

**GEOCHEMICAL MODELING FOR  
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CONTROLLING THE DISSOLVED  
MOLYBDENUM IN COAL OVERBURDEN,  
POWDER RIVER BASIN, WY, U.S.A.**

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## Geochemical modeling for predicting potential solid phases controlling the dissolved molybdenum in coal overburden, Powder River Basin, WY, U.S.A.

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**Abstract**—Surface coal mining processes may increase the dissolved Mo concentrations in overburden (mine spoils) and in nearby soils. Spoil and soil samples were subjected to solubility studies for determining potential solid phases controlling the dissolved Mo. Additionally, native soil samples were included in the study for comparison. Ion activity products (IAPs) were calculated from the total elemental concentrations of aqueous extracts and compared with solubility products ( $K_{sp}$ s) of Mo solid phases. Effects of dissolved organic carbon (DOC) on metal ion complexation were also evaluated. The pH of aqueous extracts ranged from 7.14 to 8.31. DOC in aqueous extracts varied from 17.3 to 58.7 mg/l. Molybdenum concentrations in aqueous extracts ranged between 11.5 and 35.6  $\mu\text{g/l}$  for spoils, 13.5 and 20.0  $\mu\text{g/l}$  for soils near mine site and 14.5 and 29.6  $\mu\text{g/l}$  for native soils. Initially, IAPs suggested varying degrees of supersaturation with respect to wulfenite ( $\text{PbMoO}_4$ ). However, when DOC- $\text{Pb}^{2+}$  complexes were considered, the IAPs indicated a close approach to saturation with respect to  $\text{PbMoO}_4$ . Furthermore, the IAPs suggested a high degree of undersaturation with respect to powellite ( $\text{CaMoO}_4$ ) and ferrimolybdate ( $\text{FeMoO}_4$ ). Results in this study suggest the dissolved Mo concentrations in mine spoils and soils that are near coal mine may be controlled by  $\text{PbMoO}_4$  solid phase.

### INTRODUCTION

MOLYBDENUM is an essential element for both plants and animals. However, excessive Mo in forage can cause molybdenosis, a Mo induced copper deficiency to livestock and wildlife. Several studies (ALLOWAY, 1973; STONE *et al.*, 1983) have shown that Mo concentrations  $>2.0$  mg/kg in forage can cause molybdenosis in cattle near mining areas. During surface coal mining, rock material (overburden) overlying the coal is removed. Exposure of previously buried material to surface conditions may oxidize Mo-containing sulfides and organic matter. Oxidation of such compounds may be a source for Mo in overburden (mine spoils) and soils near such mining activities. Thus, development of coal resources, particularly by surface mining, could generate spoils and soils containing high dissolved Mo. Furthermore, plants growing on such environments may accumulate high levels of Mo, which could lead to molybdenosis in animals (KUBOTA, 1975; NEUMAN *et al.*, 1987).

To predict Mo solubility in spoils and soils near

coal mines, it is essential to understand the chemical processes responsible for the release of Mo. Such information is also crucial for developing effective mineland reclamation strategies with respect to Mo. Solubility of Mo in spoils and soils near coal mines is controlled by a number of chemical processes including, solid phase equilibria (ADRIANO, 1986). The presence of sparingly soluble solid Mo phases and their possible significance in these environments have not been explored. Objectives of this study were:

(1) To examine chemical speciation of Mo in aqueous extracts of coal mine spoils and soils near coal mines;

(2) To determine the effects of DOC on the determination of IAPs of Mo solid phases; and

(3) To predict potential solid phases controlling the dissolved Mo concentrations in both mine spoils and soils near coal mines.

