

Matrix effects in the analysis of polar organic water contaminants with HILIC-ESI-MS



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Rationale

Method

Results

Conclusion

Persistent and mobile organic chemicals (PMOC) are able to penetrate natural and artificial barriers, and thus spread quickly in the water cycle [1]. It is currently considered to integrate these chemicals into REACH regulation as **persistent mobile and toxic (PMT)** or **very persistent and very mobile (vPvM)** substances [2]. Consequently, the accurate trace analysis of these chemicals is of ever increasing importance. Besides difficulties in their chromatographic separation and enrichment from aqueous matrices, several studies observed **pronounced partially highly variable matrix effects** for some very polar water contaminants [3, 4]. While matrix effects in

reversed phase chromatography – electrospray ionization (ESI) have been investigated for years, matrix effects in **hydrophilic interaction liquid chromatography (HILIC)** are still only scarcely investigated [4].

To address this issue, we investigated drinking water (DW) and waste water treatment plant (WWTP) effluent. We enriched these samples with two sample preparation methods suitable for very polar analytes, namely the evaporation of the aqueous matrix and multi-layer solid phase extraction (mISPE) method [5] and utilized **post-column infusion of 26 polar model analytes** to investigate their matrix effects throughout the chromatographic run [6].

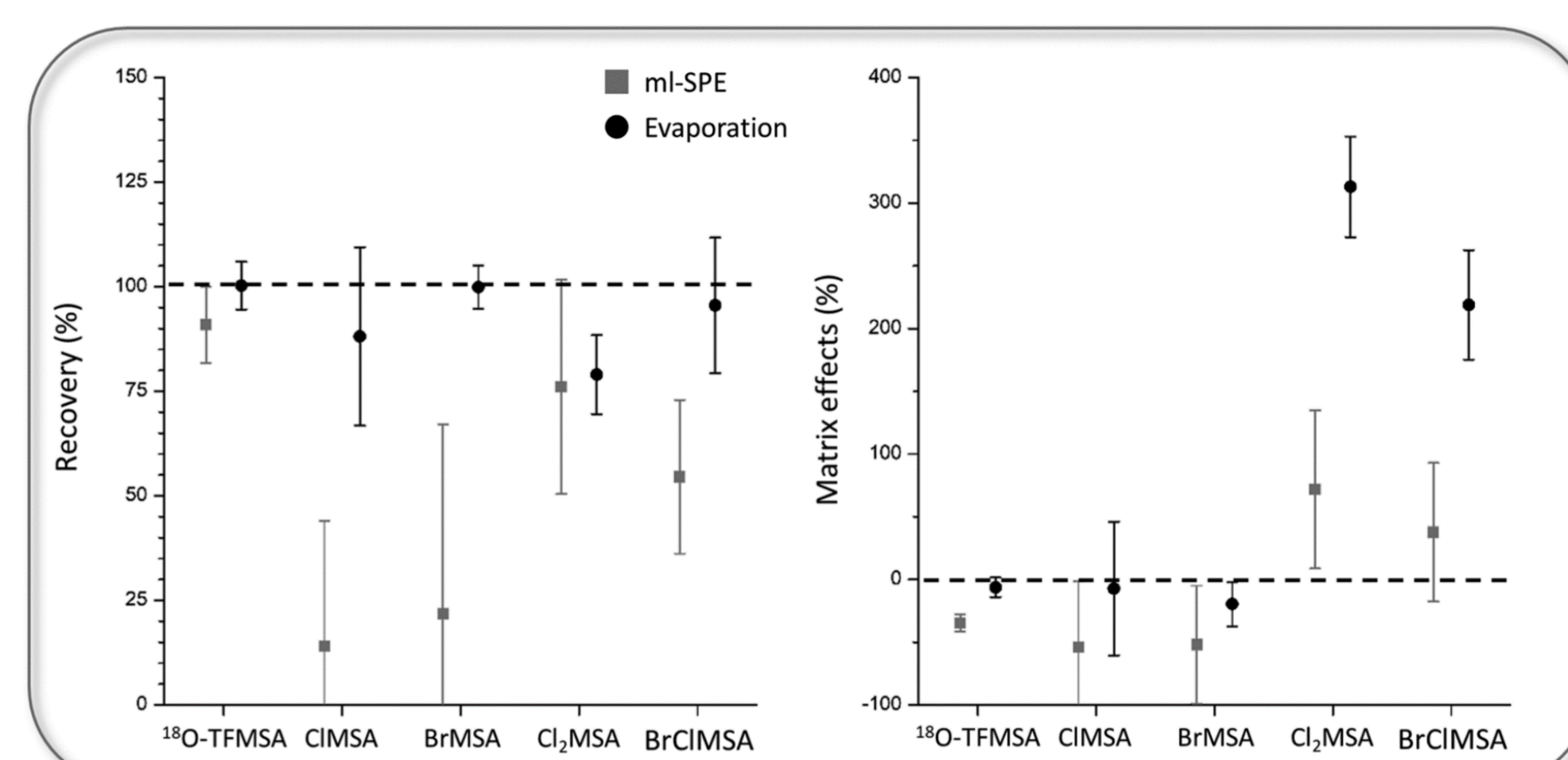


Figure 1: Recoveries and matrix effects of halomethanesulfonic acids. Taken from [3]

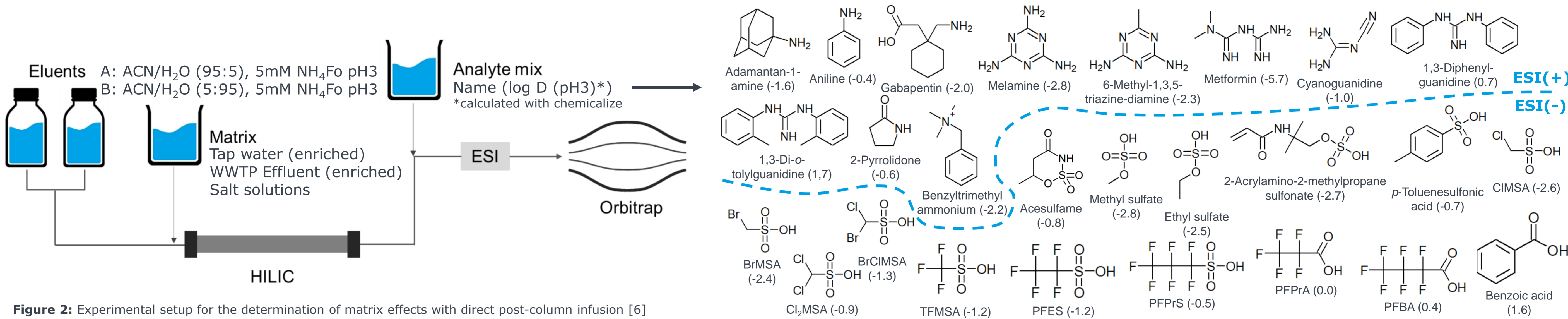


Figure 2: Experimental setup for the determination of matrix effects with direct post-column infusion [6]

