

Method development for the non-target analysis of highly polar organic substances in aqueous samples with HILIC-ESI-HRMS

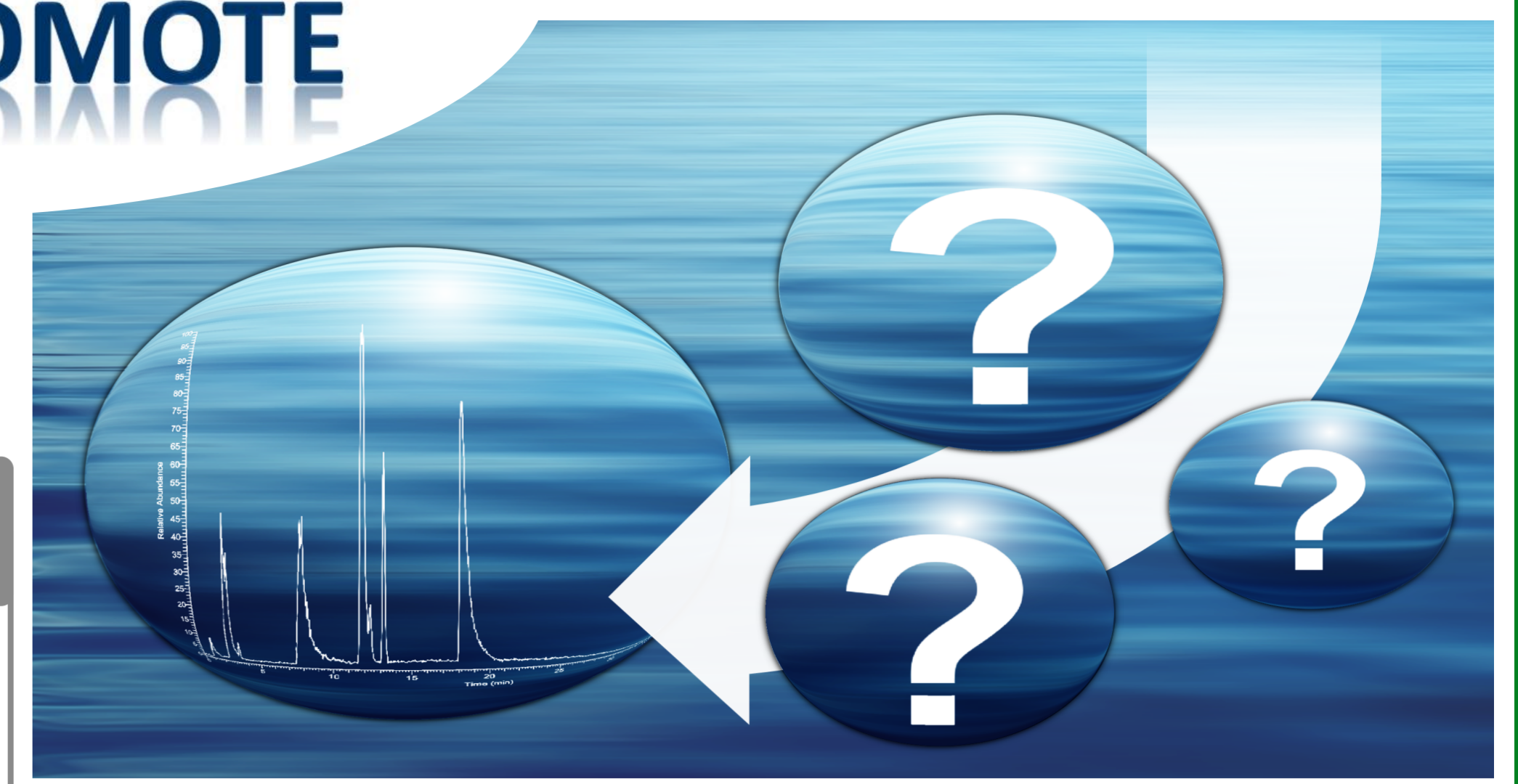
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Introduction

