GEOCHEMICAL SPECIATION AS RELATED TO THE MOBILITY OF F, Mo AND Se IN SOIL LEACHATES

K.J. Reddy   Steven P. Gloss

                                        1993
Journal Article   WWRC-93-04

In

Applied Geochemistry

K.J. Reddy and Steven P. Gloss
Wyoming Water Resources Center
University of Wyoming
Laramie, Wyoming

Geochemical speciation as related to the mobility of F, Mo and Se in soil leachates

K. J. Reddy and S. P. Gloss

Wyoming Water Resources Center, P.O. Box 3067, University of Wyoming, Laramie,
Wyoming 82071, U.S.A.

Abstract—Chemical speciation of soil leachates is necessary for evaluating a number of processes including solid phase controls, leaching potentials and toxicity problems. The objectives of this study were to examine chemical composition of soil leachates, potential solid phase controls of F, Mo and Se and evaluate their mobility in a calcareous soil. A typical calcareous soil was sampled at 10-cm increments from the surface to a depth of 70-cm. Soil leachates were extracted with distilled deionized H_2O and subjected to speciation studies. As depth of the soil increased, concentrations of F and Mo increased from 0.77 to 6.74 mg/l and 0.06 to 0.15 mg/l, respectively. Selenium concentration increased slightly (0.002–0.005 mg/l) but showed highest levels at intermediate soil depths. Chemical speciation indicated soil leachates were dominated by F^-, $MgMoO^\circ_4$ and $MgSeO^\circ_3$ species. The F and Mo concentrations, at lower depths, indicated a close approach to saturation with respect to fluorite (CaF_2) and powellite ($PbMoO_4$), respectively. Results obtained in this study suggest that as soil depth increases, the mobility of F, Mo and Se is increased due to the chemical form in which these elements are present in the soil leachates.

INTRODUCTION

ALKALINE conditions in calcareous soils often enhance the solubility of anionic elements (e.g. F, Mo, Se). An increase in the concentration of these elements may cause toxicity and leaching problems in soils. Gough *et al.* (1979) reported that F concentrations >3 mg/l in drinking water can cause fluorosis in animals and humans. Several studies (WEBB and ATKINSON, 1965; ALLOWAY, 1973) have shown that Mo concentrations >2.0 mg/kg in forage can cause molybdenosis in cattle. Although Se is not known to be an essential element for plants, it is essential for animals (OLDFIELD, 1987). However, excessive Se can be toxic to plants, animals and humans. The U.S. Environmental Protection Agency identified 0.01 mg/l Se as a primary standard for drinking water (USEPA, 1986). For any understanding of solid phase control, leaching and/or toxicity potential of any element in soil environments, it is necessary to know the chemical form in which the element is present (DREVER, 1988). Thus, the objectives of this study were:

1. To determine chemical speciation of F, Mo and Se in soil leachates;

2. To examine potential solid phases controlling the concentrations of these elements; and

3. To predict the leaching potentials of these elements in calcareous soil environments.

MATERIALS AND METHODS

A typical fine loamy, mixed, Borollic Haplargid soil was identified for sampling. These soils are extensive in the western U.S.A. and other parts of the world. The sampling site is located 1.6 km northwest of Laramie, Wyoming,

U.S.A. Surface and sub-surface samples were collected at 10 cm increments from the surface to a depth of 70 cm. Samples were sieved through a 2 mm sieve and used for subsequent experiments. Duplicate 50 g soil samples were suspended in 250 ml flasks with 100 ml of distilled–deionized H_2O. All samples were shaken at $25 \pm 0.5°C$ on a mechanical shaker at 100 oscillations per min. Three drops of toluene were added to the soil suspensions to suppress microbial activity. Laboratory air saturated with distilled–deionized H_2O was bubbled through the soil suspensions to achieve steady state conditions in a relatively short period of time (REDDY *et al.*, 1990a).

After reacting for 7 and 14 d, soil suspensions were filtered through a 0.45 μm Millipore filter. Each clear filtrate was divided into two sub-samples. One was acidified with one or two drops of concentrated HCl and one left unacidified. Acidified samples were analyzed for various cations and anions. Unacidified samples were analyzed immediately for pH, total carbonate species and Cl. These filtrates were termed as soil leachates to suggest their potential for representing the chemistry of solutions leached through the soil. The pH of soil leachates was measured with an Orion pH combination electrode. Carbonate species were measured by titrating the solutions with standardized HCl to pH 8.3 and 4.5 end points by using the pH electrode.

