Per- and polyfluorinated alkyl substances (PFASs) and total organofluorine (TOF) in sludge and water from Swedish waste water treatment plants (WWTP)

Ulrika Eriksson, Anna Kärrman, Leo W. Y. Yeung
Introduction

• WWTPs major source of PFAS to the aquatic environment
• PFASs have been monitored in Swedish WWTPs for more than a decade by the Swedish Environmental Protection Agency (EPA)
• Perfluorooctane sulfonate (PFOS) and perfluorooctanoate (PFOA) has been shown to decline following the control measures taken to reduce these compounds.
• Production and usage pattern of PFASs have changed

What are the total amount of PFASs used today and released into the environment?

• Total extractable organofluorine (EOF) analysis allows for assessment of unknown PFASs
Per- and polyfluorinated alkyl substances (PFASs) and total organofluorine (TOF) in sludge and water from Swedish waste water treatment plants (WWTP)

### Samples

<table>
<thead>
<tr>
<th></th>
<th>Henriksdal (Stockholm)</th>
<th>Gässlösa (Borås)</th>
<th>Öhn (Umeå)</th>
<th>Bergkvara</th>
</tr>
</thead>
<tbody>
<tr>
<td>Number of people served</td>
<td>Municipal, industry</td>
<td>Municipal, hospital, industry</td>
<td>Municipal, hospital</td>
<td>Municipal</td>
</tr>
<tr>
<td>Amount sludge produced (t/year)</td>
<td>14400</td>
<td>2400</td>
<td>2300</td>
<td>110</td>
</tr>
<tr>
<td>Sludge samples (n)</td>
<td>12</td>
<td>12</td>
<td>2</td>
<td>1</td>
</tr>
<tr>
<td>Water samples (n)</td>
<td>2</td>
<td>4</td>
<td>4</td>
<td></td>
</tr>
<tr>
<td>Year of collection</td>
<td>2016</td>
<td>2015-2016</td>
<td>2015-2016</td>
<td></td>
</tr>
</tbody>
</table>
Materials and methods

Sludge samples:¹⁻³
- freeze-dried
- digested with NaOH,
- followed by MeOH extraction.
- Ion pair cleanup with TBAS and MTBE

Water samples:¹
- filtered with GF/B glass fiber filters before extraction (Whatman)
- SPE using WAX sorbents, according to ISO/DIS 25101 (ISO, 2009) with some modifications.

Mass balance of fluorine

\[ C_F = n_F \times \frac{MW_F}{MW_{PFAS}} \times C_{PFAS} \]

Conversion of PFAS concentration to fluoride concentration

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**Combustion Ion Chromatography**

- **Fluorinated compounds**

  
  ![Diagram]

- **Sample introduction**
  - Solid or liquid sample is introduced on a quartz boat
  - Sample is pyrolyzed with Ar, followed by burning with O$_2$
  - Resulting gasueous compounds are passed into an adsorption solution (Milli-Q water)
  - Separation of anions on an ion exchange column
  - F$^-$ concentration analyzed using ion chromatography

- **Combustion**

- **Adsorption**

- **Ion Chromatography**

  - 920 Metrohm
  - 930 Compact IC Flex
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**LC-MS/MS Analysis**

Acquity UPLC system coupled to Xevo TQ-S triple quadropole in ESI mode (Waters)

**Perfluoroalkylacids (PFCAs)**
- PFBA (C4)
- PFPePA (C5)
- PFHxA (C6)
- PFHpA (C7)
- PFOA (C8)
- PFNA (C9)
- PFDA (C10)
- PFUnDA (C11)
- PFDoDA (C12)
- PFTrDA (C13)
- PFTDA (C14)
- PFHxDA (C16)
- PFOcDA (C18)

**Perfluoroalkylsulfonic acids (PFSAs):**
- PFBuS (C4)
- PFHxS (C6)
- PFHpS (C7)
- PFOS (C8)
- PFNS (C9)
- PFDS (C10)

**Sulfonamides**
- PFOSA
- Me-FOSA
- Et-FOSA
- Me-FOSE
- Et-FOSE

**Sulfonamide acetates**
- FOSAA
- Me-FOSAA
- Et-FOSAA

**Phosphate esters**
- 6:2 diPAP (4:2/8:2)
- 8:2 diPAP (6:2/10:2, 4:2/12:2)
- 10:2 diPAP (8:2/12:2, 6:2/14:2)
- 6:2/8:2 diPAP (4:2/10:2)
- 8:2/10:2 diPAP (6:2/12:2)
- 10:2/12:2 diPAP (8:2/14:2, 6:2/16:2)
- 12:2 diPAP (10:2/14:2, 8:2/16:2)
- SAmPAP (C8)
- diSAMPAP (C8)

**Perfluorophosphate esters**
- PFPA (C6, C8, C10, C12, C14, C16)
- PFPIA (C6/C6, C6/C8, C8/C8, C8/C10, C10/C10, C10/C12, C12, C10/C14, C14)

**Flurotelomer sulfonic acids**
- 6:2 FTSA
- 8:2 FTSA
Targeted PFAS in water 2016

Per- and polyfluorinated alkyl substances (PFASs) and total organofluorine (TOF) in sludge and water from Swedish waste water treatment plants (WWTP).

61-73% short-chained PFCAs

Concentration ng/L

- Öhn I
- Öhn E
- Gässlösa I
- Gässlösa E
- Henriksdal I
- Henriksdal E
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Targeted PFASs in sludge 2015
EOF in sludge 2015

Per- and polyfluorinated alkyl substances (PFASs) and total organofluorine (TOF) in sludge and water from Swedish waste water treatment plants (WWTP)

Gässlösa
Henriksdal
Bergkvara
Öhn

0 % 20 % 40 % 60 % 80 % 100 %

Targeted
Unidentified

87 – 91% unidentified

0 1000 2000 3000 ng/g
Temporal trend targeted PFAS in sludge
Temporal trend EOF in sludge

**Gässlösa**

![Gässlösa graph](image1)

**Henriksdal**

![Henriksdal graph](image2)

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Temporal trend EOF in sludge

Gässlösa

Unidentified
Targeted

0 % 20 % 40 % 60 % 80 % 100 %

87 – 97% unidentified

Henriksdal

Unidentified
Targeted

0 % 20 % 40 % 60 % 80 % 100 %

75 – 90% unidentified
Per- and polyfluorinated alkyl substances (PFASs) and total organofluorine (TOF) in sludge and water from Swedish waste water treatment plants (WWTP)

**Unidentified PFASs**

**Short-chained PFCAs:**

- **HFPO-DA (GenX)**
- Hexafluoropropylene oxide dimer acid

**Polyfluoroalkyl ether acids:**

- **ADONA**

**Fluorinated silanes and siloxanes:**

- $1H,1H,2H,2H$-Perfluorooctyltrietoxysilane
Summary

• A large proportion of the EOF were unidentified – 87 – 98% in water and 87 – 91% in sludge - total amount PFAS could not be explained by the targeted analytes

• Precursor compounds made a significant contribution to the total amount of PFAS in the sludge.

• Levels of short-chain PFCAs increased during the WWTP process

• The amounts of unknown PFASs have increased 2012 - 2015
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Thank you!

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Colleagues at MTM, Örebro

Contacts: Ulrika Eriksson, ulrika.eriksson@oru.se
Anna Kärrman, anna.karrman@oru.se
Leo W. Y. Yeung, leo.yeung@oru.se