

Quantification of persistent and mobile organic substances in water using supercritical fluid chromatography coupled to high-resolution mass spectrometry

Stefanie Schulze, Heidrun Paschke, Till Meier, Matthias Muschket, Thorsten Reemtsma, Urs Berger
Helmholtz Centre for Environmental Research GmbH - UFZ, Department of Analytical Chemistry, Leipzig, Germany

Introduction and Aim

Reversed-phase liquid chromatography coupled to MS is the method of choice for analysis of trace levels of polar environmental pollutants in water. However, RPLC is not suited for separation of **persistent and highly mobile substances (PM substances)**, due to low or no retention on the non-polar stationary phase.

To overcome this analytical gap, the **aim of the study** was to develop a **quantitative method** for trace analysis of PM substances based on **supercritical fluid chromatography (SFC)** coupled to **high-resolution mass spectrometry (HRMS)**. The method should be simple and quick to be suited for larger monitoring programs.

Summary and Outlook

Summary

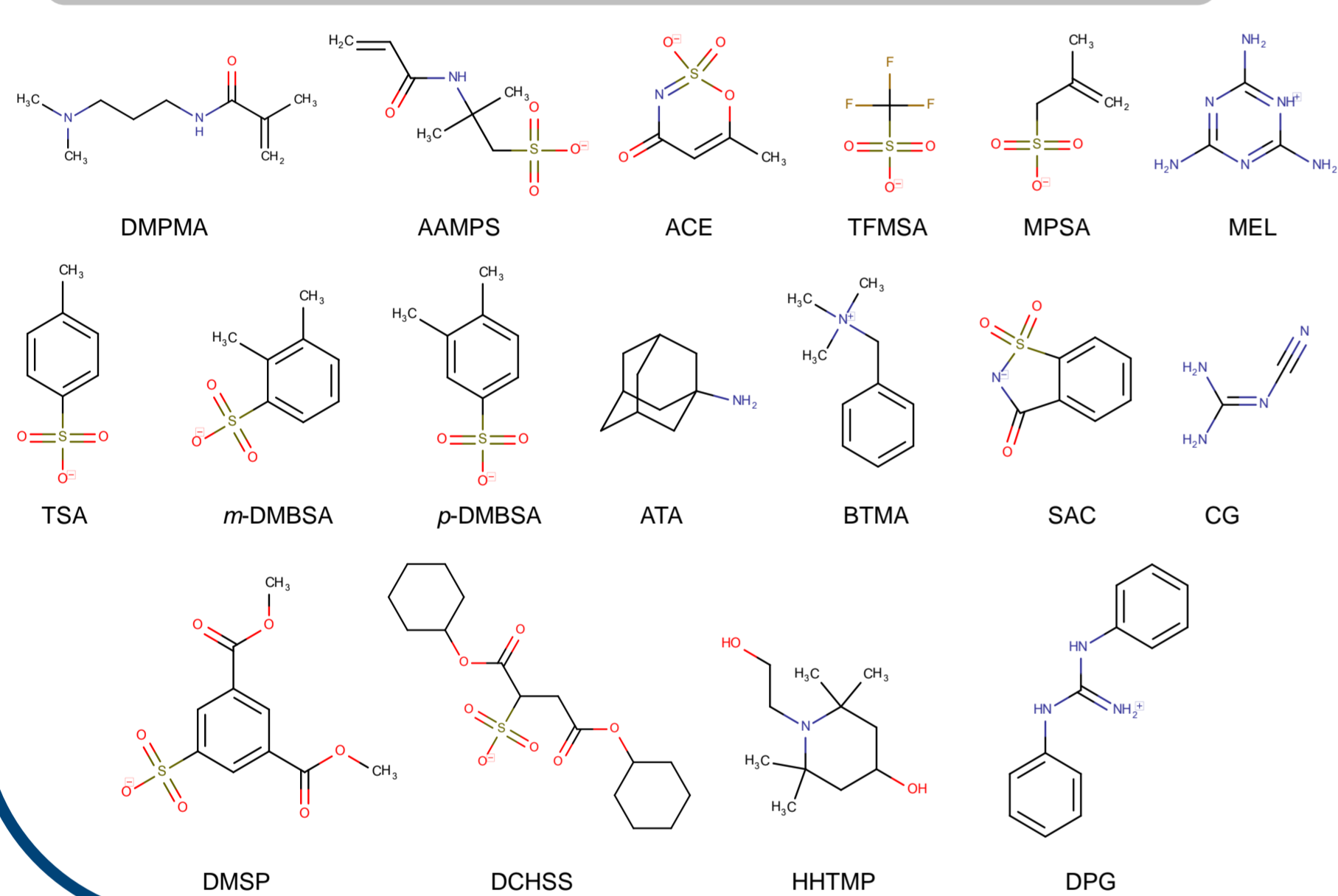
- ▶ SFC is well suited for retention and separation of PM substances.
- ▶ Matrix effects could be compensated in quantification by one matrix-matched and extracted calibration for all samples.

