Chemical and toxicological screening of large rivers using mobile passive sampling

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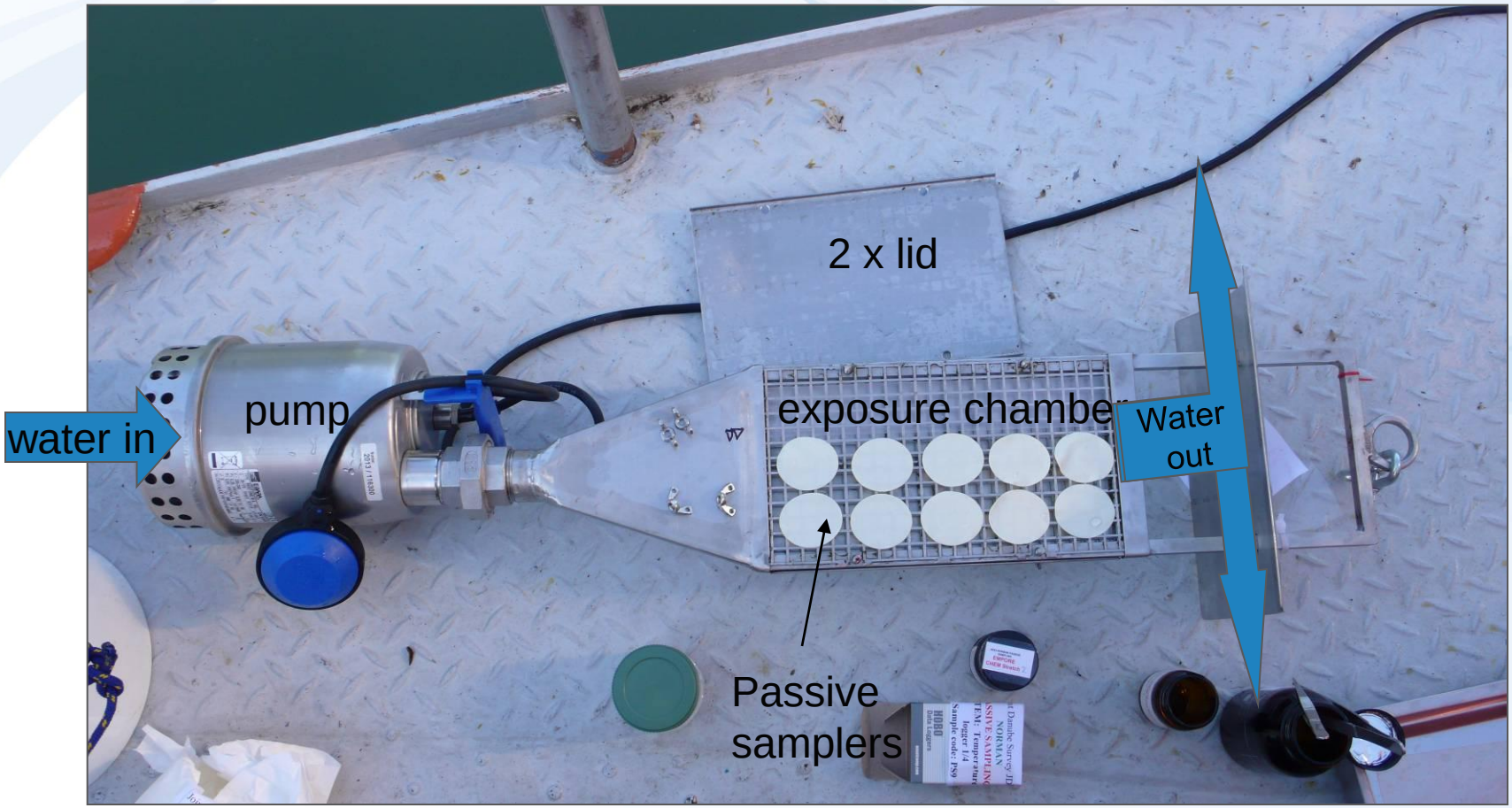
Passive sampling in the Joint Danube Survey 3

- installation of an **"active" passive sampler system** on board of the expedition ship (August-September 2013)
- temporally- and **spatially- integrative sampling approach** - pollution situation in defined stretches
- passive samplers for **hydrophobic and for polar compounds**

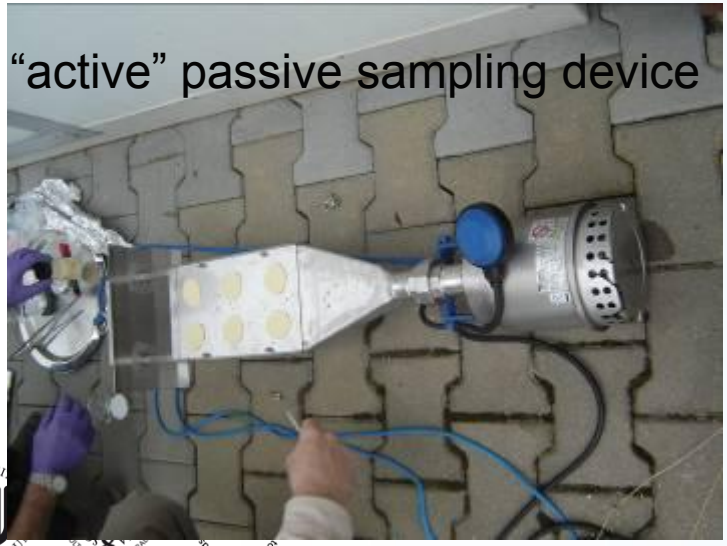
- **Target analysis** for priority substances + relevant river basin specific compounds
- **Non-target screening** analysis (GC-TOF-MS; HPLC-HR-MS(MS))
- **Toxicity profiling** – set of bioassays

