FACTORS AFFECTING THE SOIL SORPTION OF IODINE

MARSHA I. SHEPPARD, D. H. THIBAULT, JUDE MCMURRY and P. A. SMITH

Whiteshell Laboratories, AECL Research, Pinawa, MB, Canada ROE 1L0

Abstract. Iodine-129 is an important radionuclide released from nuclear facilities because of its long radioactive half-life and its environmental mobility. Its retention in surface soils has been linked to pH, organic matter, and Fe and Al oxides. Its inorganic solution chemistry indicates I will most likely exist as an anion. Three investigations were carried out to provide information on the role of the inorganic and organic chemistry during sorption of I by soil.

Anion competition using Cl^- showed that anion exchange plays a role in I sorption in both mineral and organic soils. The presence of Cl decreased the loss of I^- from solution by 30 and 50% for an organic and a carbonated sandy soil respectively. The I remaining in solution was associated primarily with dissolved organic carbon (DOC). The loss rate from solution appears to depend on two reactions of I with the soil solids (both mineral and organic) creating both a release to and a loss from solution, and the reaction of I with the DOC (from very low to high molecular weight). Composition analyses of the pore water and the geochemical modelling indicate that I sorption affects the double-charged anion species in solution the most, particularly SO_4^{--}. Iodide introduced to natural bog groundwater at three concentrations (10^{-3}, 10^{-1} and 10 meq L^{-1}) remained as I^- and was not lost from solution quickly, indicating that the association of I with DOC is slow and does not depend on the DOC or I concentration. If sorption of I to soil solids or DOC is not sensitive to concentration, then stable I studies, which by necessity must be carried out at high environmental concentrations, can be linearly extrapolated to radioactive I at much lower molar concentrations.

1. Introduction

Iodine-129 is an important radionuclide released from nuclear facilities. Because its radioactive half-life is very long (1.6×10^7 yr), understanding its environmental behaviour is of major importance to the nuclear industry. The behaviour of I in soils has been the subject of much research (Benes, 1975; Bors *et al.*, 1988; Kantelo *et al.*, 1982; Koch and Kay, 1987; Lee and Dee, 1967; Liu and von Gunten, 1988; Manzoor and Babcock, 1961; Muramatsu *et al.*, 1990; Saas and Grauby, 1976; Schuttelkopf and Pimpl, 1982; Sheppard and Thibault, 1991, 1992; Sheppard *et al.*, 1987; Tikhomirov *et al.*, 1978; Whitehead, 1973, 1974, 1978, 1984; Yoshida *et al.*, 1992; Yuita, 1992). This collective work indicates that soils rich in organic matter and iron and aluminum oxides accumulate I.

Sorption of I onto soils, in both the I^- and IO_3^- forms, occurs quickly (sorption percentages become constant in some soils after 2 days) and is dependent on the solution pH; sorption decreases as pH increases (Yoshida *et al.*, 1992). This is in keeping with the general rule that anion sorption decreases as pH increases (Mott 1981). However, the sorption of I^- can be attributed to electrostatic adsorption in some soils and not in others (Yoshida *et al.*, 1992). Yuita (1992) reported that I^- is the major I species in flooded soils but that IO_3^- is more prominent under unflooded

but still very wet (70 and 89% saturated) soil conditions. Our work in a sphagnum bog indicated that the I^- species predominated in very wet soils (Sheppard et al., 1989).

In earlier experiments, we concluded that diffusion of I^- into the fabric of organic soils played a major role in the retention of I^- (Sheppard and Thibault, 1992). In our sphagnum bog study, we noted that the soil solid/liquid partition coefficient, K_d, for I^- was dependent on the pore-water concentration (Sheppard et al., 1989). Since the K_d value decreased at high pore-water concentrations, we speculated that this could be due to saturation of the anion capacity of the soil, or due to toxicity to microbes, if microbes or the enzymes they produce (Christiansen and Carlsen, 1992) play a major role in the sorption process. The role of the inorganic, organic and biological components of the soil system have never been clearly differentiated.

This manuscript reports the results of three investigations to define the relative importance of the inorganic and organic chemistry of the soil in the I sorption process. The first investigation studied the effect that competition of another anion, particularly Cl, had on the sorption of I in a high-organic-matter, carbonated, mineral soil and a sphagnum peat soil. If the presence of Cl dramatically changed the speed of sorption or the quantity of I sorbed at steady-state, then the exchange of I with anion sites on the soil surface is a major sorption mechanism. The second experiment investigated the effect that the presence of I had on the evolving pore-water composition of the peat soil during sorption. The purpose of this experiment was twofold – to determine which anions if any, actually exchanged with the I in solution and to determine whether organic anions played a role. This experiment was supported by geochemical modelling. The geochemical modelling also addressed whether the large concentrations used, necessary because of the analytical constraints, inadvertently affected the experimental outcome through chemical precipitation of oversaturated solid phases. The third investigation examined how varying concentrations of DOC and I affected the loss of I from bog groundwater without a solid phase present.

2. Materials and Methods

2.1. SOIL SAMPLES

Two soils were used, and their most important properties are shown in Table I. The high-organic-matter mineral soil (A) is a sandy soil, chosen because the largest percentage of soils on the Precambrian Shield in Canada, the proposed location for deep disposal of nuclear fuel waste, are sandy in texture. The peat soil (P) represents soils found in topographic lows, which may correspond to terrestrial discharge zones for deep groundwater that could intersect a deep-rock disposal vault (Sheppard, 1992). The two soils represent different pH, pore-water compositions and organic matter contents.