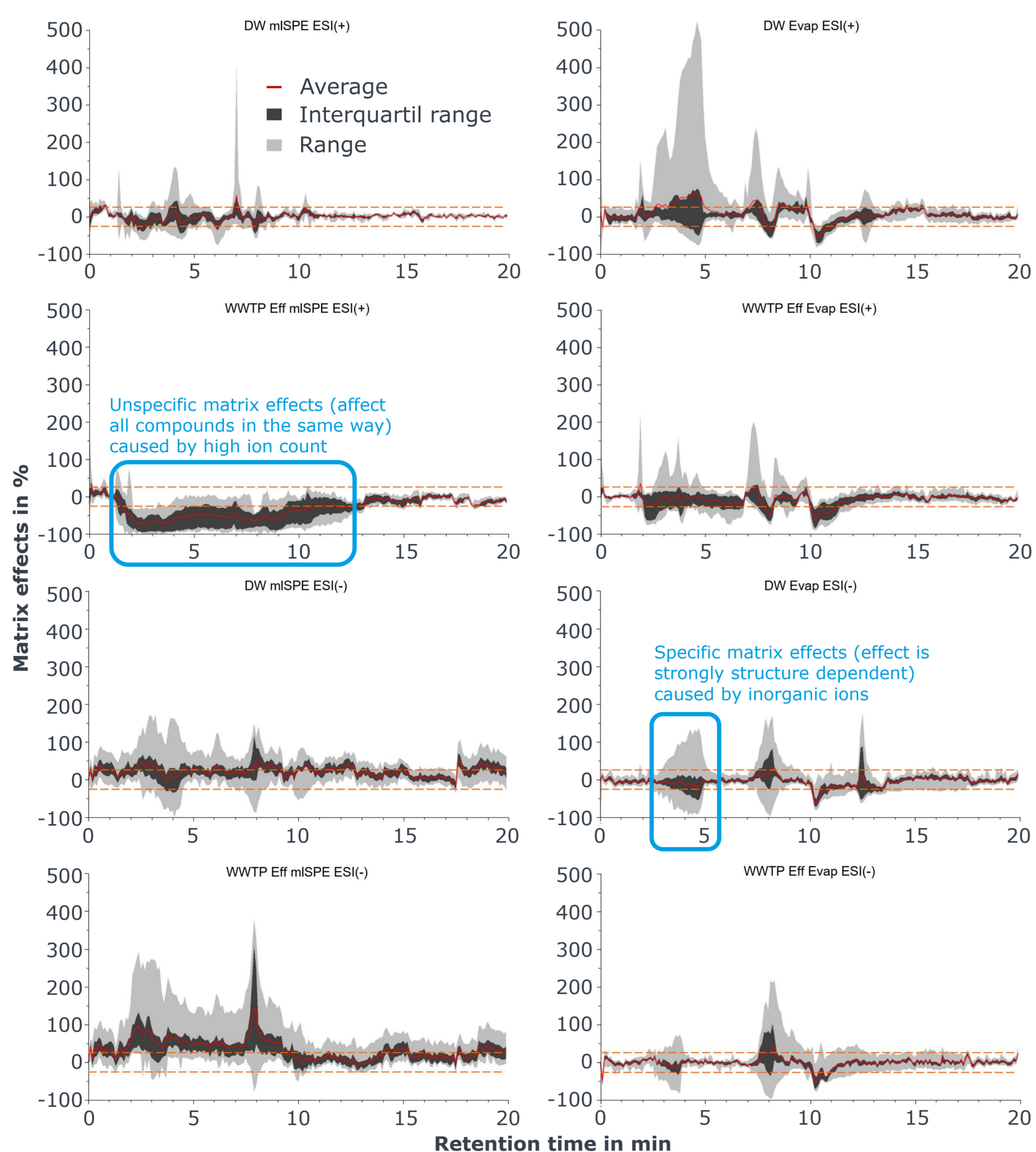
