RECETOX STRATEGY:
Chemical and toxicological profiling of large rivers using passive sampling

Klára Hilscherová, Branislav Vrana, Foppe Smedes

Research Centre for Toxic Compounds in the Environment

(RECETOX)

Masaryk University, Brno, Czech Republic

Work Programme 2016-2018 of WFD CIS - WG Chemicals:

- among the main tasks: passive sampling, effect based tools, mixtures

Passive sampling

reliable, robust and cost-effective

preconcentrate trace levels of organic pollutants

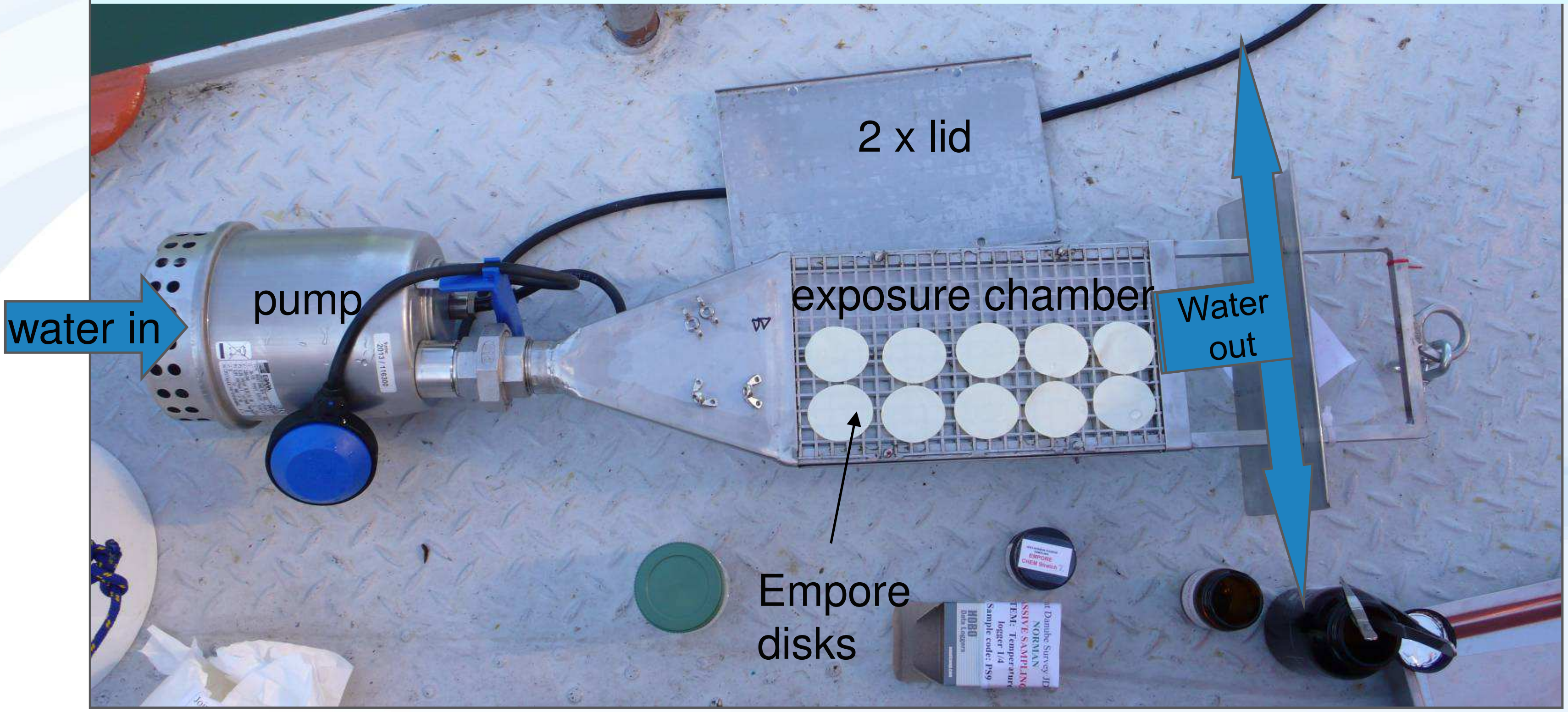
temporally- integrative

Scope: passive sampling for monitoring and toxicity profiling

- during Joint Danube Survey 4 (summer 2019)
- 10 stationary sites along the river
- 2 types of samplers covering wide range of phys-chem properties of pollutants
- ? comparison of passive and active sampling – any LVSPE planned?

- Strategy builds on the experience from mobile passive sampling in JDS3 – sampling with DYNAMIC PASSIVE SAMPLING SYSTEM during ship cruise

Design of passive sampler



Altesil® silicone rubber sheet (SR) – partitioning sampler for non-polar compounds

- sampling rate estimated by dissipation of PRCs (MW=300)

Empore discs (ED) - adsorption sampler for polar compounds based on styrene-divinylbenzene sorbent modified with sulfonic acid groups (SDB-RPS)

- sampling rate calculated from sampling velocity of SR sampler based on data on 9 PAHs - in linear uptake phase in both samplers

JDS3 - River stretches sampled with passive samplers (9 countries)

passive sampling stretch

static passive sampling site

equivalent volume of water extracted by SR

Science of the Total Environment 636 (2018) 1597–1607

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Mobile dynamic passive sampling of trace organic compounds: Evaluation of sampler performance in the Danube River

Branislav Vrana [a,*], Foppe Smedes [a], Ian Allan [b], Tatsiana Rusina [a], Krzysztof Okonski [a], Klára Hilscherová [a], Jiří Novák [a], Peter Tarábek [c], Jaroslav Slobodník [d]

[a] Masaryk University, Faculty of Science, Research Centre for Toxic Compounds in the Environment (RECETOX), Kamenice 753/5, 625 00 Brno, Czech Republic
[b] Norwegian Institute for Water Research, Gaustadalléen 21, NO-0349 Oslo, Norway
[c] Water Research Institute, Nábr. arm. gen. L. Svobodu 5, 81249 Bratislava, Slovakia
[d] Environmental Institute, Okružná 784/42, 97241 Koš, Slovakia

HIGHLIGHTS

- A dynamic passive sampling device was designed to speed up the chemical uptake
- The device was applied in the Danube river for sampling from a cruising ship
- Spatially and temporally integrated samples of dissolved compounds were obtained
- The device samples up to 5 times faster in comparison with a caged passive sampler
- Mutual comparability of three passive samplers deployed in parallel was shown

ARTICLE INFO

Article history:
Received 15 December 2017
Received in revised form 20 March 2018
Accepted 20 March 2018
Available online 30 March 2018

Editor: Kevin V. Thomas

Keywords:
Passive sampling
Mass transfer
Trace organic compounds
Joint Danube survey
Water quality

Science of the Total Environment 636 (2018) 1608–1619

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Effect-based monitoring of the Danube River using mobile passive sampling

Jiří Novák [a], Branislav Vrana [a], Tatsiana Rusina [a], Krzysztof Okonski [a], Roman Grabic [b], Peta A. Neale [c,d], Beate I. Escher [d,e,f], Miroslava Macová [e], Selim Ait-Aissa [g], Nicolas Creusot [g], Ian Allan [h], Klára Hilscherová [a,*]

