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# Chemical and toxicological profiling of large rivers using mobile passive sampling and comparison to large volume active sampling

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## Introduction and Methods:

Freshwaters often contain complex mixtures of many different pollutants, some at trace concentrations, thus the toxic potential and risk associated with these mixtures are difficult to predict. Efficient sampling methods together with sensitive effect based tools can significantly improve the risk assessment.

Novel mobile “enhanced” passive sampling system (EPS) for sampling of trace organic pollutants was successfully applied within the Joint Danube Survey 3 (JDS 3) during August and September 2013. In this device the diffusive uptake of contaminants is enhanced by jet streaming water along the sampler surface performed by a submersible pump. The EPS was installed on board of expedition ship and during a typical sampling period of 5 days the ship moved downstream along a defined stretch. The samplers accumulated water pollutants integrated in time and space over 8 river stretches. The partitioning samplers for non-polar compounds, i.e. silicone rubber sheets, and an adsorption sampler for polar compounds based on Empore SPE disks (SDB-RPS; reversed-phase sulfonate) were applied. Both samplers were extracted with organic solvents for chemical analyses and toxicological profiling.

Spot sampling of high water volumes was conducted by large volume solid phase extraction (LVSPE) at 22 sites along the river (on both the Danube River and its tributaries) during JDS 3. Up to 500 L of water were passed through large volume solid phase extraction system (Maxx GmbH, Rangendingen, Germany) consisting of a stainless-steel chamber containing neutral sorbent Chromabond HR-X, anionic exchanger Chromabond HR-XAW, and cationic exchanger Chromabond HR-XCW (Macherey-Nagel, Dueren, Germany). After extraction, each solid phase was freeze-dried and then extracted with solvents, and the eluates were combined. Extracts of samples from both EPS and LVSPE were subjected to analysis of a wide range of organic pollutants and to toxicological profiling. Bioanalytical tools were applied complementary to chemical analysis to detect the effects of complex chemical mixtures. The endpoints studied in all listed types of samples included toxic potentials for causing endocrine disruption (estrogenic, anti/androgenic), dioxin-like activity, pregnane X receptor (PXR)-mediated activity and oxidative stress-associated response.

## Results and Discussion

Passive sampling as well as application of large volume solid phase extraction enabled to identify spatial profiles of a broad range of organic pollutants and studied toxicological endpoints in the water column. In many cases the integrative character of passive sampling allowed measurement of compounds at pg L<sup>-1</sup> levels where conventional grab sampling of water applied in previous surveys failed to detect them. Besides oxidative stress response, toxic equivalents were detected in a similar range for active and passive sampling (Fig.1). The passive sampling reflected the physical-chemical characteristics of the compounds driving individual effects. While the PXR-mediated and estrogenic effect potentials were detected namely in Empore samplers, thus were elicited mainly by polar chemicals, AhR-mediated effect potential was primarily detected in silicone rubber samples, which reflects significant contribution of less polar compounds.

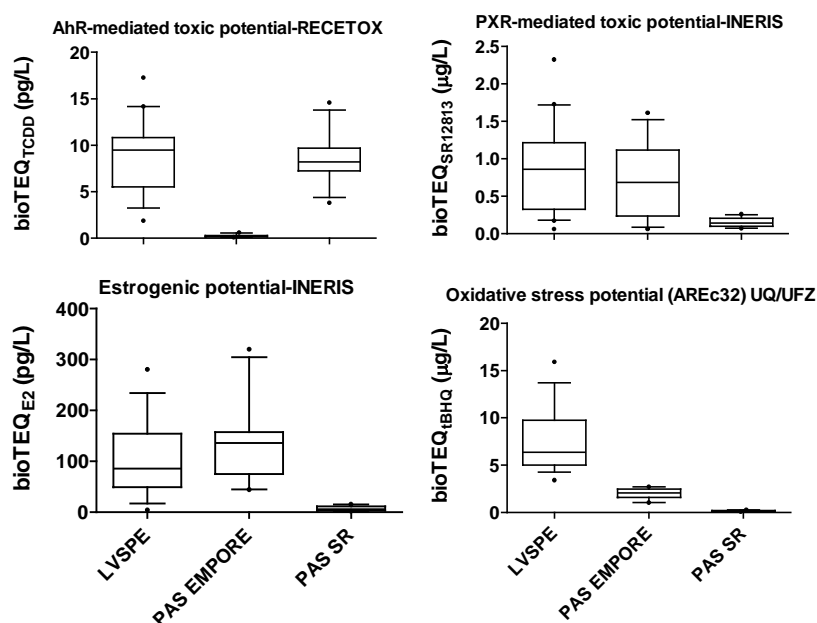


Figure 1: Comparison of toxic potentials of samples from large volume active sampling and passive sampling during JDS3