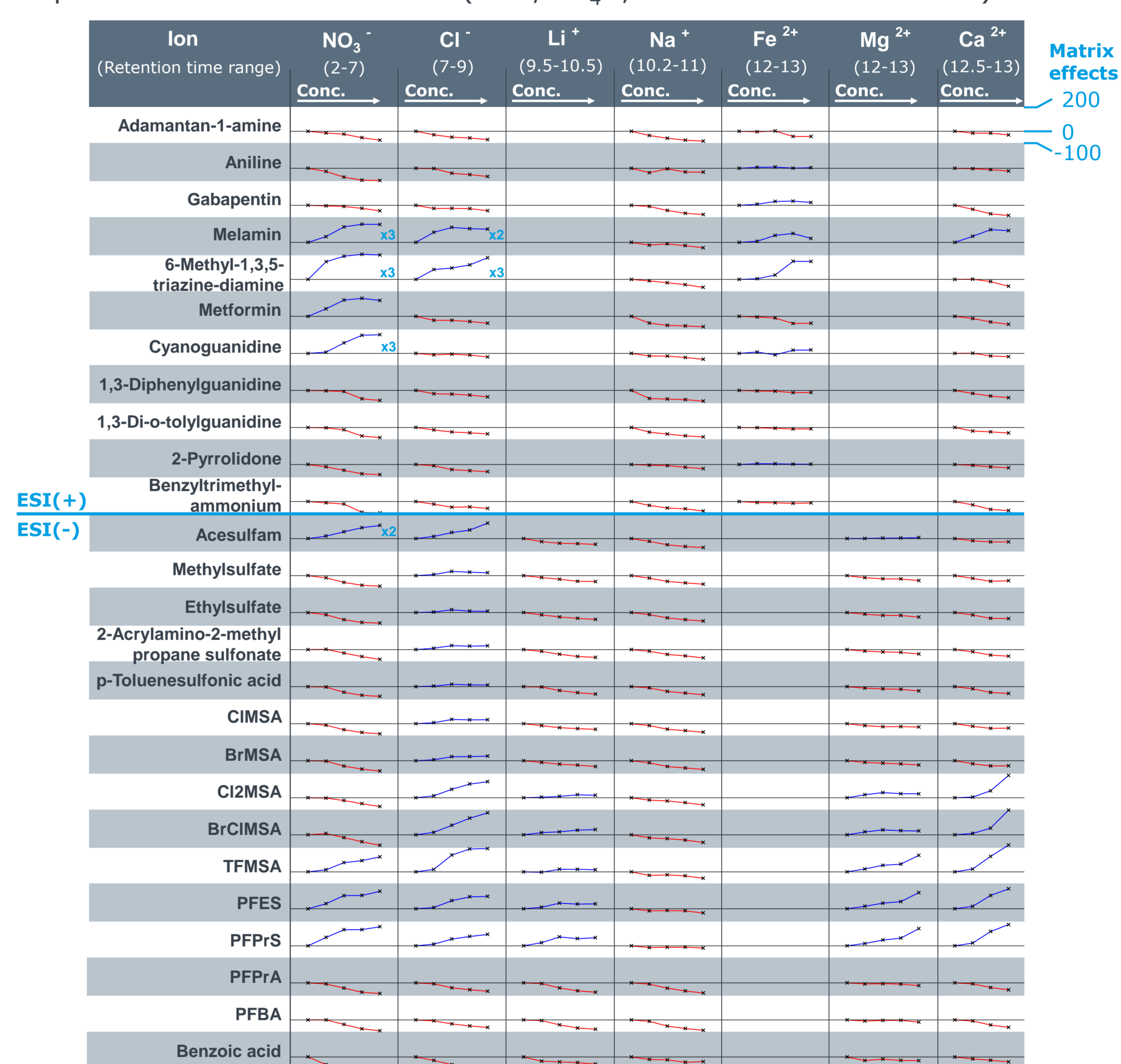


