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Schweizerisches Zentrum für angewandte Ökotoxikologie
Centre Suisse d'écotoxicologie appliquée

Ecotoxicological assessment of river sediments downstream of a firefighter training site

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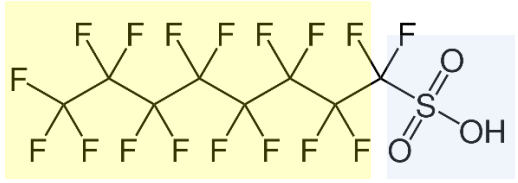
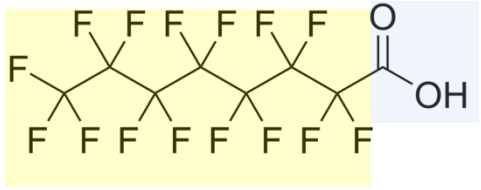
Introduction

PFAS - forever chemicals

Most famous use - firefighting foams
→ Environmental impact

- Chemicals used in industry and consumer products since the 1940s
- According to OECD, include more than 3000 substances and more than 4700 CAS numbers related to PFAS
- Specific properties
  - High persistence
  - High mobility in water
    → widespread and long-lasting contamination
- Most common
  - PFOS
  - PFOA





Fluorinated carbon chains (hydrophobic)

Functional group (hydrophilic)

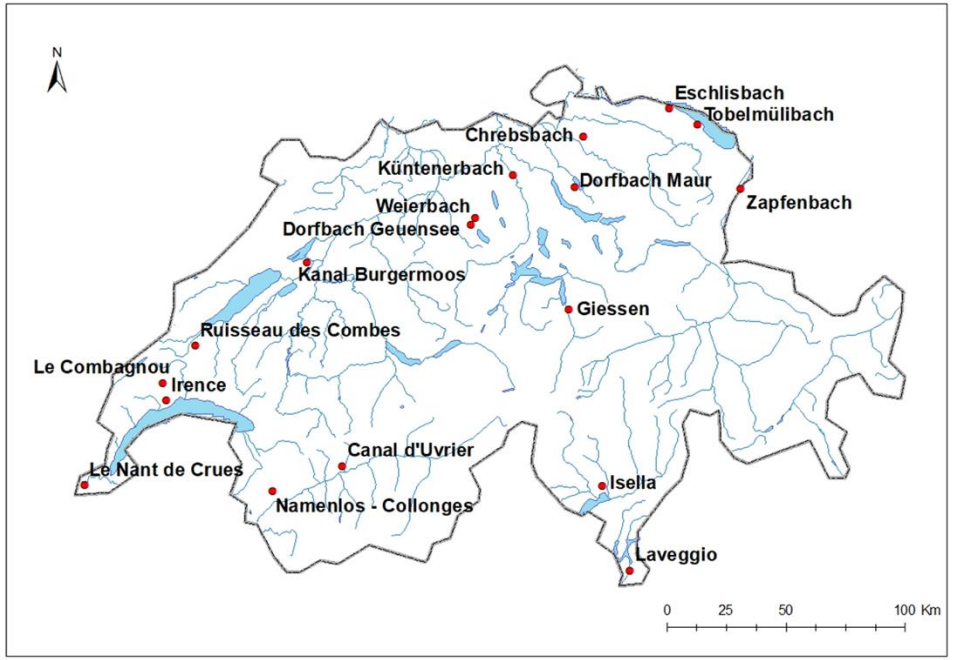
Introduction

PFAS in Swiss sediments

- PFOS in the first list of 20 priority substances, as indicator of a PFAS contamination (Casado-Martinez et al., 2018)
- Campaign 2018 - 18 streams, median values [PFOS] (µg/kg, dw) (Casado-Martinez et al., 2024)
  - 63 µm 0.61 (max 20.20, urban aeras)
  - 2 mm 0.11 (max. 2.26 , urban aeras)

- Estimation of the anthropogenic background concentration (ABC) for PFOS (µg/kg, dw) (Casado-Martinez et al., 2021)
  - 63 µm 0.68
  - 2 mm 0.32
  - → Realistic objectives for sediment managment

