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

The Argus JDS3 sampling ship

Passive sampling

“active” passive sampling device

Sampler in operation (lifted above water for the photo)
Mobile „active“ passive sampling device operation

600 l stainless steel barrel

Flow and navigation direction

Riverbed
Passive sampling on board of JDS3 ship Argus
<table>
<thead>
<tr>
<th>Stretch number</th>
<th>Stretch start and end</th>
<th>River km</th>
<th>Dates of cruise</th>
<th>Mean water temperature [°C]</th>
<th>Exposure time [d]</th>
<th>Volume extracted by SR [L]a</th>
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<tr>
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aVolume 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

<table>
<thead>
<tr>
<th>Compound class</th>
<th>Passive sampler</th>
<th>Target analysis</th>
<th>Non-target screening</th>
<th>Toxicity profiling</th>
<th>Specimen bank</th>
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</table>
| **Nonpolar compounds** | Silicone rubber sheet (SR)  
Log density polyethylene sheet (LDPE) | RECETOX/ GC/MS                     | NIVA / GC/MS          | SOLUTIONS bioassay battery | Later use in FP7 SOLUTIONS       |
| log Kow >3       |                                        |                                  |                      |                          |                                    |
| Polar compounds  | SDB-RPS Empore discs                    | RECETOX/ Waters XEVO TQ-S         | University of South Bohemia / Thermo Qxactive  
RECETOX/ AB SCIEX 5500 Q Trap | RECETOX/ Agilent 6550 QTOF        | SOLUTIONS bioassay battery | Later use in FP7 SOLUTIONS       |
| log Kow < 3      |                                        |                                  |                      |                          |                                    |

### 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

Sampler-water partition coefficient → cosolvent method

Sampling rate modeled with \( R_s = FA / M^{0.47} \)

No membrane control on uptake

Measured PRC dissipation \( f_{\text{exp}} = \frac{N_t}{N_0} \) fitted with

\[ f_{\text{calc}} = e^{\frac{FA}{K_{pw} m^{0.47}}} \]

using non-linear regression fit of \( f_{\text{exp}} \) and \( f_{\text{calc}} \)

Reference

1. Smedes et al. EST 2009
2. Rusina et al EST 2010
4. Booij and Smedes 2010

Regensburg-Passau

\( f_{\text{measured}} \) vs \( f_{\text{calc}} \)

\( R_s = 82.8 (±6.2) \)

PRC list:
- BIP-D10, PCB001, PCB002, PCB003, PCB010, PCB014, PCB021, PCB030, PCB050, PCB055, PCB078, PCB104, PCB145, PCB204
### River stretches sampled with passive samplers

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\[ V_{sampled} = R_s \times t \]

*aVolume 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

- Concentration [pg/l]
- Locations:
  - Passau-Bratislava
  - Bratislava-Budapest
  - Budapest-Vukovar
  - Vukovar-Belgrade
  - Belgrade-Turnu-Severin
  - Turnu-Severin-Ruse
  - Ruse-Braila
  - Braila-Tulcea

Spatial contaminant profiles measured by silicone rubber samplers

**PCBs**

- Organochlorine pesticides
- Musk compounds
- Alkylphenols

Comparison with older data from „classical“ passive sampling

PAH concentrations: Stretch Passau-Bratislava

Sampled using Silicon Rubber
During JDS in 2013

Sampled using SPMD (summer 2011)

* based on data < LOQ
Comparison of „mobile“ with „static“ passive sampling POPs in water column at Bratislava

Mobile „active“ passive
Passau-Bratislava

Static „active“ passive:

PAHs

PCBs

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.

![Graph showing the relationship between Silicone rubber and LDPE uptake of Chrysene]
Spatial contaminant profiles measured by Empore RPS samplers

Polar pesticides

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<tr>
<td>Alachlor</td>
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<td>Atrazine</td>
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<td>Isoproturon</td>
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<td>Simazine</td>
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Pharmaceuticals

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<td>caffeine</td>
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<td>carbamazepine</td>
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<td>diclofenac</td>
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Comparison of passive samplers: Silicone rubber vs. Empore
Surface specific uptake

Empore: 173 cm$^2$

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

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