### MATERIALS AND METHODS

The general location of the study area where spoil and soil samples were collected is shown in Fig. 1. Spoil samples (spoil 1 through 3) were collected from the Dave Johnston Coal Mine Company at the southern edge of the Powder

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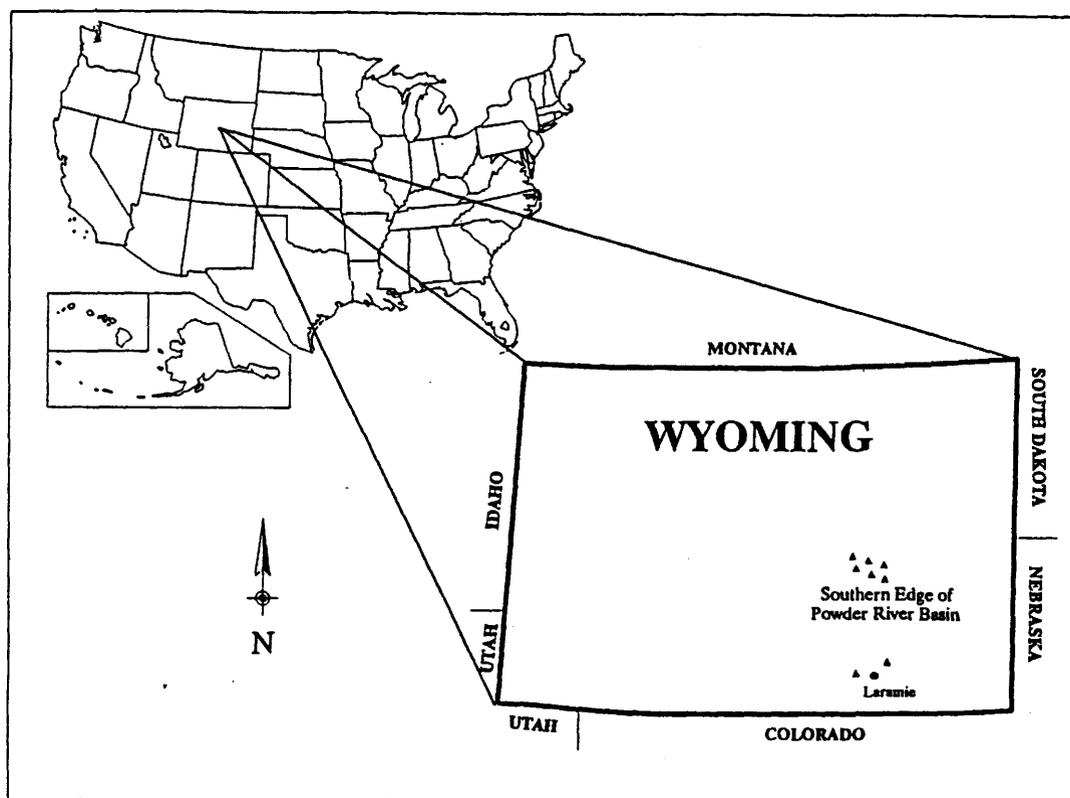


Fig. 1. General location of study area where spoil and soil samples were collected.

River Basin, Wyoming. At this particular coal company, the coal is found under overburden in the School and Badger coal seams, with average depths of 30 and 16 feet, respectively. A large dragline is used to remove the overburden to produce  $\approx 3$  million tons of coal annually. As mining progresses, top soil is removed and either directly reapplied or stored for later application. During coal removal, the remaining overburden is removed and earmarked for later use. Once mining is completed, the overburden and top soil are used to restore the land to its original condition. Soil samples (soil 1 through 3) were collected from a ranch located 2 km from the mine site. Spoil and soil samples near the mine site are classified as sandy, mixed, Ustic Torriorthents.

The climate of the Powder River Basin is temperate and semiarid. Average daily temperature varies from a low of 5°F in the winter to 90°F in July. Precipitation ranges from 11 inches in the southern part of the study area to 18 inches in the north. The geology of the Powder River Basin is the fort union and wasatch formations of early Tertiary age and consist of continental-type sediments deposited in fluvial, lacustrine and swampy environments. Strata in these formations are lenticular and consist of alternating sandstone, siltstone and claystone, with occasional coal beds (NAFTZ and RICE, 1989).