TABLE I

Properties of the soils

Property	A	P
Soil type	sandy loam	organic
pH (1:1 soil water paste)	8.0 ± 0.1[a](6)	6.4 ± 1.6 (23)
Organic carbon (% wt)	1.9 (2)	73.7 ± 2.2
Bulk density (Mg m^{-3})	1.28 ± 0.02	0.24 (2)
Field capacity moisture,		
FC (% wt)	40	318
Pore water[b]		
(mg L^{-1})		
Na	40.8 ± 6.3 (6)	27.1 ± 14.0 (6)
K	21.2 ± 8.6 (6)	5.1 ± 2.8 (6)
Ca	279 ± 52 (6)	15.8 ± 5.7 (6)
Mg	233 ± 49 (6)	4.2 ± 1.8 (6)
Fe	0.13 ± 0.03 (6)	0.4 ± 0.2 (6)
Al	–	2.0
F$^-$	60 ± 9.8 (5)	0.6
Cl$^-$	68 ± 11.8 (6)	7.9 ± 8.0 (6)
SO$_4^{--}$	200 ± 45 (6)	15.7 ± 6.4 (6)
NO$_3^-$	338 ± 258 (4)	44.6 ± 37.1 (6)

[a] All values with error terms are means ± one standard deviation. Values in parentheses give numbers of observations when they differ from three.
[b] Pore water removed from soils at FC using centrifugation. Values for the P soil include differences within one subsample and between two subsamples of the same soil.

2.2. SORPTION AND CHLORIDE COMPETITION

The sorption of I was calculated by measuring the loss of I from an initial solution of 1 mg I L^{-1}, as KI, in the presence of no-Cl, 1 mg Cl L^{-1} or 100 mg Cl L^{-1}, as KCl. The soil:solution ratio was 1:10 by weight. The sorption flasks were capped glass bottles, pre-rinsed with dilute HCl and subsequently rinsed with distilled water. During the contact time, they were uncapped and hand swirled daily to ensure aeration. Each treatment was triplicated. The bottles were incubated at 22 °C unprotected from light. The loss of I from solution was monitored at 1, 2, 9, 14, 21, 35, 56 and 93 days by removing 10 mL of solution. These solutions were filtered through a 0.80-μm Millex-PF filter and were analysed for I$^-$ by ion selective electrode (ISE) and for total I by inductively coupled plasma spectroscopy (ICP-AES). The detection level was <0.4 mg I L^{-1} for ISE and <0.03 mg I L^{-1} for ICP-AES. After 35 days, the I in solution in the P soil became undetectable, and 50 mL of this solution from the no-Cl treatment was passed through 0.5 g of

activated charcoal to collect the organic I from solution; the charcoal was analysed by neutron activation analysis. The no-Cl treatment solution of the A soil collected after 93 days and the no-Cl treatment solutions from both soils after 198 days were also passed through charcoal. All analyses were expressed as mg of I lost from solution with time per kg of soil and curves were fitted and plotted (SAS 1985). Each time solution was removed for analysis, the pH of the remaining soil slurry was measured.

2.3. PORE-WATER COMPOSITION DURING I SORPTION

Analysis of the solution composition with time should indicate whether shifts in the ion balance of the system are being accommodated by inorganic ions and which inorganic ions are involved. All experimental details, except for initial I concentration, were the same as for the first experiment. In order to see an effect on the pore-water composition, an initial solution concentration of 1000 mg I L^{-1} was used. The solution was filtered (0.45 μm) and analysed for Cl^- SO_4^{--}, NO_3^-, I^- and F^- by ion chromatography (IC), and for I, P, S, Ca, Mg and Fe by ICP, and for Na and K by atomic absorption spectrometry (AA). The detection level for I by IC was <0.1 mg I L^{-1}. The control contained no added I. Both treatments were carried out in triplicate. The cation/total data were expressed as a fraction of the sum of cation equivalents, excluding K, for Ca, Mg, Fe and Na, and the anion data were expressed as a fraction of the sum of anion equivalents, excluding I^-, for Cl^-, SO_4^{--}, NO_3^- and F^-. Analyses of dissolved inorganic carbon (DIC) and dissolved organic carbon (DOC) were also performed after 1 and 21 days.

Geochemical modelling of the soil solution using WATEQ4F (Ball *et al.*, 1991) and PHREEQE (Parkhurst *et al.*, 1990) was carried out to confirm our understanding of the measured shifts and to check whether solution or mineral saturation occurred.

2.4. PORE-WATER COMPOSITION AND DISSOLVED ORGANIC CARBON

The third investigation was an experiment to examine the effect of DOC and I concentration on the loss of I from sphagnum peat bog groundwater, the groundwater naturally in contact with the P soil. Fresh groundwater from a 1-m-deep well in a sphagnum bog (Sheppard *et al.*, 1989) was brought to the laboratory, filtered (0.45 μm) and divided for the preparation of two treatments. One treatment used the undiluted freshly filtered groundwater and the other used groundwater diluted a thousandfold with distilled water. Acid-rinsed (5% HNO_3), then distilled water rinsed glass jars containing 500 mL of the treatment waters received KI at three different concentrations (10^{-3} meq I L^{-1}, 10^{-1} meq I L^{-1} and 10 meq I L^{-1}). These concentrations correspond to 0.127 mg I L^{-1}, 12.7 mg I L^{-1} and 1270 mg I L^{-1}, encompassing the concentration range used in our previous sorption experiments (Sheppard and Thibault, 1991 1992; Sheppard *et al.* 1987 1989). After 1,

2 and 5 days, 25-mL samples were filtered (0.45 μm) and analysed for I^-, NO_3^-, F^-, Cl^- and SO_4^{--} by IC, for Ca, Mg, Fe, I, P and S by ICP, for Na and K by AA, and for N as NH_3 colorimetrically. The DIC and DOC concentrations were also determined on selected samples. Control samples of the undiluted and diluted groundwater were also sampled and analysed at the same times.

3. Results and Discussion

3.1. IODINE SORPTION AND EFFECTS OF ANION COMPETITION USING Cl

The slightly acidic organic P soil effectively removed most of the I from solution in 56 days, regardless of the presence of Cl (Figure 1). However, Cl did slow the reaction. Only 0.06 μg I L^{-1} remained in solution after 198 days. Thus 98% of the I appears to have been sorbed to the solids. The <2% remaining in solution was primarily in an organic form, as indicated by our charcoal analysis. This percentage could not be confirmed in the Cl treatments because of analytical interference between I and Cl.

