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A PFAS mass balance

impact on the sediment (re)use policy

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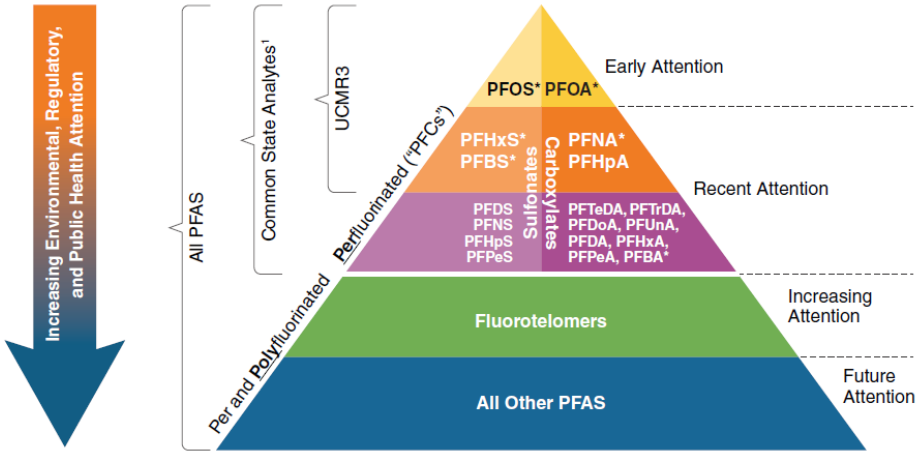
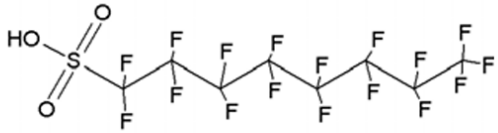
What are PFAS components?

PFAS is a group of very persistent chemicals, the per- and polyfluorinated alkyl substances (PFAS).

There are more than 4.700 chemicals within the PFAS group. They are widely used, are man-made chemicals and they accumulate over time in humans and in the environment. Most PFAS components are considered moderately to highly toxic, particularly for children's development.

In this talk the focus is on **PFOS**.



Common name	PFOS
CAS number	N.A.
EC number	N.A.
Annex I Index number	607-624-00-8
Structural formula	Acid: 
Molecular formula	$C_8F_{17}SO_3H$

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PFAS concentrations in water

For **PFOS** there are proposed individual concentration limits in water:

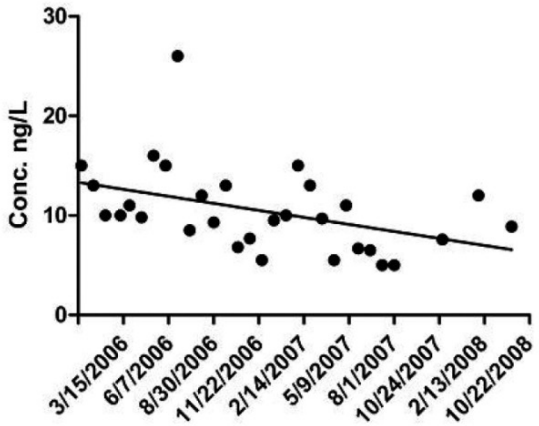
- Proposed in the 2018 recast of the EU Drinking Water Directive (EC, 2017) (PFOS limit of **400 ng/l**)
- In the EU Water Framework Directive(2013), a proposes EQS for PFOS (of **0.65 ng/l**).
- In 2022 EFSA advised to implement a surface water standards for PFOS of **0.007 ng/l** based on human fish consumption.

The used PFOS has been banned in the Stockholm convention (2009), but the EU's Persistent Organic Pollutants (POPs) Regulation has restricted it’s use 10 years earlier.

