INSTITUTE OF
CHEMICAL TECHNOLOGY PRAGUE

PERFLUORINATED COMPOUNDS LEVELS IN WILD FISH FROM THE CZECH REPUBLIC

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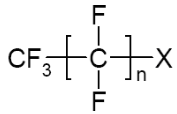
CONffIDENCE

SEVENTH FRAMEWORK PROGRAMME

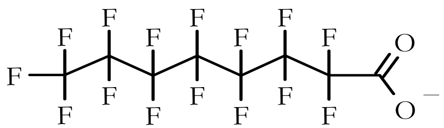
Perfluoroalkylated substances (PFAS)



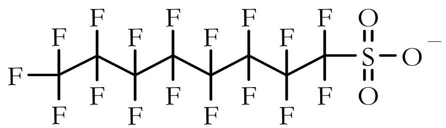
- Emerging contaminants
- Unique physico-chemical properties
  - C – F strong bond
  - High chemical stability
  - Photostability and thermostability
  - Hydrophobicity and oleophobicity – surface active compounds
- Using in various industry and household products

(Protection of textile, carpet, leather (PTFE-Teflon, Gore-Tex), fire – fighting foam)

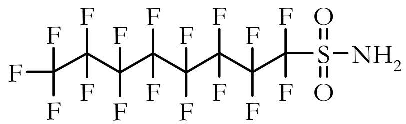


Perfluorooctanoic acid (PFOA)

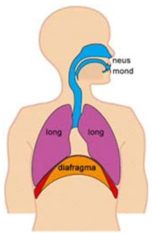


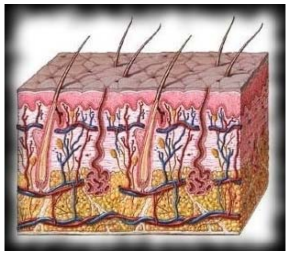
Perfluorooctanesuphonate (PFOS)



Perfluorosulphonamide (FOSA)

Exposition routes: oral, dermal and inhalation



Diverse effects:

Reproduction cycle disorder
Human evolution disorder
Hepatoxicity, spasms, weight decrease, death

Incidence of PFASs in the environment

Abiotic & biotic compartments

Sediments
(river, sea)
Sewage sludge
(Water waste treatment plants)
Water
(river, sea, tap, rain)
Dust
(home – TV, computer, carpet)
Air
(particles)

Liver
Muscle
Eggs
Kidney
Blood
(serum, plasma, cord)
Breast milk

} Animals (fish, birds, mammals), Human

PFASs → binding to proteins
X
Other halogentad POPs (e.g. PCB, BFR) → cumulation in lipids

Legislation and restrictions for PFAS

European Fo
Authority

European Commision:
recommendation 2010/161/EU

n Convention

efsa
European Food Safety Authority

Perfluorooctane sulfonate (PFOS), p
their s

Scientific Opinion of the Panel on (

(Question N° EFS

Adopted on 2:

PFOS / P

TDI - 150 / 150

L 68/22 EN Official Journal of the European Union 18.3.2010

RECOMMENDATIONS

COMMISSION RECOMMENDATION

of 17 March 2010

on the monitoring of perfluoroalkylated substances in food

(Text with EEA relevance)

(2010/161/EU)

THE EUROPEAN COMMISSION,

Having regard to the Treaty on the Functioning of the European Union, and in particular Article 292 thereof,

Whereas:

(1) Perfluoroalkylated substances (PFAS) are widely used in industrial and consumer applications including stain-resistant coatings for fabrics and carpets, oil-resistant coatings for paper products approved for food contact, fire fighting foams, mining and oil well surfactants, floor polishes and insecticide formulations. An important subset are the (per)fluorinated organic surfactants, to which perfluorooctane sulfonate (PFOS) and perfluoro-octanoic acid (PFOA) belong.

The EFSA recommended that further data on PFAS levels in food and in humans would be desirable, particularly with respect to monitoring trends in exposure.

(5) The Stockholm Convention on persistent organic pollutants (POPs) requires contracting parties to undertake monitoring of POPs, their alternatives and candidate POPs and has included PFOS, its salts and perfluorooctane sulfonyl fluoride (PFOSF) in Annex B to the Convention among the substances subject to restrictions on production and use,

HAS ADOPTED THIS RECOMMENDATION:

1. Member States should monitor during 2010 and 2011 the presence of perfluoroalkylated substances in food. The monitoring should include a wide variety of foodstuffs reflecting consumption habits including food of animal origin such as fish, meat, eggs, milk and derived products and food of plant

