Arafat,

Environment Canada
Environnement Canada

National Water Research Institute
Institut National de Recherche sur les Eaux

CHEMICAL SPECIATION OF SOLUBLE METALS IN FIVE QUEBEC LAKES

N. Arafat, AED
A. Mudroch, ECD
S. Davies, Univ. of Waterloo

FEB 2 1984

Inland Waters Directorate
Direction Générale des Eaux Intérieures

CHEMICAL SPECIATION OF SOLUBLE METALS IN FIVE QUEBEC LAKES

N. Arafat, AED

A. Mudroch, ECD

S. Davies, Univ. of Waterloo

ABSTRACT

The effect of various concentrations of fulvic acid and $Ca(OH)_2$ on the chemical speciation of soluble metals in five Quebec Lakes was examined by the computer program "Geochem". The computation showed that after the addition of the fulvic acid Ca, Mg, Na, K, Fe and Al were involved principally with the inorganic part, while Cu, Mn and Ni were associated with the organic part of the system in the water. No changes were observed in the chemical speciation of Ca, Mg, K, Na, Fe and Al after the addition of $Ca(OH)_2$. However, up to 91% of Cu and 15% of Ni were complexed by OH.

INTRODUCTION

The Noranda copper smelter was established in 1926 at the town of Rouyn-Noranda in Quebec. Its two stacks discharge annualy nearly six hundred thousand tonnes of SO_2, which is equivalent to about 70% of the province's total SO_2 production. This quantity is second only to the Inco smelter in Sudbury, Ontario for SO_2 emission in Canada (1). Heavy metals present in the sulfide ores are released upon smelting into the atmosphere along with SO_2.

The impact of the smelting operation on the aquatic environment at the Rouyn-Noranda area was investigated in 1982/83. Bottom sediment and water samples were collected to determine a number of physical and chemical parameters and the distribution of metals in several lakes in the watershed. Sediment analyses clearly showed accumulation of Pb, Zn, Cu, Ni and Cr since the beginning of the smelting operation in 1926 (2).

In this study a computer program was used to investigate the distribution of chemical species of the metals in the water from five lakes in the Rouyn-Noranda watershed. The computer program was further used to estimate the effect of various concentration levels of organic acids and lime on the chemical speciation of the metals in the water.

MATERIALS AND METHODS

The study area is shown in Fig. 1. The water was collected for trace element analyses (Cu, Ni, Mn, Al and Fe) in one liter polyethylene bottles prewashed with 10% HNO_3 and distilled water, and was acidified with 2ml of conc. HNO_3. For major ion analyses (Ca, Mg, Na, K, SO_4, Cl, SiO_2) and alkalinity, water samples were collected in 100 ml polyethylene bottles prewashed with 10% HNO_3 and distilled water. Major ions and trace elements were determined by the method described by Inland Waters Directorate, Water Quality Branch, Ottawa (3). The pH of the surface water was measured during the sampling by a Metrohm combination glass electrode.

The computer program "Geochem" , developed for the calculation of the chemical equilibria in soil solutions and other natural water systems (4), was used to predict the distribution of chemical species in the lake water. The program is based on chemical thermodynamics and the equilibria that can be calculated include complexation, precipitation, oxidation-reduction, cation exchange and metal adsorption. The details of the computations and application of the program were discussed recently (5,6).

The distribution of the metals among several possible organic and inorganic species in the lake water was calculated with the assumption that no solid phases were involved. The data bank of the "Geochem" program consists of thermodynamic data at $25^{o}C$ and 1 atmosphere. Therefore the equilibrium calculations were performed at these fixed conditions. However, the temperature of the surface lake water during the sampling ranged from 21^{o} to $23^{o}C$. This small difference in the temperature does not affect the results significantly.

