Non-target screening of highly polar organic micropolutants in environmental water samples

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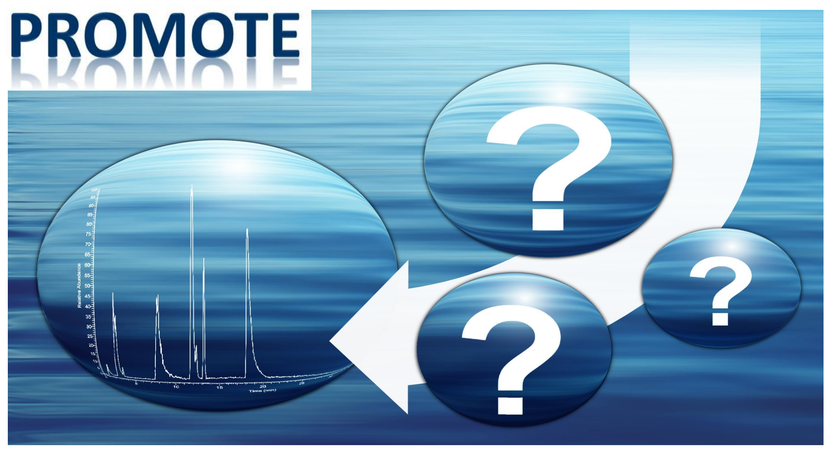
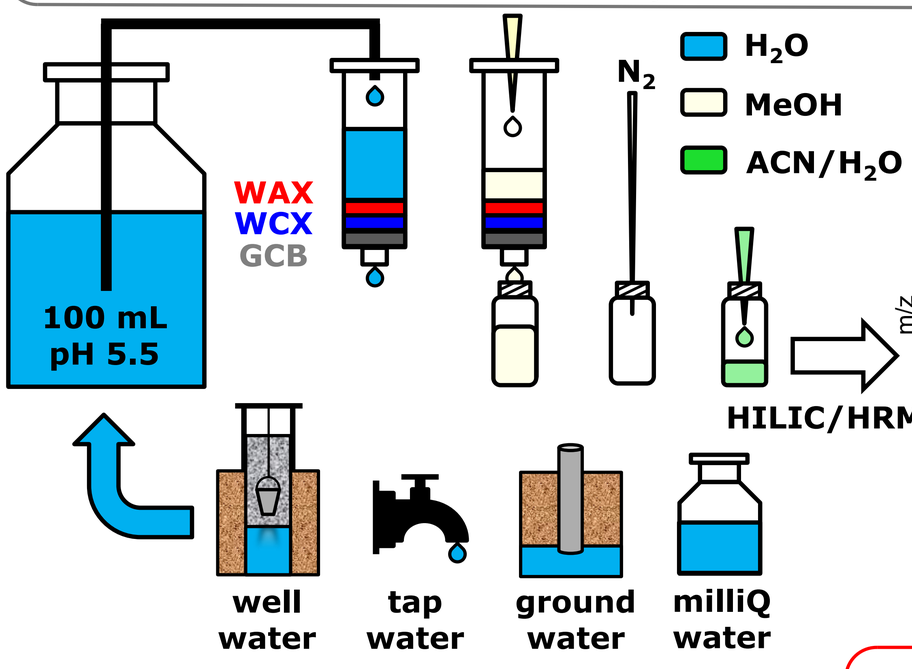
Introduction

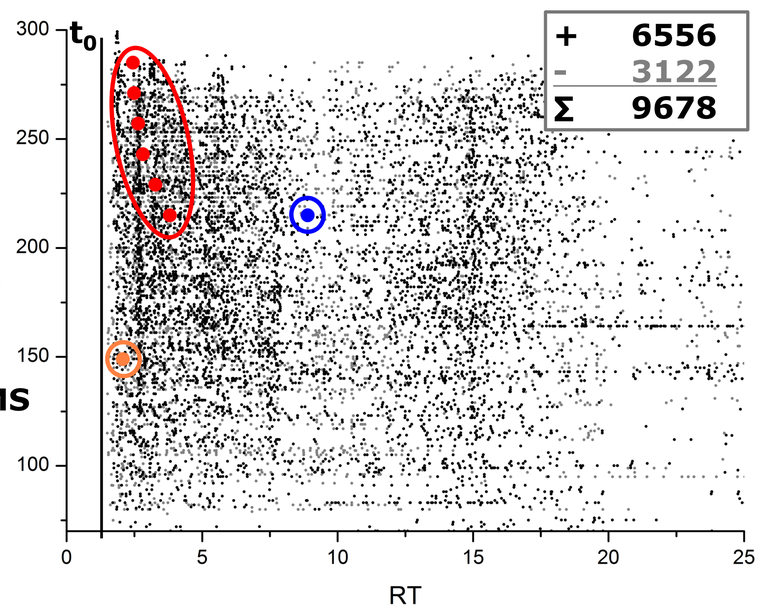
Highly polar organic substances may be able to penetrate natural and artificial barriers and are thus **mobile** in the **water cycle**. If these **mobile organic contaminants (MOC)** are **persistent (PMOC)** against microbiological and chemical degradation, their removal during waste water treatment and drinking water purification[1] may prove difficult. If these substances are present in high concentrations, toxic or undergo toxication[2], problems for the aquatic environment and human health may arise.