SC

UNEP/POPS/COP.4/38

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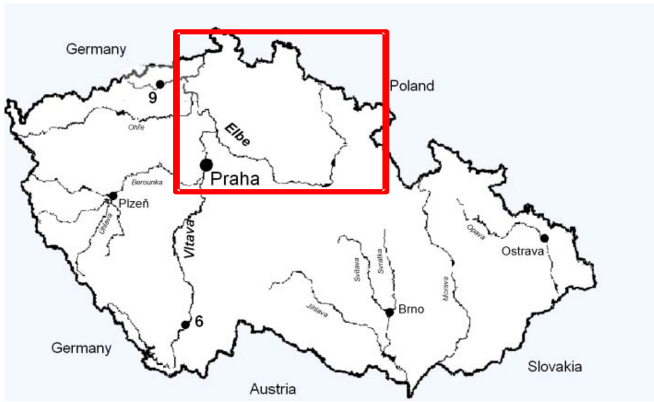
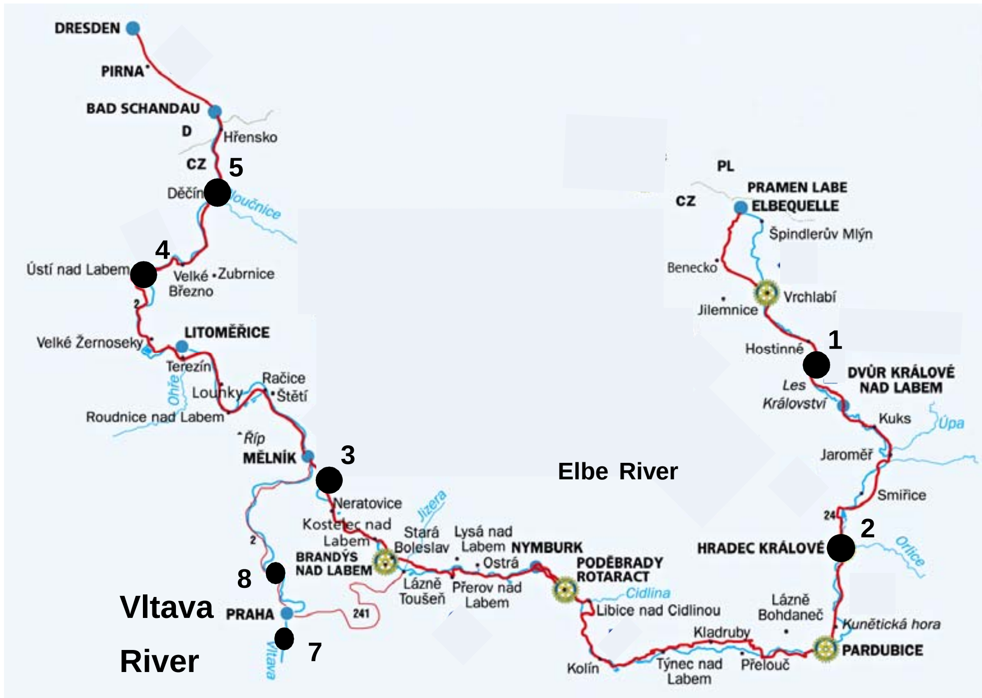
Experimental part

Sampling sites

- 9 localities
- bream, chub, crucian carp, roach, undermouth
- pooled samples – 3 categories: 100 – 300g; 300 – 900g and > 900g
- 60 samples of muscle





Elbe River:	Vltava River:
Verdek (1)	Hluboka nad Vltavou (6)
Hradec Kralove (2)	Podoli (7)
Obristvi (3)	Sedlec (8)
Usti nad Labem (4)	
Decin (5)	**Bilina River:** Trmice (9)

Target analytes

#	Analytes		
1	PFCAs	C4	PFBA
2		C5	PFPeA
3		C6	PFHxA
4		C7	PFHpA
5		C8	PFOA
6		C9	PFNA
7		C10	PFDA
8		C11	PFUdA
9		C12	PFDoA
10		C13	PFTrDA
11		C14	PFTeDA
12		C16	PFHxDA
13		C18	PFODA
14	PFSAs	C4	PFBS
15		C6	PFHxS
16		C8	PFOS
17		C10	PFDS
18	PFAPAs	C6	PFHxPA
19		C8	PFOPA
20		C10	PFDPA
21	FOSA	C8	FOSA

13 perfluorocarboxylic acids (PFCAs)

4 perfluorosufonic acids (PFSAs)

3 perfluorophosphonic acids (PFAPAs)

1 perfluorosulfonamide (FOSA)

Analytical method

Fish tissue:

2 g sample

Addition of isotopically labelled standards – $^{13}C_4$-PFOS a PFOA

EXTRACTION (6 mL methanol)

10 min

CLEAN–UP (activated charcoal)

10 min

Centrifugation (10000 rpm; 5 min)
Filtration (0.2 µm centrifuge filter; 5000 rpm; 2 min)