RESULTS AND DISCUSSION

The concentration of the major ions and trace elements and pH used as an input into the computer program are listed in Table 1. Calculated chemical species in the water are shown in Table 2. The results indicated that all metals except Fe and Al were mainly as free metals in the surface water in all five lakes studied. However, small quantities of Ca, Mg, Mn, Cu and Ni were complexed with SO_4, in particular in lakes Tremoy* and Dufault. These two lakes are close to the smelter and had highest concentration of SO_4. The Fe and Al in the water were completely complexed with OH and a small portion of Cu (2.3 to 5.9%) was also complexed with OH in all lakes.

There is no difference in the principle in the "Geochem" program between the calculation of the chemical equilibria for inorganic systems and systems that contain organic ligands. The difficulty is the identification and characterization of the organic compounds present in the system and the availability of the proper thermodynamic data. From the number of organic ligands with available thermodynamic data listed in the "Geochem"

*Lake Tremoy is sometimes called Osisko; in this report we use the name Tremoy which appears on most of the maps of the area program we selected fulvic acid to estimate the effect of soluble organic compounds on the chemical speciation of the metals in the five lakes. Fulvic acid was chosen because it is soluble under a wide range of pH conditions and abundant in natural waters. Further, the thermodynamic data for the fulvic acid in "Geochem" program were derived from a mixture of of model organic acids with measured stability constants for trace metal complexes. These values were assumed to be a good approximation of the unknown stability constants for the assembly of soil solution organics. The limitations of this provisional approach used in the program were not considered to be as serious as completely neglecting the organic speciation of trace metals in natural waters (7). In addition, we considered the fulvic acid proper for the slightly acid water (pH 6.4 to 6.9) of the five Quebec Lakes with the allochtonous organic matter derived from the watershed soils.

Since no data were available for the concentration of dissolved organic matter in the studied lakes we used 10^{-4}, 10^{-5} and 10^{-6} molar concentrations of fulvic acid in the calculation. This concentration range was selected in accordance with reported concentrations of fulvic acid in lake and river water (8). The concentration of all other parameters were the same as those in Table 2.

No changes were observed in the chemical speciation of K, Na, Al and Fe after the addition of fulvic acid in all three concentrations. The addition of 10^{-6}M fulvic acid produced complexes with up to 1.3% Mn, 0.9% Cu and 6.1% Ni (Table 3). The concentration of 10^{-5} and 10^{-4}M of fulvic acid further increased the complexation of Mn, Cu and Ni (up to 58.5%, 50.4% and 47% of the total metal, respectively). Major ions Ca and Mg were complexed up to 18.3% and 6.6% of their total concentration, respectively. Up to 60% of the added fulvic acid was complexed by Ca (Table 4) due to relatively higher concentration of this element in the lake water.

Generally, the computation showed that by the increase of the concentration of the dissolved organic matter Ca, Mg, Na, K, Fe and Al will be associated principally with the inorganic part of the system, while Cu, Mn and Ni will be associated with the organic part, in the water of the five lakes studied.

The effect of $Ca(OH)_2$ added in three different concentrations on the chemical species of the metals in the lake water is shown in Table 5. The chemical speciation of Ca, Mg, K, Na, Fe and Al did not change by increasing the concentration of $Ca(OH)_2$ from 10^{-7} to 10^{-5}M. The complexing of 91% of the total Cu by the addition of 10^{-5}M $Ca(OH)_2$ was due to OH which is one of the dominant inorganic ligands for Cu ions. A small portion of the total Mn and up to 17% of the total Ni were complexed by OH.

