



Homologue specific analysis of a polyether trisiloxane surfactant in German surface waters and study on its hydrolysis



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ABSTRACT

The occurrence of a polyether trisiloxane surfactant in the ng L^{-1} range in German surface waters is reported for the first time. The studied surfactant does not ubiquitously occur in the aquatic environment but can reach surface waters on a local scale. As a first step towards the understanding of the environmental fate, the hydrolysis was studied according to the OECD guideline 111. It confirmed that the trisiloxane surfactant is sensitive to hydrolysis and that the hydrolysis rate strongly depends on the pH and the temperature. If one takes only into account the hydrolysis, the trisiloxane surfactant could persist several weeks in river water (the half-life in water is approximately 50 days at pH 7, 25 °C, and an initial concentration of 2 mg L^{-1}). A degradation product, more polar than the initial trisiloxane surfactant, was identified by high resolution mass spectrometry.

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1. Introduction

With 236,000 tons produced in North America in 2009 (Oxford Economics for the Silicones Environmental, Health and Safety Council of North America, 2010), silicones are an important category of chemicals, represented in every segment of our every day life. Food, drugs, construction materials or personal care products contain silicones (Andriot et al., 2007). This widespread use raises the question of their environmental impact. The assessment of the environmental impact of silicones is a substantial task because of the variety of compounds. The name “silicone” refers to all chemical substances in which silicon atoms are linked via oxygen atoms, each silicon bearing one or several organic groups (Moretto et al., 2000). Three categories of silicones have been suggested to have noteworthy environmental loading (Fig. 1): volatile methylsiloxanes (VMS), polydimethylsiloxanes (PDMS), and polyethermethylsiloxanes (PEMS) (Allen et al., 1997).

The two former categories, VMS and PDMS, have been studied extensively (Graiver et al., 2003; Wang et al., 2013), but the knowledge on the environmental occurrence and fate of PEMS is lacking (Powell and Carpenter, 1997). The aim of this paper is to fill this lack with a study of the occurrence and fate of PEMS in the aquatic environment. In particular, we target one trisiloxane

surfactant (CAS: 27306-78-1) ($x = 1, y = 0, 4 < n < 12, m = 0, R = \text{CH}_3$), denoted $\text{MD}'(\text{EO}_n\text{-Ome})\text{M}$. M stands for $\text{Me}_3\text{SiO}_{1/2}$, D' for $\text{Me}(\text{R}')\text{SiO}$, and EO for $\text{CH}_2\text{CH}_2\text{O}$. Trisiloxane surfactants are increasingly used in different sectors and recent studies raised concern about their effects on non-target organisms: trisiloxane surfactants have been found to be toxic to mites (Cowles et al., 2000) and to disturb the olfactory learning of honey bees (Ciarlo et al., 2012), one of the multiple potential factors considered in regard to honey bees colony loss.

$\text{MD}'(\text{EO}_n\text{-Ome})\text{M}$ can enter the environment through various routes. It is used as an adjuvant for pesticides because it improves the activity and the rainfastness of pesticides (Venzmer, 2011). When spread on fields, $\text{MD}'(\text{EO}_n\text{-Ome})\text{M}$ may reach the soil compartment and could reach natural waters by leaching or runoff. Another possible route for $\text{MD}'(\text{EO}_n\text{-Ome})\text{M}$ to enter the environment is via the disposal of personal care products containing $\text{MD}'(\text{EO}_n\text{-Ome})\text{M}$ (Floyd, 1999). After use, they are discharged to wastewaters and $\text{MD}'(\text{EO}_n\text{-Ome})\text{M}$ reaches wastewater treatment plants (WWTPs). If the elimination in WWTPs is not complete, $\text{MD}'(\text{EO}_n\text{-Ome})\text{M}$ could reach natural waters via WWTP effluents. Also other entry routes to the aquatic environment can be hypothesized: accidental contamination or improper disposal of wastewaters coming from the washing of pesticide tanks. Once in the environment, the partitioning of $\text{MD}'(\text{EO}_n\text{-Ome})\text{M}$ depends on its physico-chemical properties. Hydrophilicity is frequently associated with mobility and preferential partition to the water phase in the environment (Food and Agriculture Organization of the United

