The role of glacial relicts in transfer of per- and polyfluoroalkyl substances (PFASs) at various trophic levels in Lake Vättern Sweden



MAN TECHNOLOGY ENVIRONMENT RESEARCH CENTRE

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Introduction

Lake Vättern is the second largest lake in Sweden and constitutes as a drinking water revenue for approximately 250 000 people. It is a deep and nutrient poor lake with favorable conditions for the Arctic char. Arctic are frequently consumed from Lake Vättern. Per- and polyfluoroalkyl substances (PFASs) are compounds of environmental concern due to their toxicity and persistence. Around Lake Vättern there are several potential point sources of PFASs, and in previous studies high levels of PFASs have been detected in fish^{1,2}. This study intends to investigate the PFAS pollution in Lake Vättern and if glacial relict crustaceans constitute a vector of transport of these

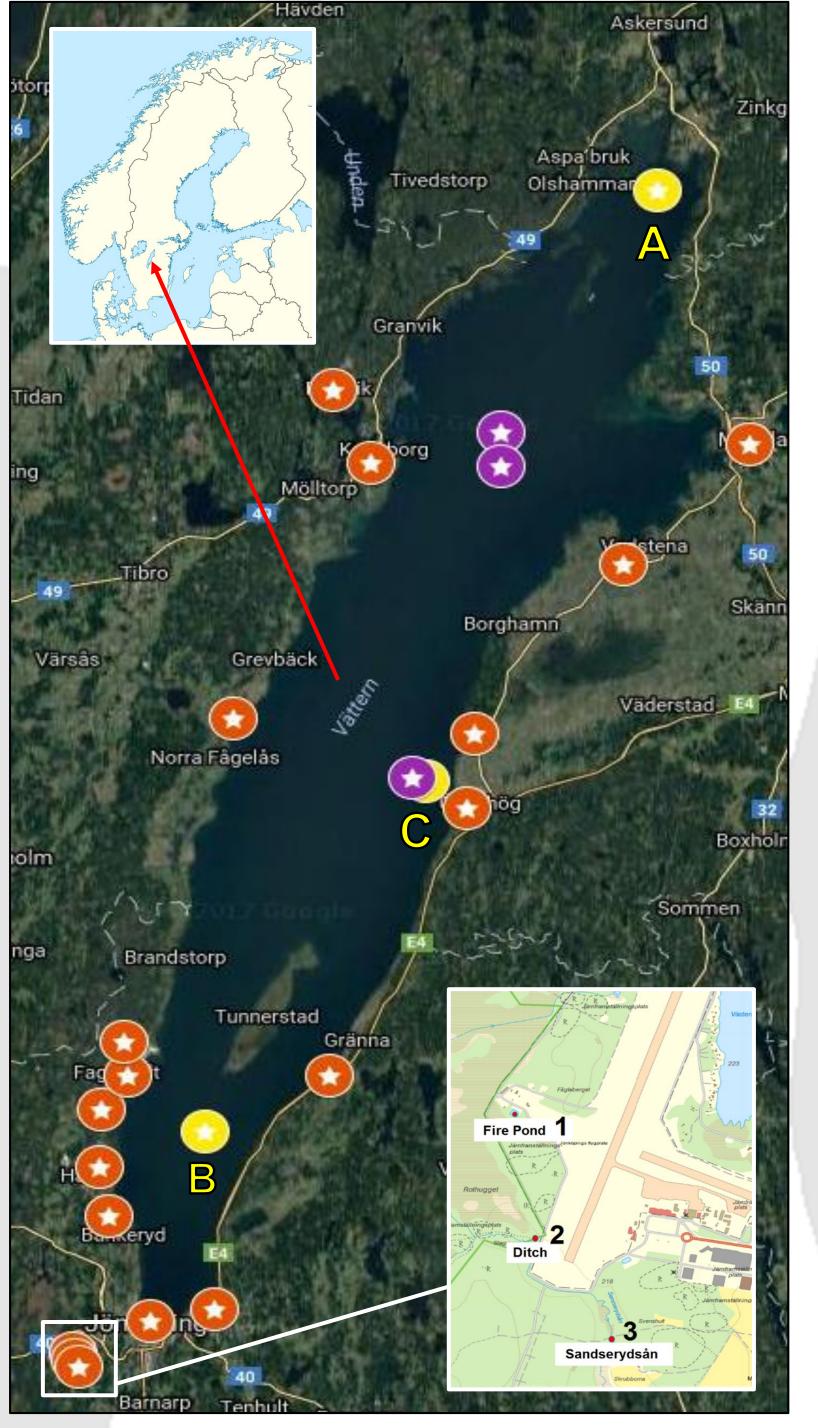
contaminants from sediments to various trophic levels.