Outlook

- ▶ The method is currently used to screen for a larger range of PM substances in the water cycle.
- ▶ It will also be used to quantify selected PM substances in the water cycle and to quantify the treatment efficiency of waste water and drinking water treatment for PM substances.

Experimental

17 Test Substances



Samples and Sample Preparation

- ▶ Surface water from different German rivers, groundwater and water from drinking water production incl. tap water
- ▶ Filtration of the sample
- ▶ Analyte enrichment (factor 40) by azeotrope evaporation with acetonitrile

Instrumental Method

- SFC** (Waters Acquity UPC²) with BEH or Torus Diol column
- ▶ Gradient: CO₂ and as co-solvent up to 40% MeOH/H₂O 95/5 with 0.2% NH₄OH
- ▶ Make-up flow: MeOH/H₂O 90/10 with 0.1% HCOOH
- HRMS** (Waters Synapt Q-TOF)
- ▶ Positive and negative ESI in full scan mode
- ▶ Two *m/z*-ratios selected per analyte

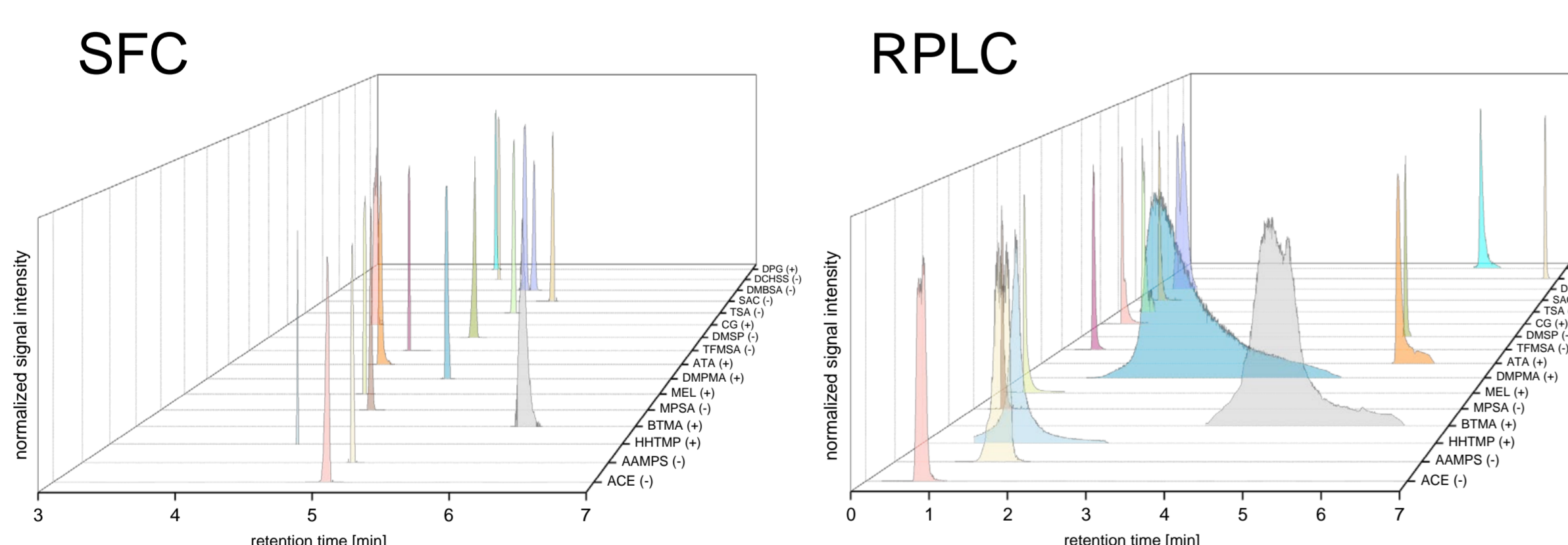
Quantification

- ▶ 5-point calibration curve in pure solvents
- ▶ Application of a compound-specific correction factor for apparent recovery (i. e. for the combination of recovery loss and matrix effect)
- ▶ The correction factor proved to be virtually independent of concentration and water matrix type