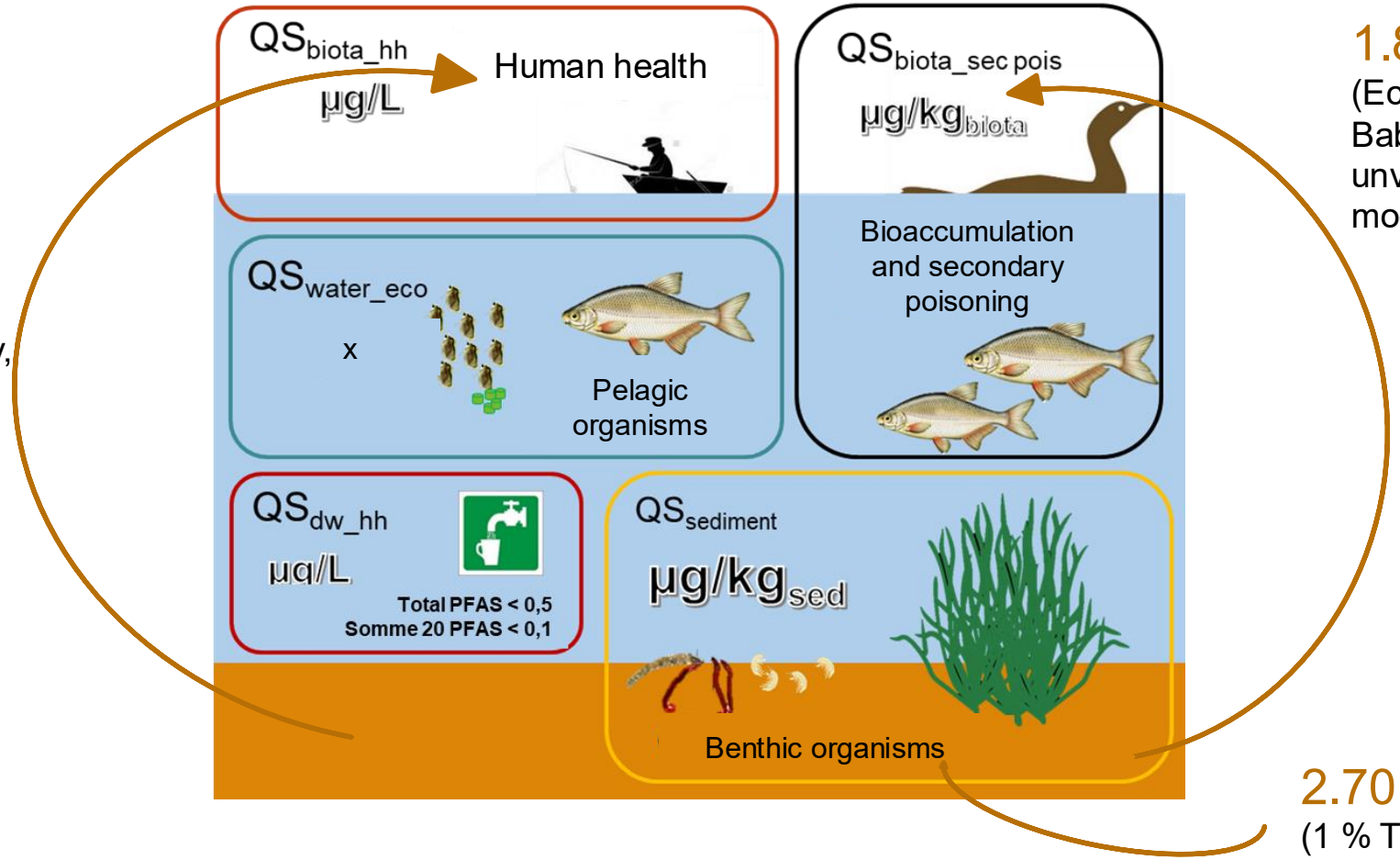
- Other PFAS measured
  - Long chain PFDA, PFHxS and PFOA
  - Short chain PFHxA and PFPeA



HPLC-MS/MS @ IRSA (IT): PFHxA, PFHpA, PFHxS, PFOA, PFOS (br,n), PFNA, PFDA, PFUnDA, PFDoDA, PFTrDA, PFTeDA, et FOSA (LOD: 0.001 - 0.020 µg/kg, dw)

Introduction

PFOS - Environmental quality standards



0.51 µg/kg, dw
(Babut, 2018) provisory, unvalidated food chain model

1.85 µg/kg, dw
(Ecotox Centre following Babut, 2018) provisory, unvalidated food chain model

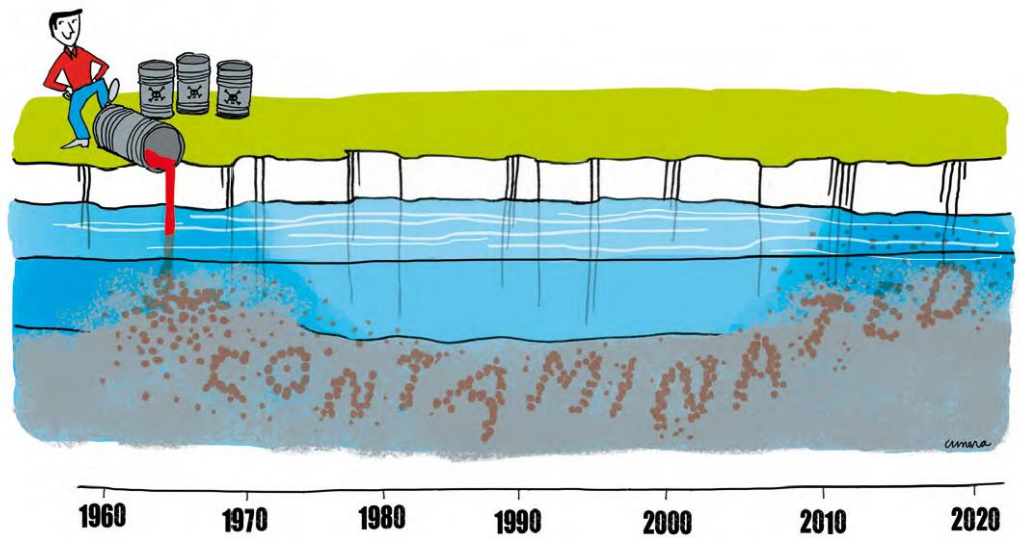
2.70 µg/kg, dw
(1 % TOC) (Ecotox Centre, 2020) provisory, insufficient data