[a] Masaryk University, Faculty of Science, Research Centre for Toxic Compounds in the Environment (RECETOX), Kamenice 753/5, 625 00 Brno, Czech Republic
[b] University of South Bohemia in České Budějovice, Faculty of Fisheries and Protection of Waters, South Bohemian Research Center of Aquaculture and Biodiversity of Hydrocenoses, Zátiší 728/II, CZ-389 25 Vodňany, Czech Republic
[c] Australian Rivers Institute, Griffith School of Environment, Griffith University, Southport, QLD 4222, Australia
[d] The University of Queensland, Queensland Alliance for Environmental Health Sciences (QAEHS), Coopers Plains, QLD 4108, Australia
[e] UFZ Helmholtz Centre for Environmental Research – UFZ, Permoserstr. 15, 04318 Leipzig, Germany
[f] Eberhard Karls University Tübingen, Hölderlinstr. 12, 72074 Tübingen, Germany
[g] Institut National de l'Environnement Industriel et des Risques (INERIS), Unité Ecotoxicologie, Parc ALATA - BP2, 60550 Verneuil en Halatte, France
[h] Norwegian Institute for Water Research, Gaustadalléen 21, NO-0349 Oslo, Norway

HIGHLIGHTS

GRAPHICAL ABSTRACT

Differences from 2013 sampling and analyses design

Passive sampling

Longer stationary exposure – up to 8 weeks - preconcentrate even lower levels of pollutants, increase sensitivity, characterization of longer term situation

Site specific – better comparability to active sampling – choose sites corresponding to previous dynamic sampling of river stretches and simultaneous active sampling

- improved approaches to estimation of sampling rates – more cross-calibration compounds

Analyses (based on collaboration with other partners and available resources):

1. Basic – priority substances (PBDEs, HCB, PAHs, HBCDD, Heptachlor, PCBs), CUPs, PFCs and RBSP

2. Wider spectra – PPCPs, alkylphenols etc.

3. Advanced – suspect and nontarget screening

4. Bioassays – reflect specific toxic potency of the whole mixture, including nonanalyzed or unknown compounds

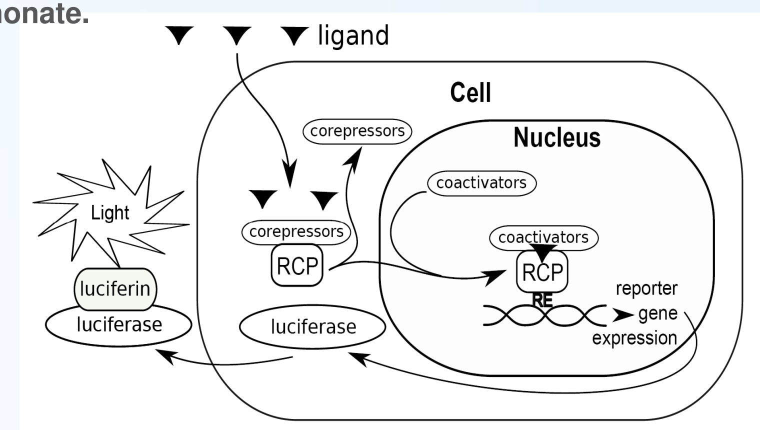
Sensitive battery from JDS3 + other additional sensitive assays from partners

Bioassays

Type of toxic action	Bioassay	Endpoint	Positive reference compound	EC value
Metabolism	CAFLUX-H4G1.1c2	Activation of AhR	2,3,7,8-Tetrachlorodibenzo-*p*-dioxin (TCDD)	EC_{20}
	HG5LN-hPXR	Activation of PXR	SR12813*	EC_{20}
Endocrine disruption	MDA-kb2	Inhibition of AR	Flutamide	IC_{20}
	MELN	Activation of ER	17β-Estradiol	EC_{20}
Adaptive stress response	ARE-bla	Oxidative stress response	tert-Butylhydroquinone	$EC_{IR1.5}$
	p53RE-bla	p53 - related genotoxicity	Mitomycin	$EC_{IR1.5}$
	NF-κB-bla	NF-κB related apoptosis	Tumor necrosis factor alpha (TNFα)	$EC_{IR1.5}$

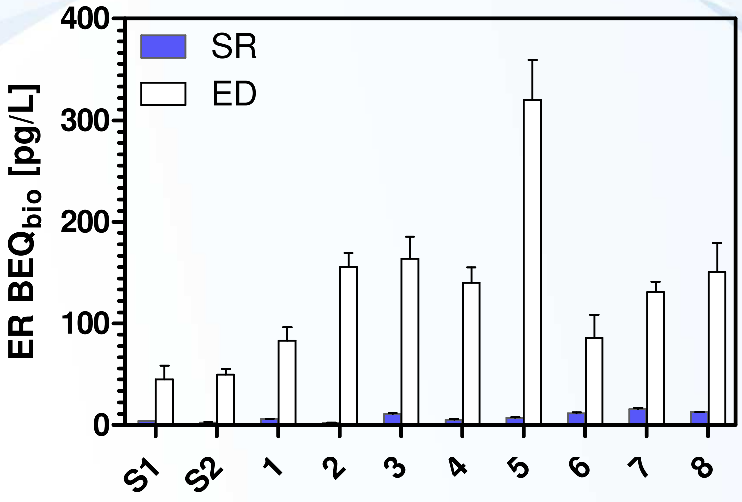
***Tetraethyl 2-(3,5-di-tert-butyl-4-hydroxyphenyl)ethenyl-1,1-bisphosphonate.**

$$BEQ_{bio} = \frac{EC_{20}\ (ref)}{EC_{20}\ (extract)} \text{ or } \frac{EC_{IR1.5}\ (ref)}{EC_{IR1.5}\ (extract)}$$

