

Development of a solid phase extraction method for the enrichment of highly polar organic contaminants from aqueous matrices

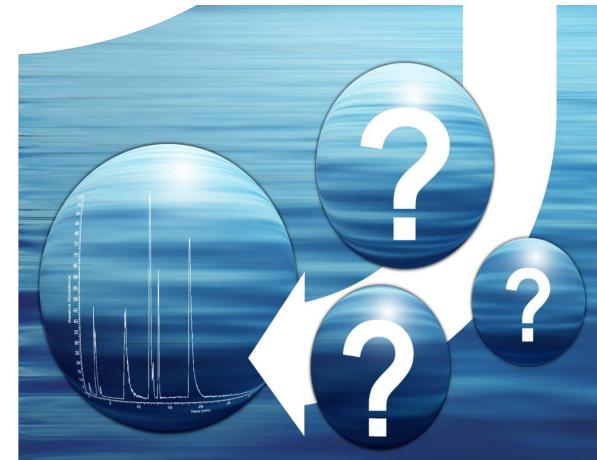
Niklas Köke, Daniel Zahn, Thomas P. Knepper, Tobias Frömel

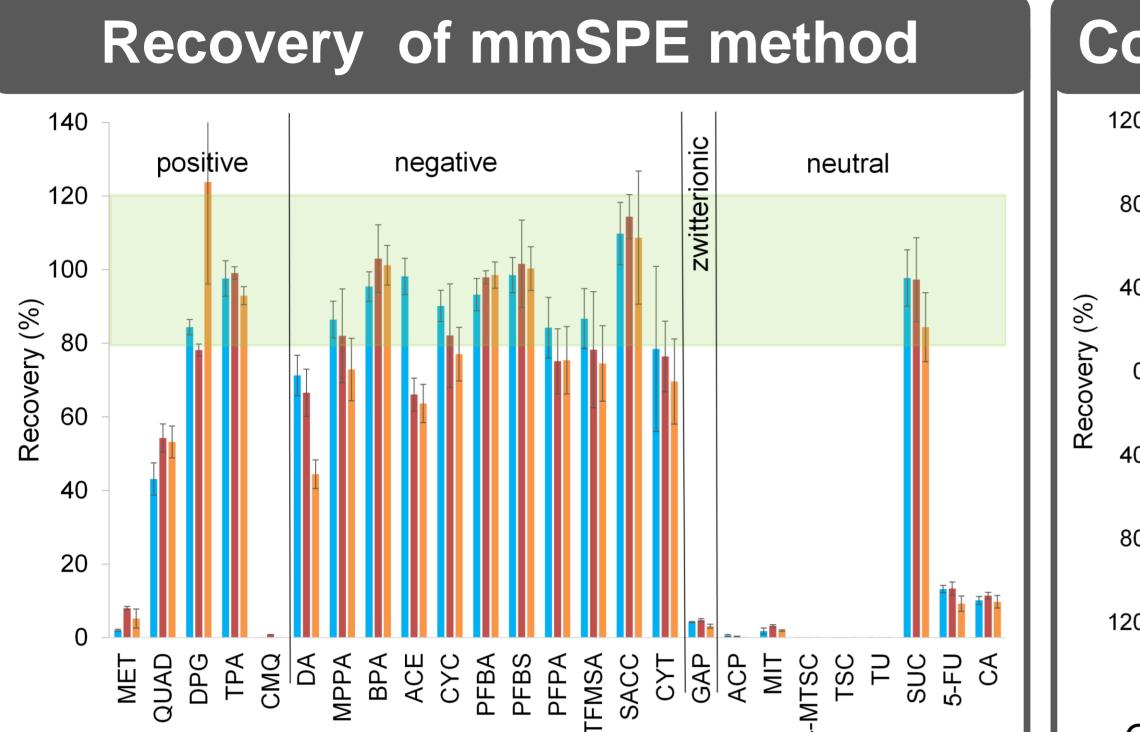
Introduction

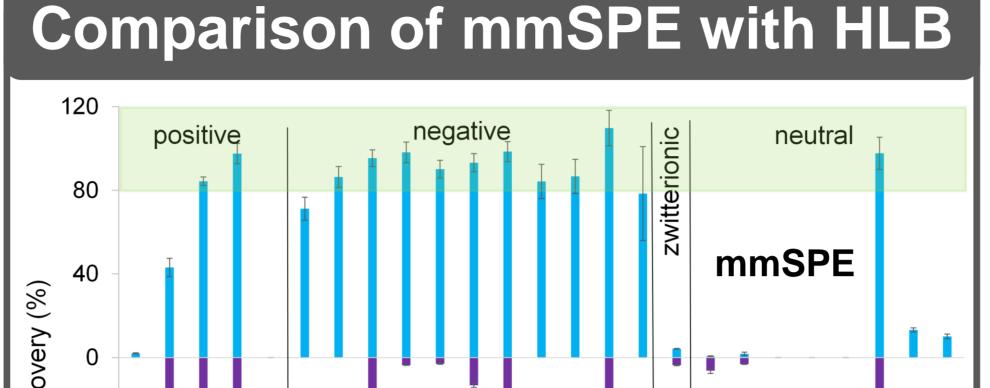
Highly polar organic contaminants are **mobile (MOCs)** in the water cycle because they are able to **pass natural and artificial barriers.** If they are **persistent (PMOCs)**, dilution is the only way of concentration reduction, and thus these substances may **reach raw and drinking waters** in significant concentrations^[1]. When PMOCs are present in high concentrations or toxic^[2], their presence in the water cycle may have **adverse effects in the aquatic environment or on human health.**

The **analysis of MOCs is acerbated** by the same physico-chemical properties^[3] that facilitate their mobility (e.g. low molecular mass and high polarity). The **lack of suitable enrichment methods** for MOCs from aqueous samples is a major problem in their trace analysis, and thus two independent methods, a **multimodal solid phase extraction method (mmSPE)** and an **evaporation method**, were developed to facilitate the analysis of MOCs.