Binding of the metals, in particular Cu, by organic and inorganic ligands significantly affects their biological and geochemical reactivity in the lake water and the toxicity to the lake biota. The following conclusions can be derived from the computation of the distribution of the chemical species in the water of the five Quebec Lakes: soluble Ca, Mg, K, Na, Mn, Cu and Ni are present mainly as free metals. Soluble organic matter, in this study represented by fulvic acid, affects the chemical species of Mn, Cu and Ni to a larger extent than those of Ca and Mg. However, the degree of complexing of the metals by the fulvic acid depends on their concentrations. The addition of the lime (in this report represented by soluble $Ca(OH)_2$) produces complexing of more than 90% of Cu by OH ions. However, the majority of Mn and Ni remains as free metals in the lake water. Recently, a procedure was developed to determine the relative toxicity of the metal speciation products (9). The results suggested that the free Cu ion and/or the neutral and cationic hydroxo complexes of the Cu are responsible for 60 to 70% of the toxicity of Cu to aquatic life. In addition, anionic hydroxo-Cu complexes contribute 15 to 18% to the total toxicity. Changes in the chemical species of the metals in the lake water should be considered together with the present knowledge of the toxicity of each species when planning any restoration of the lakes, in particular by addition of lime. Recently developed multicomponent models (6) are suitable for the prediction of trace element behaviour and for the design of experiments in the field of toxicology in an aquatic ecosystem.

REFERENCES

1. Chartrand, L. 1982. Noranda ordered to clean up. Probe Post, 1982.
2. Arafat, N., Fulop, G.J. and Glooschenko, W.A. 1983. Assessment of heavy metals. National Water Research Institute, Burlington, Ont., Report Series.
3. Inland Waters Directorate, Water Quality Branch, Ottawa, Ont. 1979. Analytical Methods Manual.
4. Sposito, G. and Mattigod, S.V. 1980. Geochem: a computer program for the calculation of chemical equilibria in soil solutions and other natural water systems. Dep. of Soil and Envir. Sci., U. of California, Riverside, CA.
5. Mattigod, S.V. and Sposito, G. 1979. Chemical modeling of trace metal equilibria in contaminated soil solutions using the program Geochem. In: Chemical Modeling in Aqueous Systems (ed. E.A. Jenne), Am. Chem. Soc., Washington, D.C., p. 837.
6. Nordstrom, D.K., Plummer, L.N., Wigley, T.M.L., Wolery, T.J., Ball, J.W., Jenne, E.A., Bassett, R.L., Crerar, D.A., Florence, T.M., Fritz, B., Hoffman, M., Holdren, G.R., Lafon, G.M., Mattigod, S.V., McDuff, R.E., Morel, F., Reddy, M.M., Sposito, G. and Thrailkill, J. 1979. A comparison of computerized chemical models for equilibrium calculations in aqueous systems. In: Chemical Modeling in Aqueous Systems (ed. E.A. Jenne), Am. Chem. Soc., Washington, D.C., p. 837.
7. Ghaseni, M. and Christman, R.F. 1968. Properties of the yellow organic acids of natural waters. Limnol. Oceanog.13, p. 583.
8. Van den Berg, C.M.G. and Kramer, J.R. 1979. Conditional stability constants for copper ions with ligands in natural waters. In: Chemical Modeling in Aqueous Systems (ed. E.A. Jenne), Am. Chem. Soc., Washington, D.C., p.115.
9. Magnuson, V.R. Harriss, D.K., Sun, M.S., Taylor, D.K. and Glass, G.E. 1979. Relationships of activities of metal-ligand species to aquatic toxicity. In: Chemical Modeling in Aqueous Systems (ed. E.A. Jenne), Am. Chem. Soc., Washington, D.C., p. 635.

