# Investigation of emerging aquatic contaminants emissions in municipal wastewaters using passive sampling

MUNI | RECETOX

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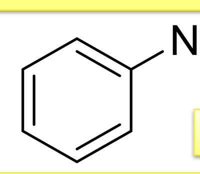
## Introduction

AAs are important industrial compounds widely used as materials and intermediates in the production of a wide range of products, e.g., dyes, plastics, pesticides and pharmaceuticals. They often enter surface water and rivers either directly from industrial emissions or indirectly from the breakdown products (metabolites) of herbicides and pesticides and have the potential to endanger aquatic ecosystems.

Due to their good solubility in water, they can easily permeate through the soil and contaminate the groundwater. They are highly toxic and have potential carcinogenic and mutagenic effects. The U.S. EPA has included them to the pollutants list subjected to environmental control.

## Objectives

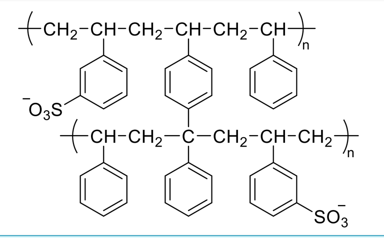


aniline

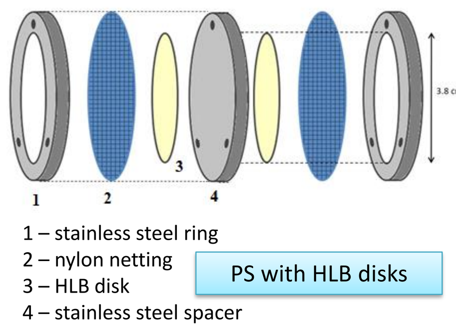
The aim of this project is to develop a selective, robust and representative method for monitoring of aromatic amines (AAs) in wastewater (WW) and recipient surface water to characterize a) their fate in the WW treatment process and b) their levels in recipient surface water related to exposure of aquatic organisms. For this purpose, monitoring techniques based on passive sampling (PS) are being developed, calibrated, tested and applied in field studies performed at municipal WW treatment plants (WWTP) and corresponding recipient water bodies.

## Active and passive sampling

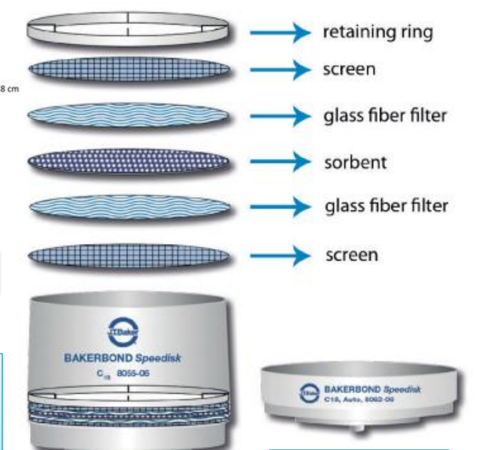
Active sampling:
- The new extraction method of AAs from the field water samples was developed and optimized using **Empore disks SDB-RPS** as sorbent.


SDB-RPS (styrenedivinylbenzene-reverse phase sulfonate)

Passive sampling:
- **HLB disks** - the HLB disk sampler consists of four solid phase extraction Affinisep AttractSPE®Disks HLB with 47 mm diameter, the surface area exposed to water is 22.7 $cm^2$
- **Speedisks** - polypropylene cylinder-shaped container, sorbent: hydrophilic divinylbenzene (ca. 600 mg, surface area 19.6 $cm^2$)



PS with HLB disks



Speedisk

Testing materials for passive sampler construction:
- Adsorbent disks diffusive properties of hydrogel (pH-dependent diffusion) – gel stacking method
- Sorptive properties of adsorbent disks (sorbent equilibration with water in laboratory)

## Field testing of passive samplers

In the field testing at WWTP, we tested suitability of wide-used HLB sorbent for AAs for further use in detection of AAs in water bodies.

Another goal was to further study characteristics of HLB disk passive sampler (PS); uptake kinetics of AA to passive sampler and AA equilibration between HLB disk sampler and water.

