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WP 2.B Contamination of rock and soil environment

Environment - Environment for Life
12. – 14. 9. 2022

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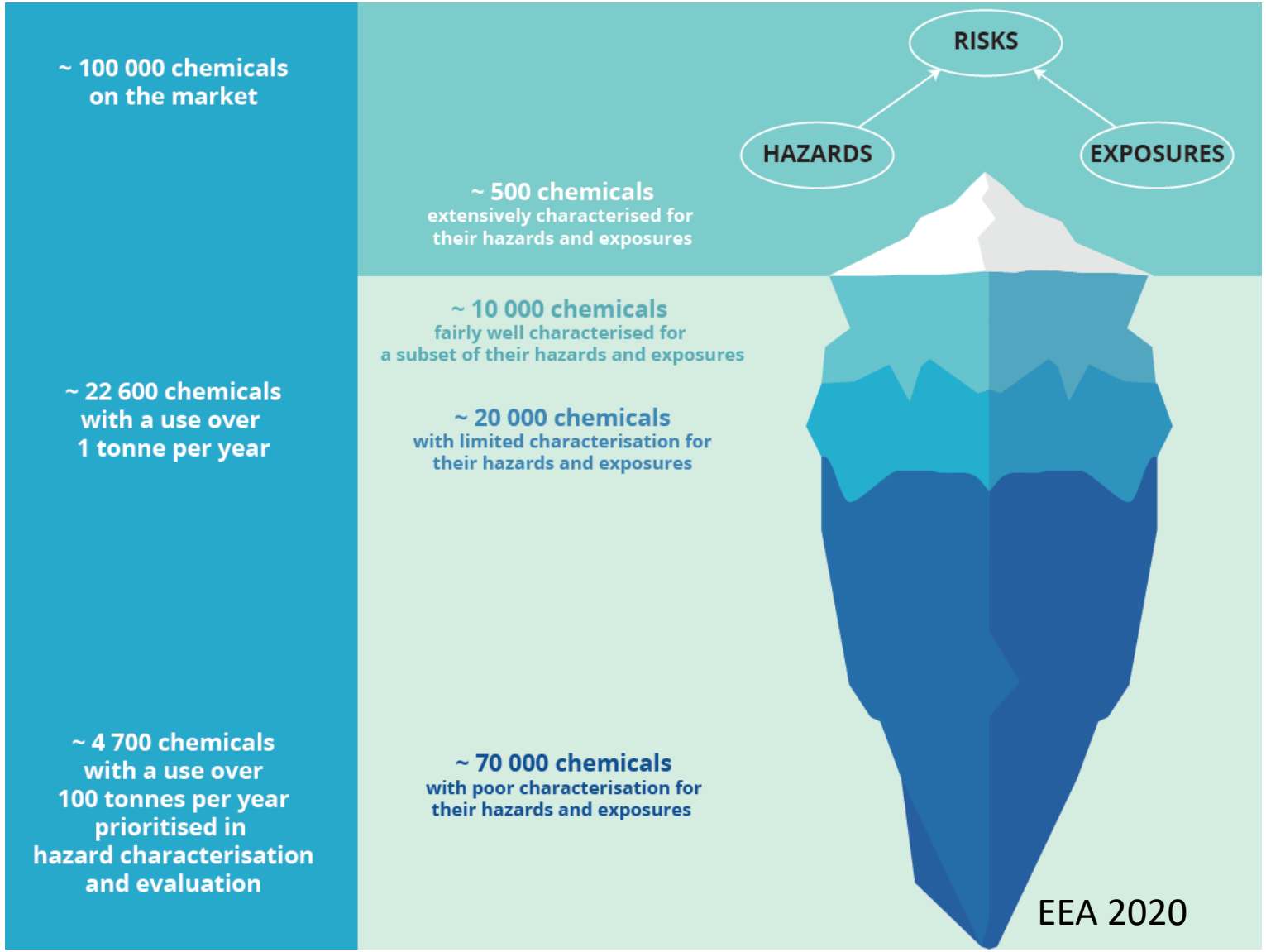
Contamination of the Czech Republic with perfluorinated and polyfluorinated substances

Tomáš Cajthaml

Institute for Environmental Studies, Faculty of Sciences, Charles University

Organic pollutants



Organic pollutants

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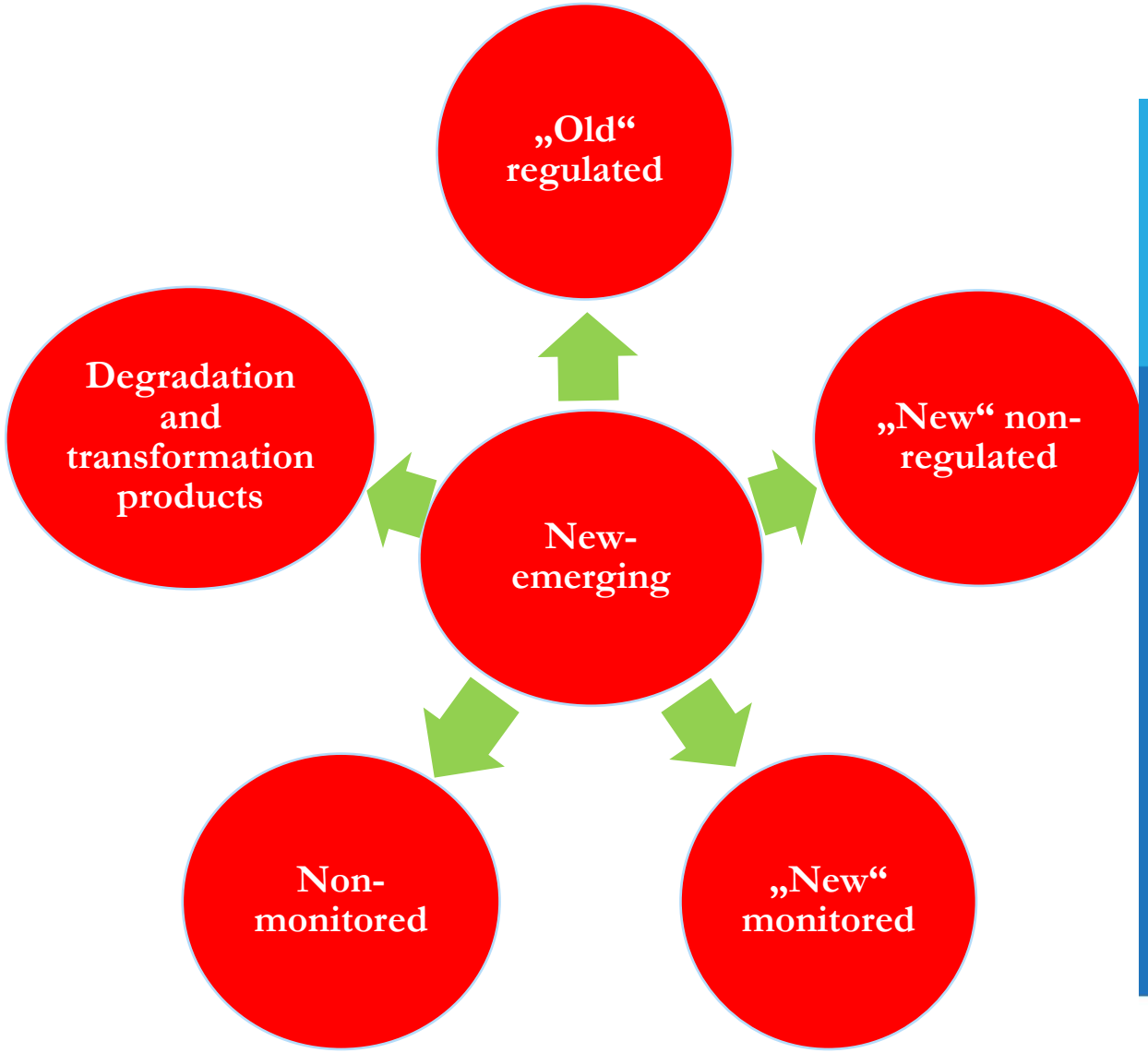
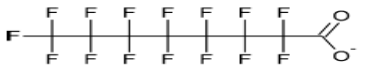
Why a compound becomes a pollutant?