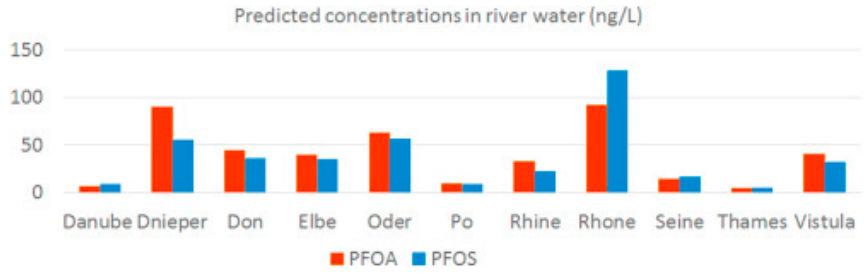
PFAS concentrations in water

The ban on PFOS has a positive but slow impact on the water quality of rivers.

Most rivers have PFOS concentrations in the range of 2 - >100 ng/l.



Eschauzier, Christian & De Voogt, Pim & Brauch, Heinz-J€ & Lange, Frank Thomas,
Polyfluorinated Chemicals in European Surface Waters, Ground-and Drinking Waters.
Polyfluorinated chemicals and transformation products - Handbook of Environmental Chemistry (2012)
http://dx.doi.org/10.1007/978-3-642-21872-9_5



J. Lindim, J. van Gils, I.T. Cousins,
Europe-wide estuarine export and surface water concentrations of PFOS and PFOA,
Water Research, Volume 103, 2016, Pages 124-132,
ISSN 0043-1354,
https://doi.org/10.1016/j.watres.2016.07.024

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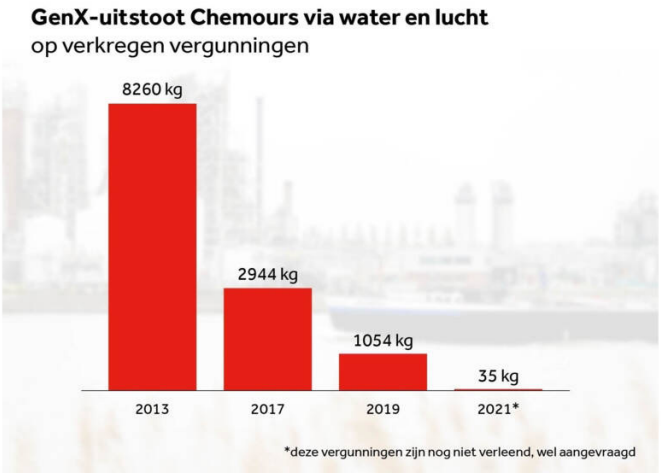
River water concentrations are in the range of 2 – 100 ng/l

The proposed EFSA EQS standards is 0.007 ng/l

What then are the sources of PFOS?

First, an example of the emission of a PFOS “avoidance” PFAS chemical; **GenX.**

The permit for **one factory** in the Netherlands:



1 kg $PFAS_x$ = 10^3 gram
= 10^6 mg
= 10^9 µg
= 10^{12} ng
= 10^{15} pg

Rhine discharge = 6.923 10^{13} liter

1 kg $PFAS_x$ = 14 pg/l $PFAS_x$

… or the **$PFAS_x$ load** for the Rhine to meet the 0.007 ng/l EQS(*) should be **less then 0.5 gram a year**.