The Eh was measured with an Orion platinum (Pt) electrode and an Ag/AgCl$_2$ reference electrode. From Eh measurements, pe ($-\log e^-$ activity) was calculated. A serious limitation of the Pt electrode is its tendency to form oxides in aerated suspensions and cause errors in Eh measurements. WHITFIELD (1974) reported that Pt oxides could form on the surface of the electrode in oxidizing solutions (pe + pH > 14.8). However, redox potential (pe + pH) measurements in the soil leachates of this study were always <14.8 and ranged between 11.71 and 12.40. Furthermore, the surface of the Pt electrode was cleaned thoroughly between measurements to minimize errors in Eh measurements. The electrical conductivity (EC) was measured with a conductivity meter. Calcium, Mg, Al, Si, Mn and B were measured with inductively coupled plasma optical emission spectrometry (ICP–OES). Sodium and K were measured with atomic emission spectrometry. Copper, Pb and Mo were measured with atomic absorption (AA) using a graphite furnace. Selenium in soil leachates was measured using the hydride generation technique

(WORKMAN and SOLTANPOUR, 1980). Specific ion electrodes were used to measure Cl and F; SO_4 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). The organic matter (OM) and $CaCO_3$ contents of soil samples were analyzed as described by CHAPMAN and PRATT (1961) and RICHARDS (1969), respectively.

The GEOCHEM (SPOSITO and MATTIGOD, 1980) model was used for chemical speciation and ion activity calculations. The thermodynamic database of GEOCHEM was updated for various elements (REDDY et al., 1990b). From ion activities, ion activity products (IAPs) were calculated and compared with solubility products ($K_{sp}s$). We assumed that IAPs within ± 0.50 log units of $K_{sp}s$ of solid phases represented equilibrium, and that the solid phase was a probable control on the concentrations of the ions involved. The variation within that range is accounted for by the uncertainty of IAP and K_{sp} measurements in the chemical literature (STUMM and MORGAN, 1981).

RESULTS AND DISCUSSION

Selected properties of soil samples are presented in Table 1. As depth of the soil increased, OM content decreased, while $CaCO_3$ content increased and then decreased. The EC increased as the depth increased. These results suggest that soil samples examined in

this study have different chemical properties. Partial chemical data from soil leachates for 7- and 14-d reaction periods are summarized in Table 2. These data suggest soil leachates approached nearly steady state within the 14 d of reaction period. The pH ranged from 7.95 to 8.12 and redox potential varied from 216 to 263 mV (pe + pH 11.80–12.40). These conditions represent alkaline and moderately reducing environments. While redox potential values may not be absolute as discussed under methods, the likelihood that they differ sufficiently to cause a change in Se species is quite small.

Chemical data of soil leachates (Table 2) show that F concentrations ranged from 0.77 to 6.74 mg/l and increased with depth, suggesting considerable downward movement of F into sub-surface soil. The F concentration in soil leachates (Table 3) was dominated by free F^- ion (84–92% of total concentration) followed by MgF^+ (5–14% of total concentration) and CaF^+ (2–3% of total concentration) complexes. A plot of ion activity products (IAP) vs soil depth (Fig. 1) suggests an initial undersaturation with respect to CaF_2. As depth increased, F concentrations increased and IAPs approached saturation with respect to CaF_2. These results are consistent with previous reports. For example, STREET and ELWALI (1983) incubated three soils with $CaCO_3$ and CaF_2

Table 1. Selected properties of soil samples (mean of duplicate samples)

Soil depth (cm)	Organic matter (%)	Calcium caronate Eq. (%)	Electrical conductivity (S/m)
10	2.0	6.5	0.214
20	1.4	9.5	0.370
30	1.3	15.6	0.330
50	0.9	21.3	0.380
60	0.6	13.4	0.470
70	0.9	12.1	0.560

Table 2. Chemical data of soil leachates (mean of duplicate samples)

| Soil depth (cm)	pH	Eh (mv)	Ca	Mg	C_{inorg}*	Pb	F	Mo	Se
						(mg/l)			
7-d reaction									
10	7.90	301	400	61	57	0.015	0.63	0.06	0.002
20	8.01	267	460	150	64	0.011	1.20	0.09	0.004
30	8.00	237	329	207	97	0.014	2.28	0.15	0.003
50	8.13	220	420	198	100	0.016	5.00	0.16	0.002
60	7.92	227	420	211	80	0.016	5.74	0.19	0.001
70	7.98	215	516	260	82	0.011	6.90	0.19	0.002
14-d reaction									
10	7.95	263	363	56	68	0.014	0.77	0.06	0.002
20	8.10	243	451	150	75	0.010	1.08	0.08	0.007
30	8.10	224	442	192	83	0.014	2.32	0.16	0.005
50	8.06	216	424	199	94	0.017	4.87	0.11	0.010
60	8.07	240	428	215	84	0.016	4.67	0.14	0.002
70	8.12	235	538	274	85	0.017	6.74	0.15	0.005

