Identification of persistent and mobile contaminants impacting raw and drinking waters

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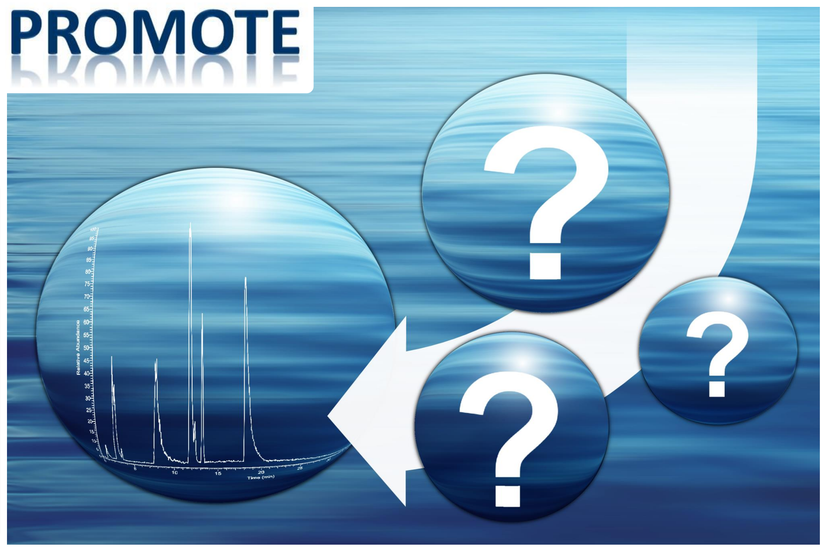
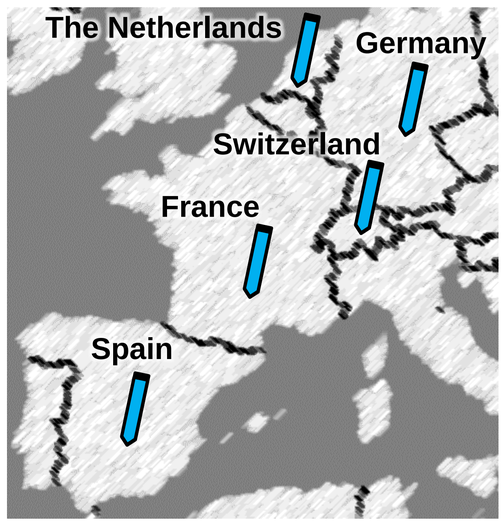
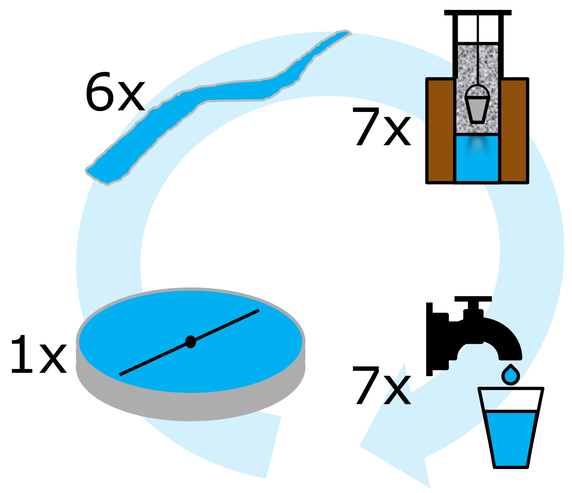


Introduction

Mobile and persistent organic micropollutants may impact raw and drinking waters and are thus of concern for human health. To identify possible substances of concern, 21 **water samples** from five European countries were enriched with **solid-phase extraction (SPE)** and analysed with a hydrophilic interaction liquid chromatography - high resolution mass spectrometry (HILIC-HRMS) **non-target screening** method. An evaluation of the screening results led to the (tentative) **identification** of seven detected features as halogenated methanesulfonic acids (H-MSA)[1]. **Semi-quantification** of these novel water contaminants gave first information about their occurrence in the environment.