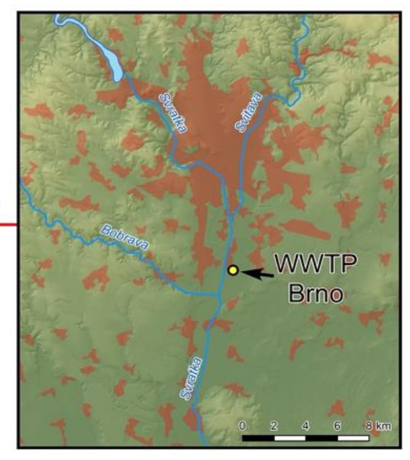

Sampler deployment in WWTP Modřice effluent


HLB disks after 1, 2, 4, 8 and 16 weeks exposure in WWTP Modřice effluent

Sampling site:
- Municipal WWTP Brno – Modřice, Czech Republic, autumn 2020
- Effluent of municipal WWTP (500,000 equivalent inhabitants)

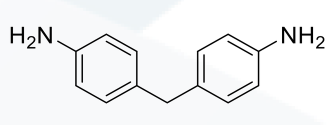
Sampler deployment design:
- Different exposure time period (1-16 weeks)
- Comparison of samplers with daily 24 h composite water samples
- Temperature: 14.3 ± 1.5 °C
- pH: 7.5 ± 0.1

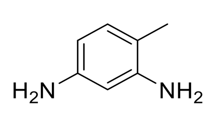
PS with HLB disk (left) and Speedisk (right)

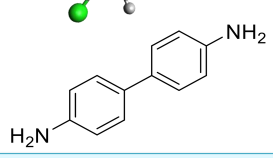



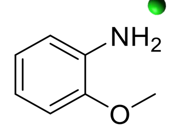

## Results

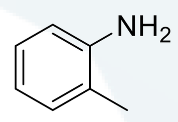
**Screening of AAs** in WWTP Modřice effluent with Empore disks SDB-RPS in summer 2021 **– 15 detected AAs:**

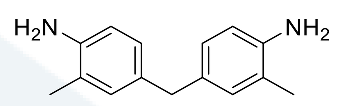

4,4'-Methylenedianiline

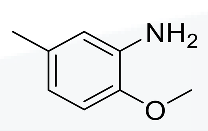

2,4-Diaminotoluene

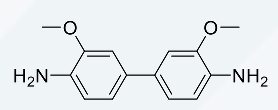

Benzidine

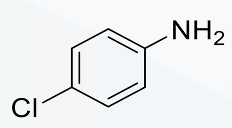

*o*-Anisidine

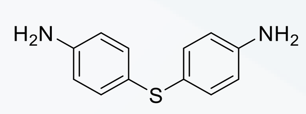

*o*-Toluidine

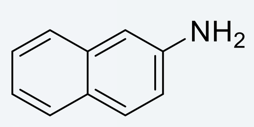

4,4-Methylene-bis(2-methyl aniline)