The carbonated, high-organic-matter, sandy A soil removed only 62% of the I from solution after 56 days, and had only removed 80 to 84% of the I from solution after 198 days. The 16 to 20% remaining in solution was collected with the charcoal, and therefore was probably in an organic form.

Our earlier work with a Brunisol litter horizon (Sheppard and Thibault, 1992) and the work of Bors *et al.* (1988) on podzolic soil horizons showed that I was generally associated with the larger humic acids. However, results with the P soil showed that the I remained very soluble and was associated with the fulvic acid fraction (Sheppard and Thibault, 1992). If I is associated more with the fulvic acid fraction in the P soil and more with the humic acid fraction in the A soil, the measured difference in loss from solution implies that sorption or complex formation with the humics is slower than with the fulvics. Also, there could be fewer anionic sorption sites available for exchange of I in the A soil than in the P soil. If the removal of I from solution is governed by iodination of the humics and fulvics (Christiansen and Carlsen, 1992), the rate of this process could differ between these soils.

The loss of I^- from solution is not a simple reaction in the presence of these two soils (Figure 1). In the no-Cl treatment of the P soil, this loss is gradual, but it is slightly faster over the first two days, and slows significantly after 36 days. In the comparable A soil treatment, there are two or perhaps three distinct I^- loss rates, one for the first two days, another reaching 21 days, and then a slower loss rate after this time. In the Cl treatments, there is an increase in I^- in solution over the first 14 days in the P soil and over the first 21 days in the A soil. This initial increase is due to I displaced from the solids in the presence of Cl. The presence of Cl either accelerated the desorption of I or slowed the I sorption process in both soils.
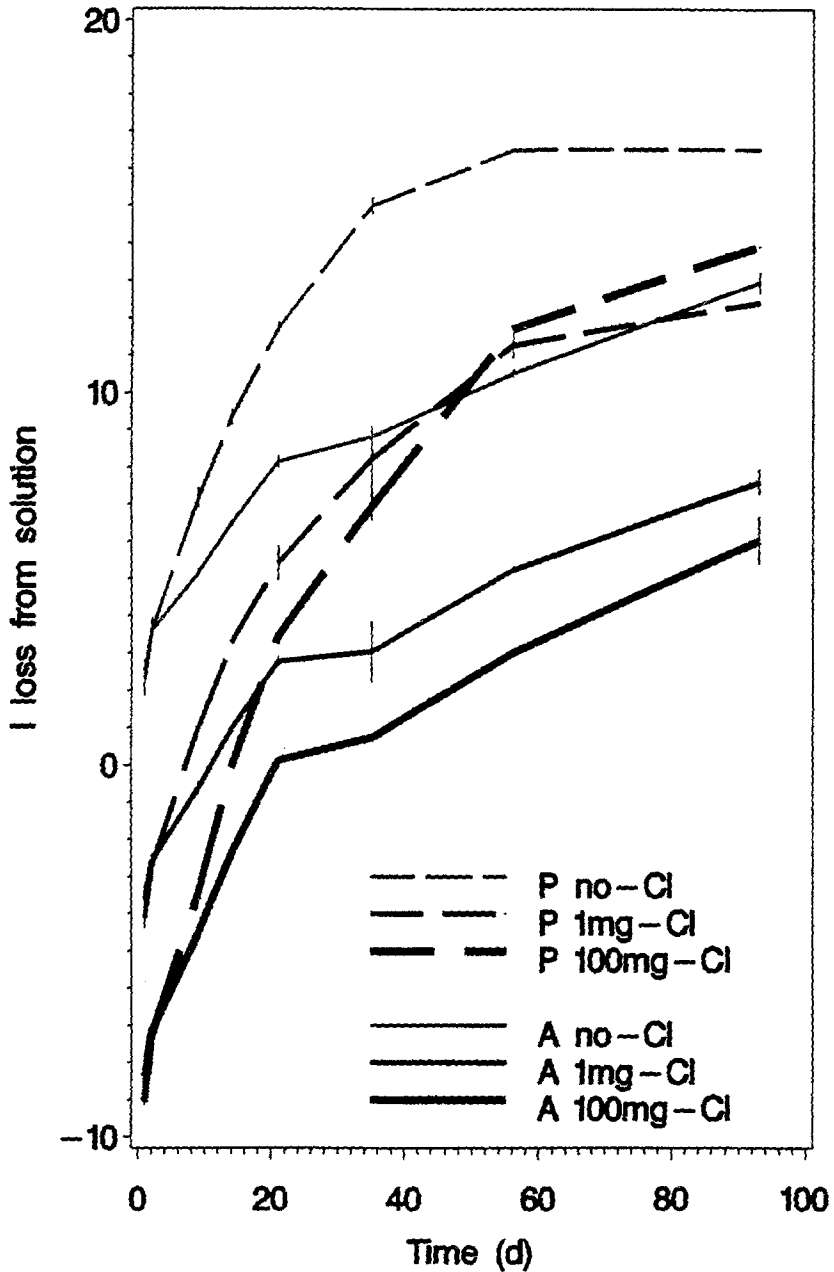
Fig. 1. Loss of I from solution (mg I kg^{-1} soil) versus time for the A (solid lines) and P (dashed lines) soils for the control or no-Cl, the 1 mg Cl L^{-1}, and the 100 mg Cl L^{-1} treatments.

