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HEAVY METAL AVAILABILITY IN SOIL IN THE PRESENCE OF ANIONIC SURFACTANTS

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INTRODUCTION

Contamination of soils with heavy metals (HM) is widespread and poses a long-term risk to ground water quality and ecosystem health. Anionic surfactants, which are widely used in the detergent industry, may complex metals and thus modify the fate and transport of HM in soil. Anionic surfactants reach the soil water system from different sources, such as pesticides formulations and irrigation with wastewater, which is becoming a common agricultural practice in regions with scarce water resources. Anionic surfactants in wastewater originate mainly from detergents, being the most abundant organic chemicals in municipal greywater (Abu-Zreig et al., 2003). Risk assessments and environmental regulations for polluted soils should take into account the mobility of HM in soils. In this study, we used batch extractions, to asses the effect of thee anionic surfactants on the mobility of Cd, Cu, Pb and Zn. Consecutive extractions were carried out as these can help evaluating continuous addition of surfactant to the soil.

MATERIALS AND METHODS

Two agricultural soils were sampled from the upper layer (0-25 cm) and sieved at 2 mm. The soil of Granada was amended with metal salts in the laboratory (Table 1).

Table 1. The pH, organic carbon content (OC), $CaCO_3$ content and heavy metal concentrations of the soils used

Location	Physicochemical properties			HM (mg·kg^{-1})			
	pH	OC (%)	$CaCO_3^-$ (%)	Cd	Cu	Pb	Zn
Brecy (France)	7.5	1.5	17.6	3.1	31.0	73.0	251.0
Granada (Spain)	7.8	1.2	24.9	18.0	246.0	638.0	877.0

The effect of anionic surfactants on heavy metal availability in soil was evaluated by performing batch experiments. Anionic surfactants (Table 2) were selected on the basis of their commercial interest and wide occurrence in agricultural and domestic products.

Surfactants were used at concentrations corresponding to 10 times their critical micelle concentration (CMC). The surfactant solution (pH=7.0) or milli-Q water (as control treatment) was added to the soil in solution:soil ratio of 10 l/kg in centrifuge tubes. The tubes were shaken end-over-end during 24 hours. The solution and solid phase were then separated by centrifugation. Four consecutive extractions were carried out for both soils, by replacing the supernatant with fresh aqueous surfactant solution.

Table 2. Surfactant properties

Surfactant (Abbreviation)	Trade Name	MW	CMC ($g \cdot L^{-1}$)	Molecular Formula [a]
Aerosol 22 (A22)	Tetrasodium N(1.2-dicarboxiethyl)-N-octadecyl sulfosuccinamate	653	0.65	$C_{26}H_{43}NO_{10}Na_4S$
SDS	Sodium dodecyl sulfate	288	2.38	$CH_3(CH_2)_{11}OSO_3Na$
Biopower (BP)	Sodium alkylether-sulfate	-	2.70	$RO(CH_2CH_2O)_nSO_3Na$

[a] R = linear or branched alkyl or alkenyl group containing 6 to 22 carbon atoms; n= integer of 1 to 10.

The concentration of heavy metals in the equilibrium solution was determined with ICP-AES, and the dissolved organic carbon (DOC) concentration was measured with a TOC-analyzer. The absorbance at 254 nm (A254) of the equilibrium solution was measured by UV-VIS spectrometry (Perkin-Elmer, Lambda 20, quartz cells), with a path length (b) of 1 cm. The specific UV-absorbance (SUVA, L g^{-1} cm^{-1}), a measure of relative aromaticity or the contribution of aromatic structures to DOC, was calculated as follows:

$$\mathrm{SUVA} = \frac{A^{254} \cdot 1000}{b \cdot [\mathrm{DOC}]} \quad (1)$$

Also the SUVA of the pure surfactant solutions was measured. As the surfactants have a different SUVA than the soil DOC, measurement of the SUVA allowed determining the source of DOC. All the assays were run in duplicate.