15 min

Identification & Quantification LC-MS/MS

15 min

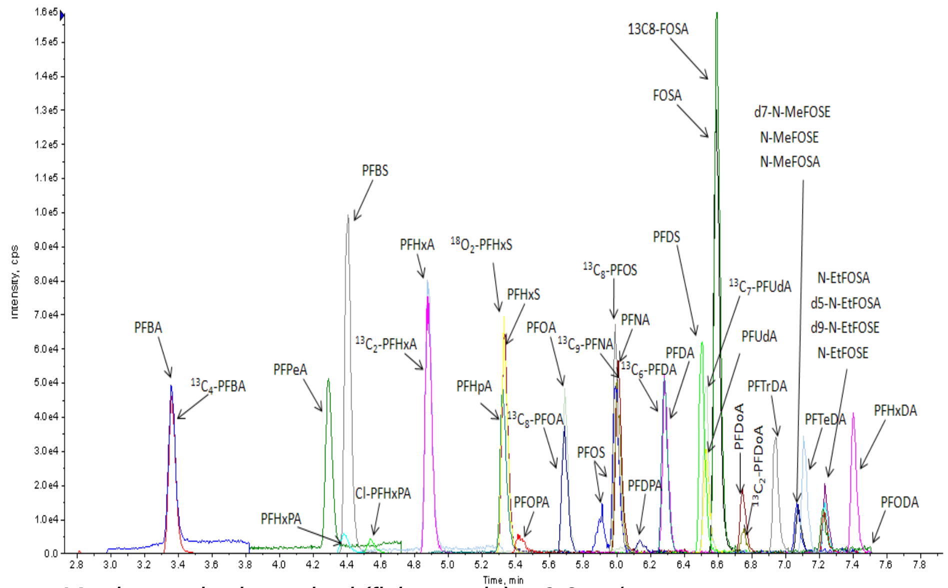
Total time: 50 min

Instrumental determination

Acquity UPLC (Waters, USA)
AB SCIEX QTRAP® 5500 (AB SCIEX, Canada)

Analytical column: HSS – 100 x 2.1 mm i.d.; 1.8 µm
Injection volume: 5 µL
Mobile phase: 5 mM ammonium acetate : Methanol
Run time: 11.5 min

Performance characteristics	
LOD (µg/kg)	**0.01–0.15**
LOQ (µg/kg)	**0.03–0.3**
Recovery (%)	**71–120**
RSD (%)	**2–7**
Linearity (µg/kg)	**0.03–15**



Matrix matched standard (fish muscle) – 0.3 ng/g

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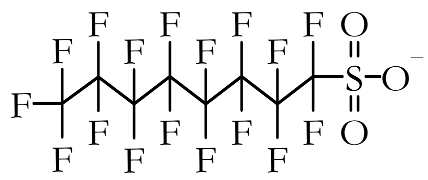
Summary of results

	PFCAs							
Analytes	**C5**	**C8**	**C9**	**C10**	**C11**	**C12**	**C13**	**C14**
Positive samples (%)	36	40	100	100	100	100	100	100
Max. concentration (µg/kg)	**0.4**	**0.4**	**0.6**	**22**	**20**	**7.8**	**3.7**	**0.9**

PFCAs with shorter chain – PFBA (C4), PFHxA (C6), PFHpA (C7) not detected

	PFSAs			FOSA
Analytes	**C6**	**C8***	**C10**	**C8**
Positive samples (%)	60	100	98	100
Max. concentration (µg/kg)	**0.1**	**136**	**0.1**	**7.8**

