In-situ measurement of free trace metal concentrations in a flooded paddy soil using the Donnan Membrane Technique

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ABSTRACT

The field Donnan Membrane Technique (DMT) has been used successfully to measure in-situ free trace metal concentrations in surface waters. However, it has not been applied previously in submerged soil systems including flooded paddy rice fields. We tested this technique in a column experiment with a flooded paddy soil contaminated with trace metals and compared the DMT measurements with predictions from a geochemical speciation model. Flooding led to a strong gradient in the redox potential (Eh) along the soil column, and the pH and concentrations of Mn, Fe, and dissolved organic carbon increased with decreasing Eh. Total dissolved trace metal concentrations decreased from the overlying water layer to the soil layers, which might be ascribed to the elevated pH outweighing the effect of the increased DOC concentrations under anaerobic conditions. Also, free trace metal concentrations were lower in the soil solution of the upper and bottom soil layers than in the overlying water layer, largely due to the increased pH under anaerobic conditions. The DMT measurements and model predictions were similar in the aerobic water layer, except for Pb. In both anaerobic soil layers, however, Cu and Pb were poorly predicted. The applied geochemical modeling approach, which is frequently being used and performs well under aerobic conditions, does not fully capture all the chemical processes occurring under anaerobic conditions. Overall, the field DMT proved to be a useful tool for the in-situ measurement of free trace metal concentrations in flooded paddy soils.

1. Introduction

Rice is the most important staple food for human beings in Southeast Asia (Meharg et al., 2013) and around 90% of the annual rice production is cropped and consumed in this area (Laborte et al., 2012). In industrialized areas throughout Southeast Asia, paddy fields for rice production are often close to industrialized sites and trace metal contamination of paddy soils has become an increasing concern (Römkens et al., 2009a). Contamination of paddy soils with trace metals can lead to an increase in the uptake of trace metals by rice plants and an accumulation of trace metals in rice grains (Simmons et al., 2005; Römkens et al., 2009b). Dietary intake of Cd through rice consumption is one of the most important exposure pathways for human beings, especially for people in Asia (McLaughlin et al., 1999; Tsukahara et al., 2003).

Apart from differences in trace metal uptake characteristics among various rice cultivars and genotypes (Römkens et al., 2009b), trace

metal uptake by rice largely depends on the bioavailability of trace metals in paddy soils. Speciation of trace metals in soils is of great importance for their bioavailability for uptake by plants. In soil solution, trace metals can be present as free metal ions or can be complexed by inorganic ligands or dissolved organic matter (DOM) (Weng et al., 2002; Koopmans et al., 2008; Koopmans and Groenenberg, 2011). The free trace metal ions in soil solution are usually considered to be the most bioavailable species for plant uptake (Bell et al., 1991; Smolders and McLaughlin, 1996; Parker and Pedler, 1997; Parker et al., 2001). To measure free trace metal concentrations in solution systems, several analytical techniques can be used including Ion-Selective Electrodes (Otto and Thomas, 1985), Cathodic Stripping Voltammetry (Xue and Sunda, 1997), Gellyfish (Senn et al., 2004), Absence of Gradients and Nernstian Equilibrium Stripping (Chito et al., 2012), Permeation Liquid Membranes (Parthasarathy et al., 1997), and the Donnan Membrane Technique (DMT; Temminghoff et al., 2000). These techniques all have their advantages and disadvantages (Batley et al., 2004; Sigg et al., 2006). In this study, we focus on the use of the DMT, because this technique does not perturb the equilibrium between free trace metal ions and other forms of trace metals in solution and it allows for measuring

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the free ion concentrations of multiple elements at the same time (Temminghoff et al., 2000).

For the so-called lab DMT developed by Temminghoff et al. (2000), the DMT cell consists of two chambers, i.e., the donor and the acceptor chamber. The donor solution, which is the solution of interest containing the free and complexed trace metals, is separated from the acceptor solution by a negatively charged semi-permeable cation exchange membrane. A peristaltic pump is used to continuously pump the donor and acceptor solutions across both chambers. Positively charged cations can pass the membrane while the transport of negatively charged ions and neutral complexes is restricted. When equilibrium is reached, the concentrations of free cations in the acceptor solution are either equal to the free cation concentrations in the donor solution or they can be calculated using a simple correction factor when a difference in ionic strength is present between the donor and acceptor solutions (Temminghoff et al., 2000). This lab DMT has been successfully used to measure the free metal concentrations in synthetic multicomponent systems (Osté et al., 2002) and in soil solution extracts (Weng et al., 2001; Koopmans et al., 2008; Koopmans and Groenenberg, 2011).