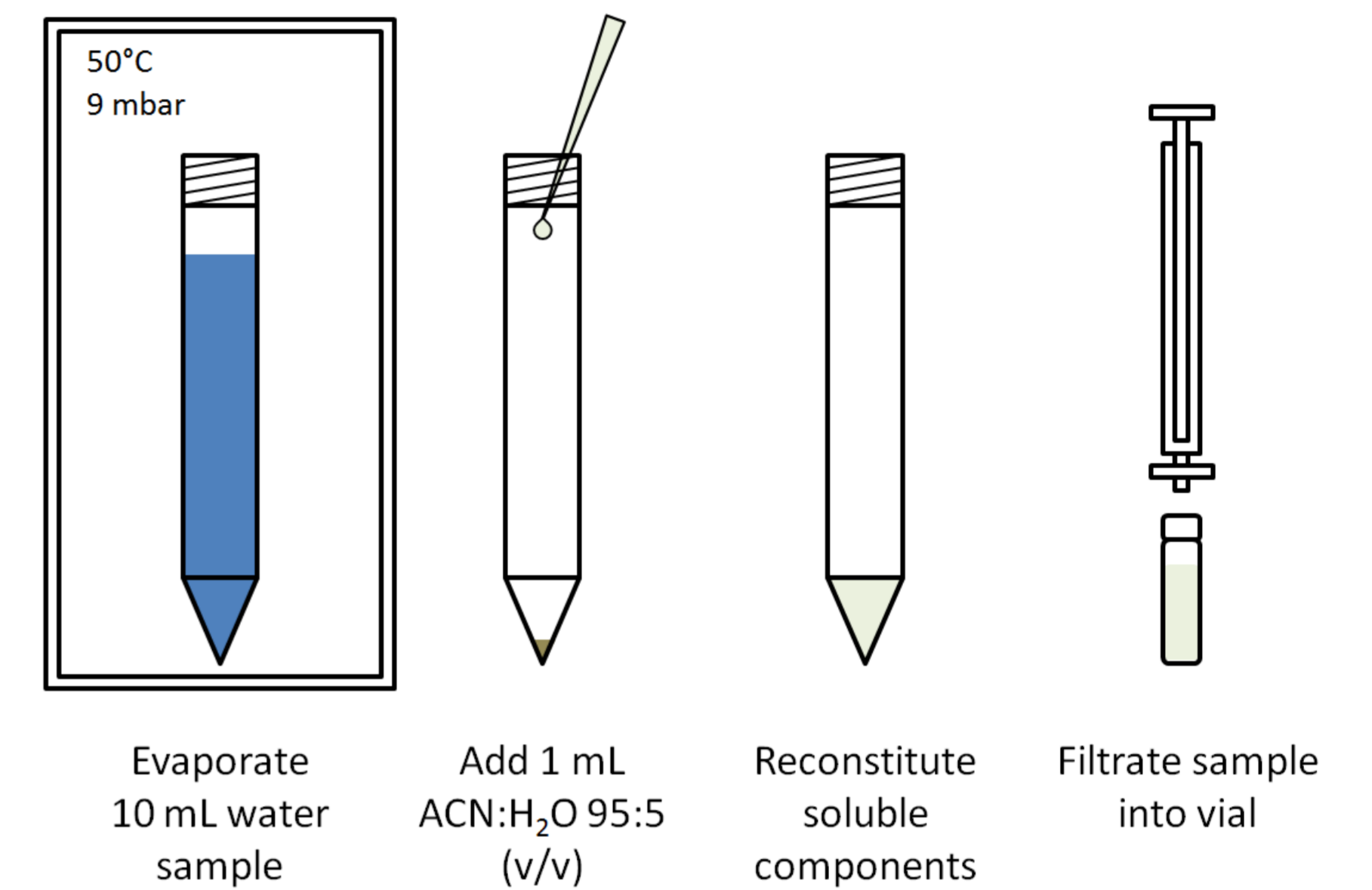
Highly polar organic substances may be able to penetrate natural and artificial barriers and are thus mobile in the water cycle. Those mobile organic contaminants (MOC) are, if persistent (PMOC) against microbiological and chemical degradation, difficult to remove during waste water treatment and drinking water purification^[1]. If these substances are present in high concentrations, toxic or undergo toxication^[2], problems for the aquatic environment 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. Within the PROMOTE project we strive to close this gap in knowledge and facilitate the protection of the aquatic environment from PMOC.

