

Interaction between organic matter and trace metals in a uranium rich bog, Kern County, California, U.S.A.

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Abstract—Surface and groundwaters, plants and organic and inorganic components of sediments from a uranium rich bog in Kern County, California were studied to determine the mechanism of uranium entrapment and concentration.

Spring waters which originate along a fault trace and contain elevated uranium concentrations (up to 293 $\mu\text{g/l}$) and other metals percolate through the waterlogged boggy meadow. Several approaches used to study the speciation of metals in the bog sediments indicate that U, unlike other metals, is predominantly associated with organic matter. In samples with high total organic carbon (>7%), uranium values range up to 1100 μm . Analyses of organic constituents of the sediments show that humic substances, and not living plant material, are responsible for U entrapment and enrichment. Infra-red studies suggest that the mechanism of entrapment is complexation of the uranyl cation in groundwaters by carboxyl functional groups on the humic and fulvic acid molecules.

Published experimental and thermodynamic data are reviewed and a mechanism to explain preferential enrichment of U over other trace metals is proposed for freshwater bog or marsh environments.



INTRODUCTION

ASSOCIATION of organic matter with trace metals of economic value is increasingly recognized as a significant mechanism in several ore forming environments. It is now apparent that the organic constituents of soils and recent sediments (humic substances) are important agents of weathering (ONG *et al.*, 1970; HUANG and KELLER, 1972; RASHID and LEONARD, 1973; SCHNITZER and KODAMA, 1976; BOYLE *et al.*, 1974; RASHID, 1974; JACKSON *et al.*, 1978; SILVERMAN, 1979; BAKER, 1986), of trace metal mobilization and transport (STUMM and MORGAN, 1970; RAMAMOORTHY and KUSHNER, 1975; MALCOLM and DURUM, 1976; REUTER and PERDUE, 1977; JACKSON *et al.*, 1978; PAGENKOPF, 1978; SHOLKOVITZ and COPELAND, 1981; LEE and JONASSON, 1983; PIOTROWICZ *et al.*, 1984) and also of element concentration (SZALAY, 1964; SZALAY and SZILAGYI, 1966; SZILAGYI, 1967; CHOWDURY and BOSE, 1970; RASHID, 1974; PAULI, 1975; JACKSON *et al.*, 1978; KERNDORFF and SCHNITZER, 1980). Several examples of trace metal sorption by humic substances in recent marine and lacustrine sediments have been reported in the literature (COOPER and HARRIS, 1974; NISSENBAUM and SWAINE, 1976; PICARD and FELBECK, 1976; JONASSON, 1976; JACKSON *et al.*, 1978; HALBACH *et al.*, 1980).

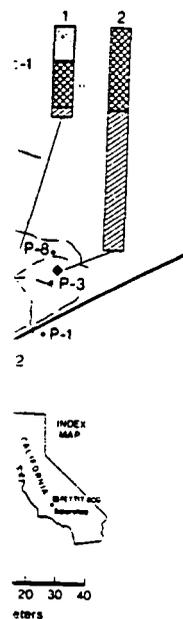
Peat bogs are environments rich in organic matter, and it is not surprising that very high concentrations of metals in bog sediments have been reported worldwide. Fe and Cu enriched bogs are found in the U.S.A. (ECKEL, 1949; FRASER, 1961; GOFF, 1983; LEVENTHAL *et al.*, 1978), in Canada (BOYLE, 1977; LETT and FLETCHER, 1980). Britain, Zambia (BOYLE, 1977), the U.S.S.R. (KOCHENOV and KRESHTAPOVA,

1967; AL'BOV and KOSTAREV, 1968), and Finland (SALMI 1967). Other metals enriched in bog sediments including Ti, Ge, Zn, Ni, Mo and V have been reported from Finland (SALMI, 1967) and the U.S.S.R. (KOCHENOV and KRESHTAPOVA, 1967; MANSKAYA and DROZDOVA, 1968).

Uranium in peat bogs has received considerable attention with occurrences reported from the U.S.A. (BOWES *et al.*, 1957; SCHMIDT-COLLERUS, 1979; CAMERON, 1985; OTTON and ZIELINSKI, 1985), the U.S.S.R. (KOCHENOV *et al.*, 1965; LOPATKINA, 1967; TITAYEVA, 1967; MANSKAYA and DROZDOVA, 1968; LOPATKINA *et al.*, 1970), Sweden (ARMANDS, 1967; WILSON, 1984), Britain (WILSON, 1984) and Germany (HALBACH *et al.*, 1980). These deposits are commonly included in the class of "young" surficial uranium deposits (CULBERT *et al.*, 1984) and are generally characterized by a marked deviation from secular equilibrium owing to their recent emplacement.

Peat rich sediments are predominantly composed of humic substances (humic and fulvic acids and humin). The mechanism of trace metal entrapment by these substances is thought to involve physical adsorption, reduction, and the formation of organometallic complexes through binding by acidic functional groups (carboxyl, phenol, hydroxyl and amino) and other oxygen containing groups such as quinone and carbonyl (SCHNITZER and SKINNER, 1965; SCHMIDT-COLLERUS, 1969; DOL *et al.*, 1975; JENNINGS and LEVENTHAL, 1977; SCHMIDT-COLLERUS, 1979; HALBACH *et al.*, 1980; TEMPLETON and CHASTEEN, 1980; DISNAR, 1981; SCHNITZER, 1978; NAKASHIMA *et al.*, 1984).