- 21 grab samples were taken from five European countries during 2015 and 2016
- Two sampling points were sampled twice, once in September 2015 (a) and once in February 2016 (b)
- A sampling blank (mineral water) was treated analogously to the February 2016 samples

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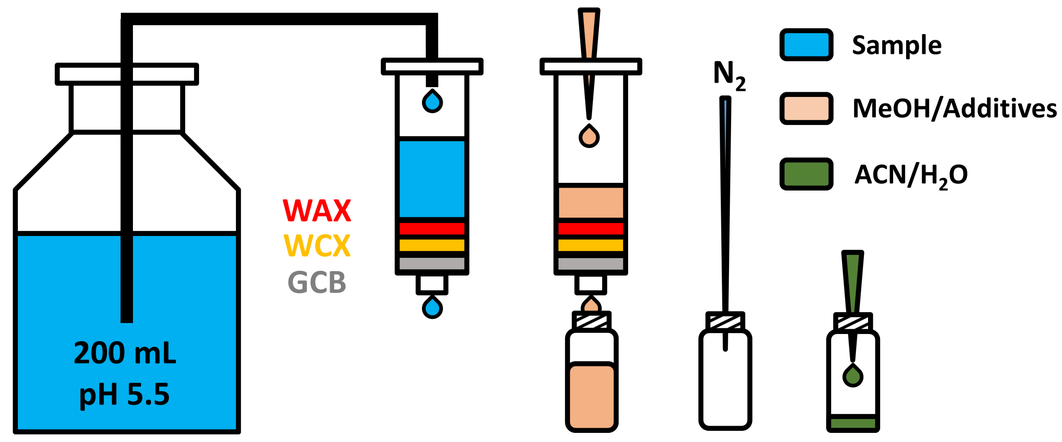

- The pH of water samples was adjusted to 5.5 with formic acid or ammonia
- SPE cartridges filled with graphitized carbon black (GCB), weak cation exchanger (WCX) and weak anion exchanger (WAX) were prepared
- Analytes were eluted with methanol (MeOH) containing different additives in the following order: 5% ammonium hydroxide (2x1 mL), 2% formic acid (2x1 mL) and 20% dichloromethane (1x1 mL)
- After evaporation samples were reconstituted in ACN/H_2O 95:5 (V:V)

Conclusion

- The broad detection of F_3-MSA indicates persistence and mobility in the water cycle, which is in compliance with the well-studied behavior of longer chain perfluoroalkane sulfonic acids
- The non-uniform distribution of chlorinated and brominated MSA congeners in different samples as well as their frequent detection in drinking water points towards drinking water disinfection as a possible source of chlorinated and brominated MSAs
- Transformation experiments and monitoring campaigns will be required to elucidate the origin, fate and distribution of HMSAs in the water cycle

