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Influence of Organic Amendments on the Mobilization of Molybdenum in Soils

S. J. Calderone and W. T. Frankenberger, Jr.

Department of Soil and Environmental Sciences, University of California,
Riverside, California 92521, USA

Recent attention has been focused on toxic levels of selenium (Se), arsenic, chromium, mercury, boron and molybdenum (Mo) accumulating in saline agricultural evaporation pond waters. Evaporation ponds are used as a means of disposal of drainage water on the west side of the San Joaquin Valley, California. Although this is an effective disposal practice for agricultural drainage water, the ponds attract wildlife and waterfowl which may create adverse environmental risks. Much of the attention has been focused on Se and its impact on the wildlife at Kesterson Reservoir (Merced Co., CA). There is also a major concern with the Mo content in these saline waters and its effect on the upper food chain. The Mo content has been reported as high as 28 mg L^{-1} in water and 21 mg kg^{-1} in sediment samples obtained from Merced County, CA (K. Tanji and M. E. Grismer, Evaporation ponds for disposal of agricultural wastewater, State Water Resources Control Board, Quarterly Report, Jan.-Feb., 1987).

Molybdenum can be fixed in soil or liberated into soil solution and become available for biotic uptake. Plant availability increases with increasing pH (Albasel and Pratt, 1989). Deficiencies in plants usually occur when the Mo content is <0.1 mg kg^{-1} in their tissues (Johnson, 1966). Molybdenosis (Mo toxicity) results when excessive amounts of Mo are taken up by ruminants. Molybdenosis of grazing animals has been observed on the west side of the San Joaquin Valley, CA (Barshad, 1948).

Molybdenum is a metallic element that can exist in different valences and oxidation states. Amin and Joham (1958) fractionated the Mo forms in soil into the following: i) water soluble (molybdate salts), ii) ammonium hydroxide soluble (Mo trioxides), and iii) the oxidizable fraction (reduced oxides of Mo). Oxidation and alkaline conditions favor Mo mobility. The objective of this study was to determine the effect of various organic materials on the solubilization and mobilization of molybdenum in soil.

Send reprint requests to W. T. Frankenberger, Jr. at the above address.

MATERIALS AND METHODS

A highly saline sediment collected from the Kesterson Reservoir (Merced County, CA) was allowed to air-dry, screened through a 2-mm mesh screen and homogenized. The chemical and physical properties of this soil were as follows: pH, 8.5; organic C, 84 g kg^{-1}; total N, 8 g kg^{-1}; EC_e, 27.0 dS m^{-1}; SAR, 6.0; Mo, 7.6 mg kg^{-1}; B, 31 mg kg^{-1}; sand, 26% and clay, 29%.

The organic amendments selected for this study included Citrus (orange) peel, cattle manure, gluten and casein. Orange peel was obtained from Sunkist Growers, Corona, CA, and cattle manure from Harris Ranch, near Coalinga, CA. Both the orange peel and manure were dried in a convection oven at 60°C. Once dry, both samples were ground to pass through a 0.53-mm mesh screen. Casein (Lot #27F0378) and gluten (#15F0182) were obtained from Sigma (St. Louis, MO). The organic materials were added to 25 g of soil well mixed with 25 g of acid-washed coarse sand (10-60 mm), homogenized, and added to glass tubes (3.4 cm dia. by 15 cm in length). A glass wool plug was placed at the base of each incubation tube, followed with the sand/sediment mixture and then a second glass wool plug above to prevent channeling upon elution. The rate of application was 30 g kg^{-1} soil for both the orange peel and cattle manure and 7.5 g kg^{-1} soil for the proteins, casein and gluten. The control received no organic amendments. There were four replicates per treatment. Each tube was incubated up to 8 weeks under ambient laboratory conditions in the dark to prevent algal growth. At weekly intervals, the soil columns were eluted with 100 ml of deionized water.

Analysis of Mo was performed using a Jarrell-Ash inductively coupled argon plasma (ICAP) optical emission spectrometer. Instrument parameters were set as follows: coolant flow, 14 L min^{-1}; sample flow, 0.5 L min^{-1}; plasma flow, 0 L min^{-1}; argon pressure to the nebulizer, 414 kPa; nebulizer type, cross flow; integration time, 17 sec, incident power, 1.25 km^2 kg s^{-3}; reflected power, <10 m^2 kg s^{-2}; observation height, 13 mm above the coil; sample aspiration rate, 1.5 ml min^{-1}.

The concentration of Mo collected in the leachate is represented in Fig. 1 as the cumulative amounts of mobilized Mo (µg Mo kg^{-1} soil). Error bars depict the cumulative standard error of the data.

RESULTS AND DISCUSSION

Figure 1 illustrates the effect of various organic amendments on the amount of soluble Mo leached from soil columns when incubated up to 8 weeks. Molybdate (MoO_4^{2-}) is not tightly bound to soil and is readily removed in alkaline media. The application of gluten enhanced the solubilization of Mo 3-fold over the

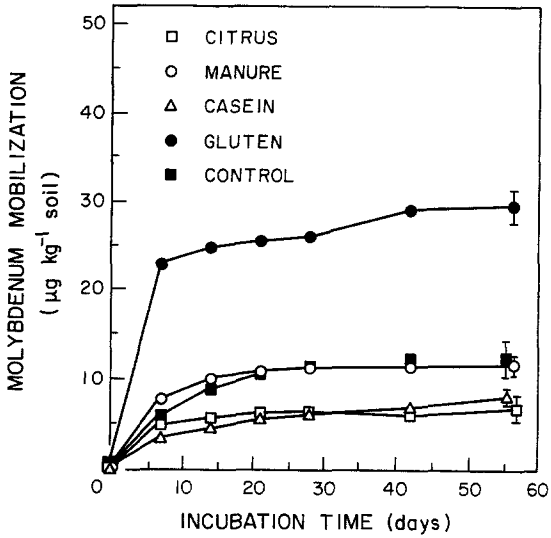

Figure 1. Effect of organic amendments on the mobilization of molybdenum in soils.

unamended control. Most of the soluble Mo was released within the first 7 days of incubation. There was no difference in the amount of soluble Mo collected in the leachate between the unamended and manure-treated soil. The application of casein and citrus peel promoted fixation of Mo in soil.

A blue color was noted in the leachate, collected from soil columns treated with ground orange peel. This reaction could have possibly been a result of Mo reduction. However, its stability in the leachate was short-lived with the loss of blue coloration in 24 h. Bautista and Alexander (1972) observed blue bacterial colonies upon reduction of either molybdate or molybdenum trioxide when present in culture media. They observed an intense blue color upon reduction of molybdenum trioxide by Pichia guillermurdii. Molybdenum blue can be associated with a number of pentavalent or hexavalent Mo species (Killeffer and Linz, 1952).

The water soluble fraction of Mo in soils is usually low and highly pH-dependent. Its solubility increases with increasing OH^- concentration. The leachate pH at the 8th week interval ranged from 8.0 to 8.4 among each of the soil columns. The application of gluten was the most active in desorption of Mo while casein and orange peel promoted fixation. Previous work in our laboratory has shown that casein and orange peel tend to lower soil pH, thus reducing the water soluble Mo subject to leaching. However, Mo could also possibly be immobilized by a pH dependent-ligand exchange reaction between oxides, organic matter, and/or the mineral clay surfaces.

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