(*) The proposed EQS is for PFOS specific, so not $PFAS_x$ generic

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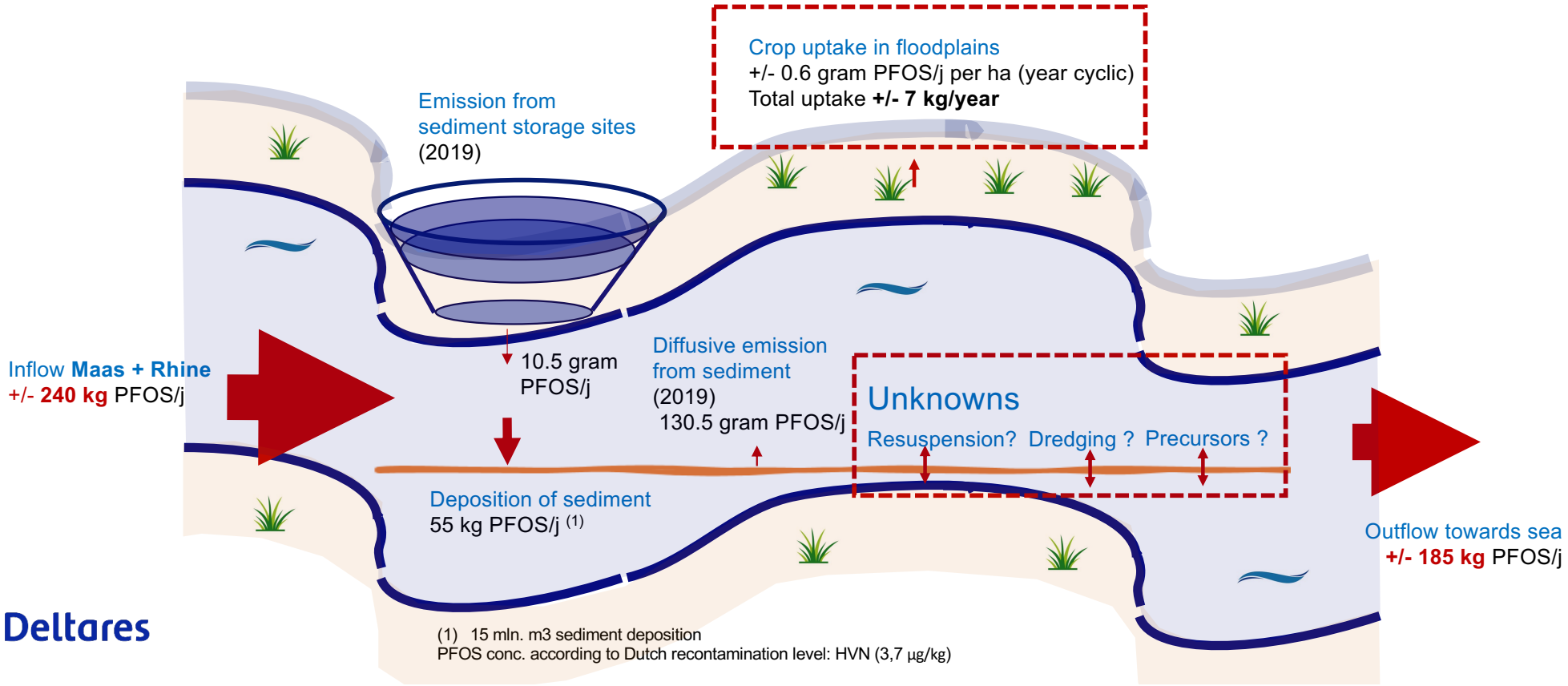
A PFOS mass balance

What can be if not having a **total ban on PFAS** components?

A mass balance without Dutch sources, based on the water and sediment quality for two rivers **for PFOS**:



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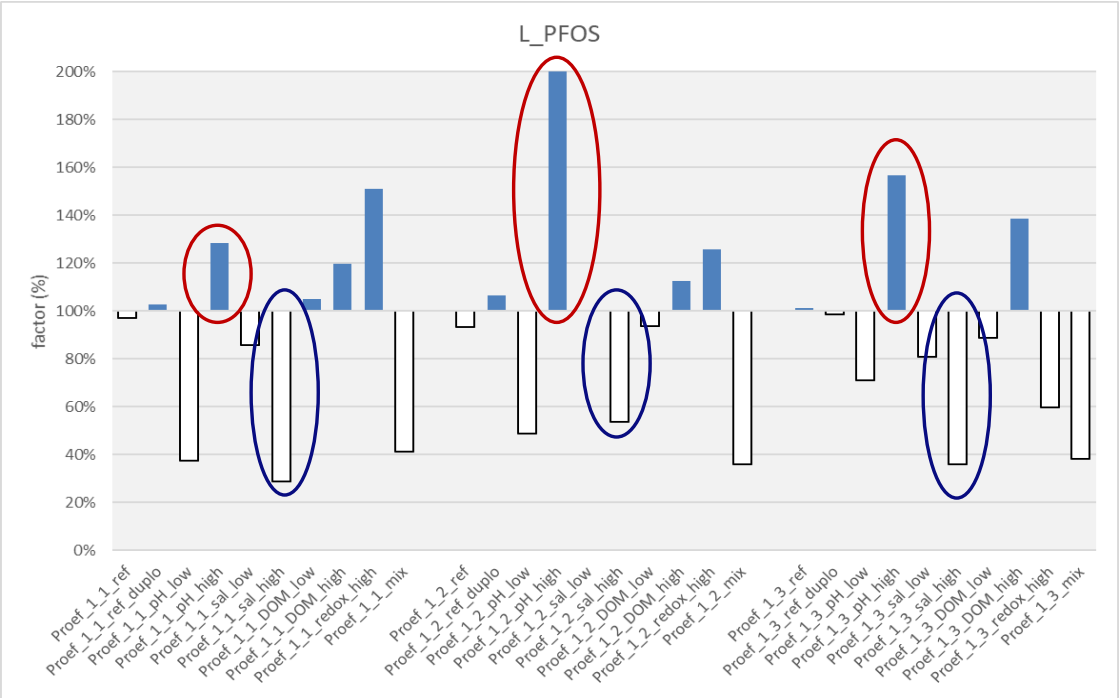
A PFOS mass balance

