



Mechanisms of enhanced mobilisation of trace metals by anionic surfactants in soil

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Anionic surfactants mobilise metals from soil through solubilisation of soil organic matter and direct complexation.

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ABSTRACT

Long-term applications of small concentrations of surfactants in soil via wastewater irrigation or pesticide application may enhance trace metal solubility. Mechanisms by which anionic surfactants (Aerosol 22, SDS and Biopower) affect trace metal solubility were assessed using batch, incubation and column experiments. In batch experiments on seven soils, the concentrations of Cu, Cd, Ni and Zn in the dissolved fraction of soils increased up to 100-fold at the high application rates, but increased less than 1.5-fold below the critical micelle concentration. Dissolved metal concentrations were less than 20% affected by surfactants in long-term incubations (70 days) up to the largest dose of 200 mg C kg⁻¹ soil. Leaching soil columns with A22 (100–1000 mg C L⁻¹) under unsaturated conditions increased trace metal concentrations in the leachates 2–4 fold over the control. Correlation analysis and speciation modelling showed that the increased solubility of metals upon surfactant application was more related to the solubilisation of soil organic matter from soil than to complexation of the metals with the surfactant. Organic matter from soil was solubilised in response to a decrease of solution Ca²⁺ as a result of Ca–surfactant precipitation. At environmentally relevant concentrations, surfactant application is unlikely to have a significant effect on trace metal mobility.

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1. Introduction

Commercial surfactants have long been considered a potential environmental hazard for soils and groundwater due to the large emission of those compounds (Eriksson et al., 2002). The worldwide annual consumption of surfactants was about 13.5 Mtons in 2006 (Zoller and Sosis, 2008). Emissions of surfactants to soil mainly occur through irrigation with municipal wastewater and application of sewage sludge. Other sources of surfactants in soil are the application of dispersants for oil spills cleaning (Ramachandran et al., 2004) and the application of pesticides formulations. The rising interest in reusing domestic wastewater for agricultural purposes has increased environmental concern about surfactants in soil. Surfactant concentrations in wastewater are typically <1 mg L⁻¹ but concentrations up to 70 mg L⁻¹ have been determined in greywater effluents (Wiel-Shafran et al., 2006). Schwuger (1996) determined that an anionic surfactant concentration between 13 and 27 mg kg⁻¹ can be reached in soil after 3

years of sewage sludge application. Surfactants generally have relatively short half-lives (<120 days) in soil, but limited information is available on the effects of surfactant degradation products (Eriksson et al., 2002; Ying, 2006).

Surfactants may be immobilised in soil through adsorption and/or precipitation processes. The extent of these processes depends on soil properties (e.g. carbonate and organic matter content) and also on surfactant type (Rodriguez-Cruz et al., 2005).

Surfactants in soil may alter the mobility and availability of potentially hazardous organic compounds (Mulligan et al., 2001; Hernández-Soriano et al., 2007) and of trace metals (Friedel et al., 1994; Doong et al., 1998; Turner and Xu, 2008). The effects of surfactants on the fate of trace metals is of environmental concern since metals and surfactants co-occur in wastewater and sewage sludge. The largest effects on metal mobilisation are in general observed for the anionic surfactants (Ramamurthy et al., 2008), but the mechanisms involved are poorly understood (Singh and Turner, 2009). Ryan and Gschwend (1994) proposed that hemimicelles of anionic surfactants adsorb onto the surface and release metal containing colloids from the solid phase through feeble forces (e.g. steric repulsion). Singh and Turner (2009) observed metal mobilisation by the anionic surfactant sodium dodecyl sulphate (SDS) in batch experiments with an estuarine sediment. They suggested

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that the mobilisation was due to complexation of the metals with SDS, as well as to solubilisation of soil organic matter. The anionic surfactants containing a carboxylic group (e.g. Aerosol 22) are likely more effective in metal complexation than sulfonate based surfactants, since the carboxylate group complexes metals more effectively than most other functional groups present in surfactants (Peters, 1999; do Nascimento et al., 2006). Moreover, carboxylic acids have been reported to affect the structure of organic matter and cause dispersion of humic aggregates (Oades, 1984), because they form complexes with polyvalent metal ions (mainly Ca, Mg, Al, Fe) that bridge organic materials.

