Halomethane sulfonic acids – standard synthesis, occurrence, and mitigation options

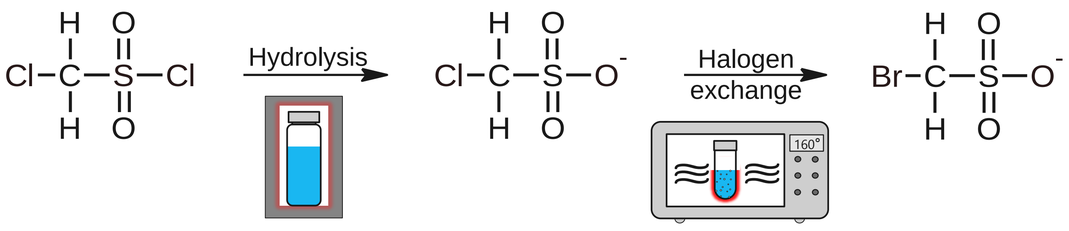
Daniel Zahn[1], Reinhard Meusinger[2], Tobias Frömel[1], Thomas P. Knepper[1]
[1]Hochschule Fresenius, University of Applied Sciences, Idstein, Germany
[2]TU Darmstadt, FB Chemie, Darmstadt, Germany

Introduction

Halomethane sulfonic acids (HMSAs) are recently discovered polar **disinfection by-products (DBPs)**[1]. So far their analysis was exacerbated by the lack of commercially available standards.

Thus we **synthesized standards** for four prevalent HMSAs and deployed them to analyze their **occurrence in drinking water production plants (DWPPs)** and **tap water samples**. In addition we determined the HMSA formation potential by chlorination of the samples to investigate the **removal** of the hitherto unknown **HMSA precursors** in DWPPs[2].

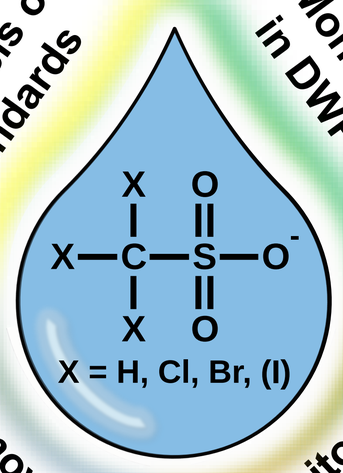
HMSAs
(Halomethane sulfonic acids)
are novel DBPs
(disinfection by-products)



- Two step synthesis of HMSAs: (1) hydrolysis of chlorinated sulfonyl chlorides and (2) halogen exchange from chlorine to bromine
- Reaction control, purity assessment, and confirmation of product structure with ion chromatography, high resolution mass spectrometry, and nuclear magnetic resonance spectroscopy (NMR), quantification with quantitative NMR
- Four HMSAs successfully synthesized:

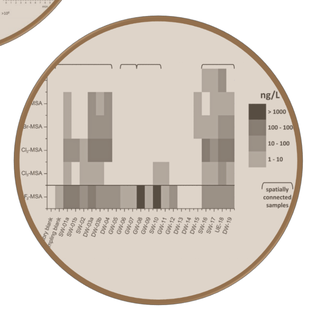
ClMSA **BrMSA** **Cl_2MSA** **BrClMSA**

Synthesis of standards
Monitoring in DWPPs
Removal of precursors
Monitoring in tap water