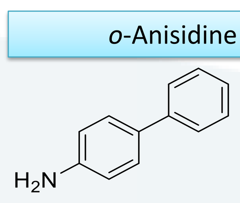

*p*-Cresidine

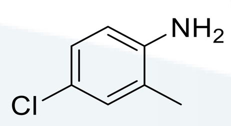

*o*-Dianisidine

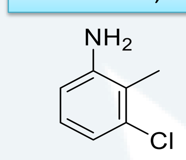

4-Chloroaniline

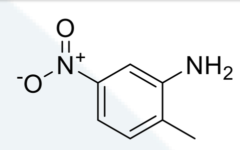

4,4-Thiodianiline


2-Naphtylamine


4-Aminobiphenyl


4-Chloro-*o*-toluidine

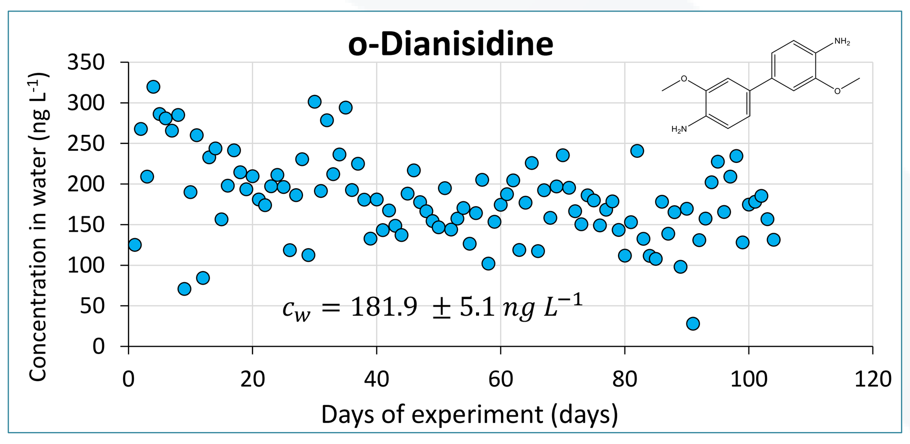

3-Chloro-*o*-toluidine

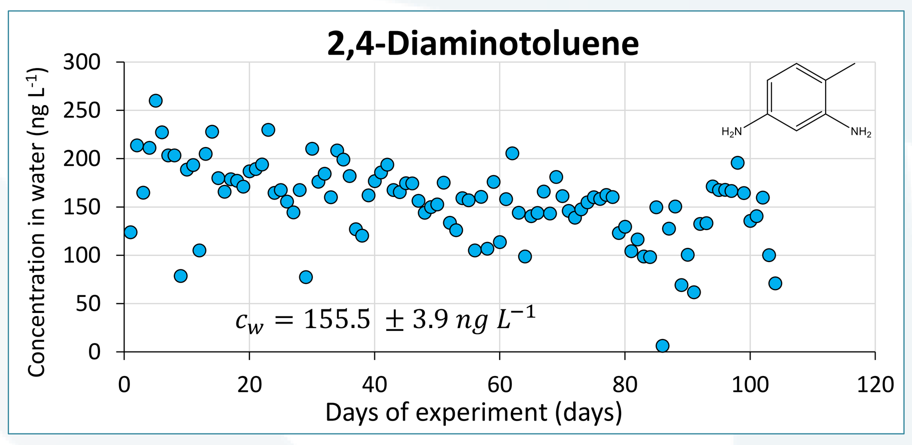

2-Amino-4-nitrotoluene

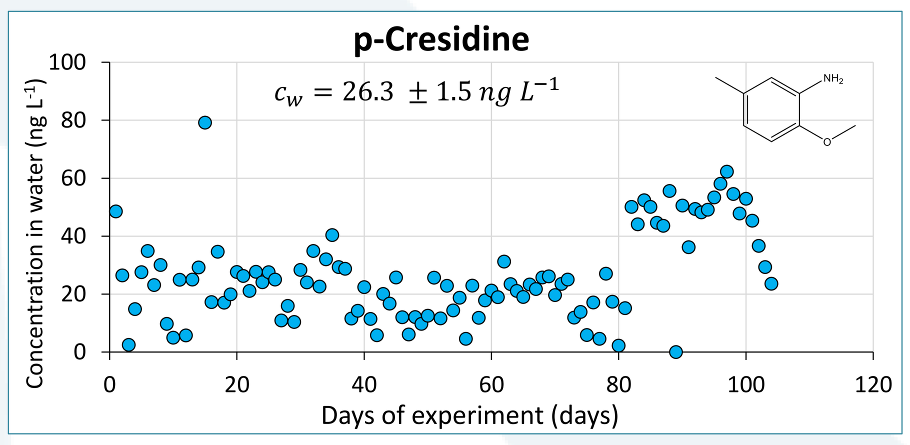

Passive sampler – Empore Disk SDB-RPS exposed – WWTP Modřice – 2 weeks

**Results from the field testing:**
The field samples (24 hours composite water samples) collected in a field study done in effluent of WWTP Modřice, 2020) were processed by new SPE method with SDB-RPS disks.

