Biogeosciences
Discussions

Open Access

Linking dissolved organic matter composition to metal bioavailability in agricultural soils: effect of anionic surfactants

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Abstract

The bioavailability of metals in soil is only partially explained by their partition among the solid and aqueous phase and is more related to the characterization of their speciation in the soil solution. The organic ligands in solution that largely determine metal speciation involve complex mixtures and the characterization of fluorescence components of dissolved organic matter (DOM) can identify pools of molecules that participate in metal speciation, this being essential for risk assessment. The bioavailability of Cd, Cu, Pb and Zn in three agricultural soils was examined in the laboratory to recreate irrigation with greywater enriched in anionic surfactants (Aerosol 22 and Biopower). Field capacity and saturation regimes were considered for this study. Irrigation with aqueous solutions of the anionic surfactants increased total DOM concentrations and metals in the soil solution ($Pb > Cu > Zn > Cd$). Significant correlation ($p < 0.05$) between the readily available pool of metals with the concentration of DOM was determined for Cu ($r = 0.67$), Pb ($r = 0.82$) and Zn ($r = 0.68$). However, speciation analysis performed with the software WHAM indicated that mobilisation of DOM and metals into the soluble phase resulted in a low concentration of free ion activities and promoted the formation of metal-organo complexes. The characterization of fluorescence components revealed that DOM in soil solution from soils irrigated with Aerosol 22 was enriched in a reduced quinone-like and a humic-like component. Besides, fluorescence quenching provided further evidence of metal complexation with organic ligands in solution. Hence, metal mobilization in soil irrigated with surfactant enriched greywater occurs with solubilisation of high affinity organic ligands, which substantially decreases the potential risk of metal toxicity.

1 Introduction

The evaluation of the potential impact of anionic surfactants in soil has received significant attention due to their increasing presence in the environment through agricultural and remediation practices (Cantarero et al., 2012; Hernandez-Soriano et al., 2011a; Konnecker et al., 2011). Soil irrigation with greywater in arid regions, application of sludge as organic amendment or soil flushing to remove pollutants (Sturges et al., 1992; Tsang et al., 2012) can introduce a broad range of surfactants in soil at concentrations ranging 1–70 mg L^{-1} (Wiel-Shafran et al., 2006; Hernandez-Leal et al., 2011). Besides, the average residence time of surfactants in soil varies with environmental conditions, this being also affected by potential adsorption of surfactants in soil or complexation with metal ions (Gonzalez et al., 2012; Okbah et al., 2013), and might result in surfactants accumulation at concentrations that can alter soil quality (Hernandez-Soriano et al., 2011b). Numerous studies on risk assessment have addressed the potential impact of anionic surfactants on trace metal solubilisation (Gonzalez et al., 2012; Jaworska et al., 2002; Tsang et al., 2012), which mostly occurs through direct metal complexation and soil organic matter (SOM) solubilisation (Hernandez-Soriano et al., 2011a). Metal speciation, which provides a more rational estimation of metal bioavailability than total concentrations (Chapman et al., 2012), has been often neglected in such studies. Otherwise, soil moisture content can affect metal mobilization processes and might influence the effect of anionic surfactants (Biasioli et al., 2010 and references therein).

Rigorous assessment of anionic surfactant effect on metal mobility can be approached through evaluation of changes in soil solution properties (Sauve et al., 2000). The composition of dissolved organic matter (DOM) largely determines metal speciation in solution and the characterization of organic ligands in the DOM might advance the relevance of speciation analysis. However, the chemical heterogeneity and complexity of SOM hampers such characterization (Bolan et al., 2011) and a limited number of approaches are available in the literature. For instance, the specific UV absorbance

(SUVA, $L\,g^{-1}\,cm^{-1}$) has been accepted as estimation of DOM aromaticity (Amery et al., 2008), which allows the identification of different sources of DOM in solution and can be related with the affinity of metals for DOM (Hernandez-Soriano et al., 2011a).

Novel research strategies assess SOM dynamics through the analysis of the molecular composition of SOM in specific soil functional pools. The examination of DOM characteristics by fluorescence spectroscopy has gained increasing attention during the last decades(Bolan et al., 2011; Chen et al., 2003), generally for water samples but more recently also for soil DOM (Borisover et al., 2012; Xue et al., 2012). Thus, excitation–emission matrix (EEM) fluorescence spectroscopy provides relevant information on DOM composition, indicating the presence of common pools of fluorophores (Zhou et al., 2013; Fellman et al., 2010). The fluorescence spectra provide semiquantitative information of DOM pools of different lability and presents sufficient sensitivity to examine subtle changes in the DOM composition upon changes in the soil water system.

The objectives of this work were to examine the effect of two anionic surfactants in: (1) Cu, Cd, Zn and Pb mobility, (2) the chemical speciation of such metals as predictor for metal bioavailability and (3) to relate metal speciation with changes in key properties of soil solution, with particular attention to DOM composition.