- High production
- Non-biodegraded
- Bioaccumulation
- Toxic

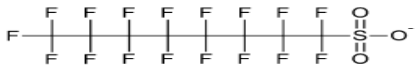
Chemicals in the environment



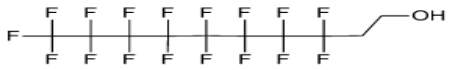
Per- and polyfluoroalkyl substances (PFAS)



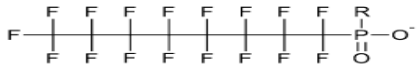
Perfluorocarboxylic acids
(ex. PFOA)



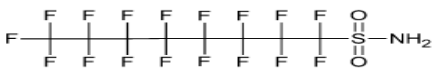
Perfluorosulfonic acids
(ex. PFOS)



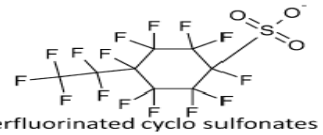
Fluorotelomer alcohol
(ex. 8:2 FTOH)



Perfluorophosphonic/phosphinic acids
(ex. If R=OH then PFOPA
If R=C8 perfluoroalkane then 8:8 PFPi)

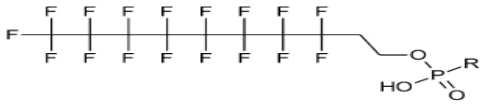


Perfluorosulfonamide
(ex. FOSA)

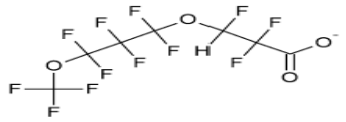


Perfluorinated cyclo sulfonates
(ex. PFECHS)

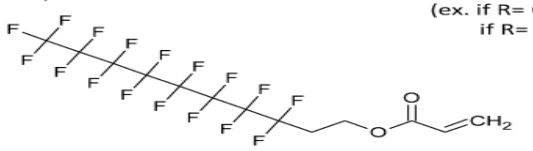
Perfluorosulfonamidoethanol
(ex. N-EtFOSE)



Fluorotelomer phosphate esters
(ex. if R= OH then 8:2 monoPAP
if R= 8:2 FTO ester then 8:2 diPAP)



Polyfluorinated ether carboxylates
(ex. 4,8-dioxa-3H-perfluorononanoate)



Polyfluorinated polymeric unit
(ex. 1H,1H,2H,2H-perfluorodecyl acrylate)

Polyfluorinated ether sulfonates
(ex. Perfluoro [hexyl ethyl ether sulfonate])

- anthropogenic chemicals that includes perfluorooctanonic acid (PFOA), perfluorooctanesulfonic acid (PFOS)

- produced and employed in various applications - persistent chemical compounds and the due to the properties of carbon-fluorine bond

- there is no natural degradation mechanism biotic. nor abiotic

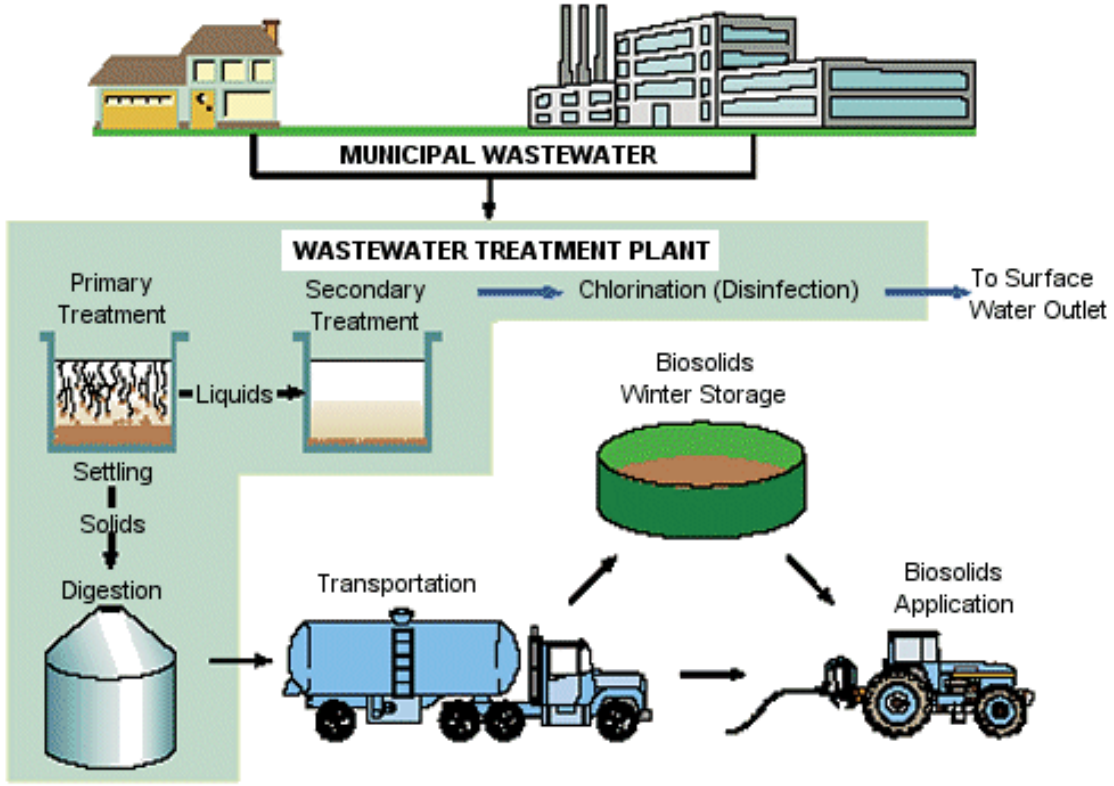
- PFAS accumulate in biota and their biomagnification properties have been also documented