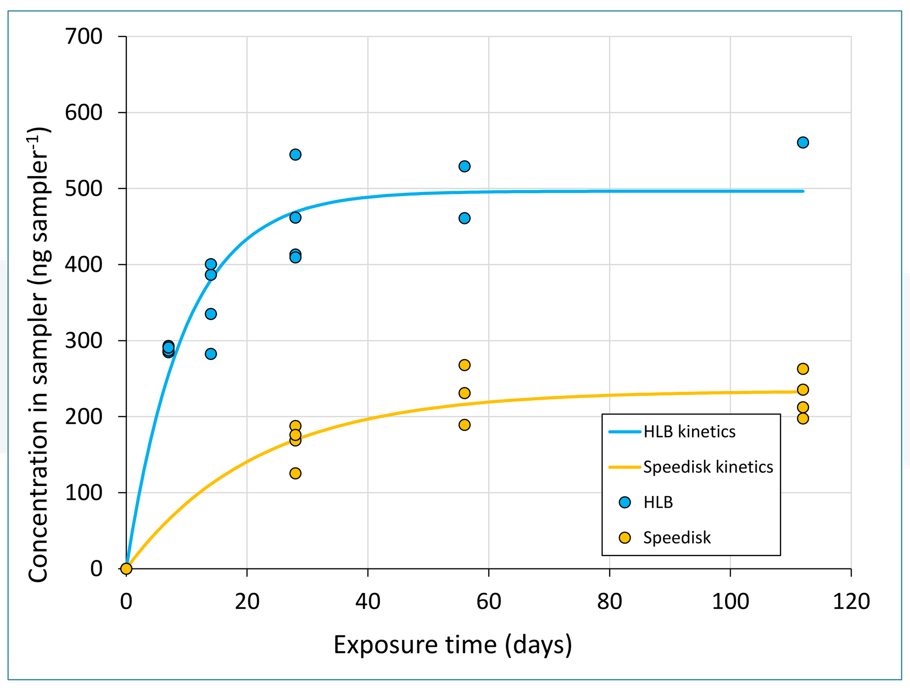
Examples of time course of selected AA in municipal WW in 24 h composite water samples using SPE

