



Effect of dissolved organic matter composition on metal speciation in soil solutions



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ARTICLE INFO

Article history:

Received 24 June 2014

Received in revised form 23 January 2015

Accepted 27 January 2015

Available online 10 February 2015

Editor: J. Fein

Keywords:

Metal speciation

Dissolved organic matter

Composition

SC-DMT

NICA-Donnan modeling

ABSTRACT

Knowledge of the speciation of heavy metals and the role of dissolved organic matter (DOM) in soil solution is a key to understand metal mobility and ecotoxicity. In this study, soil column-Donnan membrane technique (SC-DMT) was used to measure metal speciation of Cd, Cu, Ni, Pb, and Zn in eighteen soil solutions, covering a wide range of metal sources and concentrations. DOM in these soil solutions was also fractionated into humic acid (HA), fulvic acid (FA), hydrophilic acid (Hy), and hydrophobic neutral organic matter (HON) by a rapid batch technique using DAX-8 resin. Our results show that in soil solution Pb and Cu are dominant in complex form, whereas Cd, Ni and Zn mainly exist as free ions; for the whole range of soil solutions, only 26.2% of DOM is humic substances and consists mainly of fulvic acid (FA). The metal speciation measured by SC-DMT was compared to the predicted ones obtained via the NICA-Donnan model using the measured FA concentrations. The free ion concentrations predicted by speciation modeling were in good agreement with the SC-DMT measurement. Moreover, we show that to make accurate modeling of metal speciation in soil solutions, the knowledge of DOM composition, especially FA fraction, is the crucial information, especially for Cu and Cd; like in previous studies the modeling of Pb speciation is not optimal and an update of Pb generic binding parameters is required to reduce model prediction uncertainties.

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1. Introduction

Heavy metals in soil are taken up by plants and soil organisms mainly through the soil solution. To assess the mobility, bioavailability, and toxicity of heavy metals in soil solution, it is necessary to consider metal speciation rather than total dissolved concentration (Ma et al., 1999; Kalis et al., 2008). In most circumstances, free metal ion in soil solution is the key species that contributes to the metal uptake and determines metal toxicity; it is the master species from which the concentration of all other species of interest can be calculated (Ma et al., 1999; Mueller et al., 2012; Ardestani et al., 2014).

Reliable direct measurement of metal speciation in natural environment is a challenge for analytical techniques due to the low concentration expected (< nanomolar range) and the need to distinguish between species (Sigg et al., 2006), although in the last two decades numerous techniques have been applied to determine the reactive species in natural water (Sigg et al., 2006; Vega and Weng, 2013) and soil

solutions (Kalis et al., 2008; Chito et al., 2012). Soil column-Donnan membrane technique (SC-DMT) is an equilibrium method to determine multi-metal species in soil solutions with minimal disturbance of soil. The concentrations of metal ion species are quantified by separating free ions from complexed ions in equilibrium with a substrate solution via a cation exchange membrane (Weng et al., 2001b; Cancès et al., 2003; Hamilton-Taylor et al., 2011). Under certain conditions, the technique is suitable for measuring metal speciation routinely but in some cases poor detection limit, long equilibrium time or high cost prevents its use (Zhang and Young, 2005; Marang et al., 2006).

Speciation modeling is a complementary tool to predict metal species and identify the important ligands that control the degree of metal complexation in soil solution (Weng et al., 2001a; Cancès et al., 2003; Schröder et al., 2005). Various constituents in soil solution, such as dissolved organic matter (DOM), hydroxides and clay colloids, can complex with metal ions to modify their activity, and hence reduce the total metal loading to biota (Sparks, 2003). DOM is a key constituent for metal complexes in soil solution (Tipping, 2002; Zhao et al., 2007; Cornu et al., 2011), and consists of a mixture of fulvic acid (FA), humic acid (HA) and other nonhumic substances (Weng et al., 2002a). Within

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dissolved organic matter in soil solutions, humic substances (HS), including HA and FA, are the most hydrophobic fractions (Croué et al., 2002) and represent 20–60% of the bulk organics (Guggenberger et al., 1994; Amery et al., 2009; Groenenberg et al., 2010).

HS are assumed to be the most reactive fractions that control the mobility of metals in aquatic system (Benedetti et al., 1996a). Mechanistic models building on molecular-scale description of metal ion binding by HS have been developed. Model VII (Tipping et al., 2011) and the nonideal competitive adsorption–Donnan (NICA–Donnan) model (Kinniburgh et al., 1996) are at present the most widely used. However, these model predictions of natural surface water and soil solution speciation have not always been satisfactory because of the complexity of the system, the heterogeneity of DOM and the uncertainty in model parameters (Ritchie and Perdue, 2003; Groenenberg et al., 2010; Vega and Weng, 2013). Variation in natural DOM fractions is usually neglected when these models are applied, consequently resulting in large associated uncertainties in model outputs (Groenenberg et al., 2010; Baken et al., 2011; Lofts and Tipping, 2011). It is often assumed by default that the ratio of DOM to DOC (dissolved organic carbon) is 2, 65% of DOM is FA like, and 35% is inert in Model VII (Lofts and Tipping, 2011), while 82.5% of DOM is FA, and the other fraction is inert in Visual MINTEQ software (Sjöstedt et al., 2010). The proportion of active DOM can also be adjusted subjectively to obtain the optimized fits between the modeled and measured metal speciation (Dwane and Tipping, 1998).