Two native soils (soils 1 and 2) were also included in the study for comparison. The soil 1 sample was collected from the Laramie Range, Wyoming and soil 2 was collected from the stockfarm of the University of Wyoming near the Laramie River, Wyoming. Soil 1 is classified as a coarse-loamy, mixed Cumulic Haploboroll and soil 2 is classified as a sandy-skeletal, mixed Borollic Haplargid. Spoil and soil samples used in this study are representative of materials that are widespread in the U.S.A. as well as other parts of the world. Samples were ground to pass a 2 mm sieve and analyzed for pH, organic matter (CHAPMAN and PRATT,

1961),  $\text{CaCO}_3$  equivalent (RICHARDS, 1969), texture (GEE and BAUDER, 1986) and total Ca, Fe, Pb and Mo concentrations (BENNETT and OLIVER, 1976; RAO, 1971).

For geochemical modeling, duplicate 50 g samples were suspended in 150 ml of distilled-deionized  $\text{H}_2\text{O}$  in 250 ml plastic bottles. Sample suspensions were agitated on a rotary shaker at 120 rpm under laboratory conditions (i.e.  $25 \pm 1^\circ\text{C}$ ). Laboratory air saturated with distilled-deionized  $\text{H}_2\text{O}$  was continuously passed slowly through the sample suspensions to achieve steady conditions in a relatively short period of time (REDDY *et al.*, 1990a). After reacting for 7, 14, 21 and 28 d the suspensions were centrifuged and filtered through 0.45  $\mu\text{m}$  millipore filters. Each clear aqueous extract was divided into two subsamples. One was acidified with HCl to pH between 4.5 and 5.0 and the other was left unacidified. Unacidified extracts were analyzed for pH, total carbonate species, fluoride, sulfate and chloride. Acidified extracts were analyzed for various cations, anions and dissolved organic carbon (DOC).

The pH was measured with an Orion combination electrode. The Eh was measured with an Orion platinum (Pt) electrode with a Ag-AgCl<sub>2</sub> reference electrode. The Eh readings were taken over a period of 0.5–2 h until the drift was less than 3 mV. Stable readings were always obtained within 2 h. Stability of the readings was confined in selected extracts by monitoring the readings over a period of 24 h. From Eh measurements, pe ( $-\log e^-$  activity) was calculated.

Carbonate species were measured by titrating extracts with standardized HCl to pH 8.3 and pH 4.5 end points. Calcium, Mg, Si, Al, Mn and B were measured by inductively coupled plasma optical emission spectrometry (ICP-OES). Potassium and Na were measured by atomic emission. Copper, Zn, Pb and Mo were measured by atomic absorption (AA) using a graphite furnace. Specific ion electrodes were used to measure Cl and F concentrations.

Table 1. Selected properties of spoil and soil samples

Sample	Texture	pH*	OM	CaCO <sub>3</sub> equivalent (g kg <sup>-1</sup> )
Spoil 1	Sandy clay loam	7.84	12.3	21.4
Spoil 2	Sandy loam	8.39	3.9	7.8
Spoil 3	Sandy clay loam	7.87	8.6	33.0
Soil 1 near mine site	Loamy sand	6.95	9.4	8.6
Soil 2 near mine site	Sandy clay loam	7.86	23.9	29.3
Soil 3 near mine site	Sandy clay loam	8.44	13.7	69.9
Native soil 1	Sandy clay	8.18	16.1	13.4
Native soil 2	Sandy loam	7.88	14.4	41.6

\*Measured in the saturated paste

The concentration of SO<sub>4</sub><sup>2-</sup> was measured by a titrimetric method using nitrochromeazo as an indicator (RASNICK and NAKAYAMA, 1973). Phosphate was determined by the ascorbic acid molybdotartrate method (WATANABE and OLSEN, 1965) and DOC was analyzed with a coulometric technique.