What stands out? **The unknowns**

Unknown impact of resuspension and deposition for different **water quality** criteria:

Experiments with different pH and EC:



High pH (10):
Increase of PFOS emission when resuspended.

High EC:
Decrease of PFOS emission when resuspended.

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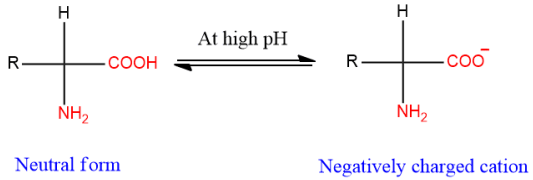
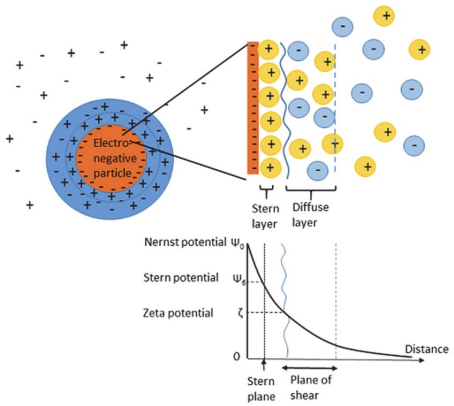
What causes this enhanced/reduced release of PFOS from sediment?

The Cation Exchange Capacity (CEC) of the **clay fraction** of the sediment:

- **pH**: The isoelectric point of the acid group shifts towards a negative charge at high pH, so no adsorption to clay takes place:



- **EC**: At a high EC (salt water) the double layer around charged clay particles is smaller, increasing the binding strength to clay particles.



