Chemical Geology 417 (2015) 279–288

Contents lists available at ScienceDirect

Chemical Geology

journal homepage: www.elsevier.com/locate/chemgeo

Molybdenum binding to soil constituents in acid soils: An XAS and modelling study

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ARTICLE INFO

Article history:
Received 30 June 2015
Received in revised form 7 October 2015
Accepted 9 October 2015
Available online 24 October 2015

Keywords:
Molybdate
Ferrihydrite
Aluminium hydroxide
Soils
Organic
Matter
Complexation

ABSTRACT

Despite its importance as a trace element, the binding mechanisms of molybdenum in soils are not well known. In this study, we studied the binding of molybdenum onto selected soil samples, and we used X-ray absorption spectroscopy (XAS) to characterize the coordination of molybdenum on three important environmental sorbents: ferrihydrite (Fh), amorphous aluminium hydroxide ($Al(OH)_3$) and fulvic acid. The X-ray near-edge structure (XANES) data showed that the added molybdenum(VI) was not reduced, although for the organic samples the coordination shifted from tetrahedral to octahedral. The EXAFS (extended X-ray absorption fine structure) analysis showed that molybdenum(VI) on Fh and $Al(OH)_3$ was dominated by edge-sharing bidentate complexes with Mo···Fe and Mo···Al distances of 2.80 and 2.62 Å, respectively. For ferrihydrite, there was a minor contribution from a corner-sharing bidentate complex at 3.55 Å. Further, geochemical modelling suggested an additional role of an outer-sphere complex at high pH. A sample from a spodic Bs horizon had XANES and EXAFS features similar to those of Mo sorbed to $Al(OH)_3$, highlighting the importance of $Al(OH)_3$-type sorbents in this soil. However, in the studied organic samples molybdenum(VI) was present in a distorted octahedral configuration as an organic complex. The results were used to improve molybdenum binding reaction equilibrium constants in the CD-MUSIC model for ferrihydrite and in the Stockholm Humic Model. Collectively the results show that acid soils may contain sorbents able to bind molybdenum efficiently, and thus prevent its leaching to waters.

1. Introduction

Molybdenum (Mo) is an essential trace element with an important role in the biogeochemical cycle of nitrogen (N), as it is required for N fixation and denitrification. The Mo-containing enzyme nitrogenase catalyses the reaction. In the most common form of this enzyme, molybdenum and iron are co-factors, where molybdenum is coordinated to a sum of about six oxygen and sulphur atoms in a distorted octahedral configuration (Burgess, 1990). Molybdenum deficiency in soils has frequently been reported, especially under P-deficient conditions (Murphy and Walsh, 1972; Wurzberger et al. 2012). However, molybdenum is also a potentially toxic contaminant that may be released from e.g. municipal solid waste incinerator bottom ash (Meima et al., 1999). The toxicity of molybdenum is related primarily to its interaction with copper and sulphur, causing copper deficiency in ruminants (Suttle, 1991).

Under conditions typical for most aerated soils, dissolved molybdenum exists primarily as dissolved molybdate (MoO_4^{2-}) ions. Adsorption to hydrous oxides is thought to be an important mechanism that restricts the mobility of molybdenum in the environment. For a long time it has been known that molybdate is bound to a variety of different iron(III) and aluminium(III) (hydr)oxides (Jones, 1957; Reisenauer et al. 1962). Examples include ferrihydrite (Gustafsson, 2003; Kashiwabara et al. 2011), goethite (Bibak and Borggaard, 1994; Arai, 2010), hematite (Goldberg et al. 1996), gibbsite (Manning and Goldberg, 1996; Miedaner et al. 2011) and alumina (Spanos et al. 1990). In addition, molybdate is bound also to titanium oxides such as titania (Bourikas et al. 2001). Molybdate adsorption is strongly pH-dependent with strong adsorption at low pH (below about 6) to weak or insignificant adsorption at higher pH. Further, competition with other anions modifies the extent of molybdate adsorption. For example, phosphate competes strongly for available adsorption sites, particularly at high pH (Gustafsson, 2003; Xu et al. 2006a). So far, relatively few studies have reported the coordination mode of adsorbed molybdate on (hydr)oxides. Goldberg et al. (2008) used attenuated total reflectance infrared (ATR-FTIR) and Raman spectroscopy and concluded that molybdate formed an inner-sphere surface complex on amorphous aluminium oxide at low pH, which shifted to an outer-sphere surface complex at high pH. Arai (2010), who studied molybdate adsorption on goethite, used extended X-ray absorption fine structure (EXAFS) spectroscopy at the Mo K edge and obtained evidence for both corner-sharing and edge-sharing bidentate complexes involving the tetrahedral molybdate anion. In addition, he observed octahedrally coordinated MoO_6