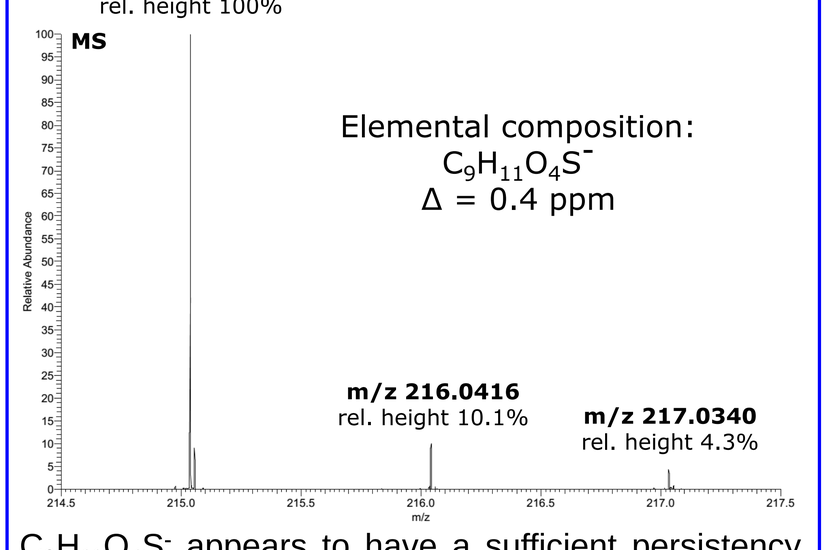
As a consequence of the lack of established analytical methods for MOC, only **limited information** about the occurrence fate and distribution of these substances is available. In the **PROMOTE** project, we strive to close this gap in knowledge.

In this work, a newly developed **SPE**[3] method that allows enrichment of **PMOC** from aqueous samples is presented and deployed in combination with a suitable **HILIC/HRMS** method to perform a non-target screening for potential **PMOC** in environmental water samples, including polluted well and ground water, tap water and milliQ water as blank. Preliminary results of the non-target screening are shown.





