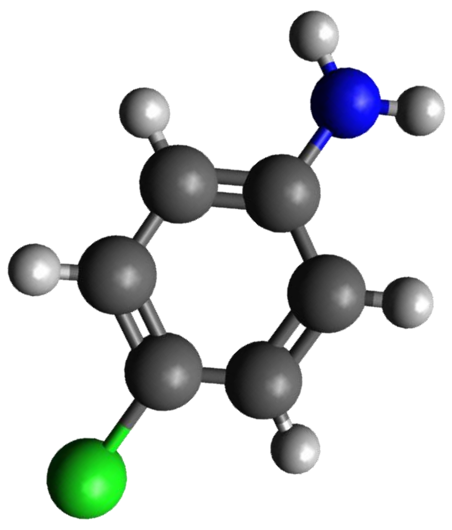

# Accumulation in textiles and release by laundry as an emission pathway for aromatic amines from indoor environments to waste- and surface water

MUNI | RECETOX


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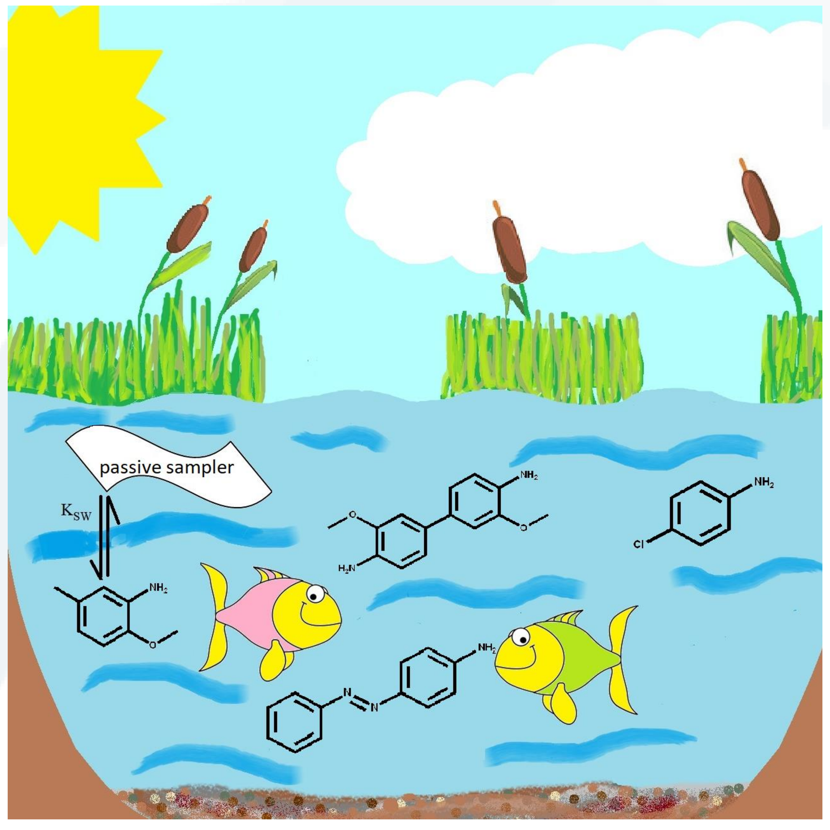
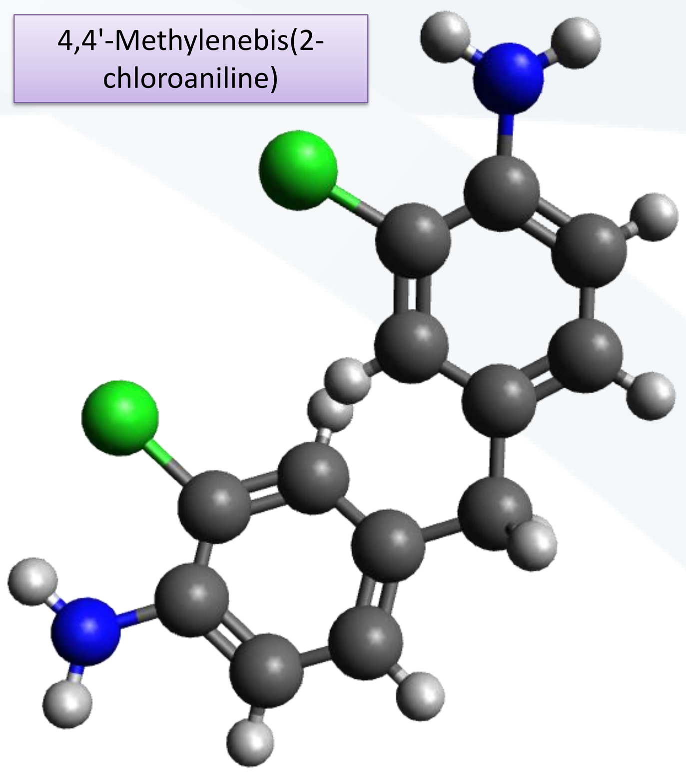
## Introduction

