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Aging effects on molybdate lability in soils

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HIGHLIGHTS

- ▶ The labile pool of MoO_4^{2-} in amended soils was observed to decrease with age in soils.
- ▶ A strong linear relationship was observed between *E* and *L* value results.
- ▶ Labile MoO_4^{2-} in Mo contaminated soils was <10% of the total Mo in soils.

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ABSTRACT

Aging reactions in soils can influence the lability and hence bioavailability of added metals in soils through their removal from labile pools into pools from which desorption is slow (non-labile pools). The aims of this study were to examine the effect of aging reactions on the lability of soluble molybdate (MoO_4^{2-}) added into soils with varying physical and chemical properties and develop models to predict changes in the labile pool of MoO_4^{2-} in soils with incubation time. Soils were spiked with soluble MoO_4^{2-} at quantities sufficient to inhibit barley root growth by 10% (EC_{10}) or 90% (EC_{90}) and incubated for up to 18 months. The labile pool of MoO_4^{2-} (*E* value) was observed to decrease in soils with incubation time, particularly in soils with high clay content. A strong relationship was observed between measures of MoO_4^{2-} lability in soils determined using *E* and *L* value techniques ($R^2 = 0.98$) suggesting *E* values provided a good measure of the potential plant available pool of MoO_4^{2-} in soils. A regression model was developed that indicates clay content and incubation time were the most important factors affecting the labile pool of MoO_4^{2-} in soils with time after addition ($R^2 = 0.70–0.75$). The aging model developed suggests soluble MoO_4^{2-} will be removed into non-labile pools more rapidly with time in neutral to alkaline clay soils than in acidic sandy soils. Labile MoO_4^{2-} concentrations in molybdenum (Mo) contaminated soils was found to be <10% of the total Mo concentrations in soils.

1. Introduction

Molybdenum is a trace element with an average concentration of 1–2 mg kg^{-1} in the Earth's crust (Taylor and McLennan, 1985). The water-soluble Mo concentrations in uncontaminated soils are generally <0.1 mg kg^{-1} (Brennan and Bruce, 1999). Molybdenum is an easily oxidised element with the dominant redox state being Mo(VI) in solutions at $E_H > 0$ V and pH > 5 (Anbar, 2004). The dominant soluble species found in oxygenated environments is the tetrahedrally coordinated oxoanion molybdate (MoO_4^{2-}).

The toxicity of soluble MoO_4^{2-} added into soils has recently been investigated using plants, invertebrate and microbial processes (Buekers et al., 2010; McGrath et al., 2010; Van Gestel et al., 2012). Total carbon content or ammonium oxalate extractable iron (Fe_{ox}) concentrations in soils were found to be the best predictors of toxicity threshold values (50% effective dose) for MoO_4^{2-} obtained using four plant species (*Brassica napus*, *Trifolium pratense*, *Lolium perenne*, *Lycopersicon esculentum*) (McGrath et al., 2010). McGrath et al. (2010) suggested the strong relationship between toxicity values and Fe_{ox} concentrations in soils indicate sorption of MoO_4^{2-} on Fe-oxides, which is pH dependent, has a large influence on MoO_4^{2-} toxicity in soils. The major soil properties governing MoO_4^{2-} toxicity in soils have recently been reported to be pH and clay content for plants and clay content for invertebrates and microorganisms (REACH Chemical Safety Report for Molybdenum, 2012).

The dominant sorbents of Mo in soils are oxides (e.g. iron (Fe), clay minerals, and organic matter) (Bibak and Borggaard, 1994; Goldberg et al., 1996, 2002). Molybdenum sorption onto soils and minerals has been shown to decrease with increasing pH (acidic to

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alkaline) (Bibak and Borggaard, 1994; Goldberg et al., 1998). Bibak and Borggaard (1994) found the sorption of Mo onto synthetic Al- and Fe-oxides and extracted humic acids to have a maximum at pH ~ 4. The sorption of Mo was found to decrease strongly with increasing pH for humic acid and decrease more gradually with increasing pH for Al- and Fe-oxides (Bibak and Borggaard, 1994).

When soluble metals are added into soils, there is an initial fast reaction for sorption onto solid phases (Ma et al., 2006a,b; Wendling et al., 2009). This initial fast reaction is followed by slower reactions that can remove metals from labile pools into a pool or pools from which desorption is slow, a process referred to as 'aging'. The immobilised metal can often still be measured using conventional techniques for bulk chemistry analysis but has essentially become unavailable for desorption/dissolution into soil solution, thus rendering it inaccessible to soil biota. Consequently, toxicity may decrease with time as the amount of actual metal exposure is reduced.

The aging of added Mo compounds into soils or oxide phases has been demonstrated by Brennan (2002, 2006) and Lang and Kaupenjohann (2003). Brennan (2006) found the residual value of a MoO_3 fertilizer added into soils to decrease with increasing contact time using wheat as a test crop. This decline in residual value was found to be more pronounced in the acidic soil, which had a larger capacity to sorb Mo. Hence, even if models are devised to assess the toxicity of soluble MoO_4^{2-} at any one time, regulators will still require models that can predict the effect of aging on metal lability in soils and its relationship to bioavailability and toxicity. This decrease in the labile or potential available pool of MoO_4^{2-} with incubation time in soils has also been reported for other anions such as arsenate and phosphate (Barrow, 1974; Song et al., 2006).