2 Material and methods

2.1 Soils characterization

The study was conducted for three agricultural soils with varying concentrations of trace metals (Table 1). Metal contamination in the soils assayed originated in atmospheric emissions from non-ferrous smelters. Total metal concentrations in soil exceeded the Dutch intervention values (CLEA, 2000) for Cd (soil S1) and Pb (soils S2 and S3). The Dutch guidelines are based on broad studies of human and ecotoxicological effects of soil contaminants and were therefore selected as reference values.

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The soil pH was measured in 0.01 M CaClR$_2$R (soil: solution ratio, 1 : 10) after shaking the soil for 1 h and settling for 30 min. The silver-thiourea method was used to measure the cation exchange capacity (CEC) and exchangeable cations were measured in this extract by ICP. The concentrations of organic C were determined by dry combustion using a CN analyzer (VarioMax). The pseudo-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). The accuracy of the method was tested using a standard reference material (sewage sludge-amended soil, CRM 143). The recovery of the metals was always between 90 and 110 %.

2.2 Soils treatments and incubation

Soils were sieved at 2 mm and air dried. Soil samples (200 g) were placed in plastic pots and irrigated with aqueous solutions of Aerosol 22 (A22, tetrasodium N(1,2-dicarboxyethyl)-N-octadecyl sulfosuccinamate) purchased from Sigma Aldrich or Biopower (BP, Sodium alkyl ether sulphate), a commercial wetting agent purchased from Bayer, corresponding to the addition of 200 mg C kg^{-1} soil day^{-1}. Soils were incubated at 25 °C in the darkness for 30 days at field capacity (FC) or saturated (ST). Irrigation with Milli-Q water at FC or ST was performed as control treatment. Moisture content was monitored and corrected to remain constant during the incubation period. Each treatment was carried out in duplicate.

The saturated soil setup was obtained by placing soil subsets on plastic columns with perforated base and saturating the soil from the bottom.

For field capacity regime, an additional subset of soils was irrigated with an aqueous solution of 7.3 mmol Na, to discriminate the genuine effect of the surfactants on metal mobility from the effect due to the addition of Na to soils. This concentration corresponded to the addition of Na equivalent to irrigation with A22 in the scenarios recreated (Reemtsma et al., 1999), provided that application of A22 supplies a larger quantity of Na to soils than BP.

2.3 Pore water analysis

Soil solution was isolated from control and surfactant or Na irrigated soils after incubation, through centrifugation using the "double chamber" method (10 min at 3000 g) (Bufflap and Allen, 1995). The soil solution was immediately filtered after centrifugation, through a 0.45 µm filter, and pH was measured. Metal concentrations were determined by ICP-OES. Dissolved organic carbon (DOC) was measured using a TOC-analyser (Analytical Sciences Thermalox).

2.4 Spectrofluorometry characterization of dissolved organic matter

Fluorescence EEMs were collected for the soil solution obtained from soils 1 and 3 after irrigation with MQ or A22 aqueous solution and incubation for 30 days. Fluorescence spectra were recorded on a Perkin-Elmer LS 50B luminescence spectrometer and using sealed quartz cuvettes. The slits were set to 5 nm for both excitation and emission. The excitation wavelengths ranged from 250 to 400 nm at 5 nm steps and the emission was measured in the range 250–500 nm at 0.5 nm steps. Blank water scans were run every 10–15 analyses.

Additionally, EEMs were obtained for S1 and S3 amended with a reference material, Pahokee peat, and incubated at described conditions. Pahokee peat, an organic soil material from Florida (USA) was obtained from the International Humic Substances Society (IHSS Bulk Solid Material #2BS103P). The EEMs were processed using the FL WinLab (Perkin-Elmer) and SigmaPlot 12.3 (Bochum, Germany).

Data from the EEMs was analyzed to obtain the main components present in the DOM according to models presented in the literature (Fellman et al., 2009). Also, the humification index (HIX) (Zsolnay et al., 1999), the $\beta : \alpha$ or freshness index (FrI) (indicative of DOM derived from microbial metabolism) (Stutter et al., 2013), the fluorescence index (FI) (terrigenous vs. microbial DOM) (Berggren et al., 2009) and the redox index (RI) (ratio of reduced : oxidized compounds) (Miller et al., 2009) were estimated from the EEMs.

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2.5 Speciation and statistical analyses

The speciation analysis was carried out for each treatment using the speciation model WHAM VI (Tipping, 1993). General specifications for data input are described elsewhere (Van Laer et al., 2006). Specific constraints were also considered for the particular scenarios assessed in this study. Thus, total DOC comprised carbon corresponding to soluble SOM plus organic carbon (OC) in solution due to the presence of surfactant, for the corresponding treatments. Since the specific UV-Absorbance (SUVA) of A22 ($0.245\,L\,g^{-1}\,cm^{-1}$) and BP ($0.120\,L\,g^{-1}\,cm^{-1}$) are much lower than that of soil-derived DOC (Table 1), the DOC concentration corresponding to the soil or surfactant can be estimated from the UV absorbance at 254 nm and total DOC measurements, as described elsewhere (Hernandez-Soriano et al., 2011a). Those calculations resulted in a rational estimation of the soluble SOM in solution, allowing for more precise input of soluble SOM in the speciation model.