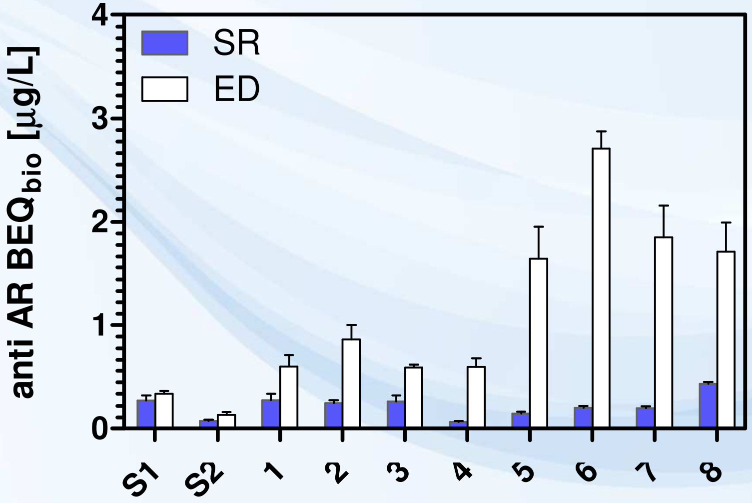


Endocrine disruptive potential

Estrogenic activity
- equivalents of E2

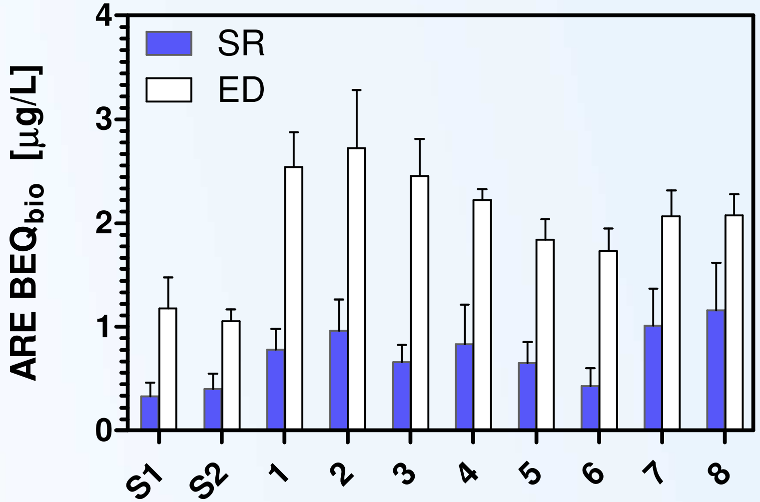


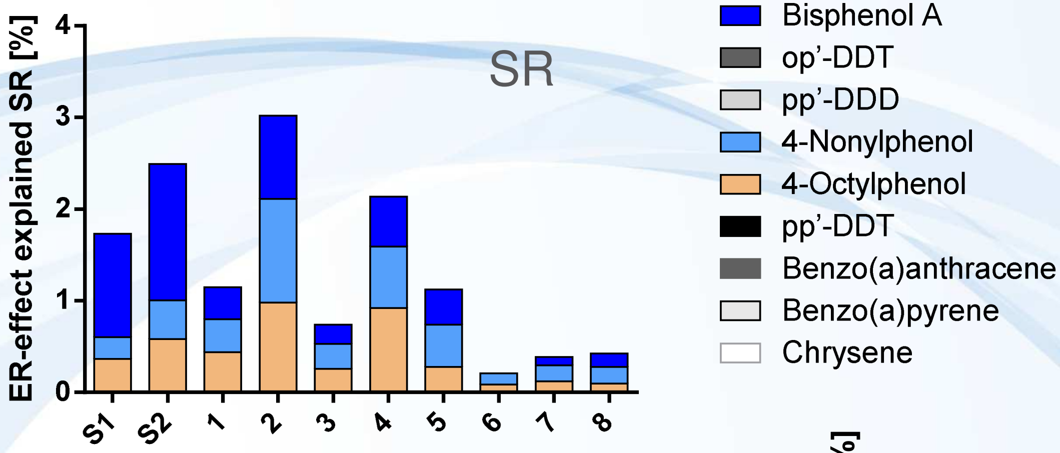
Anti-androgenic activity
- equivalents of flutamide

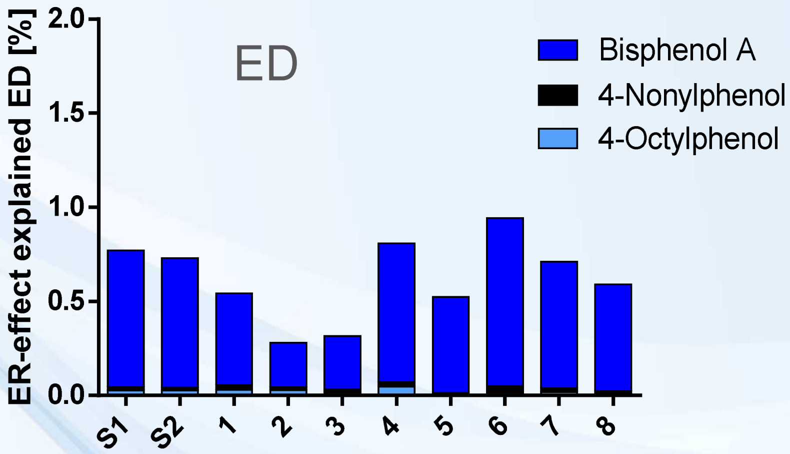


➢Studied biological effects elicited mainly by polar chemicals

Oxidative stress potential
- equivalents of tBHQ



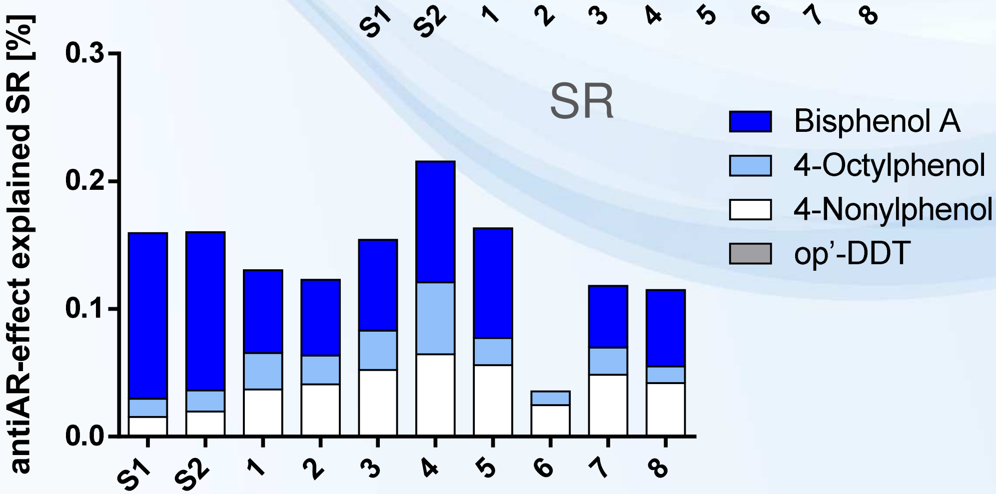




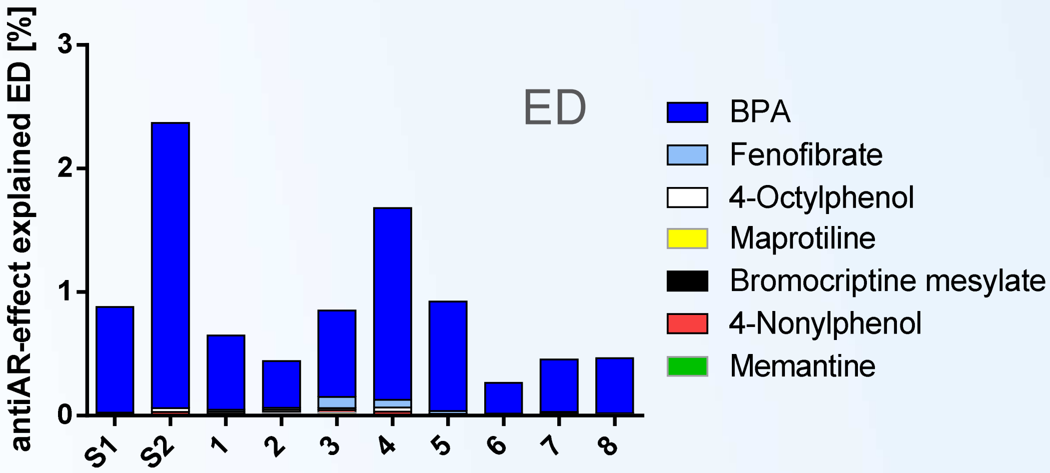
Estrogenic activity

(BEQ_{chem}/BEQ_{bio})

➢High proportion of nonanalyzed active compounds



Anti-androgenic activity



Summary

- Longer-term passive sampling
  - – effectively sample chemicals in pg/L concentration range
  - – representative picture of longer-term pollution situation on studied sites
  - – very good basis for long-term trend monitoring
- Complementarity of ED (hydrophilic bioactive compounds) and SR (bioaccumulative hydrophobic compounds) samplers
- Integrated approach: passive sampling + toxicological profiling + chemical analysis - spatial profile of pollutant mixtures, areas of concern
- Analyses of wide spectra of pollutants, suspect and nontarget screening together with bioassays (and potentially EDA) will help to identify and prioritize the effect/risc drivers