Design of an “active” passive sampler

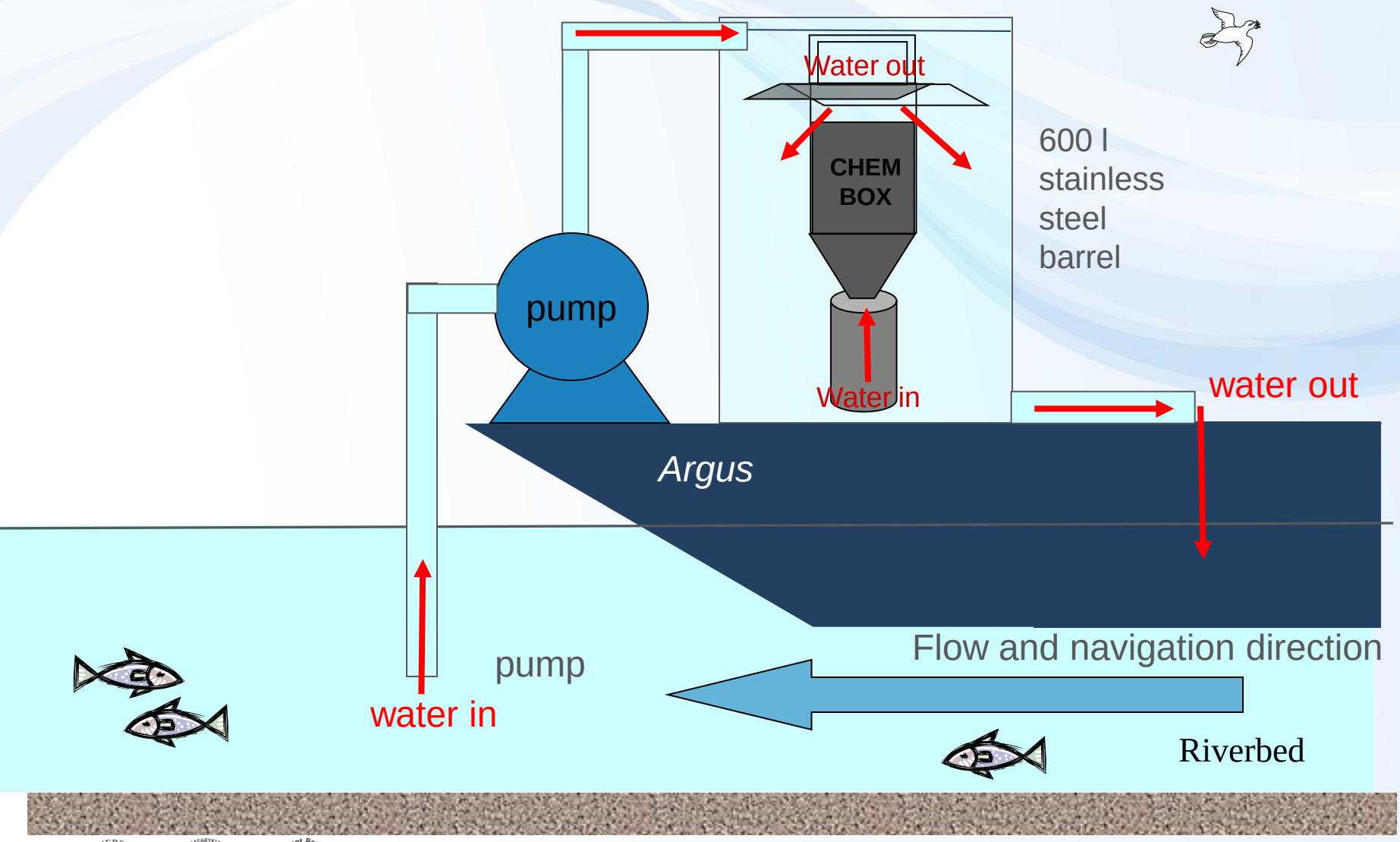


Passive samplers: Silicone rubber (SR), LDPE, SDB-RPS Empore discs

The “active” passive sampler



Mobile „active“ passive sampling device operation



Passive sampling on board of JDS3 ship Argus

River stretches sampled with passive samplers

Stretch number	Stretch start and end	River km	Dates of cruise	Mean water temperature [°C]	Exposure time [d]	Volume extracted by SR [L][a]
1	Passau-Bratislava	2203-1852	17.8.-22.8.	21.3	2.0	169
2	Bratislava-Budapest	1852-1632	22.8.-26.8.	22.0	1.2	84
3	Budapest-Vukovar	1648-1297	26.8.-2.9.	21.9	1.7	139
4	Vukovar-Belgrade	1297-1154	2.9.-6.9.	22.8	1.6	133
5	Belgrade-Turnu-Severin	1154-930	6.9.-10.9.	22.1	2.0	139
6	Turnu-Severin-Ruse	930-495	11.9.-17.9.	21.9	2.0	129
7	Ruse-Braila	495-170	17.9.-21.9.	19.2	1.4	79
8	Braila-Tulcea	170-71	21.9.-26.9.	18.7	1.3	72

[a]Volume of water extracted by the SR sampler during exposure; it is calculated for a model compound with molecular mass of 300.

