

# Polyfluorinated organic compounds (PFC) in wastewater treatment plants, fire drill sites and recipients in Norway

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## Abstract

On behalf of the Norwegian Pollution Control Authority (SFT) the Norwegian Institute for Water Research (NIVA) and the Norwegian Institute for Air Research (NILU) monitored polyfluorinated organic compounds (PFCs) in samples from wastewater treatment facilities, landfill sites, marine and freshwater sediment, blue mussel and cod liver sampled in 2007.

## Introduction

Polyfluorinated organic compounds (PFCs) are acknowledged widespread environmental contaminants, due to their manufacture over a period of decades, and release into the environment after use and disposal. The different toxicological, chemical and physical behaviour of PFCs, some of which are used as technical mixtures (formulations) containing a number of individual compounds, makes it difficult to fully assess their impact on humans and the environment. Pursuant to the SFT review material-flow there is no production of PFCs in Norway. Therefore what is marketed nationally is imported, mainly in the form of chemical-technical products or components in manufactured goods <sup>1,2,3</sup>.

Fire extinguishers (Aqueous Film Forming Foams, AFFF) and personal products like coated paper, carpets and furniture as well as all-weather clothing are the most important source of PFCs in Norway. AFFF is used for extinguishing fires associated with petroleum-products (e.g., oil, petrol) or flammable water-soluble liquids (e.g. acetone, alcohol). It is used primarily in connection with offshore installations, airports, oil refineries, tanker ships. PFCs are also used to treat clothing and other textile products in order to enhance their dirt- and water repelling quality. Direct discharge of PFCs can occur under the production of PFC containing products as well as during application, use and disposal of PFC-containing products <sup>1,2,3</sup>.

A Nordic screening investigation <sup>4</sup> indicated the presence of PFC in a broad variety of sample types with highest levels in marine mammals. The report concluded that significant concentrations of PFCs are found in the Nordic environment. In the screening survey of 2004 and 2006 <sup>2,3</sup> some PFCs were found both in freshwater and marine ecosystems including PFOS, PFOA, PFNS, PFNA and PFUnA, but little was found out about possible sources of the pollution.

In 2007, the Norwegian EPA carried out the 6th annual screening survey. In the 2007 screening survey PFCs were analysed in highly exposed environments as waste water treatment plant outlets, landfill runoffs and fire fighting drill sites. Recipients as freshwater and marine sediment, blue mussel and cod collected in close vicinity to the point sources were analysed as well and compared to reference samples unaffected by direct sources.

## Materials and methods

Waste water treatment plants:

*Bekkelaget WWTP (ca. 290 000 p.e.)*

The plant is located at Bekkelaget in Oslo municipality and treats wastewater mainly from the eastern parts of Oslo. Bekkelaget WWTP treats annually ca.40 mill m<sup>3</sup> wastewater and produces 4270 tons dry weight (2006) of sludge. The wastewater is primarily household water and light industrial wastewater (ca. 30 %).

*Saulekilen WWTP (ca. 45 000 p.e.)*

The plant treats wastewater from households, some industry (brewery) and from a inter-municipal landfill site. In 2007 the plant treated 4.7 mill m<sup>3</sup> wastewater and produced approximately 660 tons dry weight of sludge.

*Solumstrand WWTP (ca. 80 000 p.e.)*

Solumstrand WWTP receives spill water from households (ca. 70 %) and industry including a landfill site. The plant treats annually ca. 8 mill m<sup>3</sup> wastewater and produces approximately 4000 tons dry weight of sludge.

*Landfill site*

Lindum Ressurs og Gjenvinning as (Lindum) receives solid waste from the Drammen region. The average annual leachate discharge for the years 2003-2006 was 480000 m<sup>3</sup>.

*Fire drill site*

Res-Q is located in Bleivik north of Haugesund on the West Coast of Norway. It conducts fire safety and emergency preparedness courses for landbased, offshore and maritime operations, primarily for the oil industry. Res-Q is the only fire drill site in Norway where they on a regular basis use foam with FTS; ca. three to five 9-litre extinguishers per week. The run-off from the test site is collected in two consecutive sub-surface basins for sedimentation of solids followed by an oil skimmer and centrifugation.

*Freshwater sediment - Loselva*

Discharge from a car demolition plant empties into the Loselva river. From here 3 sediment samples were taken, one close to the main outlet from the plant, one upstream of this, and one downstream the outlet.

*Marine samples*

Most of the samples from the marine recipients were taken close the point of discharge from the wastewater treatment facilities described above.