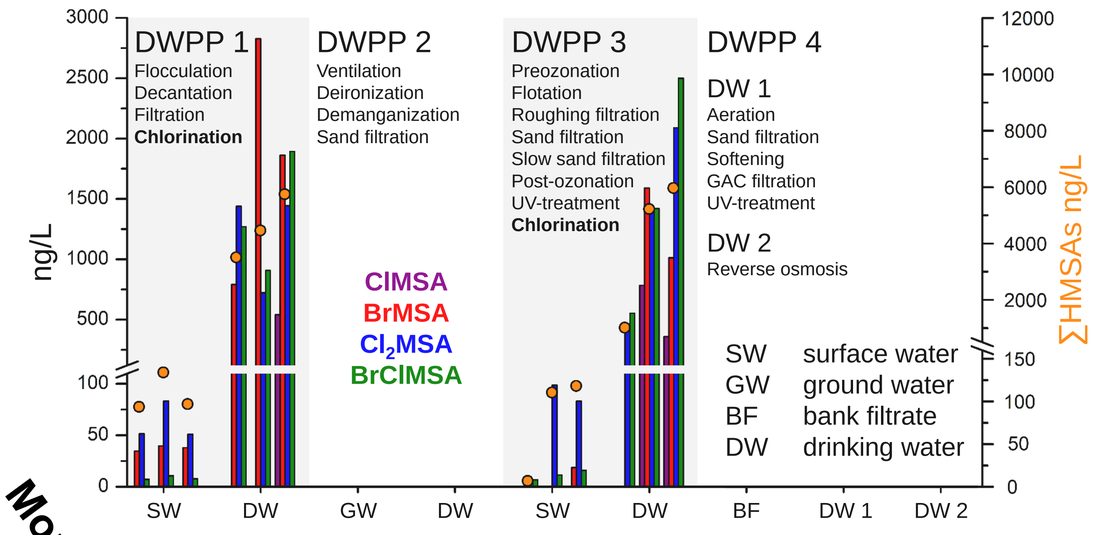


Short summary of preceding research

Development of enrichment (multi-layer SPE[3], combination of WAX, WCX, and activated carbon) and instrumental methods dedicated for the identification and quantification of very polar organic chemicals

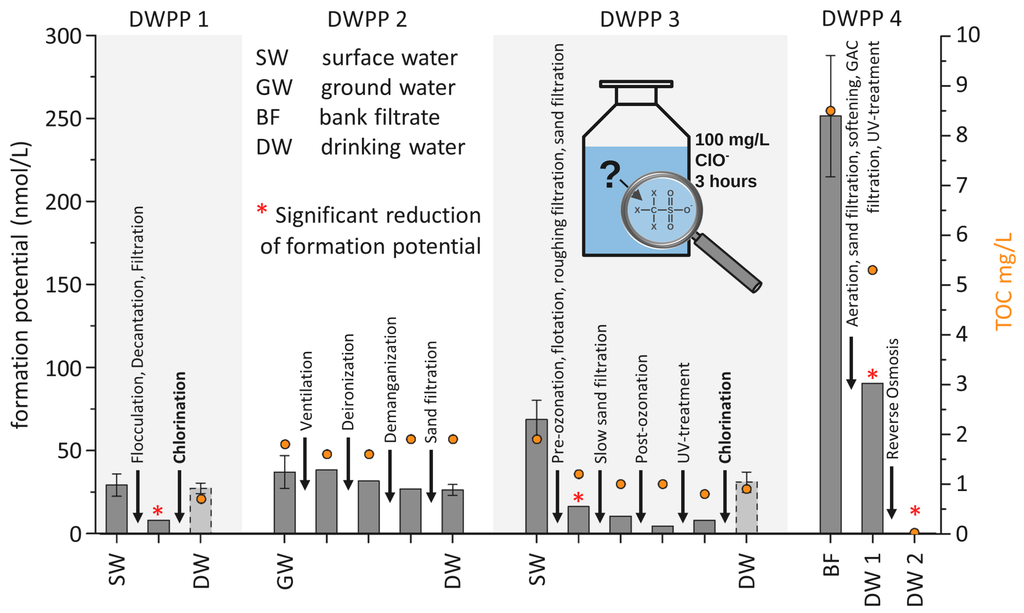


Non-target screening with these methods led to identification of halomethane sulfonic acids (HMSAs) as novel polar water contaminants[1]

