Extractable organofluorine, per/polyfluoroalkyl substances and total oxidizable precursor assay on contaminated soil

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BATTELLE|BALTIMORE|MARYLAND| 2019-04-18

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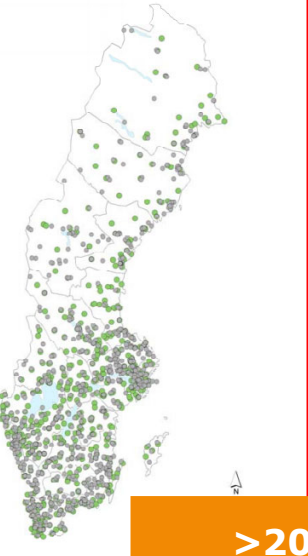
Aims and goal

- The **aim** of this presentation is to rise the awareness of PFASs and PFAS-precursors in soil.

Sub goals:

1. Investigate if PFOS the major compound in the contaminated sites?

2. Investigate how much of PFOS or other regulated PFAS are present in the contaminated sites?

3. Investigate if there are any precursor compounds of PFOS or other regulated PFAS in the contaminated sites?

4. How good mass balance of PFAS can we assemble in soil?

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Identified PFAS sources and NIRAS work with PFAS in Sweden

NATUR VÅRDS VERKET

Högfluorerade ämnen (PFAS) och bekämpningsmede

sammantagen bild av förekomsten i miljön
Redovisning av ett regeringsuppdr

RAPPORT 6709 • MARS 20

>2000 sources
Including:

- **Industries**
- **Landfills**
- **Firefighting training sites**

Flygplatser med brandövningsplats

NATUR VÅRDS VERKET

Kartan visar geografisk spridning av militära och civila flygplatser som har en brandövningsplats.
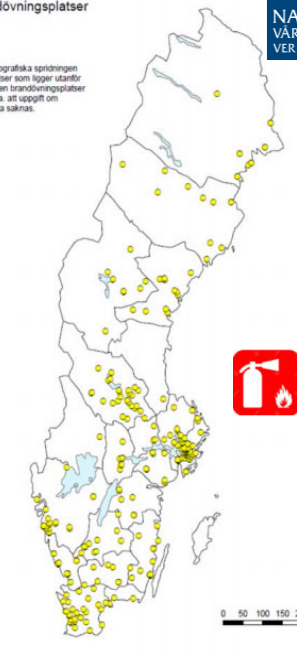
Report 6709
March 2016

0 50 100 150 200 km

28 firefighting training sites in connection with military and civilian airports have been identified in the geographical survey.
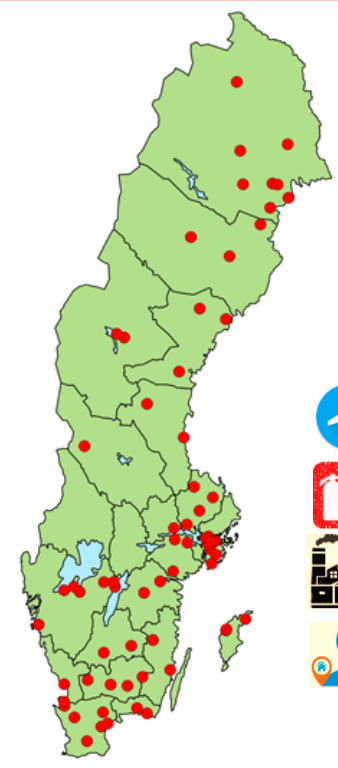

Övriga brandövningsplatser

NATUR VÅRDS VERKET

Kartan visar den geografiska spridningen av brandövningsplatser som ligger utanför flygplatser. 35 stycken brandövningsplatser saknas i kartan p.g.a. att uppgift om koordinater för dessa saknas.

0 50 100 150 200 km

According to the survey, **323 fire training sites** are in operation or dismissed in Sweden.