Analysis of passive samplers

		Type of analysis			
Compound class	**Passive sampler**	**Target analysis**	**Non-target screening**	**Toxicity profiling**	**Specimen bank**
Nonpolar compounds	Silicone rubber sheet (SR)	RECETOX/ GC/MS		SOLUTIONS bioassay battery	Later use in FP7 SOLUTIONS
log Kow >3	Low density polyethylene sheet (LDPE)	NIVA / GC/MS	NIVA / GC/TOF		
Polar compounds	SDB-RPS Empore discs	RECETOX/ Waters XEVO TQ-S	RECETOX/ Agilent 6550 QTOF	SOLUTIONS bioassay battery	Later use in FP7 SOLUTIONS
log Kow < 3		University of South Bohemia / Thermo Qexactive RECETOX/ AB SCIEX 5500 Q Trap			
Result		**Absolute or relative concentrations of compounds in the dissolved phase**	**List of compounds subject to prioritisation for identification of RBSP**	**Response and effect pattern of pollutants in water**	

Parameters to calculate water concentration from silicone rubber data

reference

Sampler-water partition coefficient → cosolvent method [1]

Sampling rate modeled with $R_s = FA / M^{0.47}$ [2]

No membrane control on uptake [3]

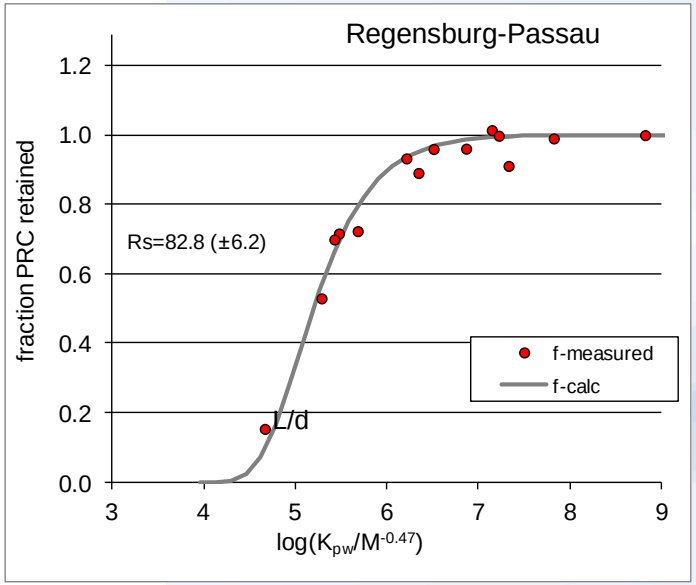
Measured PRC dissipation $f_{exp} = N_t / N_0$ fitted with

adjustable

$$f_{calc} = e^{-\frac{FA}{K_{pw} M^{0.47}} t}$$

Variable, different PRCs

using non-linear regression fit of f_{exp} and f_{calc} [4]



PRC list:

BIP-D10, PCB001, PCB002, PCB003, PCB010, PCB014, PCB021, PCB030, PCB050, PCB055, PCB078, PCB104, PCB145, PCB204

[1] Smedes et al. EST 2009

[2] Rusina et al EST 2010 [3] Rusina et al Chemosphere 2007 [4] Booij and Smedes 2010

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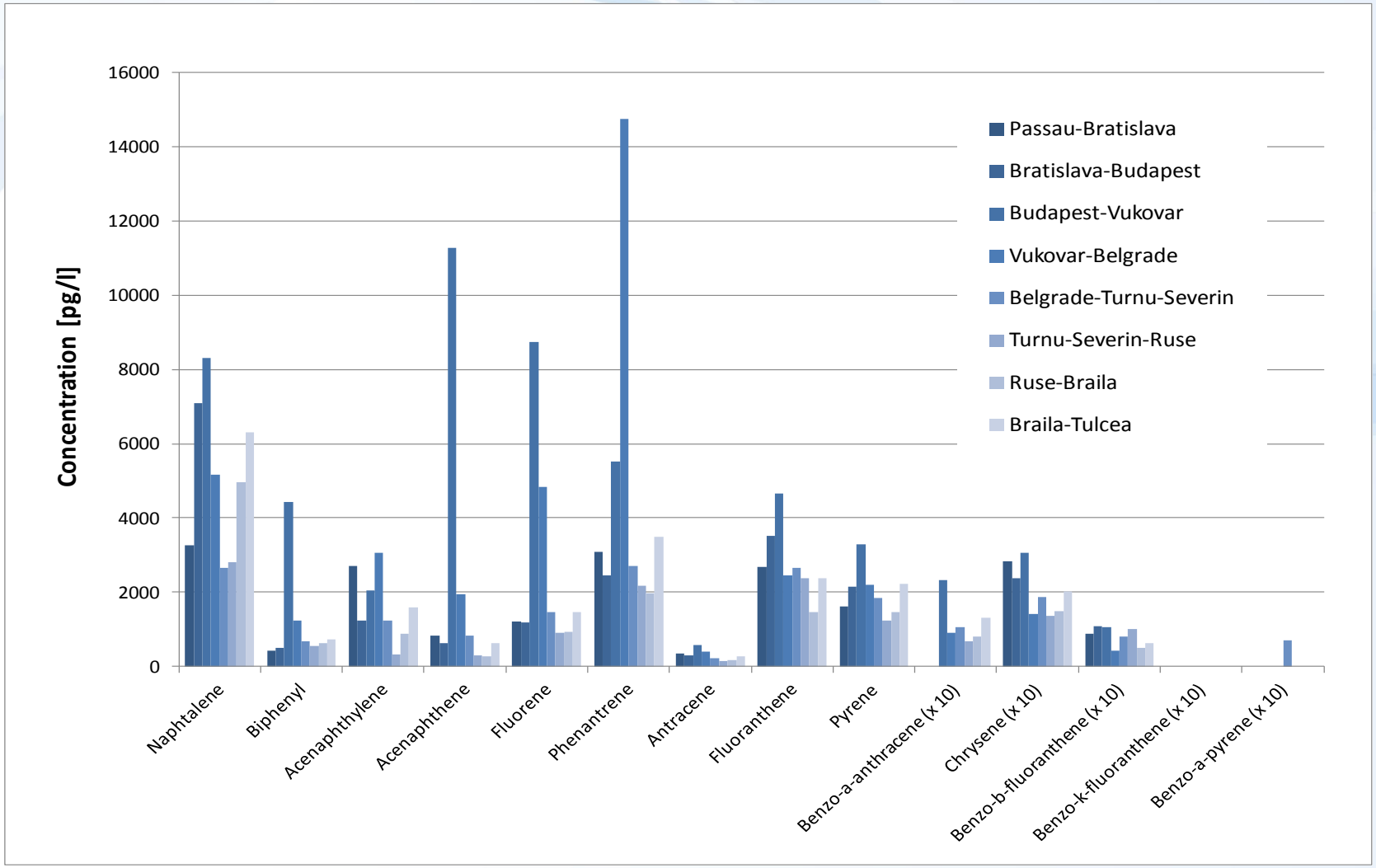
					Caged sampler (in 2days):	32