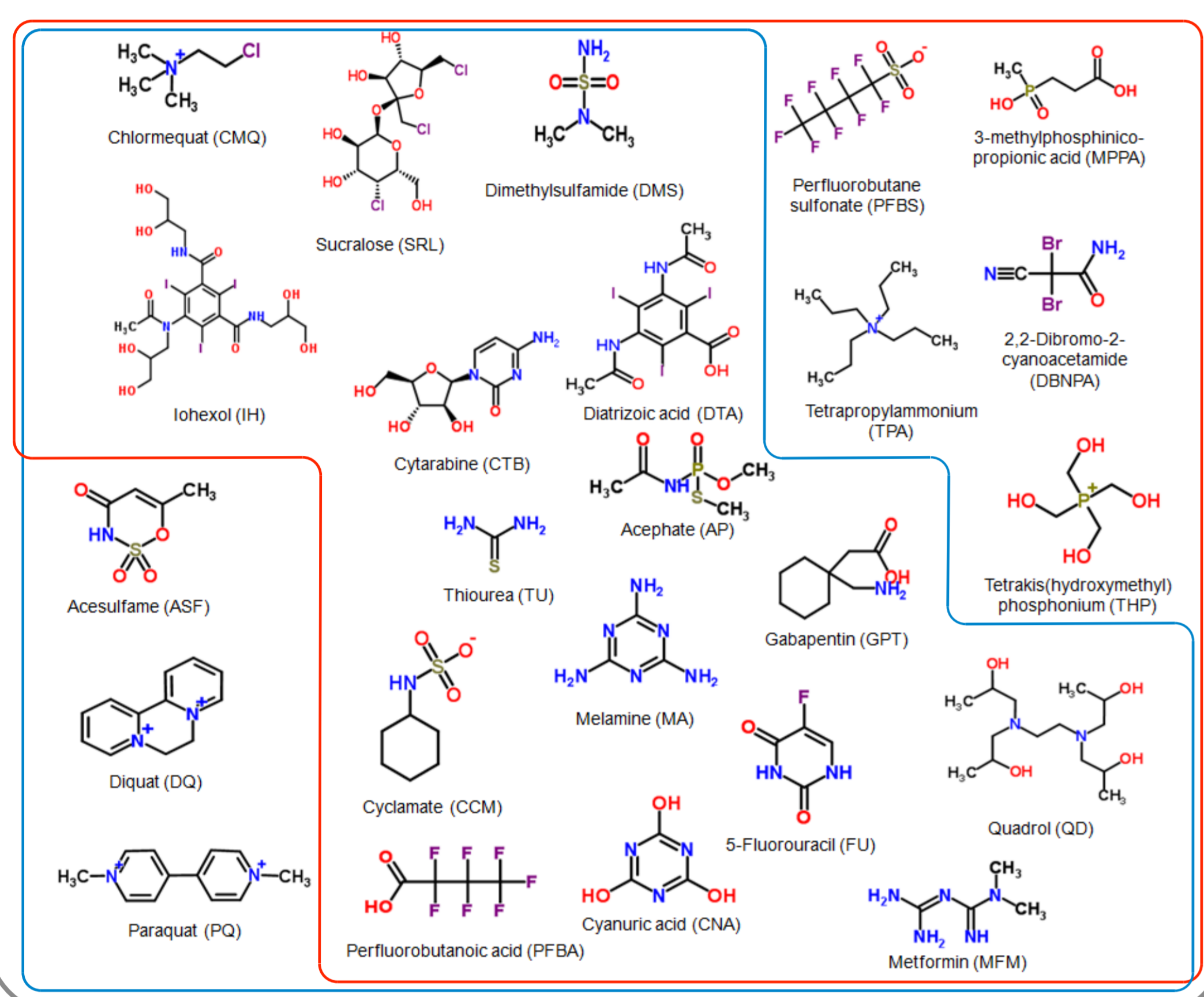
In this work, we aim to develop and test a suitable sample pre-treatment and HILIC-HRMS method for the non-target screening of MOC in aqueous samples based on a set of model analytes^[3]. The results of the method development as well as an exemplary screening result are shown to demonstrate the current capabilities and limitations of the developed method.