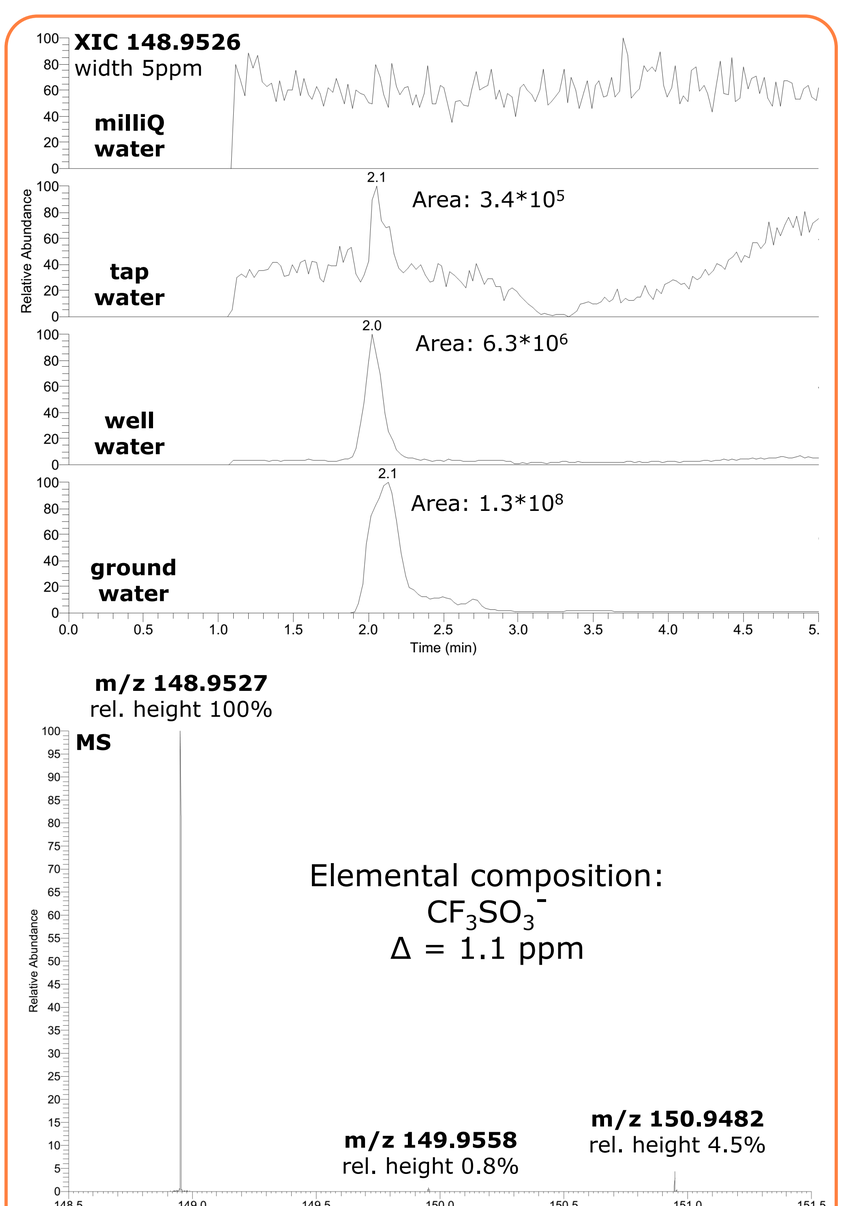




Elemental composition:
$C_9H_{11}O_4S^-$
Δ = 0.4 ppm

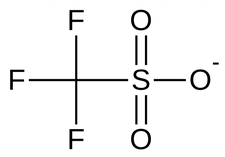
$C_9H_{11}O_4S^-$ appears to have a sufficient persistency and mobility in the water cycle to reach drinking water, and is thus classified as PMOC.

Structure and origin of $C_9H_{11}O_4S$ are still under investigation.

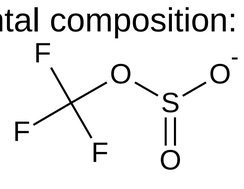


Elemental composition:
$CF_3SO_3^-$
Δ = 1.1 ppm

The unequivocal elemental composition for the ion m/z 148.9526 is $CF_3SO_3^-$. Only two chemically sound structures exist for this elemental composition:

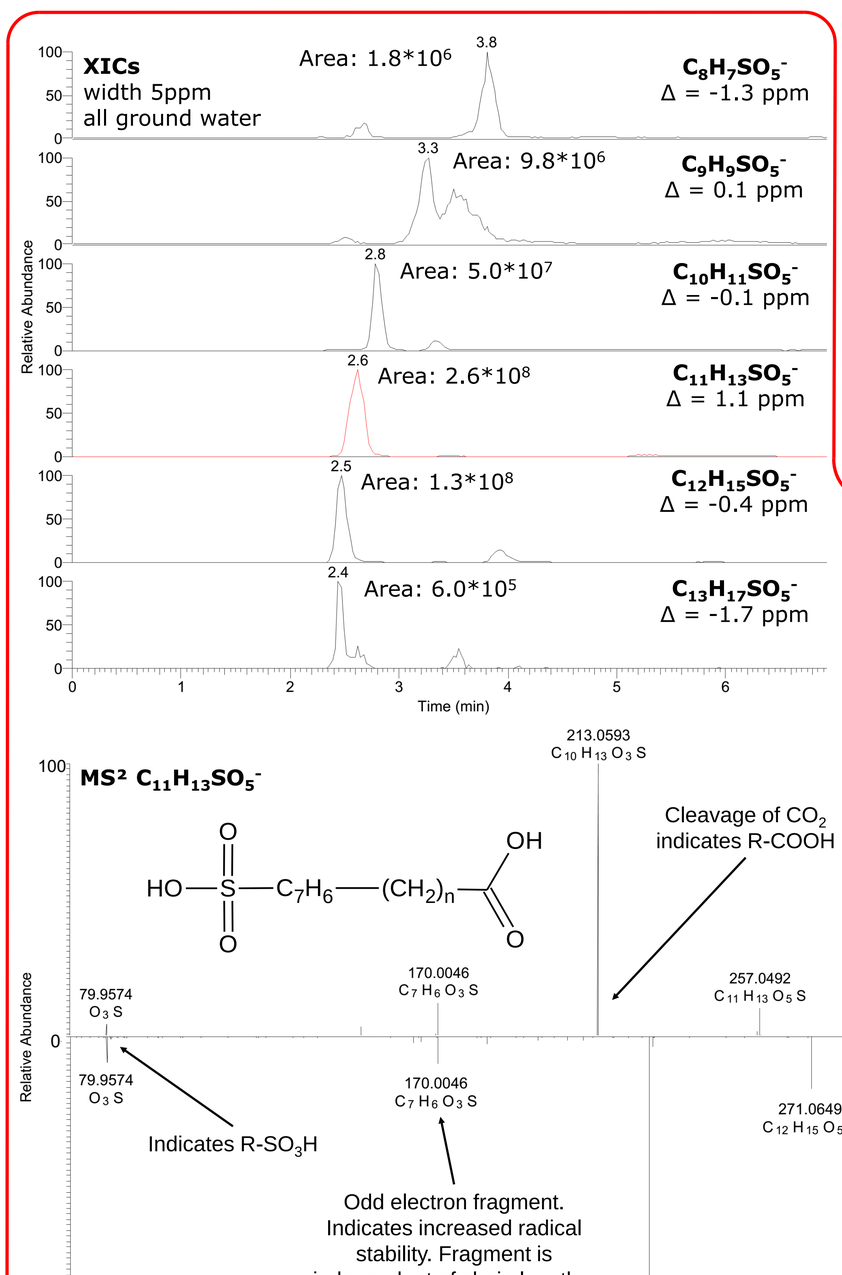


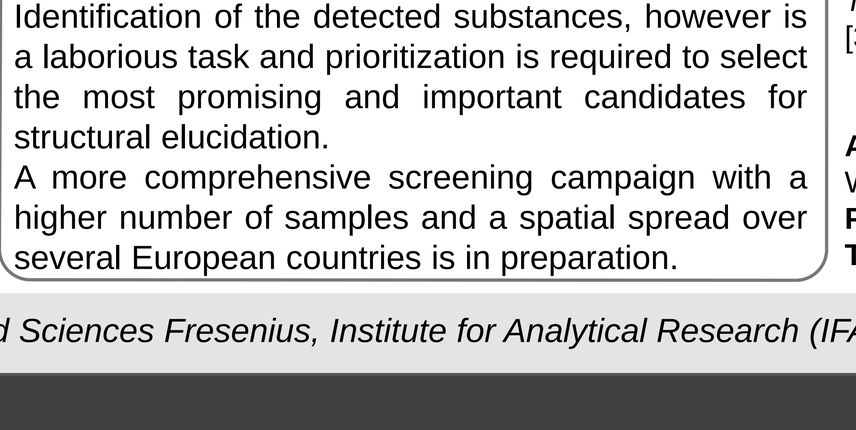
Trifluoromethanesulfonate



Trifluoromethyl sulfite

Of the two proposed structures for m/z 148.9526 Trifluoromethanesulfonate, the anion of triflic acid, is more likely to occur in environmental water samples. Triflic acid has a high production volume (> 100 t/a) and is applied in various processes including vulcanization and polymerization. A confirmation of the proposed structure is still pending.





A supposed series of homologues was observed during the non-target screening. The MS^2 spectra of the most abundant homologues (assuming a similar ESI response) were compared to facilitate structural elucidation. In addition, fractions were collected, evaporated to dryness, reconstituted in D_2O/ACN 1:1 (v:v) and measured with HRMS by direct infusion.

For both homologues a cleavage of CO_2 as well as an $SO_3^{\bullet-}$ fragment were observed, indicating the presence of a carboxylic acid and a sulfonic acid group respectively.

The fragment $C_7H_6O_3S^{\bullet-}$ is identical for both homologues and violates the even electron rule, thus indicating a position of increased radical stability in the molecule. A benzylic position appears to be most likely but other alternatives cannot be ruled out by the available spectrometric information. The mass shift of 1 Da for the deprotonated molecule after H/D exchange is in compliance with the proposed structure. Structural elucidation of these substances is still ongoing.

Conclusion and outlook

The preliminary screening results are a strong indicator that PMOC may impact drinking water.

Identification of the detected substances, however is a laborious task and prioritization is required to select the most promising and important candidates for structural elucidation.

A more comprehensive screening campaign with a higher number of samples and a spatial spread over several European countries is in preparation.

References:
[1] T.P. Knepper et al. *Waste Manage. (Oxford)* **1999**, 19, 77-99.
[2] Schmidt, C. K.; Brauch, H.-J. *Environmental Science & Technology* **2008**, *42*, 6340.
[3] Zahn, D.; Frömel, T.; Knepper, T. P. *work in progress*

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For further information about the project or a copy of the poster please visit www.ufz.de/promote or use this QR code