Increases in the Cl concentration decreased the sorption by up to 50% in the A soil and up to 30% in the P soil at steady-state, indicating that anion competition seems to occur, perhaps related to competition for a limited number of anion sorption

TABLE II

Two-stage reaction model constants describing loss of I^- from solution with time for the no-Cl and Cl treatments in the A and P soils

Treatment	Soil	R_1 (mg I L^{-1})	R_2 (mg I L^{-1})	$\lambda2$	$t^{0.99}$ (d)
no Cl	A	2.79±0.22[a]	10.54±0.46	0.028±0.003	164
	P	1.69±0.19	15.36±0.24	0.051±0.002	90
1 mg Cl L^{-1}	A	−3.40±0.30	11.12±0.54	0.031±0.004	148
	P	−2.43±1.00	15.11±1.34	0.045±0.011	102
100 mg Cl L^{-1}	A	−8.29±.0.34	14.15±0.55	0.035±0.004	132
	P	−5.74±1.76	20.38±2.66	0.037±0.013	124

[a] Estimated value using non-linear least squares and asymptotic standard error.

sites. Chloride was more effective at competing for these sites in the sandy A soil and was more dependent on the Cl concentration even though this A soil naturally contains both more Cl^- and F^- (Table I) than the organic P soil.

The amount of I^- lost from solution, SL (mg I^- kg^{-1} soil), in these two soils can be described using a two-phase reaction model such as

$$SL = R_1(1 - e^{-\lambda 1 t1}) + R_2(1 - e^{-\lambda 2 t2}) \tag{1}$$

where the first term on the right describes the longer-term steady loss of I^- from solution and the second describes the initial quick reaction and the exchange of I on the solids with Cl in solution. The value for $t2$ is so small that essentially R_2 becomes the intercept. The values for R_1, R_2 and $\lambda2$ for the three treatments and two soils are given in Table II. The values for $\lambda2$ can be used to determine times to 99% equilibrium, $t^{0.99}$, an appropriate time for calculating the K_d value. The smaller $t^{0.99}$ values for P soil confirm the P soil comes to equilibrium faster than the A soil. The smaller $t^{0.99}$ values (Table II) for the A soil in the presence of Cl^- indicate that the Cl speeds the reaction. The $t^{0.99}$ values for the P soil increase as the Cl^- concentration in the pore water increases. This indicates that reaction rates with organics may be slower and there are probably more sorption sites in the P soil than in the A soil.

Values for K_d, determined after 164 days in the A soil and after 90 days in the P soil, were 262 and 1.37×10^6 L kg^{-1}.

The pH values for the A and P soils differed significantly from one another, both as a water paste (Table I) and in the 1:10 soil solution where the average pH of control A and P samples was 8.31 ± 0.15 ($n = 8$) and 5.37 ± 0.06 ($n = 8$) over the 93 days. These means showed no systematic trend over time, and the presence of Cl had no effect on pH. Using the solution pH versus I^- sorption relationship

of Yoshida *et al.* (1992), our measured sorption for these two soils is within their range.

It is also possible that reactions with the solids occurred very rapidly, perhaps within 24 hr. In this case, the second portion of these solution-loss or sorption curves (Figure 1) perhaps describes the loss of I from this open, aerated system through degassing. This was assessed in a companion experiment that shows ^{125}I degassing, as measured through charcoal traps in a closed system, can only account for 0.07% of the iodine inventory loss over 60d. The loss from the *A* and *P* soils over the first two days was 12% d^{-1} for this very wet system. This value is much higher than expected from degassing alone, indicating that reactions with the soil solids or the DOC also occurred.

This experiment suggests that anion exchange plays a role in the loss of I from solution; but, these loss rates may not be entirely due to loss to the solid phase. Further experiments to investigate the I exchange capacity of these and other soils are under way, including studies to quantify the degassing rate of I from soils during sorption and the iodination of major soil fractions and functional groups.

3.2. SORPTION AND PORE-WATER COMPOSITION WITH TIME

This experiment contained only one I concentration in solution (1000 mg I L^{-1}) for comparison with a control (0 mg I L^{-1} added). Comparison of ionic concentrations in the control after 21 days with a fresh hand-squeezed peat pore water sample indicates that the addition of distilled water reduced most of the concentrations of the ions in the pore water, except for Fe (Table III). The anionic composition was altered more dramatically by the dilution than were the cationic or total composition. However, the presence of KI in solution generally had a much larger impact on the solution than the transition between fresh and diluted pore water. This was part of the experimental design in order to provoke shifts large enough to detect.

The anionic concentrations after 21 days showed that, in comparison to the control solution, the presence of KI caused about a twofold increase in Cl^- and a fivefold increase in F^- in solution, as well as an almost twelvefold decrease in SO_4^{--}, and a very slight decrease in NO_3^- (Table III). The Cl^- and F^- ions may have been displaced by simple exchange with I^-. However, a substantial decrease in SO_4^{--} concentrations indicates that the sulphate chemistry has been influenced. The comparable cationic or total concentrations, excluding K, show that the presence of KI caused about a fourfold increase in Ca, a fivefold increase in Mg and almost a twofold increase in Na. Impacts on the Fe concentration were not significant.

In order to standardize the concentration differences, the milliequivalent amount of each ion or the hydrogen ion equivalent was calculated, as well as this amount expressed as a fraction of the respective anion or cation equivalent total (Table III). The milliequivalent amounts of I^- and K were not included in the totals used for

TABLE III

Average ($n=3$) ionic concentrations (mg L^{-1}), milliequivalent amounts (meq L^{-1}) and fractions of their respective anion or cation equivalent totals, excluding I^- and K, in the iodine treated and control P soil after 21 days

