Trisiloxane surfactants: trace analysis in the aquatic environment and first insight into their environmental behaviour


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Introduction
Thanks to their adaptability and their high efficiency compared to traditional carbon based surfactants, silicone surfactants are a success in many different applications, from pesticides to cosmetics, polyurethane foam production, textile industry or car care products [1]. In spite of those numerous applications, no analytical method existed for their determination in environmental samples and no data were available regarding their environmental occurrence and fate. After developing and validating the first method for the trace analysis of trisiloxane surfactants in surface waters, we aim at understanding the environmental behaviour and fate of those compounds. For that purpose the analytical method is applied to the screening of environmental samples and to a lysimeter study, which will help us to understand the behaviour of trisiloxane surfactants on soil.

Our project focuses on trisiloxane surfactants, made of a siloxane backbone with three silicon atoms, and a polyethylene oxide moiety. Those compounds are used as agricultural adjuvants to enhance the activity and the rainfastness of the active substance. They are often referred as superspreaders or superwetters, because of their ability to promote rapid spreading on hydrophobic surfaces [2]. This effect is illustrated in Figure 1, together with the chemical structure of the two target substances.

Figure 1: A: Spreading of water (up) and water with 0.1% of trisiloxane surfactant (down) on a leaf. B: Chemical structure of the two targeted trisiloxane surfactants.
As a first requirement for further studies, we have developed and validated a method for the trace analysis of trisiloxane surfactants in surface waters. The next steps of our project are to use this new method to gain better knowledge on the environmental behaviour of trisiloxane surfactants, especially on soil, where they are directly released during application as agricultural adjuvants. For this purpose the Institut für Umwelt- und Verfahrenstechnik (UMTEC) in Rapperswil carried out a lysimeter test in collaboration with a silicone supplier. The experiment aims at following a trisiloxane surfactant and two degradation products during simulation of a heavy rainfall.

Material and method
The proposed method uses HPLC-MS/MS and liquid-liquid extraction with dichloromethane as extraction solvent. The chromatographic separation was achieved on a 1200 HPLC system from Agilent Technologies with a C18 reversed phase (PolymerX C18 from Phenomenex, 250 × 4.6 mm i.d., 5 µm particle size, 100 Å pore size). An elution gradient with a ternary mixture of organic solvents containing ammonium acetate was applied. The detection was carried out on a triple quadrupole mass spectrometer API 4000 Q-Trap from Applied Biosystems, used in MRM mode. Trisiloxanes surfactants were detected in positive ionisation mode as ammonium adducts [M-NH₄⁺].

The laboratory soil column used for the lysimeter test consisted in a cylinder of 30 cm diameter filled with sand over 75 cm height. Samplers were inserted horizontally at various depths. After application of the trisiloxane surfactant, together with two tracers (CsCl and acesulfame) on top of the column, a heavy rainfall was simulated by application of a water flux of 12.325 L/h/m². Samples were taken at different times and different horizontal positions during the experiment, and were analysed using the described method.

Results
The analytical method is based on liquid-liquid extraction and determination by HPLC-MS/MS. Limits of quantification (LOQ) are in the ng/L range and recoveries are higher than 80%. Each trisiloxane surfactant is a mixture of homologues containing different number of ethylene oxide groups (n), on average 7.5. The main hardship faced during method development was the lack of standards for individual homologues. Based on the mathematical model of a Poisson distribution, MS spectrum and NMR measurements, we developed a method which quantifies every homologue separately. This new approach is a reliable and simple way to overcome the lack of commercial standards for individual homologues of trisiloxane surfactants. Moreover the individual quantification of every homologue allows having information on the shape of the oligomeric distribution and avoids wrong estimation of the concentrations due to different response factors of the sample and the standard.
The method was applied to river water samples and one trisiloxane surfactant was detected in the Neckar River. An interesting observation is the change of the distribution centre in environmental samples. In river water samples, the centre of the distribution tends to shift to lower molecular weight homologues, probably because of differential sorption or degradation of low molecular weight homologues.

When used as agricultural adjuvants with pesticides, trisiloxane surfactants are spread on fields and reach the soil compartment. Due to their apolarity, they are not expected to leach through the soil column. However the structure identification of two degradation products with high resolution mass spectrometry (HPLC/ESI-TOF) has confirmed that the degradation products are more polar than the mother compound and could therefore undergo leaching through soil\[^{[4,5,6]}\]. We propose in our experiment to follow simultaneously the mother substance and two more polar degradation products during simulation of a heavy rainfall on sand.
Conclusion
Organosilicon materials have been cited many times during the last decades as emerging environmental contaminants \cite{7}. But one should always keep in mind that silicones are not limited to polydimethylsiloxane (PDMS) or cyclic siloxanes (D4 to D6) but also contain a broad range of different compounds with various applications and numerous physico-chemical properties. Silicone surfactants and among them trisiloxane surfactants are a good example of polar silicones. In spite of their numerous applications, no data existed on their environmental occurrence and fate. We have developed and validated the first method for the trace analysis of trisiloxane surfactants in surface waters and we apply it to get a first insight into the environmental behaviour of trisiloxane surfactants. For that purpose a laboratory soil column was used to simulate the behaviour of one trisiloxane surfactant on soil.

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References