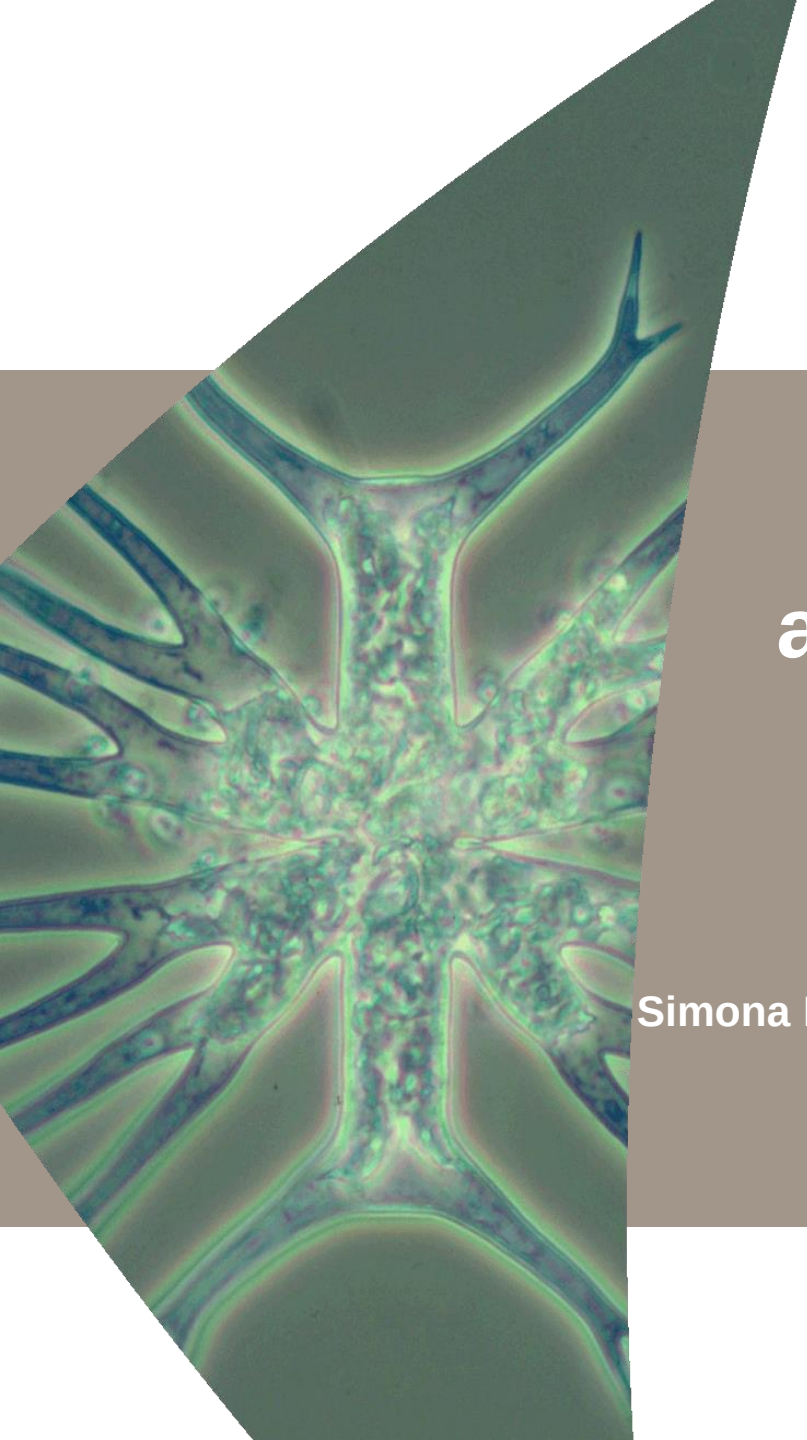

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Centre Suisse d'écotoxicologie appliquée

Sediment quality assessment framework for PFAS

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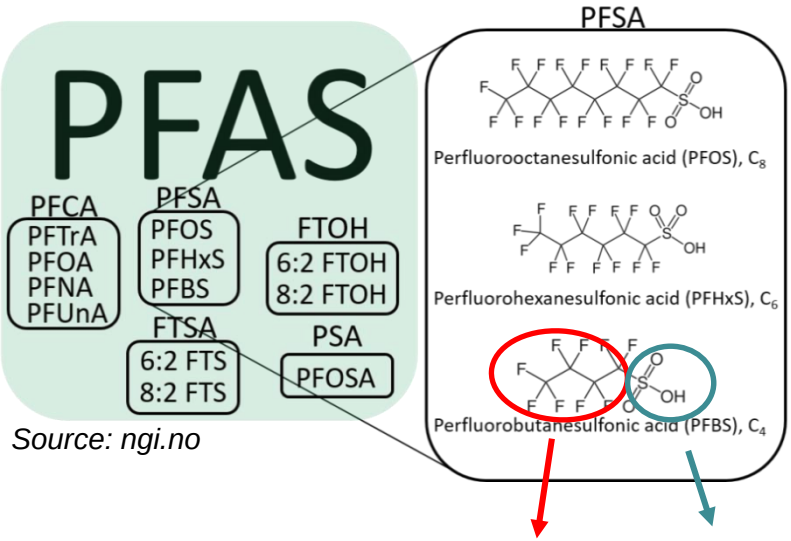
SedNet 2021