Indoor environments (IE) are contaminated with a wide variety of chemicals emitted by furniture, paints, building materials and fabrics and by human indoor activities, such as cooking, smoking, pest control, house cleaning and personal care. In IE they pose a health risk to humans due to usual high concentrations and the considerable amount of time spent indoors. However, indoor contaminants can also pose a risk to aquatic ecosystems once emitted into the water cycle. Indoor contaminants can undergo various physical and chemical processes, including deposition on and sorption to indoor surfaces like textiles such as carpets, curtains and clothes. When textiles are laundered, sorbed chemicals can be remobilized and enter the sewer system, ending up in wastewater (WW) effluent and finally, the receiving water bodies.

## Aims of this PhD study

The aim of this project is to develop a selective, robust and representative method for monitoring AAs in WW and recipient surface water in order 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 will be developed, calibrated, validated and applied in field studies performed at municipal WW treatment plants and corresponding recipient water bodies.

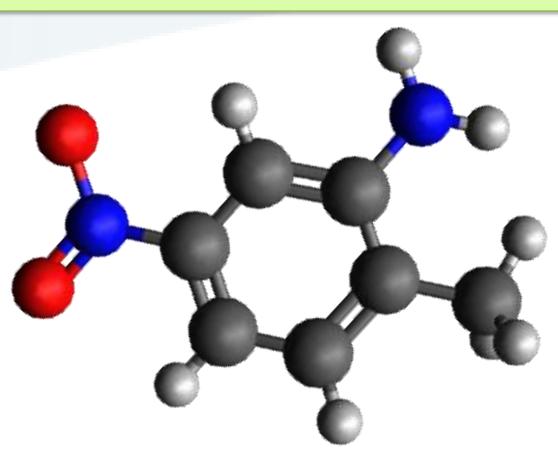


4,4'-Methylenebis(2-chloroaniline)

## HLB disk passive sampler

- The HLB disk sampler consisted of four solid phase extraction Affinisep AttractSPE®Disks HLB with 47 mm diameter
- The surface area exposed to water 22.7 cm²