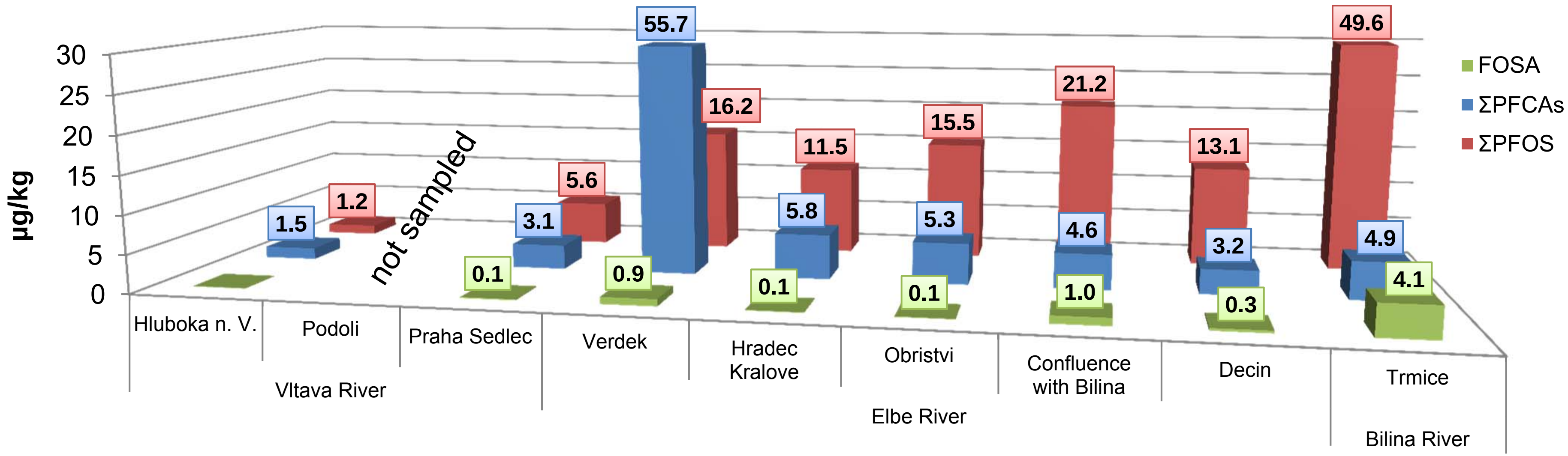


PFOS

PFBS (C4) and perfluorophosphonic acids not detected

Levels of PFASs in fish muscle

Chub (*Leuciscus cephalus*)



- Chub – the most common fish species in the Czech rivers
- Verdek/Elbe River and Trmice/Bilina River – the most polluted sampling sites
- PFASs especially PFOS, the most abundant analyte
- Sum of PFCAs – the highest concentration at Verdek