Outline

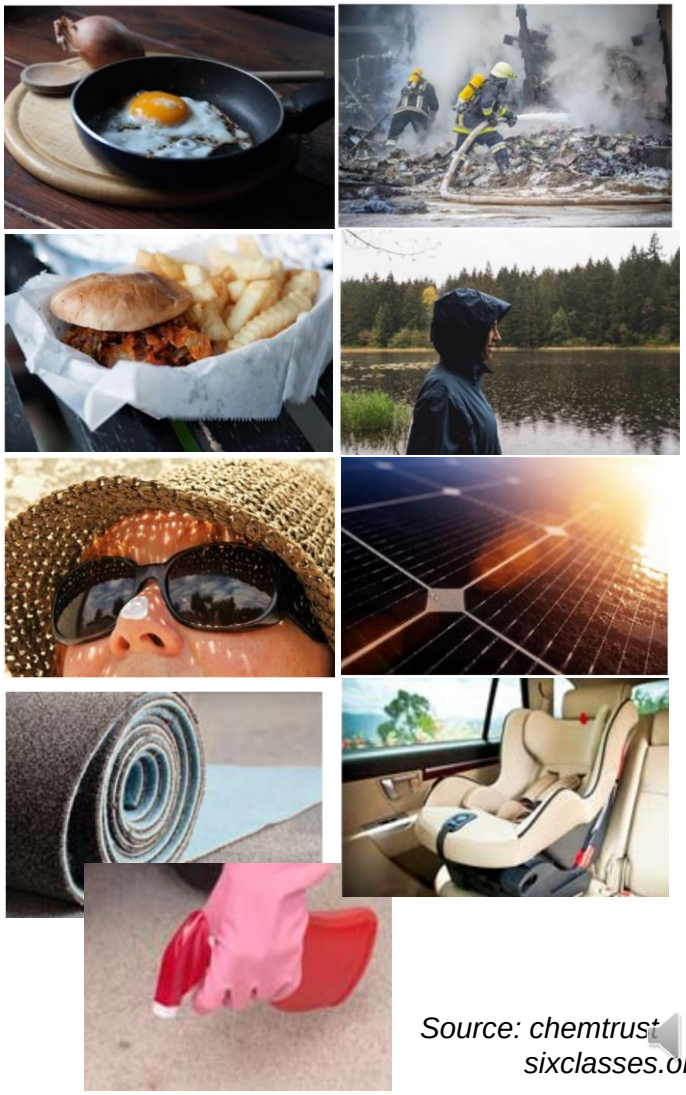
- BACKGROUND
  - Why PFAS?
  - Setting a common framework for sediment quality assessment in Switzerland
- PREPARATORY STUDY
  - Data acquisition
  - Validation of sediment quality assessment framework
- CONCLUSIONS AND PERSPECTIVES

1. PFAS

- PFAS include 3000+ substances and 4700+ PFAS-related CAS numbers.



Source: ngi.no

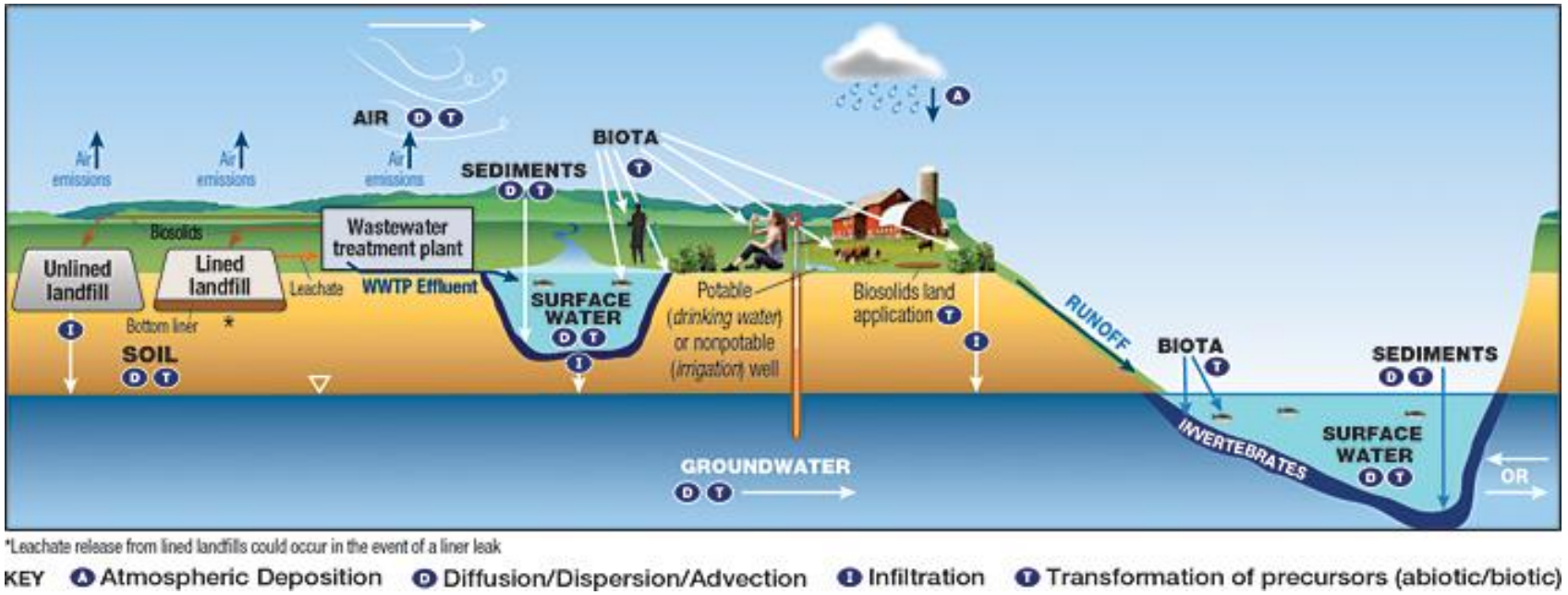


Source: chemtrust sixclasses.org

- PFOS and PFOA are regulated but many others with similar properties still in use -> **Is current regulation based on individual substances appropriate?**