The speciation model GEOCHEM (SPOSITO and MATTIGOD, 1980) was used to calculate ion activities. Significant Mo solution species were added to the GEOCHEM database to calculate accurate ion activities (REDDY *et al.*, 1993). Complete details regarding the selection of standard gibbs free energies of formation of various Mo species are reported in REDDY *et al.* (1990b). GEOCHEM utilizes total elemental concentrations and pH of aqueous extracts to calculate ion activities. From ion activities, ion activity products (IAPs) were calculated and compared with solubility products ( $K_{sp}$ s) to evaluate potential solid phases controlling the dissolved Mo concentrations in aqueous extracts. We assumed that IAPs within  $\pm 0.50$  log units of  $K_{sp}$ s of solid phases represented equilibrium, and that solid phase was a probable control on the concentration of ions involved. The variation within that range is accounted for by the uncertainty of IAP estimates and  $K_{sp}$  measurements (STUMM and MORGAN, 1981).

## RESULTS AND DISCUSSION

Table 1 summarizes the selected properties of the samples examined in this study. These results suggest a wide range of pH, texture, organic matter and CaCO<sub>3</sub> content. Total concentrations of Ca, Fe and Pb were greater than Mo concentrations (Table 2). Furthermore, the total Pb and Mo concentrations in these samples were high when compared to the selected concentration of these elements in soils. An average concentration of total Pb and Mo for soils are 10 and 2 mg kg<sup>-1</sup>, respectively (LINDSAY, 1979).

Table 2. Total concentration of selected elements in spoil and soil samples

Sample	Ca g kg <sup>-1</sup>	Fe g kg <sup>-1</sup>	Pb mg kg <sup>-1</sup>	Mo mg kg <sup>-1</sup>
Spoil 1	10.8	22.4	47.6	4.5
Spoil 2	3.0	10.2	24.8	5.0
Spoil 3	10.1	21.2	54.7	6.1
Soil 1 near mine site	2.2	12.5	22.2	4.9
Soil 2 near mine site	9.8	25.2	42.6	3.6
Soil 3 near mine site	14.0	21.2	47.4	5.6
Native soil 4	7.0	17.1	18.9	3.5
Native soil 5	17.7	25.9	20.3	5.1

The pH of spoil and soil aqueous extracts ranged between 7.0 and 8.3 and pe + pH varied from 11.85 to 14.18 (Table 3). These conditions represent somewhat alkaline and moderately oxidizing environments. Data in Table 3 also suggest that Ca, Fe, Pb and Mo concentrations in aqueous extracts reached steady state conditions within 21 d of the reaction period. Therefore, the data from the 21 d reaction period has been presented as results for discussion.

In general, mine spoils are much more reactive chemically when compared to soils because spoils are exposed to oxidizing environments during surface mining process (NEUMAN *et al.*, 1987). Such conditions may favor the dissolution of more soluble minerals and the precipitation of less soluble minerals. For Mo, only a few naturally occurring minerals are known. The most common mineral is molybdenite (MoS<sub>2</sub>). Occasionally, molybdite (MoO<sub>3</sub>) and isemannite (Mo<sub>3</sub>O<sub>8</sub>) are also found as alteration products of molybdenite. More frequently observed secondary Mo minerals are PbMoO<sub>4</sub>, CaMoO<sub>4</sub> and FeMoO<sub>4</sub> (TITLEY, 1963).

The log IAPs for PbMoO<sub>4</sub> ranged from -14.0 to -14.7 for spoil aqueous extracts whereas log IAPs ranged from -13.8 to -15.6 for soil aqueous extracts. A comparison between log IAPs and log  $K_{sp}$  of PbMoO<sub>4</sub> (i.e. -15.9, WAGMAN *et al.*, 1982) suggested varying degrees of supersaturation, indicating that PbMoO<sub>4</sub> was probably not controlling the dissolved Mo concentrations in these samples.