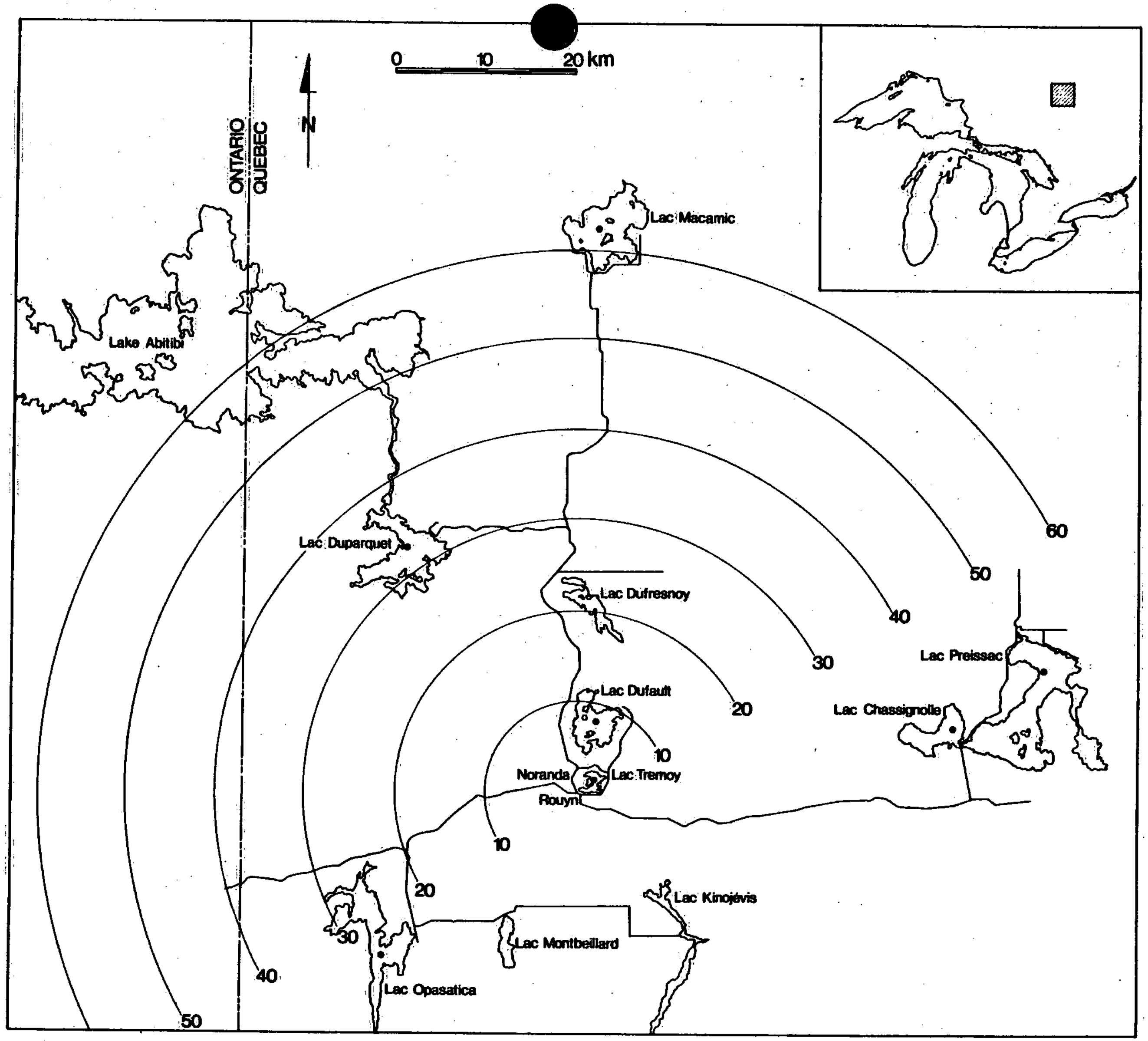
0 10 20 km
N
ONTARIO
QUEBEC
Lac Macamic
Lake Abitibi
Lac Duparquet
Lac Dufresnoy
Lac Dufault
Noranda
Lac Tremoy
Rouyn
Lac Preissac
Lac Chassignolle
Lac Kinojévis
Lac Montbeillard
Lac Opasatica
10
20
30
40
50
60

TABLE 1.