RESULTS

Concentration of the trace elements Cd, Cu, Pb and Zn in the soil solution remarkably increased in the presence of anionic surfactants for the soils studied. The three surfactants assayed showed a similar effect in the soil from Brecy (Figure 1) while for the soil amended with HM, A22 exerted larger effect than BP and SDS (Figure 2). This different behaviour may be attributed to the different origin of the HM as well as the difference in soil properties.

The first desorption step extracted most metals into solution. Nevertheless, the three next desorption steps also extracted metals in significant larger concentrations than the control treatment.

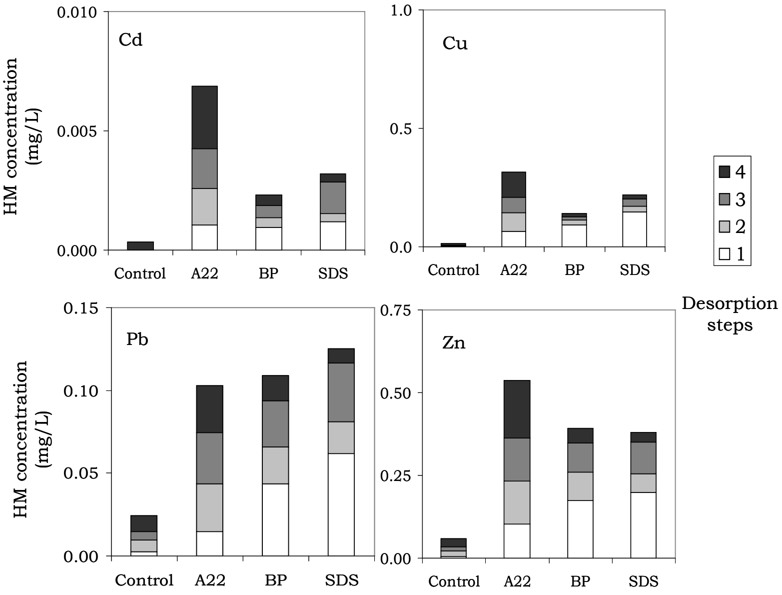

Figure 1. The concentrations of Cd, Cu, Pb and Zn in solution upon four consecutive desorption steps with anionic surfactant solutions. The control treatment was desorbed with water (Results for Brecy soil).

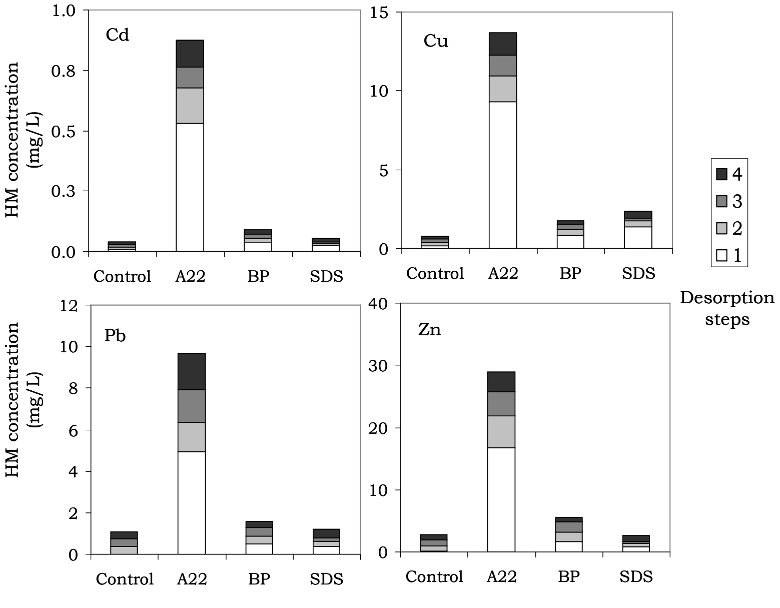

Figure 2. Idem as figure 1 (Results for Granada soil).

At high pH, heavy metals are usually strongly sorbed in soil on organic matter, oxides and clay minerals. Sorption in soil is often quantified with a solid-liquid distribution coefficient K_d, which gives the ratio of the concentration on the solid phase (s, mg/kg) to the concentration in solution (c, mg/l):

$$K_d = \frac{s}{c} \quad (2)$$

Table 2 illustrates that the K_d is indeed large in the control soil, but strongly decreases upon addition of the anionic surfactants.