2-Amino-4-nitrotoluene

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

## Design of the sampler field deployment:

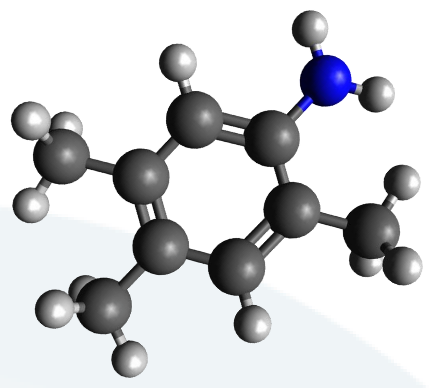
| Sampler set | Exposure time in weeks 1 V1 | 2 V2 | 3 V3 | 4 V4 | 5 V5 | 6 V6 | 7 V7 | 8 V8 | 9 V9 | 10 V10 | 11 V11 | 12 V12 | 13 V13 | 14 V14 | 15 V15 | 16 V16 | V17 | From visit | To visit | from | to |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 2* | | | | | | | | | | | | | | | | | V1 | V2 | 11-Nov-20 | 18-Nov-20 |
| 2 | | 2 | | | | | | | | | | | | | | | | V2 | V3 | 18-Nov-20 | 25-Nov-20 |
| 3 | | | 2 | | | | | | | | | | | | | | | V3 | V4 | 25-Nov-20 | 2-Dec-20 |
| 4 | | | | 2 | | | | | | | | | | | | | | V4 | V5 | 2-Dec-20 | 9-Dec-20 |
| 5 | | | | | 2 | | | | | | | | | | | | | V5 | V6 | 9-Dec-20 | 16-Dec-20 |
| 6 | | | | | | 2 | | | | | | | | | | | | V6 | V7 | 16-Dec-20 | 23-Dec-20 |
| 7 | | | | | | | 2 | | | | | | | | | | | V7 | V8 | 23-Dec-20 | 30-Dec-20 |
| 8 | | | | | | | | 2 | | | | | | | | | | V8 | V9 | 30-Dec-20 | 6-Jan-21 |
| 9 | | | | | | | | | 2 | | | | | | | | | V9 | V10 | 6-Jan-21 | 13-Jan-21 |
| 10 | | | | | | | | | | 2 | | | | | | | | V10 | V11 | 13-Jan-21 | 20-Jan-21 |
| 11 | | | | | | | | | | | 2 | | | | | | | V11 | V12 | 20-Jan-21 | 27-Jan-21 |
| 12 | | | | | | | | | | | | 2 | | | | | | V12 | V13 | 27-Jan-21 | 3-Feb-21 |
| 13 | | | | | | | | | | | | | 2 | | | | | V13 | V14 | 3-Feb-21 | 10-Feb-21 |
| 14 | | | | | | | | | | | | | | 2 | | | | V14 | V15 | 10-Feb-21 | 17-Feb-21 |
| 15 | | | | | | | | | | | | | | | 2 | | | V15 | V16 | 17-Feb-21 | 24-Feb-21 |
| 16 | | | | | | | | | | | | | | | | 2 | | V16 | V17 | 24-Feb-21 | 3-Mar-21 |
| 17 | 2 | | | | | | | | | | | | | | | | | V1 | V3 | 11-Nov-20 | 25-Nov-20 |
| 18 | | | 2 | | | | | | | | | | | | | | | V3 | V5 | 25-Nov-20 | 9-Dec-20 |
| 19 | | | | | 2 | | | | | | | | | | | | | V5 | V7 | 9-Dec-20 | 23-Dec-20 |
| 20 | | | | | | | 2 | | | | | | | | | | | V7 | V9 | 23-Dec-20 | 6-Jan-21 |
| 21 | | | | | | | | | 2 | | | | | | | | | V9 | V11 | 6-Jan-21 | 20-Jan-21 |
| 22 | | | | | | | | | | | 2 | | | | | | | V11 | V13 | 20-Jan-21 | 3-Feb-21 |
| 23 | | | | | | | | | | | | | 2 | | | | | V13 | V15 | 3-Feb-21 | 17-Feb-21 |
| 24 | | | | | | | | | | | | | | | 2 | | | V15 | V17 | 17-Feb-21 | 3-Mar-21 |
| 25 | 4 | | | | | | | | | | | | | | | | | V1 | V5 | 11-Nov-20 | 9-Dec-20 |
| 26 | | | | | 4 | | | | | | | | | | | | | V5 | V9 | 9-Dec-20 | 6-Jan-21 |
| 27 | | | | | | | | | 4 | | | | | | | | | V9 | V13 | 6-Jan-21 | 3-Feb-21 |
| 28 | | | | | | | | | | | | | 4 | | | | | V13 | V17 | 3-Feb-21 | 3-Mar-21 |
| 29 | 4 | | | | | | | | | | | | | | | | | V1 | V9 | 11-Nov-20 | 6-Jan-21 |
| 30 | | | | | | | | | 4 | | | | | | | | | V9 | V17 | 6-Jan-21 | 3-Mar-21 |
| 31 | 20 | | | | | | | | | | | | | | | | | V1 | V17 | 11-Nov-20 | 3-Mar-21 |