Results

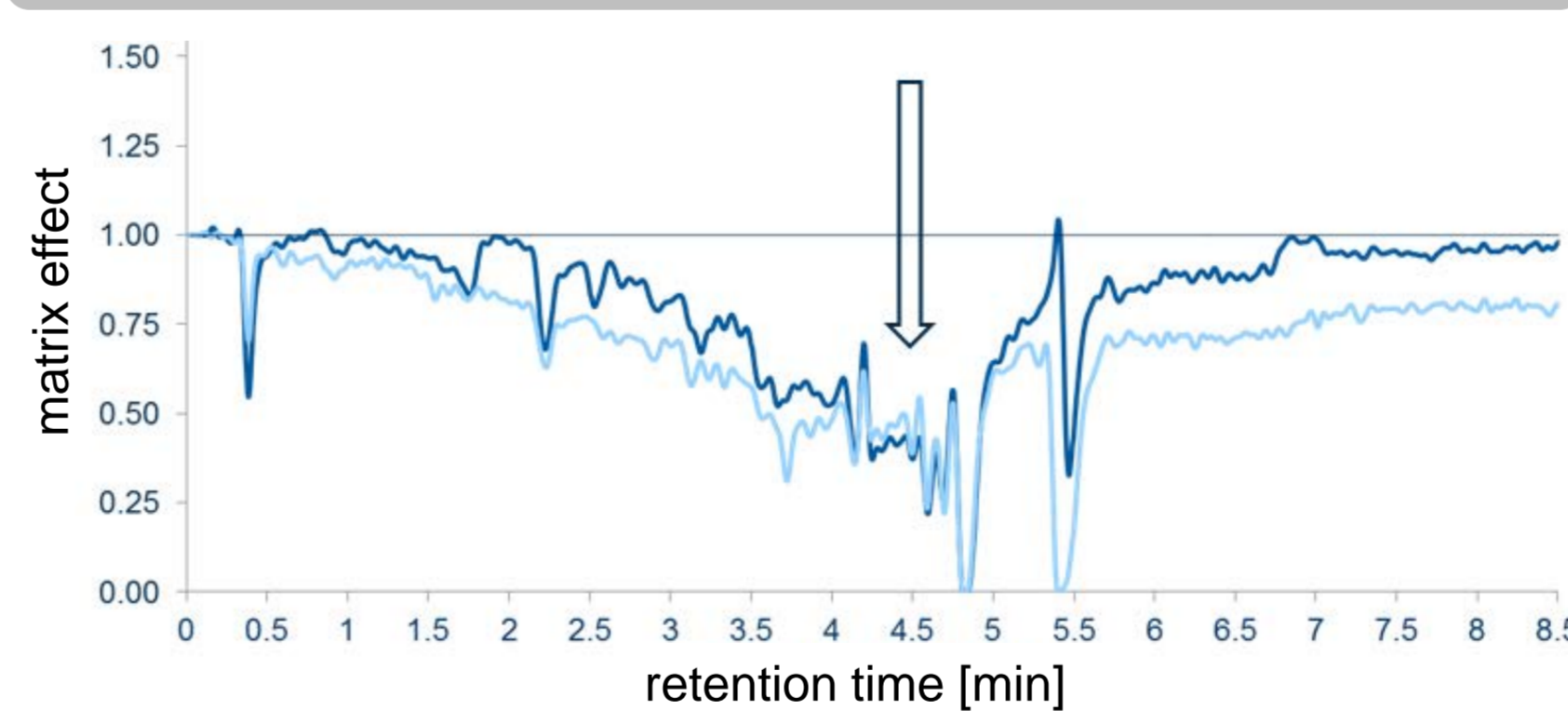
Method Validation

Chromatography



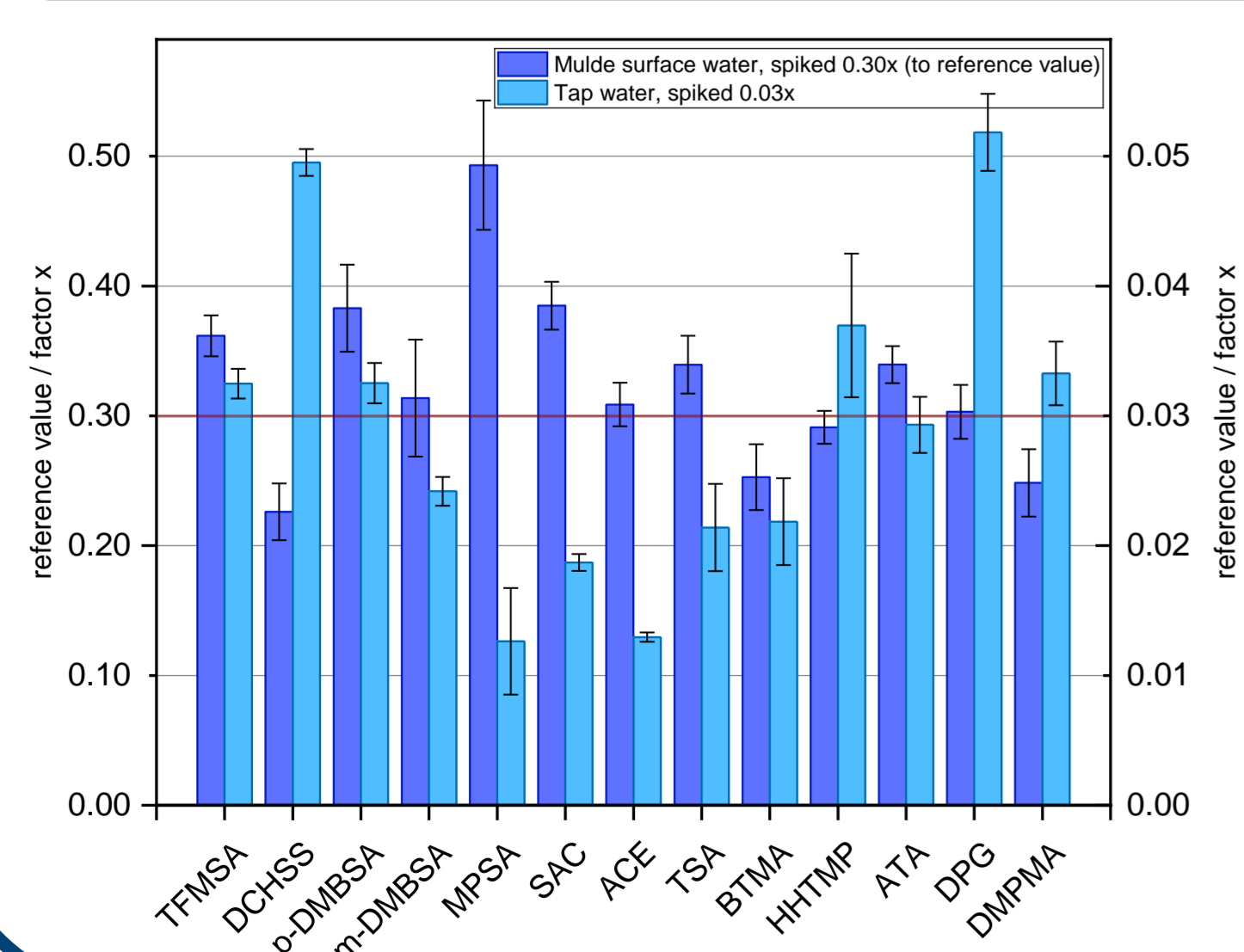
Chromatographic separation by SFC compared to RPLC. Note the different scale of the x-axis.

Matrix Effects



Post-column infusion of DPG (*t_R* 4.5 min, arrow) after injection of a surface water (dark blue) or a groundwater (light blue) extract.

Precision and Trueness



Precision (error bars represent standard deviations, *n*=4) and trueness (closeness to spiked concentration, red line) of quantification of PM substances based on the apparent recoveries determined in another surface water sample at a concentration factor 1x.