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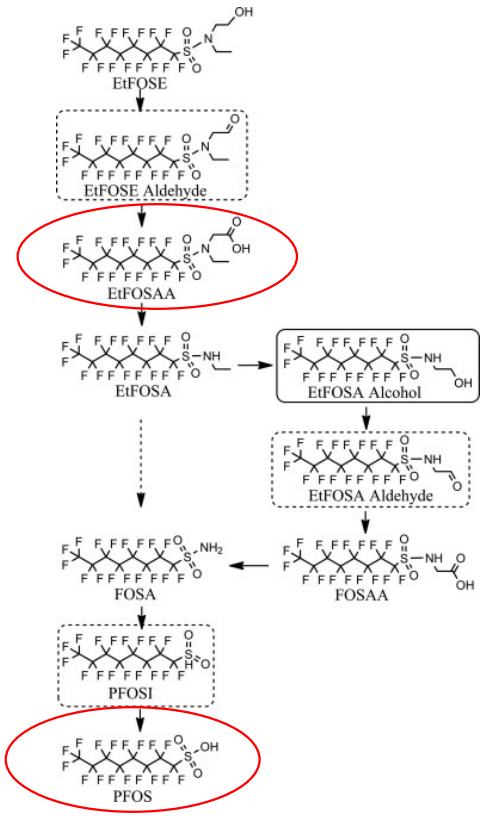
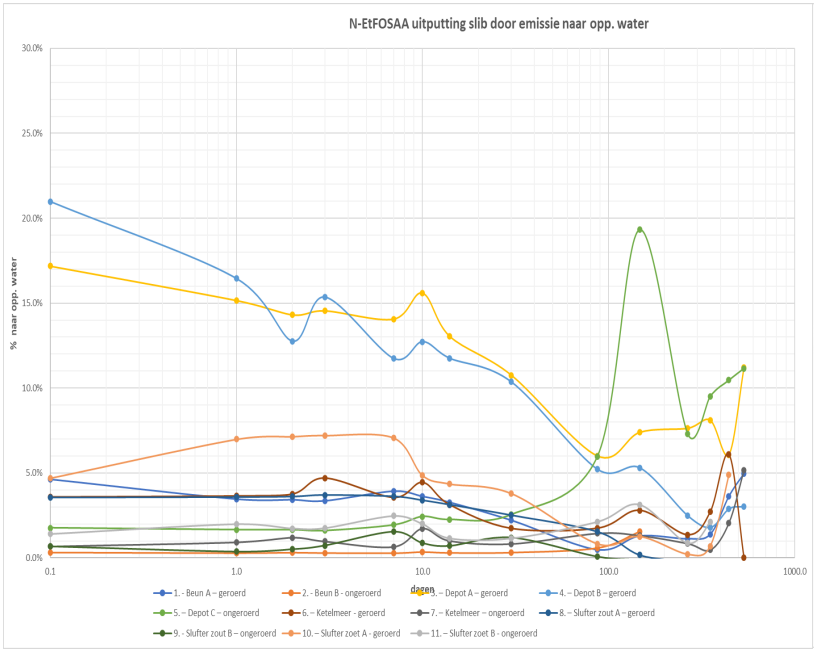
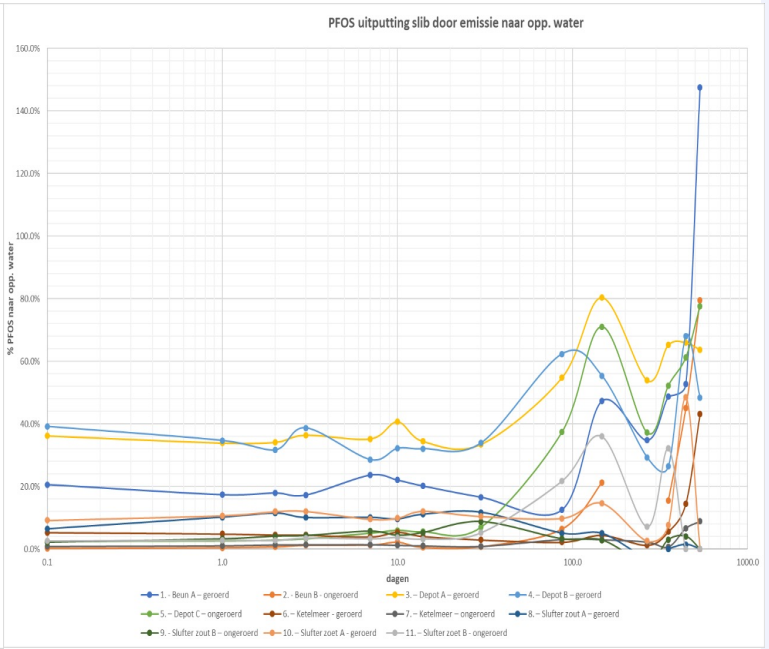
Unknown: Precursors