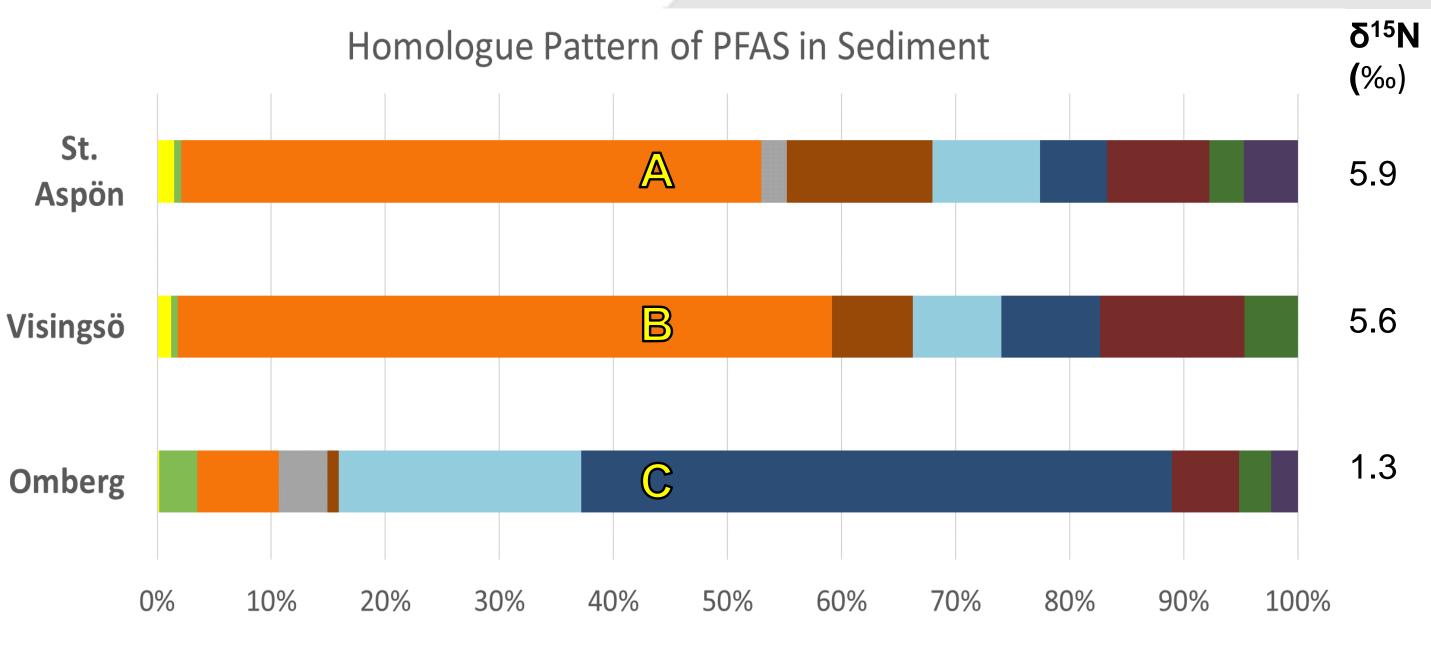
Samples

All sampling locations included in the study are depicted in Figure 1. Data is available from water samples (n=3; enlargement in Figure 1) collected from Jönköpings airport, sediment samples (n=3), smelt (n=10), vendace (n=10), Arctic char (n=6) and whitefish, burbot, Black trout (n=1). Surface water and glacial relict crustaceans³ have not yet been analyzed.

