

Screening of extractable organofluorine (EOF) and per- and polyfluoroalkyl substances in sediments close to paper industries

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1 Introduction

Per- and polyfluoroalkyl substances (PFAS) is a large group of anthropogenic compounds used in a wide range of commercial and industrial applications due to their unique physicochemical properties such as stability, water-, oil- and dust repellence (KemI, 2015). Several PFAS have been found to pose a risk to the environment and humans due to their persistency, mobility, toxicity and bioaccumulative potential (Silva et al., 2021; Fenton et al., 2021).

PFAS are used in numerous industrial processes to create non-friction surfaces together with water- and oil-repellency. In the paper industry PFAS are mostly known to be used for manufacturing grease- and water-repellent paper. Paper products that might contain PFAS includes food packaging (plates, popcorn bags and pizza cartons) and other paper packaging materials such as cartons, containers and masking paper. Studies on food packaging materials have shown contents of polyfluoroalkyl phosphate esters (PAPs) (Trier et al. 2011) as well as fluorotelomer alcohols (FTOHs) (Liu et al. 2014). According to register, database and inventory lists (compiled by KemI 2015) there are numerous PFAS used in the global paper industry market including polymers/polymer raw materials, mainly polyfluorinated/perfluorinated (meth)acryl polymers and monomers, and poly/perfluorinated alkyl thiols, poly/perfluorinated alkyl sulfonamide derivatives, and poly/perfluorinated alkyl phosphorus compounds. Because of the known environmental risks associated with long-chain PFAS, a shift in the general production of PFAS has been noticed to more short-chain alternatives, for example 6:2 fluorotelomers, perfluorobutane sulfonyl fluoride (PBSF)-based PFAS, and perfluoropolyethers (PFPE), which are alternative process chemicals for fluoropolymer production (Wang et al. 2013).

Studies on environmental emissions as a result of paper manufacturing are scarce. Recent screening studies from Norway reported high levels of PFAS in sediment nearby a closed paper industry (Norwegian Environment Agency, 2019; Langberg et al., 2019). There are currently 49 pulp and paper mills in Sweden. The paper production consists of widely different products such as cardboard, liquid cardboard, writing paper, sack paper, hygiene paper (tissue), etc. In addition, there are also numerous closed paper industries. Current and historical use of PFAS in paper industries are not known and there is no information regarding environmental occurrence of PFAS due to emissions from Swedish paper industries. The purpose of this study was to assess if paper industries could be an important point source for PFAS in Sweden by analysis of the occurrence of PFAS in sediment located nearby paper industries. Since possible target PFAS are numerous, and analytical standards are partly lacking, the assessment was done by combining target analysis of selected PFAS with analysis of extractable organofluorine (EOF).

2 Materials and Methods

A total of 50 non-polymer PFAS were targeted in the study, divided into the subgroups perfluoroalkyl acids (PFCAs), perfluoroalkyl sulfonic acids (PFSAAs), perfluoroalkylsulfonamides (FASA), polyfluorotelomer sulfonic acids (FTSA), polyfluoroalkyl phosphate esters (PAPs), and perfluoroether acids/sulfonic acids (PFECA/PFESA). In addition, EOF was targeted. Native and labeled standards were from Wellington Laboratories (Guelph, Canada).

Sediment core samples were taken during 2021-2022 and others were retrieved from frozen archives. In total, 39 samples from 8 sites in Sweden sampled during the time period 2015-2022 are presented here. The samples originated from both fresh water and marine recipients located outside active paper factories. Sediment was stored at -20 °C and was freeze-dried prior extraction.

All samples were extracted in duplicates, where the first replicate was intended for target PFAS analysis and was subsequently fortified with isotopically labelled internal standards (IS). The second replicate was analysed for EOF and was therefore not fortified with IS since the labelled standards will also contribute to EOF in the sample. Approximately 0.5 g freeze-dried sediment was treated with alkaline methanol (0.2 M) before solid-liquid extraction with methanol using three consecutive portions and a total of 10 mL methanol. The extract solution was neutralized by addition of formic acid. Clean-up was performed using ENVI-carb (100 mg, Supelco) and weak anion exchange (300 mg Oasis WAX, Waters Corporation, Milford, USA) sorbents. Extra washing steps were applied during the WAX clean-up (5 mL 0.01% aqueous ammonium hydroxide, 3 mL laboratory produced ultra-pure water, 2 mL aqueous ammonium acetate buffer (pH<4) and 2 mL 20% methanol in ultra-pure water) to remove water soluble interferences, and specifically inorganic fluoride.