Table 2. The solid:liquid distribution coefficient of the metals (Kd; in l/kg) in water (control) or in the surfactant solutions (first desorption step) (Results for Brecy soil)

	Cd	Cu	Pb	Zn
Control	>1000	338	2450	2570
A22	306	49	514	254
BP	324	34	167	145
SDS	263	21	120	129

The DOC concentrations in the surfactant solutions were very large (>3000 mg DOC L^{-1}) since the surfactants contain carbon. To assess whether soil organic matter was mobilized by addition of the surfactants, the UV absorbance of the treatment, control and pure surfactant solutions was measured. As the specific UV absorbance of the surfactants (SUVA< 0.2 L g^{-1} cm^{-1}) and of the soil organic matter (SUVA > 15 L g^{-1} $cm^{-1)}$ is very different, measurement of the UV absorbance allowed determining whether the increase in DOC in the treatments (where surfactant was added) was solely derived from the surfactant or was also partly caused by solubilization of the soil organic matter. These measurements indicated that the surfactants solubilized soil organic matter. The estimated DOC derived from soil organic matter was between 100 and 600 mg L^{-1}. The amount of soil organic matter solubilized by the surfactant decreased with increasing extraction number and was largest for the treatments with A22 (Figure 3). Yang et al. (2001) also showed that addition of surfactants may result in mobilization of organic matter.

There are several possible mechanisms that may explain the increase in heavy metal solubility upon addition of surfactant. The anionic surfactants may mobilize the metals because they form soluble complexes with the metals. The increase in heavy metal concentration may also be due to the solubilization of organic matter with which the heavy metals are complexed (Yang et al., 2001). Solubilization of carbonate minerals in which metals are coprecipitated, could also partly explain the observed increase. However, there was only a small increase in inorganic carbon concentration upon addition of the surfactants, so this is probably not an important mechanism.

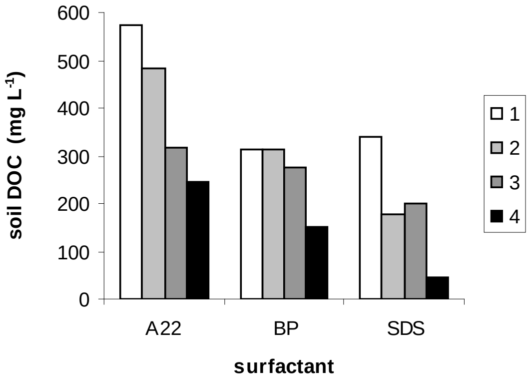

Figure 3. The amount of soil organic matter solubilized (expressed as dissolved organic carbon) in four consecutive desorption steps with anionic surfactant solutions. (Results for Brecy soil).

CONCLUSION

Significant concentrations of anionic surfactants in soil can be expected due to continuous application of these compounds, which are not easily degradable due to their large molecular weight or complex structure (Table 2). Because of their multi-ligand potential, anionic surfactants may act as chelates for HM, and thus increase their concentration in soil solution. Besides, anionic surfactants may increase the solubility of soil organic matter and thus mobilize metals that are sorbed on organic matter. We observed indeed large concentrations in metal solubility upon addition of anionic surfactants to soil.

However, the concentrations of surfactants used in this study were much larger than concentrations that may occur in the field. In an ongoing experiments, we test the effect of surfactants under more realistic conditions, in a dynamic system (soil columns) with a continuous supply of surfactant in low (field-relevant) concentrations.

REFERENCES

ABU-ZREIG M., RUDRA R.P., DICKINSON W.T. (2003). Effect of application of surfactants on hydraulic properties of soils. Biosyst. Eng. 84: 363-372.

YANG Y., RATTE D., SMETS B.F., PIGNATELLO J.J., GRASSO D. (2001). Mobilization of soil organic matter by complexing agents and implications for polycyclic aromatic hydrocarbon desorption. Chemosphere 43: 1013-1021.