*Total inorganic bicarbonate and carbonate species.
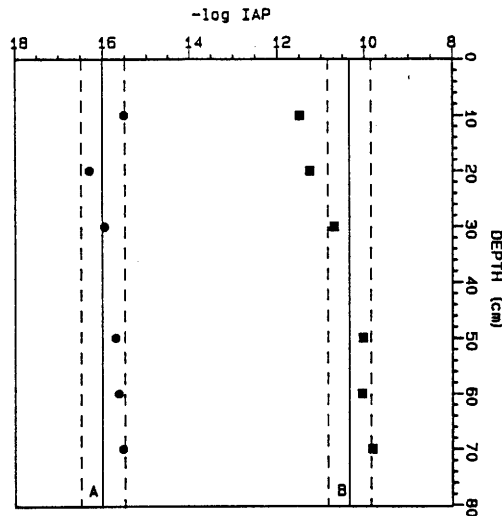
FIG. 1. Potential solid phases controlling the concentrations of F and Mo in soil samples. A = PbMoO$_4$, K_{sp} = 10$^{-16.0}$ and B = CaF$_2$, K_{sp} = 10$^{-13.35}$.

for six weeks before measuring the F solubility. After incubation, the F solubility in these soils was controlled by the fluorite. TRACY et al. (1984) irrigated a calcareous soil with high F water to grow alfalfa in lysimeters and reported that soil extracts and leachates were in equilibrium with CaF$_2$.

Molybdenum concentrations ranged from 0.06 to 0.16 mg/l in soil leachates (Table 2) and increased with depth, suggesting that Mo is mobile and leaching from surface and sub-surface soils. The chemical speciation of Mo (Table 3) suggested that leachates were dominated by the MgMoO$^°_4$ ion pair (41–70% of total concentration), followed by CaMoO$^°_4$ (15–38% of total concentration) and MoO$_4^{2-}$ (7–16% of total concentration) species. The IAPs in soil leachates showed a close approach to saturation with respect to PbMoO$_4$ (Fig. 1), particularly at lower depths. LINDSAY (1979) developed solubility relations for different solid phases of Mo in soils and reported PbMoO$_4$ as the most stable solid phase in

calcareous soils. Recently, WANG et al. (1992) examined potential solid phases controlling the solubility of Mo in soils and reported that PbMoO$_4$ probably controlled Mo concentrations in alkaline soils.

Selenium concentrations in soil leachates increased from 0.002 to 0.010 mg/l (Table 2) and then decreased from 0.010 to 0.005 mg/l as depth of the soil increased. The Se was probably solubilized and mobilized from surface soil and accumulated in the sub-surface soil. Soil leachates were (Table 3) dominated by the MgSeO$^°_3$ (62–87% of total concentrations) ion pair followed by CaSeO$^°_3$, SeO$_3^{2-}$ and SeO$_4^{2-}$ species. The IAPs of different Se solid phases (e.g. PbSeO$_3$, Fe$_2$(SeO$_3$)$_3$, MnSeO$_3$, PbSeO$_3$ and Cu$_2$Se) in soil leachates were compared with K_{sp}s to examine the possibility that one of these solid phases may be controlling the Se concentrations in leachates. Results indicated that IAPs were highly undersaturated and were not controlling the Se concentrations. However, as the depth of the soil increased, the Se concentrations appeared to be controlled by Cu$_2$Se.

To examine the above possibility, the log of IAPs were plotted against soil depth (Fig. 2). Initially IAPs for Cu$_2$Se were highly undersaturated; however, as depth of the soil increased, IAPs appeared to reach saturation with respect to Cu$_2$Se in sub-surface soil where Se was accumulated. These results suggested that as depth in soil increased, redox potential (Pe + pH) decreased, Se concentration increased, and possibly reached saturation with respect to Cu$_2$Se. It is possible that as depth in the soil increases, O$_2$ concentration may decrease and such anaerobic conditions would favor precipitation of reduced Se solid phases such as Cu$_2$Se (ELRASHIDI et al., 1987; MASSCHELEYN et al., 1990). While results shown in Fig. 2 are not conclusive they indicate that Cu$_2$Se has the potential to precipitate in sub-surface soils. In surface soil leachates Se concentrations probably were controlled by adsorption process rather than precipitation process. Several kinetic studies have shown that Se adsorption onto oxide surfaces as a major control for Se in soils (YATES and