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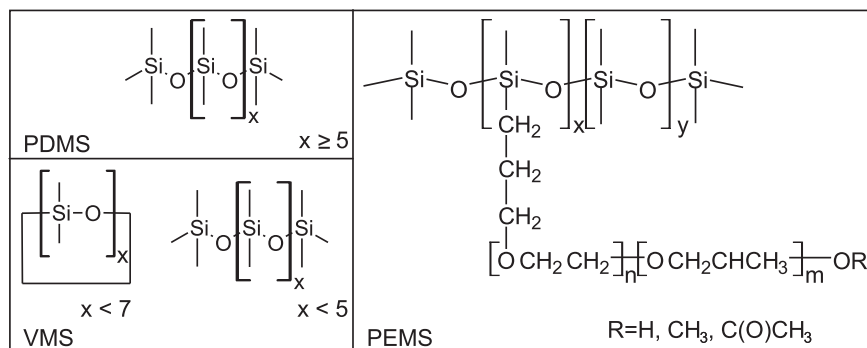


Fig. 1. Chemical structures of the silicones considered to have noteworthy environmental loading.

Nations, 1989). With a short hydrophobic part (three silicons) and a highly hydrophilic organic moiety (no polyoxypropylene groups), MD'(EO_n-OMe)M is one of the most hydrophilic PEMS. Based on the expected entry routes to the environment and its hydrophilicity, MD'(EO_n-OMe)M is expected to reach the aquatic environment.

In the aquatic environment, hydrolysis is thought to be an important elimination mechanism. This hypothesis is based on several studies showing that trisiloxane surfactants are sensitive to hydrolysis. However, most of those studies have been focused on the stability in pesticide formulations, under acidic conditions, and at high concentrations (Knoche et al., 1991; Radulovic et al., 2009, 2010). Moreover, the hydrolysis has been investigated by measuring the evolution of surface tension over time, but since nothing is known on the surface activity of the by-products and degradation products, those measurements are not specific and could have led to a wrong interpretation of the results.

Regarding the toxicity of trisiloxane surfactants to the aquatic environment, data are scarce and only the acute toxicity has been investigated. The LC₅₀ values of one trisiloxane surfactant (MD'(EO_n-OAc)M) ($m = 0$, $R = \text{C(O)CH}_3$) have been determined for an aquatic invertebrate (41 mg L⁻¹ for the water flea, *Daphnia magna*) and for a fish (4 mg L⁻¹ for fathead minnow, *Pimphales promelas*) (Powell and Carpenter, 1997). To the best of our knowledge, no data are available for MD'(EO_n-OMe)M.

Generally speaking, the knowledge on the environmental occurrence, fate and toxicity of trisiloxane surfactants is scarce. The aim of this paper is to provide the first measurements of a trisiloxane surfactant in surface waters, to investigate the importance of hydrolysis as an elimination mechanism from the aquatic environment and to provide a tentative identification of degradation products by high resolution mass spectrometry.

2. Experimental

2.1. Chemicals and standards

Reference substance of the trisiloxane surfactant was purchased from ABCR (Karlsruhe, Germany). Stock solutions were prepared at 11 g L⁻¹, 1 g L⁻¹, 10 mg L⁻¹, 1 mg L⁻¹, and 0.1 mg L⁻¹ (total surfactant concentration) in methanol and were stored at -18 °C. The alkylphenol ethoxylate (Triton™ X-100 laboratory grade, average molecular weight: 625 g mol⁻¹) was obtained from Sigma-Aldrich (Steinheim, Germany). All organic solvents used for the analysis were HPLC-grade. Their purity was at least 99.8%. Methanol and dichloromethane were provided by Carl Roth GmbH (Karlsruhe, Germany), tetrahydrofurane and isopropanol were purchased from Merck (Darmstadt, Germany) and acetonitrile was obtained from Scharlau S.L. (Sentmenat, Spain). Ultrapure water was produced by an Arium 611 UV laboratory water purification system from Sartorius (Göttingen, Germany). Ammonium acetate was purchased from Fluka (Steinheim, Germany, purity > 98.0%), sodium hydroxide, potassium chloride, potassium dihydrogen phosphate, boric acid, and calcium chloride were obtained from Merck (Darmstadt, Germany) and had a purity of minimum 99%. All glassware was treated in a pyrolysis oven (model LHT6/120 from Carbolite (Hope Valley, United Kingdom) at 550 °C for 60 min before use.