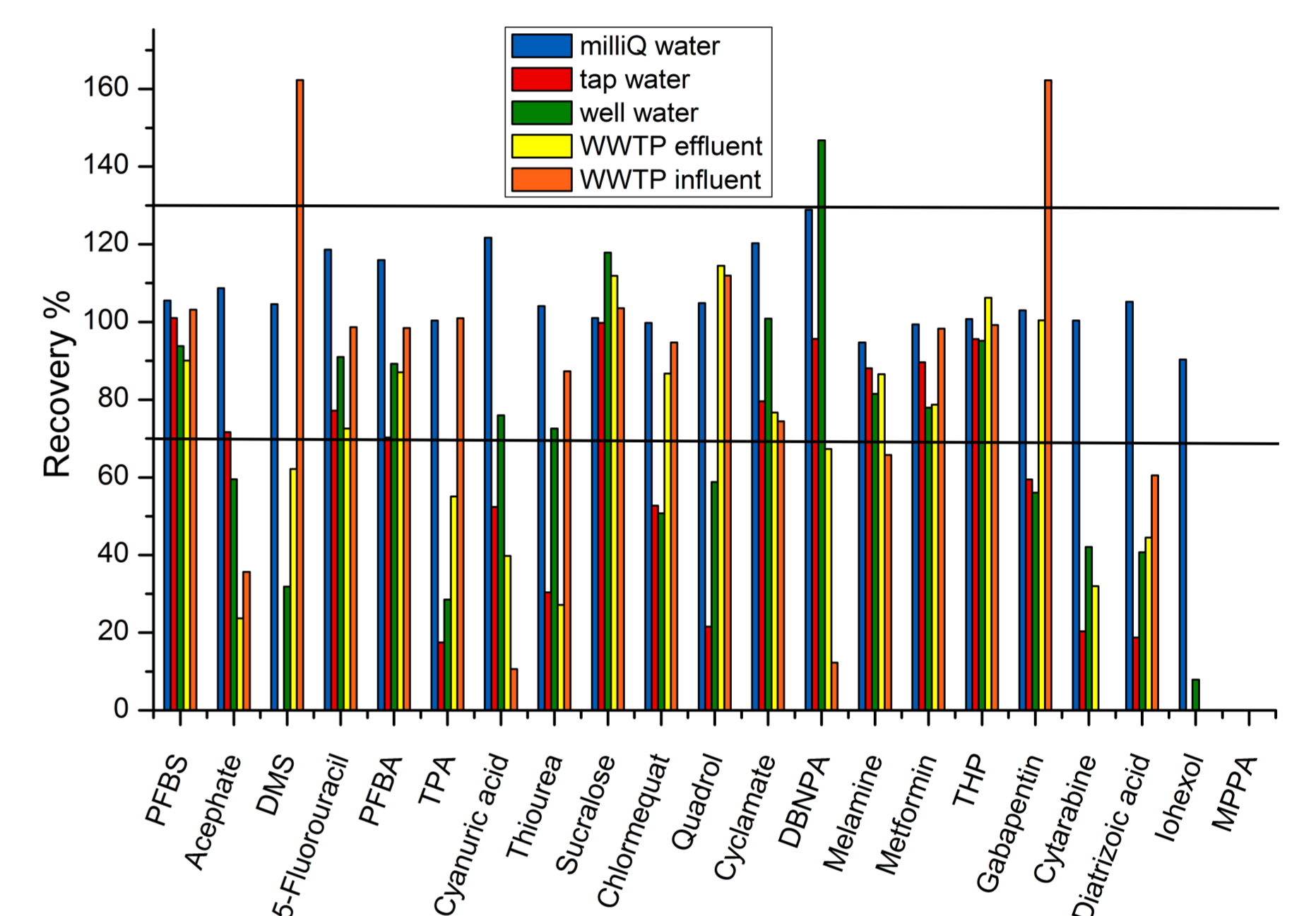