Moreover, the nonhumic, hydrophilic fractions, generally representing 40–70% of the DOM in soil solutions, have been found to be dominant ligands in complexing metals in some cases (Croué et al., 2002; van Schaik et al., 2010; Pernet-Coudrier et al., 2011). However, due to the difficulties of their isolation, little exploratory work has been reported in the literature regarding the metal binding properties of hydrophilic fractions and the range of variability of their quality and quantity in the environment, which is related to the source of DOM (i.e., autochthonous and anthropogenic) (Baken et al., 2011). Therefore, we believe that the heterogeneity of DOM will have an influence on metal binding, and characterization of DOM composition is needed for the improvement of model prediction (Amery et al., 2007; Baken et al., 2011).

The objectives of this study are to (1) evaluate the reliability and performance of SC–DMT by comparing measured Cd, Cu, Ni, Pb, and Zn speciation in soil solutions with NICA–Donnan calculation for a wide range of metal sources and concentrations; (2) demonstrate the importance of DOM composition variations in the validation of NICA–Donnan model prediction of metal speciation in soil solutions

against experiment data. SC–DMT was used to measure metal ion species in soil solution samples at pH 4.4–7.6, and DOM fractions in soil solution collected from SC–DMT experiment were determined by measurement of the HA, FA, hydrophilic acid (Hy) and hydrophobic neutral organic matter (HON) concentrations (van Zomeren and Comans, 2007).

2. Materials and methods

2.1. Soil samples

Eighteen contaminated and uncontaminated soils were collected from France and China, encompassing a wide range of soil physical properties, metal sources and concentrations. The detailed description of soil sampling is shown in Table A1.

The salient soil characteristics can be found in Table 1. The total Cd, Cu, Ni, Pb, and Zn concentrations ranged between 0.07 and 54.9, 7.0 and 1015, 5.1 and 20850, 4.8 and 2378, and 15.5 and 2284 mg·kg⁻¹, respectively. The elevated Cd content was found in the soils collected from Zn smelter industrial sites in Nord–Pas–de–Calais, France and tin mining area in Gejiu, China. The highest Cu content was observed in soils contaminated by agricultural activities from Aquitaine, France. High Pb and Zn almost occurred together in geogenically enriched soils (soil 4 and 5) and mining contaminated soils (soil 10–12 and soil 15–18). Total Ni content was lower than 100 mg·kg⁻¹ in most soils except soil 6, which was inherited from the ultramafic bedrock in New Caledonia, France.

2.2. Soil analysis

All soil samples were air-dried and sieved through 2 mm mesh. Part of the samples was finely crushed for organic C and total metal contents analysis. Analytic pure and supra pure chemicals, ultrapure acids and ultrapure water (Milli-Q, 18.2 mΩ) were used throughout this work.

Soil pH was measured at a 1:2.5 soil-to-water ratio with a Hanna 211 pH meter. Clay content (<2 μm) was determined according to the ISO 11277 standard by sieving and sedimentation for the French soils (soil 1–14), while the sieve and pipette method (Day, 1965) was used for the Chinese soils (soil 15–18). The contents of total organic carbon (TOC) and carbonate-C were determined according to ISO 10694 standard and ISO 10693 standard, respectively. Total carbon concentration in soils was first measured by dry combustion with CHNS Automatic Elemental Analyzer (Thermo Flash 2000). Some soil subsamples were then acid-treated with ultrapure H₃PO₄ to remove carbonates prior to

Table 1
Selected characteristics of the soil samples.

Soil	pH	Clay	TOC	Carbonate-C	Amor-Fe	Cry-Fe	CEC	Total metal content mg·kg ⁻¹				
	H ₂ O	%	%	%	g·kg ⁻¹	g·kg ⁻¹	cmol·kg ⁻¹	Cd	Cu	Ni	Pb	Zn
1	5.40	14.4	3.08	0.33	14.18	89.94	9.49	0.38	88.7	92.50	4.8	275.1
2	6.29	3.5	0.93	0.04	0.47	2.22	2.25	0.25	14.3	63.25	20.1	15.5
3	6.74	6.4	4.26	0.50	13.90	84.76	23.29	0.31	120.4	90.50	6.6	328.6
4	7.44	39.6	4.92	1.70	5.49	50.18	22.86	3.20	236.6	27.00	908.4	826.0
5	5.92	20.2	1.59	0.12	6.04	21.54	10.58	1.11	124.0	35.75	497.4	995.3
6	5.00	13.5	0.12	0.31	5.52	487.43	0.47	0.07	31.1	20850.00	5.1	341.8
7	5.96	3.7	1.17	NM ^a	0.65	1.16	2.97	3.04	24.6	17.00	49.2	55.5
8	8.23	6.1	0.27	1.44	0.80	2.35	3.94	4.00	7.0	6.75	40.8	95.74
9	6.92	8.6	3.49	4.54	5.50	3.67	8.71	5.86	366.8	27.25	726.9	1383.5
10	5.45	11.3	1.03	0.19	2.55	3.83	5.05	3.30	14.5	11.31	91.9	350.5
11	7.63	45.7	3.65	2.77	8.44	10.96	45.17	8.49	25.2	39.44	89.8	370.0
12	6.64	10.0	1.62	0.13	2.34	3.34	8.55	20.50	23.0	9.38	269.4	1670.7
13	6.97	6.7	1.07	NM	1.60	2.25	2.84	0.10	1015.2	5.13	23.6	42.32
14	5.60	11.7	1.72	NM	3.17	5.04	3.84	0.29	442.4	11.40	86.0	65.57
15	4.46	27.3	2.19	1.36	1.51	7.65	7.91	0.70	34.8	12.73	162.5	246.0
16	4.84	24.6	1.53	0.01	4.86	49.26	14.51	1.09	429.8	15.13	468.6	270.4
17	7.81	23.5	2.34	0.61	6.53	37.62	6.56	1.86	58.7	22.56	767.9	715.4
18	6.81	67.1	0.60	NM	17.85	65.89	30.54	54.87	526.7	158.27	2378.1	2284.3

^a NM: not measurable.

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