Ion	Concentration		Hand-squeezed pore water	Milliequivalent amount		Equivalent fraction of total	
	I	Control		I	Control	I	Control
Cl^-	4.15±2.27	1.69±0.41	15.6±13.7	0.18	0.20	0.585	0.603
SO_4^{--}	0.47±0.13	5.47±0.32	13.9±0.12	0.04	0.05	0.169	0.235
NO_3^-	0.51±0.10	0.55±0.15	7.7±0.4	0.024	0.018	0.095	0.079
F^-	0.64±0.0	0.12±0.03	0.3±0.2	0.031	0.026	0.150	0.083
I^-	796.7 ±20.2	<0.05	<0.5	6.42	–	30.450	0.045
HCO_3^-	<1.0	<1.0	<1.0	–	–	–	–
CO_3^-	<1.0	<1.0	<1.0	–	–	–	–
Ca	34.8 ±0.25	7.91±0.20	9.9±0.2	1.86	0.29	0.674	0.514
Mg	8.0 ±0.04	1.59±0.04	2.5±0.05	0.73	0.10	0.264	0.180
Fe	1.1 ±0.55	1.27±0.09	0.6±0.06	0.019	0.040	0.007	0.067
Na	3.3 ±1.46	2.03±0.13	4.6±0.4	0.153	0.127	0.055	0.239
K	132.1 ±1.08	0.94±0.03	1.4±0.01	3.56	0.19	1.294	0.375

these fractions. Figure 2 shows the total anion/cation balance, including K and I^-, for the experimental system. Ideally, the data, which include each treatment (I and control), each of the 3 replicates and each of the 5 sampling times, would fall on the one-to-one line. The measured anion equivalents in the control solution were low with respect to the cation equivalents. The charge balance in this solution may have been satisfied by organic anions that were not measured. However, the treatment containing I showed more anion equivalents in solution than cation equivalents. This seems to confirm that anion exchange was occurring and also indicates that organic anions do not appear to have played a large role and may even have been salted out at high concentrations.

The milliequivalent fractions for the cations were much larger in the treatment than the control, including their respective errors, throughout the 21 days. The presence of KI increased the milliequivalent fraction attributable to Ca and Mg, and decreased the fraction attributable to Na and Fe. The KI appeared to exchange with the sites holding double-valence cations in preference to single- and triple-valence cations. It appears that Ca and Mg are displaced to balance the charge. It is possible that unmeasured cations, such as NH_4^+, Si^{++} and Al^{+++} or complex ions contributed to the cation imbalance.

When I is present, the anions could be associated with functional groups or organics and may not be measured as inorganic anions, causing the charge to
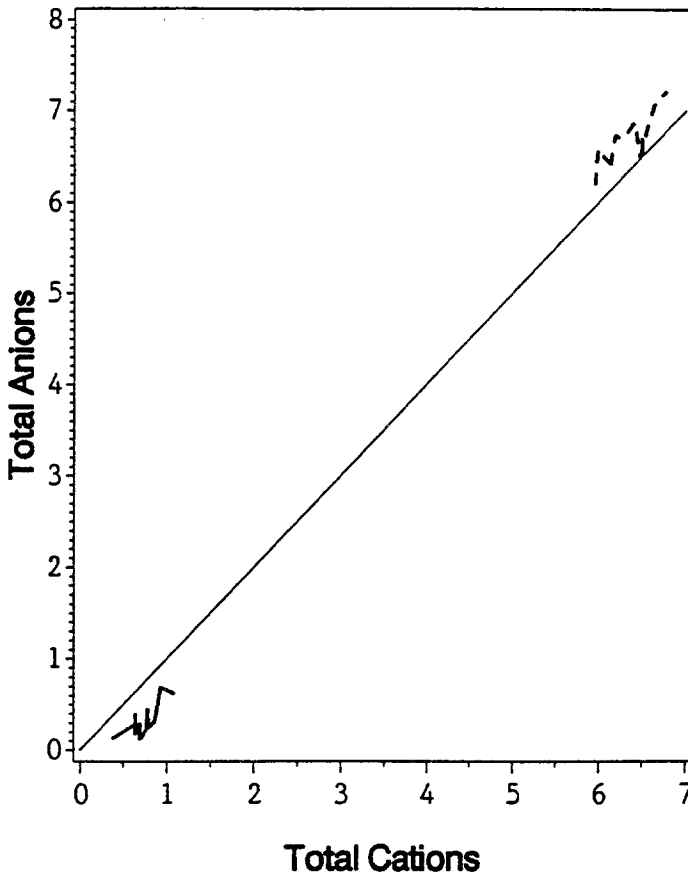
Fig. 2. Total anion versus total cation balance, expressed as milliequivalents, for P soil, including K and I^-.

appear to be underbalanced with respect to anions and overbalanced with respect to cations. Since the values of I^- by IC and total I by ICP are similar, this suggests that complexes of I are not forming in this system. Since the anion fraction of the total decreases and the cation or total fraction of the total increases with time, this indicates that neutral ions or complex species of other ions, perhaps S, are creating this shift.

Several modelling studies were completed to evaluate the aqueous geochemistry of the A and P soil pore-water solutions. Starting solutions were derived from chemical analyses of a hand-squeezed pore water from a fresh sample of the P soil and of a centrifuged pore water from the A soil (Table I). Two geochemical modelling codes, WATEQ4F (Ball et al., 1991) and PHREEQE (Parkhurst et al., 1990) were used to determine the speciation and saturation of these solutions in simulations of these the experiments. Only inorganic species were considered in the simulations.
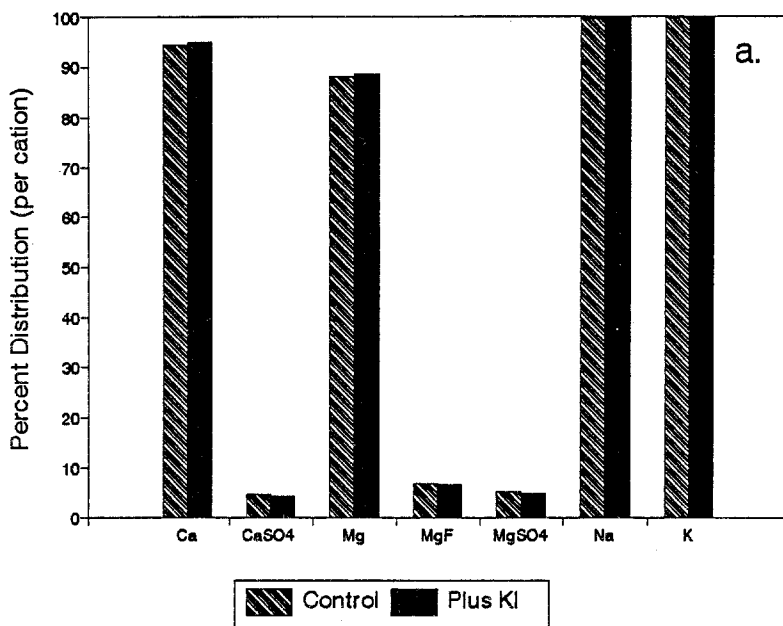
Fig. 3a.