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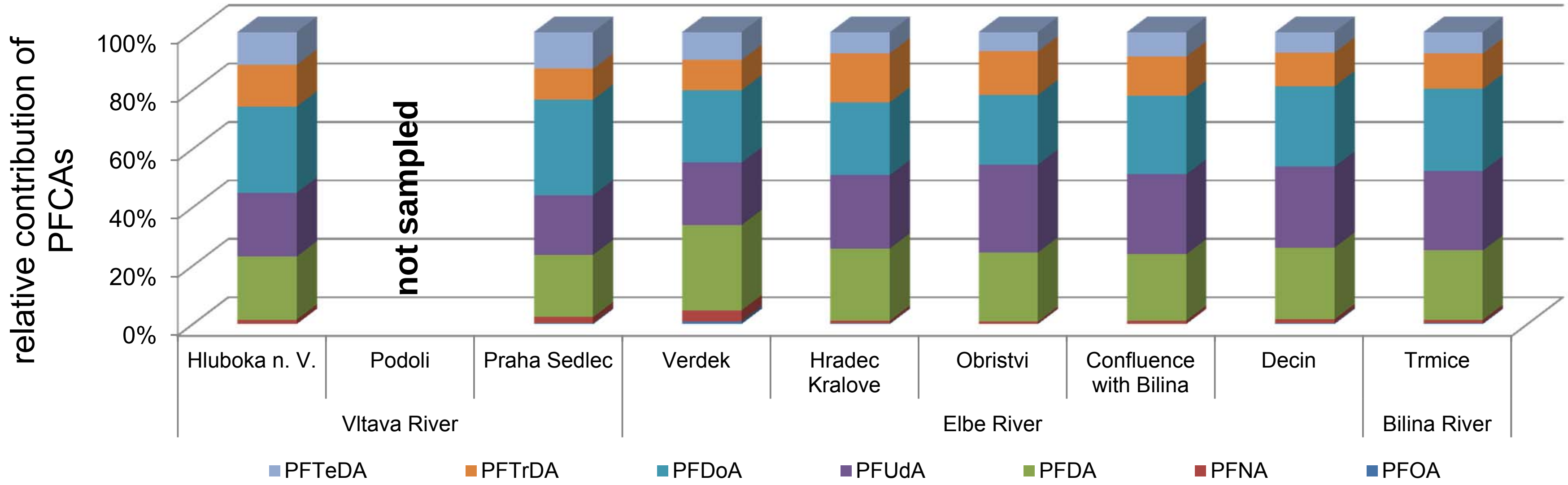
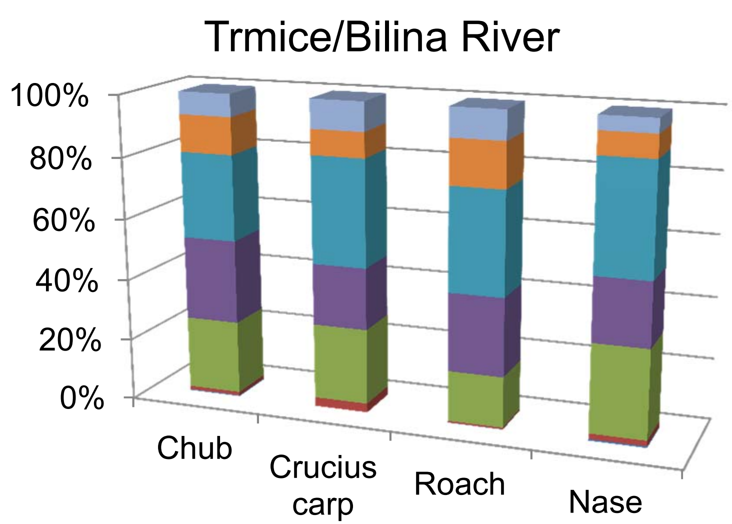
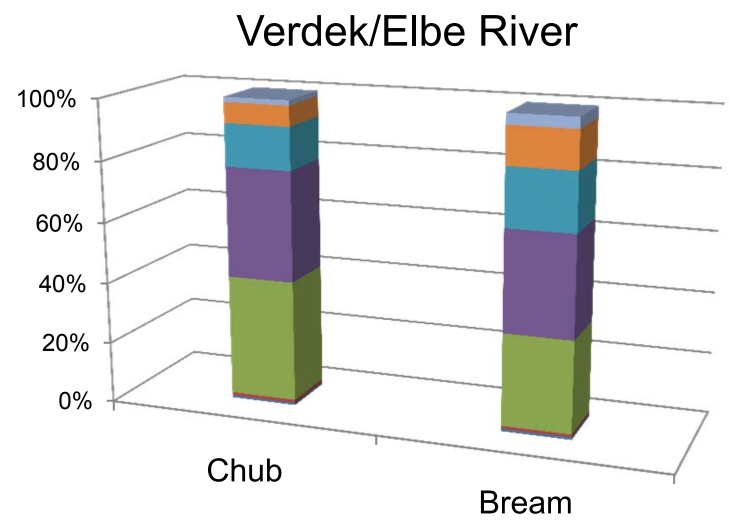
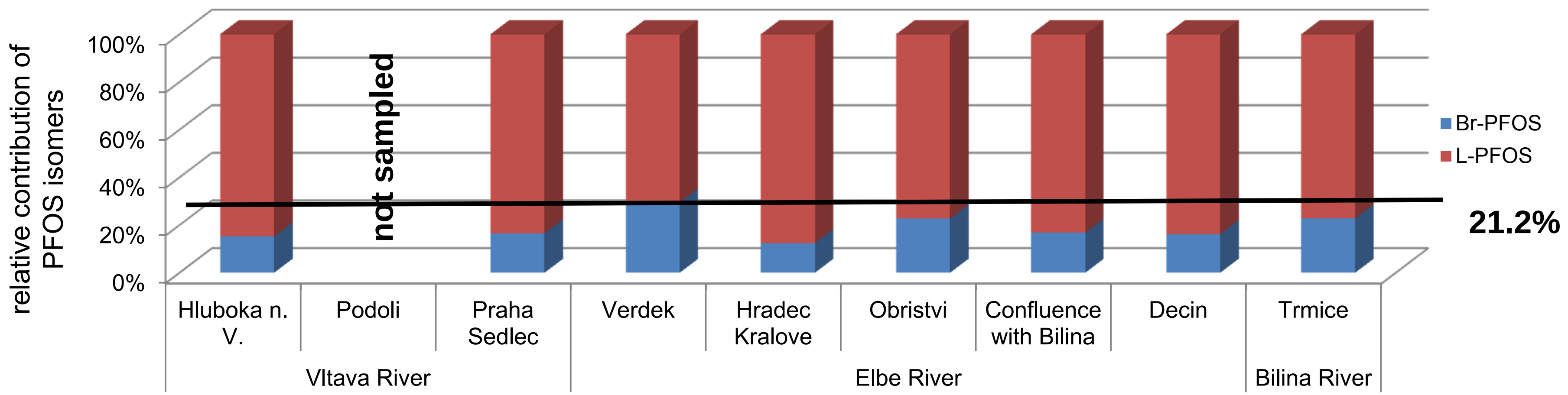
Contribution of individual PFCAs to Σ PFCAs