- applications: stain- and water-resistant fabrics and carpeting. cleaning products. paints. and fire-fighting foams (approx. 10,000 individuals,from the 1940s)

Per- and polyfluoroalkyl substances (PFAS)

- produced and employed in various applications from the 1940s
- At the beginning 3M and DuPont (Parkersburgu in Ohio)
- 3M tested toxicity on rats and stopped production in 60s
- Dupont aware about toxic consequences from 60s and kept this undisclosed
- Wilbur Earl Tennant, a farmer in Parkersburg lost his cow herd, neighboring to a dumpsite of Dupont (officially 700 tones of waste)
- Panel C8 established – after seven years of an epidemiological study health consequences reported: **testicular cancer, kidney cancer, thyroid disease, ulcerative colitis, pregnancy-induced hypertension and high cholesterol**

Case Study 1:
Wastewater sludge as a potential source of PFAS in vegetables



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Screening for 32 per- and polyfluoroalkyl substances (PFAS) including GenX in sludges from 43 WWTPs located in the Czech Republic - Evaluation of potential accumulation in vegetables after application of biosolids

Jaroslav Semerád [a, b], Nicolette Hatasová [b], Alena Grasserová [a, b], Tereza Černá [a, b], Alena Filipová [a], Aleš Hanč [c], Petra Innemanová [b, d], Martin Pivokonský [e], Tomáš Cajthaml [a, b, *]

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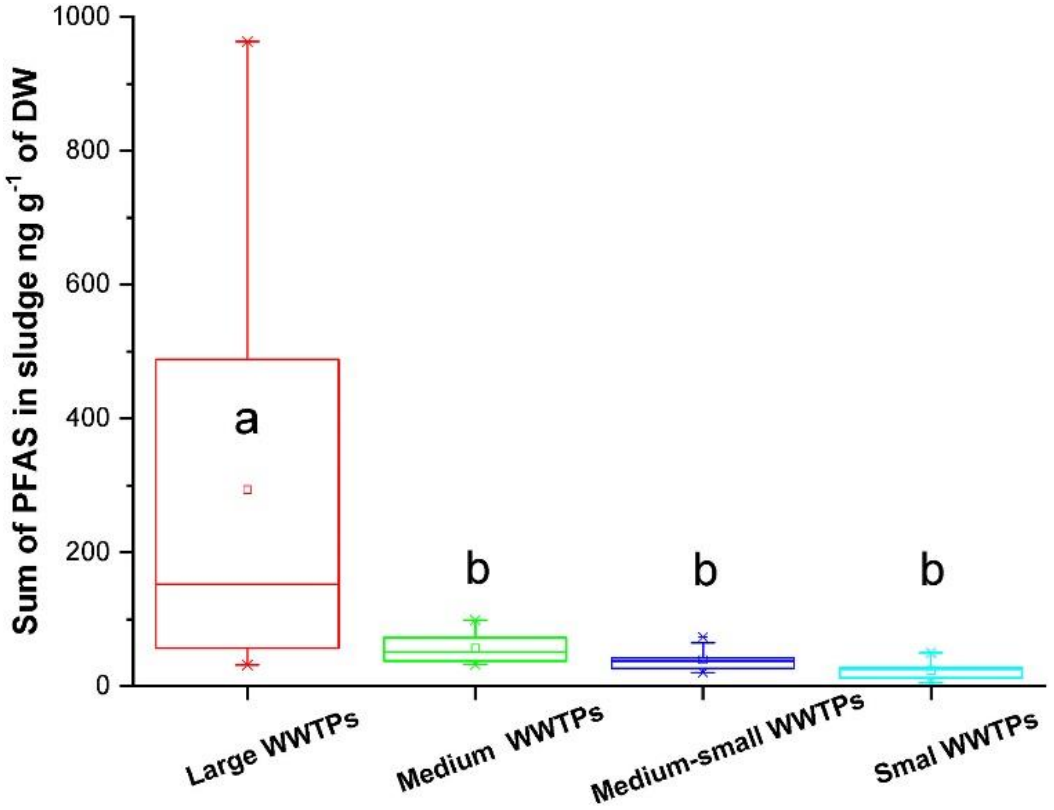
[b] Institute for Environmental Studies, Faculty of Science, Charles University, Benátská 2, CZ-128 01, Prague 2, Czech Republic
[c] Department of Agro-Environmental Chemistry and Plant Nutrition, Czech University of Life Sciences Prague, Kamýcká 129, CZ-165 00, Prague 6, Czech Republic
[d] Dekonta a.s., Dřetovice 109, CZ-273 42 Stehelčeves, Czech Republic
[e] Institute of Hydrodynamics of the Czech Academy of Sciences, Pod Patankou 30/5, CZ-166 12, Prague 6, Czech Republic