An EtFOSAA decrease and PFOS increase in mesocosm experiments





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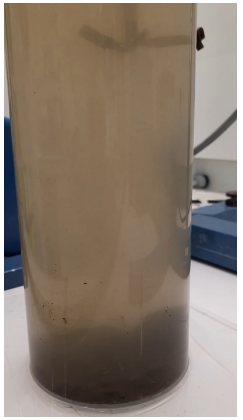
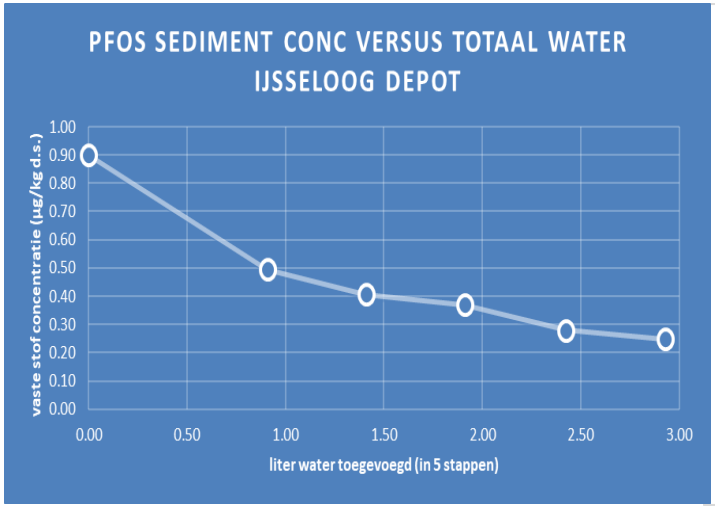
Voettekst van de presentatie

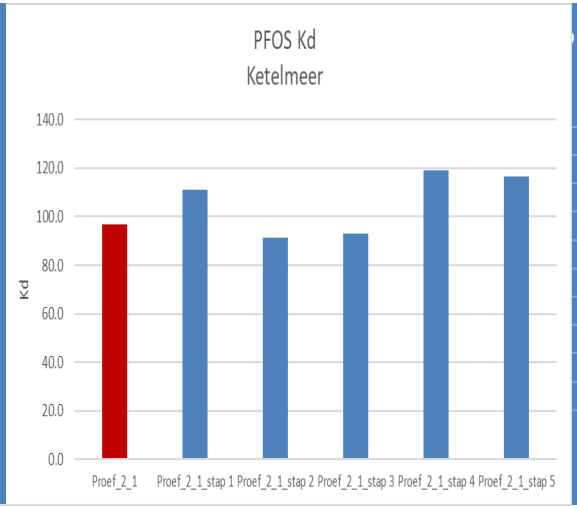
A PFOS mass balance

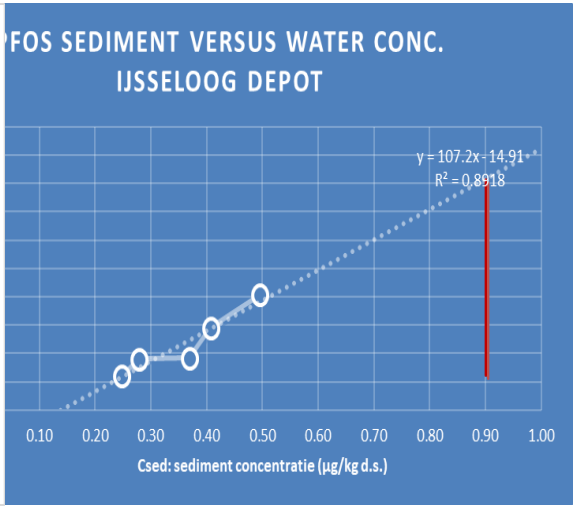


Unknown: Shear (when resuspended due to erosion or dredged)

Tested by adding and refreshing surface water in 5 steps:







40% of the sediment bound **PFOS was mobilized** in step 1 -> **resuspension/dredging impacts the emission to surface water**

