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Identification of Fluorinated Methylsiloxanes in Environmental Matrices Near a Manufacturing Plant in Eastern China

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Abstract : Recently, replacing some of the methyl groups in polydimethylsiloxanes with other functional groups has been extensively explored to obtain modified polymethylsiloxanes with special properties that enable new industrial applications. Fluorinated polysiloxanes, one type of these modified polysiloxanes, are based on a siloxane backbone with fluorinated groups attached to the side chains of polysiloxanes. As a commercially significant material, poly[methyl(trifluoropropyl)siloxane] (PMTFPS) has sufficient fluorine content to be useful as a fuel-and oil-resistant elastomer, which combines both the chemical and solvent resistance of fluorocarbons and the wide temperature range applicability of organosilicones. PMTFPS products can be used in many applications in which resistance to fuel, oils and hydrocarbon solvents is required, including use as lubricants in bearings, sealants, and elastomers for aerospace and automotive fuel systems. Fluorinated methylsiloxanes, a type of modified methylsiloxane, include tris(trifluoropropyl)trimethylcyclotrisiloxane (D3F) and tetrakis(trifluoropropyl)tetramethylcyclotetrasiloxane (D4F), both of which contain trifluoropropyl groups in the side chains of cyclic methylsiloxanes. D3F, as an important monomer in the manufacture of PMTFPS, is often present as an impurity in PMTFPS. In addition, the synthesis of PMTFPS from D3F could form other fluorinated methylsiloxanes with low molecular weights (such as D4F). The yearly demand and production volumes of D3F increased rapidly all over world. Fluorinated methylsiloxanes might be released into the environment via different pathways during the production and application of PMTFPS. However, there is a lack of data concerning the emission, environmental occurrence and potential environmental impacts of fluorinated methylsiloxanes. Here, we report fluorinated methylsiloxanes (D3F and D4F) in surface water and sediment samples collected near a fluorinated methylsiloxane manufacturing plant in Weihai, China. The concentrations of D3F and D4F in surface water ranged from 3.29 to 291 ng/L and from 7.02 to 168 ng/L, respectively. The concentrations of D3F and D4F in sediment ranged from 11.8 to 5478 ng/g and from 17.2 to 6277 ng/g, respectively. In simulation experiment, the half-lives of D3F and D4F at different pH values (5.2, 6.4, 7.2, 8.3 and 9.2) varied from 80.6 to 154 h and from 267 to 533 h respectively. $CF_3(CH_2)_2MeSi(OH)_2$ was identified as one of the main hydrolysis products of fluorinated methylsiloxanes. It was also detected in the river samples at concentrations of 72.1-182.9 ng/L. In addition, the slow rearrangement of D3F (spiked concentration = 500 ng/L) to D4F (concentration = 11.0-22.7 ng/L) was also found during 336h hydrolysis experiment.

Keywords : fluorinated methylsiloxanes, environmental matrices, hydrolysis, sediment
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