1. PFAS

- **PFAS: the «forever chemicals»**
  - C-F bound extremely stable
  - Accumulation in humans through food consumption and drinking water
- **Important challenges for the management of PFAS contaminated sites**



Source: envirowiki "Conceptual Site Model for landfills and WWTPs. Adapted from figure by L. Trozzolo, TRC, used with permission."

2. Sediment quality assessment strategy in Switzerland

Expected publication date: end 2021.

2. Sediment quality assessment strategy in Switzerland

Study design and sampling strategy

Study design (Chapter 5.1)

Definition of objectives
Collection and evaluation of available information
Selection of target compounds
Matrix selection
Requirements for chemical analyses
Field quality control

Sampling strategy (Chapter 5.2)

Selection of sites
Replicate and composite samples
Frequency and time of sampling
Equipment
Measures to take before fieldwork

Field sampling (Chapter 5.3)

Preliminary measures
Collection of sediment
Homogenization, sieving and bottling
Transport
Preservation and storage

Analysis (Chapter 5.4)

Sample pre-treatment
Sediment properties
Metals
Organic (micro-pollutants)

2. Sediment quality assessment strategy in Switzerland

Priority substances for sediment monitoring

CAS	Substance	Type	Use
330-54-1	Diuron	Herbicide	Herbicide, biocide in urban areas, vineyards, fruits production
2921-88-2	Chlorpyrifos	Insecticide	Insecticide in fruits, vineyards, beets Restrictions as from 2019
52315-07-8	Cypermethrin	Insecticide	Insecticide in fruits, vineyards, beets
107534-96-3	Tebuconazole	Fungicide	Fungicide in wood treatment, cereal crops
85721-33-1	Ciprofloxacin	Antibiotic	Human and veterinary medicine
50-28-2 53-16-7 57-63-6	E2 [a] E1 EE2	Hormones	Contraceptive, breast cancer
3380-34-5	Triclosan	Bactericide	Disinfectant Personal care product, human health Restrictions as from 2015
NA	PBDEs [b] (8 indicators)	Organobromines	Flame retardants
1763-23-1	PFOS [c]	Fluorosurfactant	Industrial and consumer applications
117-81-7	DEHP [d]	Phtalate	Plasticizer
NA	Nonylphenols	Phenols	Nonionic surfactants used in detergents, paints, pesticides, personal care products, and plastics
NA	Octylphenols	Phenols	Synthesis intermediates
21145-77-7	Tonalide	Synthetic musk	Perfumes, cosmetics and laundry detergents
87-68-3	HCBD [e]	Halogenated aliphatic compound	Solvent
NA	PAHs [f] (16 indicators)	Polycyclic aromatic hydrocarbons	Release through pyrolysis
NA	PCBs [g] (7 indicators, PCB 118)	Polychlorinated biphenyls	Banned
7440-50-8	Cu	Trace metal	Materials, agriculture, chemistry
7440-66-6	Zn	Trace metal	Materials, agriculture, chemistry
7439-97-6	Hg	Trace metal	Regulated use
7439-92-1	Pb	Trace metal	Batteries, ammunition

2. Sediment quality assessment strategy in Switzerland

Level 1: classification system based on EQS_{sed} comparison

Classification		Class definition ($RQ = MEC/EQS_{sed}$)	Meaning
Very good	The measured concentration in the sediment is at least 10 times lower than the quality criterion (EQS_{sed})	$RQ < 0.1$	EQS_{sed} met
Good	The measured concentration in the sediment is between 1 and 10 times lower than the quality criterion (EQS_{sed})	$0.1 \leq RQ < 1$	
Moderate	The measured concentration in the sediment is lower than two times the quality criterion (EQS_{sed})	$1 \leq RQ < 2$	EQS_{sed} exceeded
Unsatisfactory	The measured concentration in the sediment is lower than 10 times the quality criterion (EQS_{sed})	$2 \leq RQ < 10$	
Bad	The measured concentration is equal or higher than 10 times the quality criterion (EQS_{sed})	$RQ \geq 10$	

Level 2: assessment refinement

2. Sediment quality assessment strategy in Switzerland

- **The recommended matrix for analysis and type of evaluation depend on the study objective.**

