Research centre
for toxic compounds
in the environment

Challenges in ship-based sampling and extraction of per- and polyfluorinated alkyl substances from open sea water

Miroslav Brumovský[1], Pavlína Karásková[1], Luca Nizzetto[1,2]

[1] RECETOX, Brno, Czech Republic

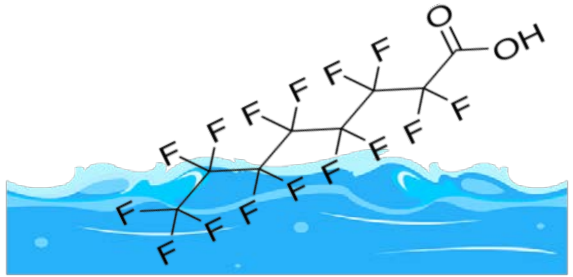
[2] NIVA, Oslo, Norway

brumovsky@recetox.muni.cz

3rd March 2016

Why PFASs in seawater?

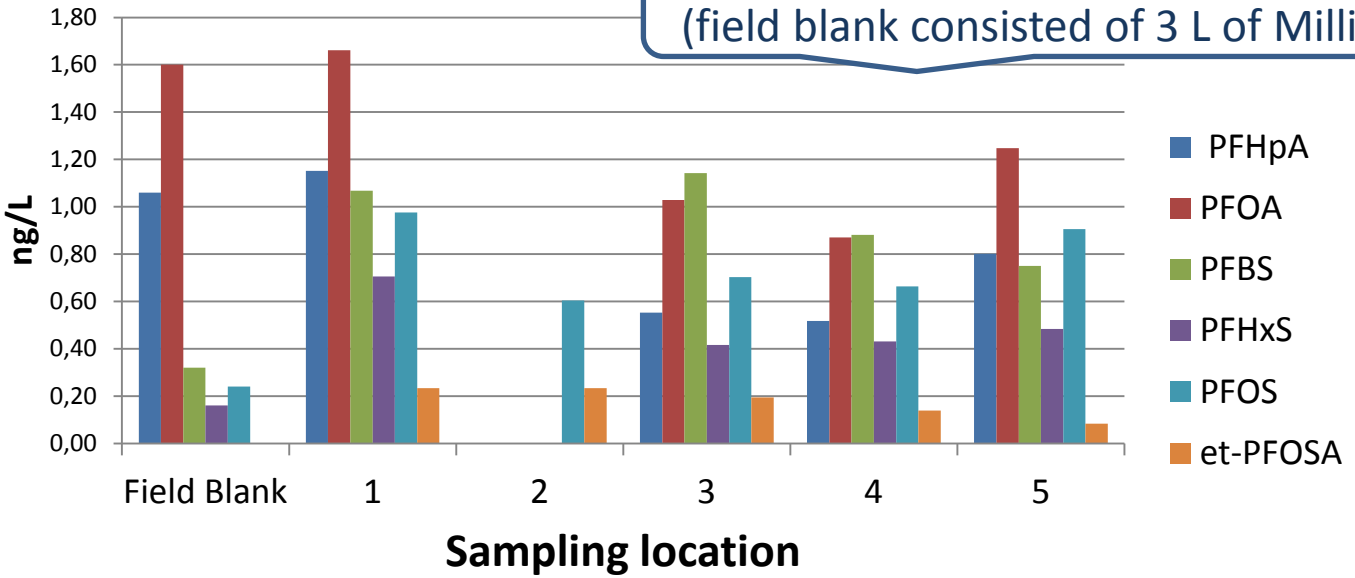
- Persistent contaminants
- Some are bioaccumulative
- Potential toxic effects
- Detected in all environmental compartments
- Some regulated at national/international level
- Need for monitoring
- Marine waters are their main environmental reservoirs



PFAS background on the FerryBox

Data from the North Sea

Procedural blank subtracted
(field blank consisted of 3 L of Milli-Q water)