Principal component analysis (PCA) was performed to explore the relationship between factors (soil pH, CEC and OC content, soil solution pH, OC concentration, ionic strength and concentrations of Al, Fe and Mn) with responses (concentration of Cd, Cu, Pb and Zn in solution for the different treatments assayed). Projection to latent structures (PLS; $p < 0.05$) by means of partial least squares method (Eriksson et al., 2001) was applied.

Correlation or regression analyses were used to estimate relationships among the studied variables. Dunnett's test was selected to determine significant differences between the treatments and the control while Tukey test was used to compare treatments. Kruskal–Wallis test was used when the variables did not meet the ANOVA normality assumption.

For all tests, significant correlation was considered for $p < 0.05$. Statistical analysis was performed with the software package SPSS 17.0 (Illinois, USA).

3 Results

3.1 Soil characterization

The chemical characterization of the soils selected for this study is summarized in Table 1. Overall, S2 and S3 are neutral soils, while S1 is slightly alkaline. S1 and S2 present high CEC values but different content in total organic carbon (OC). S3 present low values for both CEC and OC content. Total Cd (S1) and Pb (S2 and S3) concentrations are above the intervention reference values (12 and 530 mg kg^{-1} respectively) observed in the Dutch guidelines (CLEA, 2000). Besides, Cd, Cu and Zn levels in S2 are above the target values as indicated in the Dutch guidelines (0.8 mg kg^{-1} for Cd, 36 mg kg^{-1} for Cu and 140 mg kg^{-1} for Zn), which are underpinned by an environmental risk analysis wherever possible.

3.2 Pool of potentially bioavailable metals

The evaluation of the potential risks of metals in soils is not directly related to their total concentration in the soil and requires an assessment of the fraction of the total metal that is in a mobile and potentially bioavailable form. Thus, soils S2 and S3 present a similar background of Cd but a larger fraction was in the soil solution for S2 (Table 1). Likewise, S1 and S3 presented similar total concentrations of Cu but concentrations determined in the soil solution were lower for S1 than for S3 (Table 1). Otherwise, comparable amounts of Zn were found in the soil solution for S2 and S3, despite the difference in total Zn concentration (Table 1).

Concentrations of Cd, Cu, Pb and Zn in the soil solution for the treatments assayed after 30 days of incubation are presented in Table 2. Additionally, Table 2 summarizes the percentage of Cd and Zn in solution present as free ion, the most readily bioavailable metal specie (Lofts et al., 2004), according to speciation analysis performed with WHAM. Results from the speciation analysis indicated that Cu and Pb in the soil solution were mostly bounded to soil-derived OM ($\geq$ 99 %) for the soils and treatments

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evaluated. Accordingly, data corresponding to the percentage of Cu and Pb existing as free ions has not been included in Table 2. To simplify data interpretation concentrations of soluble metal lower than $20\,\mu g\,L^{-1}$ have not been discussed.

3.3 Field capacity regime

Irrigation of soils with aqueous solutions of A22 or BP under FC regime increased Cd concentrations in soil solution circa 7-fold for the Cd-contaminated soil (S1) with no significant effect ($p > 0.05$) on Cd mobility for S2 (Table 2). Mobility of Cu and Zn increased up to 14-fold for S2 > S3 > S1 when irrigated with A22, except for Zn in soil S3. Although S2 and S3 present similar total concentrations of Pb, the increase of Pb concentration in solution for S2 and S3 was different: circa 20 times for A22 and 30 times for BP for S2 and 10-fold for A22 and 14-fold for BP for S3.

The variation in the concentration of Cd and Zn chemical species among different treatments and relative to control assays is summarized in Fig. 1, as well as the relative variation in ionic strength (I) and soil-derived DOM in the soil solution. Overall, for treatments at FC, the speciation analysis indicated a decrease on the percentage of Cd and Zn as free ions for soils irrigated with A22 compared to control soils (relative increase < 1), while irrigation with BP increased the ratio of those metals as free ions (relative increase circa 1.4) for S2 and S3 (Fig. 1a). Irrigation with either A22 or BP yielded a 2–3.5 times relative increase in the ratio of Cd and Zn as organo-metal complexes for S1, consistently with higher concentrations of soil-derived DOM in solution (Fig. 1c).

The effect of soil irrigation with Na aqueous solution evaluated for treatments at FC was generally comparable to the addition of BP for S2 (Fig. 1a and c).

3.4 Saturation regime

Comparison of metal solubility in control soils for FC and ST regimes indicates that soil concentrations of Cu (2-fold) and Zn (3-fold) in solution decreased under saturated

conditions for S3 while mobility increased two (Cu) to six (Zn) times in S2. Besides, for ST regime the solubility of Pb in S2 and S3 increased up to six times compared to FC regime (Table 2).

Cadmium solubility did not vary significantly for S1 ($p > 0.05$) increasing for samples irrigated with A22 or BP aqueous solutions and incubated under saturated conditions. Concentrations of Cd in solution for S2 and S3 were negligible for those treatments.