Flow proportional composite water samples were collected over a 7 days period from the influent and effluent the municipal wastewater treatment plants. The samples were collected using the plant's stationary automatic samplers set at collecting a sub-sample every 30-60 min which was immediately refrigerated for storage. Every 24 hours a fraction of the collected water was transferred to the final sample bottles, the volume being determined by the actual amount of wastewater being treated within that period. One litre samples were collected in 2-litre polypropylene bottles that were stored cold. At the end of the sampling period a 100 g van Veen grab sludge sample was collected of the final dewatered/dried sludge and transferred to an annealed glass bottle.

Two sediment samples (Res-Q Firedrill-1 and Res-Q Firedrill-2) were collected in connection with a drill using FTS foam and taken from the sediments in the two primary run-off ditches from that area. The next two samples were collected at the end of the primary sedimentation basin (Res-Q Sedim-1) and in the last of the sedimentation basins before discharge (Res-Q Sedim-2) using a small (12.5x15 cm) van Veen grab sampler. Sampling was done right before the annual emptying and disposal of sediments in the two basins. The fifth sediment sample was collected with the van Veen grab sampler through the last manhole on the transfer line before discharge to sea (Res-Q out.d).

At the landfill site Lindum Ressurs og Gjenvinning AS all sediment samples were collected as duplicates from the upper sediments in the pump pit before leachate discharge to the WWTP Solumstrand using a small (12.5x15 cm) van Veen grab sampler. It was tried to sample during a typical dry period (22 June) and a typical wet period (29 August). The daily average leachate flows were relatively low in the two weeks periods preceding both sampling times; 726 m<sup>3</sup>/d (560 m<sup>3</sup>/d at sampling day) and 1093m<sup>3</sup>/d (660 m<sup>3</sup>/d at sampling day), respectively. The average daily leachate flow from Lindum is approximately 1300 m<sup>3</sup>/d (1417 m<sup>3</sup>/d in 2007).

### **Sample preparation and analysis**

Prior extraction, samples were homogenised and internal standard was added to all samples. Sediment and sludge samples were treated with acid and neutralized again prior extraction with acetonitrile in an ultrasonic bath. Water samples were filtered in order to collect the particles. Particles were weight and treated similar to sediments. Biota samples were homogenised and extracted directly. After centrifugation, the supernatant solution was concentrated and added to 25 mg ENVI-Carb and 50µL glacial acetic acid. After additional centrifugation an aliquot of the solution was transferred in an autoinjector vial and a recovery standard (3,5-bis(trifluoromethyl)phenyl acetic Acid, 20µL of a 0.25 ng/µL solution in methanol) and aqueous ammonium acetate was added. For quantitation 13C labelled PFOS and PFOA were used as internal standard.

Aliquots (50  $\mu\text{L}$ ) were injected automatically on a HPLC (Agilent 1100; Agilent Technologies, Palo Alto, CA) coupled to ESI time-of-flight-high-resolution MS in the negative ion mode (LCT, Micromass, Manchester, England). Compounds were separated on an ACE C18 column (150 x 2.1 mm, 3  $\mu\text{m}$  particle size) (ACT, Aberdeen, U.K.) using a gradient of 200  $\mu\text{L}/\text{min}$  methanol and water (both with 2 mM  $\text{NH}_4\text{OAc}$ ). The initial mobile phase condition was 50:50 methanol/water, followed by a 5 min ramp increase to 85:15, a 5 min hold at 85:15, a 0.5 min ramp to 99:1, and hold until reverting to initial condition after min 15. Full scan ( $m/z$  165-720) high resolution mass spectra were monitored throughout the chromatograms.

## Results and Discussion

There were 18 samples from three domestic WWTP (influent, effluent and sludge samples), one fire drill site (five sediment samples) and one landfill site (four sediment samples) were analysed for 27 different ionic PFCs. All 18 samples contained appreciable concentrations of ionic PFCs amounting to a total of 0.74-2.17 ng/l in water samples, 1.55-12.1  $\mu\text{g}/\text{kg}$  dry weight in sludge samples and 5.17-157  $\mu\text{g}/\text{kg}$  dry weight in sediment samples. PFOS was the only compound found in all samples (Table 1). The highest sludge concentration was found at Bekkelaget WWTP, while the highest sediment concentrations were found at the fire drill site Res-Q after the drilling campaign.