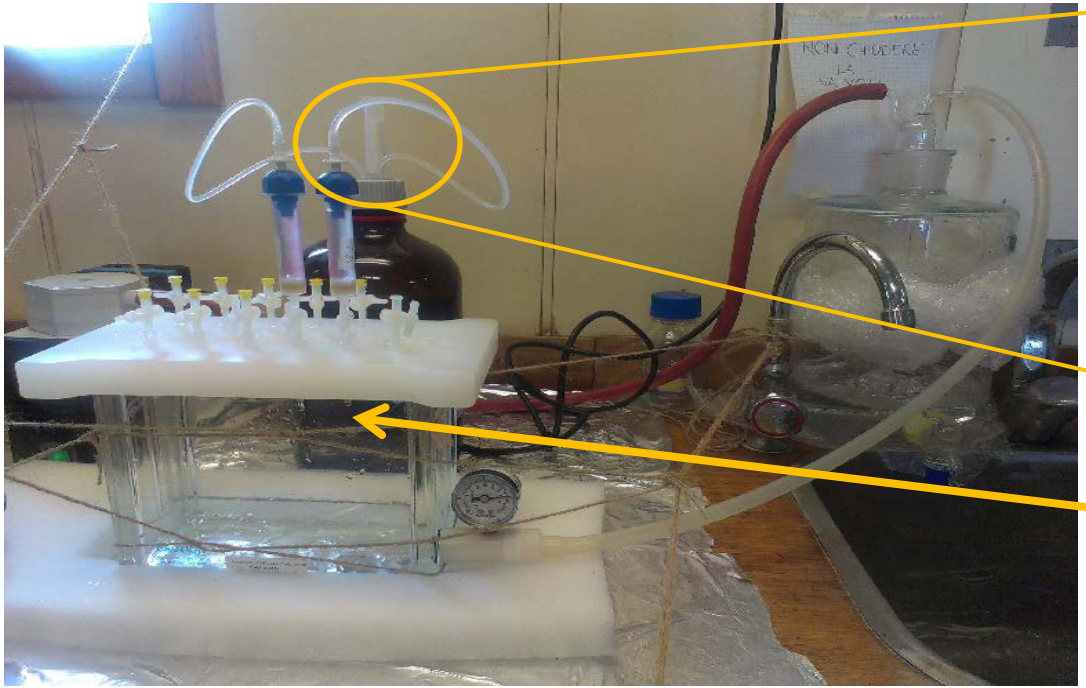


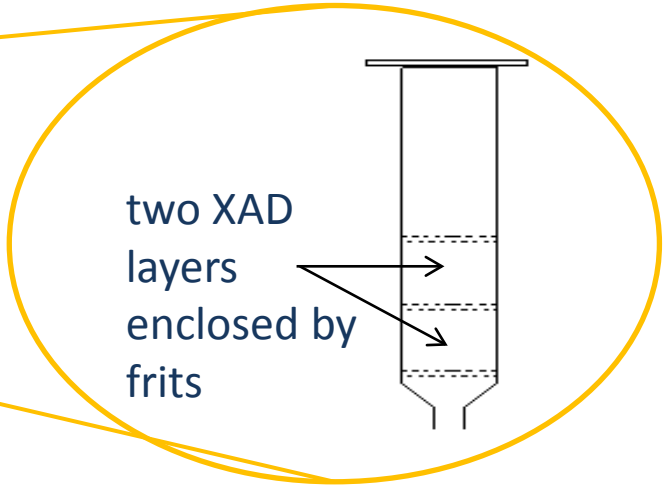
brumovsky@recetox.muni.cz

Contamination in the field

- PFASs contamination may originate from:
  - fluoropolymers in the sampling device
  - surrounding air
  - storage and transport
- Field blank design
  - water contamination → inconsistencies
- Our approach:
  - avoid all fluoropolymer materials
  - avoid sample contact with the surrounding air (use filters)
  - extraction on board