Table 3. Distribution of F, Mo and Se species in soil leachates as predicted by GEOCHEM speciation model (mean of duplicate samples and data for 14-d reaction period)

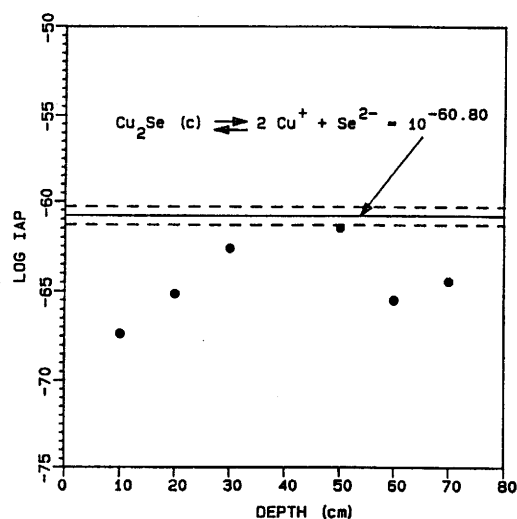| Species	10	20	30	50	60	70 cm
(−log mg/l)						
F$^+$	4.42	4.29	3.97	3.64	3.68	3.52
MgF$^+$	5.70	5.27	4.86	4.51	4.53	4.31
CaF$^+$	5.84	5.73	5.46	5.13	5.10	5.07
MgSeO$^°_3$	7.80	7.16	7.24	6.97	7.59	7.30
CaSeO$^°_3$	8.04	7.72	7.94	7.69	8.26	8.16
SeO$_3^{2-}$	9.70	9.37	9.55	9.29	9.93	9.70
SeO$_4^{2-}$	13.92	14.07	14.81	14.90	14.70	14.52
MgMoO$^°_4$	6.60	6.32	5.89	6.14	6.04	5.92
CaMoO$^°_4$	6.63	6.68	6.47	6.66	6.51	6.62
MoO$_4^{2-}$	6.89	6.87	6.59	6.77	6.69	6.66
NaMoO$^°_4$	8.84	7.83	7.29	7.53	7.60	7.59

FIG. 2. Ion activity products of $Cu_2Se(c)$ in surface and
sub-surface soils.

HEALY, 1975; CORNELL and SCHINDLAR, 1980; BALIS-
TRIERI and CHAO, 1987).

The results of the experiments reported here
suggest that as soil depth increases, the solubility and
mobility of F, Mo and Se in leachates of calcareous
soils are enhanced. A plausible explanation is that in
sub-surface soils CO_2 concentrations increase due to
biological activity. Increased CO_2 will dissolve car-
bonates, which will increase the pH (i.e. OH^- ions)
of soil leachates. The hydroxyl ions are known to
replace fluoride ions from the surface of Al and Fe
hydroxides (PARFITT and RUSSELL, 1977; OMUETI and
JONES, 1977). Such desorption reactions may contrib-
ute to the leaching of F^- in soils. The observed
leaching for Mo and Se may be related to the pre-
dominance of neutral species such as $MgMoO^\circ_4$,
$CaMoO^\circ_4$, $MgSeO^\circ_3$ and $CaSeO^\circ_3$. These species
may not be adsorbed onto oxides or hydroxides as a
charged species, and are therefore subject to leach-
ing.

CONCLUSIONS

As depth of the calcareous soil increased, concen-
trations of F, Mo and Se increased in the leachates.
Chemical speciation suggested that F^-, $MgMoO^\circ_4$,
and $MgSeO^\circ_3$ were predominant species in leachates.
The F and Mo concentrations in sub-surface soils
indicated a close approach to saturation with respect
to CaF_2 and $PbMoO_4$, respectively. However, Se
concentration in soil solutions may be controlled by
adsorption reactions. Mobility of these elements is
related to the chemical form in which the element is
present in the leachates. Although soil leachate equi-
libria do not prove or disprove the existence of
mineral phases, it is a convenient method for evaluat-
ing the relative importance of mineral reactions con-
tributing to leaching of elements in soils.