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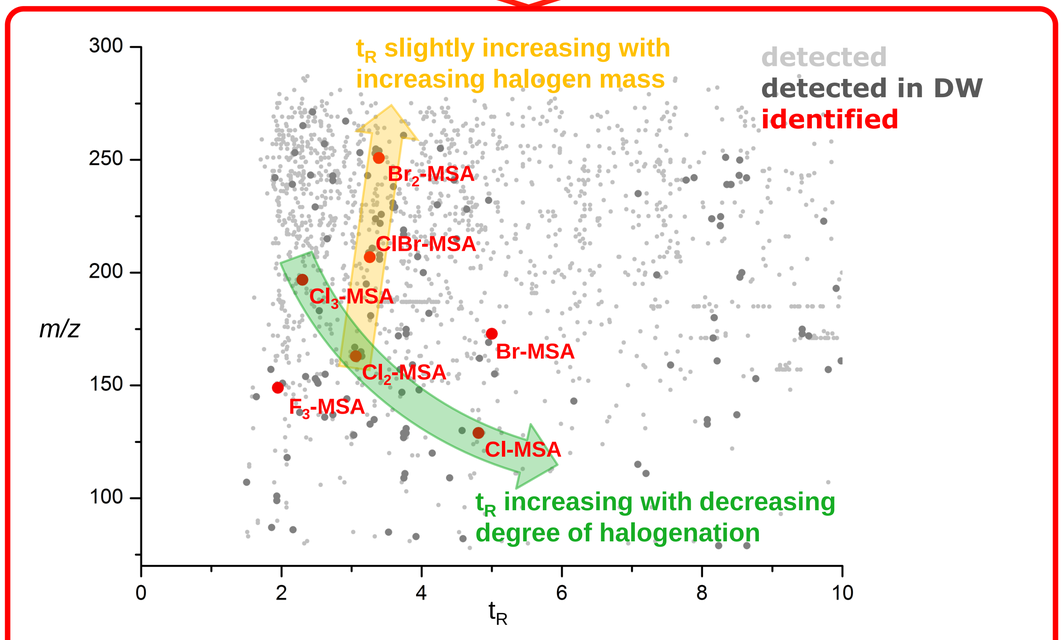

- LC-HRMS was performed with an Orbitrap Velos pro and a Nucleodur HILIC column (150*2 mm; 5 µm)
- More than 2000 features were detected with negative ionization
- 194 of the detected features were detected in drinking water
- Seven of the detected features were (tentatively) identified

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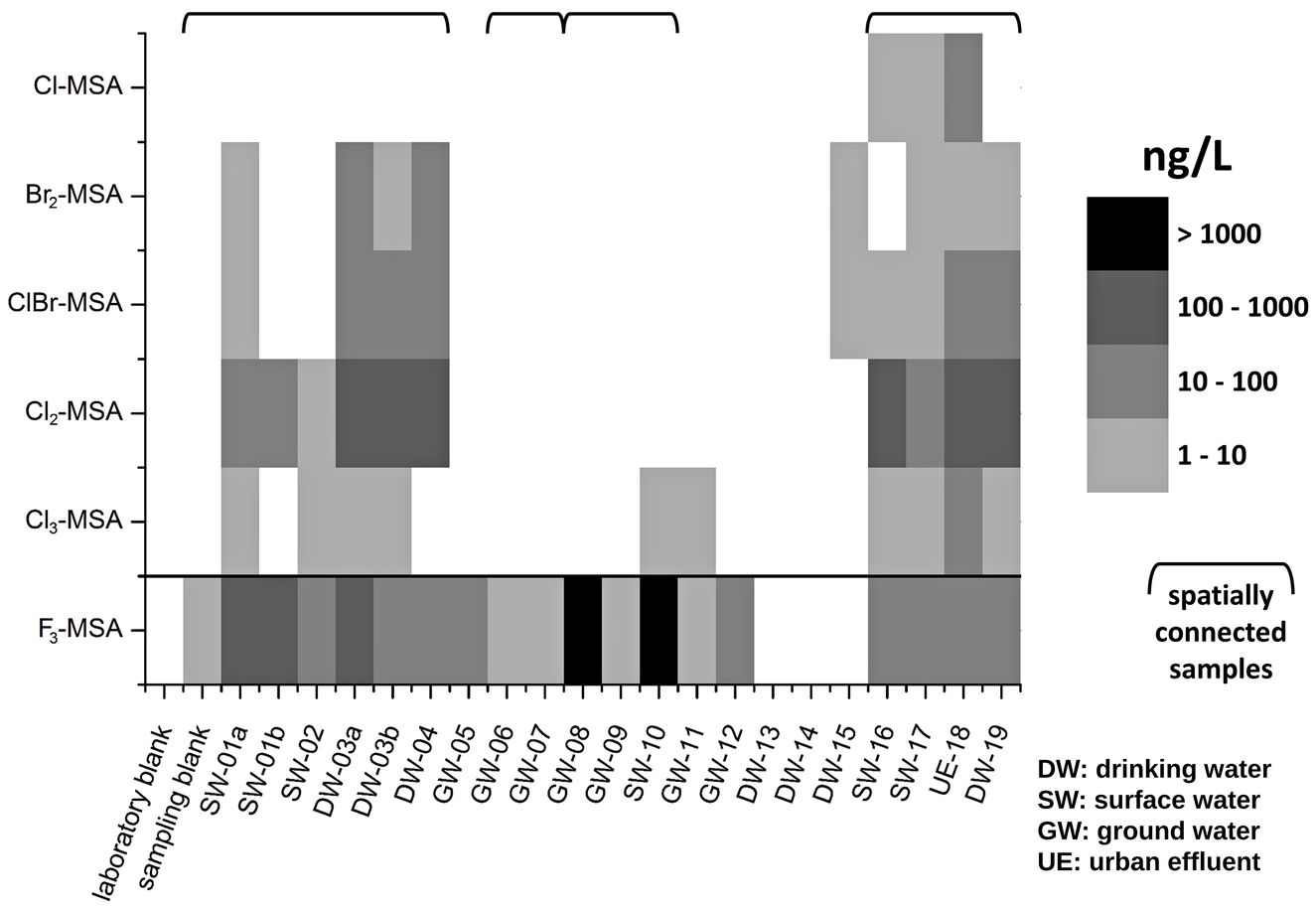