Objective			**Monitoring of sediment quality**	**Diagnosis: identifying the causes of known biological impairment**	**Assessment & monitoring of potential biological impairment at known hot spots**	**Trend monitoring**
Problems to solve			1) Obtain an overview of biological impact of sediment quality on a cantonal or regional scale, both spatially and temporally 2) Find indication for biological impacts of sediment quality	2) Test for contribution of sediments to known ecological impairment (e.g. bad score in MSK modules)	1) Monitor the impact at identified hot spots (e.g. point-sources or known discharges) 2) Prioritize sites on the basis of sediment quality 3) Remediation planning and success control	1) Identify spatial and temporal trends of sediment contamination 2) Prioritize sites based on chemical contamination
Type of assessment			Ecotoxicological			Chemical
Matrix for analysis	% sediment <63 µm in 2 mm fraction	< 5%	Assessment not recommended [a]			
		< 20%	< 2 mm			< 63 µm
		20-80%				(< 63 µm or) 2 mm [b]
		> 80%				2 mm [c]
Evaluation			Classification of sediments into 5 classes through comparison with EQS_{sed}			Classification by comparison with EQS_{sed} or other established threshold [d]

[a] Sampling sites for sediment monitoring should ideally have more than 5% fine fraction (<63 µm) (EC 2010).
[b] The fraction <2 mm can already identify point sources of pollution and spatial trends in sediment contamination when the sediment contains at least 20% fines (< 63 µm) but this may not hold true of all instances.
[c] According to the results from field trials for sites that have high proportion of fines, the measurements are representative for the entire matrix, and hence results can be used for comparison to EQS_{sed}.
[d] For non-ionic substances EQS_{sed} are normalized for organic carbon content, accounting for the matrix effect on bioavailability to some extent. Else, measured concentration values have to be compared with established thresholds from older measurements in the region or alternative thresholds values (Chapter 6).

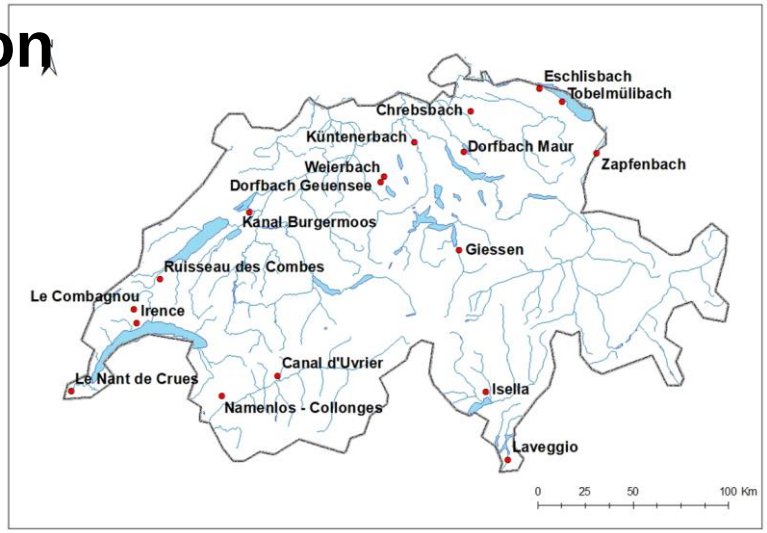
2. Sediment quality assessment strategy in Switzerland

Action categories (information needs)

	CATEGORY			
	1	2/4	3	5
Situation	Exposure and risk known	Exposure is not/hardly known	Risks difficult to evaluate	Exposure known, low risk
Criteria	Concentrations in CH known, available SQG, Identified risk (RQ≥1)	Substances measured occasionally in CH or in other EU countries	Substances mesurées occasionnellement en CH ou l'UE, données écotoxicologiques manquent	Substances avec RQ <1, concentrations décroissantes ou interdites en CH
Reccommended action	Candidate for sediment monitoring	Data acquisition campaign	Improvement of ecotoxicological knowledge	Candidate for reduced monitoring, if no other information available
Substances	PCBs, PAHs, DEHP, metals	PPP, pharmaceuticals, PFAS	Personal care products, PFAS	Lindane, endosulfan, heptachlor,

3. Preparatory study

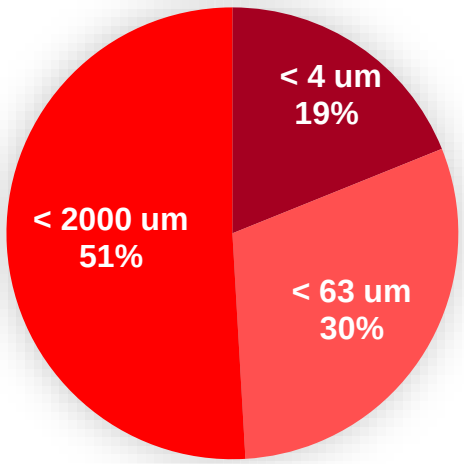
- **Data acquisition in 18 small streams**
- Different **sources of contamination**
  - Urban settlements: 0 – 43.2%
  - High-intensity agriculture : 0 – 71.1%
  - Low-intensity agriculture: 0.42%
  - Forest: 1.1 – 94%
  - Unproductive: 0 – 9.1%