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

Acknowledgements

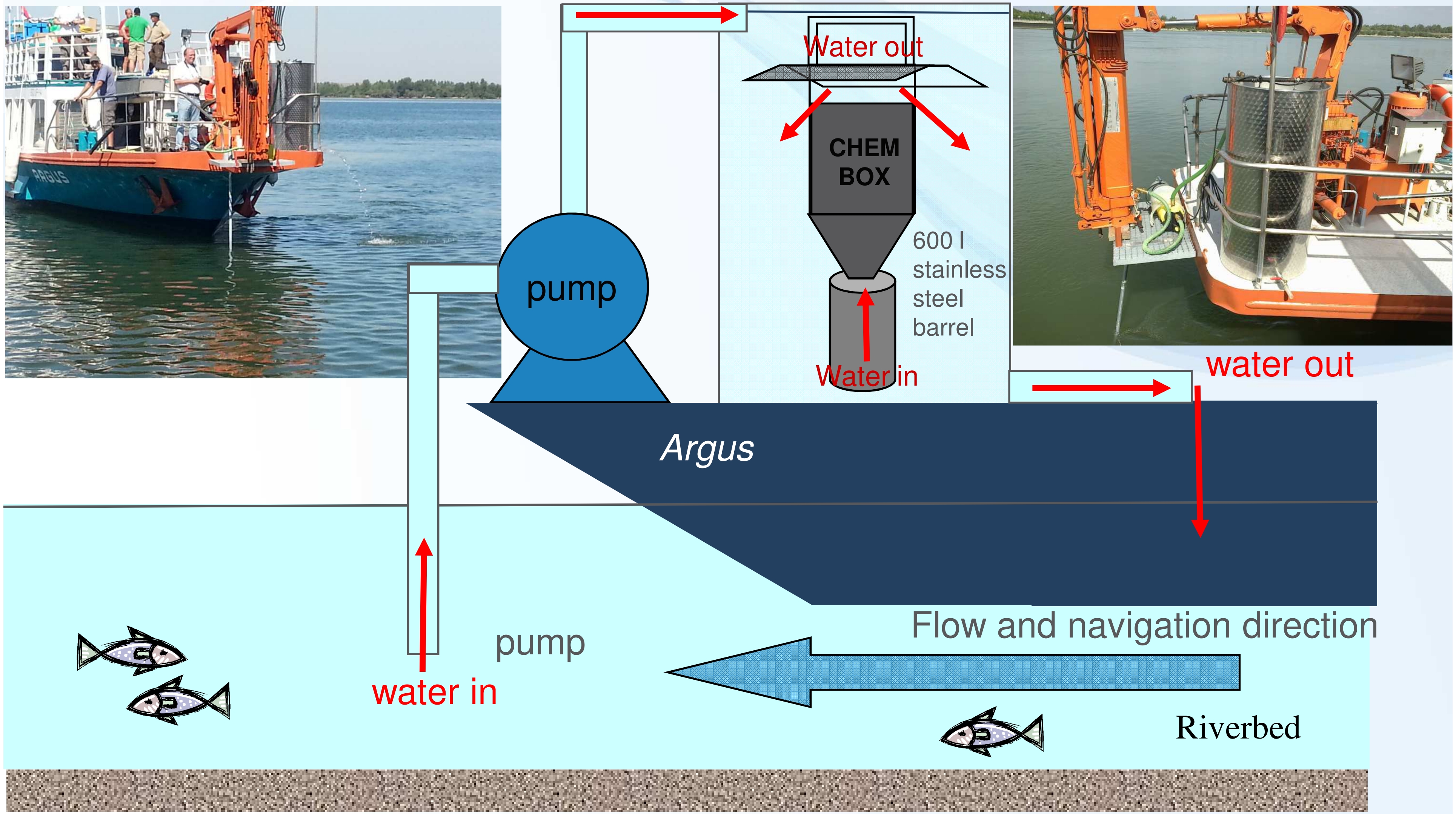
NORMAN association www.norman-network.net

The FP7 SOLUTIONS project funded from the European Union's Seventh Framework Programme for research, technological development and demonstration under grant agreement no. 603437)

Collaborators from UFZ, INERIS, RWTH, WRI, EI, RECETOX, University of South Bohemia are acknowledged for participating in sampling, chemical and toxicological analysis.

Mobile sampling device operation

passive sampling with active water exchange ~ 5 times more effective



River stretches sampled with passive samplers

Stretch number	River stretch	River km	Dates of sampling (2013)	Mean water temperature [°C]	Exposure time [d]	Volume extracted by SR [L][a]	Volume extracted by ED [L][b]
S1	Cunovo	1852	19.8.-23.8.	21.3	4	245	90
S2	Cunovo	1852	23.8.-28.8.	21.3	5	264	97
1	Passau-Bratislava	2203-1852	17.8.-22.8.	21.3	2.0	169	62
2	Bratislava-Budapest	1852-1632	22.8.-26.8.	22.0	1.2	84	31
3	Budapest-Vukovar	1648-1297	26.8.-2.9.	21.9	1.7	139	51
4	Vukovar-Belgrade	1297-1154	2.9.-6.9.	22.8	1.6	133	49
5	Belgrade-Turnu-Severin	1154-930	6.9.-10.9.	22.1	2.0	139	51
6	Turnu-Severin-Ruse	930-495	11.9.-17.9.	21.9	2.0	129	47
7	Ruse-Braila	495-170	17.9.-21.9.	19.2	1.4	79	29
8	Braila-Tulcea	170-71	21.9.-26.9.	18.7	1.3	72	26

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

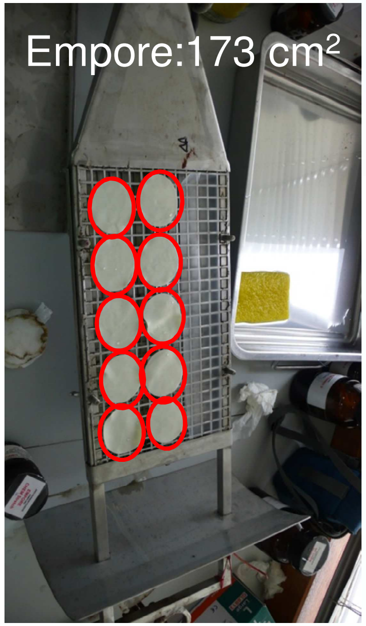
[b] Volume of water extracted by the ED sampler; estimated based on comparison of levels of 9 PAHs in SR and ED samplers

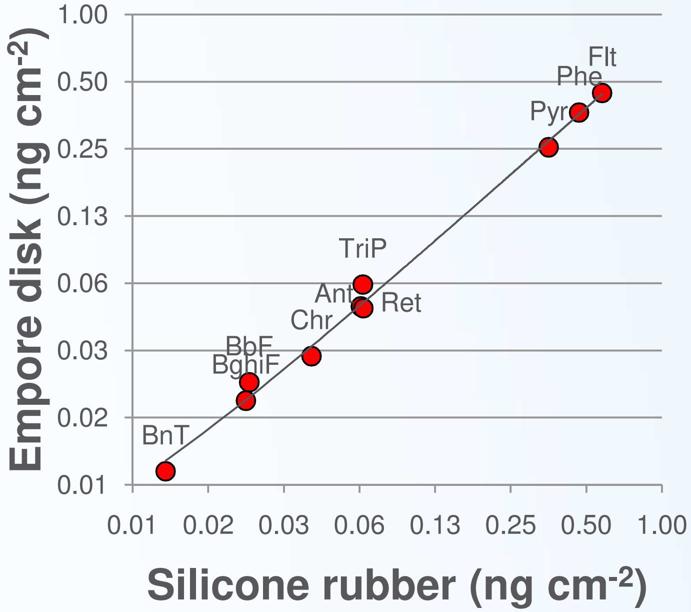
Comparison of passive samplers: Silicone rubber vs. Empore Surface specific uptake