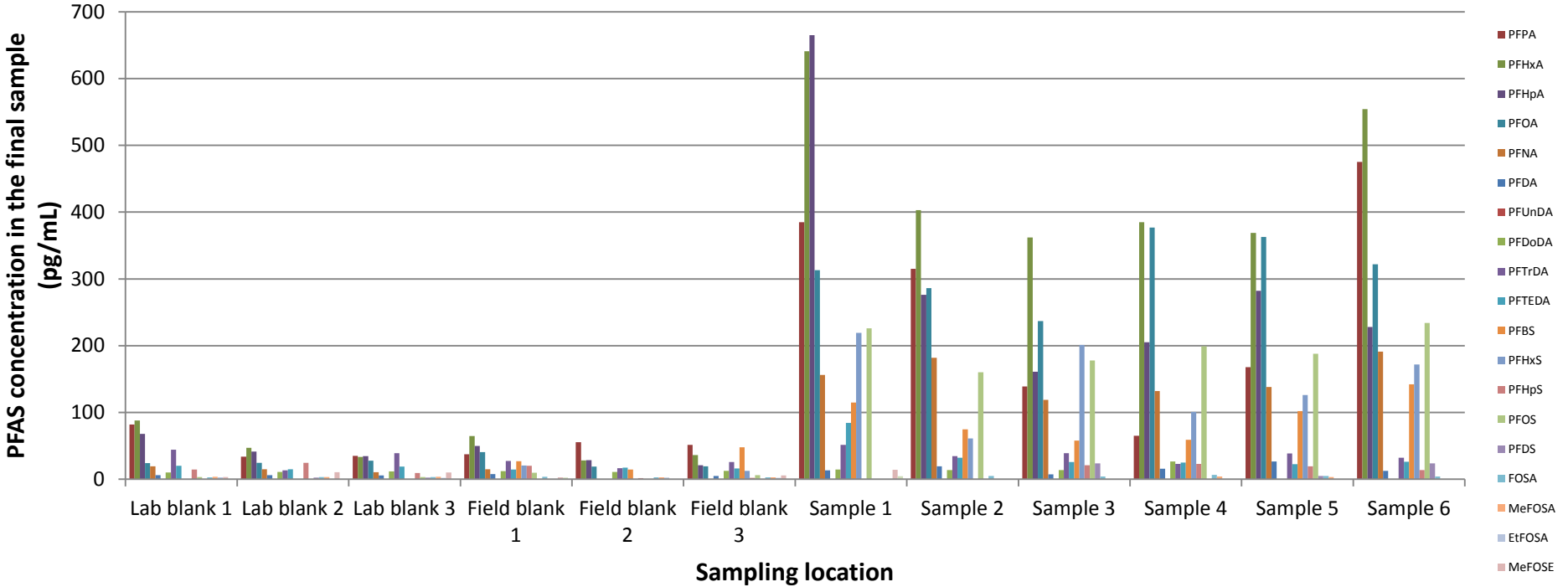
Mediterranean campaign setup



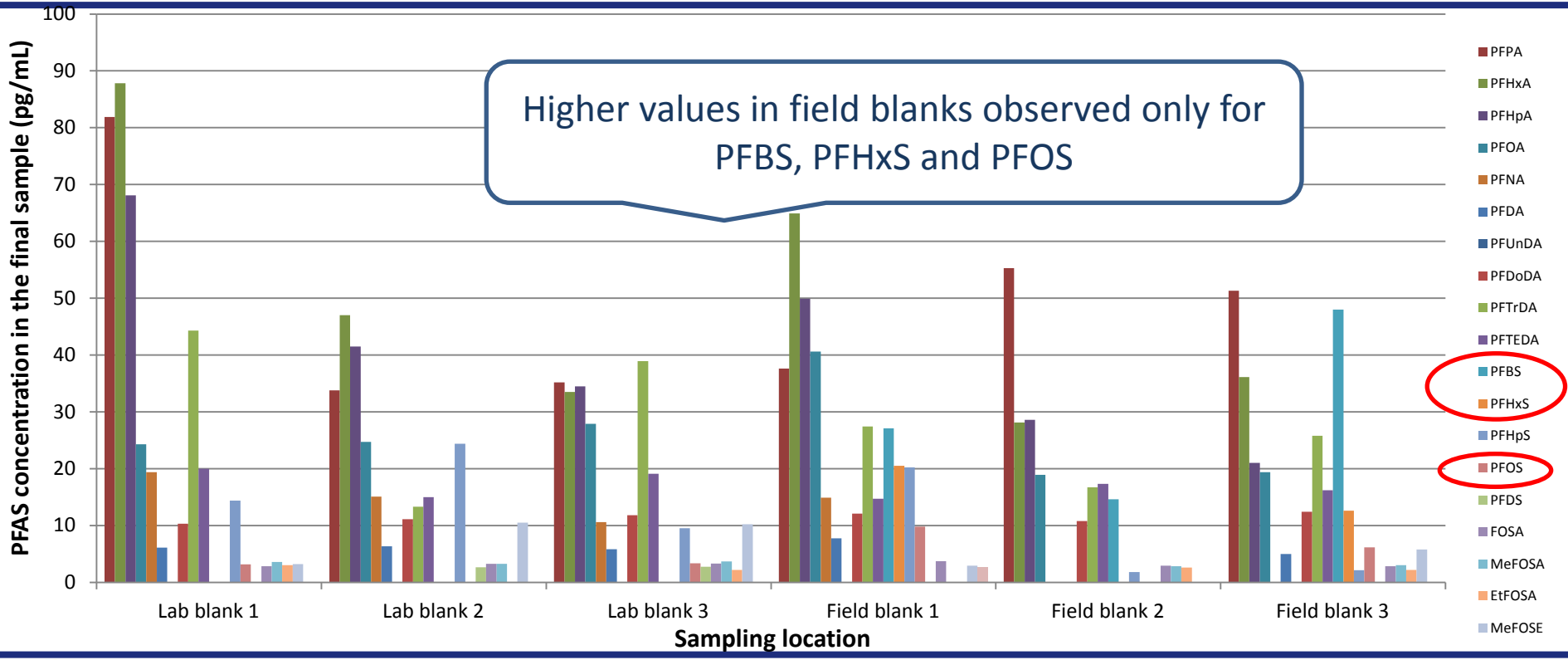


extraction on board using Oasis WAX cartridges

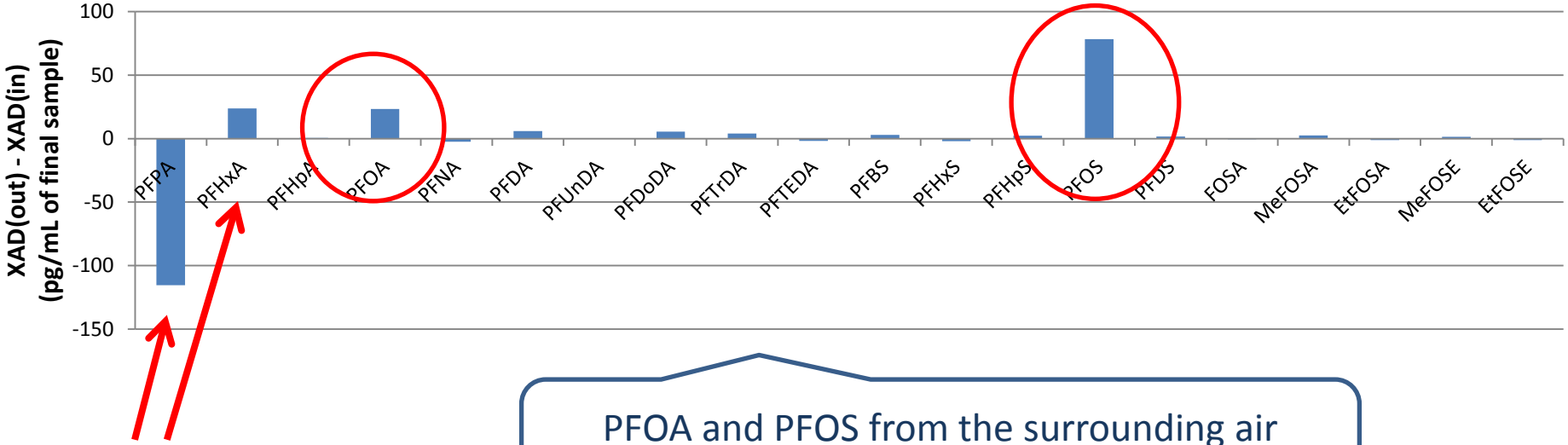
PFAS in the Western Mediterranean



Closer look at the blanks



Performance of XAD air filters



high levels in XAD blanks

PFOA and PFOS from the surrounding air trapped in the first XAD layer

Method overall performance

- LODs determined by instrument sensitivity, blank levels and noise (data in pg/L of seawater)

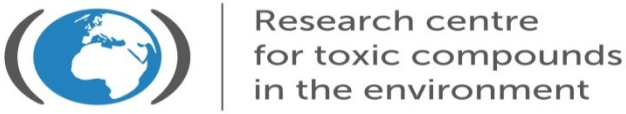
Analyte	PFPA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnDA	PFDoDA	PFTrDA	PFTeDA	PFBS	PFHxS	PFHpS	PFOS	PFDS	FOSA	MeFOSA	EtFOSA	MeFOSE	EtFOSE
Instrument LOD	0.2	0.6	0.8	1.7	1.6	0.8	6.2	1.5	0.9	2.5	2.4	1.0	0.2	0.6	0.4	0.2	0.2	0.2	0.2	0.2