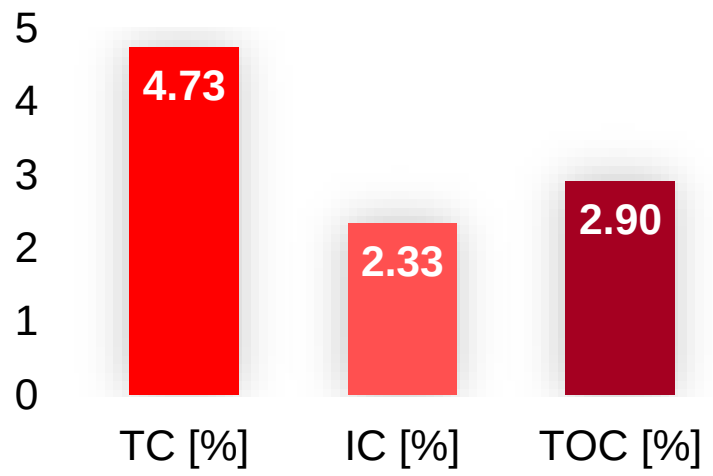
3. Preparatory study

- Different **types of substrate**
  - Grain size: fines 4.5-68%
  - Organic carbon: 0.5-13%

Average grain size



Average TOC



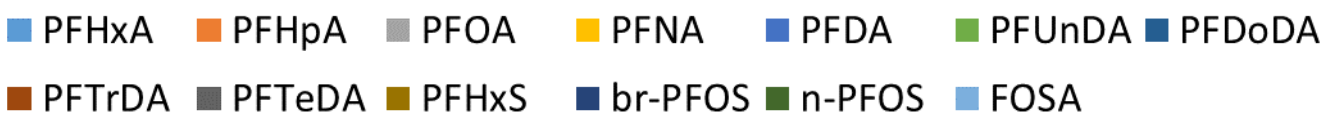
3. Preparatory study

- **Sampling and sample pre-treatment**
  - Sieving < 2 mm in the field
  - Wet sieving < 63 um in the lab

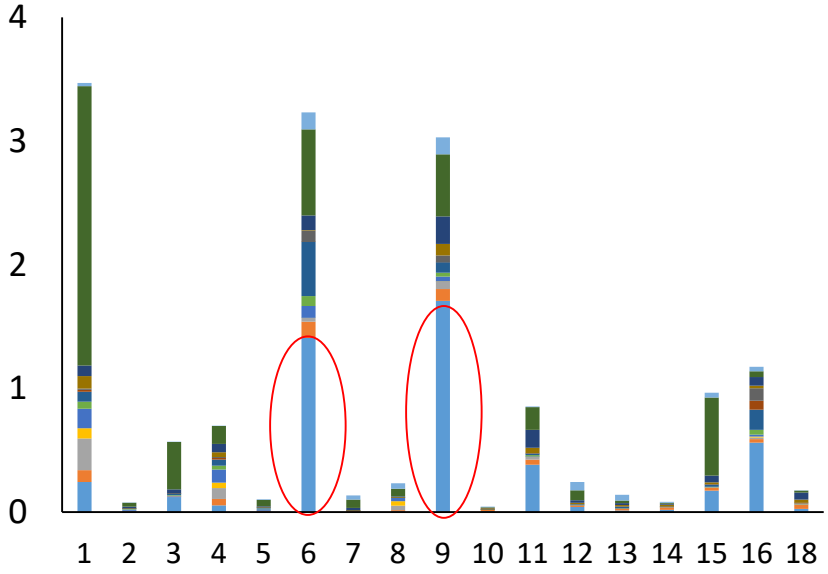
- **Quantification** of perfluoroalkyl compounds:
  - PFHxA, PFHpA, PFHxS, PFOA, branched PFOS (br-PFOS), linear PFOS (n-PFOS), ΣPFOS (calculated as br-PFOS + n-PFOS), PFNA, PFDA, PFUnDA, FOSA, PFDoDA, PFTrDA and PFTeDA
  - Quantified at IRSA (IT) by liquid chromatography tandem mass spectrometry (HPLC-MS/MS) coupled to on-line turbulent flow chromatography (TFC) for on-line purification of extracts
  - Method detection limits: 0.001 to 0.020 ng/g d.w. depending on the compound

3. Preparatory study

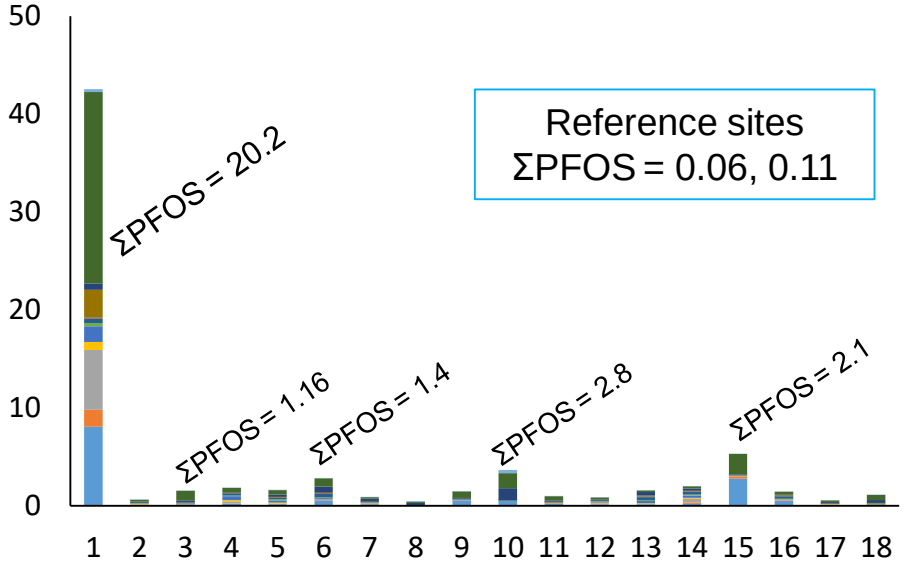
Measured concentrations of PFAS in sediments (ng/g dw)