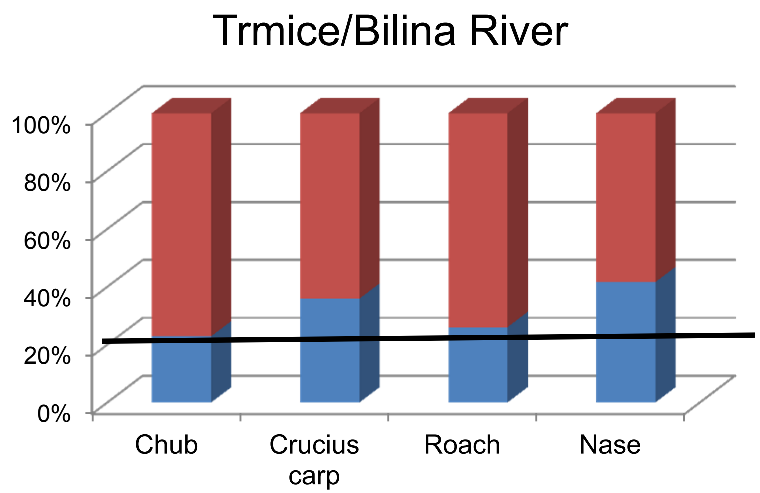


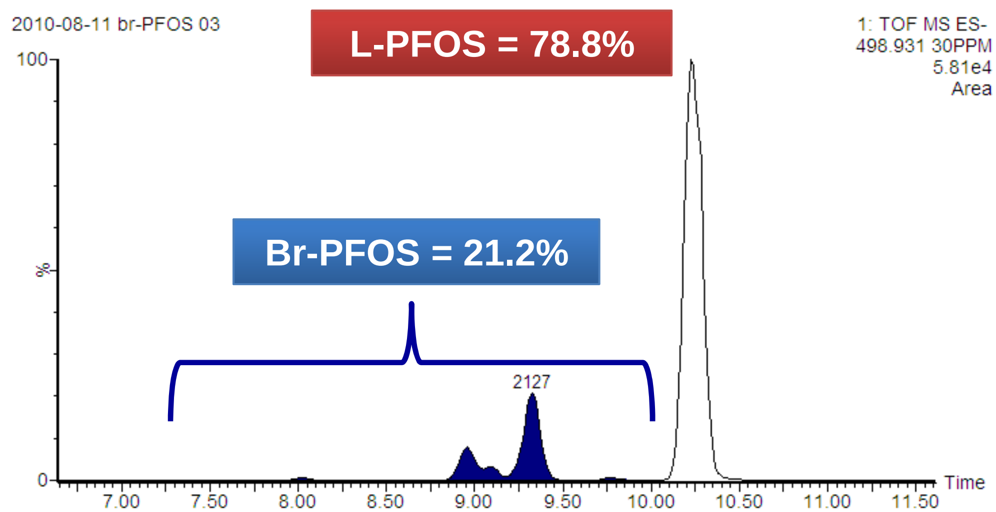


Contribution of PFOS isomers to Σ PFOS



Technical mixture PFOS





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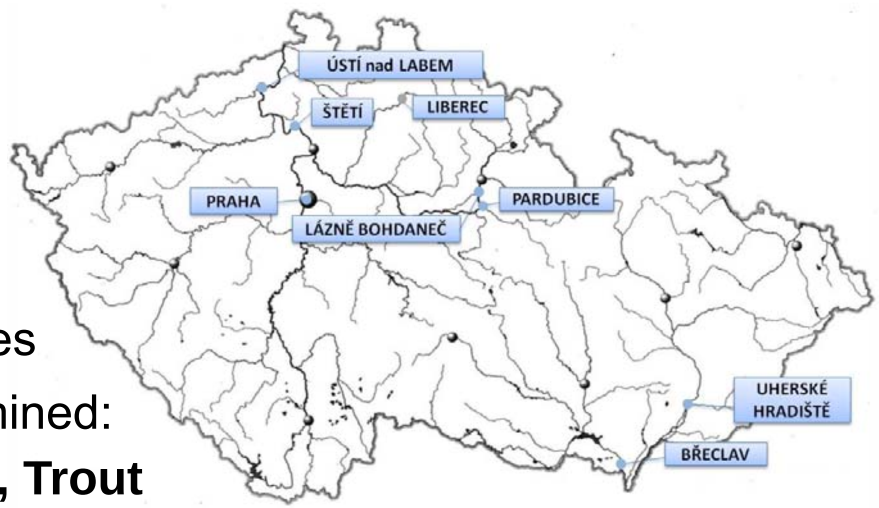
Follow-up study

- ❑ Pooled samples
- ❑ Altogether 72 fish muscle samples
- ❑ In selected localities also individual samples
- ❑ The most common fish species were examined:

Bream, Chub, Roach, Perch, Crucian carp, Trout



(Abramis brama)