SR - partitioning sampler for non-polar compounds
- sampling rate estimated by dissipation of PRCs (MW=300)

ED - adsorption sampler for polar compounds
- sampling rate calculated from sampling velocity of SR sampler based on data on 9 PAHs - in linear uptake phase in both samplers

$$\frac{R_S\,(\text{Empore})}{A\,(\text{Empore})} = 0.83\,\frac{R_S\,(\text{silicone rubber})}{A\,(\text{silicone rubber})}$$

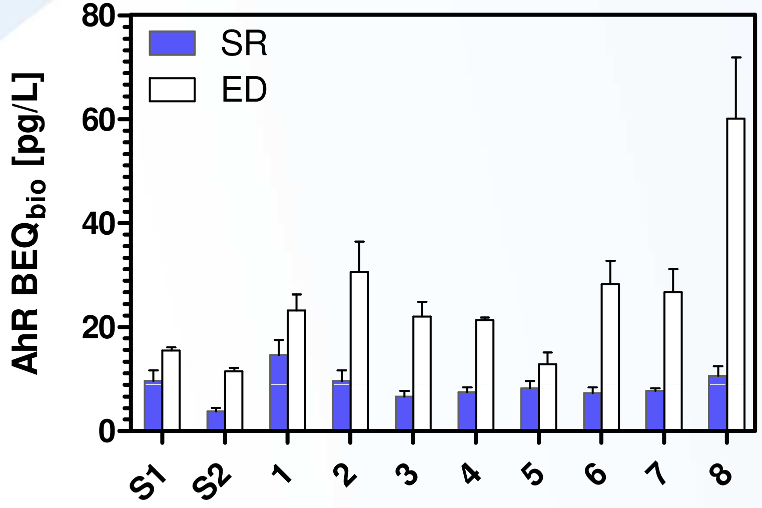




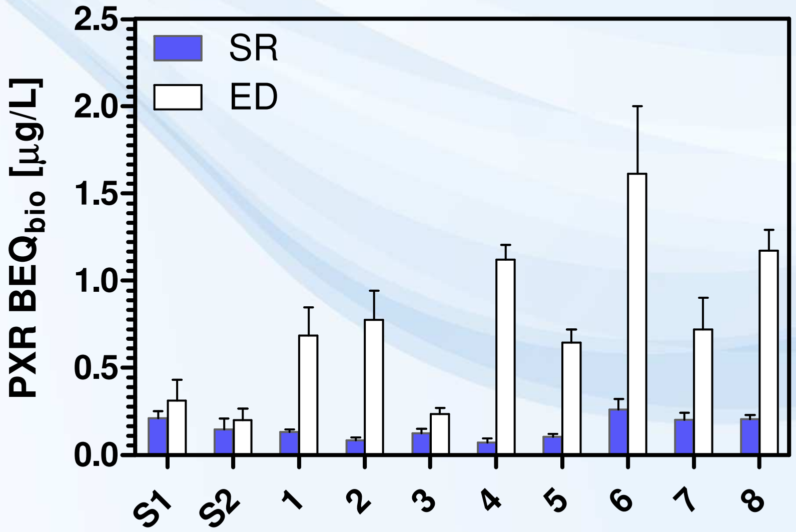
Vrana et al. 2016. Guidelines describing passive sampling and analytical aspects of the procedure for relevant compounds. Deliverable SOLUTIONs project:
http://www.solutions-project.eu/wp-content/uploads/2017/01/SOLUTIONS_Guidelines_Passive_Sampling.pdf :
Jalova et al. 2013. *Env.Int. 59: 372-383*

Bioanalytical data

Dioxin-like activity
- equivalent of TCDD



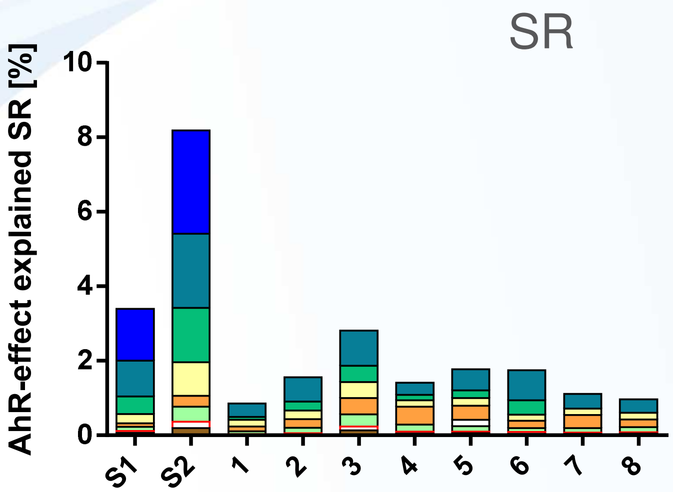
PXR-mediated activity
- equivalent of SR12813

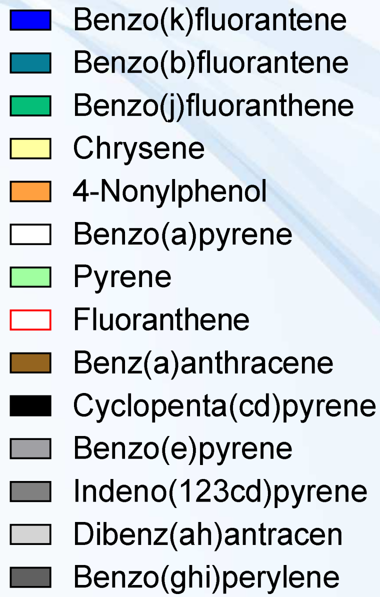


➢Studied biological effects elicited mainly by polar chemicals

Contribution of detected chemicals to biologic potentials

AhR-mediated activity (BEQ_{chem}/BEQ_{bio})