$$V_{sampled} = R_s \times t$$

[a]Volume of water extracted by the SR sampler during exposure; it is calculated for a model compound with molecular mass of 300.

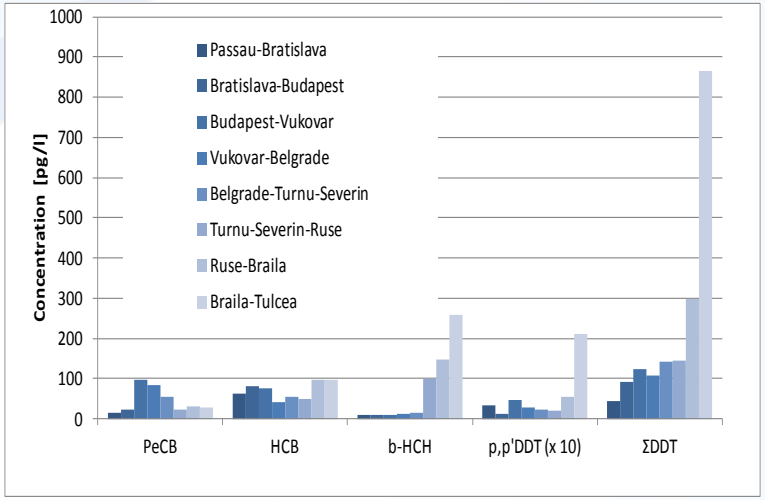
Spatial contaminant profiles measured by silicone rubber: PAHs



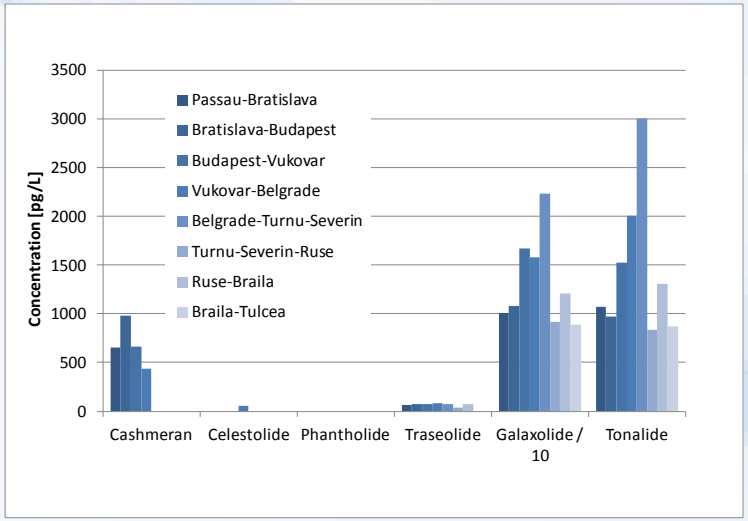
Report: www.icpdr.org/main/activities-projects/jds3