Lack of ecotoxicological data / high uncertainty

Introduction

PFAS hazard in sediments

- Sediments : source and sink of PFAS
- Bioavailability and toxicity to benthic organisms
- Enter aquatic food webs → biomagnification in top predators
- Remobilization potential (release to water)
  - pH change, oxidoreduction state
  - perturbation through dredging, floodings



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Case study:
Ecotoxicological assessment of river sediments downstream of a firefighting training site

Introduction

Case study

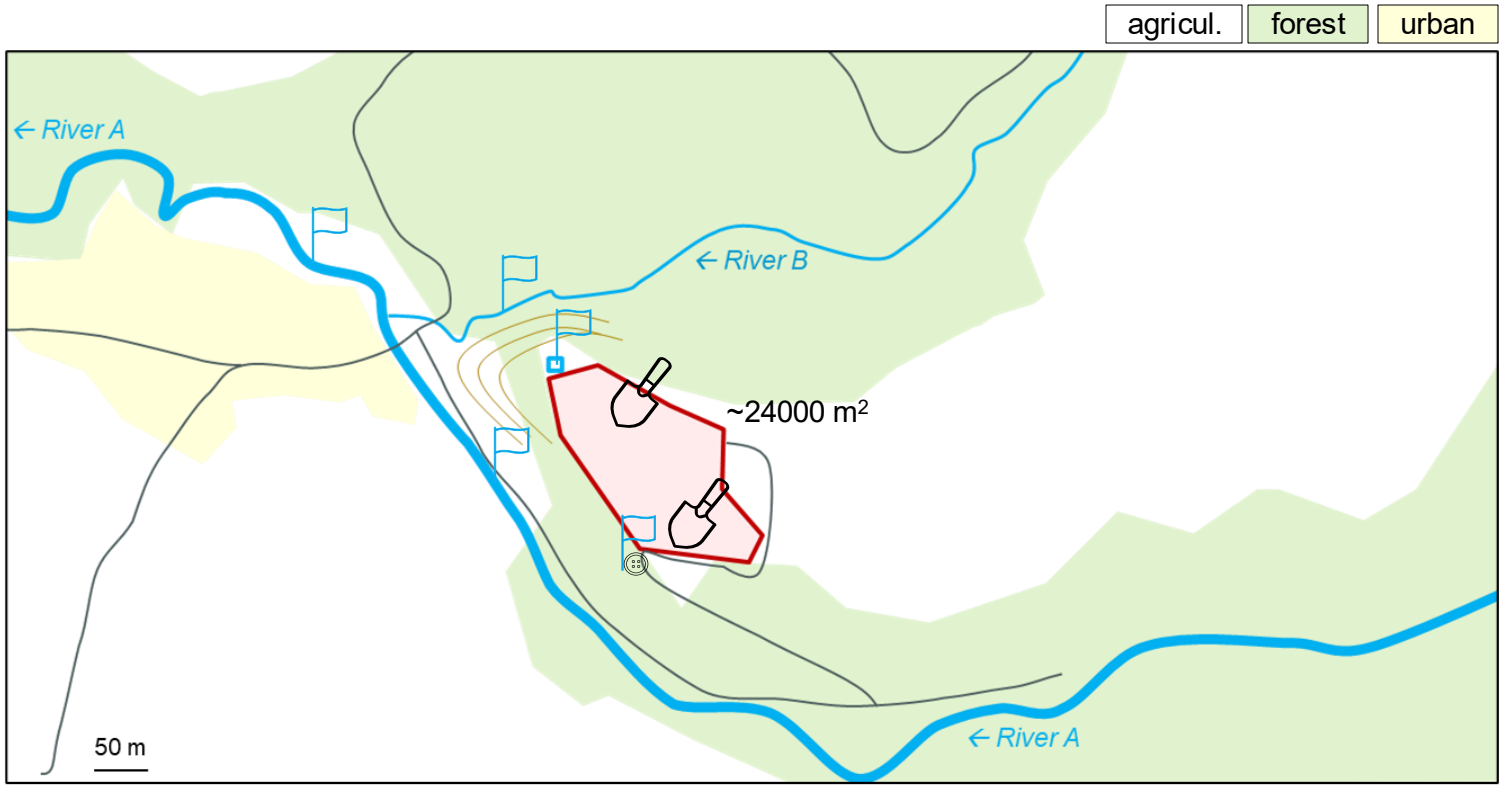
- Firefighter training site constructed in the 80s - use of different types of firefighting foams
- The use of firefighting foams can lead to the dispersion of PFAS into the environment (soil, water)
- Registered as polluted site → cantonal authority asks for investigation