The bioanalytical equivalent concentration (BEQ) approach was used to characterize the contribution of the detected chemicals to observed toxic potentials and identify the main toxicity drivers. The fraction of biological effects explained by the detected chemicals in samples from mobile “enhanced” passive sampling of water from the Danube river differed depending on the studied effect and the type of sampler (Fig. 2). For example, estrogenicity and AhR-mediated potential were explained relatively well in Empore sampler (mainly polar compounds), with  $17\beta$ -estradiol and  $17\alpha$ -ethinyl estradiol being responsible for most of the calculated estrogenic potential. On the other hand, most of the estrogenicity and AhR-mediated potential in silicon rubber samples (non-polar chemicals) was not explained by the measured chemicals. The detected chemicals contributed only little to some other endpoints, such as oxidative stress-associated response.

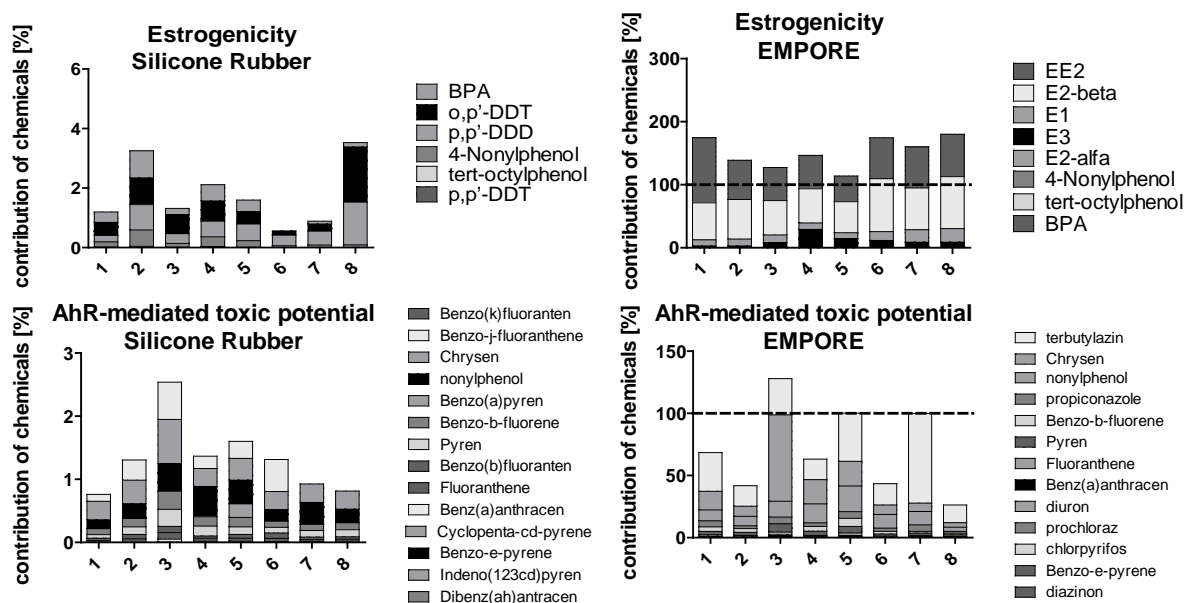


Figure 2: Fraction of toxic potentials in passive samples from the 8 river stretches explained by levels of detected chemicals

Our study demonstrates the utility of the integrated approach using toxicological profiling to characterize fresh water pollutant mixtures along with chemical analysis in monitoring of fresh water quality and the very good applicability of both passive sampling and large volume solid phase extraction in this assessment.

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