The results of this modelling indicated that the changes in speciation caused by adding a total of 1308 mg I L^{-1} to the solution were minor and there was no significant change in the saturation state for any solid phase. The modelled addition of KI caused the concentration of a minor species, KSO_4^-, to increase, which in turn had a slight effect on the amount of SO_4 that was available to complex with other cations. The anions Cl^-, I^-, and NO_3^- remained largely uncomplexed in all solutions. In the A soil pore-water solution, WATEQ4F predicted that adding the KI would cause a minor Fe species, $FeOH^+$, to disappear from solution, but no other species were removed or added as a result of the increase in K and I in any of the solutions modelled. The increase in ionic strength due to the addition of the KI resulted in a slight relative decrease in the proportions of neutral or paired complexes such as $MgSO_4^0$ and MgF^-, with a corresponding increase in the proportions of free ionic species such as Mg^{++}, SO_4^{--}, and F^-. These shifts, all less than 2%, are shown for the A soil in Figure 3. This effect on SO_4^{--}, shown by the model, was also the largest effect measured in the pore water of the A soil during sorption.

WATEQ4F also calculates the saturation state of a number of minerals and other solid phases with respect to the modelled solution. The P pore-water solution was not oversaturated with any phases, either before or after the addition of KI. The A pore-water solution was reported to be oversaturated in ferrihydrite, fluorite and goethite initially, and the addition of KI did not change the oversaturated nature of
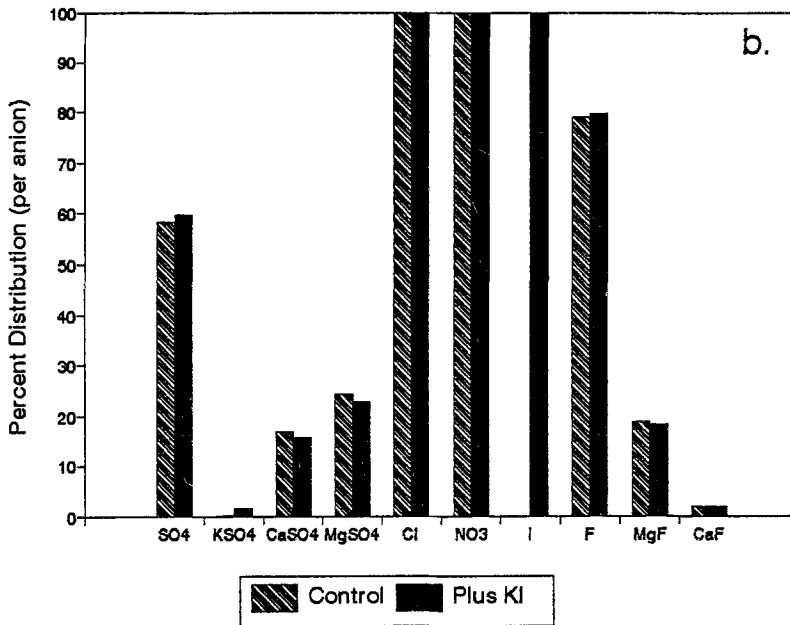
Fig. 3b.

Figs. 3(a)–(b). Percent distribution of the major elements in the A soil pore water grouped by a) cation species and b) anion species naturally (control) and in the presence of KI (plus KI).

these phases, nor did WATEQ4F indicate that any additional solid phases became oversaturated as a result. WATEQ4F contains limited thermodynamic data for the I solids, so further solubility modelling was performed with an expanded version of PHREEQE using the CHEMVAL thermodynamic database (Chandratillake *et al.*, 1992), which contains data for crystalline KI, CaI_2, MgI_2 and I_2. PHREEQE simulations showed all of these iodide phases were undersaturated in the solutions being modelled, both before and after the addition of 1308 mg L^{-1} KI. The geochemical modelling helps to confirm, albeit with less than ideal databases for I, that solid-phase saturation is unlikely.

The DOC results show that there was very little organic carbon after the first day of the experiment (Table IV). However, the DOC was easily measured after 21 days and it was fivefold higher in the control than in the presence of KI. This indicates that either the peat released DOC to the solution with time or a microbial population flourished in this interval. The high ionic strength may have caused the humics to degrade in the KI solution or inhibited microbial growth. Although the humics may have changed their conformation or microbes flourished in this *P* soil solution after 21 days, the sorption results indicate that some I still remained in solution.

TABLE IV

Dissolved inorganic (DIC) and organic (DOC) carbon (μg L^{-1})

Slurry type	Day 1 DIC/DOC	Day 21 DIC/DOC
Peat + distilled water	0 / 0	0 / 116
Peat + distilled water + KI	0 / 0	0 / 22

3.3. SORPTION VERSUS DOC

Our pore-water composition results and the results showing a marked increase in DOC during sorption prompted this experiment with a range of iodide concentrations and two DOC concentrations. Three I concentrations (10^{-3}, 10^{-1} and 10 meq L^{-1} or 0.127, 12.7 and 1270 mg I L^{-1}) were used. Although, these were thought to be high concentrations for simulated pore waters, the concentration of I was 39.3 mg I L^{-1} in the sphagnum bog groundwater sampled from a pit and used to introduce the natural DOC. This may be a result of the earlier experiment in this bog (Sheppard *et al.*, 1989), but, no elevated I concentrations were ever measured in the groundwater near this pit or in the surface water of this pit, located some 20 m from the injection of the KI spike. The concentration of K in this groundwater was 1.31 mg K L^{-1}. The concentrations of I and K in the thousandfold dilution using distilled water were <0.10 mg I L^{-1} and 0.12 mg K L^{-1}.