The abundant literature dealing with the effect of surfactants on trace metal mobility has mostly focused on their potential for soil remediation (Doong et al., 1998; Shin and Barrington, 2005; Ramamurthy et al., 2008). These studies have, in general, shown enhanced metal mobility at large surfactant concentration, generally well above the surfactant critical micelle concentration (CMC) and there is little information regarding whether surfactants may also affect metal mobility at the environmentally relevant surfactant concentrations that are found in wastewater- or sludge-amended soils. In addition, most studies have used batch experiments (Chen et al., 2006; Ramamurthy et al., 2008) and column studies are rare (Wang and Mulligan, 2004). Column experiments include field relevant mechanisms not encountered in batch, such as biodegradation of the surfactant and rate limiting sorption and desorption reactions (Voegelin et al., 2003; Hauser et al., 2005).

The overall objective of this study is to unravel mechanisms by which surfactant affect trace metal mobility in soil. We postulate that this relates directly to the metal–surfactant complexation reactions and, indirectly, to the effects of surfactant on mobilising dissolved organic matter (DOM) from soil which also facilitates leaching. Anionic surfactants were selected for this study and their fate (sorption and precipitation) and trace metal complexation properties are studied separately. A range of soils with contrasting properties is studied in batch extraction test. A 70-d incubation test and a column study were set-up to test longer-term effects. We assessed the effects of the surfactants on the metals Cd, Cr, Cu, Ni, and Zn. However, the solution concentrations of Cd, Cr, and Ni were below detection limit for some soils. Therefore, we mainly focus on Cu (representative for metals with high affinity for organic matter) and Zn (representative for metals with moderate affinity for organic matter).

2. Material and methods

2.1. Soils and surfactants

Eight topsoils with contrasting soil properties were selected (Table 1). Total C concentrations were determined by dry combustion using a CN analyzer (VarioMax). Inorganic carbon was analyzed from the pressure increase after adding a mixture of HCl/FeSO₄ to a soil sample in a sealed container. The organic C content was calculated from the difference in total C and inorganic C. The 'total' metal concentrations were determined by aqua-regia digestion. Metal concentrations in the digests were measured by Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES, Perkin–Elmer, Optima 3300 DV). Two soil samples with certified aqua-regia extractable metal concentrations (OVAM 8 and Ter Munck) were analyzed as quality control (recovery of metals within 10% of certified values). Two internal lab standards (a polluted and an unpolluted soil) were analyzed with each digestion. These standards were verified against a soil sample with certified metal content (sewage sludge-amended soil, CRM 143 from the Central Bureau of Reference of the European Union). The recovery of the metals studied for these internal lab standards was always between 90% and 110%.

Soil Z and N are not metal contaminated. Soil K is enriched with metals from atmospheric emissions of non-ferrous smelters and soil Lo received sewage sludge application in the 1960s. Soils G, L, C and S were uncontaminated at sampling, but were spiked with Cd, Cu, and Zn in the laboratory. The soil spiking occurred by hand mixing stock solution of the metal chloride salts followed by air drying and storage.

Three anionic surfactants (Table 2), were purchased from Sigma–Aldrich (A22, SDS) or Bayer (BP) as Na-salts.

Table 1
Soils and selected properties.

Name	Location	pH ^b	OC (%)	CaCO ₃ (%)	Aqua-regia extractable metal content (mg kg ⁻¹)				
					Cd	Cr	Cu	Ni	Zn
G	Granada (Spain) ^d	7.6	1.2	24	18	6.1	246	5.8	877
L	Leuven (Belgium) ^a	7.0	0.9	0	20	24	318	11	343
	Leuven (Belgium) ^c	7.0	0.9	0	1.3	24	24	11	134
C	Cordoba (Spain) ^d	7.6	0.9	18	20	nd	351	nd	374
S	Souli (Greece) ^d	7.4	2.6	47.4	20	53	334	83	351
Z	Zegveld (The Netherlands)	4.7	23.3	0	0.9	38	70	27	191
B	Brecy (France)	7.5	1.5	17.6	3.1	54	31	109	251
K	Kruikebe (Belgium)	5.5	5.7	0	21	58	107	30	194
Lo	London (UK)	6.3	4.3	0	20	108	724	80	876

^a Soil amended with metal salts in the laboratory.