Dissolved organic carbon is usually divided into fulvic and humic acids. Fulvic acid is known to complex Pb<sup>2+</sup> in natural waters (GAMBLE, 1970; REUTER and PERDUE, 1977; STEVENSON and WELCH, 1979; SARR and WEBBER, 1980; SPOSITO *et al.*, 1981). Determination of Pb in spoil and soil aqueous extracts with ICP or AA probably included both inorganic and organic species of Pb. The Pb<sup>2+</sup> activities calculated using total concentration of Pb in these extracts, without correcting for organic complexes, would result in overestimation of Pb<sup>2+</sup> activities.

Data summarized in Table 4 show that the concentration of DOC for spoil aqueous extracts ranged from 46.6 to 51.7 mg/l. DOC concentration ranged from 17.3 to 54.7 mg/l for soil aqueous extracts. Concentration of DOC ranged between 35.3 and

Table 3. Partial chemical data of aqueous extracts

Reaction time (d)	pH		DOC	Ca	Fe (-log mol l <sup>-1</sup> )	Pb	Mo
	pe + pH						
Spoil 1							
7	7.97	12.64	2.40	2.64	5.57	6.77	6.70
14	7.91	12.15	2.40	2.62	5.60	6.75	6.66
21	7.91	11.99	2.36	2.62	5.29	6.76	6.66
28	7.92	11.85	2.33	2.62	5.25	6.76	6.65
Spoil 2							
7	7.70	14.18	2.41	3.37	3.71	6.77	6.92
14	7.34	14.01	2.39	3.22	3.74	6.75	6.92
21	7.92	14.03	2.41	3.22	3.74	6.76	6.92
28	7.96	13.95	2.45	3.22	3.74	6.76	6.94
Spoil 3							
7	8.17	12.54	2.39	2.63	5.20	6.72	6.45
14	8.05	12.47	2.40	2.57	5.34	6.74	6.43
21	8.20	12.35	2.37	2.55	5.38	6.74	6.43
28	8.15	12.52	2.37	2.53	5.34	6.73	6.44
Soil 1 near mine site							
7	6.78	13.69	2.29	3.49	3.64	6.55	6.78
14	6.87	13.75	2.27	3.46	3.48	6.80	6.81
21	7.14	13.49	2.34	3.47	3.44	6.74	6.69
28	7.08	13.14	2.33	3.40	3.37	6.61	6.69
Soil 2 near mine site							
7	8.07	13.02	2.78	3.15	5.00	7.19	6.80
14	8.18	13.15	2.85	3.03	4.83	7.09	6.82
21	7.80	13.70	2.69	3.06	4.87	7.14	6.85
28	7.80	13.85	2.67	3.01	4.93	7.13	6.93
Soil 3 near mine site							
7	8.32	12.46	2.97	3.18	4.70	7.13	6.98
14	8.23	12.53	2.95	3.17	4.73	7.10	6.92
21	8.31	12.71	2.83	3.13	4.76	7.08	6.83
28	8.31	12.80	2.80	3.10	4.83	7.09	6.76
Native soil 1							
7	7.63	13.43	2.40	3.06	5.15	6.98	7.05
14	7.99	13.72	2.34	3.04	5.10	7.04	6.87
21	8.03	13.55	2.31	3.03	4.93	7.09	6.82
28	8.07	13.61	2.33	3.04	4.86	7.09	6.83
Native soil 2							
7	8.17	13.84	2.40	2.78	5.96	7.01	6.55
14	8.28	13.89	2.44	2.76	5.96	6.95	6.52
21	8.25	13.73	2.53	2.75	6.04	6.95	6.51
28	8.24	13.38	2.53	2.75	6.14	6.95	6.50

Table 4. Effect of DOC-Pb<sup>2+</sup> complexation on Pb<sup>2+</sup> activities in aqueous extracts from 21 d reaction period