Saturation regime diminished the solubilizing effect of A22 and slightly enhanced BP effect on Cd solubility for S1 (Table 2). For the three soils, ST diminished the effect of both surfactants on Cu solubility up to 10 times (S2). The concentrations of Pb in solution for S2 and S3 indicate that irrigation with A22 and BP has largely depleted the content of Pb in soil for both moisture regimes, although the ST regime decreased the solubilizing effect for both surfactants in S2 while increasing such effect in S3. For Zn, ST decreased the solubilizing effect of BP 2–3 folds in S2 and S3, while no significant effect was determined for soil treated with A22 ($p > 0.05$). Besides, ST induced an inversion of A22 and BP effect for Cd (S1) and Zn (S3), i.e. reducing A22 effect and promoting the BP-enhanced metal solubilisation.

Overall, the ratio of Cd and Zn as free ion decreased under saturated conditions (relative increase < 1), except for S2 irrigated with BP, which resulted in a relative increase circa 1.4 (Fig. 1b). Soil saturation resulted in a lower relative increase in DOM and ratios of Cd and Zn as organo-metal complexes (Fig. 1d) compared to treatments performed at FC.

3.5 Metal bioavailability in relation to the properties of bulk soil and soil solution

The relationships between Cd, Cu, Pb and Zn concentrations in solution and the selected soil and soil solution properties as obtained from PCA are summarized in Fig. 2. The two first principal components extracted explained 56–59 % of the variability in the metal concentration measured for the different treatments assayed. Thus, changes in Cd solubility were positively related to soil and soil solution pH as well as solution *I* and

negatively related to the concentration of OC in soil solution. The solubility of Cu, Pb and Zn was positively related to soil and soil solution concentrations of OC and negatively related to soil and soil solution pH. Additionally, the solubility of Pb and Zn was also positively related to the variation in the concentration of Al, Fe and Mn in solution.

Relative variation of I depicted in Fig. 1a for FC regime illustrates an increase in I for S2 (1.2–1.7 fold) comparable to the relative increase in free ion concentration of Cd and Zn, particularly for soil irrigation with Na (1.7 fold). For S1 and S3, irrigation with A22 and BP resulted in a 2-fold decrease in I, consistent with a decrease in free ion activities, except for BP applied to S3, with no variation determined for the application of Na. Similar trends in I were determined for soils under ST regime (Fig. 1b).

Otherwise, irrigation with A22 and BP under FC regime increased DOM circa 2–3 times, generally consistent with increasing rates of Cd and Zn organo complexes in S1 and S3 (Fig. 1c), while this effect was lower in soils under ST regime (Fig. 1d).

Irrigation with Na solution had a lower effect on SOM solubilisation than surfactant addition, while the effect on the solution I was similar or larger (S1) than the irrigation with A22 or BP (Fig. 1a and c).

Regression analysis performed for results obtained from all the treatments confirmed that total concentration of Cd, Cu, Pb and Zn in solution was significantly correlated ($p < 0.05$) with soil pH ($r_{Cd} = 0.716$; $r_{Cu} = -0.651$; $r_{Pb} = -0.622$; $r_{Zn} = -0.639$) and soil-derived DOC ($r_{Cd} = -0.450$; $r_{Cu} = 0.669$; $r_{Pb} = 0.817$; $r_{Zn} = 0.676$). Significant correlations ($p < 0.05$) were also determined for the solubility of Cu, Pb and Zn and total soil OC content ($r_{Cu} = 0.712$; $r_{Pb} = 0.531$; $r_{Zn} = 0.715$). Additionally, Cu and Pb solubility were significantly correlated ($p < 0.05$) with soil solution pH ($r_{Pb} = -0.537$; $r_{Zn} = -0.522$), Al concentration in solution ($r_{Pb} = 0.473$; $r_{Zn} = 0.472$) and Mn concentration in solution ($r_{Pb} = 0.748$; $r_{Zn} = 0.655$).

The relative increase of Al, Fe and Mn concentrations in solution compared to control soils was lower for soils incubated under ST compared to treatments carried out at FC. Furthermore, regression analysis performed for the set of data corresponding to soils incubated under FC regime revealed significant correlations for Cu, Pb and Zn

solubility with concentrations in solution of Al ($r_{Cu} = 0.632$; $r_{Pb} = 0.942$; $r_{Zn} = 0.954$), Fe ($r_{Cu} = 0.626$; $r_{Pb} = 0.983$; $r_{Zn} = 0.930$) and Mn ($r_{Pb} = 0.754$; $r_{Zn} = 0.840$) as well as a significant correlation for DOC concentration with Al ($r = 0.679$) and Fe ($r = 0.836$) concentrations in solution. However, for the data set obtained from the ST regime, significant correlations were only determined for concentration in solution of Cd with soluble Al ($r = 0.814$) and for Pb solubility with soluble Mn ($r = 0.893$), while DOC concentration was significantly correlated with Fe and Mn in solution ($r_{Fe} = 0.770$; $r_{Mn} = 0.801$).

3.6 Evaluation of dissolved organic matter composition

Excitation–emission matrices obtained for S1 and S3 (Fig. 3) provided a fingerprint of DOM composition for non-amended soil and soil treated with the surfactant A22 or the reference material Pahokee peat. The fluorescence intensity was scaled to range 0–450 for all the EEMs.