Investigations performed by **NIRAS** in Sweden encompassing various sectors such as: fire training sites , industries and private sector.
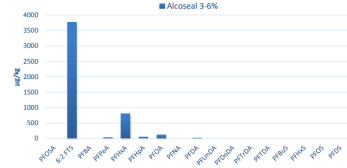
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PFAS IN AFFF

The complex degradation pathways of selected PFAS-precurosrs

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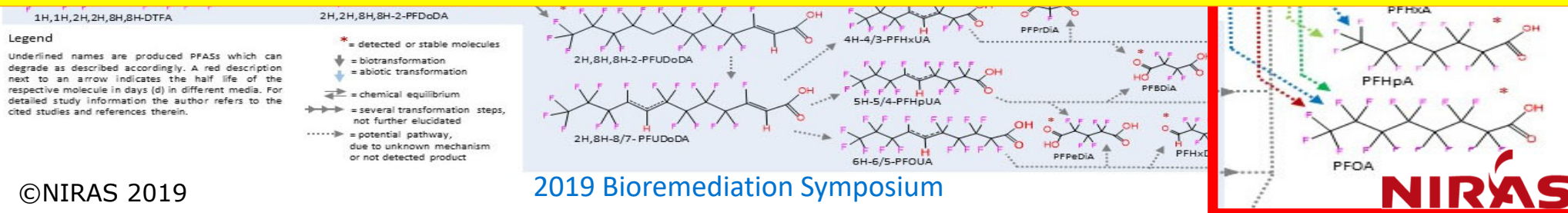
Swedish guidelines for riskassesment of PFAS contaminated land

Vägledning om att riskbedöma
och åtgärda PFAS-föroreningar
inom förorenade områden

RAPPORT 6871 • JANUARI 2019

The Swedish EPA has, in collaboration with the Swedish Geotechnical Institute (SGI), developed a joint guidance document regarding risk assessment and remediation of sites contaminated by highly fluorinated substances (per- and polyfluorinated alkyl substances, PFAS).

This guidance document is primarily intended for authorities that conduct regulatory supervision on contaminated sites.

The Swedish preliminary guideline **values for PFOS**:
- **in soil**:
  - **3**µg/kg d.w. for areas of sensitive land use
  - **20**µg/kg d.w. for less sensitive land use
- **in groundwater: 45 ng/L**

*Potable water: Swedish National Food Agency suggest guideline values (**90 ng/L and 900 ng/L**) ∑11 PFASs Sum of PFBS, PFHxS, PFOS, 6:2 FTSA, PFBA, PFPeA, PFHxA, PFHpA, PFOA, PFNA and PFDA*

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Are available evaluation methods for PFAS-contaminated areas sufficient?

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Sample information

- **Ten potential PFAS hot-spot areas** were investigated within one airport.

- **Training with PFAS containing AFFF since 1970s.**

- **Aqueous film forming foams (AFFFs) are and have been** historically used at the investigated site.

- In total >200 top soil samples were collected whereas **10 samples were selected for the current investigation.**

Figure illustrated by Andreas Ekoutsidis©

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Methods of measuring unidentified PFAS

Total oxidizable precursor (TOP) assay

G
F F
F F n
C_6F_{13}—R + OH• → + $C_nF_{2n+1}COO^-$
C_5F_{11}

n = 6, 8, 10

| C6 Fluorotelomer precursor | PFHxA | C5 and shorter PFCAs |

Concentration ng/mL

- 40
- 30
- 20
- 10
- 0

Before   After
Oxidative conversion

- PFPeS
- PFHxS
- PFHpS
- PFOS
- FOSA
- PFBA
- PFPeA
- PFHxA
- PFHpA
- PFOA
- PFNA
- PFDA
- PFUnDA
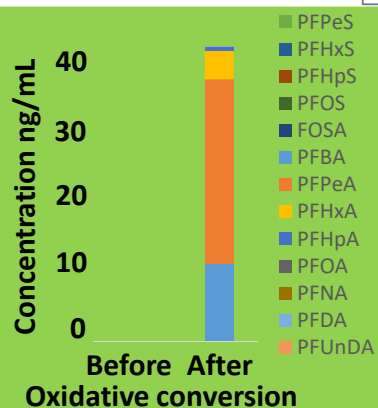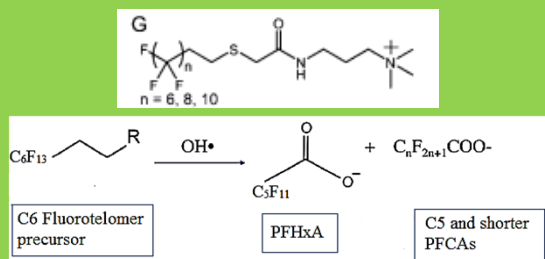
Houtz and Sedlak 2012. Environ. Sci. & Technol., 46. 9342.