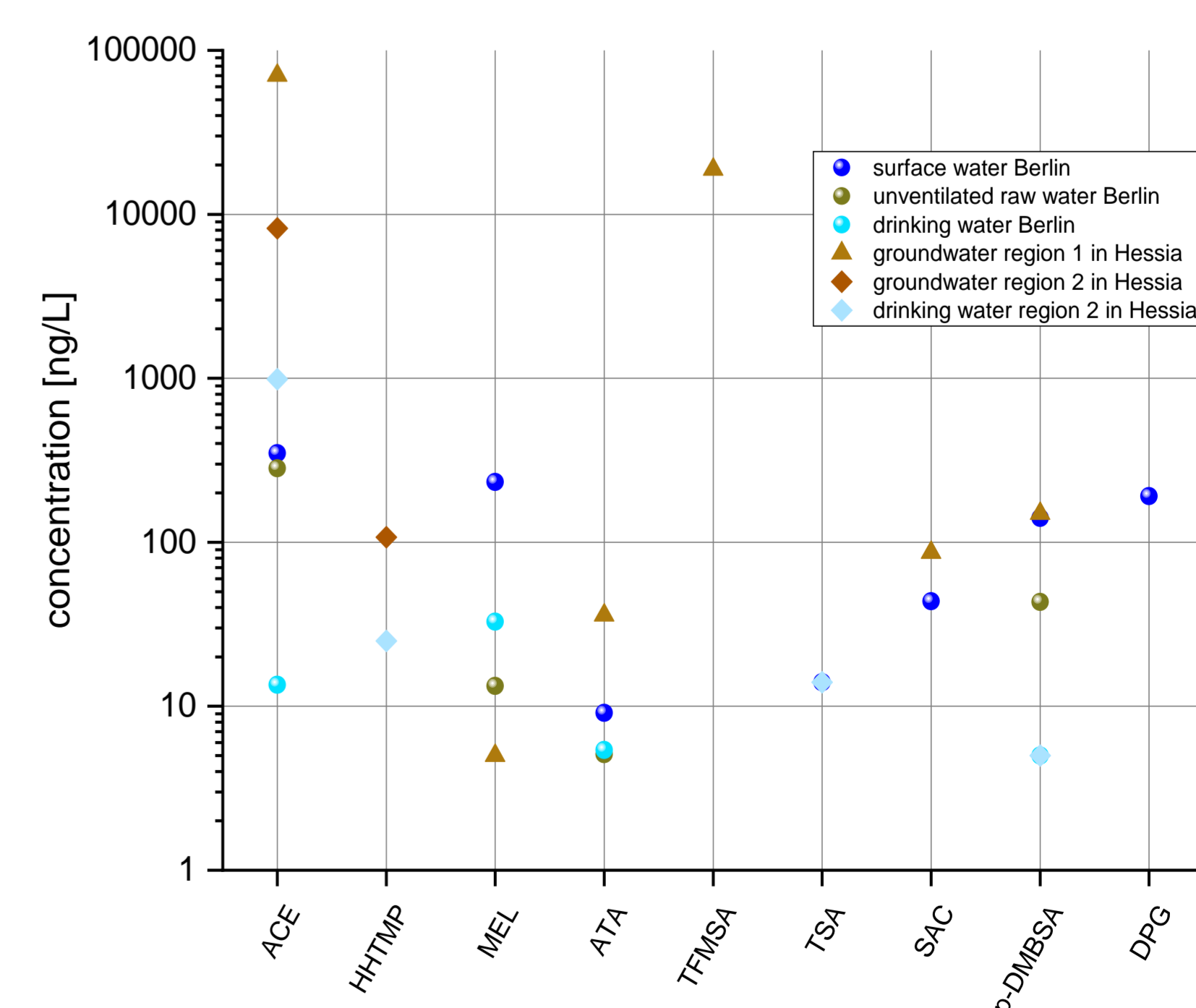
Method Detection Limits

Analyte	MDL [ng L ⁻¹]	Analyte	MDL [ng L ⁻¹]
ACE (-)	14	DMSP (-)	10
AAMPS (-)	10	CG (+)	30
HHTMP (+)	5	TSA (-)	14
BTMA (+)	3	SAC (-)	15
MPSA (-)	50	<i>p</i> -DMBSA (-)	5
MEL (+)	4	<i>m</i> -DMBSA (-)	26
DMPMA (+)	3	DCHSS (-)	10
ATA (+)	2	DPG (+)	33
TFMSA (-)	4		

Method detection limits (MDL). (+) or (-) indicate analysis in the ESIpos or ESI_{neg} mode, respectively.

Method Application

The method was successfully applied to six drinking water relevant samples from Berlin and Hestia (Germany) including surface water, groundwater, raw water for drinking water production and drinking water.



Concentration data of PM substances in environmental samples. Note the logarithmic y-axis.