Quaternary phosphonium compounds: new toxic compounds present in sediments and suspended matter

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Introduction: The contamination of water bodies with a multitude of emerging contaminants is one of the key problems facing water management today.[1] Although most of these contaminants are present at low concentrations, many of them raise considerable (eco)toxicological concerns, particularly because they are present in complex mixtures. One powerful tool to detect and identify emerging organic contaminants in the environment is nontarget analysis.[2] This technique covers all substances that are accessible with the chosen analytical detection method. For polar surface water contaminants the usage of LC-HRMS systems is currently seen as most powerful approach.[3]

Methods: A non-target method was established for the analysis of daily-composite water samples taken over a time span of 14 months from the river Rhine at Koblenz. For mass spectrometric detection a SCIEX (TripleToF 5600, Darmstadt, Germany) hybrid quadrupole time of flight mass spectrometer (QToF) system equipped with a DuoSpray ion source and a TurboIonSprayTM probe for ESI experiments was used in positive and negative ionization mode. Furthermore, a target method was developed and validated for 25 quaternary phosphonium compounds (QPCs) and derived phosphine oxides (POs).

Sediment from the river Rhine near Ehrenbreitstein was used for an aerobic degradation experiment with four quaternary phosphonium compounds (QPCs) to investigate their biological degradation.

Results: By fragmentation experiments, chemical data bank searches and eventually a confirmation with authentic standards, five QPCs were identified for the first time as new contaminants occurring in German rivers and streams. These compounds are used worldwide by the chemical industry to synthesize alkenes via Wittig reaction.[4] Point emissions from the chemical industry are therefore probably responsible for contamination of the rivers. To investigate the overall occurrence and fate of 25 quaternary phosphonium compounds (QPCs) in the aquatic environment, water, suspended solids and sediments from the rivers Rhine and Elbe were analyzed, as well as samples from tributaries bearing significant loads of QPCs. The quaternary phosphonium compound tetrabutylphosphonium (Bu_4P^+) e.g. was detected in the river Elbe with concentrations up to 1000 µg/kg (sediment). Analysis of a time series of suspended solids (2005-2015) showed that QPCs have been present in the Elbe and Rhine catchment for at least one decade, with partly rising tendency. A degradation experiment with Rhine sediment revealed that triphenylphosphonium compounds ($R\text{-}Ph_3P^+$) and Bu_4P^+ are persistent in contact with sediment and suspended solids and tend to sorb onto sediment particles. Despite having data from “only” German rivers and streams, we assume that with the analytical method described, QPCs could be found in streams of other industrial nations as well due to their relevance in Wittig-type reactions and as phase transfer catalysts.

Discussion: Several biological studies attest that QPCs are able to penetrate double layer lipid membranes, although under the given distribution experiment conditions hydrophilic properties seem to dominate their behavior.[5] However, toxicological studies (determination of cytotoxicity, Ames test, Micronucleus test) showed that all investigated phosphonium compounds exhibited (baseline) cytotoxicity and $MeOCarbMe\text{-}Ph_3P^+$, Bu_4P^+, $MeOMe\text{-}Ph_3P^+$ and Ph_3PO genotoxic potential at elevated concentrations, which emphasizes the need for an emission regulation of these compounds. Due to (partly) high concentrations of QPCs in surface water and/or sediment, drinking water should be investigated to ensure that critical concentrations are not exceeded.

References: [1] Krauss, et al., *Anal. Bioanal. Chem.* **2010,** *397*, (3), 943-951. [2] Schymanski, et al, *Anal. Bioanal. Chem.* **2015**, 1-19. [3] Schlüsener et al. (2015), *Environ. Sci. Technol.* ***49***, 14282–14291. [4] Pommer, *Angew. Chem. Int. Ed. Engl.* **1977**, *16* (7), 423-429. [5] Brand et al, (2018), Water Research, 136, 207-219.