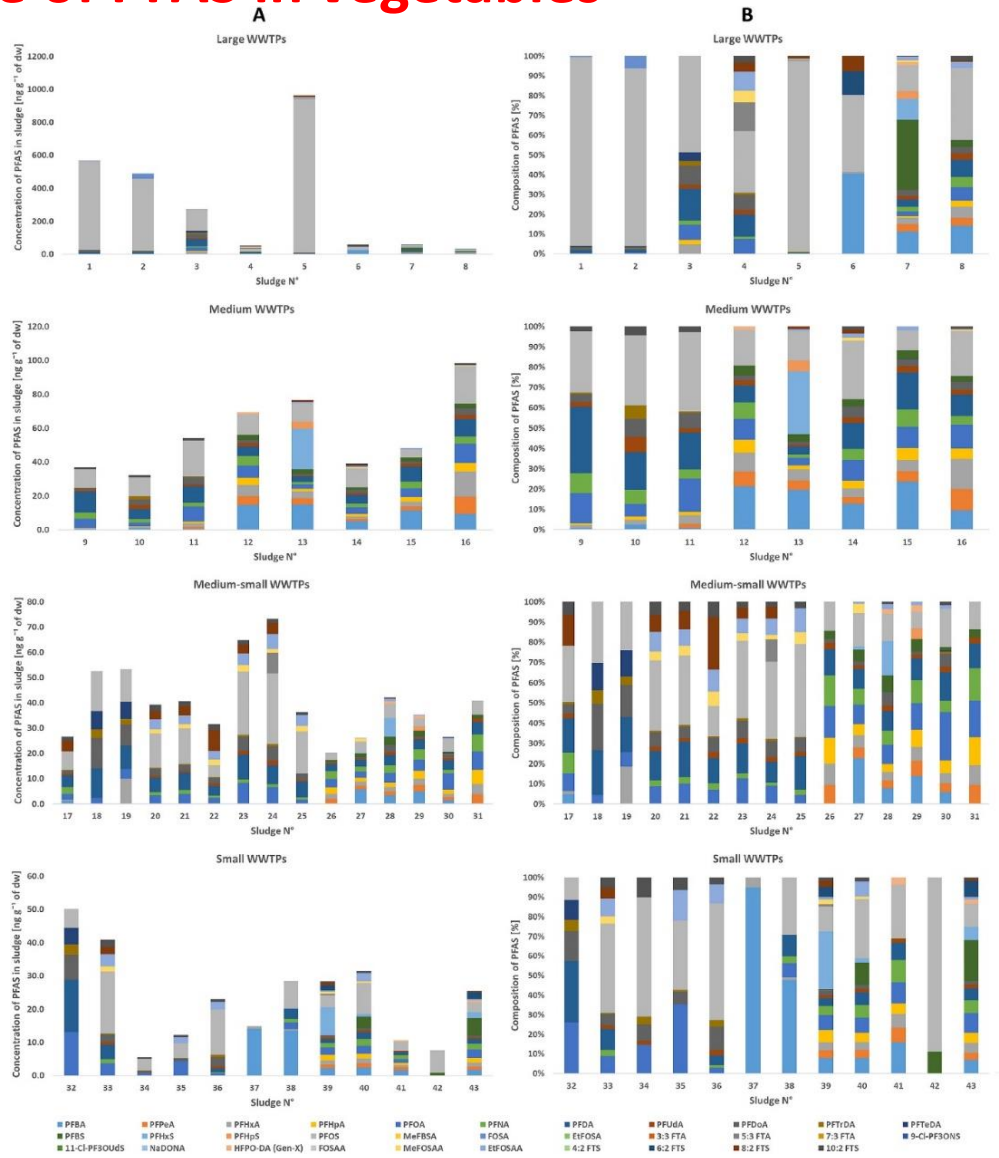
- ≈ 60 000 tons of sludge is used in agriculture in the Czech Republic (30% of total production)

Goals:

- To evaluate the contamination of PFAS in sludge from Czech wastewater treatment plants
- Is it safe to use sludge in agricultural applications?
  - No current legislation concerning PFAS in the Czech Republic

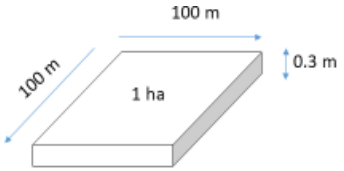
Case Study 1:
Wastewater sludge as a potential source of PFAS in vegetables





Case Study 1:
Wastewater sludge as a potential source of PFAS in vegetables

$$c_s = \frac{m_{sludge}\,[g]}{m_{soil}\,[g]} = \frac{m_{max}}{V * \rho}$$



c_S	maximal concentration of sludge in agricultural soil [ng/g]
m_{sludge}	amount of sewage sludge [g]
m_{soil}	amount of exposed soil [g]
m_{max}	maximal allowed amount of sewage sludge for the use as a fertilizer (10t per 1 ha)
V	volume of soil affected by sludge (recalculated to 1 ha)
ρ	theoretical density of soil (1.5 kg/L)

$$c_{plant}[ng/g] = c_{PFOS}[ng/g] * F_{BC}$$

$$c_{PFOS}[ng/g] = \frac{c_{PFOS\ in\ sludge}\,[ng/g] * m_{sludge}[g]}{m_{soil}\,[g]}$$

c_{plant}	concentration of *PFOS* in edible plant parts [ng/g]
c_{PFOS}	concentration of PFOS in soil [ng/g]
$c_{PFOS\ in\ sludge}$	concentration of PFOS in sludge [ng/g]
F_{BC}	bioconcentration factor in edible plant parts

Sludge N°	Concentration of PFOS in sludge [ng g^{-1}]	Concentration in vegetable [ng kg^{-1} of edible parts dw]		
		Oat grains	Celery shoots	Lettuce leaves
1	543	270	1678	2015
2	439	219	1357	1630
3	135	67	416	500
4	16	8	50	60
5	933	464	2882	3462
6	22	11	68	82
7	7	4	23	28
8	11	6	36	43
median	78	39	242	291

EFSA LIMITS

In 2020, the European Food Safety Authority (EFSA) reduced the Tolerable Weekly Intake (TWI) of: PFOA, PFOS, PFNA, PFHxS to 4.4 ng / kg human weight

70 kg human → 308 ng PFAS with respect to EFSA limit

European Food Safety Authority

Case Study 2:
Monitoring of PFAS in river fish species in the Czech Republic

Aquatic organisms

Common nase
(*Chondrostoma nasus*)

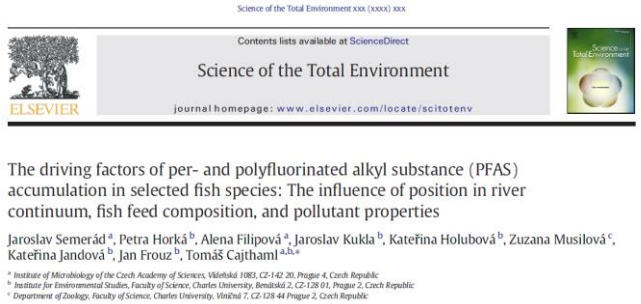
Common chub
(*Squalius cephalus*)

Common roach
(*Rutilus rutilus*)

Goals:

- To evaluate the contamination of PFAS in common river fish species in the Czech Republic
- To estimate an influence of the trophic position on the contamination

Case Study 2:
Monitoring of PFAS in river fish species in the Czech Republic



The driving factors of per- and polyfluorinated alkyl substance (PFAS) accumulation in selected fish species: The influence of position in river continuum, fish feed composition, and pollutant properties

Jaroslav Semerád [a], Petra Horká [b], Alena Filipová [a], Jaroslav Kukla [b], Kateřina Holubová [b], Zuzana Musilová [c], Kateřina Jandová [b], Jan Frouz [b], Tomáš Cajthaml [a,b,*]