REFERENCES

ALLOWAY B. J. (1973) Copper and molybdenum in sway-
back pastures. *J. agri. Sci.* **80**, 521–524.
BALISTRIERI L. S. and CHAO T. T. (1987) Selenium adsorp-
tion by geothite. *Soil Sci. Soc. Am. J.* **51**, 1145–1151.
CHAPMAN H. D. and PRATT P. F. (1961) The methods of soil
analyses for soils, plants and waters. Univ. of California,
Div. of Ag. Sci., pp. 44–45.
CORNELL R. M. and SCHINDLAR P. W. (1980) Infrared study
of the adsorption of hydrocarboxylic acids on FeOOH
and amorphous Fe (III) hydroxide. *Colloid Polymer Sci.*
258, 1171–1175.
DREVER J. I. (1988) *The Geochemistry of Natural Waters.*
Prentice Hall.
ELRASHIDI M. A., ADRIANO D. C., WORKMAN S. M. and
LINDSAY W. L. (1987) Chemical equilibria of selenium in
soils: a theoretical development. *Soil Sci.* **44**, 141–152.
GOUGH L. P., SHACKLETTE H. T. and CASE A. A. (1979)
Element concentrations toxic to plants, animals and man.
U.S. Geol. Surv. Bull. 1466.
LINDSAY W. L. (1979) *Chemical Equilibria in Soils.* Wiley
Interscience.
MASSCHELEYN P. H., DELAUNE R. D. and PATRICK W. H. JR
(1990) Transformations of selenium as affected by sedi-
ment oxidation–reduction potential and pH. *J. envir. Sci.
Tech.* **24**, 91–96.
OLDFIELD J. E. (1987) The two faces of selenium. *J. Nutrit.*
177, 202–208.
OMUETI J. A. L. and JONES R. L. (1977) Fluoride adsorption
by Illinois soils. *J. soil Sci.* **28**, 264–272.
PARFITT R. L. and RUSSELL J. D. (1977) Adsorption on
hydrous oxides. IV. Mechanisms of adsorption of various
ions on goethite. *J. soil Sci.* **28**, 297–305.
RASNICK B. A. and NAKAYAMA F. S. (1973) Nitrochromeazo
titrimetric determination of sulfate in irrigation and other
saline waters. *Comm. Soil Sci. Plant Anal.* **4**, 171–174.
REDDY K. J., DREVER J. I. and HASFURTHER V. R. (1990b)
Application of geochemical model to the prediction of the
chemistry of extracts from non-recarbonated and recar-
bonated spent shales. U.S. Dept Energy. DC-FC-21-
86M11076.
REDDY K. J., LINDSAY W. L., WORKMAN S. M. and DREVER
J. I. (1990a) Measurement of calcite ion activity products
in soils. *Soil Sci. Soc. Am. J.* **54**, 67–71.
RICHARDS L. A. (1969) Diagnosis and improvement of
saline and alkaline soils. Agri. Hand book, No. 60, U.S.
Dept Agric.
SPOSITO G. and MATTIGOD S. V. (1980) GEOCHEM: a
computer program for the calculation of chemical equili-
bria in soil solutions and other natural water systems. The
Kearney foundation of soil science, Univ. of California,
Riverside.
STREET J. J. and ELWALI A. M. O. (1983) Fluorite solubility

in limed acid sandy soils. *Soil Sci. Soc. Am. J.* **47**, 483–485.

STUMM W. and MORGAN J. J. (1981) *Aquatic Chemistry.* Wiley Interscience.

TRACY P. W., ROBBINS C. W. and LEWIS G. C. (1984) Fluorite precipitation in a calcareous soil irrigated with high fluoride water. *Soil Sci. Am. J.* **48**, 1013–1016.

USEPA (1986) Maximum contaminant levels (Subpart B of Part 141, National Interim Primary Drinking Water Regulations), U.S. Code of Federal Regulations, Title 40, pp. 524–528.

WANG L., REDDY K. J. and MUNN L. C. (1992) Potential solid phases controlling the solubility of molybdenum in coal mine spoils and soils. *J. environ. Qual.* (in review).

WATANABE F. S. and OLSEN S. R. (1965) Test of ascorbic acid method for determination of phosphorus in water and NaHCO₃ extracts from soil. *Soil Sci. Soc. Am. Proc.* **29**, 667–678.

WEBB J. S. and ATKINSON W. J. (1965) Regional geochemical reconnaissance applied to some agricultural problems in Colorado. *Nature* **208**, 1056–1059.

WHITFIELD M. (1974) Thermodynamic limitations on the use of the platinum electrode in Eh measurements. *Limnol. Oceanog.* **19**, 857–865.

WORKMAN S. M. and SOLTANPOUR P. N. (1980) Importance of pre-reducing selenium (VI) to selenium (IV) and decomposing organic matter in soil extracts prior to determination of selenium using hydride generation. *Soil Sci. Soc. Am. J.* **44**, 1331–1332.

YATES D. E. and HEALY T. W. (1975) Mechanism of anion adsorption at the ferric and chromic oxide/water interfaces. *J. Colloid Inter. Sci.* **52**, 222–228.