Filling the knowledge gap: Comparative suspect screening for over 1400 persistent and mobile chemicals with SFC- and HILIC-HRMS in environmental water samples

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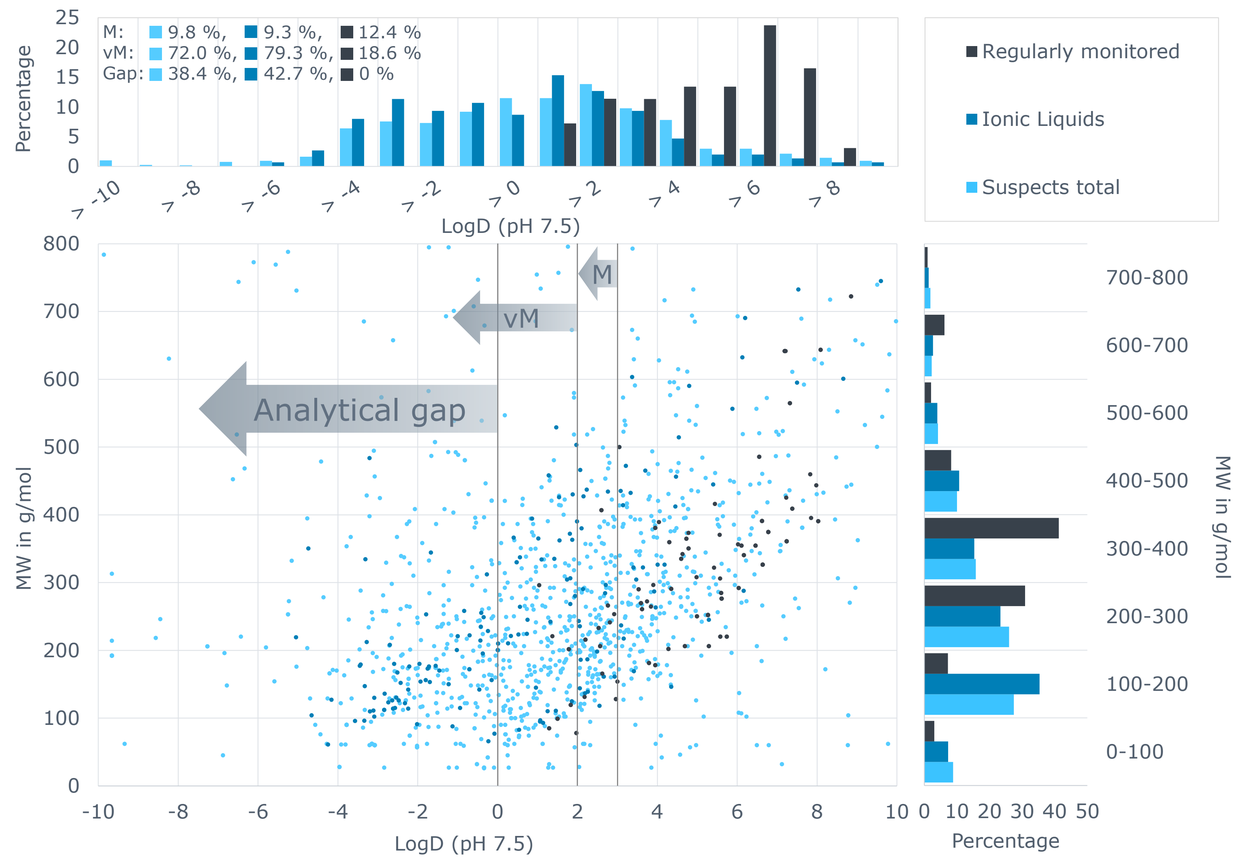
Introduction

A large variety of **anthropogenic substances** may enter the aquatic environment [1] daily. Chemicals that combine persistency, high aquatic mobility and potential toxicity **(PMT) are exceptionally problematic**, since their removal from partially closed water cycles is difficult [2]. Their aquatic mobility and thus **high polarity** also severely **exacerbates their analysis**. While recent improvements in sample preparation, chromatographic and mass spectrometric methods facilitate their analysis [3], there is likely still a severe **lack of knowledge** about the presence of these chemicals in the aquatic environment.