Experimental

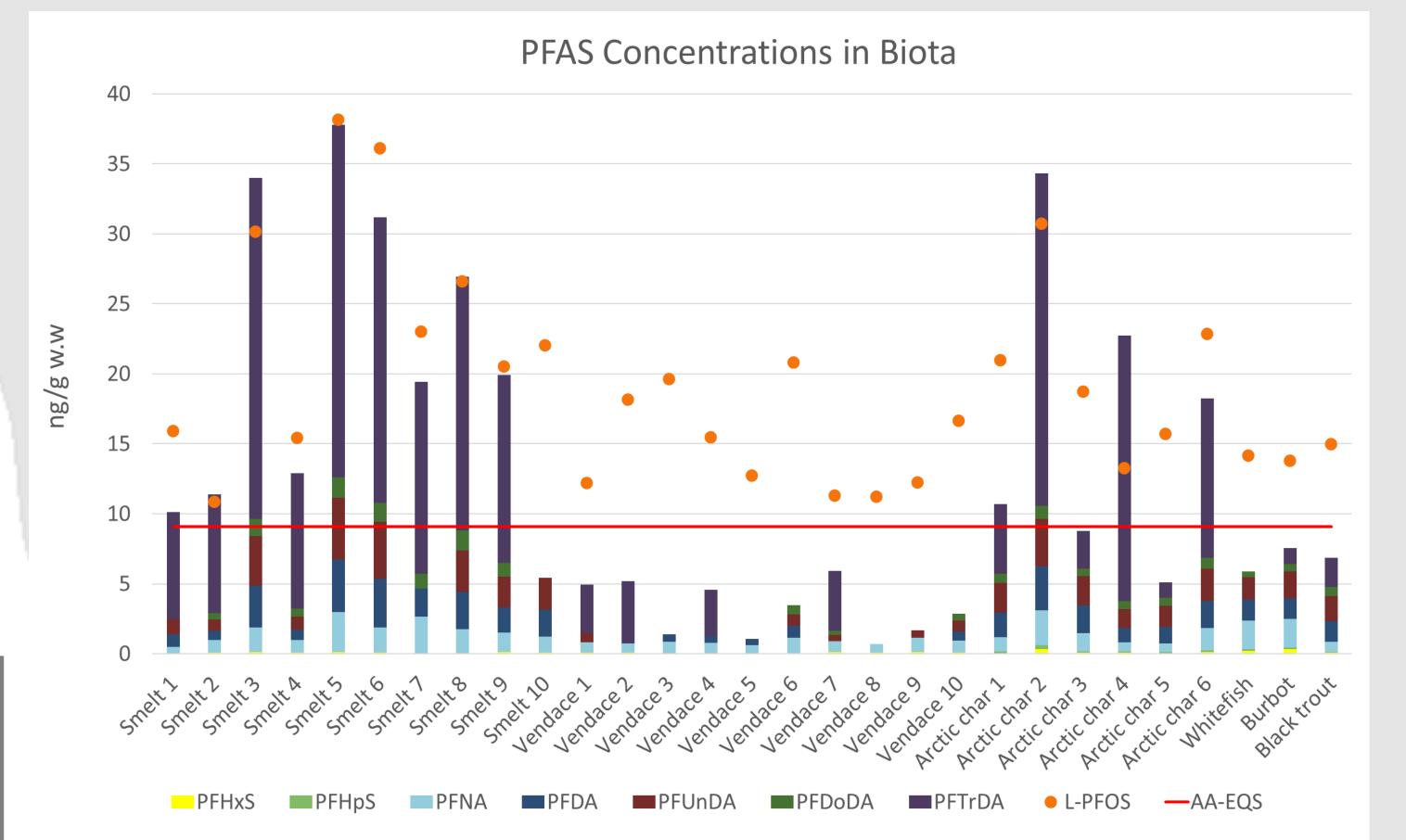
Sediment and biotic samples were extracted using alkaline digestion. Further clean-up was performed by using EnviCarb and solid phase extraction (SPE Oasis WAX). Water samples were extracted using SPE. Instrumental analysis was performed using UPLC-MS/MS. Biomagnification data was assessed by stable isotope analysis of δ^{15} N.