- F_3-MSA is present in all compartments of the water cycle and was detected in concentrations up to the µg/L range
- Chlorinated and brominated methanesulfonic acids seem to co-occur and were frequently detected in drinking waters
- Samples from identical sampling points (taken in September 2015 (a) and February 2016 (b)) showed similar levels of contamination, indicating that the investigated substances are consistently present in the water cycle and did not originate from random events (e.g. spillage)

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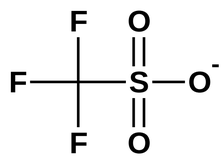
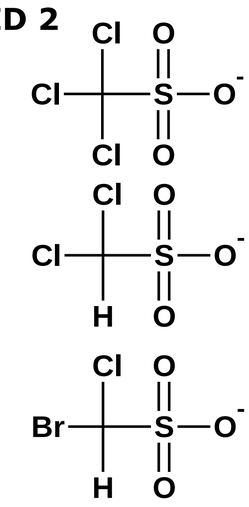
ID 1



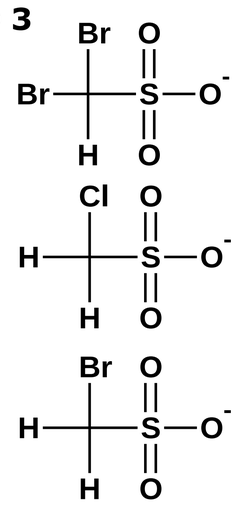
HRMS, MS/HRMS, comparison with reference material

ID 2



HRMS, MS/HRMS, detected after chlorination of MSA

ID 3



HRMS, MS/HRMS

- The structure of one substance was confirmed with a reference standard (F_3-MSA,ID level 1)[2]
- A probable (Cl_3-MSA, Cl_2-MSA and ClBr-MSA, ID level 2) or tentative (Br_2-MSA, Cl-MSA and Br-MSA, ID level 3) structure could be assigned to chlorinated and brominated MSA
- A chlorination experiment was performed with MSA, Br^- and OCl^-

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[1]Zahn, D.; Frömel, T.; Knepper, T. P. submitted
[2]Schymanski, E. L.; Jeon, J.; Gulde, R.; Fenner, K.; Ruff, M.; Singer, H. P.; Hollender, J. *Environmental Science & Technology* **2014**, *48*, 2097-2098.

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