The concentrations of Cl$^-$, NO$_3{}^-$ and Mg stabilized within 24 hours of the KI addition to the natural groundwater, and did not change significantly over the 5 days. Concentrations of anions and cations were measured after 24 hr (Table V). The addition of KI to the natural groundwater elevated the I$^-$ and K concentrations in proportion to the additions; however, Cl$^-$ was not affected even though it was affected significantly in the earlier pore-water composition experiment. This suggests that the Cl$^-$ in the peat sorption experiment was displaced from the peat solids. The NO$_3{}^-$ concentrations increased directly with an increase in I$^-$, but by less than twofold. The Mg concentrations were not affected significantly by the presence of KI in the natural groundwater, but the Mg concentrations almost doubled at low I concentrations in the dilute groundwater. Sulphate concentrations increased at the lower I concentrations by 37%. The total S, Ca and Fe did no differ significantly across the I concentrations in the natural groundwater, but, the concentrations of these elements were up to twofold larger for Ca and Fe in the low DOC water and more than threefold larger for S. Ratios of measured-to-added (including background) I concentrations after 24 hr were usually greater than 1. Thus, more I was found in solution than was added, and the ratios were consistently highest at low I concentrations and lowest at high I concentrations. Iodine did not

TABLE V

Selected ion concentrations in bog groundwater 24 hr after contact with
10^0, 10^{-1} and 10^{-3} mg I L^{-1} as KI (mg L^{-1})

Treatment	I^-	I	F^-	Cl^-	NO_3^-	SO_4^{--}	K	Na	Mg	Ca	P	S	DIC	DOC	DIC/DOC
Natural	41	44.1	<0.1	1.48	0.26	0.73	1.64	3.72	8.60	26.5	<0.08	0.72	19.81	30.07	0.65
10^{-3}	43	44	<0.1	1.89	0.24	1.00	1.97	2.77	8.56	26.5	<0.08	0.68	18.61	27.41	0.68
10^{-1}	52	44	<0.1	1.26	0.33	0.70	4.69	4.21	8.36	25.9	<0.08	0.72	18.31	28.57	0.64
10	1300	1320	<0.1	0.98	0.43	0.76	398	3.92	7.61	24.7	<0.08	<0.06	17.84	26.42	0.67
Thousandfold Dilution	<0.5	<0.5	<0.1	<0.13	0.19	0.27	0.17	2.87	0.019	0.45	<0.08	<0.06	2.83	15.67	0.18
10^{-3}	1.26	<0.5	<0.1	0.21	0.21	0.70	0.50	2.13	0.031	0.56	<0.08	0.13	1.3	19.14	0.07
10^{-1}	13.2	13.2	<0.1	0.21	<0.16	0.71	4.23	3.06	0.035	0.83	<0.08	0.13	1.84	18.14	0.10
10	1260	1260	<0.5	<0.13	<0.16	1.54	410	2.83	0.020	0.79	<0.08	0.18	1.47	9.38	0.16

seem to react with the DOC at low concentrations, but it did react slightly at the highest concentrations, giving measured-to-added ratios of 0.98 to 0.93. Total I and I^- concentrations are similar, indicating that any reactions with the DOC are slow and most of the I added remains as I^- in solution, as in the experiment containing the P soil.

These experimental measurements and the geochemical modelling suggest that I speciation and sorption are not sensitive to solution concentration or DOC concentration, and very high I concentrations must be attained before saturation of the solid phase occurs. Sheppard and Evenden (1988) reported a linear relationship between the I in soil leachate and the total soil I concentration over eight orders of magnitude for a peat soil, confirming that extrapolations can be made. Our experiments indicate that I appears to be most closely linked to the sulphate chemistry.

Analyses of dissolved inorganic (DIC) and organic carbon (DOC) on these groundwaters shows that the thousandfold dilution reduced the DIC/DOC ratio by one-third. This reduction in the ratio is primarily caused by a large decrease in the DIC upon dilution. Comparison between samples filtered through a 0.2 and a 0.45 μm filter indicated that about 2% of the total carbon was in the 0.2 to 0.45 μm size range in the natural groundwater and about 12% was in the 0.2 to 0.45 μm size range in the dilute groundwater. There was no trend of particle size with increasing I concentrations. This means that the higher ionic strength did not cause the humics to disaggregate as we noticed in our earlier field study (Sheppard *et al.*, 1989). However, there is a difference between the inorganic/organic carbon ratio. The I^- concentration of these samples filtered through a 0.2- or 0.45-μm filter were the same, indicating no preferential association of I^- with the smaller or the larger particulate.

4. Conclusions

Based on anion competition with Cl^-, it is evident that anion sorption plays a role in the retention of I in both mineral and organic soils. The I remaining in solution after 198 days (<2% in the P soil and <20% in the A soil) was primarily in an organic form. More sorption of I was observed in the P soil, the soil at the lower pH, characteristic of classic anion exchange behaviour in mineral soils.

The loss of I from solution in contact with soil is not a simple reaction and it has been successfully described for our A and P soils using a two-stage reaction model. There is a very fast initial reaction followed by a slower reaction. Slower reaction rates in the A soil than the P soil indicate that perhaps the reaction or complex formation with one humic form is slower than with another. These different reaction rates could be attributed to completely different reactions between the liquid and solid phases (both mineral and organic) or reactions with different DOC (from very low to very high molecular weight). Very slow reactions of I with DOC may bias

batch sorption experiments, including those carried out with fresh soil or simulated pore water. The loss of I from solution due to degassing is minimal.