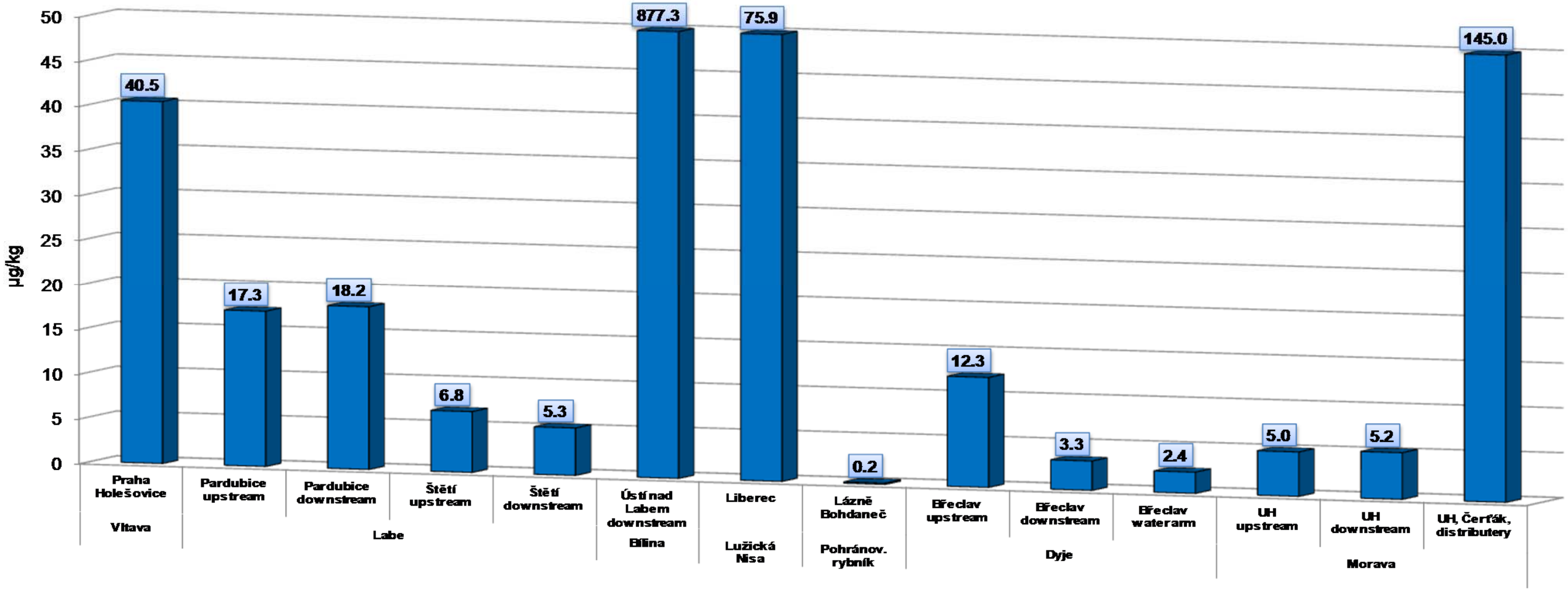
(Rutilus rutilus)

(Leuciscus cephalus)

(Cyprinus carpio)

- ❑ Sampling sites – Elbe River, Vltava, Bilina, Lužická Nisa, Morava, Dyje and in pond (Podhradský)
- ❑ The sampling localities upstream and downstream from the potential source of PFASs

Results – follow–up survey



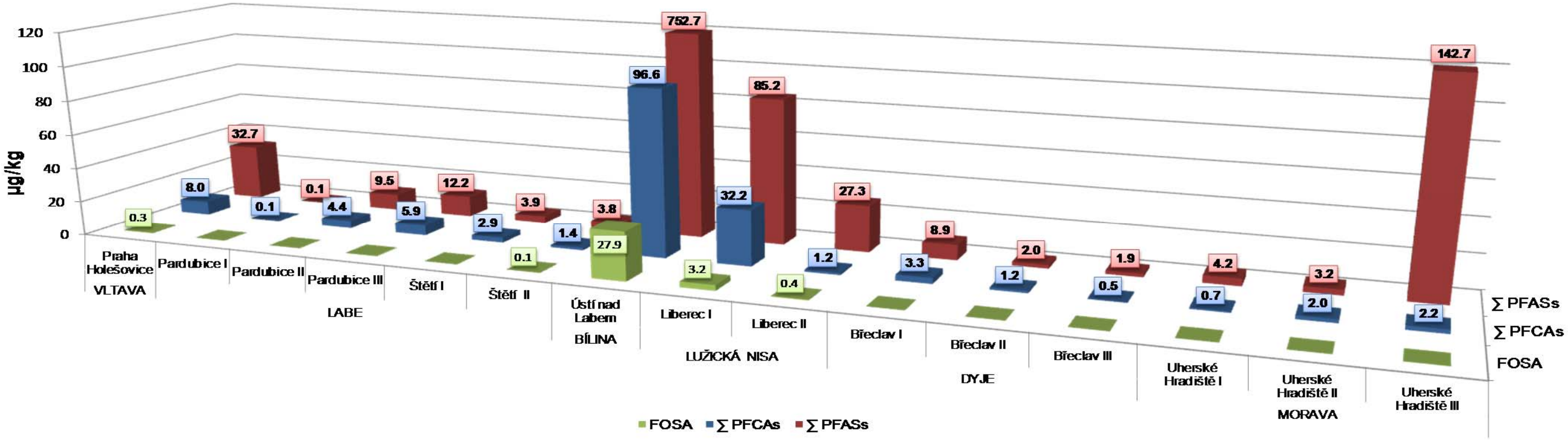
- ❑ Localities on Bilina River, Lužická Nisa and Morava (distributary) – the most contaminated