In < 2 mm sediment



In < 63 um sediment

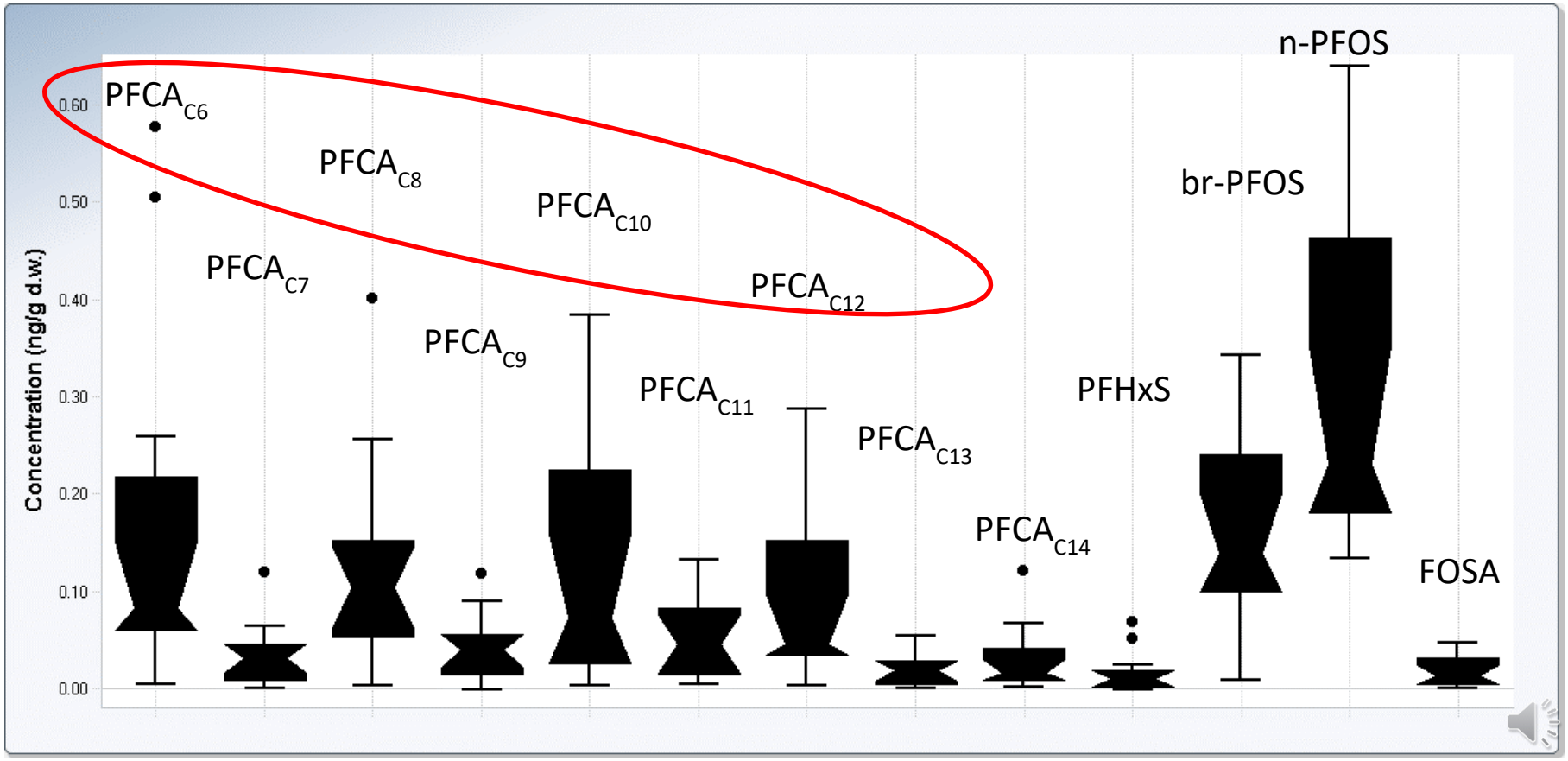


SITES

Highest proportion of urban settlements

3. Preparatory study

- **Distribution of congeners in < 2 mm sediments according to number of C for PFCAs**