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http://dx.doi.org/10.1016/j.chemgeo.2015.10.016

polymers at low pH. In another Mo K-edge EXAFS study, molybdate adsorption on ferrihydrite was found to involve mostly outer-sphere complex formation, as there was only a minor contribution from second-shell Fe (Kashiwabara et al. 2011); however, it should be noted that the pH value was high (8), which may be important when interpreting these results.

Molybdenum(VI) may also be bound to natural organic matter (NOM). Already in 1967, sorption of molybdate to humic acid was observed (Szilagyi, 1967). Consistent with this, Bibak and Borggaard (1994) observed significant molybdate adsorption to organic matter especially at low pH (<5). Wichard et al. (2009) added molybdate to leaf litter and soil samples. They used Mo K-edge EXAFS and XANES (X-ray absorption near edge structure) spectroscopy to identify the reaction products. Their interpretation was that molybdenum formed complexes with tannins and tannin-like compounds, as well as to iron oxides. Additional evidence for the importance of natural organic matter for molybdenum binding has recently been obtained using stable isotopes (Siebert et al. 2015).

Surface complexation models have frequently been used to describe molybdate adsorption to hydrous oxides. Most previous attempts, however (e.g. the CD-MUSIC model of Gustafsson, 2003) did not constrain the model based on structural observations, and may therefore rely on incorrect assumptions as regards the coordination environment of the bound molybdate. Goldberg et al. (2008) were the first (and until now the only) authors who attempted to design such a model based on spectroscopic observations (in their case vibrational spectroscopy); they used the triple layer model to optimize surface complexation constants and found that the model agreed well with data for iron(III)/aluminium (hydr)oxides and mineral soils. As concerns molybdenum complexation onto natural organic matter, no model currently exists.

The objective of this work was to obtain information on the coordination of adsorbed molybdate on selected sorbents, ferrihydrite, amorphous aluminium hydroxide, and natural organic matter, all of which are likely to be of importance for Mo binding in acid soils, and to investigate whether the coordination of molybdate added to two soil horizons from a Spodosol could be understood based on these observations. Moreover, we investigated whether it was possible to use the spectroscopic data to design complexation models that capture the binding of molybdate to ferrihydrite and to natural organic matter in acid soils.

2. Materials and methods

2.1. Soils

Soil samples were collected from 4 soils from different locations in central Sweden. Two of these were Albic Podzols (Risbergshöjden and Storå), one was a Eutric Arenosol (Björkby Sand), and one was a Fibric Histosol (Paskalampa), according to IUSS Working Group WRB (2014). From the Risbergshöjden and Storå soils, O as well as Bs horizons were sampled. Selected chemical properties are shown in Table 1. The soils were sieved immediately after collection.

Table 1
Properties of investigated soil samples.

Soil	$pH(H_2O)$	Organic C	Clay	Fe_{ox}[a]	Al_{ox}[a]	Si_{ox}[a]	Al_{pyp}[b]
		%	%	mmol kg^{-1}			mmol kg^{-1}
Paskalampa Oi	3.8	46.7	<1	39	16	0	14
Risbergshöjden Oe	3.8	47.9	<1	13	30	0	22
Storå Oe	3.8	48.7	<1	8	21	0.1	16
Björkby sand A	4.5	6.4	14	65	67	3	61
Risbergshöjden Bs2	5.7	0.8	4.0	74	519	233	43
Storå Bs	5.3	1.3	2.9	63	350	121	79

[a] Extracted with 0.2 M oxalate buffer at pH 3.0 (van Reeuwijk, 1995).
[b] Extracted with 0.1 M $Na_4P_2O_7$ (van Reeuwijk, 1995).