Targeted analysis was done with an Acquity UPLC coupled to a Xevo TQ-S triple quadrupole mass spectrometer in negative electrospray ionization mode, with a BEH C18 column (1.7 μ m, 100 \times 2.1 mm, all from Waters Corporation, Manchester, UK). The mobile phase consisted of 2 mM ammonium acetate in water and methanol. Extractable organofluorine was assessed by measuring fluoride via conductivity using a combustion ion chromatograph (CIC) with a combustion module from Analytik Jena, (Germany), and an ion chromatograph from Metrohm (Switzerland). Injection (100 μ L) was done on a quartz boat and the oven was operated at 1000–1050 $^{\circ}$ C) under hydropyrolytic conditions. Anions were separated with an ion exchange column (Metrosep A Supp 5–150/4), carbonate buffer eluent (64 mmol/L sodium carbonate and 20 mmol/L sodium bicarbonate) and isocratic elution.

To calculate how much target analytes contributed to the organofluorine concentration, a fluorine mass balance was performed by comparing EOF to quantified, but not recovery-corrected, target PFAS concentration.

3 Results

The first results from the screening study shows a wide range of the sum target PFAS 50, between <LOD to 1415 μ g/kg dry weight (dw) in sediments close to paper industries in Sweden. Figure 1 shows the average sum PFAS 50 concentrations in surface sediments from the eight sites presented in this study. The homologue distribution of detected PFAS also varied between sites (Figure 2). The groups of PFCA, PFSA, FASA and derivatives, FTSA and PAPs were represented in one or several sediment samples. The overall dominant PFAS-class was PAPs.

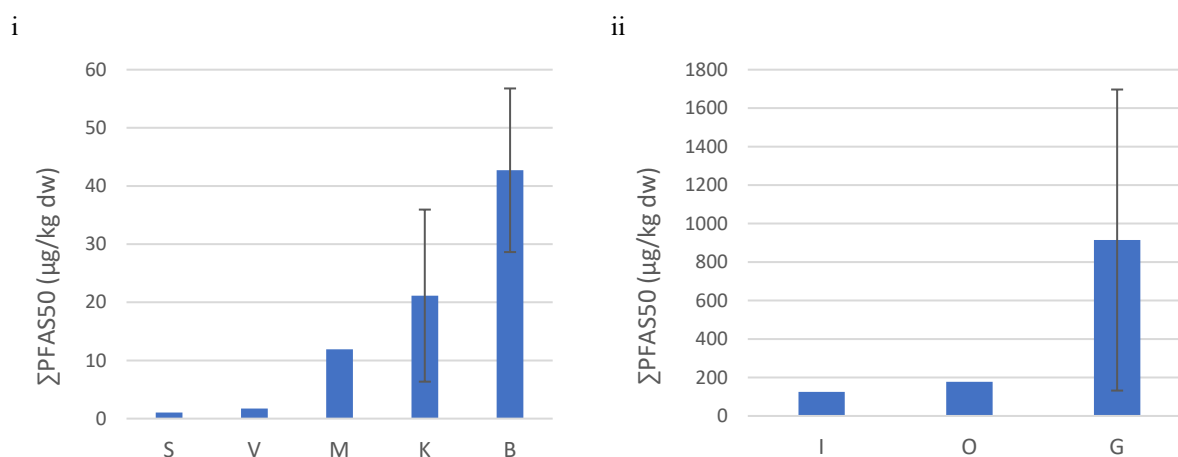


Figure 1: Average concentrations of sum PFAS 50 (μ g/kg dw) in surface sediments (0-5* cm) from eight different sites in Sweden close to paper factories, divided into two groups (i and ii) based on concentration. Multiple surface samples ($n > 2$) were taken from sites K, B and G and standard deviation is illustrated by error bars. (* O and I 0-15 cm, M 0-20 cm)