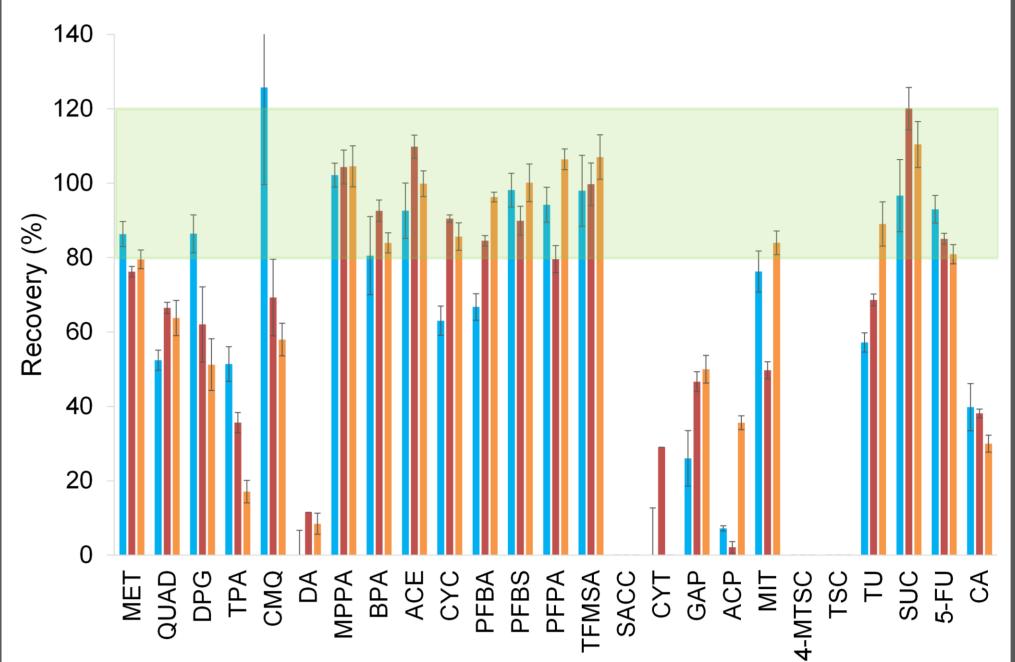




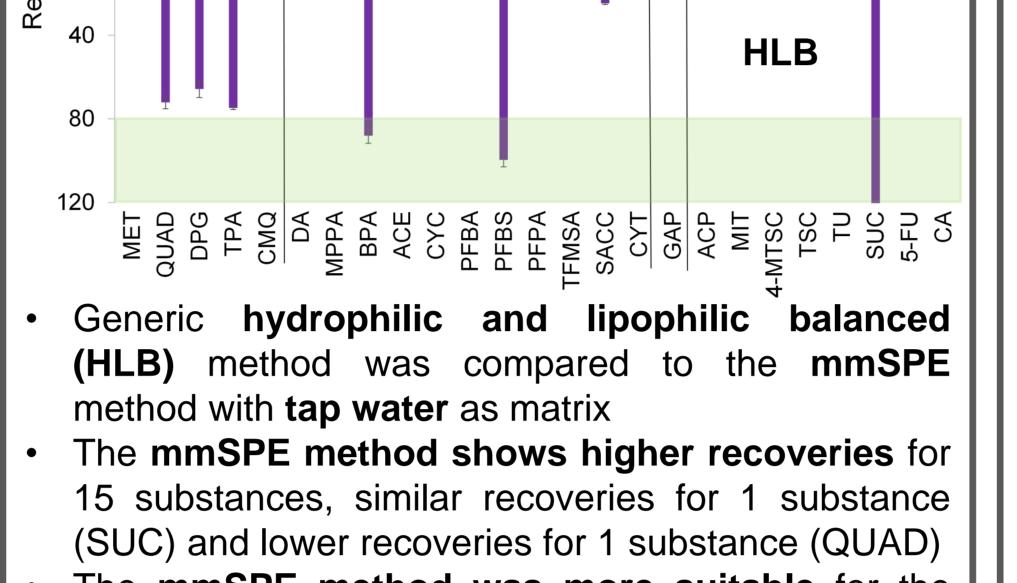




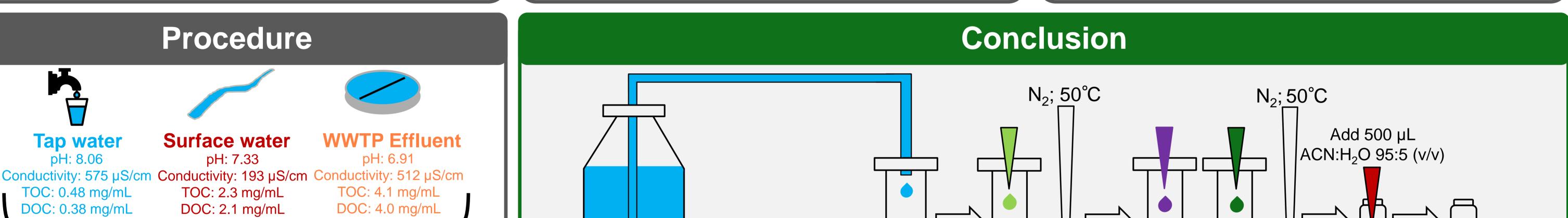
Recovery of evaporation method

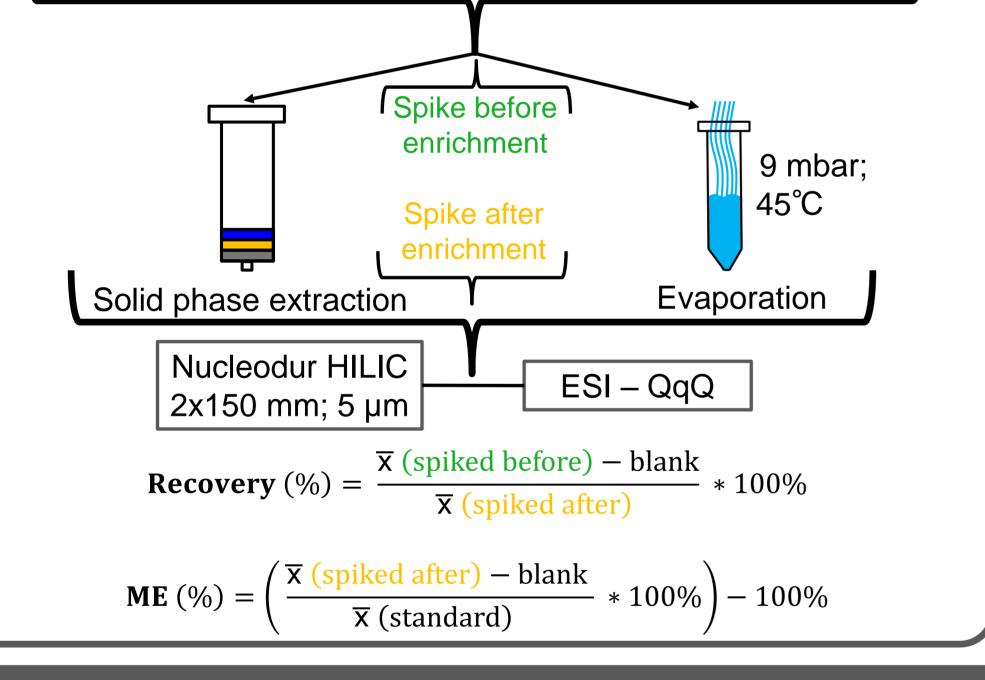


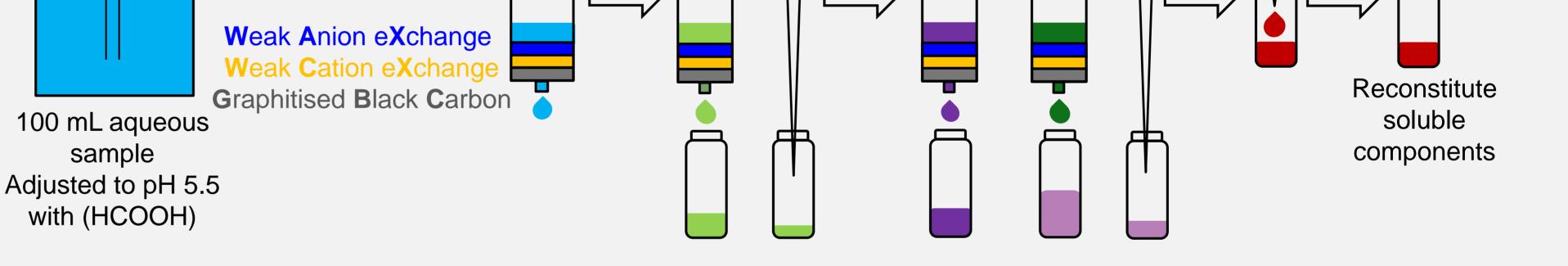
- Successful enrichment of 15 of 25 model substances with a recovery above 40%
- MET, CMQ, GAP, ACP, MIT, 4-MTSC, TSC, TU, 5-FU and CA could be identified as critical substances
- MET and CMQ may undergo transformation since their recovery is above 80%, when enriched from milliQ H₂O (data not shown)
- Nearly **no interactions** of TU, TSC and 4-MTSC with the solid phase material, which led to **no enrichment**



- The mmSPE method was more suitable for the enrichment of highly polar organic substances from aqueous matrices, compared to the generic HLB method
- Successful enrichment of 18 of 25 substances with a recovery above 40%
- Compared to the mmSPE method, GAP, MIT, CMQ, MET, 5-FU, CA and TU showed acceptable recoveries
- DA, SACC, ACP, 4-MTSC and TSC were the most critical substances in terms of enrichment
- Possible hydrolysis of 4-MTSC and TSC during 48 h evaporation process (data not shown)