*number of deployed passive sampler replicates

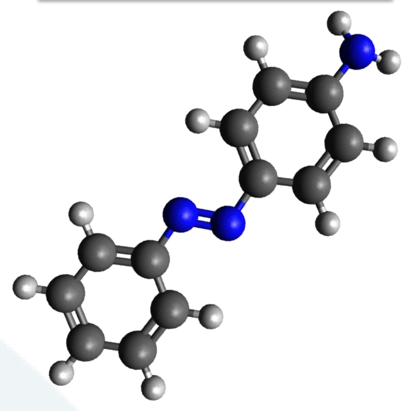
## Aromatic amines

Aromatic amines (AAs) are important industrial compounds widely used as materials and intermediates in the production of a wide range of products, e.g., 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 the entire aquatic ecosystem.

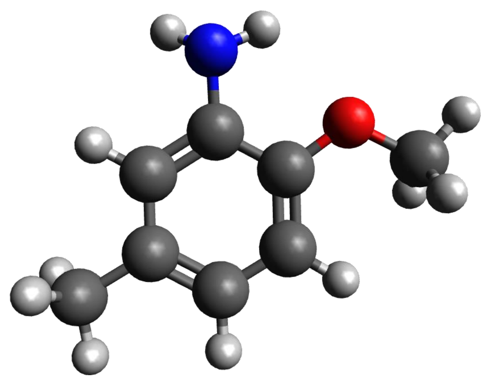
Due to their high solubility in water, they can easily permeate through the soil and contaminate the groundwater. They are highly toxic and have potential carcinogenic and mutagenic effects. The U.S. EPA has included them to the pollutants list subject to environmental control.



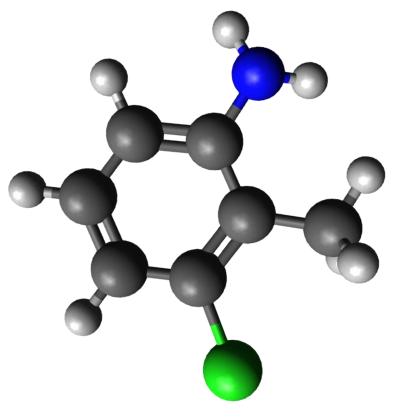
2,4,5-Trimethylaniline



p-Aminoazobenzene



p-Cresidine



3-Chloro-o-toluidine

## Analytical methods development

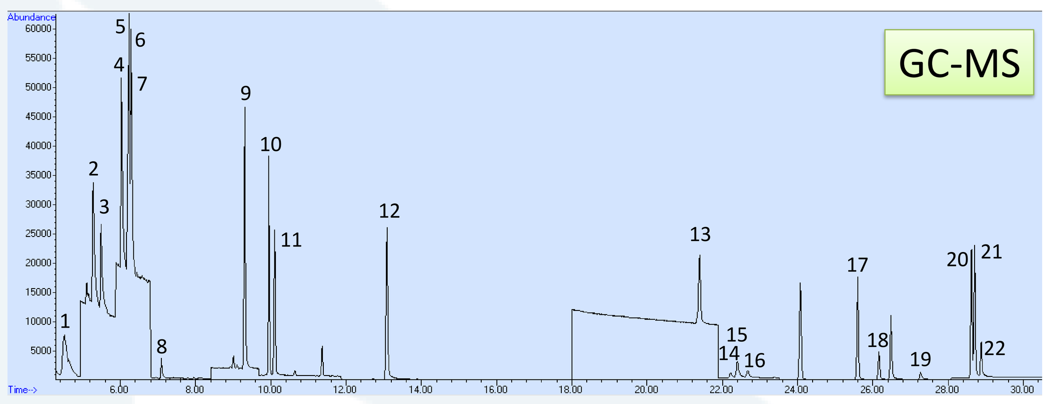
GC-MS method:

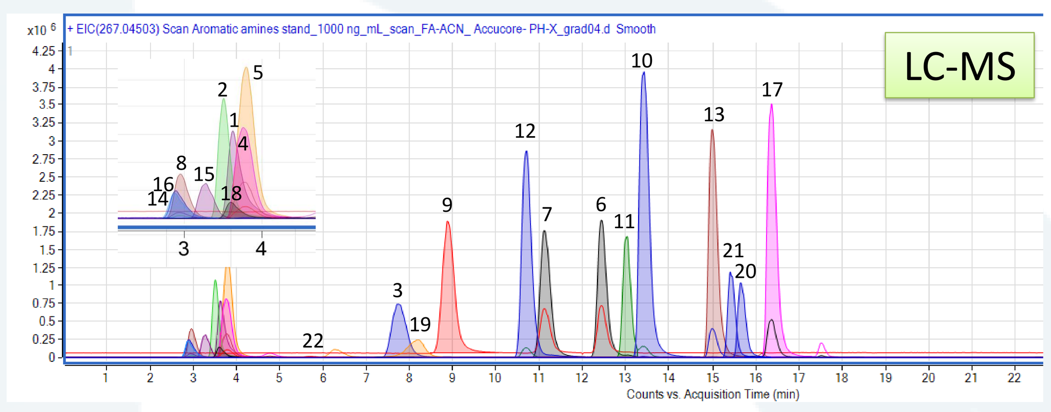
- Inlet: Gerstel Thermal desorpion unit (TDU) + cold injection system (CIS4), solvent venting mode
- Gas chromatograph: Agilent 6890N
- GC column: HP-5MS 5% Phenyl Methyl Siloxane
- Mass spectrometric detector: Agilent 5973
- EI ionisation, single ion monitoring mode

LC-MS method:

- Liquid chromatograph: Agilent 1260
- LC column: Thermo Accucore Phenyl-X, gradient elution
- Mass spectrometer: Agilent LC Q-TOF 6550
- Ionisation mode: Electrospray (ESI+)
- Detection: Time of flight mass spectrometer

| No. | Compound | Retention time GC | Retention time LC |
|---|---|---|---|
| 1 | o-Toluidine | 4,50 | 3,63 |
| 2 | o-Anisidine | 5,28 | 3,51 |
| 3 | 4-Chloraniline | 5,48 | 7,75 |
| 4 | p-Cresidine | 6,03 | 3,76 |
| 5 | 2,4,5-Trimethylaniline | 6,20 | 3,80 |
| 6 | 3-Chloro-o-toluidine | 6,23 | 12,48 |
| 7 | 4-Chloro-o-toluidine | 6,28 | 11,12 |
| 8 | 2,4′-Diaminotoluene | 7,09 | 2,96 |
| 9 | 2-Naphtylamine | 9,30 | 8,87 |
| 10 | 2-Aminobiphenyl | 9,95 | 13,42 |
| 11 | 2-Amino-4-nitrotoluene | 10,10 | 13,02 |
| 12 | 4-Aminobiphenyl | 13,07 | 10,70 |
| 13 | p-Aminoazobenzene | 21,40 | 15,00 |
| 14 | 4,4′-Oxydianiline | 22,23 | 2,88 |
| 15 | Benzidine | 22,39 | 3,28 |
| 16 | 4,4'-Diaminodiphenylmethane | 22,68 | 2,90 |
| 17 | o-Aminoazotoluene | 25,60 | 16,37 |
| 18 | 4,4′-Methylene-bis(2-methyl aniline) | 26,16 | 3,60 |
| 19 | 4,4′-Thiodianiline | 27,06 | 8,16 |
| 20 | 3,3′-Dichlorbenzidine | 28,62 | 15,65 |
| 21 | 4,4'-Methylenebis(2-chloroaniline) | 28,71 | 15,41 |
| 22 | o-Dianisidine | 28,87 | 5,71 |