2.2. Sample preparation and analysis by liquid chromatography–mass spectrometry

The sample enrichment and the analysis by HPLC-ESI-MS/MS were performed according to Michel et al. (2012). Briefly, the sample was extracted by liquid–liquid extraction with dichloromethane, the extract was blown down to dryness and reconstituted with 300 μL of a mixture of 80% ACN/10% MeOH/10% THF 10 mM ammonium acetate and 200 μL aqueous 10 mM ammonium acetate solution. The HPLC unit is a 1200 HPLC system (Agilent Technologies, Waldbronn, Germany) equipped with a solvent cabinet, a micro vacuum degasser, a binary pump, a high-performance autosampler with 54 vial plates and a temperature controlled column compartment. The separation was carried out on a PolymerX C18 (250 mm × 4.6 mm i.d., 5 μm, 100 Å) from Phenomenex with a flow rate of 800 μL min⁻¹. The eluents were: A: a quaternary mixture including 40% of aqueous 10 mM ammonium acetate solution, 48% ACN, 6% THF, and 6% MeOH and B: THF. The gradient started with 100% of eluent A over 8 min, decreased to 40% over 16 min and was held for 3 min before going back to 100%. The detection was achieved with a triple quadrupole mass spectrometer API 4000 Q-Trap (Applied Biosystems/MDS Sciex Instruments, Concord, Canada) equipped with an ESI source and used in multiple reaction monitoring (MRM) mode. The mass spectrometer was operated in positive ionization mode and silicone surfactants were detected as ammonium adducts. Data acquisition was performed with the Analyst software (version 1.5.1). An extracted ion chromatogram was generated for every homologue and the area obtained by integration of the peak was used for quantification.

2.3. Sampling method

The sample collection procedure followed the DIN standard 38402-15 (Deutsches Institut für Normung, 2010). Due to their structures, surfactant molecules tend to accumulate at boundary layers: water/air or water/sediments (González-Mazo et al., 2003; Knepper et al., 2003; Van der Linden, 1992). Special care was therefore taken not to sample the water/air surface and not to change the suspended solids fraction around the sampling point, for instance by moving the bottom sediments. Samples were taken approximately at 20 cm from the surface by introducing the bottle upside down in the water and by inverting it at 20 cm depth, allowing the water to flow in. The bottles were filled without headspace and were immediately stored in an ice-box. Generally speaking, it was avoided to collect samples where the water quality was not typical of the water body (close to the river side, in stagnant zones, or, generally, in any zone where the water is non-homogeneous). To fulfill this requirement, the samples were taken directly in the middle of the water bed when possible or at least 3 m away from the river bank by using a 3 m long arm. After arrival in the lab, the samples were stored at 4 °C and were analyzed within a week. The stability of MD'(EO_n-OMe)M during storage of river water samples was tested by analyzing one Neckar sample (Esslingen (10), 16.07.12, Table 1 and Fig. 2) directly after arrival in the lab and after one week of storage. For all homologues, the two determined concentrations were not significantly different (4.1 ± 0.1 ng L⁻¹ and 4.2 ± 0.2 ng L⁻¹ for example for the homologue $n = 7$), indicating that no significant degradation occurs in this time scale under the applied storage conditions.

2.4. Quality control

2.4.1. Calibration blanks

Every sequence of environmental samples began with two direct injections of deionized water to check the absence of contamination in the solvents or in the HPLC-MS/MS system. A blank sample (direct injection of deionized-water) was also always run after the calibration to verify that no memory effect occurred. The absence of peak in any of the blanks confirms the absence of contamination and memory effect in the HPLC-MS/MS system.

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