PFHxS ■ PFHpS ■ L-PFOS ■ PFHpA ■ PFOA ■ PFNA ■ PFDA ■ PFUnDA ■ PFDoDA ■ PFTrDA

Figure 2. Homologue patterns of 10 PFASs in sediment samples from Lake Vättern. Mean isotopic ratios (n=2) of $\delta^{15}N$ (‰) are presented to the right of each sample site.



Preliminary Results

Figure 1. Samples included in present study:

Sediment (Figure 2): In sediment samples, homologue patterns of 10 detected PFASs showed similar distribution in St. Aspön (A) and Visingsö (B).

- δ¹⁵N for site A (5.9‰), B (5.6‰) and C (1.3‰) correlate to homologue pattern
- L-PFOS (40-1600 pg/g d.w) was the most prominent compound, followed by PFDA (150-300 pg/g d.w), PFNA (120-250 pg/g d.w) and PFUnDA (30-370 pg/g d.w)

Biota (Figure 3): Among the 13 PFCAs and 9 PFSAs, 8 compounds showed levels above the MDL and met the confirmation criteria in the biotic samples.

- L-PFOS was the most abundant compound and ranged from 11 to 38 ng/g, exceeding the AA-EQS value for PFOS and its derivatives of 9.1 ng/g fish and biota⁴
- PFTrDA ranged from 1.1 to 25 ng/g and PFDoDA ranged from 0.3 to 1.5 ng/g, however, the recovery was >150% (20-229%) for these compounds

Figure 3. Concentrations (ng/g w.w) of detected PFCAs and PFSAs where L-PFOS is compared to the the Annual Average Environmental Quality Standard (AA-EQS) value for PFOS and its derivatives of 9.1 ng/g fish and biota⁴.

Table 1. Concentrations of \sum_{11} PFAS in surface water samples from Jönköpings airport (Jan 2017), compared to previous measurements and the Swedish limit value in drinking water.

∑ ₁₁ PFAS (ng/L)	Fire Pond (1)	Ditch (2)	Sandserydsån (3)
Limit Value ⁵	90	90	90
Nov 2016 ⁶	n/a*	1400	110
Jan 2017	20 000	2100	230
*n/a = not available data			