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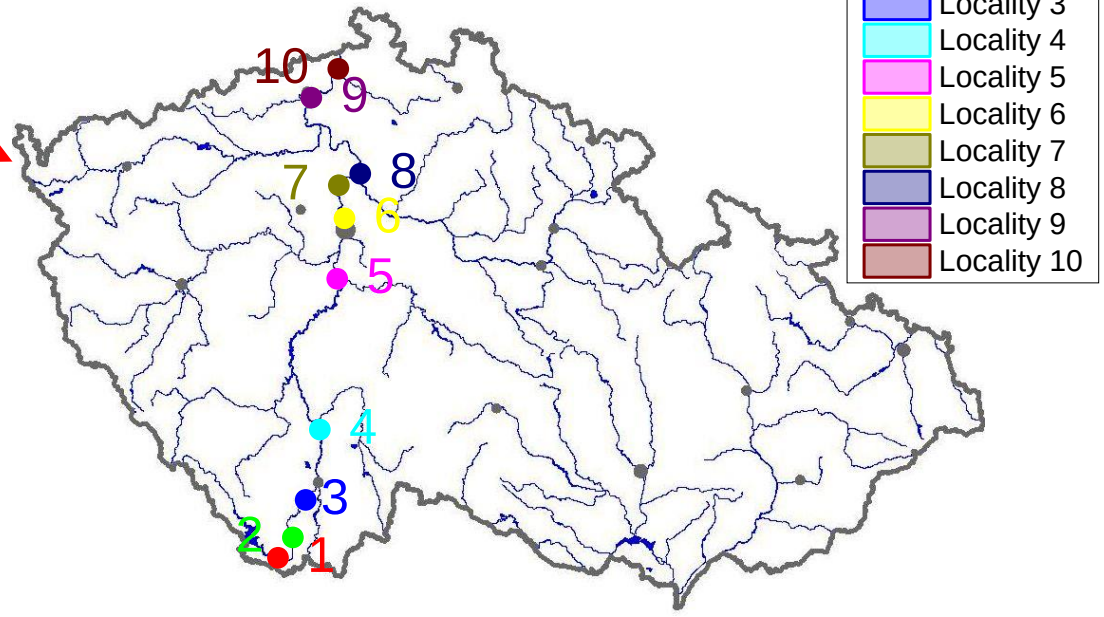
[b] Institute for Environmental Studies, Faculty of Science, Charles University, Benátská 2, CZ-128 01, Prague 2, Czech Republic
[c] Department of Zoology, Faculty of Science, Charles University, Viničná 7, CZ-128 44 Prague 2, Czech Republic



Case Study 2:
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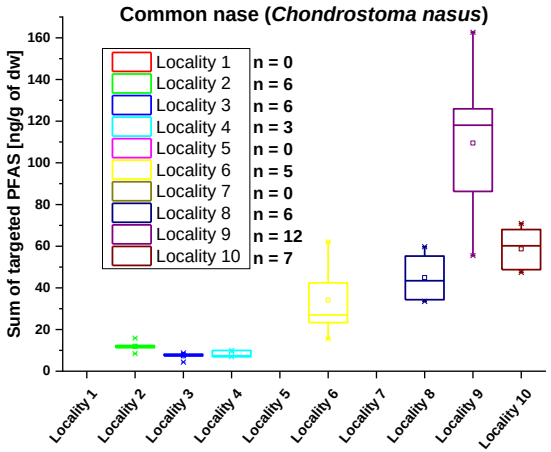
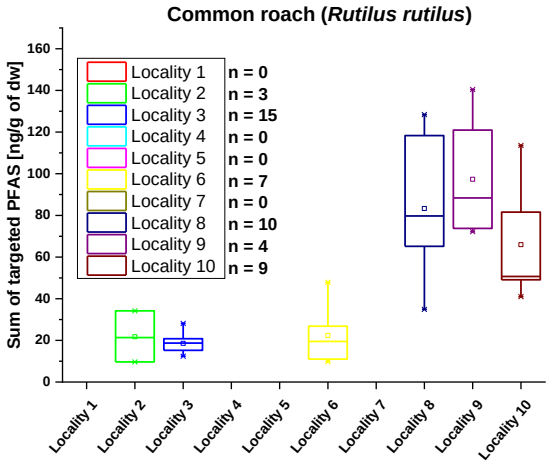
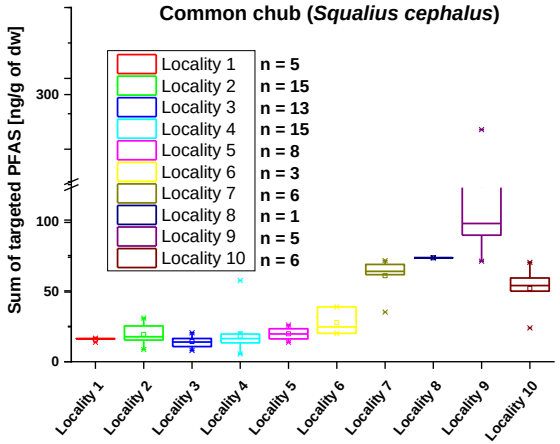




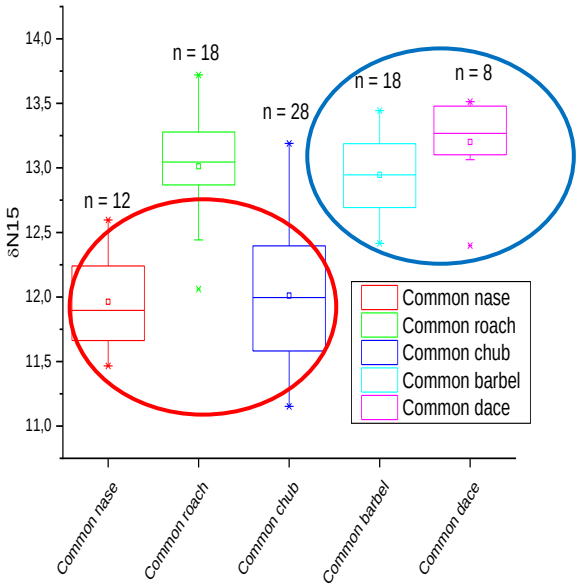


EFSA LIMITS

In 2020, the European Food Safety Authority (EFSA) reduced the Tolerable Weekly Intake (TWI) of: PFOA, PFOS, PFNA, PFHxS to 4.4 ng / kg human weight

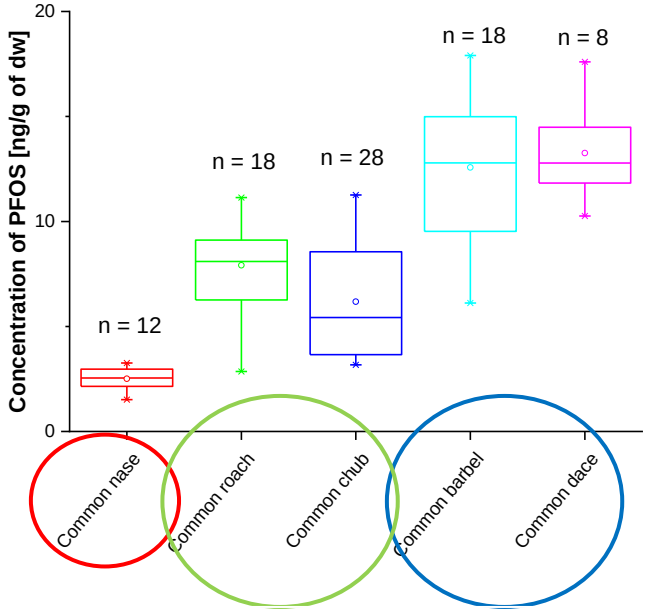
70 kg human → 16 g of fish meat in average with respect to EFSA limit

