux aquatiques, et ce même dans des endroits isolés tels les Iles Féroé.

Ce mémoire a pour but d'observer l'évolution de la contamination par 18 PFAS d'une population d'Ombles Chevaliers (*Salvelinus Alpinus*) d'un lac isolé situé sur l'île de Streymoy aux Iles Féroé. Ce lac est (à notre connaissance) exempt de toute contamination anthropogénique directe.

Les échantillons (muscles prélevés sur le filet droit) ont été analysés à l'aide d'une chromatographie en phase liquide et d'un spectromètre de masse.

Les résultats auraient du être mis en relation avec des données météorologiques du Landversk ; le transport par voie aérienne et les dépositions humides étant les voies de contaminations principales suspectées, ceci aurait pu permettre de voir si la contamination des poissons suit effectivement l'évolution des précipitations.

Les précipitations variant énormément d'un endroit à l'autre au sein des Iles Féroé, des échantillons d'eau ont été prélevés dans 9 lacs. Ceux-ci ont été concentrés et nettoyés *via* extraction en phase solide et auraient du être analysés par UPLC et MS. Les résultats auraient été mis en parallèle avec des données météo afin de voir si la contamination des lacs semble suivre les différents taux de précipitations.

Suite à un problème technique (une pompe de l'UPLC n'est plus fiable), les échantillons d'eau n'ont pas pu être analysés. Les analyses des échantillons de poissons sont quant à elles non fiables.

Les conclusions, basées sur des résultats non fiables, sont que les concentrations de PFAS étaient croissantes jusqu'à 2009 et semblent diminuer à partir de 2011. Aucune donnée météo n'était disponible jusqu'à 2006, et les données pour la période 2006-2009 se sont avérées inexploitables. Restent donc 2010 à 2014, mais les échantillons de poisson analysés datent de 2011 au plus tard ; les résultats n'ont donc pas pu être mis en lien.

Mots-clés : substances polyfluorées (PFAS), dépositions humides, PFOS/PFOSA, environnement reculé, Ultra Performance Liquid Chroamtography (UPLC), Spectrométrie de Masse (MS), Extraction en Phase Solide (SPE)