Analytical methods for emerging contaminants: advanced tools to understand environmental and technical processes.

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Emerging contaminants such as UV-stabilizers, biocides, industrial chemicals, pharmaceuticals, hormones or household chemicals are omnipresent in treated wastewater, since they are only partially removed during processes of industrial and municipal wastewater treatment plants. Furthermore, many chemicals are directly released by technical products in contact with water. Due to the improvement of advanced analytical methods based on mass spectrometry coupled to LC, GC or IC, a wide range of extremely polar to very lipophilic compounds can be identified and quantified in all kinds of matrices, such as wastewater, surface water, soil, sediments or biota down to a few ng/L and ng/g range. Individual groups, such as hormones, can even be quantified in the lower pg/L range. Furthermore, it has to be noted that biological and chemical degradation does not lead to a mineralization, but rather to the formation of a multitude of transformation products, which have frequently not been known before. The transformation products and transformation pathways elucidated are extremely helpful to understand the technical and environmental processes occurring and to implement measures for their improvement. A couple of examples will be presented in the lecture to highlight the capabilities of advanced analytical techniques to identify and quantify emerging contaminants including transformation products.

For instance, a novel approach for assessing the leaching of emerging contaminants from polyurethane (PU) and epoxide coatings used in hydraulic structures will be presented. Based on MS^2 spectra from LC-QTOF-MS measurements, a variety of 31 substances released from PU coatings were tentatively identified. These substances belong to four chemical groups: derivatives of i) p-toluenesulfonyl, ii) 4,4′-methylenediphenyldiisocyanate (4,4′-MDI), iii) toluene diisocyanate (TDI) and iv) poly(ethylene carbonate) ($[C_2H_4O]_n$). The longer the hardening duration the lower were the losses of compounds used for polymerization.
Another example is the development of a non-target and target methods to analyze water samples taken from the River Rhine as well as form the Elbe. A hybrid quadrupole time of flight mass spectrometer (QToF) system equipped with a DuoSpray ion source and a TurboIonSpray probe for ESI experiments was used in positive and negative ion mode. By fragmentation experiments, chemical data bank searches and confirmation with authentic standards quaternary phosphonium compounds (QPC) such as triphenyl methoxymethyl phosphonium were identified for the first time as new contaminants occurring in German rivers and streams. OPCs are used worldwide by the chemical industry to synthesize alkenes via the Wittig reaction and have already been present in the aquatic environment for at least the last decade. In addition to the Wittig QPCs another quaternary phosphonium compound, tetrabutylphosphonium, was detected in the River Elbe with concentrations up to 1000 µg/kg (sediment). Tetrabutylphosphonium is mainly used as phase transfer catalyst during polymerization. Thus, in addition to regulated compounds, many other emerging chemicals of concern are present in environmental matrices resulting from technical processes and chemical synthesis.