Data analysis yielded two fluorophores corresponding to a humic (FC1) and a reduced quinone-like (FC2) component (Fellman et al., 2009). The variation in the percentage of FC1 and FC2 and the values estimated for the HIX, FrI, FI and RI indexes are presented in Table 3.

The EEMs obtained for S1 and S3 treated with A22 presented a slight attenuation of the fluorescence intensity (FI) compared to EEM obtained for control soil and soil treated with the peat, likely due to fluorescence quenching by metal complexation with organic compounds in solution, according to results presented in Table 2 and Fig. 2. Besides, the presence of non-humified SOM corresponding to A22-derived DOC may have a dilution effect that also explains the broadening of the signal. For A22-treated soils, FC1 and FC2 in solution increased about 20 % compared to non-amended control soils (Table 3), likely related to the enhanced SOM solubilisation (Fig. 2). The higher presence of humified compounds (FC1) in solution for A22-treated soil was further confirmed by increased values of HIX (2 to 3-fold) and a modest decrease in FrI values. The slight decrease in RI values supported the increase in the reduced quinone-like component (FC2).

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Interactive Discussion

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Soil addition with Pahokee peat, a highly humified material, slightly reduced the FI and FrI for both soils whilst the impact on the percentage of FC1 and FC2 was substantially different among S1 and S2. Thus, the percentage of FC1 and FC2 strongly decreased for S1 with a negligible change in the HIX and RI while increasing 10–19 %
5   for S3, with a 3-fold increase in HIX and a moderate increase in RI.

4   Discussion

4.1   Anionic surfactants enhance solubility of metals

The effect of anionic surfactants in metal mobilisation rates was associated to changes in soil and soil solution properties and substantially related to the solubilisation of SOM
10   (Figs. 1 and 2). The SOM functions as a carrier of trace metals, particularly for Cu and Pb (Fig. 2), as previously reported in the literature (Hernandez-Soriano et al., 2011a).
Several mechanisms contribute to surfactant-enhanced solubility of metals. Micellar solubilisation of OM (A22 and BP) and sequestration of polyvalent metal ions (A22) that act as a bridge between charged sites in OM (mainly Ca, Mg, Al, Fe) can explain the in-
15   crease on metal mobility linked to OM solubilisation (Hernandez-Soriano et al., 2011a; Temminghoff et al., 1998). Besides, A22 can increase metal solubility by direct complexation (Hernandez-Soriano et al., 2011a; Sarathy and Allen, 2005). The application of anionic surfactants introduces Na in the soil, which can increase SOM solubilisation (Reemtsma et al., 1999), although the effect of Na in total metal solubility was only sig-
20   nificant for S2 and likely related to an increase on solution I (Fig. 1), particularly for Cd, as previously reported by Pinheiro et al. (2000), and Zn. Finally, changes in solution pH and I might promote the presence of soluble inorganic complexes in solution (Jacobs and Foreman, 2005).

4.2 Concentration and composition of dissolved organic matter is altered by soil treatment with anionic surfactants

The concentration of SOM in solution consistently increased for all the treatments evaluated (Fig. 2), according to the SUVA values estimated for the soil solutions. Results indicated that SOM solubilisation was mainly related to increasing concentration of Al, Fe and Mn in solution, their colloids being known to substantially control SOM chemical stability (Dolfing et al., 1999). Therefore, the mobilisation of such cations in solution by direct complexation with A22 (Hernandez-Soriano et al., 2011a), sulphate-induced dissolution by BP (Flaathen et al., 2010) or changes in solution pH or I (Pinheiro et al., 2000) likely accounts for the increase of soil-derived DOM. Irrigation with surfactants causes different and simultaneous effects, such as direct complexation and increase in soil solution pH for A22, which explains the large ratio of SOM solubilisation determined in soils treated with surfactants.

For ST regime, anaerobic metabolism could promote the reduction of carboxylic functions (Lovley et al., 1996), likely resulting in a lower ratio of A22-enhanced solubilisation of SOM. Similarly, anaerobic conditions can promote the reduction of the sulphate group in BP, reducing its effect on the solubilisation of Al, Fe and Mn colloids.

The solubilization of SOM will be largely determined by SOM and soil properties. Thus, the solubilizing effect of compounds such as anionic surfactants might be more significant in soils where SOM is poorly humified or soil offers low chemical protection (Wagner et al., 2007; Six et al., 2002), while highly humified materials such as Pahokee peat can be strongly retained in soils with a higher CEC (Fig. 3).

Up to date, the evaluation of anionic surfactants effect in SOM has been limited to the determination of changes in DOM concentration and aromaticity (Hernandez-Soriano et al., 2011a), with the most significant effect observed for soil treatment with A22. Spectrofluorometry analysis performed in this study has revealed that A22 preferentially increases the solubilization of humic and reduced quinone-like components (Ta-

ble 3, Fig. 3). These results provide the first description of changes in the composition of DOM for soils treated with anionic surfactants.