Soil

2 soil sampling sites
∑9 PFAS = 6 / 41 µg/kg, dw

Leachates
∑9 PFAS = 228 / 679 ng/L

→ Remediation values exceeded (OSol ordinance)



Water

∑PFAS

retention tank 159 ng/L, drain 539 ng/L

No PFAS in River A

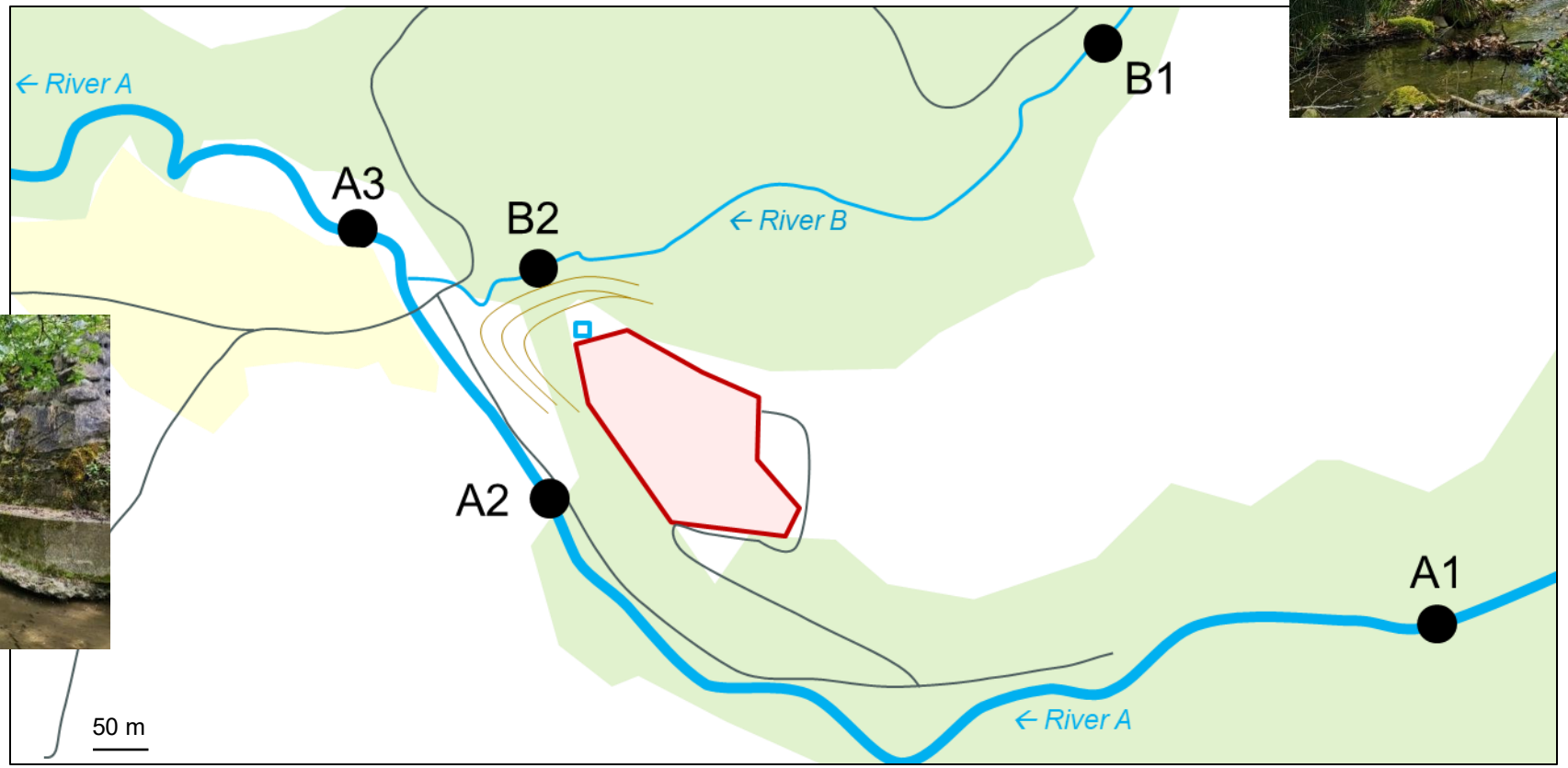
87 ng/L (18 - 30 ng/L) (PFHxA, PFHxS, PFOA, PFOS) in River B

