Identification of emerging pollutants in the environment

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Introduction:

With the increasing production volume, organic chemicals are continuously discharged into the environment through various routes. Due to the regulatory scrutiny of the currently applied chemicals, the application of new alternative products has led to the release of new compounds into the environment. The unknown pollutants including byproducts, transformation products which might possess higher toxicity than the main products or their precursors. Therefore, the coexistence of the resultant environmental contaminations and emerging pollutants has become a rising concern and have attracted increasing attention. Recently we have focused on the investigation of emerging pollutants using both the targeted or non-targeted analysis. On one hand, we have developed sample-preparation method, including extraction, concentration, clean-up and derivatization for the investigation of new persistent organic pollutants (POPs). On the other hand, we have also applied high-resolution mass spectrometry to identify previous unknown emerging contaminants.

Results and discussion

New POPs

We have established a method for isotope dilution-high resolution gas chromatography-high resolution mass spectrometry for the determination of polybrominated diphenol ethers (PBDEs) in multiple environmental compartments. The characteristics of the distribution of contaminated PBDEs in activated sludge of sewage treatment plants (STPs) was investigated.[1] The metabolic debromination and elimination of PBDEs in the aquatic species was observed. To screen the bioindicators of new POPs, we have determined the PBDEs in Mollusks. We unveiled that Ost and Myt could be applied as bioindicators of PBDEs.[2] Concentrations of PBDEs showed the negative correlation with the TL of the selected mollusks.

Due to their unique properties, perfluorinated compounds (PFCs) has been widely applied in a wide spectrum of applications, including polymers, textile coatings, food packaging, and firefighting foams etc..[3, 4] Via the monitoring of the concentrations of PFCs in the ambient environment near an industrial manufacturing plant, we found that only perfluorooctanesulfonate (PFOS) and perfluorooctanoic acid (PFOA), and perfluorohexane sulfonate (PFHxS) occurred in the samples, including abiotic and biotic ones.[5] We have for the first time measured PFCs in samples of whole human blood collected in China. We observed that PFOS and PFHxS in males were higher than that in females and PFOS was the most abundant PFCs followed by PFHxS.[6]

To investigate the occupational exposure pathway to PFC isomers, we have then analyzed the concentrations of PFCs in indoor dust, total suspended particles (TSP), diet, and drinking water samples and human serum and urine samples. According to the concentrations of PFCs in the serum and urine of occupational workers, we found that the proportions of PFCs in the serum were higher than the that in urine. Branched PFAA isomers could be cleared by the renal route more rapidly than did their linear counterparts. Molecular docking modeling implied that linear

PFCs showed a stronger potential to interact with human serum albumin than branched isomers did which might explain the proportions of linear PFOS in the serum.[7]

Under oxidative conditions in the environment, precursors of PFCs might be a possible source for the occurrence of certain polyfluorinated alcohols, aldehydes, and carboxylic acid derivatives. We have identified a group of volatile PFCs, including four perfluorinated iodine alkanes (FIAs) and three polyfluorinated telomer iodides in the environment. A wide range of concentration of FIAs in the ambient air near the manufacturing plant has been detected. However, most of these PFIs were below detection limits regarding surface soils, suggesting that PFIs are more prone to release into the atmospheric compartments easily.[8] F-53B, as an alternative to PFOS, is A 6:2 chlorinated polyfluorinated ether sulfonate (6:2 Cl-PFAES). As the environmental behaviors and potential adverse effects of the 6:2 Cl-PFAES is not fully understood, we have applied high resolution mass spectrometry to determine the occurrence and distribution of perfluorobutane, perfluorohexane, perfluorooctane, and perfluorodecanesulfonates, 6:2 and 8:2 FTSAs, and the emerging 6:2 Cl-PFAES in municipal sewage sludge samples.[9] We identified 8:2 and 10:2 Cl-PFAESs as the emerging polyfluorinated contaminants. Using the commercial and custom-purified standards, we measure the concentrations of these fluorinated agents. 8:2 Cl-PFAES showed higher hydrophobicity and showed increased capacity in the sorption in the sludge.[9] We then evaluated the susceptibility of Cl-6:2 PFESA to reductive dehalogenation and identified a hydrogen-substituted polyfluoroalkyl ether sulfonate (1H-6:2 PFESA) as the predominant product. This is also the first to report on the occurrence of the polyfluoroalkyl sulfonates in the environment.[10]