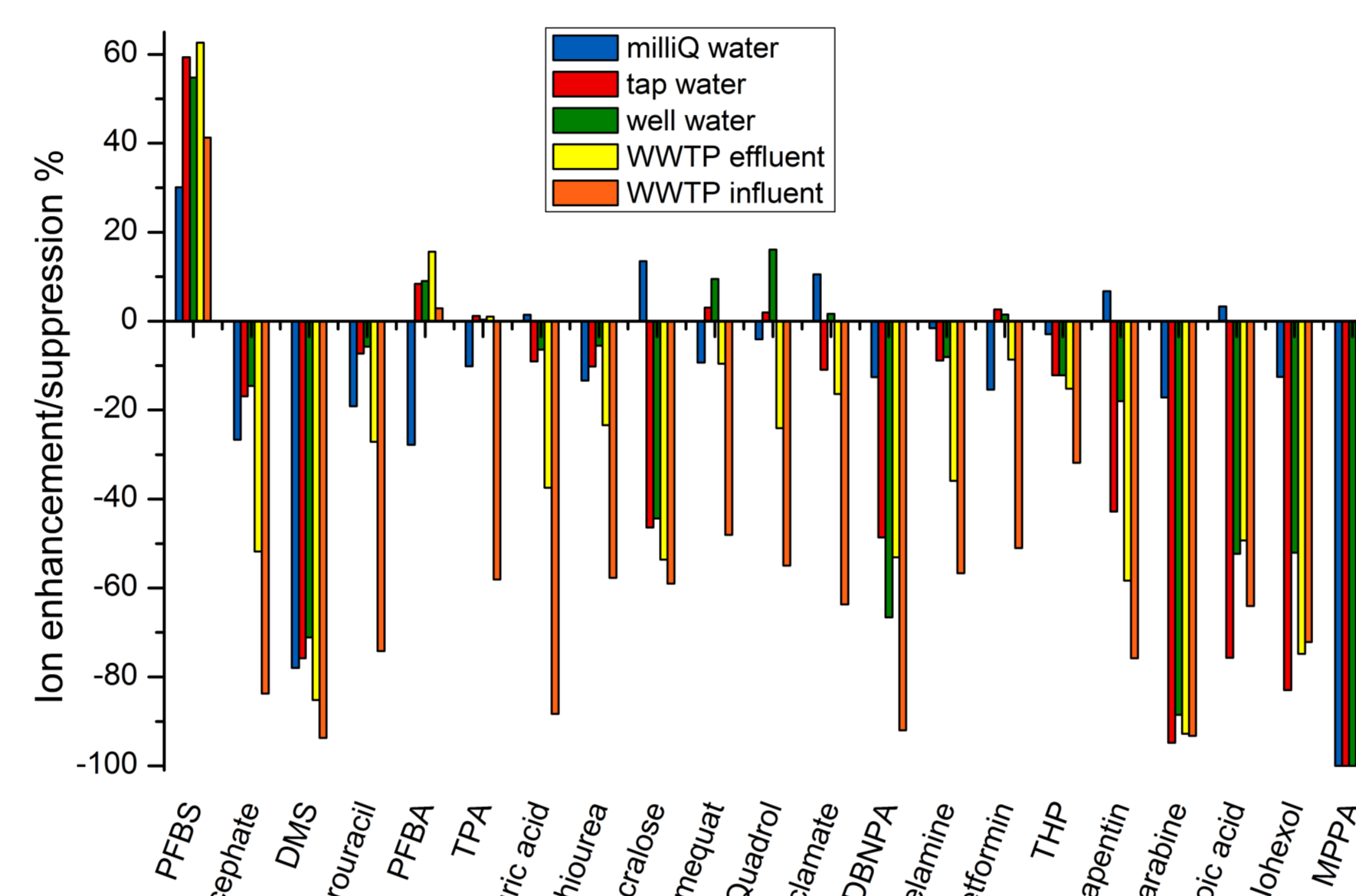
Sample Pre-treatment Method