No Swiss guideline values
EQS-annual average 0.65 ng/L

→ **Investigation of sediments - how is the environment impacted?**

Material and methods

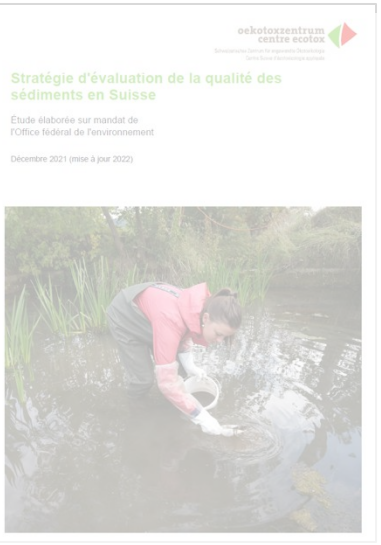
- Sediment sampling sites



Material and methods

1. Collection of fine sediments according to the Ecotox Center guidelines (composite samples sieved on-site to 2 mm).

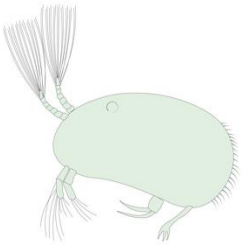
   - 2 in river A, 2 in river B, 1 after their confluence in river A
   - chemical analyses (20 PFAS substances# (“European list”, private laboratory), total organic carbon content, grainsize distribution
   - PFAS risk assessment: comparison of concentrations with available sediment quality criteria

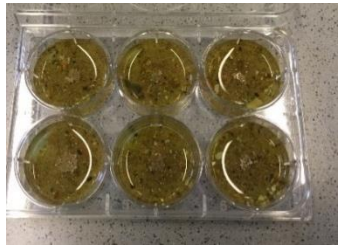


Casado et al., 2022

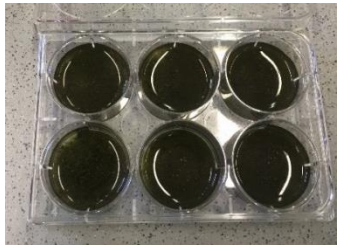
2. Bioassay with the epibenthic crustacean *Heterocypris incongruens*

   - Relevant benthic invertebrate, abundant in freshwater bodies, wide distribution
   - Commercial test kit (Micro BioTests Inc.), no culture needed
   - ISO standard 14371 (ISO, 2012) for freshwater sediment toxicity
   - survival and/or growth affected by exposure to sediments (5 samples)?

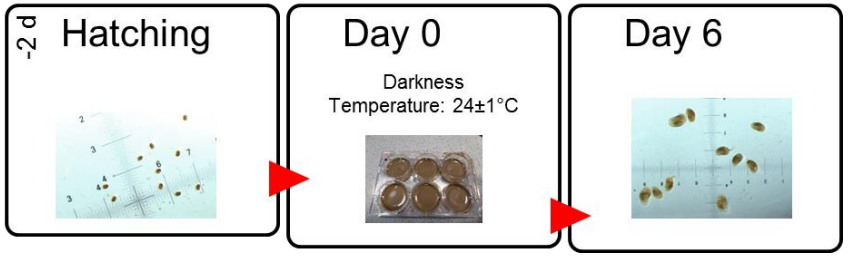




Control



Sediment



: PFBA, PFPeA, PFHxA, PFHpA, PFOA incl. branched, PFNA, PFDA, PFUnA, PFDoDA, PFTrDA, PFBS, PFPeS, PFHxS incl. branched, PFHpS, PFOS incl. branched, PFNS, PFDS, PFUnS, PFDoDS, PFTrS

Results and discussion

- Chemical analyses

  Sediment samples (µg/kg, dw)

	upstream	downstream	downstream confluence	upstream	downstream
Substance / Site	A1	A2	A3	B1	B2

Results and discussion

- Chemical analyses

  Sediment samples (µg/kg, dw)

	upstream	downstream	downstream confluence	upstream	downstream
Substance / Site	A1	A2	A3	B1	B2
PFOS					
PFDA					
PFOA		<LOQ	<LOQ	<LOQ	
PFHxA	<LOQ			<LOQ	
PFHxS	<LOQ	<LOQ	<LOQ	<LOQ	
PFPeA	<LOQ	<LOQ	<LOQ	<LOQ	

Results and discussion

- Chemical analyses

  Sediment samples (µg/kg, dw)

	upstream	downstream	downstream confluence	upstream	downstream
Substance / Site	A1	A2	A3	B1	B2
PFOS	0.1	3.7	3.9	0.4	34.1
PFDA	0.1	0.4	0.7	0.3	0.5
PFOA	0.5	<LOQ	<LOQ	<LOQ	0.8
PFHxA	<LOQ	0.2	0.2	<LOQ	0.2
PFHxS	<LOQ	<LOQ	<LOQ	<LOQ	0.4
PFPeA	<LOQ	<LOQ	<LOQ	<LOQ	0.2
∑PFAS	0.7	4.3	4.8	0.7	36.2

× 6

× 50 !!