Figure 3: Statistical evaluation of matrix effects in tap water (DW) and waste water treatment plant (WWTP) effluent after enrichment with two sample preparation methods [6]

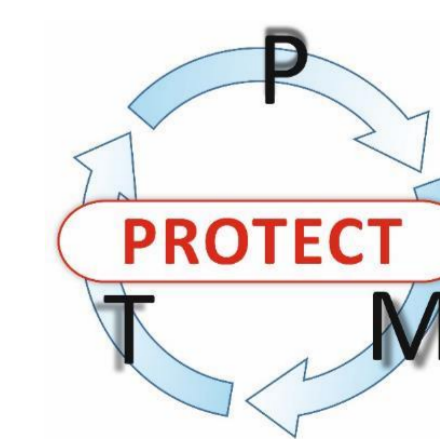
- Unspecific ion suppression coincided with a high ion count, thus the excess charge was identified as limiting factor
- Structure-specific matrix effects were mostly accompanied by ion clusters of inorganic anions (e.g. $[Mg^{2+} + 3HCOO^-]$)
- Inorganic ions were confirmed as cause of structure specific matrix effects by experiments with salt solutions (Fe^{3+} , PO_4^{3-} , and K^+ showed no effect)



- There are structure-specific and unspecific matrix effects.
- In this study, unspecific matrix effects predominantly coincided with a high ion count. The excess charge seems to be the limiting factor in ion formation.
- Structure-specific matrix effects were traced back to inorganic anions and cations, which eluted over a significant fraction of the chromatographic run time with this setup. They were much more pronounced when evaporation of the aqueous matrix is utilized for sample preparation
- Even structurally similar compounds like perfluorinated sulfonic and carboxylic acids as well as mono- and dihalogenated methanesulfonic acids may react entirely differently to some inorganic ions (e.g. Ca^{2+}).
- Coelution with inorganic ions and the resulting matrix effects should be considered in the development of HILIC-ESI-MS methods for polar analytes. Different column chemistries and method variations may be utilized to reduce or even circumvent the coelution of specific inorganic ions and especially critical analytes (e.g. pronounced matrix effects, no isotope-labelled standard available).

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