Stable and radioactive isotope dilution techniques have been used with success to assess the labile or potentially bioavailable pool of cations and anions in soils (e.g. cobalt (Co), copper (Cu) and phosphorus (P)) (Hamon and McLaughlin, 2002; Oliver et al., 2006). The labile pool of metals in soils can be directly assessed by sampling the solution phase (*E* value) or through the use of a biological component (e.g. plant or earthworm) grown directly in the labelled soil (*L* value) (Scott-Fordsmand et al., 2004; Oliver et al., 2006; Wendling et al., 2009).

The aims of this study were to examine the effect of aging reactions on the lability of soluble MoO_4^{2-} added into soils and develop models that can be used to predict changes in MoO_4^{2-} lability and hence potential bioavailability in soils with incubation time. The effectiveness of the *E* value technique to measure the potential bioavailable pool of MoO_4^{2-} in soils was assessed by comparing concentrations with those measured using isotope dilution with a plant biological component (ryegrass) (*L* value).

2. Materials and methods

2.1. Soil physical and chemical characteristics

Fifteen soils with varying physical and chemical characteristics were selected for this study (Table 1). These soils were collected from various locations in Europe and Australia. The soils were selected to cover a range of physical and chemical properties (e.g. pH and Fe_{ox} content) likely to be important in the partitioning and availability of MoO_4^{2-} in soils (Table 1). All soils were collected from the top 20 cm of the soil profile. The soils were air-dried at 25 °C and sieved to <2 mm.

2.2. Soil spiking with soluble MoO_4^{2-}

Soils were spiked with soluble MoO_4^{2-} ($Na_2MoO_4{\cdot}2H_2O$) at quantities sufficient to inhibit barley root growth by 10% (EC_{10}) or 90% (EC_{90}). The EC_x values for the ten European soils were supplied by Rothamsted Research, United Kingdom (Table 2). The EC_{10} and EC_{90} concentrations for the five additional soils (four Australian and Vault de Lugny) were estimated by comparing their Fe_{ox} contents with European soils for which EC_{10} and EC_{90} values for MoO_4^{2-} had been determined (Table 2). Air-dried soils were wetted to 60% of their moisture content at pF 2.0 and stored at 25 °C in 4.5 L polypropylene containers for the duration of the aging experiment. Soils were maintained daily at 60% of their moisture contents at pF 2.0 through the addition of ultrapure deionized water. The spiked soils were aged for 0, 0.5, 1, 3, 6, 12, and 18 months at 25 °C in a temperature controlled environment.

2.3. Porewater MoO_4^{2-} concentrations in soils with age

Porewater samples were collected from soils using the procedure outlined in McLaughlin et al. (1997). Triplicate 20–30 g subsamples (equivalent dry mass basis) for each soil at aging periods were weighed into 20 mL syringes containing acid-washed glass wool. The syringes were placed into 50 mL centrifuge tubes with a plastic stopper placed in the bottom and ultra pure deionized water (Milli-Q, Millipore) added to each soil to increase their water content to pF 1.7. After 24 h the syringes were centrifuged at 1200 g for 40 min and the supernatants filtered to <0.2 μm (Sartorius). Total Mo concentrations in filtered solutions were determined using inductively coupled plasma-optical emission spectroscopy (ICP-OES) (SPECTRO ARCOS) (Zarcinas et al., 1996) or inductively coupled plasma-mass spectrometry (ICP-MS) (Agilent 7500ce) (helium collision cell gas = 4 ml min^{-1}; double charged < 2% (m z^{-1} 70/m z^{-1} 140) and oxides < 1% (m z^{-1} 156/m z^{-1} 140)).

2.4. Ammonium nitrate extractable MoO_4^{2-} concentrations in soils with age

Triplicate 10.0 ± 0.02 g sub-samples (equivalent dry mass basis) for each soil at each aging period were weighed into 50 mL centrifuge tubes and mixed on an end-over-end shaker for 2 h with 25 mL of 1.0 M ammonium nitrate (NH_4NO_3) (Sigma). Samples were then centrifuged at 1200 g for 20 min and supernatants filtered to <0.2 μm (Sartorius). Total Mo concentrations in filtered solutions were determined using ICP-OES or ICP-MS.

2.5. Ammonium Bicarbonate – diethylenetriaminepentaacetic acid extractable MoO_4^{2-} concentrations in soils with age

Triplicate 5.0 ± 0.02 g sub-samples (equivalent dry mass basis) for each soil at each aging period were weighed into 50 mL vials and shaken for 15 min with 15 ml of ammonium bicarbonate-diethylenetriaminepentaacetic acid (AB-DTPA) (pH 7.6) (Sims, 1996). Samples were centrifuged at 1200 g for 20 min and supernatants filtered to <0.2 μm (Sartorius). Total Mo concentrations in filtered solutions were determined using ICP-OES or ICP-MS.

2.6. Isotopically exchangeable MoO_4^{2-} concentrations in soils (*E* value) with age

Quadruplicate 2.0 ± 0.02 g sub-samples (equivalent dry mass basis) for each soil at each aging period were weighed into 50 mL centrifuge tubes and mixed end-over-end for 48 h with 20 mL of ultrapure deionized water (Milli-Q, Millipore). Samples were then spiked with 100 μl of $^{99}MoO_4^{2-}$ ($t_{1/2}$ 67 h) (25 kBq, ANSTO Radiopharmaceuticals and Industrials) and mixed end-over-end for a further 72 h. After this spike equilibration period, samples were centrifuged at 1200 g for 20 min and supernatants filtered to <0.2 μm (Sartorius).