Concentration of metals and ligands used in the computation
(-log molar concentration)

	Lake				
	Tremoy	Dufault	Macamic	Preissac	Opasatica
Ca	3.15	3.24	3.58	3.81	3.63
Mg	3.52	3.75	3.89	4.16	3.82
K	4.23	4.59	4.48	4.71	4.55
Na	3.20	3.68	4.08	4.16	3.93
Fe^{3+}	5.40	5.67	4.57	5.03	5.46
Mn^{2+}	5.74	5.93	6.44	6.44	6.44
Cu^{2+}	6.57	6.55	7.10	7.10	7.10
Ni	7.17	7.77	7.77	7.77	7.77
Al	6.25	6.02	4.39	4.93	5.28
CO_3^{2-}	5.8	5.5	5.2	5.4	5.2
SO_4^{2-}	3.07	3.23	4.02	4.06	3.88
Cl^-	3.28	4.15	4.32	4.47	4.17
pH	6.9	6.5	6.4	6.7	6.6

TABLE 2.

Distribution of chemical species of soluble metals in lake water (percent of total metal)

	Lakes:	Tremoy	Dufault	Macamic	Preissac	Opassatica
Ca	as a free metal	92.1	93.8	98.7	98.8	98.3
	bound with SO_4	7.8	6.1	1.3	1.2	1.7
	bound with Cl	0.1	*	*	*	*
Mg	as a free metal	93.6	95.0	99.0	99.0	98.6
	bound with SO_4	6.3	4.9	1.0	1.0	1.4
	bound with Cl	0.1	*	*	*	*
K	as a free metal	99.5	99.7	99.9	99.9	99.9
	bound with SO_4	0.4	0.3	*	*	*
Fe	bound wit OH	100.0	100.0	99.9	100.0	99.9
Mn	as a free metal	92.1	93.8	98.8	98.7	98.2
	bound with SO_4	7.8	6.1	1.3	1.2	1.7
Cu	as a free metal	83.5	87.6	91.1	89.5	88.2
	bound with CO_3	1.7	2.6	5.2	4.5	6.2
	bound wth SO_4	8.9	7.2	1.5	1.4	1.9
	bound with OH	5.9	2.6	2.3	4.6	3.6
Ni	as a free metal	92.0	93.7	98.3	98.4	97.8
	bound with CO_3	0.1	0.2	0.4	0.3	0.5
	bound with SO_4	7.8	6.1	1.3	1.2	1.7
Al	bound with OH	100.0	100.0	100.0	100.0	100.0

*less than 0.1%

note: "bound with" means in complexed form and does not include solids (same in Tables 3 to 5)

TABLE 3.

Distribution of chemical species of soluble metals in lake water after the addition of fulvic acid (distribution as percent of total metal)