Spatial contaminant profiles measured by silicone rubber samplers

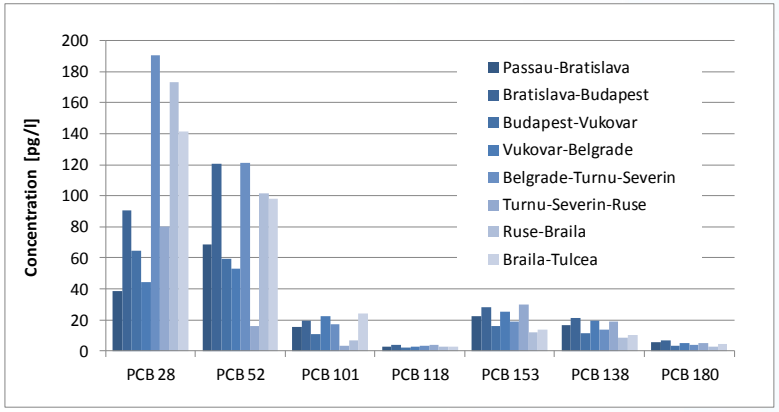
Organochlorine pesticides



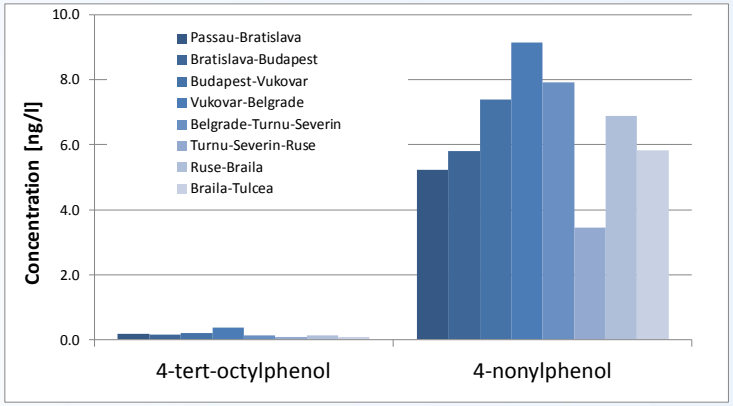
Musk compounds



PCBs



Alkylphenols



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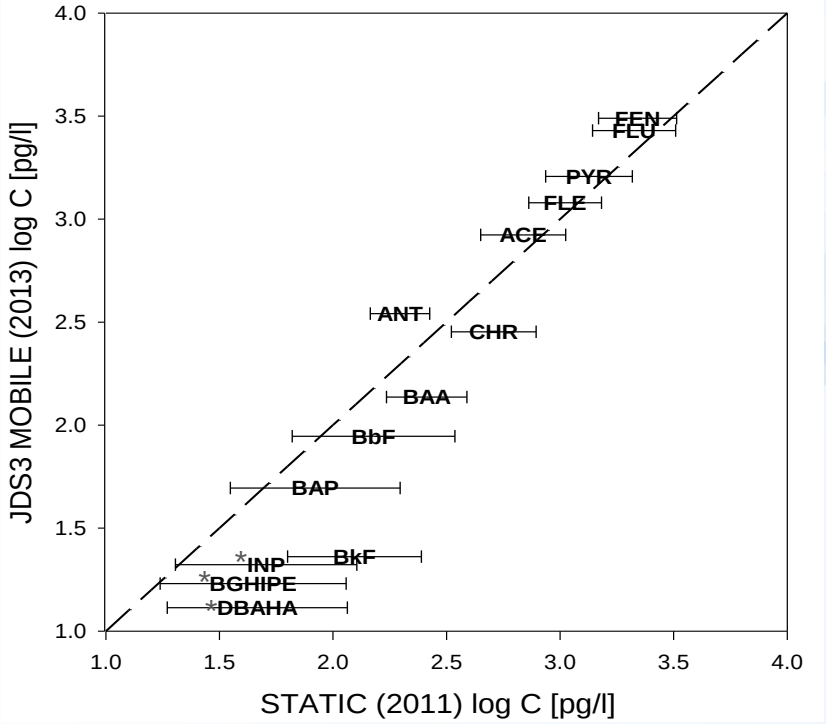
Comparison with older data from „classical“ passive sampling

PAH concentrations: Stretch Passau-Bratislava

Sampled using Silicone Rubber
During JDS in 2013



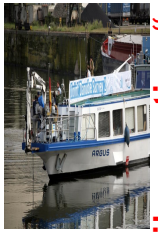
* based on data < LOQ

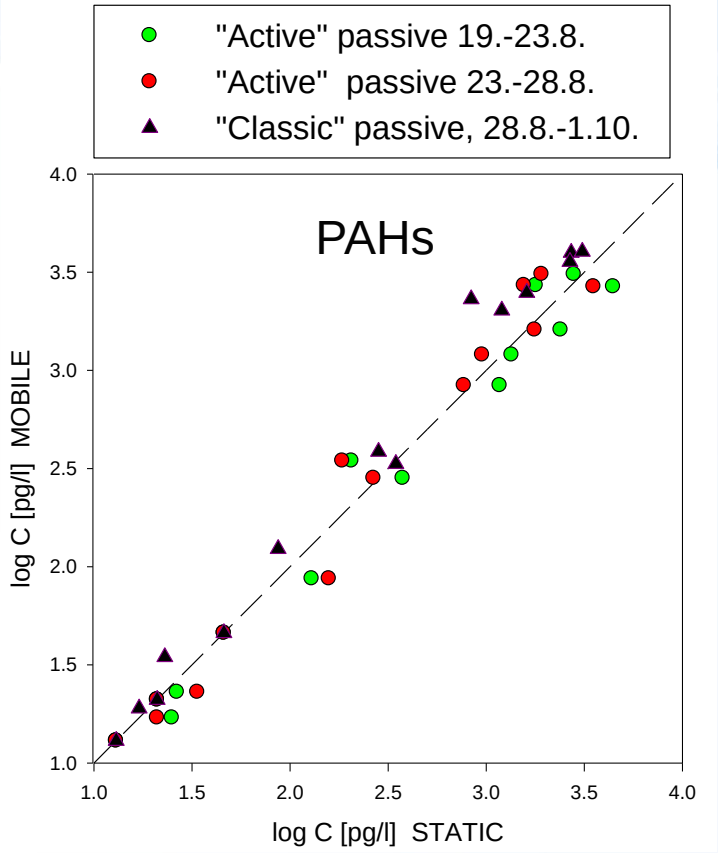
Sampled using SPMD (summer 2011)