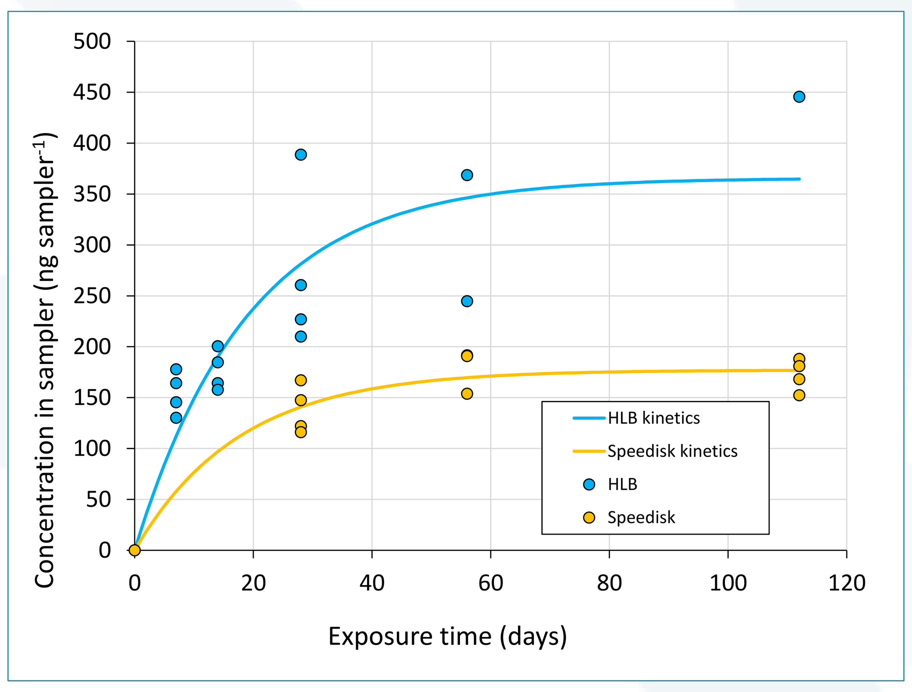


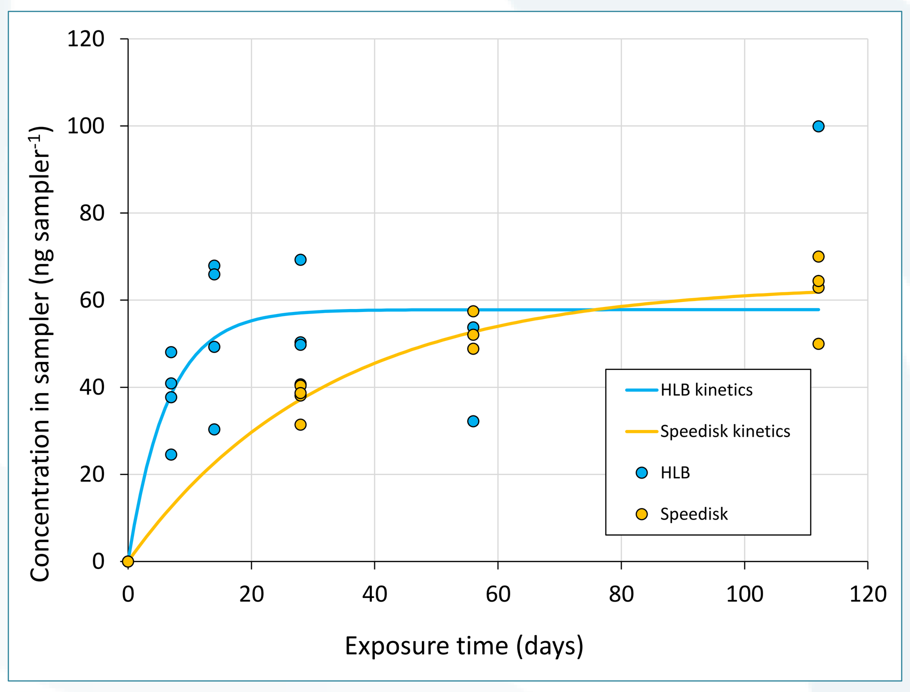




Examples of parallel passive sampler exposure: naked HLB disks and Speedisks – demonstrates sorptive properties




o-Dianisidine:

| | HLB | Speedisk |
|---|---|---|
| log $K_{sw}$ | 3.97 ± 0.02 | 3.33 ± 0.06 |
| Sampler capacity (L) | 2.73 ± 0.15 | 0.63 ± 0.08 |
| Sampling rate (L $d^{-1}$) | 0.28 | 0.06 |

2,4-Diaminotoluene:

| | HLB | Speedisk |
|---|---|---|
| log $K_{sw}$ | 3.90 ± 0.05 | 3.28 ± 0.05 |
| Sampler capacity (L) | 2.35 ± 0.27 | 0.56 ± 0.06 |
| Sampling rate (L $d^{-1}$) | 0.12 | 0.06 |

p-Cresidine:

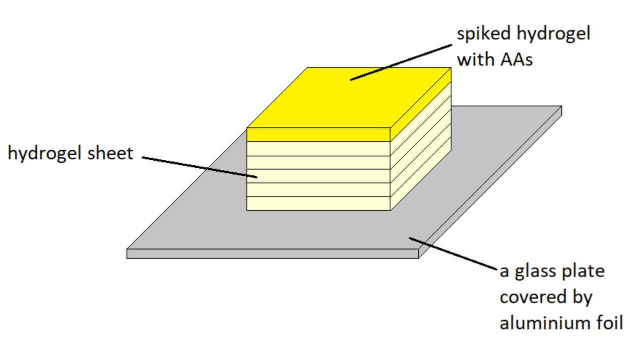
| | HLB | Speedisk |
|---|---|---|
| log $K_{sw}$ | 3.87 ± 0.10 | 3.61 ± 0.10 |
| Sampler capacity (L) | 2.20 ± 0.50 | 1.19 ± 0.27 |
| Sampling rate (L $d^{-1}$) | 0.34 | 0.08 |