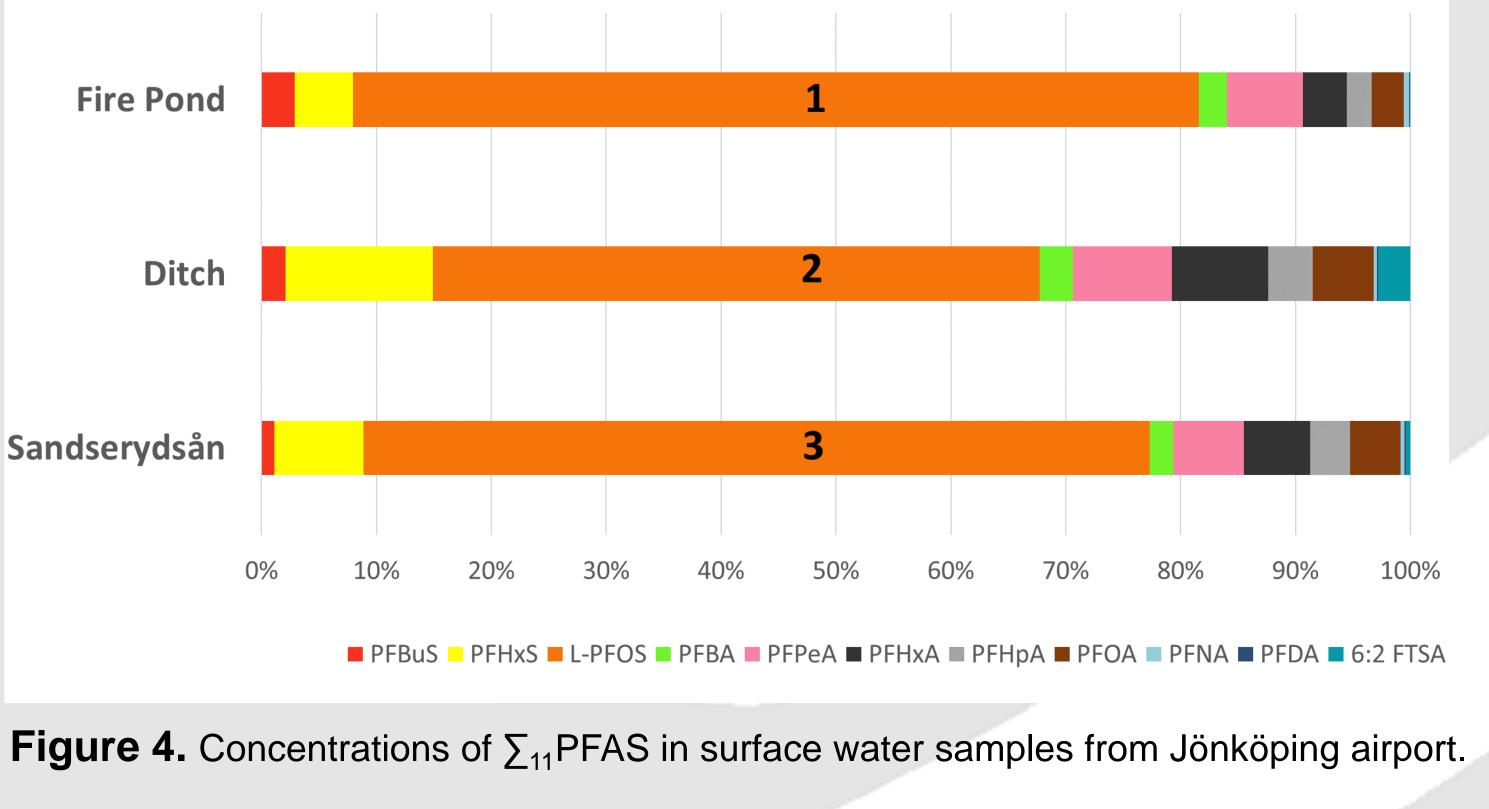
Homologue Pattern of PFAS in Water

Water (Table 1 and Figure 4): \sum_{11} PFAS (ng/L) in water samples exceed the Swedish limit value (90 ng/L).

 L-PFOS was the most prominent compound in all sites, in concentrations ranging from 160 to 14 500 ng/L, exceeding the 0.65 ng/L⁴ AA-EQS for PFOS in freshwater

QA/QC

In sediments, the recovery of ¹³C-labelled internal standards ranged from 80 to 95% for PFSAs (C_6 , C_8), 65 to 90% for PFCAs (C_8 - C_{11}), 85 to 180% for PFHpA and from 30 to 120% for PFCAs (C_{12} - C_{13}). For spiked sediment samples (duplicate), 17 compounds were within 8% RSD, while PFTrDA and PFUnDA ranged from 20 to 30%. Recovery of ¹³C-labelled internal standards ranged from 68 to 100% for PFCAs and 66 to 100% for PFSAs in biotic samples. RSD of inhouse biotic reference sample: 3 to 8% of detected PFASs. Recoveries in water samples ranged from 70 to 150% for PFCAs (C_6 - C_{10}); 90 to 145% for PFSAs; 40 to 80% for PFBA and 80 to 300% for 6:2 FTSA which was >150% in one sample.



References

¹ Berger, U. et al. (2009). "Fish consumption as a source of human exposure to perfluorinated alkyl substances in Sweden – Analysis of edible fish from Lake Vättern and the Baltic Sea." *Chemosphere*, *76*(6), 799–804.
² Norström, K. (2015). "Analys av PFAS i vatten och fisk och ytvatten." *IVL Svenska Miljöinstitutet*, *46*(0).
³ *Mysis relicta, Pallasea quadrispinosa and Monoporeia affinis*⁴ EU Directive No. 2013/39
⁵ Swedish National Food Agency limit value ∑₁₁PFAS in drinking water (2016)
⁶ Jönköping County Administrative Board (2016-11-16)

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