 $3x 1 \text{ mL MeOH} + 5\% \text{ NH}_4\text{OH}$ 3x 1 mL MeOH + 2% HCOOH

- The mmSPE method offers adequate recoveries for many highly polar organic contaminants (15 of 25 with recoveries above 40%)
- The **mmSPE** method shows **less matrix effects** than the evaporation method, and thus allows realisation

of higher enrichment factors

Enrichment of **neutral substances is still problematic** with the mmSPE method, which can be attributed to **little interaction** of these substances with the solid phase materials

 $3x 0.5 \text{ mL MeOH:} CH_2 CI_2 80:20 (v/v)$

Matrix effects of mmSPE and evaporation method

- Low matrix effects for 17 of 25 substances for the evaporation method. Only DA, SACC and SUC show significant matrix effects with more than 70 % ion suppression
- An increased enrichment factor leads to significantly more pronounced matrix effects for the evaporation method
- mmSPE method allows realisation of higher enrichment
 - Solid phase extraction enrichment factor 200

20

factors before matrix effects become critical

- It is assumed that TOC and DOC influence the matrix effects of the mmSPE method more significantly than dissolved salts
- For the evaporation method, the salt content seems to influence the matrix effects more strongly than the TOC and DOC

Evaporation enrichment factor 50

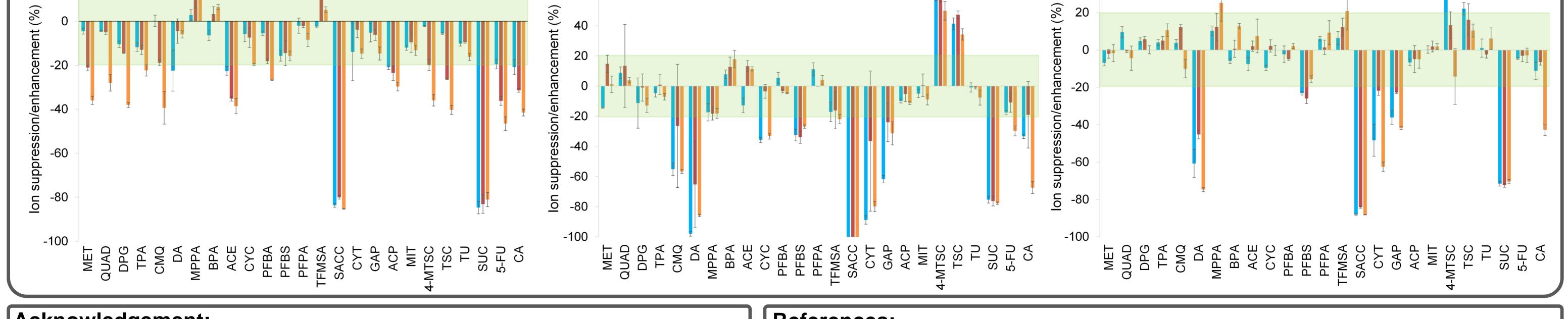
Significance of matrix effects for the **mmSPE** method ♥ < /<

Significance of matrix effects for the evaporation method



Evaporation enrichment factor 10

60



Acknowledgement: This work has been funded by the BMBF (02WU1347B) in the frame of the collaborative international consortium WATERJPI2013 - PROMOTE of the Water Challenges for a Changing World Joint Programming Initiative (Water JPI) Pilot Call.

References:

[1] Reemtsma, T. *et al. Environmental Science & Technology* 2006, 40, 5451-5458
[2] Schmidt, C. K.; Brauch, H.-J. *Environmental Science & Technology* 2008, 42, 6340
[3] www.promote-water.eu; 12.05.2016

Hochschule Fresenius, University of Applied Sciences, Institute for Analytical Research (IFAR), Idstein, Germany | Corresponding e-mail address: froemel@hs-fresenius.de