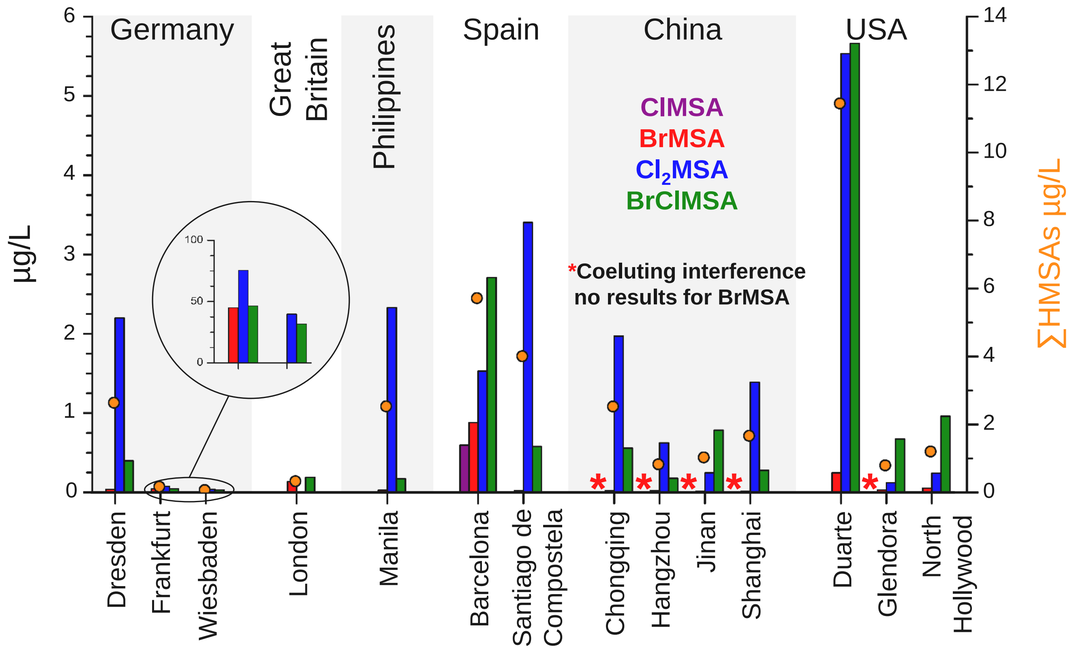


- HMSA were formed in the µg/L range during drinking water chlorination
- HMSA were present in two surface waters in the 100 ng/L range
- Seasonal trends in HMSA formation correspond roughly with TOC of raw water (exception month 1 in DWPP 3)

- HMSA formation potential (sum parameter for HMSA precursors) was utilized to indirectly assess removal of HMSA precursors
- Original disinfection in DWPPs led to more efficient HMSA formation
- Significant HMSA precursor removal coincides with TOC reduction
- Ozonation, granular or powder activated carbon filtration and reverse osmosis most efficient treatment options for HMSA precursor removal



- HMSAs were detected in all 14 tap water samples (0.07 µg/L – 11.5 µg/L)
- Dihalogenated congeners were more prevalent in tap water than in DWPPs. This may be caused by further reaction of mono-halogenated species with residual chlorine in the pipe system
- High concentrations in Duarte may partially be attributed to sulfonic acid based water softener at sampling site



References:
[1] Zahn, D., *et al. Water Research* **2016**, *101*, 292-299.
[2] Zahn, D., et al., submitted
[3] Köke, N., *et al. Analytical and Bioanalytical Chemistry* **2018**, 9, 2403-2411
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HMSA synthesis strategy was successful

HMSAs are widely spread and frequently present in the µg/L range in tap water

The HMSA formation potential is a valuable tool for the study of hitherto unknown precursors

HMSAs may also be very polar environmental contaminants (potential vPvM or PM(T))

HMSAs are not amenable to adsorbable organic halogen (AOX) analysis and thus demonstrate a polarity gap[4] for the AOX

Next steps:

- Extension of analyte spectrum (e.g. iodinated HMSAs)
- Further optimization of methods
- Large scale monitoring in tap water and environmental water samples
- Experimental assessment of toxicity
- Investigation of mISPE to extend polarity range of AOX

Corresponding author: daniel.zahn@hs-fresenius.de

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