Chlorinated paraffins (CPs), as halogenated contaminants in the environment, showed very high complexity. The coexistence of media chain CPs (MCCPs) and short chain CPs (SCCPs) in CP industrial products indicated that SCCPs are difficult to be controlled without the regulatory control of MCCPs.[11] Because CPs can not be separated by chromatography, which also generated the same mass/ charge ratio, it is difficult to determine the concentrations of CPs in the environment.[12] We have started the studies on short chain CPs at 2011 and found that effluents from STP were important sources where SCCPs released to the ambient environment and wastewater. Lower chlorinated (C5-6) and shorter chain (C10-12) congeners tend to migrate to deeper soil layers comparing to their longer chain counterpart. High bioaccumulation of SCCPs was detected in the sampled aquatic species and SCCPs.[13] We have investigated the concentrations of SCCPs collected from the surface sediments and sediment cores collected from the East China Sea to study their environmental behavior. The C10 homologue was the most predominant carbon chain group, followed by C11, C12, and C13 homologue groups. Significant linear relationship was found between total organic carbon (TOC) and total SCCP concentrations ($R\text{-}2 = 0.51$, $p < 0.05$). Although possessing a decreasing trend along with the distance from the coast was, we observed the highest value in a distal mud area far away from the land. Spatial distributions and correlation analysis indicated that TOC, riverine input, ocean current, and atmospheric deposition was deeply involved in the controlling of the distribution of in sediments. We demonstrated that SCCPs are being distributed by long-range atmospheric or ocean current transport.[14] However, SCCPs did not biomagnify in mollusks collected from the Chinese Bohai Sea.[11] We have reported data on the human exposure to CPs. With human placentas as target samples, SCCPs were positively detected in all the samples. A significant positive correlation between the SCCPs and MCCPs concentrations was observed.[15] MCCPs might decompose into SCCPs through environmental chemical processes that result in a breakdown of carbon-carbon bond or dechlorination. These processes include multiple degradation pathways such as ultraviolet radiation exposure, ozone oxidation, and chlorine disinfection. Collectively, the MCCPs fraction in CPs products are expected to increase worldwide, and the emission of MCCPs to the environment will likely increase in the near future.[11]

Emerging novel pollutants

Tetrabromobisphenol A (TBBPA) has been widely used as additives in industrial products as flame retardants. as the most widely used brominated flame retardants (BFRs).[16] Using effect-directed analysis, we have identified TBBPA bis (allyl) ether (TBBPA BAE) was the main toxicant in real environmental samples collected near a BFR manufacturing plant.[17] We have developed methods based on liquid chromatography coupled with tandem mass spectrometry (LC-MS/MS) and liquid chromatography coupled with quadrupole time-of-flight mass spectrometry (LC-QTOF-MS) to determine TBBPA BAE levels in the samples. Our findings showed that derivatives of TBBPA were present in various environmental compartments. Through the elucidation of mass spectrum, the byproducts of TBBPA derivatives, TBBPA mono(allyl ether)(TBBPA MAE) and (TBBPA-MAE), TBBPA mono(2-bromoallyl ether)(TBBPA-MBAE) were identified in the technical products.[18] Via the analysis of environmental samples including soil, sediments and mollusks, we confirmed the occurrence of these contaminants in samples. The detection frequencies of TBBPA MAE and TBBPA MDBPE in mollusks collected from the Chinese Bohai Sea ranged from 41% and 32%, respectively.[18] The distribution patterns and trophic transfer properties of TBBPA/S and analogs in various biological samples collected from the Chinese Bohai Sea were then investigated. TBBPA/S analogs displayed detection frequencies higher than 86% and showed a trophic dilution tendency. The occurrence of these novel TBBPA-MAE, TBBPA-MBAE, TBBPA-MDBPE, TBBPS-MAE, TBBPS-MBAE, and TBBPS-MDBPE could occur not only as byproducts, but also as the degradation or transformation products of commercial industrial TBBPA/S derivatives.[19] We firstly identified series of novel transformation products. Ether bond breakage and debromination have been demonstrated to contribute to the transformation of TBBPA derivatives and the existence of the novel transformation products was identified.[20] We have identified other new BFRs in the environment. For instance, we have identified hexabrominated heterocyclic tris-(2,3-dibromopropyl) isocyanurate (TBC) in the natural environment.[21] Similar to TBBPA derivatives, in mollusks, trophic dilution trend TBCs in the aquatic food chains was observed.[22]

Photoinitiators (PIs) are widely used additives in the industrial polymerization process, the contamination of which through migration into foodstuffs has been subjected to increasing public scrutiny. Our results demonstrated the existence of the novel PIs in products including UV curable resins and food contact materials, as well as indoor dust and sewage sludge samples. Analysis of physical-chemical properties of PIs showed that the overall persistent half-lives for the PI contaminants were up to 500 days, indicating a potential regional distribution of these chemicals once released from the contaminated site.[23] Synthetic phenolic antioxidants (SPAs) belongs to another group of frequently applied additive chemicals. We identified the existence of SPAs in STP samples. Among the 12 frequently used SPAs and metabolites, 11 SPAs were positively detected. We identified 8 novel SPA compounds for the first time in the environment. BHT, 4-tert-octylphenol (4-tOP), and 2,4,6-tri-tert-bultylphenol (AO 246) were the most abundant in the samples.[24]

We have observed the occurrence of hexachlorobutadiene (HCBD) in the sewage sludge from 37 WWTP collected from 23 cities for the first time. The risk assessment of HCBD was performed based on the concentrations detected in soil and plant. We identified the occurence of HCBD in sludge sample. Levels of HCBD were not correlated with the capacity of the WWTPs and total organic carbon.[25] We have determined the occurrence of PCNs in stack gas and fly ash samples collected from 13 typical iron foundry plants. We evaluated the emission factors of PCNs and the average mass emission factors of PCNs were 44 μg/t.[26] Successive reductions in the abundance of homologues were observed to occur with the increase in chlorine substituted

numbers. The levels of congeners containing more beta-position chlorines were higher than those containing more alpha-position chlorines implicated the preference of beta-positions for chlorination.[26]

Taken together, our investigation provided new insights into the emerging pollutants in environmental compartments. Although these contaminants, especially new pollutants, have been identified in various types of environmental compartment, nontargeted analysis and identification strategies warrant further optimization for the finding of these products.

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