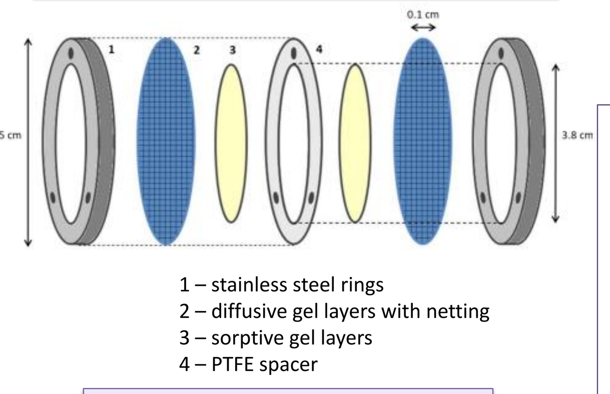
Field study in WWTP Modřice, autumn 2020:
20 AAs analysed, 12 detected:

| Detected compounds | HLB | Speedisk | Water |
|---|---|---|---|
| **2,4-Diaminotoluene** | + | + | + |
| 2-Amino-4-nitrotoluene | + | + | - |
| 3-Chloro-o-toluidine | - | + | + |
| 4,4'-Methylenebis(2-chloroaniline) | - | - | + |
| 4,4'-Methylenedianiline | + | - | - |
| 4,4-Thiodianiline | - | - | + |
| 4-Aminobiphenyl | - | - | + |
| 4-Chloraniline | + | + | - |
| o-Anisidine | - | + | + |
| **o-Dianisidine** | + | + | + |
| o-Toluidine | - | - | + |
| **p-Cresidine** | + | + | + |

## Diffusion coefficients in hydrogel

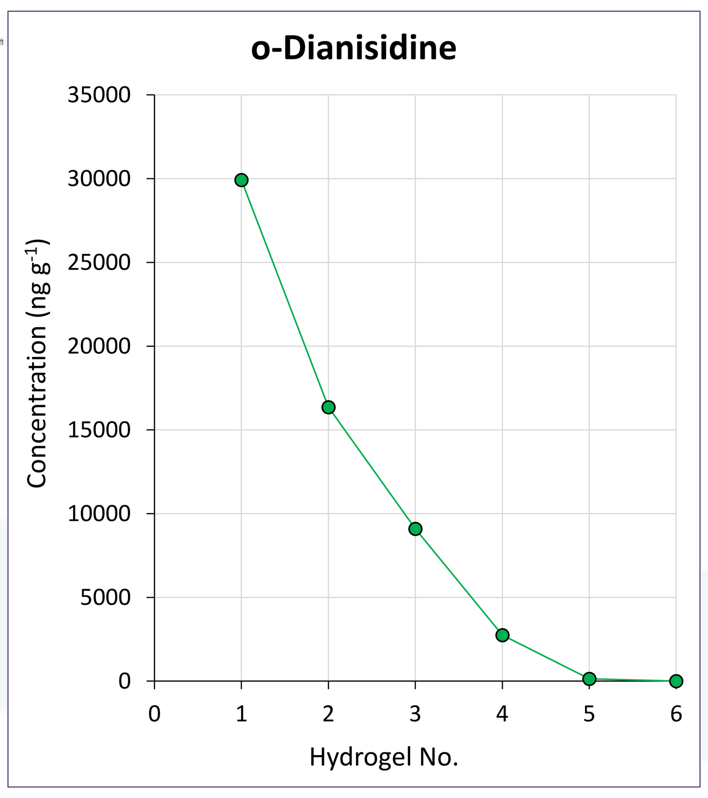
Application of diffusive hydrogel can improve stability of sampling rate, making it less susceptible to variation of hydrodynamics.