^b In CaCl₂ 0.01 M (S:L 1:10 kg L⁻¹)

^c Unspiked soil used for the column experiment; nd: not determined.

2.2. Solubility of surfactants in artificial soil solutions

Batch experiments were carried out to assess how the solubility of the anionic surfactants is affected by the presence of calcium in solution and how this affects trace metal solubility. Duplicate solutions were prepared with either A22, SDS or BP at a concentration of 300 mg C L⁻¹ (corresponding to 1 mM or 1 CMC for A22, 2.1 mM or 0.25 CMC for SDS, and circa 1.25 mM or 0.22 CMC for BP), metal salts at a concentration of 1 μM (CuCl₂, CdCl₂ and ZnCl₂) and Ca(NO₃)₂ ranging from 0 to 20 mM or NaNO₃ at 20 mM. The solutions were equilibrated on an end-over-end shaker (30 rpm) for 24 h. After centrifugation at 3000 g to remove precipitates, the solutions were analyzed for Ca, Cu, Cd and Zn by ICP-OES and for dissolved organic carbon (DOC) using a TOC-analyzer (Analytical Sciences Thermalox).

2.3. Metal complexation by surfactants

The complexation of the anionic surfactants with metals was measured under standardized conditions, using a one-step resin exchange method modified from Amery et al. (2007). In this method, Chelex is used to control the metal activities in solution at low, environmentally relevant, free ion activities. Upon addition of metal-complexing ligands (in our study, the surfactants), metal is mobilised from the Chelex resin because of complexation with the ligand. The amount of metal on the resin is however much larger than the amount of metal in solution, and the resin therefore acts as a buffer of the free metal ion activity.

Chelex-100 resin (Bio-Rad; 0.62 mmol_c g⁻¹ wet weight) was equilibrated with a solution containing metals salts and NaOH to attain equivalent Cu:Zn:Ca:Ca fractions of 0.2:0.2:0.1:0.5 and a pH of 7.0. The solution with the resin was filtered, and the resin was rinsed several times with a 0.5 mM Ca(NO₃)₂ solution and resuspended in 0.5 mM Ca(NO₃)₂. Centrifuge tubes were filled with 1 mL of this resin suspension (corresponding to 0.2 g of Chelex) and 20 mL of 0.5 mM Ca(NO₃)₂ with A22 (100, 300 or 1000 mg C L⁻¹, i.e. 0.33, 1 and 3.3 mM or CMC), BP (1000 mg C L⁻¹, i.e. circa 5 mM or 0.75 CMC) or SDS (1000 mg C L⁻¹, i.e. 7 mM or 0.84 CMC) or without surfactant (control treatment). Each treatment was carried out in duplicate. The solutions were equilibrated on an end-over-end shaker for 7 days (in the darkness at 20 °C). After equilibration, the tubes were centrifuged (3000 g, 15 min) and the pH was measured. The supernatant was sampled and analyzed for DOC. A subsample was acidified to pH 1 with HNO₃ and analyzed by ICP-OES. The metal concentrations in the control treatment were negligible (below the detection limit of 1–3 μg L⁻¹). The metal concentrations in the surfactant treatments were therefore assumed to correspond to the concentration of metal complexed by the surfactants. The free ion activities at which the resin buffered the solution, were determined by extracting the same resin with 0.5 mM Ca(NO₃)₂ and 0.1 mM NTA (nitrilotriacetic

Table 2
Selected characteristics of the anionic surfactants.

Trade name	Abbreviation	Chemical name	MW	CMC (g L ⁻¹ /g DOC L ⁻¹)
Aerosol 22	A22	Tetrasodium N (1,2-dicarboxiethyl) N-octadecyl sulfosuccinamate	653	0.65/0.31
SDS	SDS	Sodium dodecyl sulphate	288	2.38/1.19
Biopower	BP	Sodium alkyl ether sulphate	328–480	2.70/1.35

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