Blank level LOD	11.0	13.7	10.1	7.4	2.7	0.7	6.2	0.5	7.3	1.3	10.1	4.6	5.6	2.0	0.2	0.2	0.4	0.4	2.4	0.5
S/N LOD	19.1	9.9	22.2	8.1	6.3	1.8	6.2	1.6	0.9	2.5	2.5	3.3	1.2	15.8	0.7	0.2	0.7	0.7	0.9	0.5
LOD (max)	19.1	13.7	22.2	8.1	6.3	1.8	6.2	1.6	7.3	2.5	10.1	4.6	5.6	15.8	0.7	0.2	0.7	0.7	2.4	0.5
Avg. field C (pg/L)	44.6	80.6	52.4	58.0	28.1	2.4	6.2	1.8	7.3	4.4	14.0	26.8	5.6	38.2	1.9	0.4	0.7	0.7	2.4	0.5
Vmin (detection) (L)	0.4	0.2	0.4	0.1	0.2	0.8	1.0	0.9	1.0	0.6	0.7	0.2	1.0	0.4	0.4	0.7	1.0	1.0	1.0	1.0
Vmin (quantification) (L)	**1.4**	**0.6**	**1.4**	**0.5**	**0.7**	**2.5**	**3.3**	**2.9**	**3.3**	**1.9**	**2.4**	**0.6**	**3.3**	**1.4**	**1.2**	**2.2**	**3.3**	**3.3**	**3.3**	**3.2**

- Detection and quantification limits driven mainly by low S/N ratio
- Increased noise due to matrix background
- Sample volume > 1 L necessary

Summary

- To minimize PFAS contamination risk during sampling of marine water:
  - avoid fluropolymer materials
  - pre-clean all equipment with methanol
  - limit sample exposure to surrounding air
- Extraction on board:
  - facilitates sample storage and transport
  - enables simpler and more accurate field blank design
- Matrix background reduction is important to lower LODs

Acknowledgements



Jitka Becanova, Roman Prokes, Ondrej Sanka

Mireno Borghini, Stefania Sparnocchia, Sara Durante

Wilhelm Petersen


Thank you for your attention

Summary

- To minimize PFAS contamination risk during sampling of marine water:
  - avoid fluropolymer materials
  - pre-clean all equipment with methanol
  - limit sample exposure to surrounding air
- Extraction on board:
  - facilitates sample storage and transport
  - enables simpler and more accurate field blank design
- Matrix background reduction is important to lower LODs