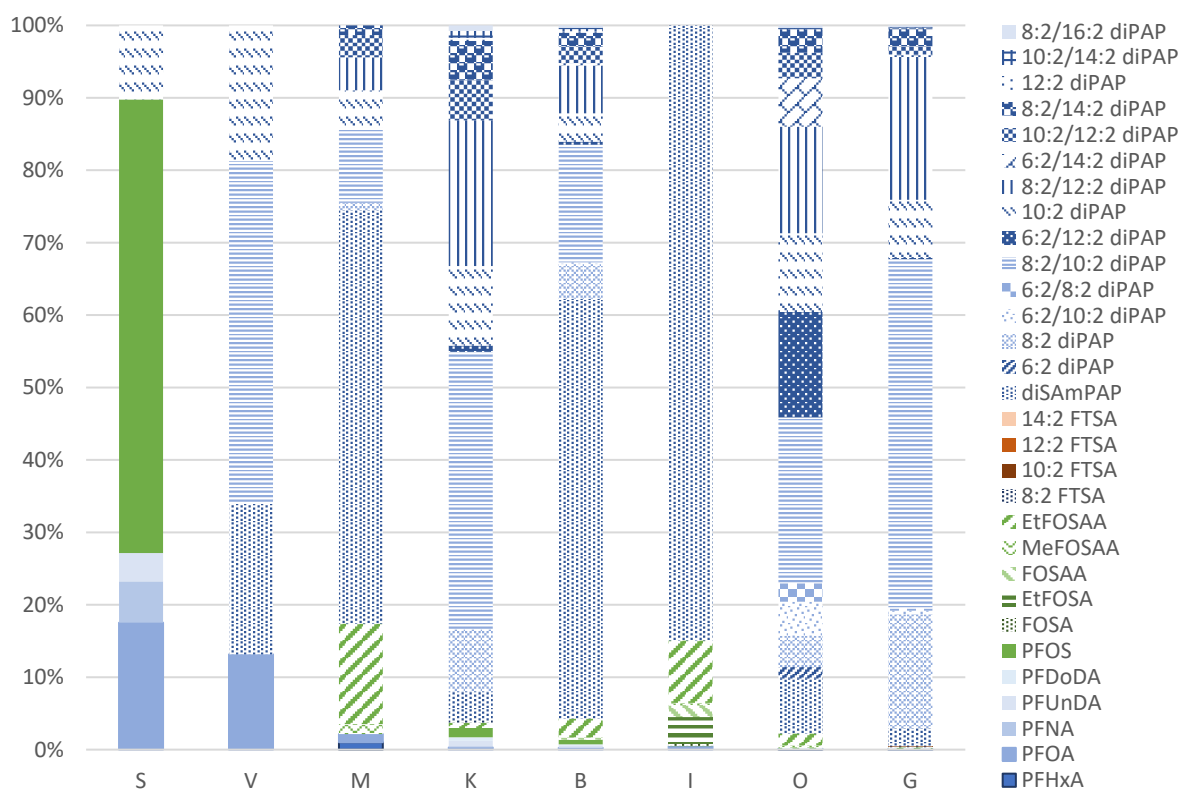


Figure 2: Homologue profile of the target PFAS detected in surface sediments (0-5* cm) from eight different sites in Sweden close to paper factories. (* O and I 0-15 cm, M 0-20 cm)

About 50% of the samples showed detectable levels of EOF, with the maximum level of 1415 $\mu\text{g/kg dw}$. The detection limit for EOF varied between extraction batches due to varying reagent blank levels but was in general around 220 $\mu\text{g/kg dw fluoride}$. Only minor part of the EOF could be attributed to target PFAS, with a contribution ranging from <1% to 15%. The only exception was for sediment samples from site G3 where an average of 78% of the EOF was explained by sum of PFAS 50. The PAPs dominated the profile at site G (Figure 2).

The influence of depth on PFAS concentrations is displayed in Figure 3 for the multiple sediment core sections available in the current study. All four sediment cores showed an increase in concentration with increasing sediment depth, suggesting a higher historical emission rate.