Model Analytes

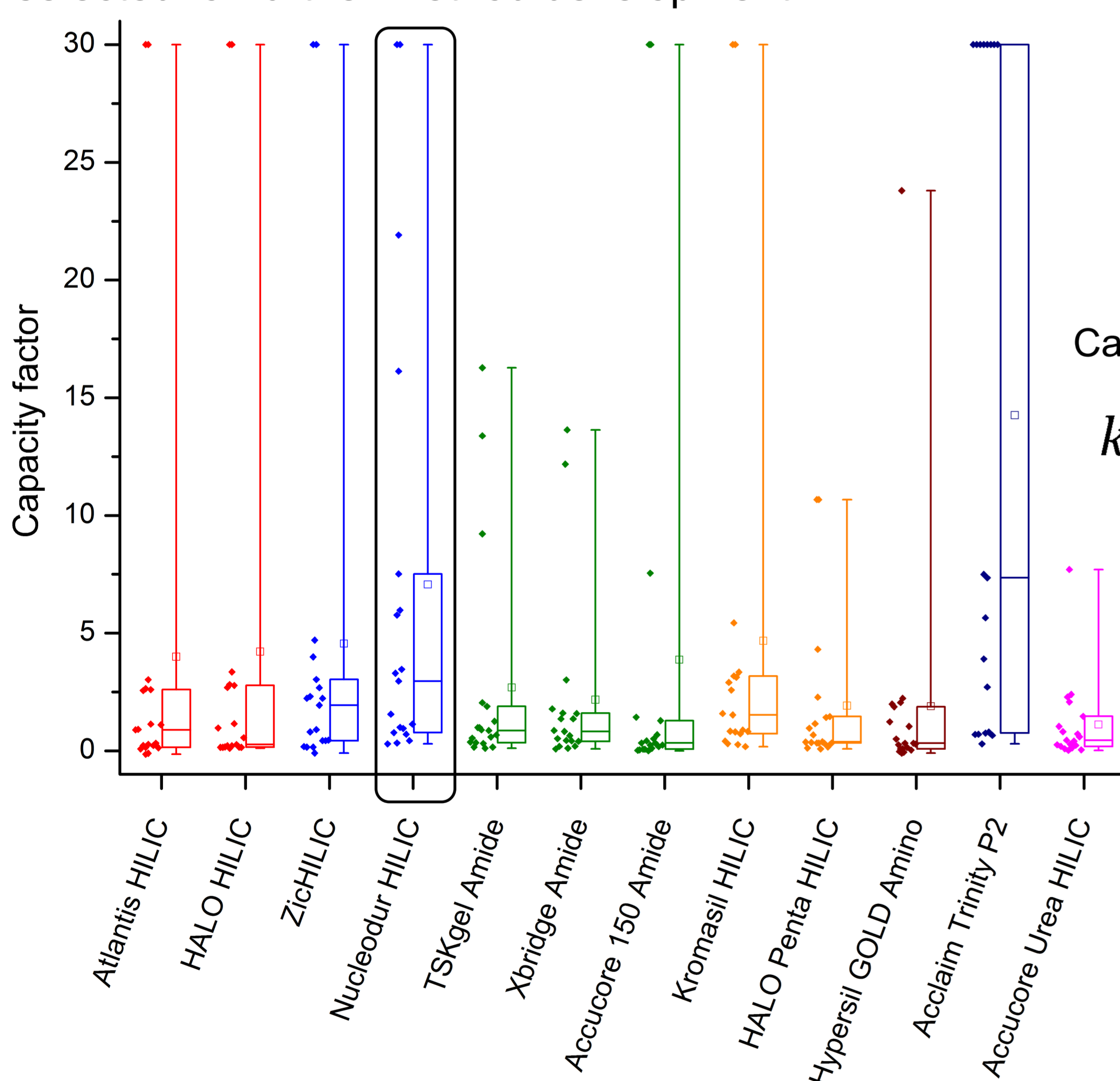


To reliably enrich a variety of MOC and perform the necessary solvent exchange, a simple approach based on evaporation and reconstitution was tested with 5 different matrices. Cytarabine, iohexol and MPPA could be identified as critical in most matrices.



HILIC-HRMS Method

A mixture of model analytes, differing in molecular mass, polarity and charge state, was analyzed on 12 HILIC columns. The most suitable column for further method development was identified to be the Nucleodur HILIC column. The column was chosen due to good retention of analytes of all charge states and no necessity for high salt concentrations to ensure elution. The Nucleodur HILIC column was selected for further method development.