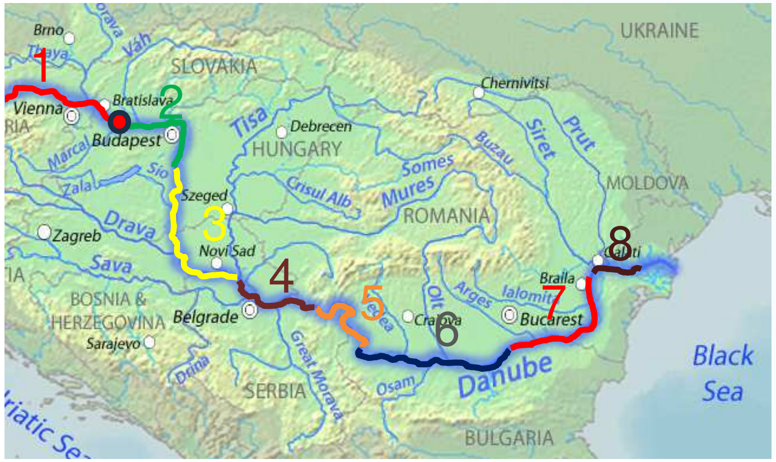


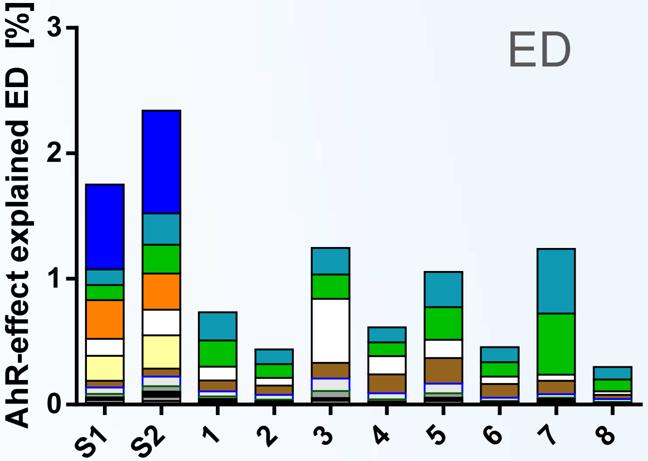


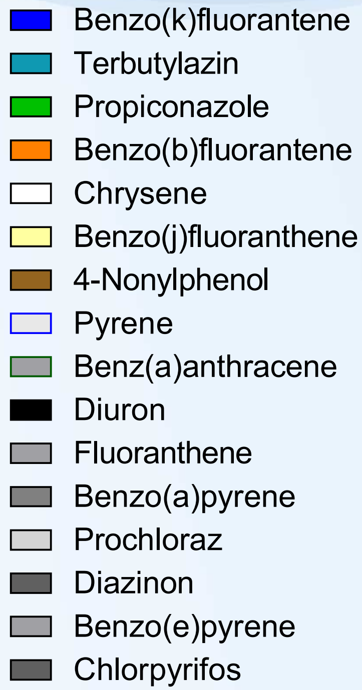
concentration addition model

$$BEQ_{chem} = \sum_{i=1}^{n} REP_i \cdot C_i$$

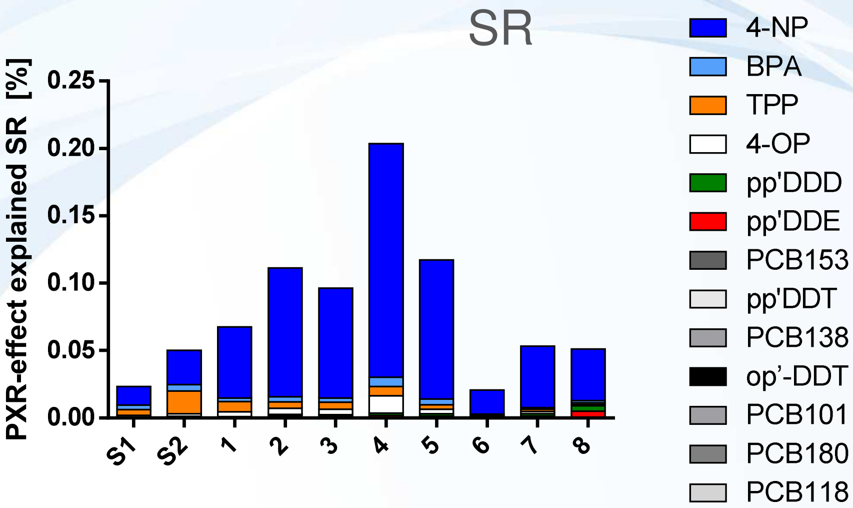
➢ High proportion of nonanalyzed active compounds, need REP for analyzed compounds

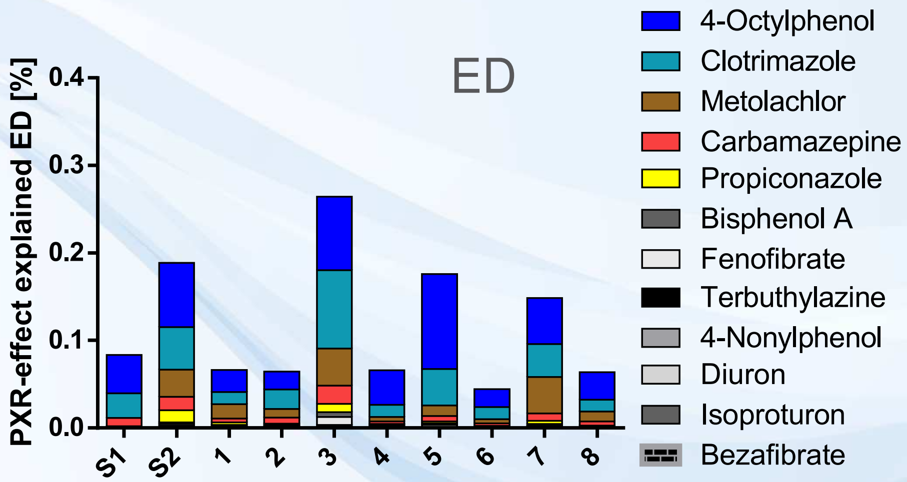




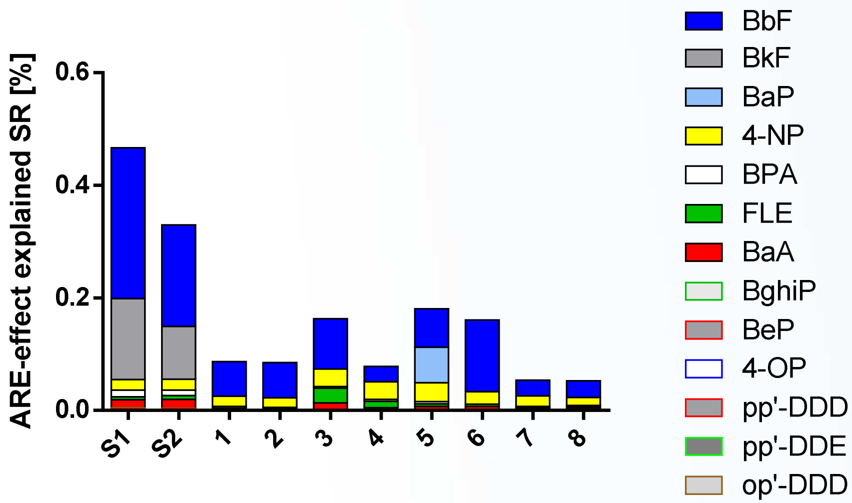


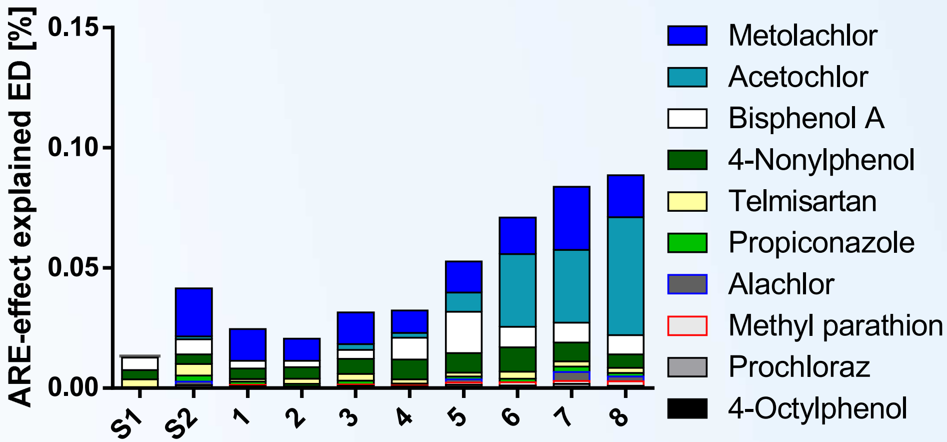
PXR-mediated activity (BEQ_{chem}/BEQ_{bio})