Lakes	Tremoy			Dufault			Macamic			Preissac			Opasatica		
Fulvic a.[1]	4	5	6	4	5	6	4	5	6	4	5	6	4	5	6
Ca as a free metal	84.3	91.3	92.0	84.5	92.9	93.8	83.9	97.1	98.6	80.7	96.7	98.5	83.3	96.7	98.1
bound with SO_4	7.3	7.7	7.8	5.7	6.1	6.1	1.1	1.2	1.3	1.0	1.2	1.2	1.5	1.7	1.7
bound with Cl	0.1	0.1	0.1	*	*	*	*	*	*	*	*	*	*	*	*
bound with Ful.a.	8.2	0.8	*	9.8	1.0	0.1	14.9	1.6	0.2	18.3	2.0	0.2	15.1	1.6	0.2
Mg as a free metal	90.8	93.3	93.6	91.7	94.7	95.0	93.7	98.5	98.9	92.4	98.4	98.9	93.3	98.1	98.6
bound with SO_4	6.3	6.3	6.3	4.9	4.9	4.9	1.0	1.0	1.0	0.9	1.0	1.0	1.3	1.4	1.4
bound with Cl	0.1	0.1	0.1	*	*	*	*	*	*	*	*	*	*	*	*
bound with Ful.a.	2.8	0.3	*	3.3	0.3	*	5.3	0.5	*	6.6	0.7	*	5.4	0.5	*
K as a free metal	99.5	99.5	99.5	99.7	99.7	99.7	99.9	99.9	99.9	99.9	99.9	99.9	99.9	99.9	99.9
bound with SO_4	0.5	0.4	0.4	0.3	0.3	0.3	o.3	*	*	*	*	*	*	*	*
Na as a free metal	99.2	99.3	99.3	99.5	99.5	99.5	99.5	99.9	99.9	99.9	99.9	99.9	99.9	99.9	99.9
bound with SO_4	0.7	0.7	0.7	0.5	0.5	0.5	*	*	*	*	*	*	*	*	*
Fe bound with OH	100	100	100	100	100	100	99.9	99.9	99.9	100	100	100	99.9	99.9	99.9
Mn as a free metal	58.8	87.5	91.7	55.7	88.2	93.2	46.8	89.5	97.7	4o.9	87.3	97.5	46.2	88.9	97.2
bound with SO_4	5.1	7.4	7.8	3.7	5.8	6.1	0.6	1.1	1.3	0.5	1.1	1.2	0.8	1.5	1.7
bound with Ful.a.	36.0	5.0	0.5	40.5	6.0	0.6	52.5	9.3	1.0	58.5	11.6	1.3	53.0	9.5	1.0
Cu as a free metal	59.3	80.4	83.1	58.0	83.6	87.1	50.2	84.7	90.4	44.3	81.8	88.7	48.9	82.1	87.6
bound with CO_3	1.2	1.6	1.7	1.7	2.5	2.6	2.8	4.8	5.1	2.2	4.1	4.4	3.5	5.8	6.2
bound with SO_4	6.5	8.6	8.9	4.9	6.9	7.5	0.8	1.4	1.5	0.7	1.3	1.4	1.1	1.8	1.9
bound with Ful.a.	28.8	3.7	0.4	33.6	4.5	0.5	44.8	7.0	0.7	50.4	8.6	0.9	44.5	6.9	0.7
bound with OH	4.2	5.7	5.9	1.7	2.5	2.6	1.3	2.1	2.3	2.3	4.2	4.6	2.0	3.4	3.6
Ni as a free metal	67.8	89.0	91.7	65.4	90.0	93.3	58.0	92.4	97.7	52.1	90.9	97.6	57.3	91.8	97.2
bound with SO_4	5.9	7.5	7.8	4.4	5.9	0.2	0.8	1.2	1.3	0.7	1.1	0.8	1.0	1.6	1.7
bound with Ful.a.	26.2	3.2	0.3	30.3	3.9	6.1	41.0	6.1	0.6	47.0	7.6	1.2	41.4	6.2	0.6
bound with CO_3	*	0.1	0.1	0.1	0.2	0.3	0.2	0.3	0.4	0.2	0.3	0.3	0.3	0.4	0.5
Al bound with OH	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100

[1] -log molar concentration fulvic acid

* less than 0.1 %

TABLE 4.

Distribution of fulvic acid complexes in lake water (in percent of total fulvic acid)

Lake	Tremoy			Dufault			Macamic			Preissac			Opasatica		
Fulv.a.[1]	4	5	6	4	5	6	4	5	6	4	5	6	4	5	6
Free ligand	32.9	31.7	31.5	37.3	35.7	35.5	53.7	5o.9	50.6	66.9	63.5	63.1	56.1	53.4	53.1
Bound with Ca	57.9	59.1	59.2	56.1	57.7	57.9	39.3	42.1	42.4	28.3	31.5	31.9	35.5	38.3	38.6
Bound with Mg	8.4	8.2	8.1	6.0	5.7	5.7	6.8	6.6	6.6	4.6	4.5	4.5	8.1	7.9	7.9
Bound with Mn	0.7	0.9	1.0	0.5	0.7	0.7	0.2	0.3	0.4	0.2	0.4	0.5	0.2	0.3	0.4
Bound with Cu and Ni	← less than 0.1 →														

[1]-log molar concentration fulvic acid

TABLE 5.