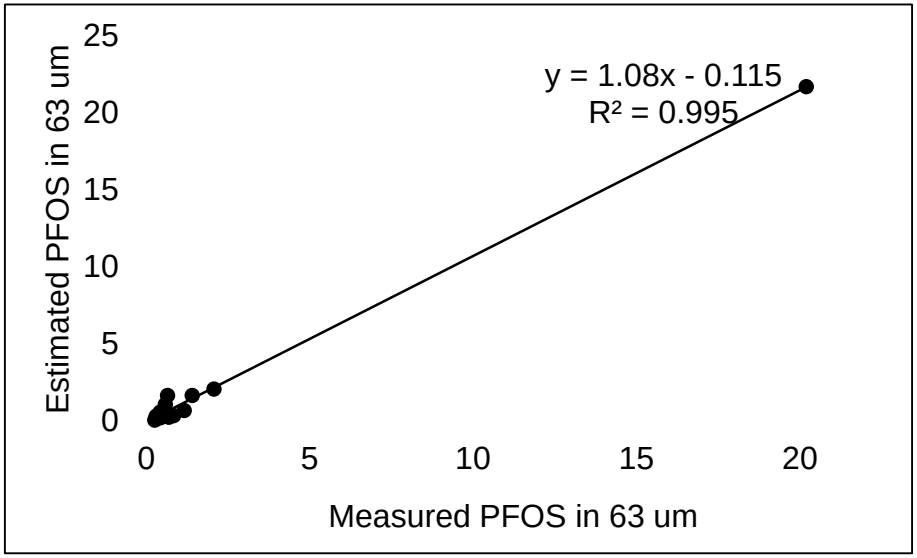
3. Preparatory study

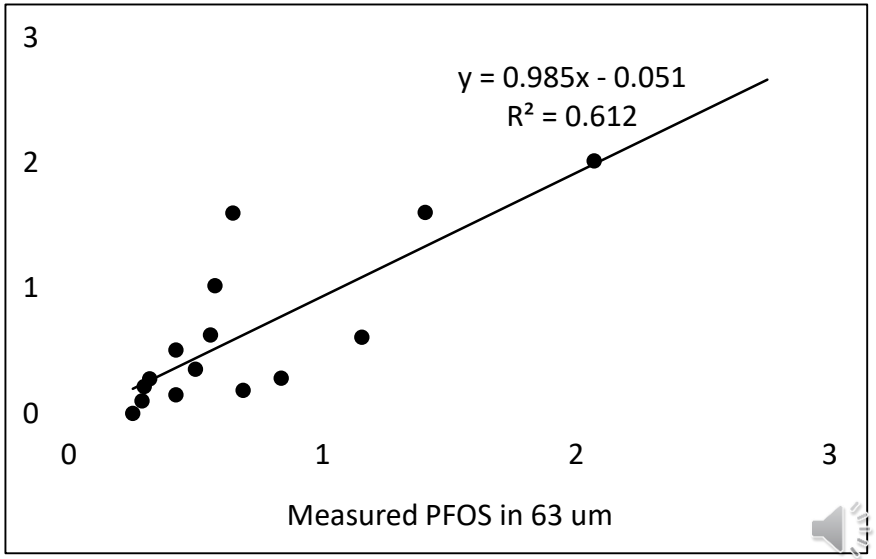
- **Estimation of anthropogenic background concentrations (ABC) of PFOS in sediments**

This study **90th PC ref+low impacted sites**	**ΣPFOS:** **0.680 ng/g d.w. (63 um)** **0.316 ng/g d.w (2mm)** **PFHxA:** **0.455 ng/g d.w. (63 um)** **0.545 ng/g d.w. (2 mm)**
Lowest concentrations Lake Geneva (Switzerland) (CIPEL 2017)	PFOS: 0.64 ng/g d.w.
Maximum at Lake Constance Danube (Austria) (Clara et al. 2009)	PFOS: 1 ng/g d.w. (<63 µm) Alpine Lakes < DL
Marine sediments in Norway (Bakke et al. 2010)	PFOS: 0.17 ng/g d.w.
90th PC (2 MS, 34 sites, N=62) (EC 2011)	PFOS: 3.12 ng/g d.w. (1.98 ng/g including 22 non-detects)

3. Preparatory study

- **WFD-CIS Guidance n. 25 on sediment and biota monitoring (EC 2010):**
  - "whole sediment "may give a direct reflection of pollutant distribution only if the sediments have homogeneous bulk composition" -> recommends the analysis of the <63 µm sediment fraction.
  - Suspended matter is an alternative to water samples for monitoring certain (organic) non polar pollutants when levels of concentrations in the water phase are below quantification limits or when water quality criteria are challenging for compliance check (EC 2010).





3. Preparatory study

- **Derivation of environmental quality criteria for sediments (EQS_{sed}) following the EU TGD for EQS development (EC 2018)**

Description	Value	Development method	Uncertainty	Reference
ABC_{2mm}	0.32	PC90 at reference and low impacted sites computed for the sediment fraction <2 mm	Not effect-based	This study
Direct toxicity				
(1) $QS_{sed,AF,eco}$	**13.5**	EU TGD (EC 2018): based on NOEC for *Monoporeia affinis* survival of 1300 ng/g d.w.(1350 ng/g d.w. for a sediment with 5% OC) and AF of 100	Too few effect data from spiked sediment toxicity tests, high AF to account for uncertainty	This study
(2) $QS_{sed,EqP,eco}$	22.1	EU TGD (EC 2018): derived using the EqP and a $QS_{freshwater}$ of 230 ng/L	Preliminary QS	This study

3. Preparatory study

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(2) $QS_{sed,EqP,eco}$	22.1	EU TGD (EC 2018): derived using the EqP and a $QS_{freshwater}$ of 230 ng/L	Preliminary QS	This study
Secondary poisoning for top predators				
(3) $QS_{sed,EqP,sec.pois.}$	0.19	EU TGD (EC 2018): derived using the EqP and a $QS_{freshwater}$ of 2 ng/L	Preliminary QS	This study
(4) $QS_{sed,sec.pois.}$	**1.85**	Babut (2018): derived from a QS_{biota} of 33 ng/g w.w. to protect top predators from fish consumption	Derivation method not validated Relatively small BSAF database	This study
Secondary poisoning for human health				
(5) $QS_{sed,hh\ food}$	0.51	Babut (2018): derived from a EQS_{biota} of 9.1 ng/g fish w.w.	Derivation method not validated Relatively small BSAF database	Babut (2018)