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Extractable organofluorine (EOF) analysis

TF □ Known PFAS ▨ IF

Foam 12
Faom 11
Foam 10
Foam 9
Foam 8
Foam 7
Foam 6
Foam 5
Foam 4
Foam 3
Foam 2
Foam 1

0   5000   10000   15000   20000
Concentration ($\mu g\ F\ mL^{-1}$)
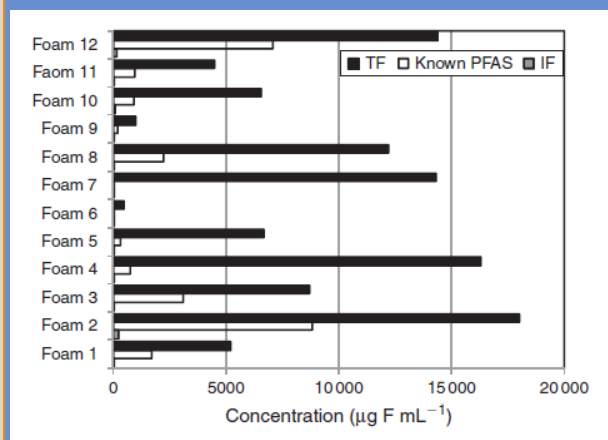
Weiner et al. 2013 Environ Chem 10, 486

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Mass Balance of PFAS

Measurable PFAS

EXTRACTABLE ORGANO-FLUORINE (EOF)
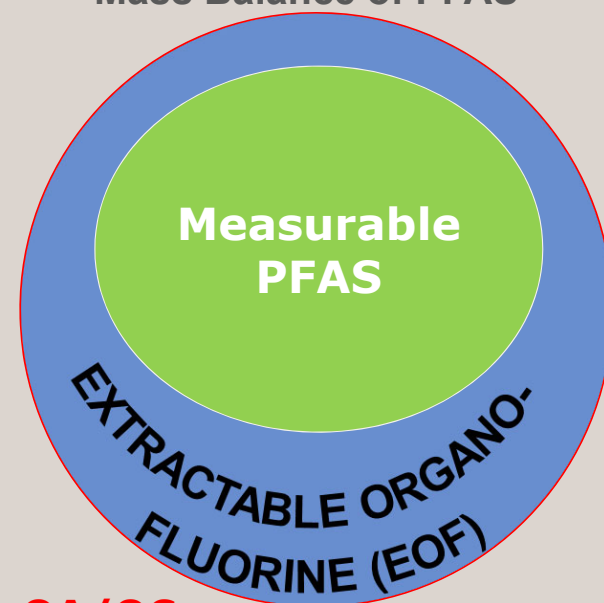
QA/QC

- Extraction blank
- Samples were extracted in duplicate (RSD % of the measured levels <10% for PFAS and <20% for EOF)
- Recoveries: 85 – 103%

PFAS levels –TOP assay

Total PFAS levels (ng/g d.w.) in soil samples
from different locations

1. Investigate if PFOS the major compound in the contaminated sites?
2. Investigate how much of PFOS or other regulated PFAS are present in the contaminated sites?

92%

0

1   2   3   4   5   6   7   8   9   10
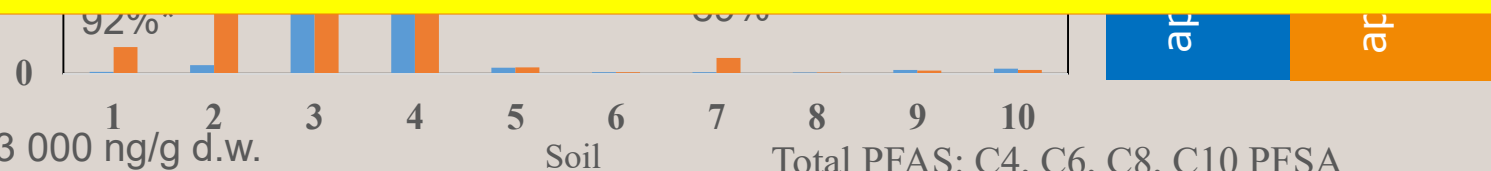
Soil

Before TOP: 51 – 23 000 ng/g d.w.
After TOP: 47 – 23 200 ng/g d.w.