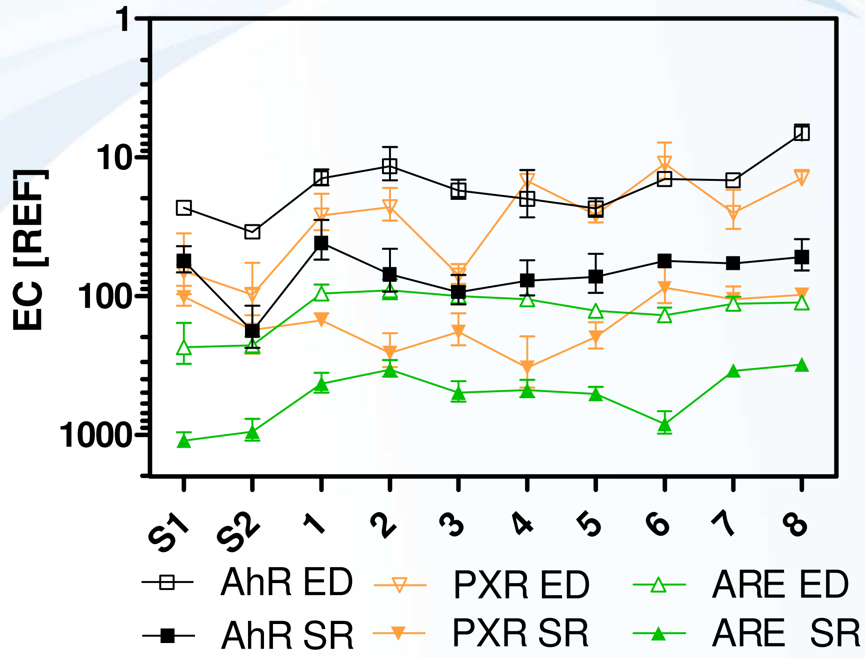
ARE-mediated oxidative stress

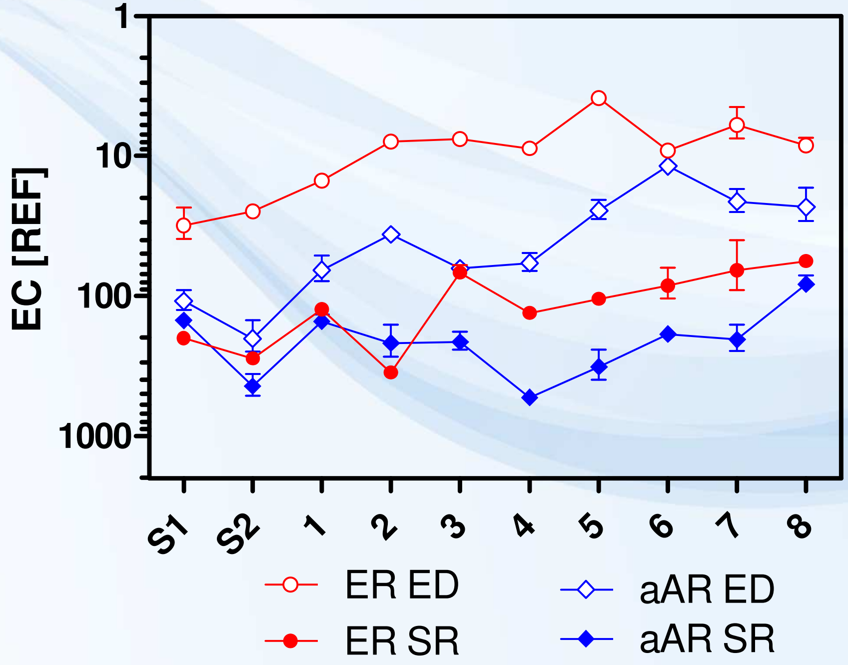




Corresponds to Neale et al. (2015) *Environ.Sci.Technol.* 49 (24): 14614–14624

Bioanalytical data

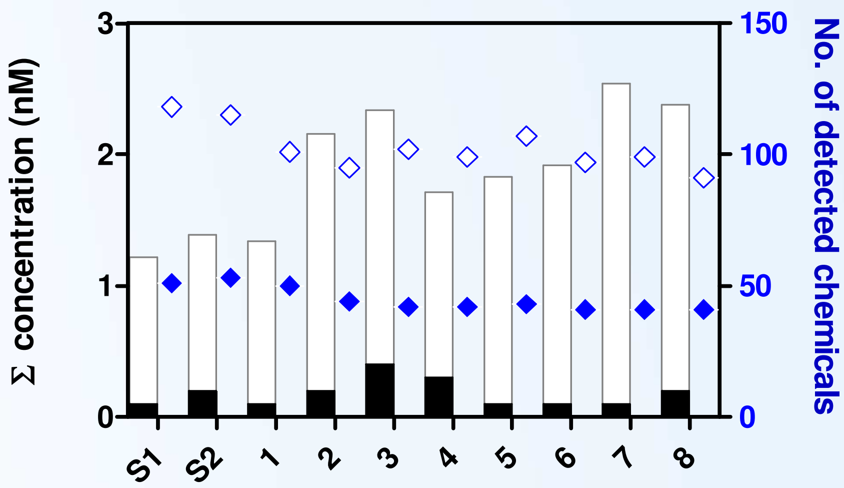




EC values in units of relative enrichment factor (REF) compared to sampled water

Chemical analyses

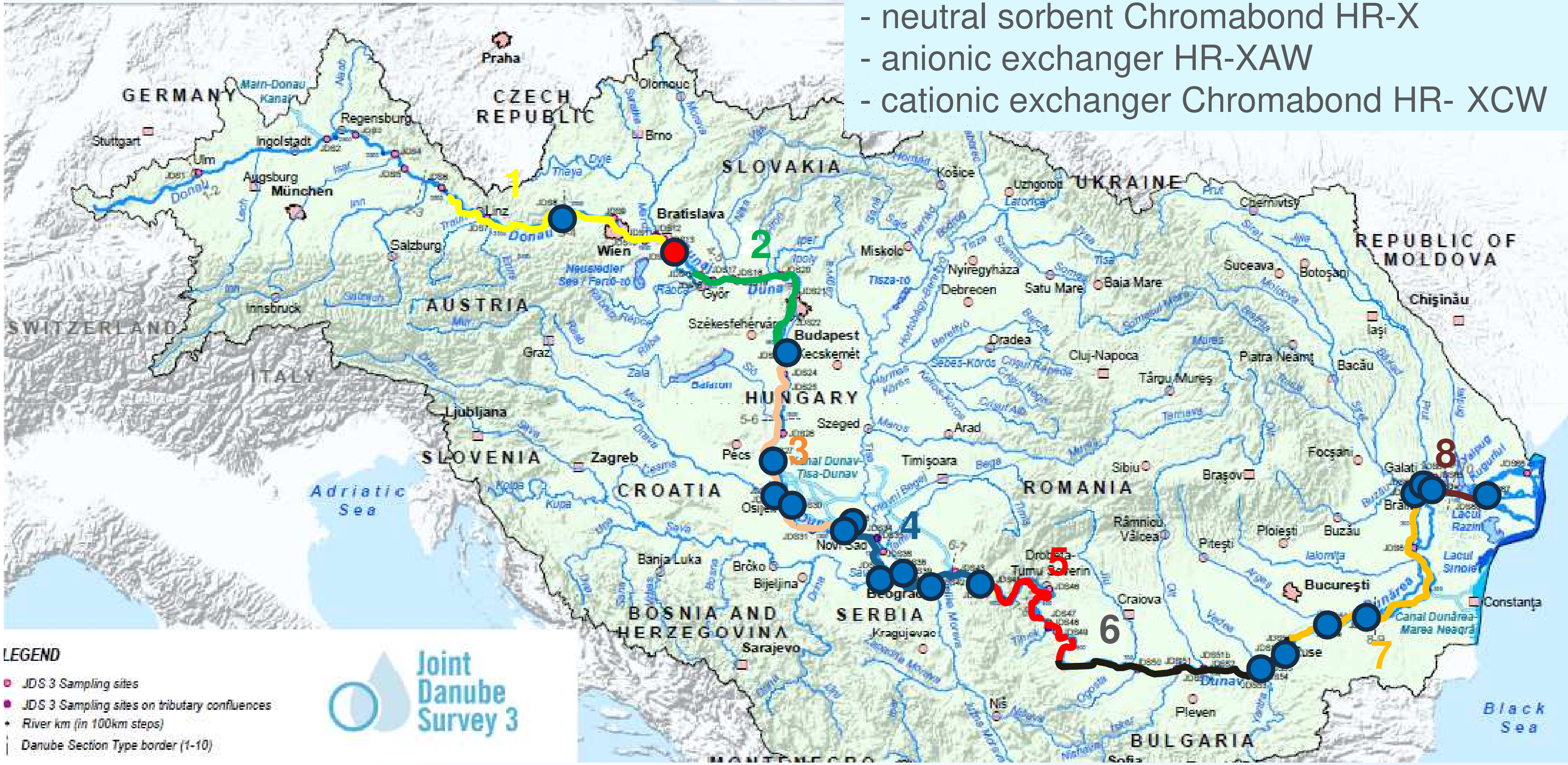
Chemicals (pg/L)	No.	S1	S2	1	2	3	4	5	6	7	8
ATBs	*31*	12151	11974	10940	23122	22568	16900	21014	12103	31949	28454
Cardiovascular	*15*	14183	14964	11748	19693	21649	11367	11730	7262	10764	11026
Psychoactive	*30*	13151	10851	8217	14306	12215	8845	11249	9248	13562	11449
Antihistamins	*8*	255	91	275	<LOD	112	348	242	<LOD	583	<LOD
Antifungals	*8*	4099	4898	4121	8291	8146	8476	10560	10466	10582	9297
Antidiabetics	*4*	31	4	32	42	98	35	20	21	97	27
Statins	*4*	289	318	286	400	1259	1031	1219	418	590	507
Other pharm.	*4*	290	248	<LOD	<LOD	122	533	<LOD	295	<LOD	<LOD
CUPs	*40*	17543	28746	33152	20492	32509	17067	27033	28373	67140	41961