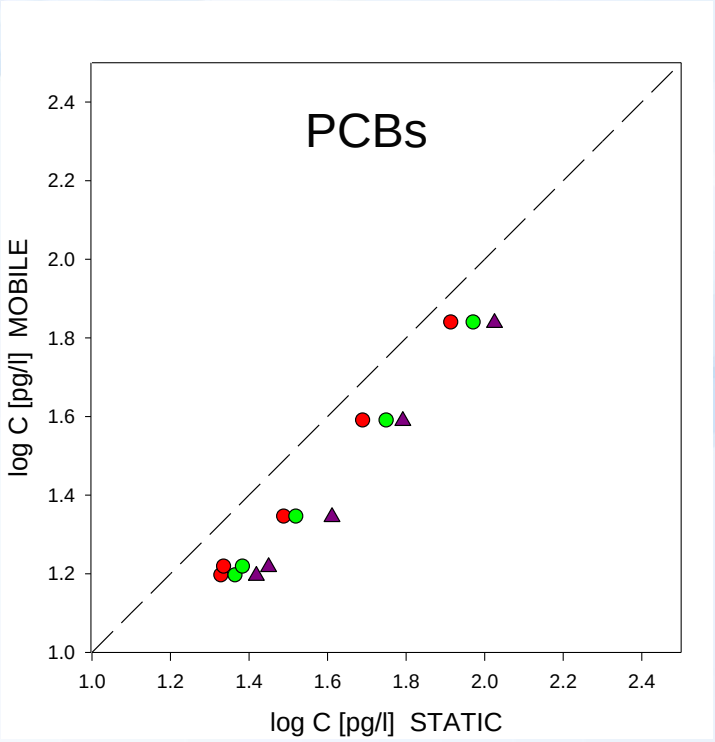
Comparison of „mobile“ with „static“passive sampling

POPs in water column at Bratislava

Mobile „active“ passive
Passau-Bratislava





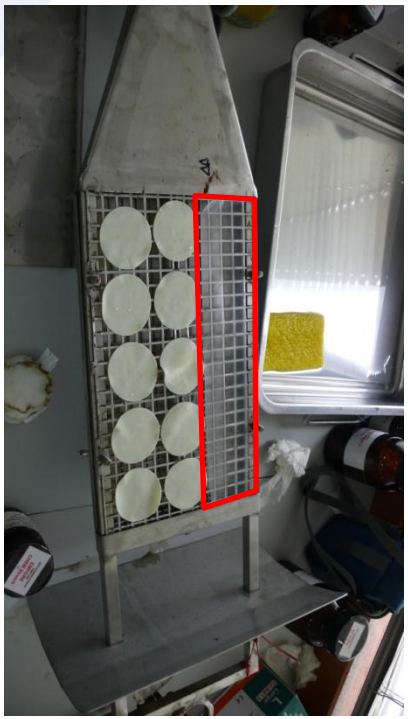


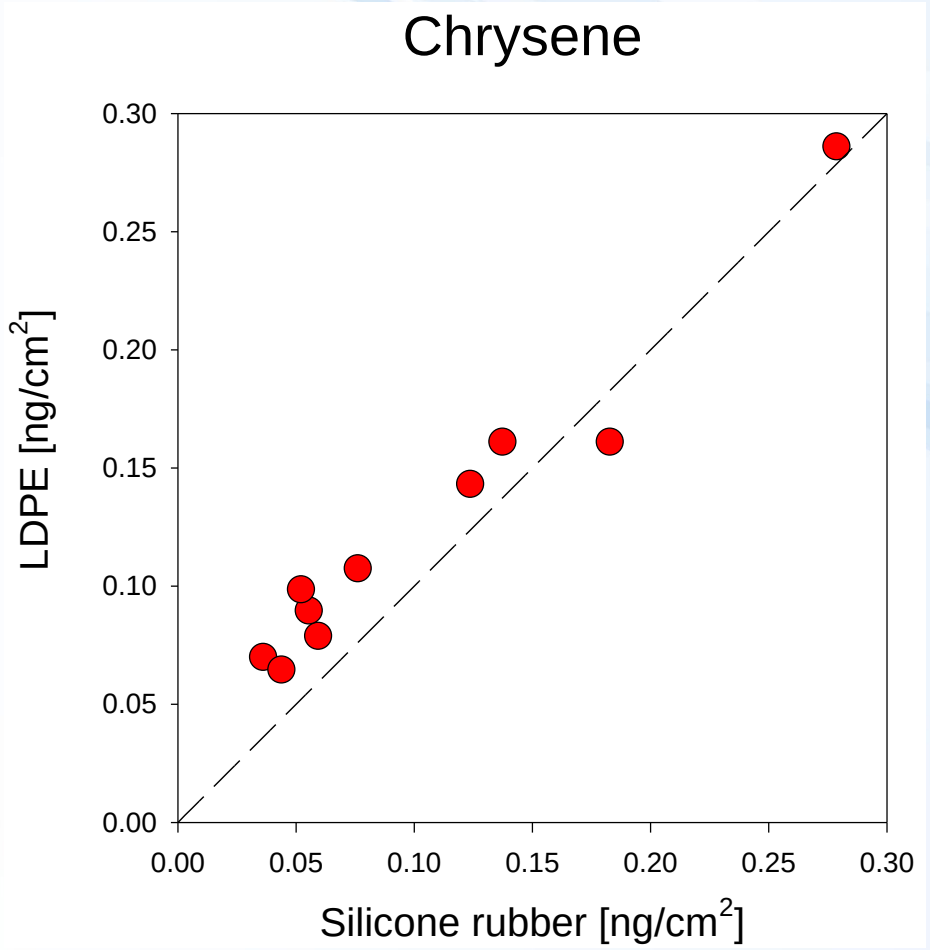
Static „active“ passive:

Static „classic“ passive:

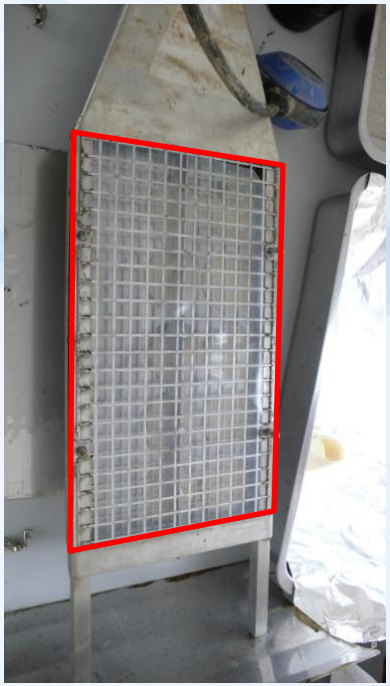
Comparison of passive samplers: Silicone rubber vs. LDPE
Surface specific uptake

LDPE:112 cm^2





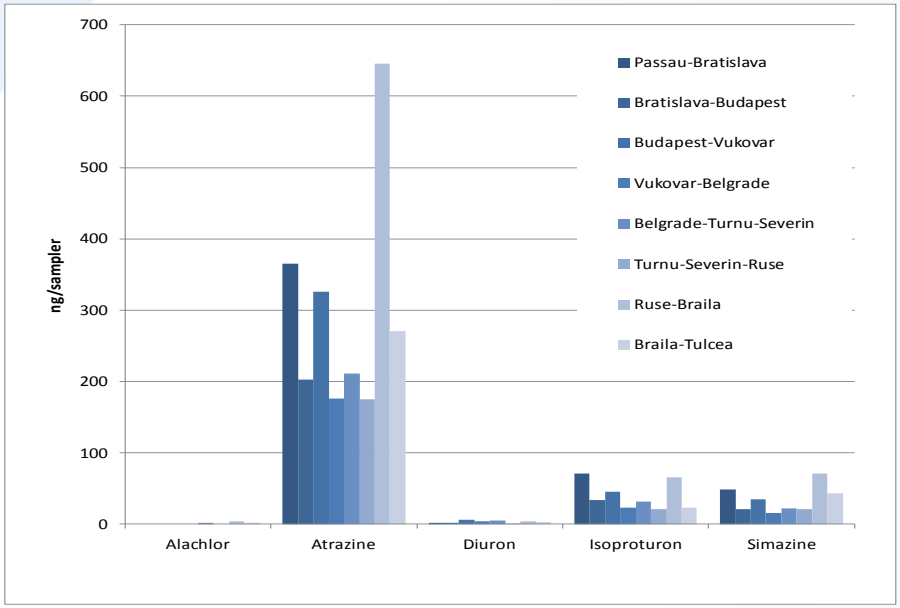
SR:392 cm^2



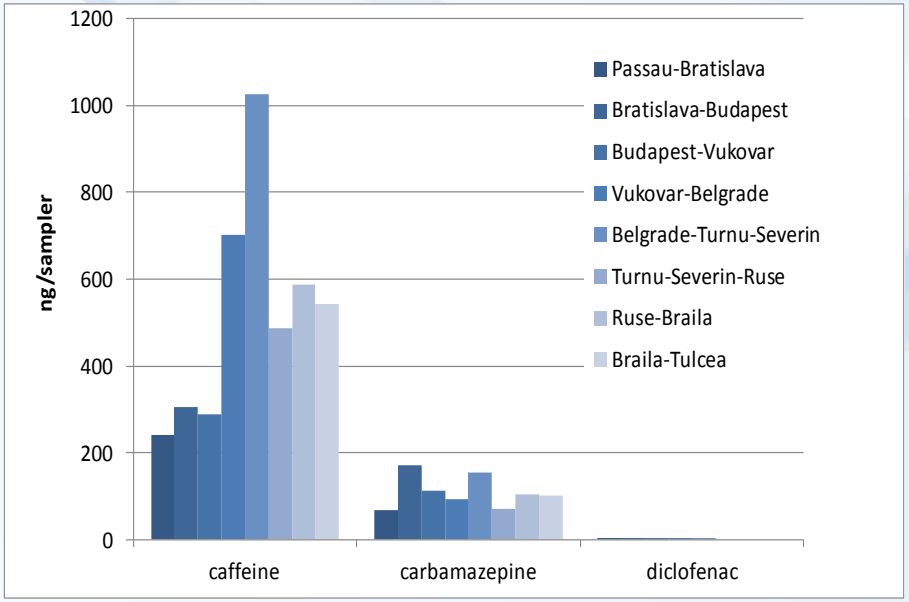
Chrysene – a compound in linear uptake phase in both samplers.