Case Study 2:
Monitoring of PFAS in river fish species in the Czech Republic



Higher trophic position
- More „animal“ sources in feed

Lower trophic position
- More „plant“ sources in feed



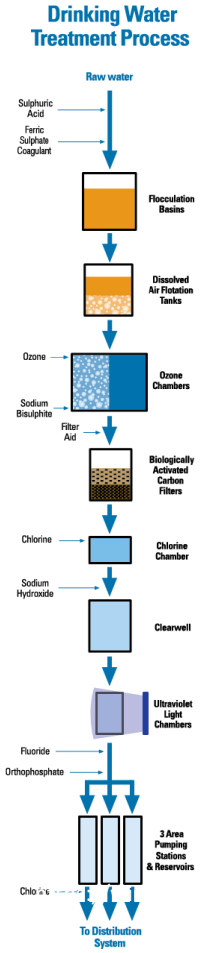
Herbivors
algae
plants

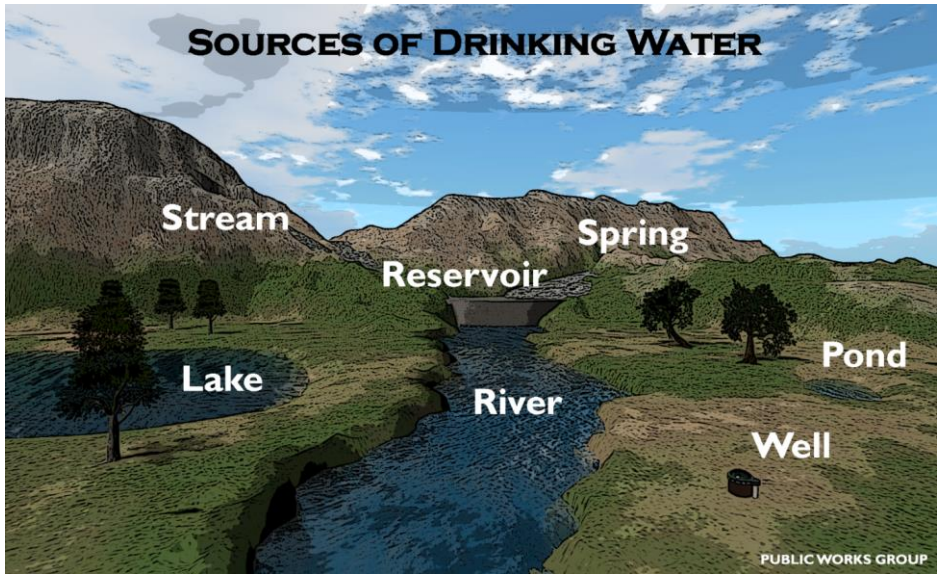
Omnivors
plants
invertebrates
worms
mollusks

Omnivor/carnivor
benthic
crustaceans
insect larvae
mollusks
small fish

- A significant relationship was detected between the $\delta^{15}N$ and the concentration of PFAS (PFOS) for the common nase (low $\delta^{15}N$, low concentration of PFAS)
- As well as for the common barbel and the common dace (higher $\delta^{15}N$ and high concentration of the targeted pollutants in the muscle tissue).

Case Study 3:
Contamination of Czech drinking water sources and ineffectivity of PFAS elimination during treatment processes





http://www.publicworksgroup.com

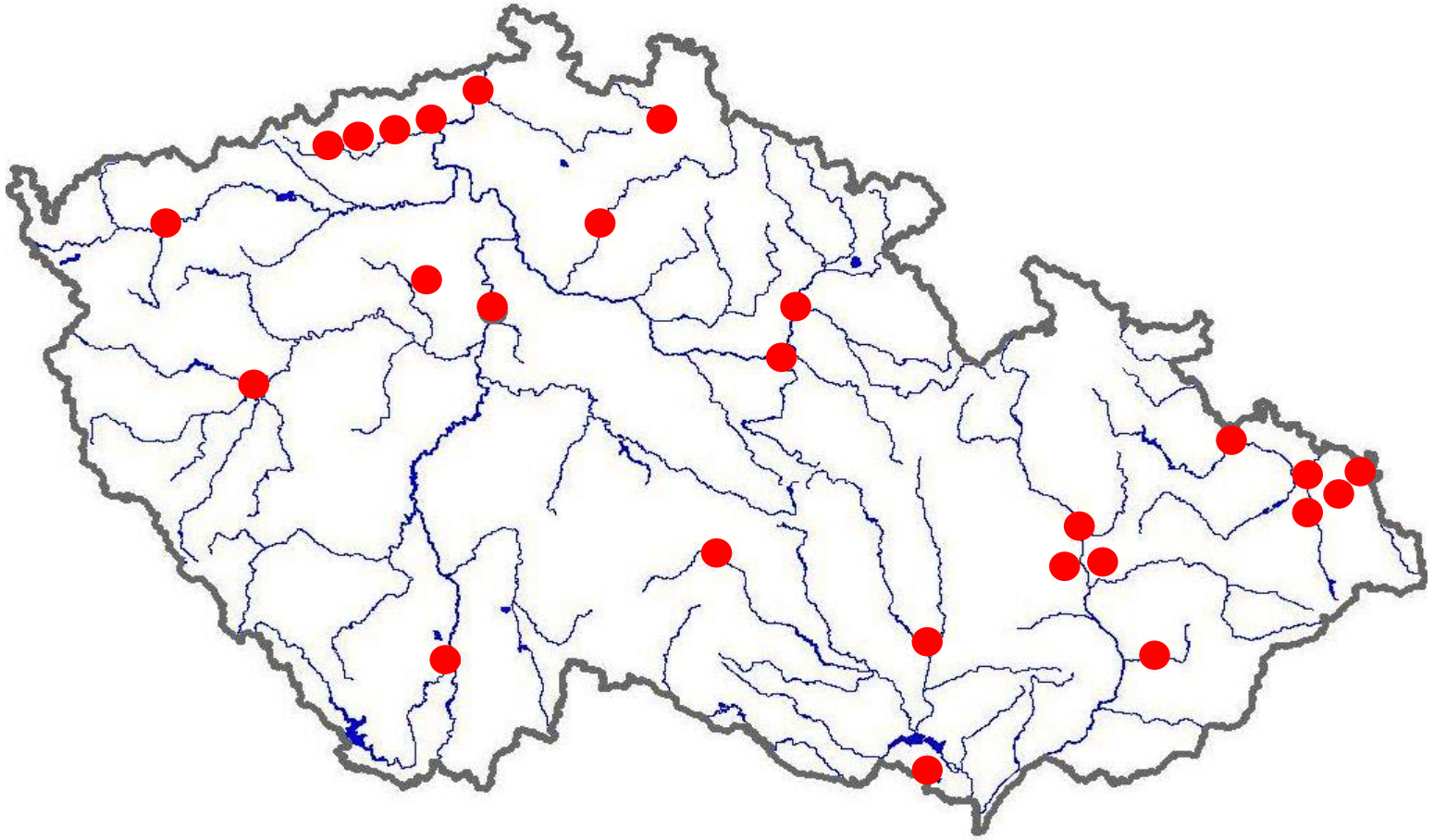
- the production of drinking water in the Czech Republic ≈ 400 000 000 m^3 per year
- different sources (50:50 ground:surface water)
- different treatment technologies