4.3 Metal bioavailability in surfactant-treated soils is determined by metal complexation with dissolved organic compounds

Soil addition with anionic surfactants, unintentional or for remediation purposes, will have a variable effect on metal mobility and bioavailability depending on soil properties. These effects are strongly related to variations induced in soil solution properties and consequently in the chemical speciation of metals (McBride et al., 1997; Kinniburgh et al., 1999). Thus, analysis of metals speciation in solution provides a rational estimation of their bioavailability (Nolan et al., 2009), which is largely controlled by the solubility and composition of SOM, as well as pH and I.

The increase in soil solution pH for all the treatments assayed (Table 2) may result in the hydrolization and polimerization of Al(III) ions associated to OM (Nierop et al., 2002; Scheel et al., 2007), which would result in available binding sites in SOM for other elements present in solution. Accordingly, Fig. 3 shows enrichment in the fulvic-like component upon soil amendment with A22, which might provide a pool of ligands of high-moderate affinity for metal ions that will promote formation of organo-metal complexes and decrease the presence of metals as free ions. Further confirmation of metal complexation with organic compounds was derived from the attenuation in the fluorescence intensity, or quenching (Mounier et al., 2011), in soils treated with A22 (Fig. 3).

The substantial increase of soluble organic ligands for the treatments evaluated yielded surprisingly large percentages of Cd and Zn as organo complexes (Fig. 2), presumably due to the occurrence of sites of high affinity in the DOC (Kinniburgh et al., 1999). This was particularly significant for soils irrigated with A22.

4.4 Opportunities for sustainable agriculture and risk assessment

The increasing intensity of agricultural exploitation due to food demands of world population has resulted in the implementation of practices such as wastewater irrigation and systematic application of pesticides to secure satisfactory crop yields worldwide (Singh et al., 2012; Muyen et al., 2011). However, quality requirements for the use of wastewater in agricultural fields differ among countries (Hanjra et al., 2012), and the composition, including concentration of metals or anionic surfactants, can largely vary depending on protocols observed in the treatment plants. Otherwise, the concentration of metals in soils is also highly variable, and the exploitation of contaminated soils for agricultural activities is frequently reported in the literature (Liu et al., 2011).

The mobilization of metals towards the soluble phase and the amount of metal readily available highly determine potential metal toxicity and nutrients availability for soil microorganisms and plant uptake (Degryse et al., 2009; Chapman et al., 2012). The results presented in this study indicate that the potential effect of anionic surfactants in crucial soil processes such as metal bioavailability can be rationally predicted by metal speciation analysis and characterization of concentration and composition of DOM. Overall, this methodological approach can be directly implemented for a more sensible reuse of wastewater in agricultural fields (Singh et al., 2012), environmental risk management research (Hanjra et al., 2012) or soil remediation activities (Tsang et al., 2012).

5 Conclusions

The presence of anionic surfactants in soil alters the partition of Cd, Cu, Pb and Zn between free ion species and metal-organo complexes in solution. This is being promoted by an increase of anionic ligands in solution with high affinity for the metals following addition of anionic surfactants to soil. Generally, free ion activities are accepted as the chemical forms of metals most readily available for living organisms but labile metal

complexes in solution might largely govern the pool of bioavailable metals. The spectrofluorometric characterization of DOM suggested that anionic surfactants promote the complexation of metals in solution with humified compounds which might limit their availability for plant or microorganisms uptake.

Overall, the results presented highlight the necessity of implementing a rational characterization of DOM composition for modelling trace metal mobilization in soils, which has become an essential tool in risk assessment and environmental research.

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Table 1. Soil properties, total and soil solution content of Cd, Cu, Pb and Zn of soils. Values in bold indicate concentrations above intervention values (Dutch guidelines, CLEA, 2000).

Soil (Location)	Physicochemical properties							[e]Trace metal content			
	pH	[b]PCEC (cmol$_c$ kg^{-1})	[c]OC (%)	[d]SUVA	Sand (%)	Silt (%)	Clay (%)	Cd	Cu	Pb	Zn
S1 (Hungary)	7.5	25	2.7 [28]	15	32	23	45	**118** [5.4]	21 [1.0]	n.d.	48 [2.1]
S2 (France)	6.8	26	6.5 [200]	57	13	69	18	1.1 [2.3]	57 [16]	**5550** [57]	245 [14]
S3 (Belgium)	7.1	15	2.3 [110]	35	35	53	12	0.6 [0.3]	17 [12]	**5460** [42]	74 [13]
Dutch thresholds[e] (mg kg^{-1})								0.8 [12]	36 [190]	85 [530]	140 [720]

[a] Target values. Intervention values are indicated in brackets.

[b] CEC: cation exchange capacity.

[c] OC: organic carbon; numbers in brackets correspond to soil organic matter in solution (mg L^{-1}).

[d] Specific UV-absorbance (SUVA) (L g^{-1} cm^{-1}).

[e] Aqua-regia extractable metal content (mg kg^{-1}). Numbers in brackets correspond to metal concentration in soil solution (µg kg^{-1}).