The sulphate chemistry is most affected by the presence of I in solution. Double-valence anions and cations, more so than single- or triple-valence ions, were affected by the addition of KI. Organic anions and neutral species or complexes may play a role in I retention. Analyses by IC and ICP indicate that this is not a direct effect, but may come as an indirect effect on the sulphate chemistry. Geochemical modelling confirmed that the highly charged species, particularly SO_4^{--}, were the most clearly affected by the presence of KI and its accompanying high-ionic-strength pore-water solution. The WATEQ4F and PHREEQE models indicated the solid-phase saturation state of the minerals did not occur at these high concentrations.

Dissolved organic carbon analyses showed that after the I addition the P soil either released DOC to the pore water with time or that microbes flourished. Filter size comparisons showed that the high ionic strength did not cause the humics to flocculate and indicates no preference of I with the smaller or larger humics.

These experiments and the geochemical modelling confirm that the speciation of I is not sensitive to the ionic strength of the pore water, and that very high I concentrations would have to be attained before solid-phase saturation occurs. We conclude that experiments using elevated concentrations of stable I, to assure detection, provide valid data that can be meaningfully extrapolated to very low concentrations using linear principles.

Several follow-up experiments are foreseen to help elucidate the iodine chemistry of soils. These include determinations of loss of I from pore water to specific soil functional groups and specific DOC size fractions, the role of microorganisms in I soil sorption, including attention to the sulphate chemistry of the system, determination of anion exchange capacities using I for a range of soils, and data improvements for I to geochemical databases.

Acknowledgements

References

Ball, J. W. and Nordstrom, K. D.: 1991, User's manual for WATEQ4F, with revised thermodynamic data base and test cases for calculating speciation of major, trace, and redox elements in natural waters. U.S. Geological Survey, Open-File Report 91–183.

Benes, J.: 1975, *Chem. Commun.* **40**, 2012.

Bors, J., Martens, R. and Kuhn, W.: 1988, *Radiochim. Acta* **44/45**, 201.

Christiansen, J. V. and Carlsen, L.: 1992, *Radiochim. Acta.* **52/53**, 327.

Chandratillake, M., Falck, W. E. and Read, D.: 1992, CHEMVAL Project Guide to the CHEMVAL Thermodynamic Database, DOE (U.K.) Report DOE/HMIP/RR/92/094.

Kantelo, M. V., Tiffany, B. and Anderson, T. J.: 1982, in *Environmental Migration of Long-Lived Radionuclides*, International Atomic Energy Agency, Vienna, p. 495.

Koch, J. T. and Kay, B. D.: 1987, *Can. J. Soil Sci.* **67**, 353.

Lee, K. D. and Lee, S. K.: 1976, *Indian J. Appl. Chem.* **30**, 80.

Liu, Y. and von Gunten, H. R.: 1988, Technischer Bericht 88–29, Paul Scherrer Institut, University of Bern, Switzerland.

Manzoor, E. R. and Babcock, K. L.: 1961. *Soil Sci.* **91**, 1.

Mott, C. J. B.: 1981, 'Anion and Ligand Exchange' in *The Chemistry of Soil Processes*, John Wiley and Sons Ltd., Chichester, Greenland, D. J. and Hays, M. H. B. (eds.), p. 179.

Motycka, M. and Stephenson, M.: 1993, *Methods of Iodine Preconcentration and Speciation*, Atomic Energy of Canada Limited report, AECL-XXXXX, (in prep).

Muramatsu, Y., Uchida, S., Sriyotha, P. and Sriyotha, K.: 1990, *Water, Air, and Soil Pollut.* **49**, 125.

Parkhurst, D. L., Thorstenson, D. C. and Plummer, L. N.: 1990, *PHREEQE - A Computer Program for Geochemical Calculations.* U.S. Geological Survey, Water - Resources Investigations 80–96.

SAS, Statistical Analysis System, Inc.: 1985, *Statistical Analysis System Users Guide: Statistics*, SAS Institute, Cary, NC.

Saas, A. and Grauby, A.: 1976, *Health Physics* **31**, 21.

Schuttelkopf, H. and Pimpl, M.: 1982, in *Environmental Migration of Long-Lived Radionuclides*, International Atomic Energy Agency, Vienna, p. 395.

Sheppard, M. I.: 1992, *The Soil Submodel, SCEMR1, for the Assessment of Canada's Nuclear Fuel Waste Management Concept*, Atomic Energy of Canada Limited Report AECL-9577, COG-91-194.

Sheppard, M. I. and Thibault, D. H.: 1991, *J. Environ. Qual.* **20**, 101.

Sheppard, M. I. and Thibault, D. H.: 1992, *Appl. Geochem.* **7**, 265.

Sheppard, M. I., Thibault, D. H. and Mitchell, J. H.: 1987, *J. Environ. Qual.* **16**, 273.

Sheppard, M. I., Thibault, D. H. and Smith, P. A.: 1989, *Appl. Geochem.* **4**, 423.

Sheppard, S. C. and Evenden, W. G.: 1988, *J. Environ. Radioactivity* **7**, 221.

Tikhomirov, F. A., Kasparov, S. V., Prister, B. S. and Kurbatov, V. M.: 1978, *Soviet Soil Sci.* **10**, 717.

Whitehead, D. C.: 1973, *J. Soil Sci.* **24**, 260.

Whitehead, D. C.: 1974, *J. Sci. Fd. Agric.* **25**, 73.

Whitehead, D. C.: 1978, *J. Soil Sci.* **29**, 88.

Whitehead, D. C.: 1984, *Environ. Intern.* **10**, 321.

Yoshida, S., Muramatsu, Y. and Uchida, S.: 1992, *Water, Air, and Soil Pollut.* **63**, 321.

Yuita, K.: 1992, *Soil Sci. Plant. Nutr.* **38**, 281.