Goals:

- To evaluate the contamination of PFAS in sources of drinking water located in the Czech Republic
- To evaluate the effectivity of current technologies in drinking water treatment processes

Case Study 3:
Contamination of Czech drinking water sources and ineffectivity of PFAS elimination during treatment processes

- Screening of drinking water in county towns in the Czech Republic 2021



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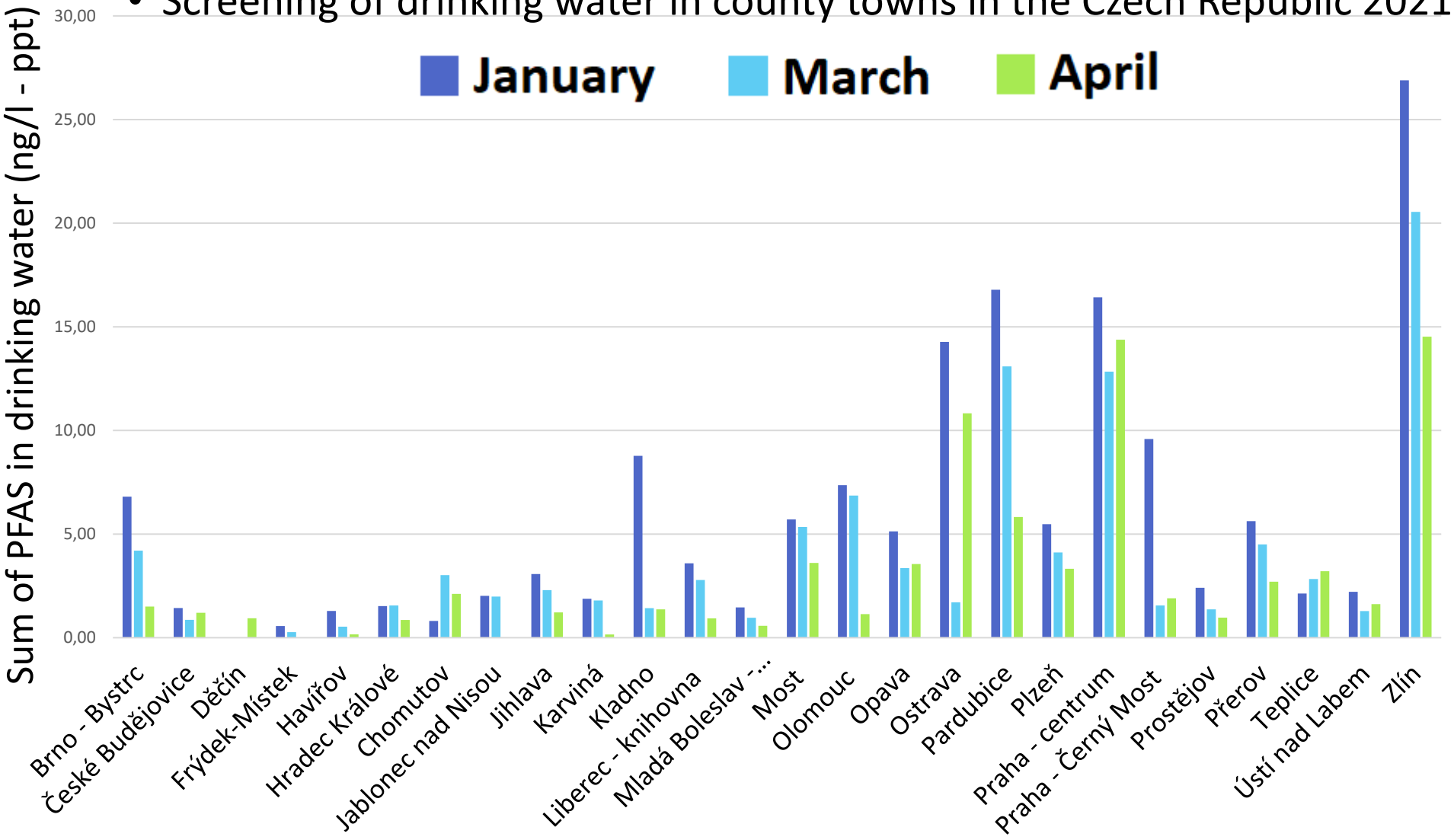
Ostrava
Pardubice
Plzeň
Praha - centrum
Praha - Černý Most
Prostějov
Přerov
Teplice
Ústí nad Labem
Zlín

Case Study 3:
Contamination of Czech drinking water sources and ineffectivity of PFAS elimination during treatment processes