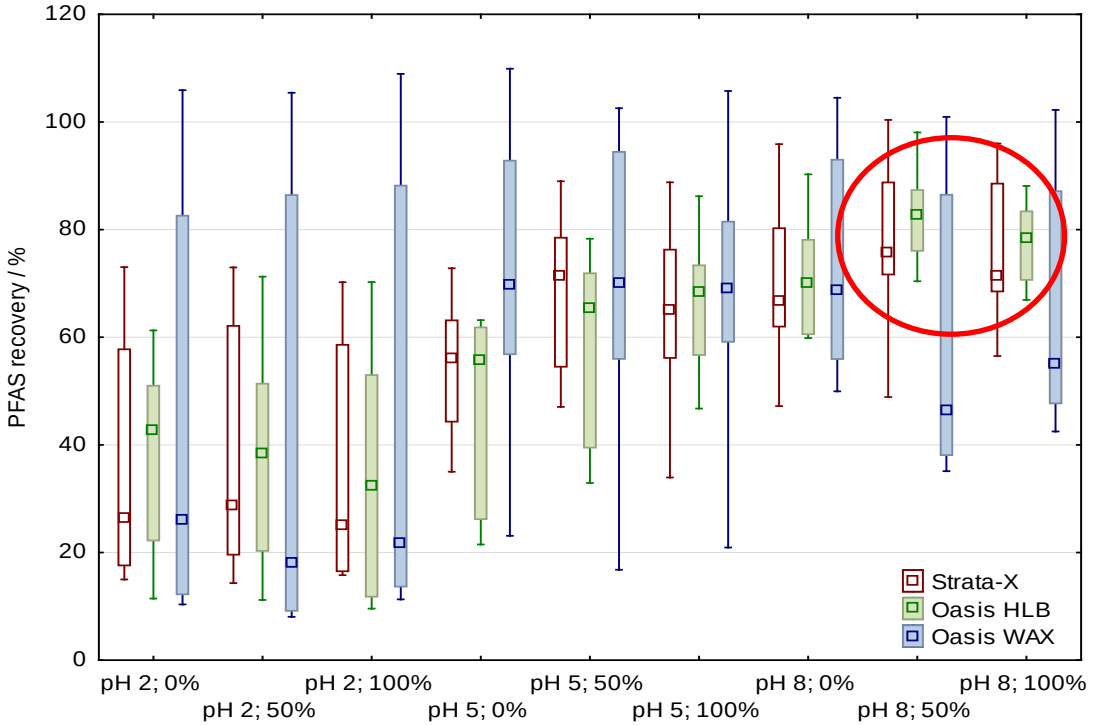
SPE procedure to extract PFAS

- pooled samples (total volume 5 L)
- pH adujsted to 4
- SPE using 5x150mg Oasis WAX cartridges
  - conditionning: 8 mL of 0.1% ammonia in MeOH, 5 mL MeOH
  - equilibration: 5 mL of Milli-Q water
  - drying under vacuum for 15 mins
  - wash: 4 mL of 25 mM acetate buffer
  - spinning on a centrifuge (2 min at 3250 g)
  - two-step elution: 6 mL MeOH followed by 8 mL basic MeOH

Recovery test procedure

- matrices of different pH and salinity levels (100 mL)
- spiking level 100 ng/L
- 3 sorbents: Strata-X (200 mg), Oasis HLB (200 mg) and Oasis WAX (150 mg)
- SPE
  - conditionning: 6 mL 0.1% ammonia in MeOH, 6 mL MeOH
  - equilibration: 6 mL of tap water of appropriate pH
  - loading of the test solution
  - wash: 12 mL of tap water of appropriate pH
  - drying under vacuum (15 mins)
  - two-step elution: 4 mL MeOH, 4 mL MeOH:acetone 1:1 (Strata-X and Oasis HLB)
  - two-step elution for Oasis WAX: 6 mL MeOH, 8 mL basic MeOH

Is ion-exchange the best approach?



Preliminary results of recovery test from seawater

- 3 sorbents
- 3 pH levels
- 3 salinity levels (0, 50 and 100% seawater)

- High recoveries observed for Strata-X and Oasis HLB at natural seawater conditions
- Noise to be evaluated