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Table 2. Concentrations of Cd, Cu, Pb and Zn in the soil solution isolated from soils irrigated with aqueous solutions of the anionic surfactants Aerosols 22 (A22) and Biopower (BP) or a solution of Na. Values in brackets indicate the percentage of free metal ion estimated with WHAM VI.

Soil	Treatment	Soluble metal (μg L^{-1}) at field capacity					Soluble metal (μg L^{-1}) at saturation				
		pH	Cd	Cu	Pb	Zn	pH	Cd	Cu	Pb	Zn
S1	Control	7.5	38 [34]	7.4	n.d.	15 [27]	7.8	47 [25]	8	n.d.	4 [23]
	A22	7.8	287 [12]	31	n.d.	22 [13]	8.1	115 [3]	34	n.d.	26 [4]
	BP	7.7	229 [12]	66	n.d.	32 [14]	7.8	317 [20]	33	n.d.	50 [18]
	Na	7.2	234 [26]	8.1	n.d.	71 [23]					
S2	Control	6.8	16 [12]	114	398	95 [14]	7.7	**2**	275	2415	627 [7]
	A22	6.7	15 [7]	1487	7464	625 [10]	7.6	**7**	476	6543	618 [2]
	BP	5.7	18 [17]	1627	9973	1440 [19]	7.0	**7**	851	7259	591 [9]
	Na	7.5	4.1 [20]	1915	718	188 [18]					
S3	Control	7.1	**1.8 [20]**	86	291	90 [21]	8.0	**2**	41	1708	20 [19]
	A22	7.7	**3.2 [2]**	351	2818	70 [4]	7.4	**6**	60	3623	103[4]
	BP	4.5	**9.4 [18]**	255	4238	306 [28]	7.6	**5**	213	5814	67 [8]
	Na	7.7	**3.3 [12]**	139	845	21 [15]					

Percentages of free metal ion for Cu and Pb were < 1 % in all cases.
n.d. = below detection limit.

Table 3. Fluorescence indexes and percentages of fluorescent components in soil solution from soils irrigated with an aqueous solution of the anionic surfactant Aerosol 22 (A22) or amended with Pahokee peat. Fluorescent components correspond to a reduced quinone-like (FC1) and a humic-like (FC2) component.

Soil	Treatment	Fluorescence indexes				Fluorescent components (%)	
		HIX	FrI	FI	RI	FC1	FC2
S1	Control	3.72	0.81	1.51	0.34	57	63
	A22	7.06	0.61	1.43	0.41	80	80
	Pahokee peat	3.83	0.70	1.41	0.37	3	2
S3	Control	3.30	0.86	1.58	0.35	46	50
	A22	15.4	0.64	1.45	0.40	70	70
	Pahokee peat	16.3	0.65	1.43	0.41	65	60

HIX: humification index; FrI: freshness index; FI: fluorescence index; RI: redox index.

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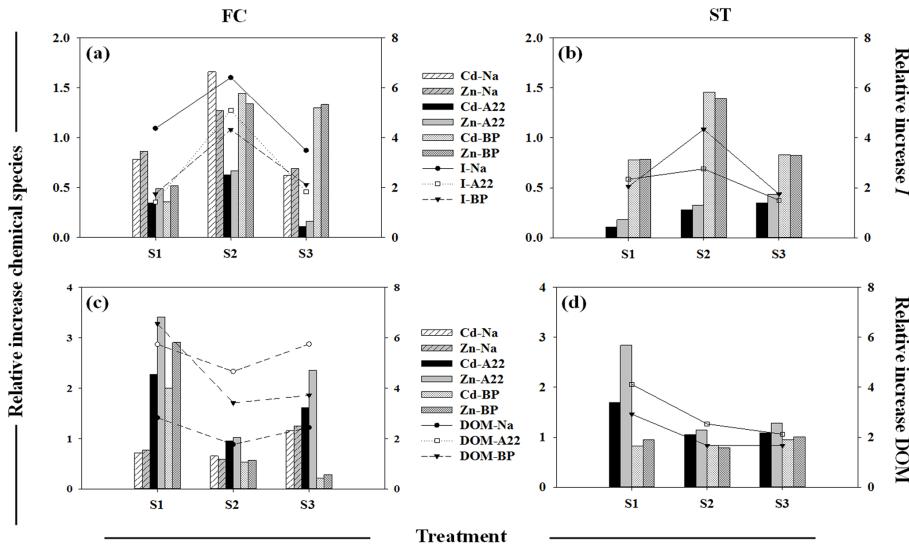
Figure 1. The relative increase in Cd and Zn chemical species: free ion **(a, b)**, organo-metal complexes **(c, d)**, and the relative increase in the ionic strength of the solution (*I*) and soil-derived dissolved organic matter (DOM), for the three soils (S1, S2, S3) irrigated with Na, Aerosol 22 (A22) or Biopower (BP) aqueous solutions. Soils were incubated at field capacity (FC, **a** and **c**) or under saturated conditions (ST, **b** and **d**).