- Screening of drinking water in county towns in the Czech Republic 2021



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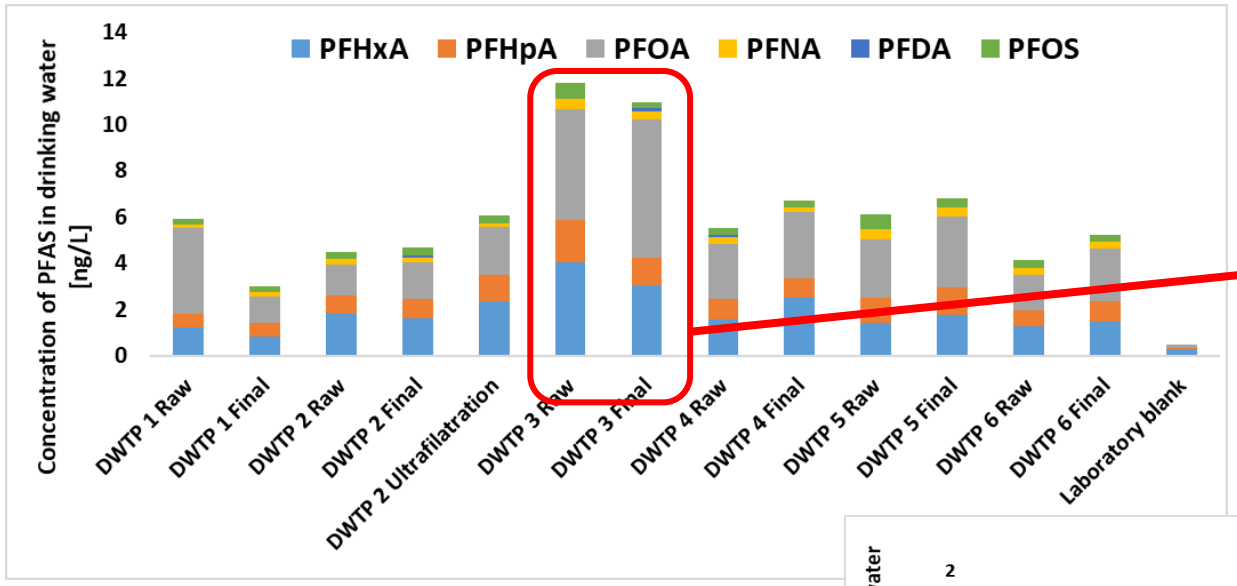
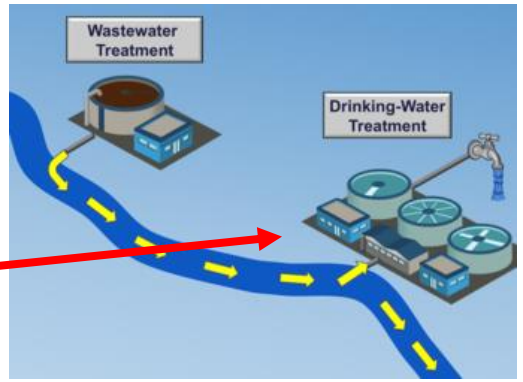
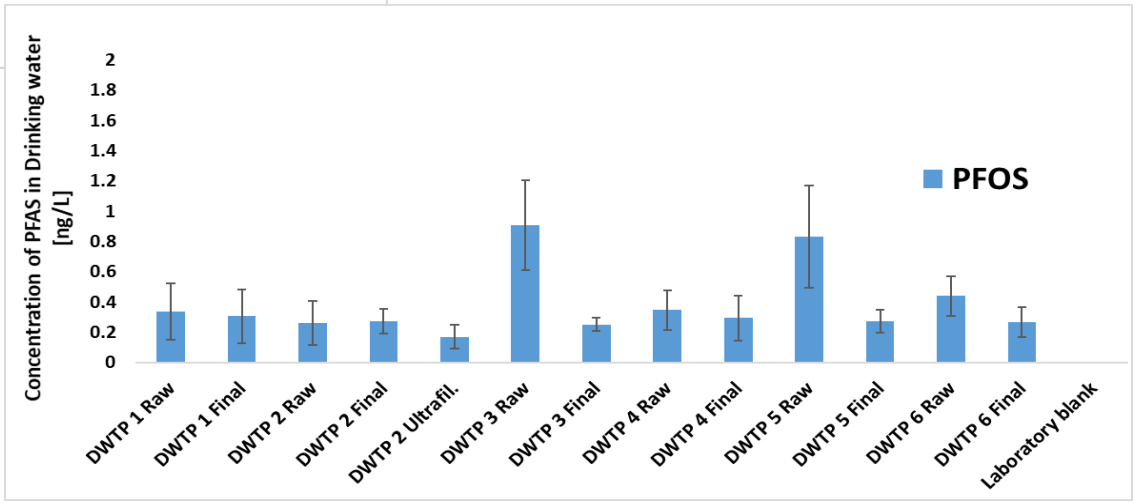
Case Study 3:
Contamination of Czech drinking water sources and ineffectivity of PFAS elimination during treatment processes





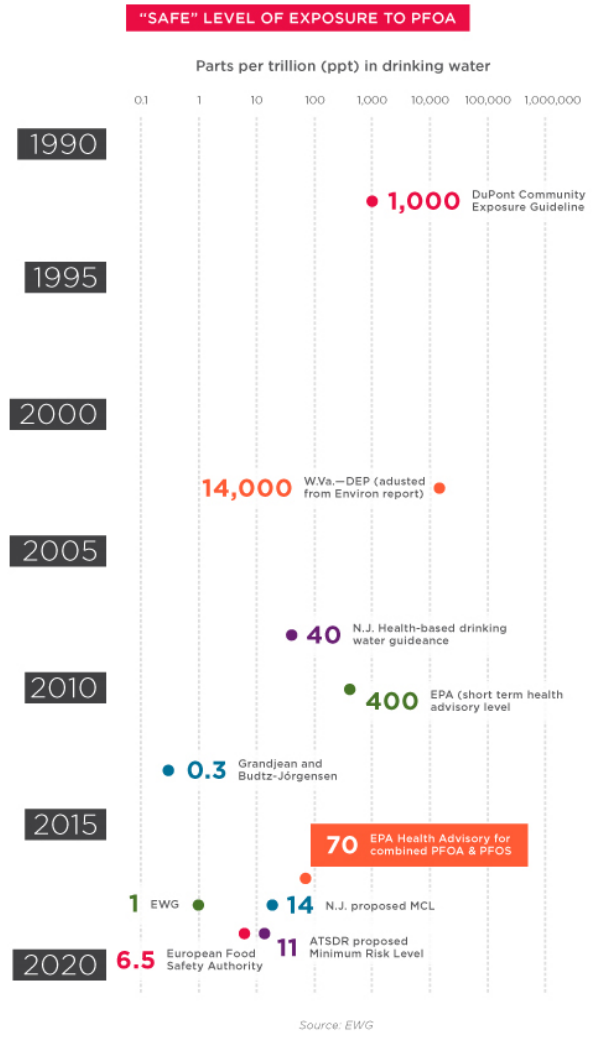


Case Study 3:
Contamination of Czech drinking water sources and ineffectivity of PFAS elimination during treatment processes

Detected Levels of PFOA and PFOS in Czech drinking water

PFOS: 0.17 – 0.91 ng/L
PFOA: 1.14 – 5.97 ng/L

- Small non-representative sample series
- The risk is real …



70 kg person… 7 days… drinks 2 L H_2O ➔ 22 ng / L PFAS in drinking water with respect to EFSA limit

Conclusions:

- The environment is contaminated with PFAS
- Setting legislation limits will be difficult to reach already recommended levels by EFSA
- EU legislation proposal 100 ng/L ??????
- Regulated PFAS still detectable
- Producers replace the „old“ with new-ones
- PFAS must be systemically monitored
- Decontamination methods???