The use of the lab DMT to measure free metal concentrations in the soil solution of flooded paddy soils is difficult. For lowland rice production in paddy soils, flooding conditions prevail during almost the entire rice cropping period because lowland rice is extremely sensitive to water shortage (Kögel-Knabner et al., 2010). During the flooding of paddy soils, the redox potential (Eh) decreases and subsequently various reduction processes take place. For example, short-range ordered Mn- and Fe-(hydr)oxides will be reductively dissolved causing elevated Mn^{2+} and Fe^{2+} concentrations in soil solution (Tack et al., 2006; Grybos et al., 2007; Pan et al., 2014), while organic matter will be released leading to elevated DOM concentrations in soil solution (Kaiser et al., 1997; Vink et al., 2010; Pan et al., 2014). Therefore, a decrease in the reactive surface of these soil constituents might lead to an increase of the trace metal concentrations in soil solution (Ponnamperuma, 1972; Tack et al., 2006; Grybos et al., 2007). The presence of sulfide as a result of sulfate reduction, however, might lead to the formation of poorly soluble precipitates with trace metals exhibiting a low solubility (de Livera et al., 2011; Khaokaew et al., 2011; Fulda et al., 2013a). In addition, the pH of acid soils can increase after flooding, because reduction processes consume protons (Ponnamperuma, 1972; Kögel-Knabner et al., 2010), thereby increasing trace metal adsorption to reactive surfaces of soil organic matter (SOM) and short-range ordered metal-(hydr)oxides. Hence, changes in the Eh as induced by flooding of paddy soils can have a large influence on the free trace metal concentrations in soil solution. In such a complex and dynamic system, it is difficult to use the lab DMT to measure free trace metal concentrations, because it is a complicated task to sample flooded paddy soils without perturbing the Eh and maintaining anaerobic conditions during the DMT experiment in the laboratory. Therefore, it would be preferable to measure free trace metal concentrations in-situ without significantly disturbing the system. The so-called field DMT, which is a modified version of the lab DMT, has been developed for in-situ measurements. In this field DMT cell, only one chamber containing the acceptor solution with two cation exchange membranes on both sides is used, without any pumping (van der Stelt et al., 2005). The use of an additional membrane in the field DMT cell is expected to facilitate a faster cation exchange between the donor and the acceptor solutions (Kalis et al., 2006). The field DMT has been successfully used in-situ to measure free nutrient concentrations in slurries of animal manure (van der Stelt et al., 2005), free metal concentrations in simulated milk ultrafiltrate and reconstituted skim milk (Gao et al., 2009), and free trace metal concentrations in surface waters (Kalis et al., 2006; Sigg et al., 2006; Unsworth et al., 2006; Chito et al., 2012; Vega and Weng, 2013). Before the field DMT can be used in paddy fields, this analytical technique first needs to be tested since it has not been used previously to measure free trace metal concentrations in-situ in flooded soils.

The first objective of our study was to test the potential of the field DMT to measure the free trace metal concentrations in-situ in soil solution of a flooded paddy soil under anaerobic conditions. In our experimental approach, we carefully designed a soil column experiment with a field-contaminated paddy soil.

Speciation modeling can be a useful tool to investigate the underlying mechanisms of trace metal speciation in soil solution. Trace metal binding with inorganic ligands can be predicted based on known stability constants of metal complexes with such ligands and advanced models such as the Model VI (Tipping, 1998) and the Non-Ideal Competitive Adsorption Donnan (NICA-Donnan) model (Kinniburgh et al., 1999) can be used to predict complexation of trace metals with DOM (Weng et al., 2002; Koopmans et al., 2008; Koopmans and Groenenberg, 2011). Performing speciation calculations of trace metals for aqueous environmental systems is a complex task, due to the heterogeneity in the composition of DOM and the uncertainty and lack of model parameters (Groenenberg et al., 2010; Vega and Weng, 2013). Consequently, it is important to validate these models with regard to their ability to predict trace metal speciation under a wide variety of geochemical conditions, which can be done by comparing model results with independent DMT measurements of the free trace metal concentrations. Therefore, our second objective was to compare the field DMT measurements of free trace metal concentrations in both the aerobic and anaerobic layers of the soil column experiment with predictions of the free trace metal concentrations obtained by speciation modeling, using the Objects Representing CHEmical Speciation and TRAnsport (ORCHESTRA) framework (Meeussen, 2003), which includes the NICA-Donnan model.

2. Materials and methods

2.1. Soil sampling and physical–chemical soil properties

Soil with a clay loam texture was sampled from the 0–20 cm layer of a paddy field nearby a former transformer and electronic waste stripping and recycling factory in the vicinity of Taizhou city in Zhejiang Province in the southeast of China. This soil was air-dried, sieved through a 2 mm nylon sieve to remove stones and plant residues, and stored at room temperature of around 20 °C until further use for physical–chemical analyses and the column experiment in which the field DMT was tested. The pH was measured in a settling 1:10 (w:v) suspension of soil in 0.01 M $CaCl_2$, SOM by loss-on-ignition (550 °C), and clay by the sieve and pipette method (Houba et al., 1997, 2000). Short-range ordered (hydr)oxides of Al, Fe, and Mn were determined by using the acid ammonium oxalate extraction method (Novozamsky et al., 1986). Concentrations of Al, Fe, and Mn in the extracts (i.e., Al-ox, Fe-ox, and Mn-ox) were measured by inductively coupled plasma-atomic emission spectrometry (ICP-AES; IRIS Intrepid II). Total soil contents of trace metals were determined by digestion with Aqua Regia (Houba et al., 1997). Concentrations of Cd, Cu, Ni, Pb, and Zn in the digests were measured by ICP-AES. All these soil properties were determined in triplicate and average ± standard deviation is presented in Table 1.

2.2. Field DMT

The field DMT was used to measure the free trace metal concentrations in-situ in the overlying water layer and soil solution of the flooded paddy soil in a soil column experiment. The design of the field DMT cell used in this study was slightly modified from the field DMT cell as used by van der Stelt et al. (2005) and Kalis et al. (2006). In our modified version of the field DMT cell (Fig. 1), we added a polytetrafluoroethylene (PTFE) ring to the outer shell of the Perspex ring on both sides of the cell so as to enable us to mount a nylon membrane with a pore size of 20 μm to both sides of the cell. This modification was done to prevent soil particles from blocking and damaging the cation exchange