3. Preparatory study

- **Sediment quality assessment at the studied sites**

Site	Protection objective		
	Direct toxicity	Sec. Pois.	Human health
1			
2			
3			
4			
5			
6			
7			
8			
9			
10			
11			
12			
13			
14			
15			
16			
18			

Classification		Class definition ($RQ = MEC/EQS_{sed}$)	Meaning
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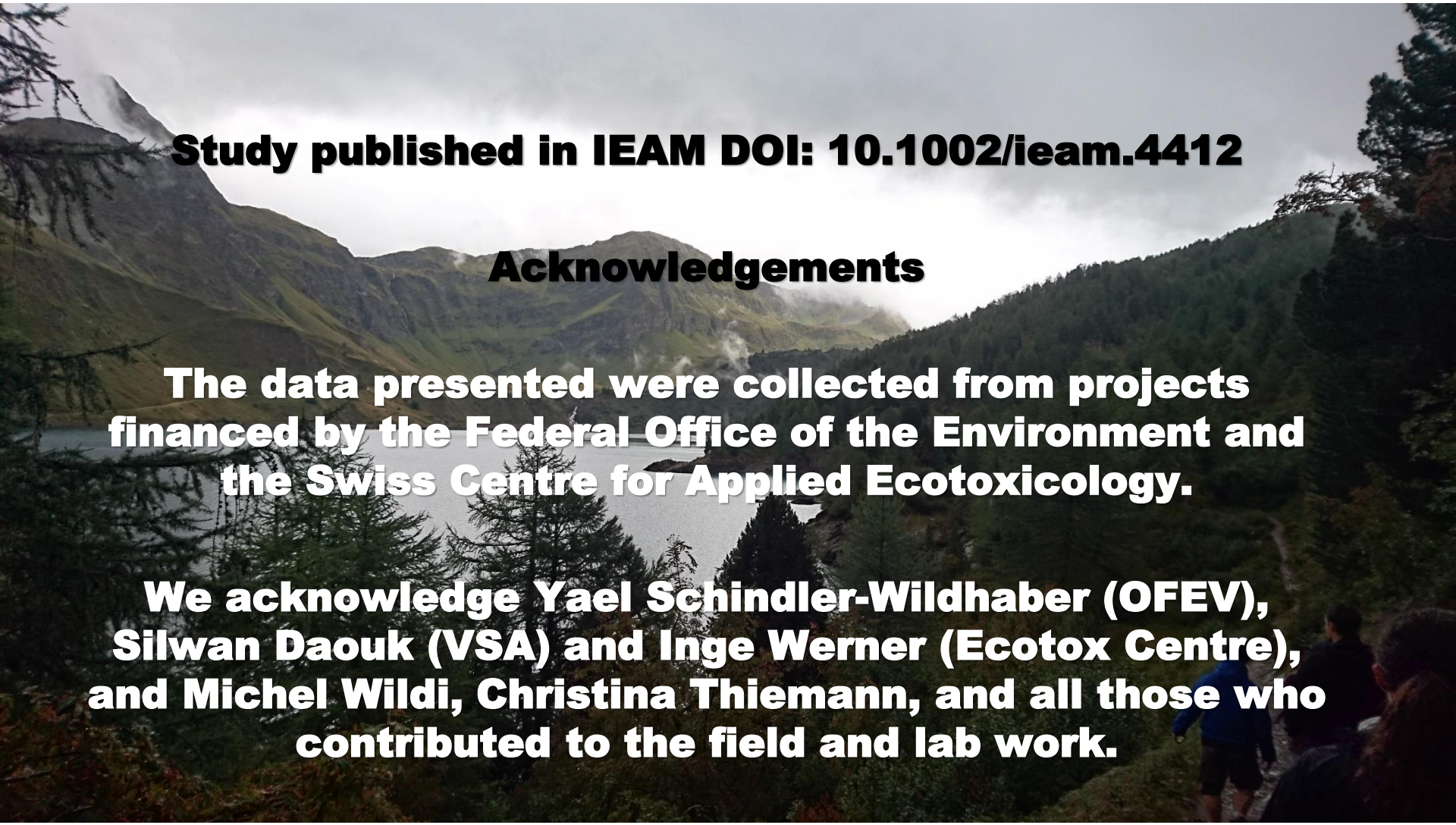
Level 2: assessment refinement

4. Conclusions and perspectives

- PFOS: suitable indicator for monitoring PFAS contamination in sediment quality assessment in Swiss small streams
  - Most commonly detected PFAS
  - EQS_{sed} could be derived
  - Normalization for the fine fraction for comparison among campaigns targeting different matrices
    - If not possible, anthropogenic background concentration are proposed for sediment quality assessment (not safe concentration benchmarks!)

4. Conclusions and perspectives

- PFOS: suitable indicator for monitoring PFAS contamination in sediment quality assessment in Swiss small streams
  - Most commonly detected PFAS
  - EQS_{sed} could be derived
  - Normalization for the fine fraction for comparison among campaigns targeting different matrices
    - If not possible, anthropogenic background concentration are proposed for sediment quality assessment (not safe concentration benchmarks!)
- Need of further data for deriving sound threshold values
  - Sediment toxicity studies for direct toxicity assessment
  - Validation of food webs models to link sediment contamination and secondary poisoning in top predators
- Need of appropriate strategies for PFAS risk assessment as a whole



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