Alkylphenols	*3*	7630	7790	12225	12484	15209	26311	34513	20982	22399	19817
PAHs	*29*	17342	23000	18215	21063	51067	37296	15975	12002	13965	20704
PCBs	*7*	217	244	171	291	167	172	369	158	307	295
OCPs	*12*	188	223	156	244	372	313	358	465	808	1872
BDEs	*9*	4	6	22	2	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD



Sum concentration and number of detected chemicals
white symbol - ED (chemicals analysed: 185)
filled symbol - SR (chemicals analysed: 81)

Passive and active (LVSPE) sampling sites

LVSPE: large volume solid phase extraction - up to 500 L
Stainless-steel chamber:
- neutral sorbent Chromabond HR-X
- anionic exchanger HR-XAW
- cationic exchanger Chromabond HR- XCW

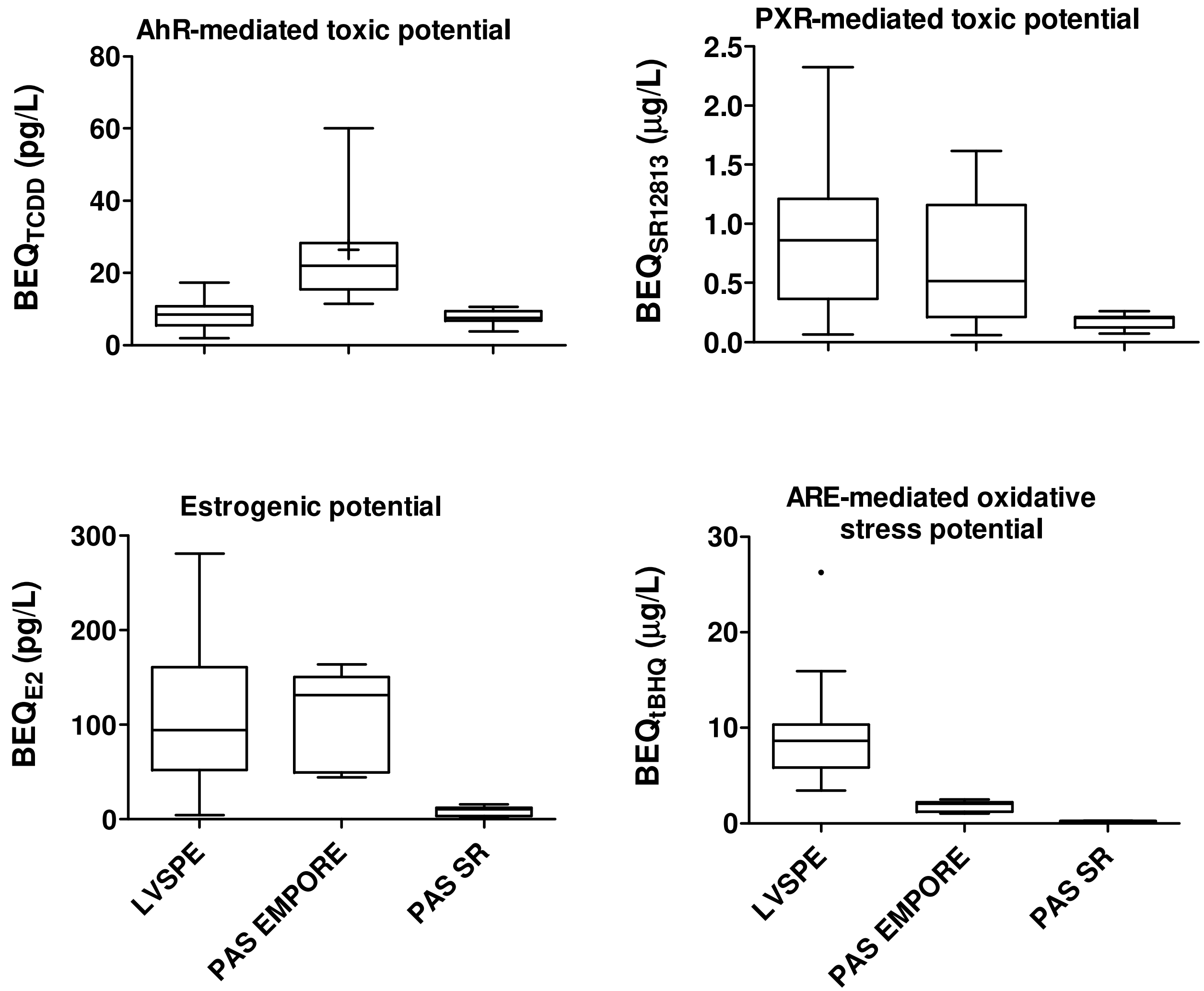


mobile passive sampling stretch

static passive sampling site

LVSPE sampling sites (Neale *et al.* (2015) *Environ.Sci.Technol.* 49 (24))

Comparison of BEQ_{bio} from passive and LVSPE sampling



- Sampled volume estimates for passive samplers correspond to data from LVSPE

Neale et al. (2015) *Environ. Sci. Technol.* 49 (24): 14614–14624