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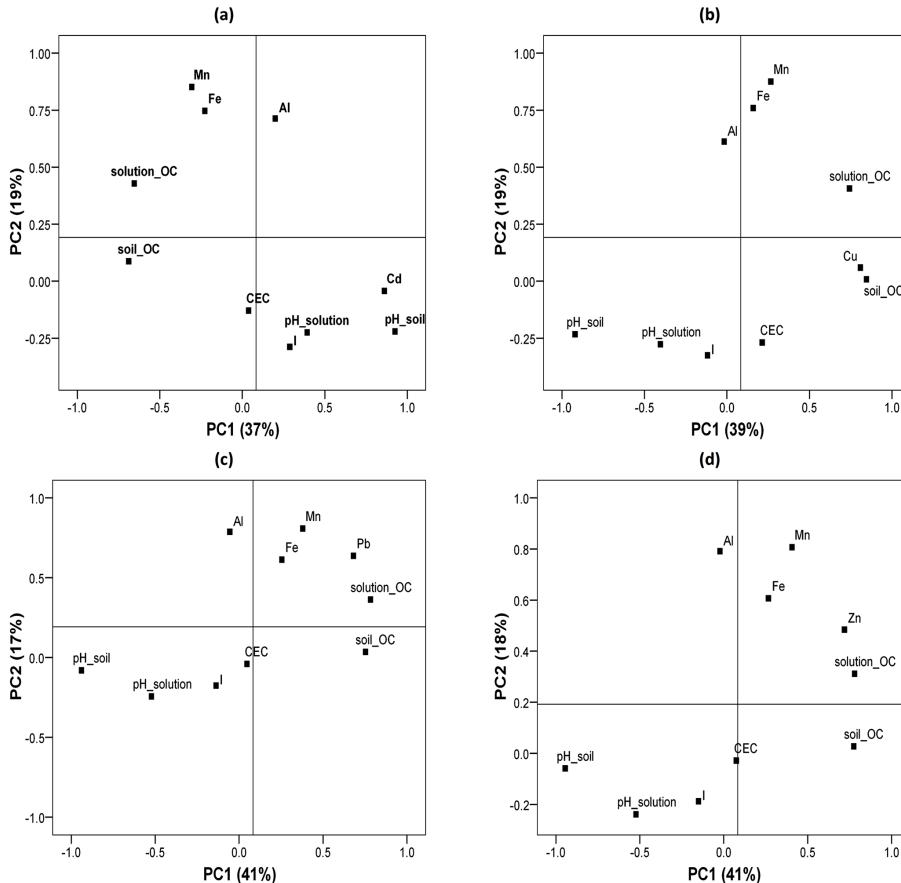
Figure 2. Multivariate data analysis PLS (partial least squares) loading scatter plots for the responses Cd **(a)**, Cu **(b)**, Pb **(c)** and Zn **(d)** concentration in solution and the factors soil pH, cation exchange capacity (CEC) soil organic carbon (OC) content, soil solution pH, soil solution OC concentration, ionic strength (I) and solution concentrations of Al, Fe and Mn.
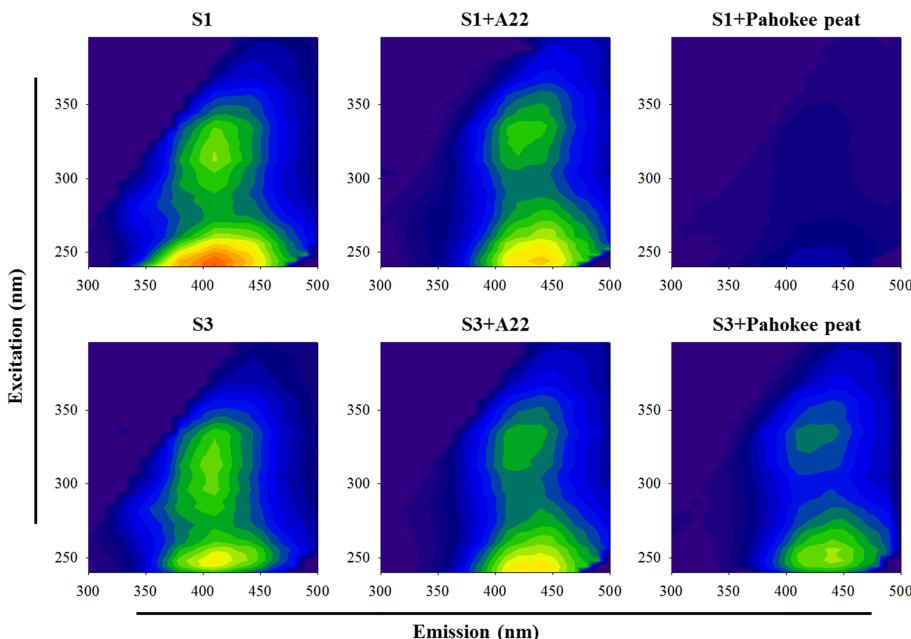
Figure 3. Excitation-emission matrices for non-amended soil 1 (S1) and soil 3 (S3) incubated at field capacity and for S1 and S3 amended with Aerosol 22 (A22) or Pahokee peat. Fluorescence intensity ranges 0–450 for all the matrices.