Sample	DOC (mg/l)	Pb <sup>2+</sup> activity (-log)		% Pb-DOC complex
		Without DOC	With DOC	
Spoil 1	51.7	7.78	8.83	86.0
Spoil 2	46.4	6.49	8.04	92.8
Spoil 3	50.6	7.47	8.45	84.7
Soil 1 near mine site	54.7	6.20	8.42	95.6
Soil 2 near mine site	24.0	8.09	8.72	45.3
Soil 3 near mine site	17.3	7.96	8.65	35.8
Native soil 1	57.5	7.00	8.37	84.8
Native soil 2	35.3	7.47	8.29	83.0

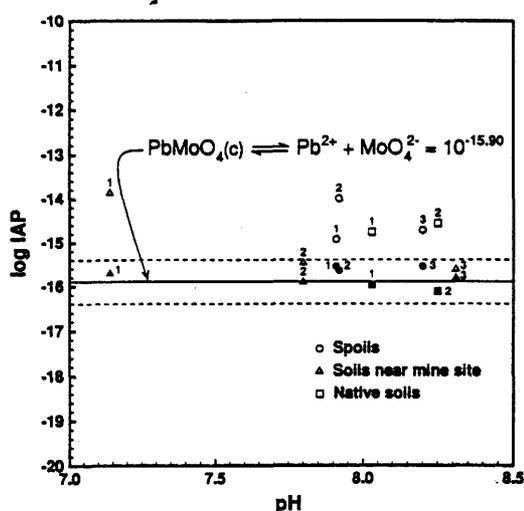


FIG. 2. IAPs of  $\text{PbMoO}_4$  for spoil and soil extracts. Open symbols represent IAPs without considering DOC- $\text{Pb}^{2+}$  complexes. Closed symbols represent IAPs considering DOC- $\text{Pb}^{2+}$  complexes.

57.5 mg/l for aqueous extracts from native soils. Determination of concentration of individual organic compounds in natural waters is very hard because they are complex and difficult to analyze (DREVER, 1988). SARR and WEBBER (1980) reported that fulvic acid has greater affinity for binding  $\text{Pb}^{2+}$  than humic acid in soils. Therefore, we assumed DOC concentrations in spoil and soil aqueous extracts as fulvic acid for modeling ion activities of  $\text{Pb}^{2+}$ . However, we suggest that readers should observe caution regarding these assumptions.

Two types of calculations were made with GEO-CHEM to determine the effects of fulvic acid on IAPs of  $\text{PbMoO}_4$ . First,  $\text{PbMoO}_4$  IAPs were calculated without considering fulvic acid as an input to the model. Second,  $\text{PbMoO}_4$  IAPs were calculated by including fulvic acid in the model (MATTIGOD and SPOSITO, 1979). The activity of  $\text{Pb}^{2+}$  decreased significantly when DOC was considered for ion activity calculations (Table 4). The percentage of Pb complexed with DOC is summarized in Table 4. The percentage of total Pb in aqueous extracts bound with DOC was greater than 50% for all samples except for soil 2 and 3 from near the mine.

Calculated IAPs for  $\text{PbMoO}_4$  were plotted against pH (Fig. 2) to explore the possibility that  $\text{PbMoO}_4$  is probably controlling the dissolved Mo concentrations in spoil and soil aqueous extracts. When DOC was considered as a ligand for ion activity calculations, log IAPs for  $\text{PbMoO}_4$  in aqueous extracts were very close to its log  $K_{sp}$  and ranged from -15.55 to -16.11 with a mean value of -15.8, suggesting that the dissolved Mo concentrations were probably controlled by  $\text{PbMoO}_4$ . Additionally, results presented in Table 4 and Fig. 2 suggest that as DOC decreased, the difference of log IAPs and log  $K_{sp}$  for  $\text{PbMoO}_4$  also decreased. Thus, the initially

observed high degree of supersaturation of IAPs with respect to  $K_{sp}$  of  $\text{PbMoO}_4$  for spoil and soil samples may suggest overestimation of  $\text{Pb}^{2+}$  activities due to organic complexes.