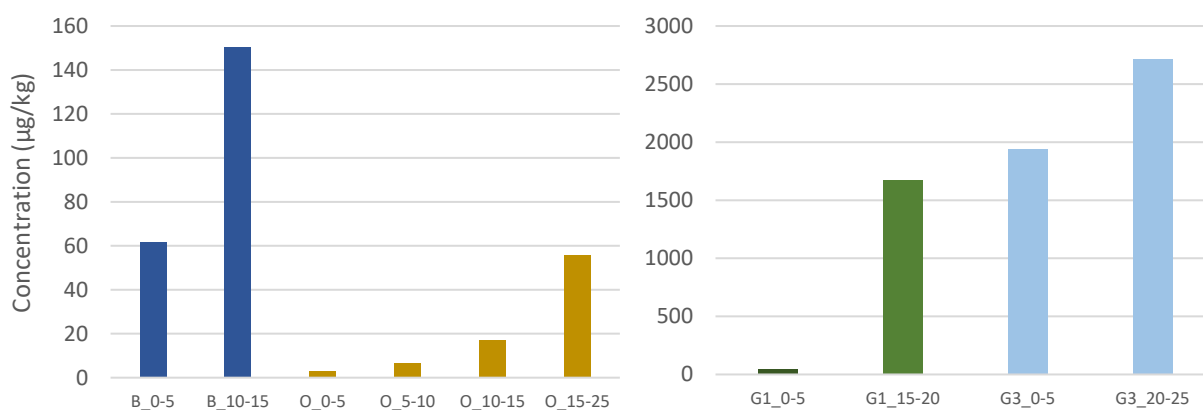


Figure 3: Concentration of sum PFAS 50 ($\mu\text{g/kg dw}$) in sediment core sections (cm) from three sites (B, O, G). The core section depth is given in the sample name. Two core samples were taken from the same site (G1 and G3).

4 Discussion

Sediments from all included sites showed PFAS pollution. Levels in sediments with the lowest contamination (sites S, V, M) were comparable to PFAS levels found in offshore sediments 2020-2021 in Sweden (Josefsson 2022). However, it should be noted that the number of target PFAS in current study (sum PFAS 50) was higher compared to Josefsson (sum PFAS 11). The sites in current study showing elevated PFAS concentrations (Figure 1ii) are in the same range as the recipient lake sediment concentrations outside a closed paper factory in Norway (6.1-207 µg/kg, sum PFAS 29) and the river sediments from the factory area (2450 µg/kg) (Langberg et al., 2021).

The PFAS homologue profile in sediments disclose different types of emissions. The site with the lowest PFAS concentration (site S) was dominated by PFOS and long-chain PFCAs while the contaminated site in Norway was dominated by the precursor compounds FTSA and FASA (including derivatives). Precursor compounds, especially PAPs including diSAmPAP, dominated the homologue profile for all studied sites in Sweden except for site S, which indicates that there is a point source nearby those sample sites. In contrary to the Norwegian study, only a small part of the total PFAS belonged to the classes FTSA and FASA which indicates application and use of different PFAS. Other sources for PFAS in the sediments besides the nearby paper factories cannot be entirely ruled out. Another important emission source of PFAS is aqueous film forming foams (AFFF). Sediment core samples from an AFFF-contaminated lake in Sweden showed PFAS concentrations between <1 µg/kg dw and 76 µg/kg dw, where PFOS and PFHxS had an average contribution of ~71% and ~23% of the detected PFAS (Mussabek et al. 2019).

The mass balance between EOF and target PFAS indicates that there are potentially more fluorinated compounds in the sediments, although the mass balance was almost closed for the highest contaminated site using an analysis method returning the sum of PFAS 50.

5 Conclusions

Findings in the initial screening motivates further analysis of emission patterns, release history, manufacturing processes for paper, and environmental implications. Paper industries can be a substantial point source of PFAS in Sweden, considering that there are 49 active factories and more historical sites. Further analysis of possible influence by other sources than the manufacturing process at the sites are needed. Characterization of PFAS using a broader analysis approach would also shed light on the incomplete mass balance of organofluorine.

6 Acknowledgments

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7 References

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