- ✓ Upstream ABC exceeded
- ✓ Impact of the polluted site
- ✓ PFAS are present in River A

blanks <0.1-1.0 µg/kg, dw
ABC 0.32 µg/kg, dw

Results and discussion

- Risk assessment

PFOS - provisory SQC, different protection objectives

2.7 µg/kg, dw (1% COT)

1.85 µg/kg, dw (sec. poisoning)

	US	DS	DS-conf	US	DS
Substance / Site	A1	A2	A3	B1	B2
RQ - PFOS	0.01			0.07	
RQ - PFOS sec. p.	0.05			0.22	
RQ - ∑PFAS	0.09	0.33	0.64	0.12	6.27
RQ - ∑PFAS sec. p.	0.38	2.24	2.59	0.38	19.6

RQ, risk quotient

Sediment quality assessment system based on SQC comparison.

Classification	Numerical evaluation		Class definition (RQ = MEC/SQC)	Meaning
Very good	0.8 – 1	The measured concentration in the sediment is at least 10 times lower than the quality criterion (SQC)	RQ < 0.1	SQC met
Good	0.6 - <0.8	The measured concentration in the sediment is between 1 and 10 times lower than the quality criterion (SQC)	0.1 ≤ RQ < 1	
Moderate	0.4 - <0.6	The measured concentration in the sediment is lower than two times the quality criterion (SQC)	1 ≤ RQ < 2	SQC exceeded
Unsatisfactory	0.2 - <0.4	The measured concentration in the sediment is lower than 10 times the quality criterion (SQC)	2 ≤ RQ < 10	
Poor	0 - <0.2	The measured concentration is equal to or higher than 10 times the quality criterion (SQC)	RQ ≥ 10	

Casado et al., 2022

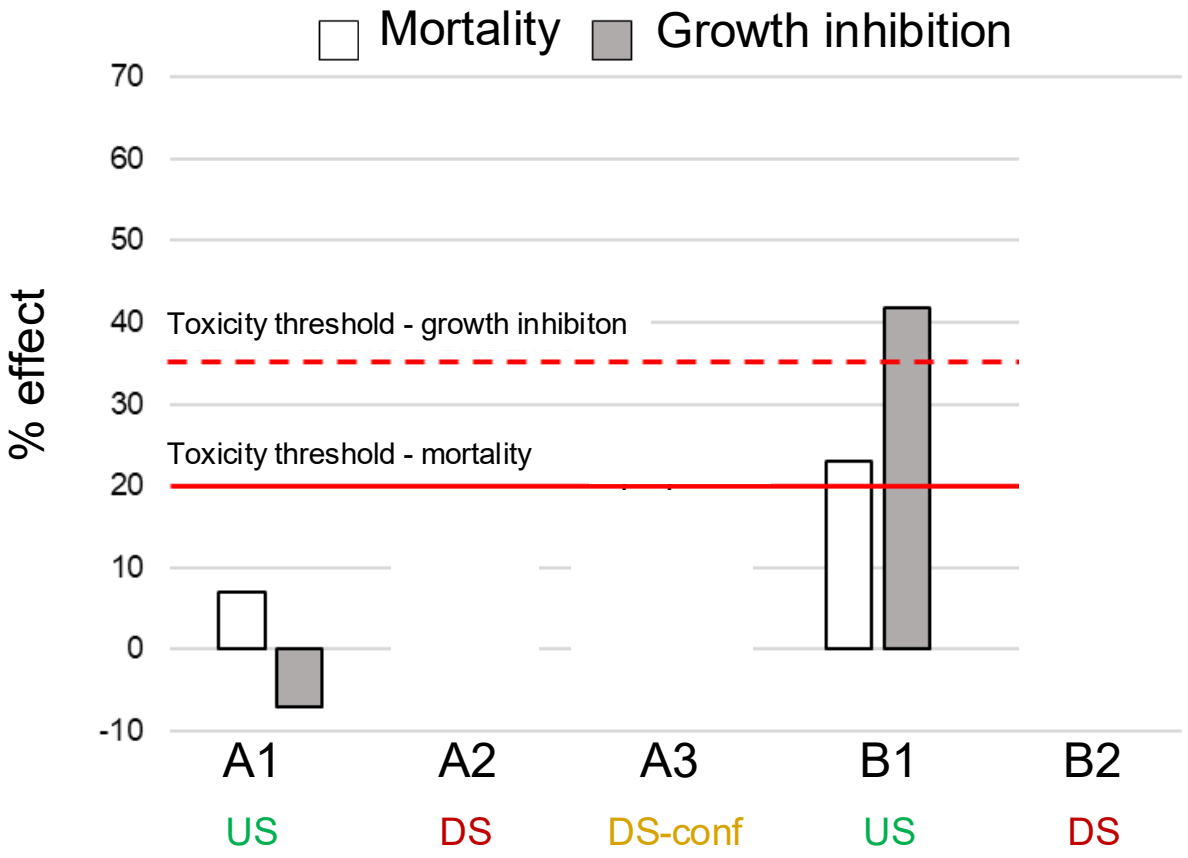
✓ Significant impact on sediments in River B, less significant impact in River A
✓ Provisional quality criteria, need of toxicity data on benthic organisms → perform ecotoxicological tests