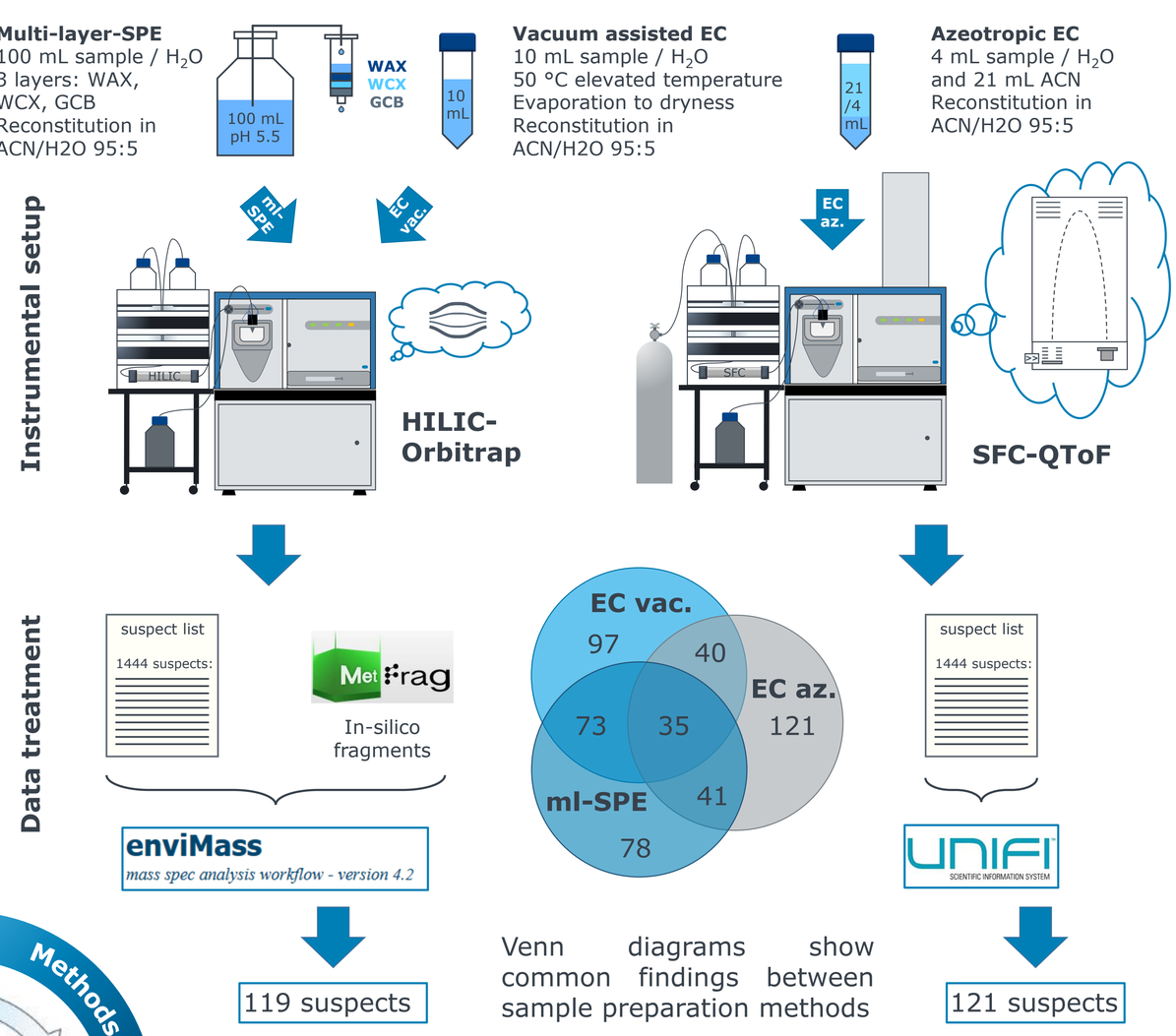
To narrow the knowledge gap on PMT substances, we conducted a **suspect screening** by combining **various methodological approaches**. Three sample preparation techniques (multi-layer SPE, vacuum-assisted evaporative concentration and azeotropic evaporative concentration) and two analytical instrumentations (HILIC-Orbitrap-HRMS and SFC-QToF-HRMS) were applied. A **large suspect list** containing more than 1400 potential PM(T) substances was compiled from various sources.