For  $\text{PbMoO}_4$  to form in spoil and soil samples, an adequate source of Pb is necessary. The concentration of Pb in these samples was much higher than Mo (Table 2). These results suggest that spoil and soil samples examined in this study have an adequate source of Pb for  $\text{PbMoO}_4$  to precipitate. However, identification of a minor solid phase like  $\text{PbMoO}_4$  in these samples with X-ray diffraction (XRD) or scanning electron microscope (SEM) would be difficult and such techniques are generally successful only when the solid phase content is greater than approximately 5%.

VLEK and LINDSAY (1977) examined the solubility of solid Mo phases in soils. The pH of soils ranged from 5.5 to 7.7. Their data for alkaline soil suggested near saturation with respect to  $\text{PbMoO}_4$ . Recently, REDDY and GLOSS (1993) also suggested that dissolved Mo concentrations in aqueous extracts from alkaline soils are probably controlled by  $\text{PbMoO}_4$ . Other studies have shown that  $\text{PbMoO}_4$  could occur in active and abandoned mine tailings from semi-arid environments (ROSEMEYER, 1990; BIDEAUX, 1990). It is probable that, because the spoil samples were from a coal mine site, which is located in a semi-arid environment and soil samples were from the vicinity of this coal mine,  $\text{PbMoO}_4$  may originate from mine spoils.

Overall, results in this study suggest that  $\text{PbMoO}_4$  probably controls dissolved Mo concentrations in spoils and soils that are near coal mining activity. If  $\text{PbMoO}_4$  controls Mo solubility, the concentration and availability of Mo in these environments will increase as pH increases (VLEK and LINDSAY, 1977), which may represent a potential for Mo toxicity and contamination.

Calcium molybdenate and  $\text{FeMoO}_4$  are often proposed as solid phase controls for the dissolved Mo concentrations in soils (SARAFIAN and FURBISH, 1965; REYES and JURINAK, 1967). A comparison of IAPs with  $K_{sp}$ s for these solid phases (Table 5) demonstrated the experimental IAPs were highly undersaturated, suggesting that these solid phases were not controlling the dissolved Mo concentrations in the spoils and soils examined in this study.

## CONCLUSIONS

Solubilities of Mo solid phases were examined in coal mine spoils, soils near a coal mine site and native soils. Samples used in this study had different pH, texture, organic matter and  $\text{CaCO}_3$  contents. Total Pb and Mo concentrations in these samples were much higher than the mean concentration of these elements in average soils. Dissolved Mo concentrations suggested a close approach to saturation with

Table 5. Solubilities of Pb, Ca and Fe molybdate solid phases in aqueous extracts for 21 d reaction period

Sample	PbMoO <sub>4</sub>	(-log IAP) CaMoO <sub>4</sub>	FeMoO <sub>4</sub>
	(-log K <sub>sp</sub> = 15.9)	(-log K <sub>sp</sub> = 8.1)	(-log K <sub>sp</sub> = 7.7)
Spoil 1	15.55	10.28	20.02
Spoil 2	15.65	10.82	14.73
Spoil 3	15.55	10.31	20.88
Soil 1 near mine site	15.70	10.15	12.49
Soil 2 near mine site	15.90	10.50	19.55
Soil 3 near mine site	15.80	10.55	20.98
Native soil 1	15.96	10.66	17.83
Native soil 2	16.11	10.78	18.31

respect to PbMoO<sub>4</sub>, when DOC-Pb<sup>2+</sup> complexes were considered for ion activity calculations. The IAPs for all extracts were undersaturated with respect to CaMoO<sub>4</sub> and FeMoO<sub>4</sub>. Results from this study suggest that the dissolved Mo concentrations in mine spoils and soils near coal mining areas may be controlled by PbMoO<sub>4</sub>. If PbMoO<sub>4</sub> controls the dissolved Mo concentrations, then Mo availability and mobility in these environments should increase as pH increases.

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