In influent water samples taken the WWTPs with PFOS being the only ionic PFCs found at appreciable concentrations. The effluent ionic PFC concentrations from these WWTPs were at similar levels. These concentrations were more than one order of magnitude lower than what was found in the effluents from Bekkelaget and Saulekilen WWTPs in the 2004 screening (Fjeld *et al.*, 2005); 37.5 ng/l and 10.4 ng/l, respectively. PFDCs was detected in all three sludge samples. PFOA was not detected in the WWTP samples, owing to the high water solubility of this compound. The estimated discharge of ionic PFCs in effluent water from the three WWTPs together was 1.5 g per day.

Elevated PFC concentrations were found in the sediment samples collected at the fire fighting drill site Res-Q; sumPFC varied between 106-332  $\mu\text{g}/\text{kg}$ . In the samples taken from settled materials in the ditch directly on the test site even-numbered PFCA and 6:2 FTS completely dominated, though some PFOS was also detected (0.7-0.8  $\mu\text{g}/\text{kg}$ ). This change in PFC pattern is caused by the substitution of the now-banned PFOS containing fire fighting foam. In the samples taken from the sedimentation basins, however, 6:2 FTS and PFOS dominate (80 and 31.5  $\mu\text{g}/\text{kg}$ ) with also an elevated concentration of PFNS (11.3  $\mu\text{g}/\text{kg}$ ) in one of these samples. PFOSA, PFHxS, PFHpS and PFDS were also detected at appreciable concentrations. However, the considerable total PFC concentration (106  $\mu\text{g}/\text{kg}$ ) was found in the sample taken from the last manhole on the transfer line before discharge to the sea, hence, representing sediments that have travelled through the whole treatment process at Res-Q or coming from the mechanical WWTP Res-Q, treating only household wastewater. In this sample PFUnA (12.3  $\mu\text{g}/\text{kg}$ ) and PFOS (59  $\mu\text{g}/\text{kg}$ ) dominated, but elevated levels of 6:2 FTS (11.6  $\mu\text{g}/\text{kg}$ ), PFUnS (6.3  $\mu\text{g}/\text{kg}$ ), PFOSA (3.6  $\mu\text{g}/\text{kg}$ ) and PFDS (2.6  $\mu\text{g}/\text{kg}$ ) were also detected (Figure 1).

Table 1: Average PFC values in WWTP and sediment samples (WWTP-in and WWTP-out: ng/L; WWTP sludge, Res-Q-sediment and landfill sediment  $\mu\text{g}/\text{kg}$ ).

Sample ID	WWTP-in	WWTP-out	WWTP sludge	Res-Q-sediment	Landfill
6:2 FTS	nd	nd	nd	82.7	2.37
PFOSA	nd	nd	nd	1.80	nd
PFBS	nd	nd	nd	nd	0.13
PFHxS	nd	nd	0.09	0.65	0.38
PFHpS	nd	nd	nd	0.41	nd
PFOS	0.96	0.99	3.61	30.1	7.41
PFNS	0.33	nd	nd	11.3	nd
PFDS	0.49	nd	3.64	0.51	nd

PFOA	nd	nd	0.15	nd	nd
PFOA	nd	nd	3.24	nd	nd
PFOA	nd	nd	nd	nd	4.62
PFNA	nd	nd	nd	nd	3.26
PFTTrA	nd	nd	nd	12.9	nd

In the sediment samples taken from the pump ditch at the landfill site *Lindum Ressurs og Gjenvinning AS*, the total PFCs concentrations summing compounds detected were within the range 5.2-17.2 µg/kg with PFOS (3.8-7.5 µg/kg) and PFHxS (0.4-0.9 µg/kg) being found in all samples and PFOA (4.6 µg/kg), PFNA (3.3 µg/kg), PFTTrA (5.1 µg/kg), PFTA (5.0 µg/kg), 6:2 FTS (2.4 µg/kg), PFDS (0.15-0.17 µg/kg) and PFBS (0.13 µg/kg) being found in two or fewer samples. Lindum was not included in the 2004 screening (Fjeld *et al.*, 2005), but the total PFC content in sediment samples from the seven different landfills included in that study was 1.3-23.5 µg/kg with PFOS, PFOA and PFHxS as dominating compounds.

#### *Recipients*

Sediments from Loselva, Drammensfjord and Bekkelaget all show elevated values for PFOS relative to the reference sample from Lista. Highest level was found at Bekkelaget Station 1 (up to 20 times higher than at Lista).

Quantifiable concentrations of PFOS in mussels varied in the range 0.2-1.9 µg/kg wet weight among the 7 samples analysed. Highest level was found outside the Res-Q fire fighting facility at Haugesund. All mussel samples except one had quantifiable levels of PFOSA in the range 0.4-2.9 µg/kg wet weight.