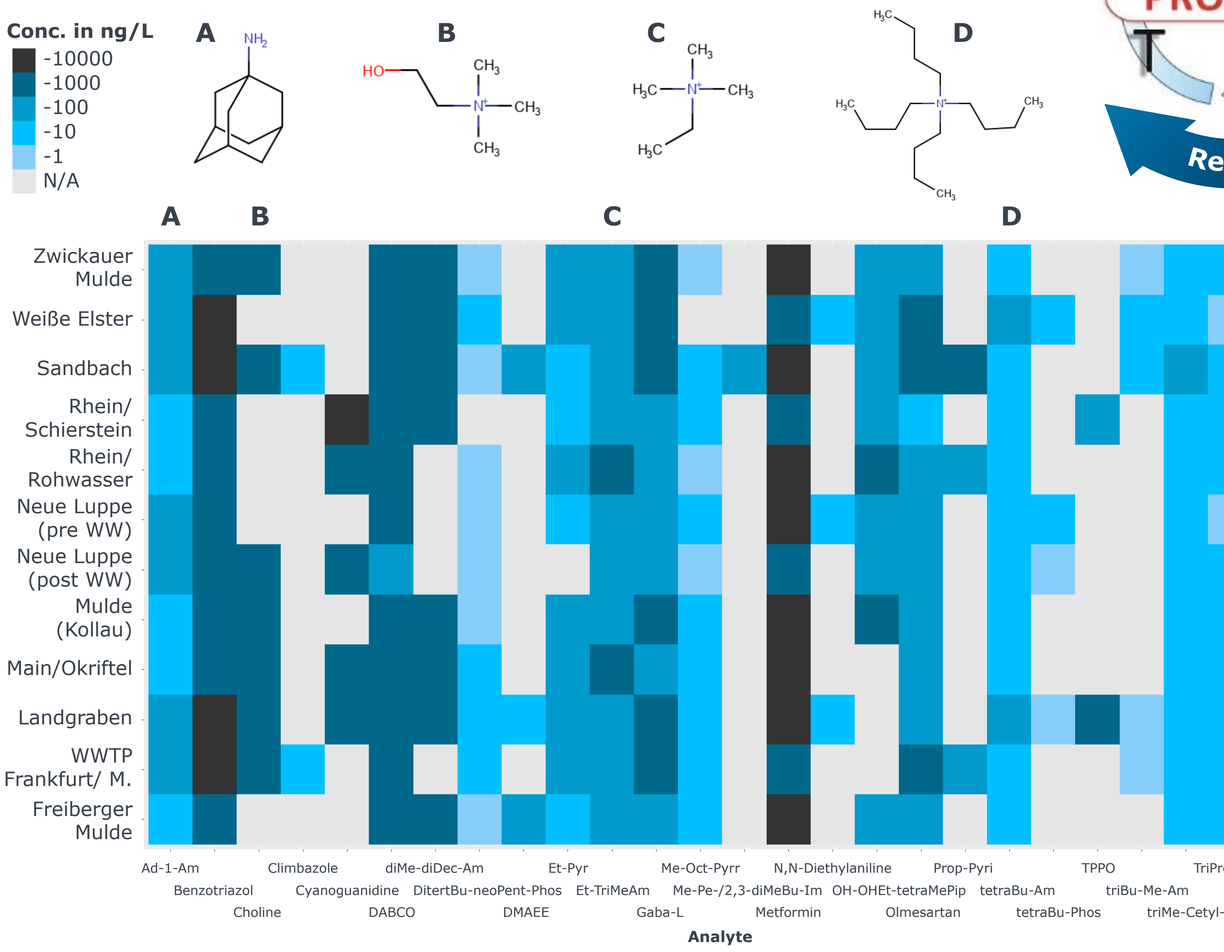
Conclusion

- The analytical methods used are **complementary** to each other (maximum intersection 34%), may partially be caused by differences in data treatment
  - Total **202 detected suspects** (**55 ionic liquids)**, of which 137 were compared to reference standards
    - **43** were already **confirmed** (ongoing work)
- **More than half** of identified substances are **not yet known** as environmental contaminant or only **scarcely investigated** in environmental samples, many of them were **ionic liquids**
- Besides the known ones (benzotriazole, metformin, nitrobenzenesulfonic acid), PF_6^- was **ubiquitously detected** in the 0.1 µg/L range or above



- Suspect list had to be compiled from several prioritization approaches [4-8]
- Including extensive literature research for ionic liquids [9]
- Selected suspects differ significantly from regularly monitored substances in logD and MW
- Few regularly monitored substances are mobile or very mobile and none fall into the analytical gap
- Suspects above min. logD of 4 are predominantly attributed to proposed PM(T) precursors





- Heatmap of all identified substances in positive and negative ESI that were compared to a reference standard
- concentration estimation was performed based on a standard mixture
- Well-kown environmental contaminants were included as markers for positive control

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