- ❑ Low levels of PFASs – Dyje River

- ❑ No significant differences between localities upstream and downstream from the „source“

Levels of PFASs in fish muscle

Bream (*Abramis brama)*



- High PFASs levels on the Bilina River confirmed
- The highest concentration of Σ PFASs exceeded 850 µg/kg
- PFOS, the most abundant analyte
- Σ PFCAs – the highest concentration at Bilina River

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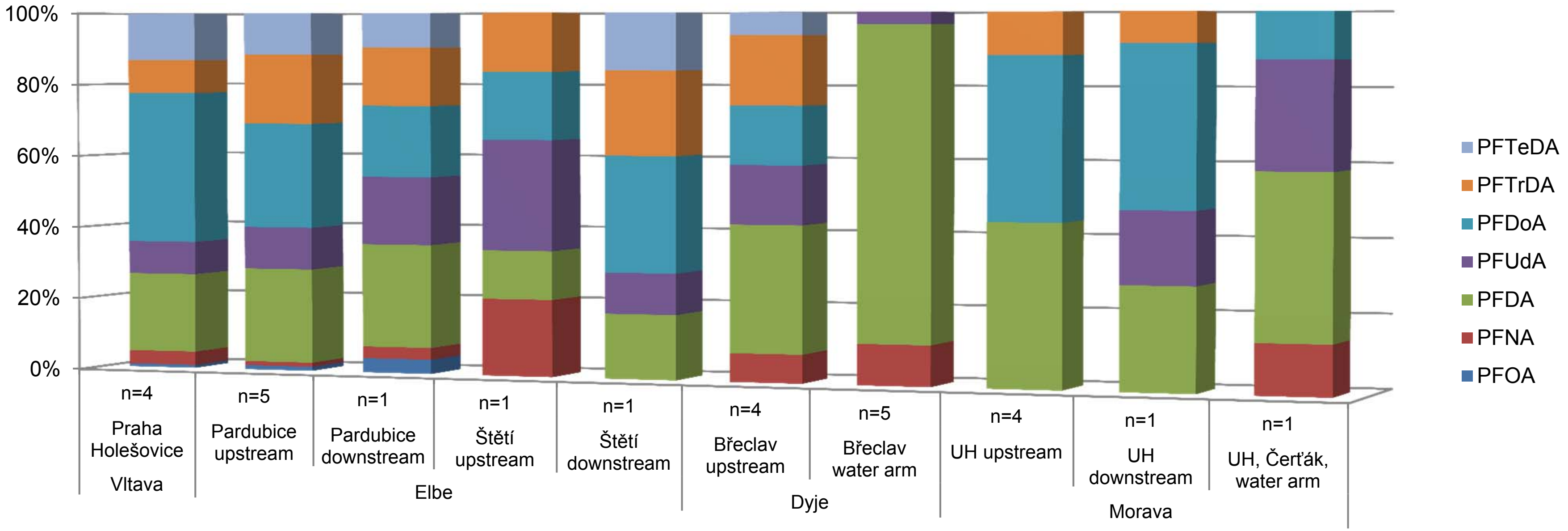
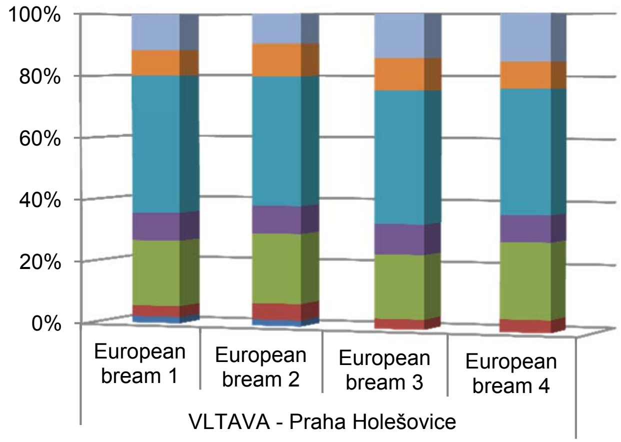
Contribution of PFCAs in bream muscle





- Comparison of the PFCAs profile in the different localities
- The contribution of individual PFCAs depend on locality / potential source ?
- Similar profile in one locality

CONCLUSIONS

- For the first time, the extensive monitoring study was conducted in the Czech Republic.
- PFOS was the most abundant analyte, not only from the group PFSAs.
- The acids with longer carbon chain (C8 >), especially PFNA, PFDA, PFUdA (C11) and PFDoA (C12), represented PFCAs.
- The potencial sources of PFCAs in Verdek / Elbe River and PFOS in Trmice / Bílina River, were located.
- The follow–up study confirmed the previous results and the most polluted localities.

Thank for your attention