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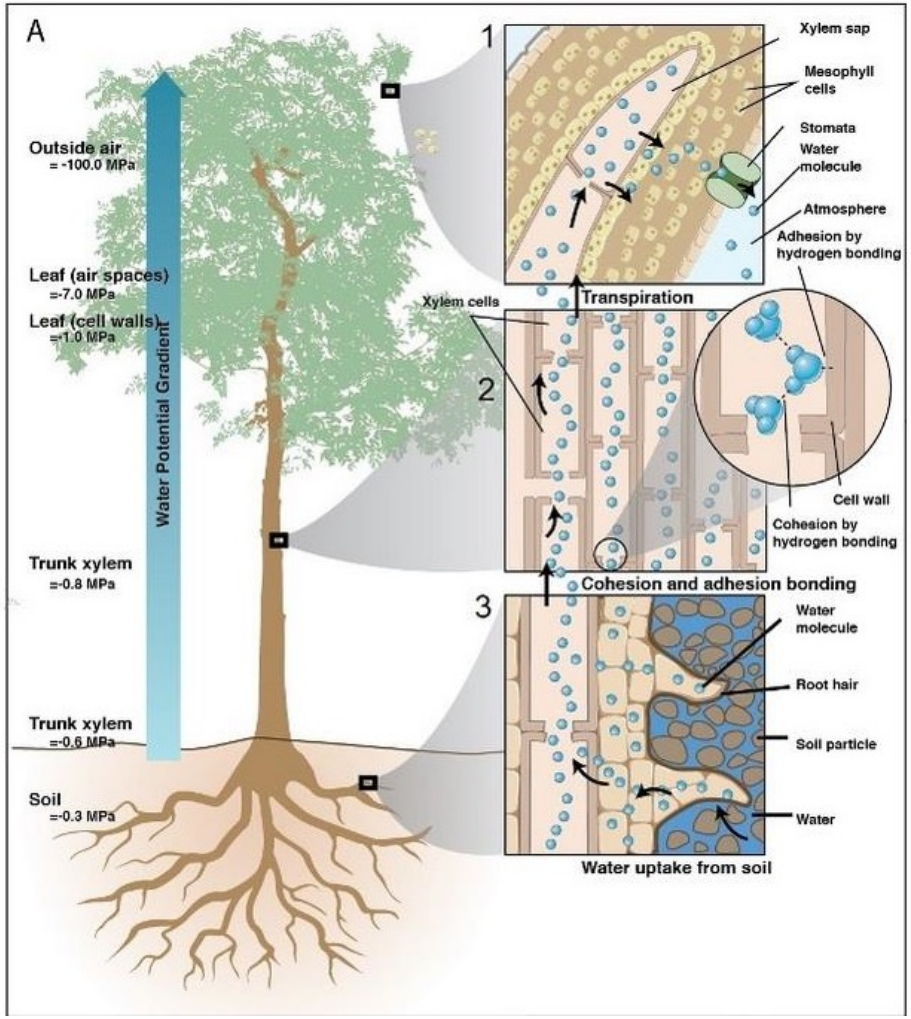
A PFOS mass balance

Biological uptake of PFAS

PFAS does not break down in plants, but due to evapotranspiration PFAS accumulated in the leafs.



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Biological uptake of PFAS – enrichment rates

Sampling date	N	PFBA	PFPeA	PFHxA	PFHpA	PFOA	PFNA	PFDA
16-6-2022	17	419	483	-	-	-	-	3742
18-8-2022	7	0	463	51	0	30	147	2449
16-9-2022	6	250	294	52	55	43	333	542
25-10-2022	6	346	13	40	20	12	41	28

Sampling date	N	PFBS	PFPeS	PFHxS	PFHpS	PFOS	6:2 FTS	GenX
16-6-2022	17	-	-	-	-	571	-	-
18-8-2022	7	0	0	0	0	857	0	0
16-9-2022	6	36	0	62	617	324	539	421
25-10-2022	6	21	0	40	0	43	83	561

Fotocollage van de verschillende veldwerken

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In summary

- Based on the proposed EFSA standard for PFOS (0.007 ng/l) in surface water only a total ban on PFAS helps to improve the water quality sufficiently.
- Even with a ban it will take decades to meet the PFAS water quality standards in surface water.
- Part of the reason for the slow water quality transition is the erosion and sedimentation of PFAS containing sediments. Especially shear (friction) enhanced the release of PFAS.
- Water quality parameters like pH and EC influence the sediment/water exchange .
- Emissions form sediments ‘in equilibrium’ (undisturbed) are negligible on a system balance scale.
- Water quality managers can use plant harvesting to improve the PFAS water quality somewhat.

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