For field-moist mineral soils a 4 mm sieve was used in accordance with standardized leaching test procedures (ISO TS 21268:2; ISO, International Organization for Standardization, 2007), while for organic soils an 8 mm sieve was used to facilitate the removal of coarse roots and branches. The soil samples were stored in a field-moist state at +5 °C for a maximum of three months before the experiments. The spodic B horizons (Risbergshöjden Bs2 and Storå Bs) were both characterized by low clay content ($\leq 4\%$). Both had appreciable amounts of oxalate-extractable Si (Table 1) and an $(Al_{ox} - Al_{pyp})/Si_{ox}$ ratio of 2.0 and 2.2, respectively. These observations suggest that imogolite-type materials, mostly allophane, are the predominant secondary Al phases in these soils (Gustafsson et al. 1995; Gustafsson et al. 1999). Imogolite-type materials were also identified in the Risbergshöjden Bs horizon by Kleja et al. (2005).

2.2. Model sorbents

2-Line ferrihydrite (Fh) was prepared according to Gustafsson et al. (1999) and Karltun et al. (2000). A mixture of 36 mmol L^{-1} $Fe(NO_3)_3$ and 12 mmol L^{-1}$NaNO_3$ was brought to pH 8.0 through dropwise addition of 4 mol L^{-1} NaOH (prepared immediately before use). The resulting suspension was aged for 16 h at 20 °C. Iron (hydr)oxide particles from such a suspension have been confirmed to be Fh using Fe K-edge EXAFS spectroscopy (Gustafsson et al., 2007); moreover, the use of X-ray diffraction confirmed the presence of Fh (data not shown). After synthesis the Fh suspension was back-titrated with 0.1 mol L^{-1} HNO_3 to pH 4.6 and stirred for about 30 min just before starting the batch experiments to avoid the presence of excessive CO_2 in the suspensions.

Amorphous aluminium hydroxide ($Al(OH)_3$) was prepared in a similar way as 2-line ferrihydrite, i.e. by mixing 36 mmol L^{-1} $Al(NO_3)_3$ and 12 mmol L^{-1} $NaNO_3$. The solution was then brought to pH 7.0 with 4 mol L^{-1} NaOH, and then the suspension was aged for 16 h. After synthesis, the $Al(OH)_3$ suspension was back-titrated to pH 5, and stirred for about 30 min before the batch experiments. X-ray diffraction confirmed that the formed $Al(OH)_3$ was amorphous in nature (data not shown).

2.3. Batch experiments

Briefly, either 1.00 g (for Risbergshöjden Oe and Storå Oe) or 2.00 g (other soils) field-moist soil was suspended in 30 mL solutions of variable composition in polypropylene centrifuge tubes, and then shaken for 7 days in a shaking water bath at 8 °C. This temperature was chosen for two reasons: (i) it represents the mean annual air temperature at the site, and (ii) it ensures that the microbial activity remains low during the equilibration period. The molybdenum(VI) binding following a Mo addition of 50 μmol L^{-1} Na_2MoO_4 was studied. This corresponds to molybdenum(VI) additions of 5.88, 5.88, 6.00, 0.83, 0.87, and 1.7 mmol Mo kg^{-1} dw for Risbergshöjden Oe, Storå Oe, Paskalampa Oi, Risbergshöjden Bs2, Björkby Sand A and Storå Bs, respectively. To produce a range of pH values in the suspensions, various amounts of acid (as HNO_3) or base (NaOH) were added, so that each system was studied at eight different pH values. For the organic soils (Risbergshöjden Oe, Paskalampa Oi and Storå Oe), the concentration of added Na_2MoO_4 was varied to investigate the influence on the equilibrium molybdenum(VI) solution concentration on the amount adsorbed. All experiments were made using a background electrolyte of 0.01 mol L^{-1} $NaNO_3$. However, for Risbergshöjden Oe experiments were carried out also in 0.1 mol L^{-1} $NaNO_3$ to study the effect of ionic strength. To evaluate possible competition effects from phosphate on molybdenum(VI) adsorption to organic matter, an additional data set was produced for the Paskalampa Oi sample in which 50 μmol L^{-1} molybdenum(VI) was added together with 1.4 mmol L^{-1} NaH_2PO_4.

After equilibration, the suspensions were centrifuged at 5000 *g* for 20 min, the pH values of the aqueous phases were measured (with a Radiometer glass combination electrode), and they were filtered (Acrodisc