Total PFAS: C4, C6, C8, C10 PFSA
+ C4-C18 PFCAs

10

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PFAS levels –TOP assay

Total PFSA levels (ng/g d.w.) in soil samples from different locations

Total PFCA levels (ng/g d.w.) in soil samples from different locations

o PFOS is the dominating compound in some soils reflecting usage of different AFFF at the different areas.

o PFSAs levels are within the range of method uncertanity.

o PFCAs show a significant increase in 6 soil samples but not all!
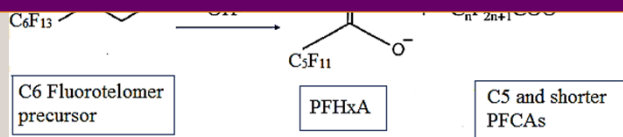
C_6F_{13}		$C_nF_{2n+1}COO$
C6 Fluorotelomer precursor	C_5F_{11} PFHxA	C5 and shorter PFCAs

PFSAs: C4, C6, C8, C10
PFCAs: C4-C18

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3.Investigate if there are any precursor compounds of PFOS or other regulated PFAS in the contaminated sites?

10%

0%

| 1 | 2 | 3 | 4 | 5 | 7 |

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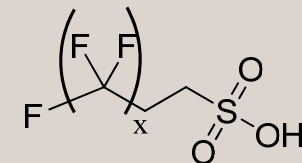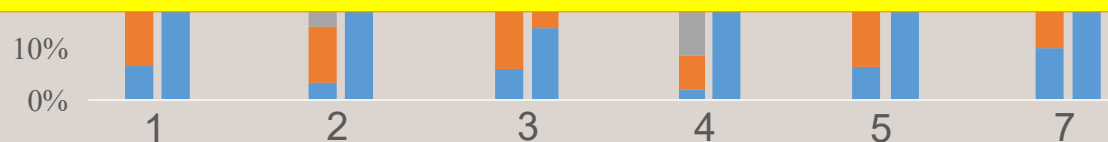
PFAS composition – pre/post TOP assay
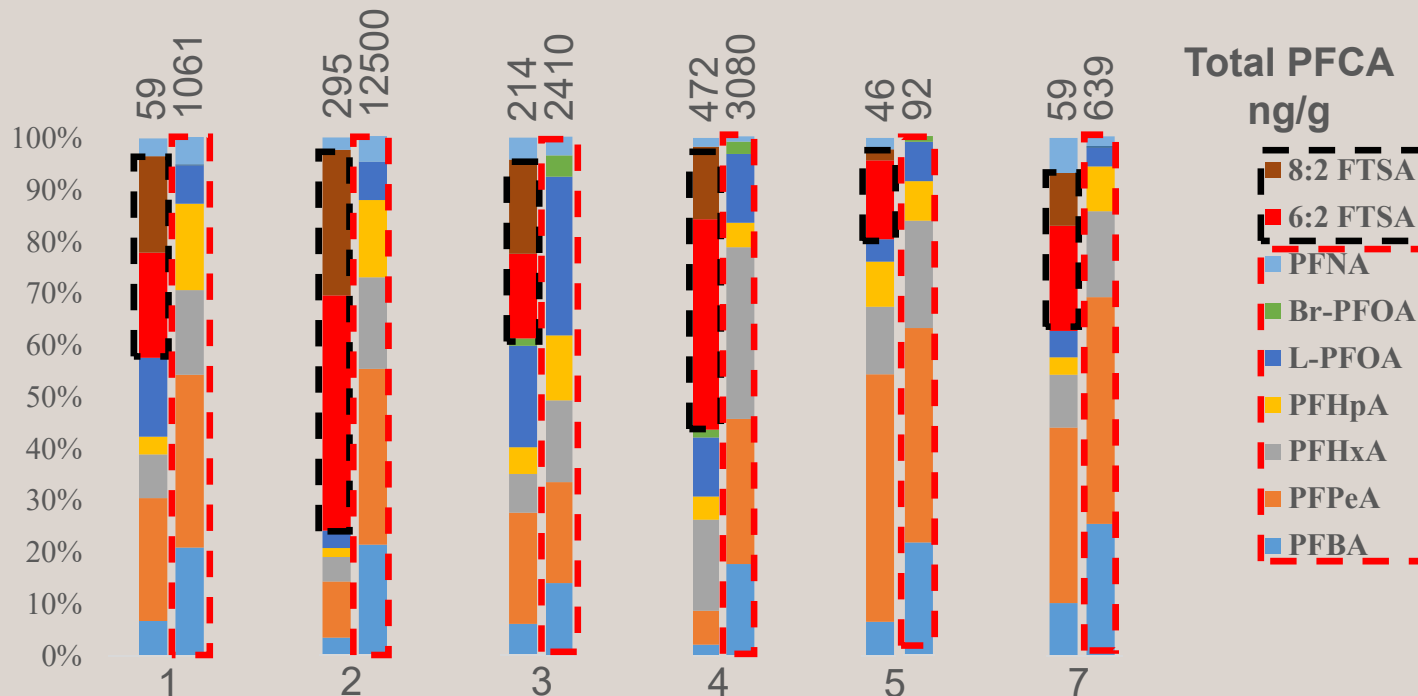
Total PFCA ng/g