Distribution of chemical species of soluble metals in lake water after the addition of $Ca(OH)_2$
(distribution as percent of total metal)

	Lake	Tremoy			Dufault			Macamic			Preissac			Opasatica		
	$Ca(OH)_2$ [1]	5	6	7	5	6	7	5	6	7	5	6	7	5	6	7
Ca	as a free metal	90.8	90.9	90.9	92.9	92.9	92.9	98.5	98.6	98.6	98.6	98.7	98.7	98.1	98.1	98.1
	bound with SO_4	9.0	9.0	9.0	7.1	7.1	7.1	1.4	1.4	1.4	1.3	1.3	1.3	1.8	1.8	1.8
	bound with Cl	0.1	0.1	0.1	*	*	*	*	*	*	*	*	*	*	*	*
Mg	as a free metal	92.5	92.6	92.6	94.1	94.3	94.3	98.7	98.8	98.9	98.8	98.9	98.9	98.3	98.5	98.5
	bound with SO_4	7.3	7.3	7.3	5.7	5.7	5.7	1.1	1.1	1.1	1.0	1.0	1.0	1.5	1.5	1.5
	bound with Cl	0.1	0.1	0.1	*	*	*	*	*	*	*	*	*	*	*	*
	bound with OH	0.1	*	*	0.1	*	*	0.2	*	*	0.2	*	*	0.2	*	*
K	as a free metal	99.5	99.5	99.5	99.6	99.6	99.6	99.9	99.9	99.9	99.9	99.9	99.9	99.9	99.9	99.9
	bound with SO_4	0.5	0.5	0.5	0.4	0.4	0.4	*	*	*	*	*	*	*	*	*
Na	as a free metal	99.2	99.2	99.2	99.4	99.4	99.4	99.9	99.9	99.9	99.9	99.9	99.9	99.9	99.9	99.9
	bound with SO_4	0.8	0.8	0.8	0.6	0.6	0.6	0.1	0.1	0.1	*	*	*	0.1	0.1	0.1
Fe	bound with OH					← 100 →										
Mn	as a free metal	88.5	90.8	90.9	90.4	92.7	92.9	95.3	98.2	98.5	95.6	98.3	98.6	94.9	97.8	98.1
	bound with CO_3	0.2	*	*	0.4	*	*	0.8	0.1	*	0.5	*	*	0.8	0.1	*
	bound with SO_4	8.8	9.0	9.0	6.9	7.1	7.1	1.4	1.4	1.4	1.3	1.3	1.3	1.8	1.8	1.8
	bound with OH	2.3	0.2	*	2.3	0.2	*	2.5	0.2	*	2.5	0.2	*	2.5	0.3	*
Cu	as a free metal	6.2	45.5	80.7	5.9	43.9	80.7	5.6	42.7	81.7	5.6	43.9	84.2	5.5	42.1	81.1
	bound with CO_3	1.9	2.4	1.8	3.8	5.0	3.9	8.0	10.7	8.6	5.2	7.1	5.7	7.8	10.5	8.5
	bound with SO_4	0.8	5.7	10.1	0.6	4.2	7.7	0.1	0.8	1.5	*	0.7	1.4	0.1	1.0	1.9
	bound with OH	91.1	46.4	0.1	89.7	46.9	7.7	86.3	45.9	8.3	89.0	48.3	8.7	86.5	46.3	8.4
Ni	as a free metal	74.8	89.6	90.7	73.3	90.9	92.5	70.8	95.0	97.8	73.8	95.9	98.1	70.4	94.6	97.3
	bound with CO_3	2.7	0.5	0.1	5.8	1.0	0.3	12.2	2.3	0.7	8.3	1.5	0.5	12.1	2.3	0.7
	bound with SO_4	7.4	8.9	9.0	5.6	6.9	7.0	1.0	1.4	1.4	1.0	1.3	1.3	1.3	1.8	1.8
	bound with OH	15.0	1.1	0.1	15.4	1.2	0.1	15.9	1.3	0.1	17.0	1.3	0.1	16.2	1.3	0.1
Al	bound with OH					← 100 →										

[1] -log molar concentration of $Ca(OH)_2$

* less than 0.1%

Date Due

JUL 13 1999			