In cod liver highest levels of PFOS were found in the two samples from Bekkelaget (19.8 and 28.0 µg/kg wet weight), whereas the reference sample from the Kari Sea, facing the open North Sea, had only 4.4 µg/kg wet weight, indicating elevated exposure due to emission of PFC to the coastal waters.

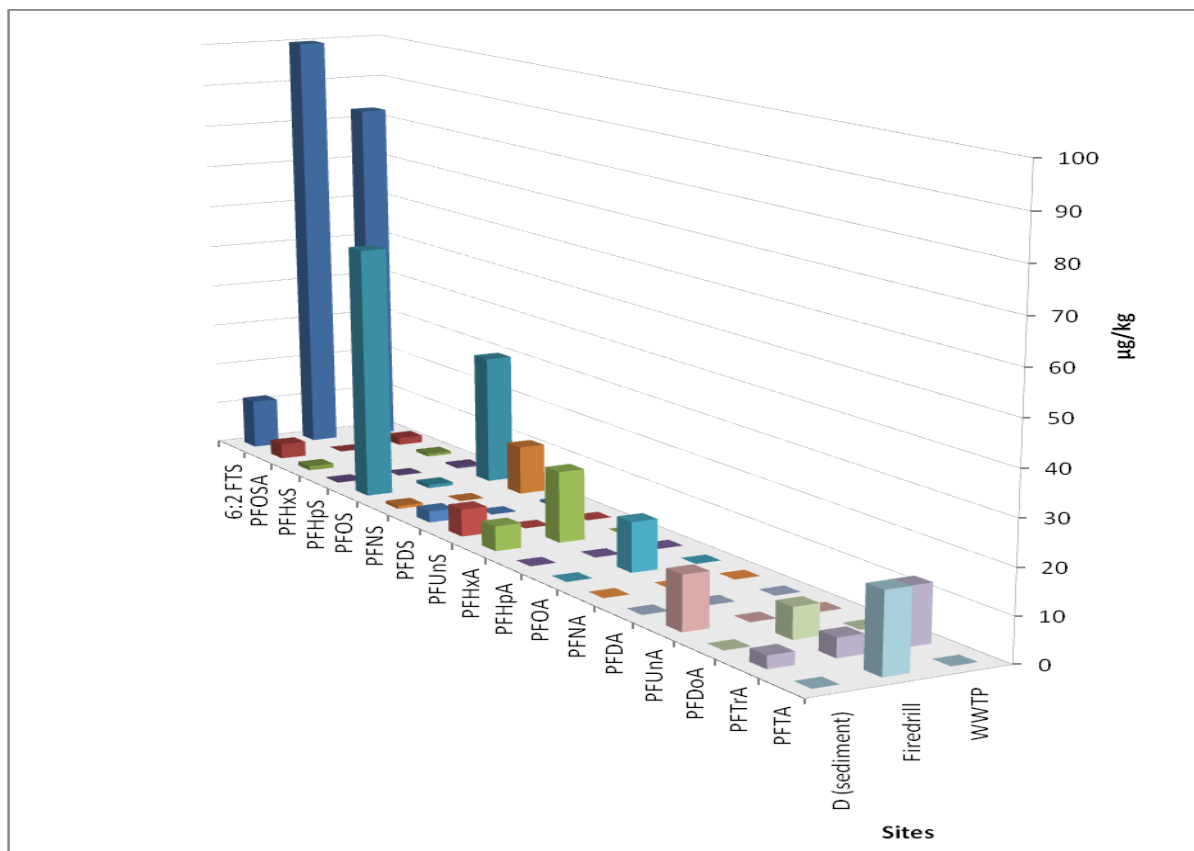


Figure 1: PFC concentrations in three sediments from a fire fighting drilling site (WWTP: from treatment plant sedimentation basin connected to site, Fire drill: settled material in the ditch directly after a drill session; D: sediment from last manhole in the transfer line before discharge to the sea).

#### References

- (1) SFT. Kartlegging av utvalgte nye organiske miljøgifter 2004. SFT and Norway. 927/2005. 2005.
- (2) SFT. Kartlegging av perfluoralkylstoffer (PFAS) i utvalgte tekstiler. ISBN 82-7655-285-4. 2006.
- (3) SFT. Undersøkelse av PFAS-utslipp fra PTFE-belegningsindustri. TA 2233/2007; ISBN 978-82-7655-297-3. 2007.
- (4) Kallenborn R; Berger U; Järnberg U Perfluorinated Alkylated Substances (PFAS) in the Nordic Environment. *Norden, Nordic Council of Ministers, Copenhagen 2004* **2004**, TemaNord 2004:552.