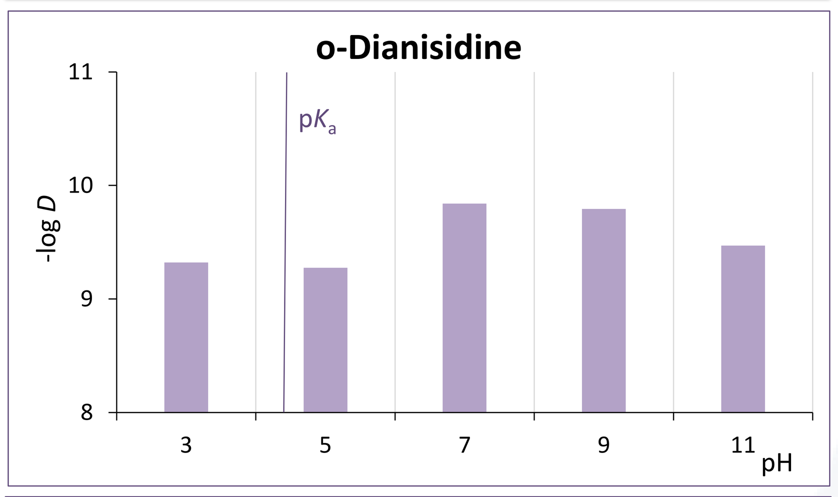



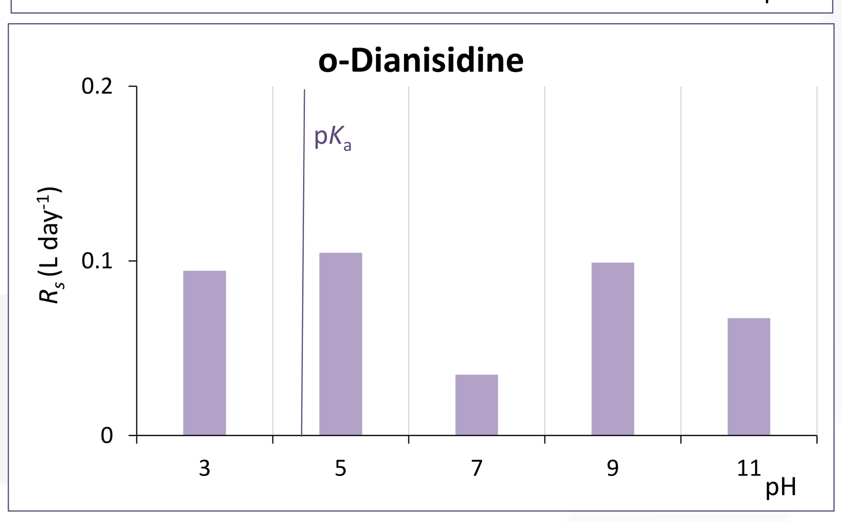

Hydrogel based passive sampler design by Urík & Vrana, 2019[2].

Diffusion of AAs in agarose hydrogels – optimization for AAs of gel stacking method described by Urík et al., 2020[1] and calculation of diffusion coefficients.




Diffusion coefficients of selected AA pH dependent – and estimation of sampling rate from diffusion coefficients




## Conclusions

Passive samplers without membrane accumulated investigated AAs integratively from WW up to 7 days of exposure and equilibrated within 53 days.

Maximum uptake capacity of HLB disks for investigated AAs was 2.73 ± 0.15 litres water – it can potentially be improved by using sorbents with cation exchange moieties (e.g. WAX (weak anion exchange) or SDB-RPS with sulphonate groups).

Application of a diffusive hydrogel layer potentially reduces the sampling rate of *o*-dianisidine from 0.28 to less than 0.1 L $day^{-1}$. Application of diffusive hydrogel reduces the effect of hydrodynamics on compound uptake and potentially extends the integrative uptake period of a passive sampler.

## References

[1] – Urík J, Paschke A, Vrana B. Diffusion coefficients of polar organic compounds in agarose hydrogel and water and their use for estimating uptake in passive samplers. Chemosphere. 2020 Jun;249:126183. doi: 10.1016/j.chemosphere.2020.126183. Epub 2020 Feb 13. PMID: 32088466.

[2] – Urík J, Vrana B. An improved design of a passive sampler for polar organic compounds based on diffusion in agarose hydrogel. Environ Sci Pollut Res Int. 2019 May;26(15):15273-15284. doi: 10.1007/s11356-019-04843-6. Epub 2019 Mar 30. PMID: 30929173.

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