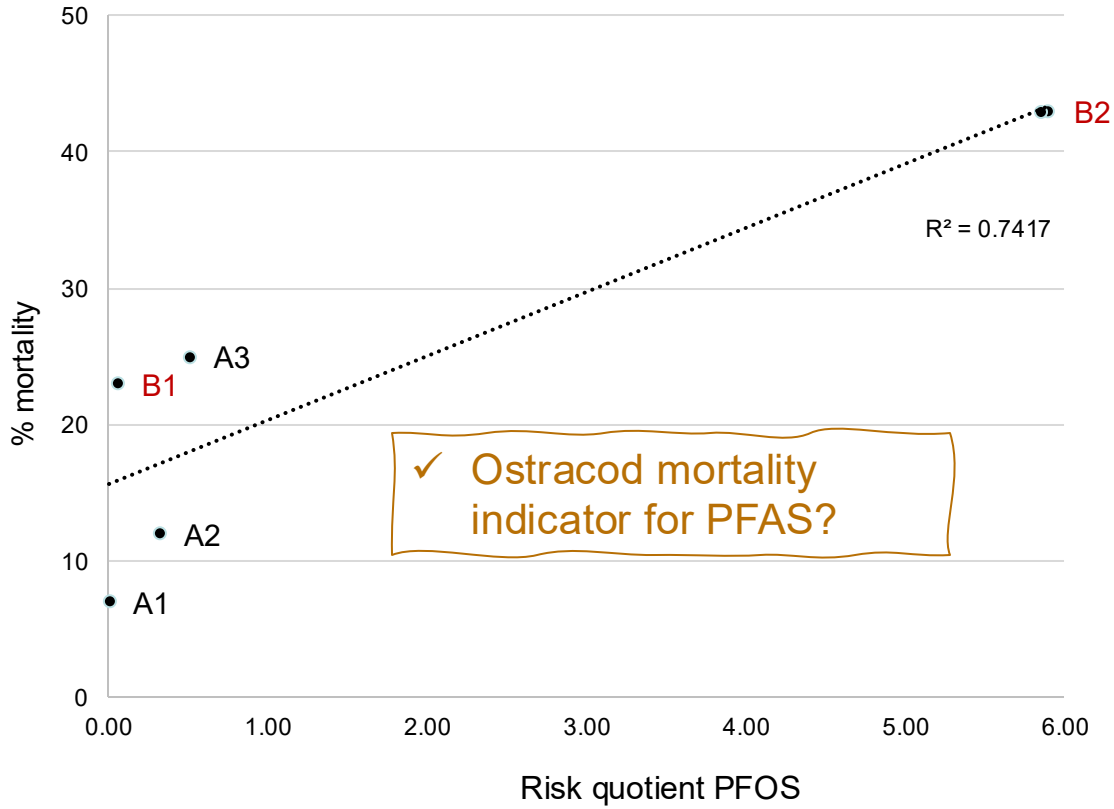
Results and discussion

- Bioassay with the ostracod *H. incongruens*

Results and discussion

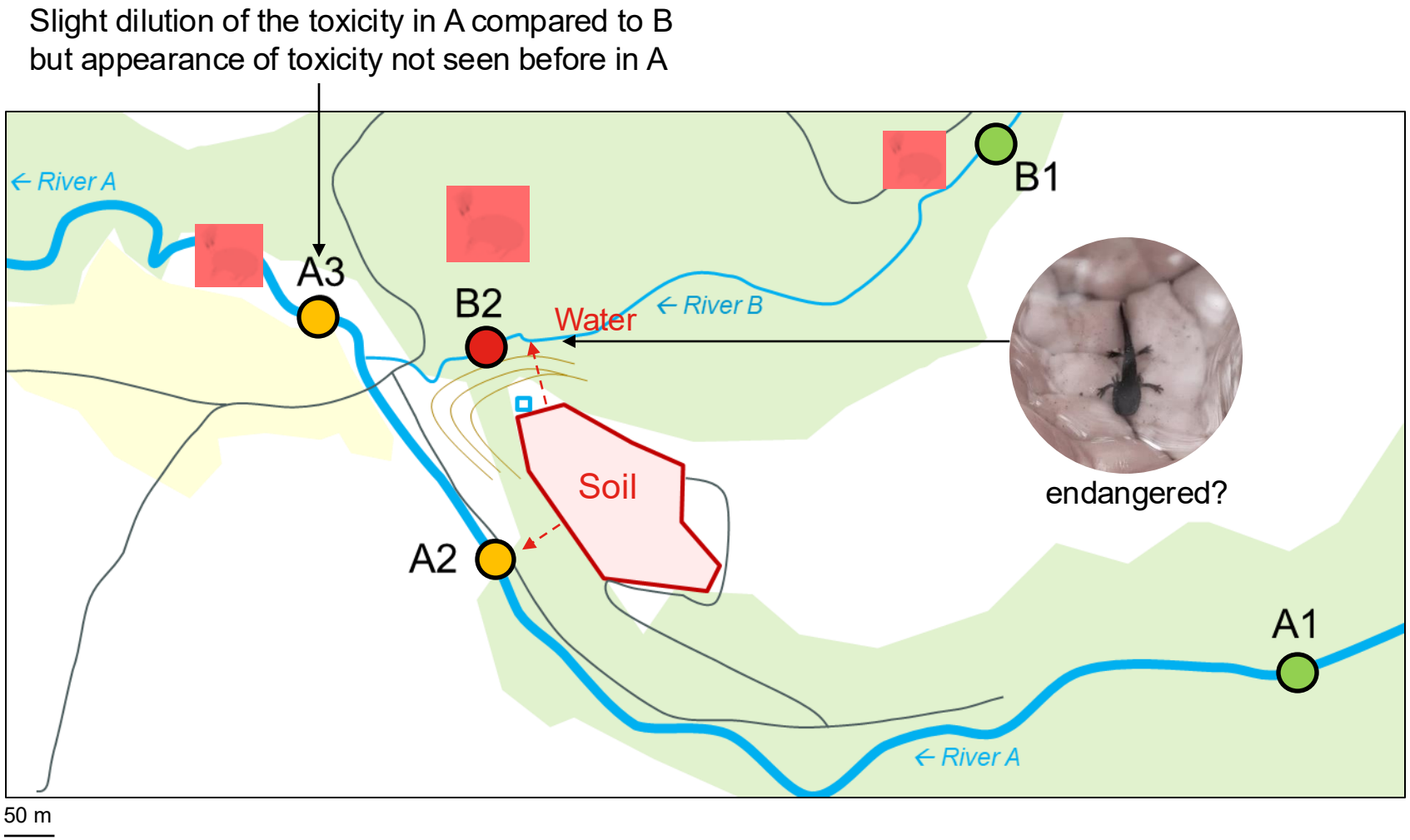
- Bioassay with the ostracod *H. incongruens*





✓ Same gradient as for [PFAS]: impact on benthic organisms at B2 but also impact upstream (sediment properties and/or chemical pressure already upstream - other than PFOS?)

Summary



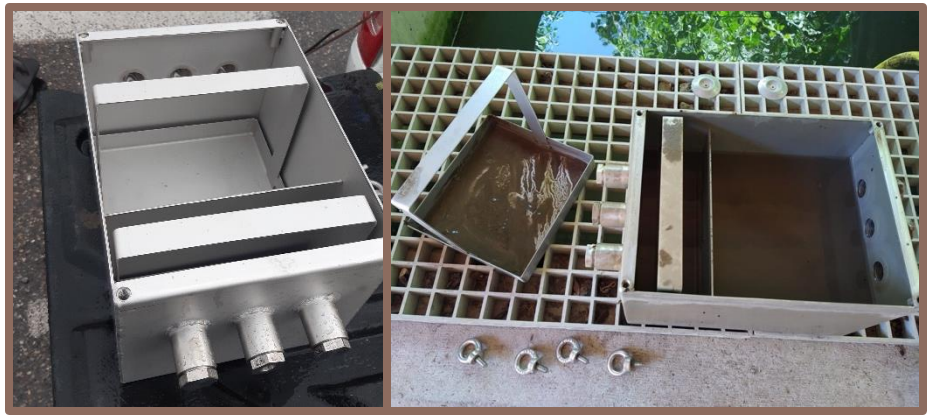
Risk assessment using the EQS for secondary poisoning $PFOS_{emp.sec.}$ for the ∑[PFAS] («worse case»)

Ostracod mortality

Conclusions

- **First study** in Switzerland on PFAS contamination of sediments in connection with a **firefighter training site**.
- Both the risk assessment based on chemical analyses and the bioassay converge in showing an **impact on sediment quality** downstream of the firefighting training site.
  - Chemical analyses showed a significant difference between upstream and downstream, especially for the **smallest watercourse**.
  - **Ostracod mortality** showed a clear upstream-downstream response in both rivers, with the highest mortality was observed in the sediment with the highest concentration of PFOS (and ∑PFAS).
  - For B2, the risk assessment indicates a significant risk to benthic life downstream of the site and **risk of secondary poisoning** of aquatic fauna.
- Ostracod mortality sensitive for detecting effects related to the presence of PFAS in complex sediment samples?

- Follow-up project with the support of the authority
  - How far spreads the contamination downstream
  - Use of a biotestbattery
  - Investigations on suspended particulate matter



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