8:2 FT-based => PFNA + PFOA + PFHpA + PFHxA + PFPeA + PFBA
6:2 FT-based => PFHpA + PFHxA + PFPeA + PFBA

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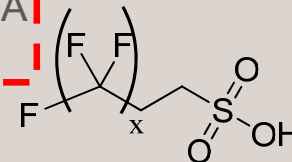
PFAS composition – pre/post TOP assay

						Total PFCA ng/g
59 / 1061	295 / 12500	214 / 2410	472 / 3080	46 / 92	59 / 639	

o There is a high presence of PFAS-precursors of multiple regulated PFAS.

o We observe an increase of Br-PFOA after TOP-assay in some samples. We assume that there might be presence of PreFOS.

o Increasing the number of target precursors might improve the understanding of PreFOS in the samples.

0%   1   2   3   4   5   7

Formation of branched PFOA is probably due to precursors produced by ECF which could potentially include PreFOS compounds.

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Mass balance analysis

o By combining the TOP-assay we are able increase the percentage of measurable PFAS to extractable organofluorine (EOF).

o EOF shows a high presence of neutral/cationic PFAS which we are not meassuring in our current HPLC-MS/MS method.

o EOF fractination of neutral/cationic and anionic PFAS can be used as tool to better understand which PFAS-groups we lack knowledge about.

Measurable PFAS (after TOP)/EOF	%	24.2	33.6	42.9	77.9	11.1	7.1	17.3	7.6	17.3	29.2

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Conclusion

- This investigation highlighted the range and levels of known PFAS showed huge variation among AFFF polluted site. PFOS is not always the most dominant PFAS in soil.

- **TOP assay** "visualized" unknown precursors to a varying extent in several samples.

- After TOP assay, substantial increases were observed for **C4–C6 PFCAs** with the greatest level for **PFPeA**. Results were consistent with the **degradation pattern of 6:2 precursors**, and that suggest the 6:2 structures, the **backbone of more modern AFFF**, present in the contaminated soils.

- The **PFAS/EOF** demonstrated that the degree of explanation is highly dependent upon the PFAS and precursor composition.

- **The F budget** showed that the **TOP-assay increases** the **explanation** level of **EOF**.

NIRAS

The research team

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Thank you
for your attention

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REVIEW

A review of contamination of surface-, ground-, and drinking water in Sweden by perfluoroalkyl and polyfluoroalkyl substances (PFASs)

Stefan Banzhaf, Marko Filipovic, Jeffrey Lewis, Charlotte J. Sparrenbom, Roland Barthel

Abstract Perfluoroalkyl and polyfluoroalkyl substances (PFASs) are found in aquatic systems, flora, and fauna worldwide. These potentially harmful compounds are also frequently detected in Sweden and have already resulted in (PFCAs) and perfluoroalkane sulfonic acids (PFSAs). PFCAs and PFSAs, including their precursor, have shown to be persistent in the environment. Recent studies have shown that some PFASs are toxic for both animals and

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The power to question
is the basis of all
human progress.

Indira Ghandi

Lets progress

Question time!

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