Spatial contaminant profiles measured by Empore RPS samplers

Polar pesticides



Pharmaceuticals



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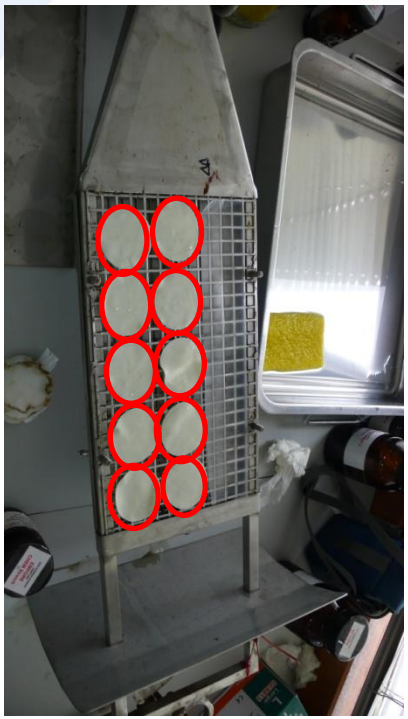
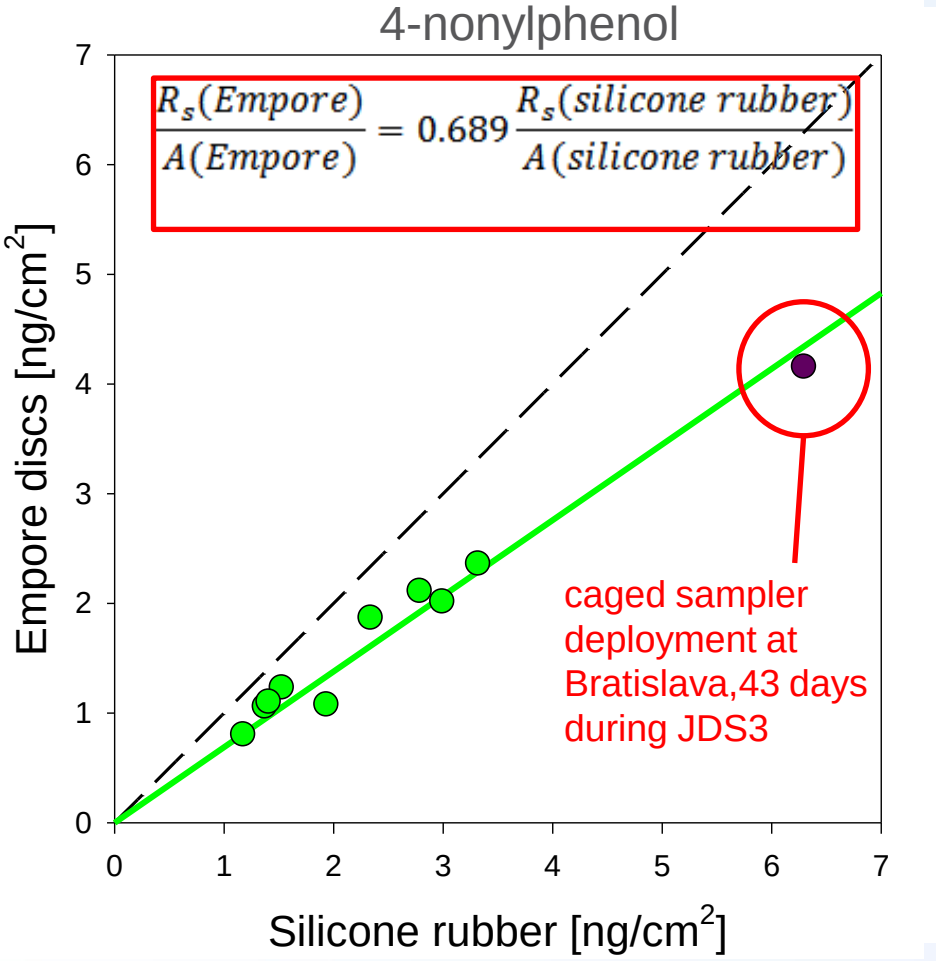
Comparison of passive samplers: Silicone rubber vs. Empore
Surface specific uptake

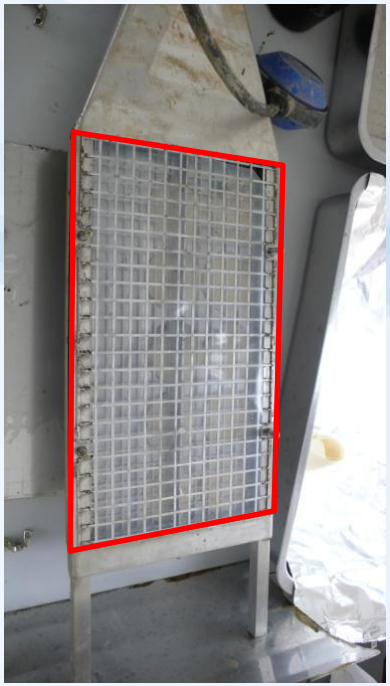
Empore:173 cm^2



4-nonylphenol



SR:392 cm^2



4-nonylphenol – a compound (likely) in linear uptake phase in both samplers.

Conclusions

- **Mobile passive sampling** enabled to clearly identify spatial profiles of a broad range of organic pollutants in the water column of Danube
  - POPs: PCBs, organochlorine pesticides, PAHs, brominated flame retardants
  - Alkylphenols, alkylphosphates, musks
  - polar pesticides, pharmaceuticals
- **„Active“ vs. „caged“ passive sampling:** cca. 5-fold increase of sampling rate
  - Measurement down to pg l^{-1} levels in only 2 days of sampling
- **A good comparability** of various passive sampling approaches
  - mobile and static sampling (concurrent and historical data)
  - co-deployed passive samplers (SR and LDPE)
- Sampling rates in the **SDB-RPS Empore-disk** sampler can be estimated from the correlation with uptake to co-deployed silicone rubber
- Current research: the combination of passive samplers with **bioassays** for identification of areas of concern for further investigation

Report: www.icpdr.org/main/activities-projects/jds3

Acknowledgements

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Thank you for your attention !