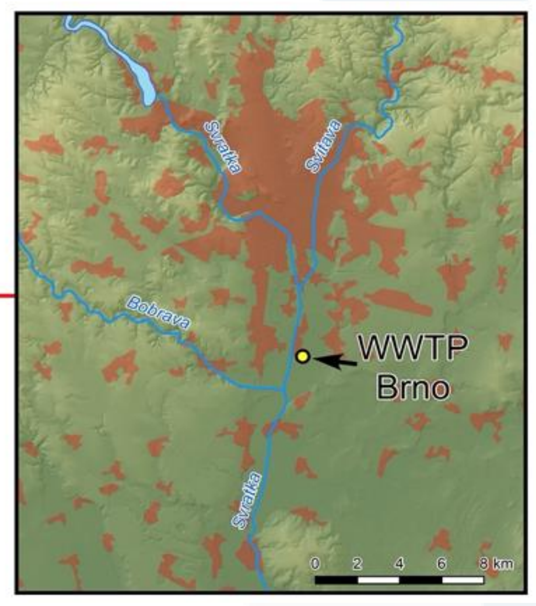

## Field testing of passive samplers

Sampling site:

- Effluent of municipal WWTP Brno – Modřice, Czech Republic (500,000 equivalent inhabitants)

Sampler deployment design:

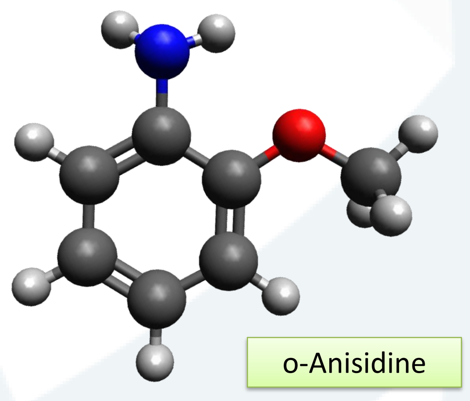
- Different time period of exposure (1-16 weeks)
- Comparison of samplers with daily 24 h composite water samples
- Temperature: 14.3±1.5 °C
- pH: 7.5 ±0.1


## Study objectives

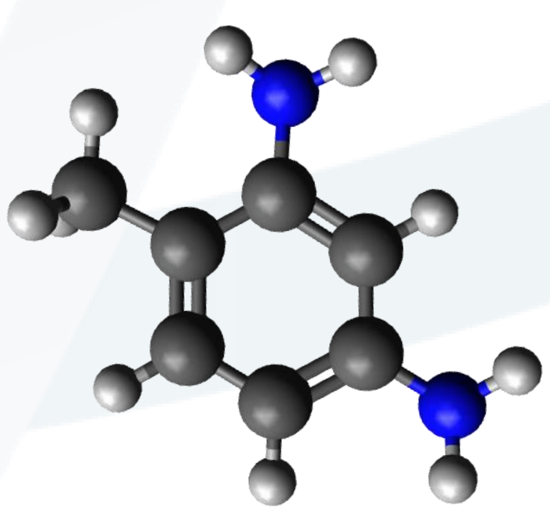
In the field testing we wanted to test suitability of wide-used HLB sorbent for AAs for further use in detection of AAs in water bodies

Then further study characteristics of HLB disk passive sampler – uptake kinetics and equilibration time in water



o-Anisidine

2,4-Diaminotoluene



Sampler deployment in WWTP effluent