$$k = \frac{t_R - t_0}{t_0}$$

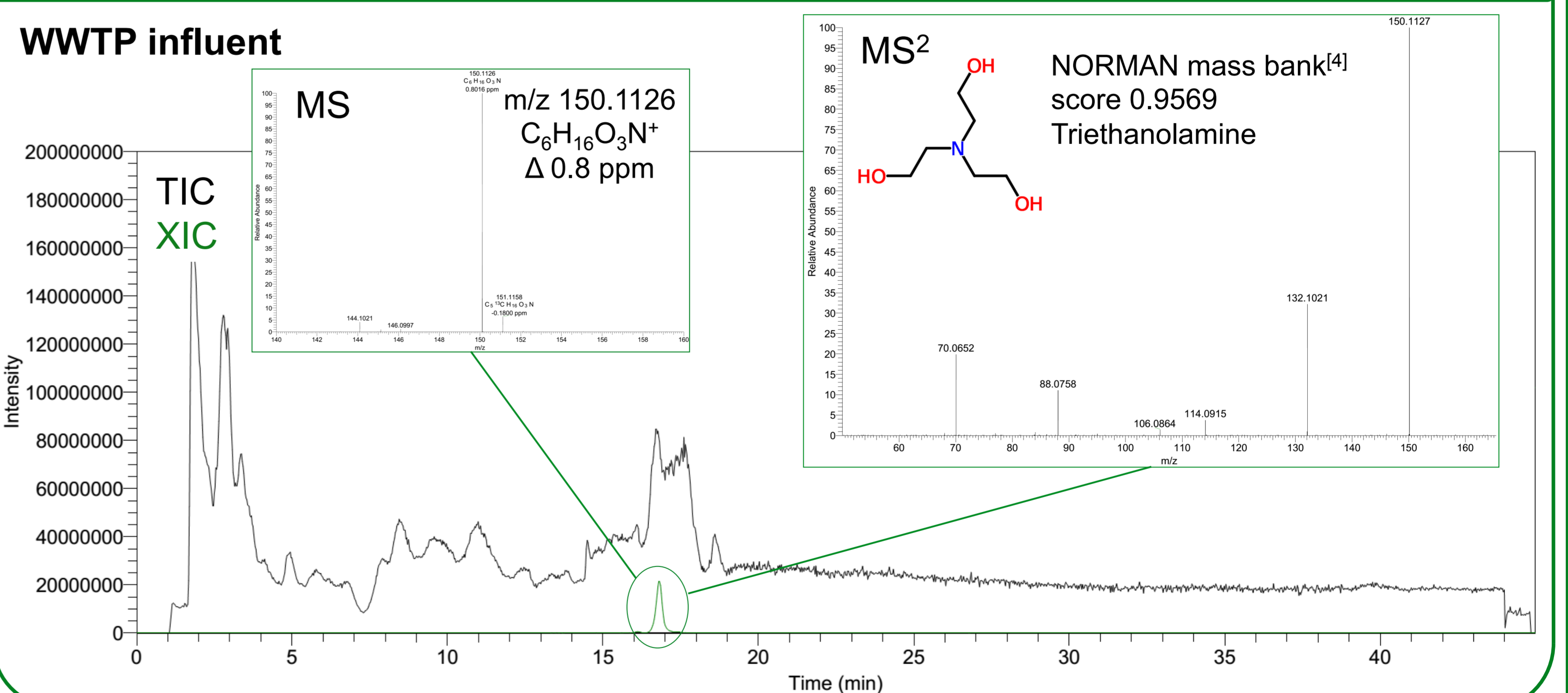
With the selected column a linear H₂O/ACN gradient from 2.5 to 60% H₂O was developed. 2.5% MeOH were added during the initial isocratic step to increase retention and ensure sufficient wetting of the stationary phase. At any time the solvent mixture contained 5 mM NH₄Fo.

The developed chromatographic method was coupled to an Orbitrap mass spectrometer, where HRMS as well as data-dependent HCD MS/HRMS data was generated

Conclusion and Perspective

- The developed HILIC method offers suitable retention and peak shapes for the majority of the model analytes
- Analyte enrichment and solvent exchange are possible by means of evaporation.
- Recovery and matrix effects are often within an acceptable range for milliQ, tap and well water
- The applicability of the developed methods was demonstrated by the exemplary identification of triethanolamine in a WWTP influent
- Further development of the enrichment method is required to enhance its performance for critical analytes and complex matrices

Exemplary Unknown Screening



References:

- [1] Scheurer, M. *et al. J. Environ. Monit.* **2011**, *13*, 966.
- [2] Schmidt, C. K.; Brauch, H.-J. *Environmental Science & Technology* **2008**, *42*, 6340.
- [3] Zahn, D.; Frömel, T.; Knepper, T. P. *work in progress*
- [4] massbank.ufz.de/MassBank

Acknowledgement:

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