The early experimental work by SZALAY (1958; 1964) confirmed the ability of peat-derived humic



Millipore filters to remove particulate matter, stored in clean polyethylene bottles after acidification with 0.1N HCl and subsequently analyzed for U by DNA, and other trace metals by inductively coupled plasma emission spectroscopy (ICPES). Living plant samples were collected from within the bog and from outside the area of known U enrichment (as controls), washed in the laboratory to remove any residual soil and freeze dried. Samples were subsequently ground to a fine mesh in a glass ball mill and analyzed for U (by DNA) and for other elements by optical emission spectroscopy (OES). Ashing was avoided and results are on a dry-weight basis. Grass samples were separated from their roots in order to minimize soil contamination. Tree samples consisted solely of needles and new (1–2-year-old) twigs.

Fifteen sediment cores of varying depth were taken from different parts of the bog using a hand-driven piston corer. The cores were collected in plastic liners, air dried and sectioned. Each section, ranging from 15 to 25 cm in length, was homogenized and stored in cleaned glass sample jars. Compaction of the waterlogged sediment inside the corer necessitated determination of a compaction factor ($\times 2$) in order to estimate depths of the samples. Finely ground (80 mesh) sediment was analyzed for U directly by DNA and for other trace metals by ICPES. For the ICPES analysis, 15 mg of each sample was digested in a 25 ml mixture of concentrated HF:HCl:HClO₄ (2:5:2), and evaporated to dryness. The residue was then taken up in 5 ml of concentrated HNO₃ diluted to a volume of 50 ml with ultrapure water (Barnstead Nanopure II purification system) and analysed. A multivariate technique of R-mode factor analysis (Bio-Medical Data Package statistical software, UCLA) was used to examine relationships among the various elements analysed in sediment and water samples in an attempt to establish possible correlations and to infer factors or processes controlling their distribution. Organic carbon contents of 29 sediments were determined manometrically on a vacuum line utilizing the routine combustion at 900°C procedure used for sample preparation for stable isotope analysis (STUERMER *et al.*, 1978). The bitumen fraction of the bog sediments was extracted with CH₂Cl₂, separated chromatographically on an activated silica gel column and the *n*-alkane fraction eluted with hexane. The *n*-alkanes were analysed on a Hewlett Packard 5830A gas chromatograph, and the total bitumen fraction was analysed for U and other elements by DNA and ICPES respectively. Humic and fulvic acids were extracted using dilute alkali (SCHNITZER and KHAN, 1972). Briefly, 5–10 g of dried bog sediment was extracted for 6 h with 0.2N NaOH in sealed polyethylene bottles in which the air had been displaced by N₂. The samples were repeatedly extracted until no color remained in the extractant, each centrifugation. After filtration through a 0.8 μ m glass fibre filter paper to remove finely suspended sediment, the alkaline solutions were acidified to pH 1.0 with 6N HCl to precipitate humic acid (HA). Following centrifugation (3000 rev/min for 40 min) the supernatant was decanted, filtered through 0.45 μ m Millipore filter and passed through an Amberlite XAD-7 resin column (3 cm diameter, 40 cm length). The sorbed fulvic acid (FA) was eluted from the XAD-7 resin with a 1:1 mixture of 0.1N NH₄OH and MeOH, concentrated to a small volume by rotary evaporation and freeze dried. The coagulated humic acid (HA) was washed with nanopure water several times and freeze dried. The XAD-7 passed solution (containing organic compounds not sorbed by the resin) was kept for analysis of low mol. wt organic acids and trace metals by DNA and OES. Eight samples from which the HA and FA (the alkali soluble fraction) had been extracted, were demineralized using a 1:5 mixture of HF:HCl (38% and 6N respectively) in order to obtain the insoluble Humin (HU) fraction. Elemental C, H and N contents of HA, FA and HU were determined using a vacuum line manometer and standard stable isotope sample preparation procedures (MINAGAWA *et al.*, 1984). Gas samples collected during this

procedure were analyzed for stable isotopes of C, H and N to characterize the source of the organic matter. Molecular weights of HA and FA samples were determined using size exclusion chromatography (HPLC). Infra-red spectra of HA, FA and HU samples were run on a Perkin Elmer 521 spectrometer using KBr discs (0.5 mg sample, 200 mg KBr) pressed at 15000 psi pressure. Functional group analyses (total acidity, carboxyl and phenolic groups) were determined by using methods suggested by SCHNITZER and KHAN, 1972).

RESULTS

Radiometric measurements

A radiometric survey (Geometrics GR 410 spectrometer) of the greater drainage area of the bog indicates typical values of 2.0–3.0 ppm eU (equivalent U) and 10 to 18 ppm eTh for outcropping quartz diorite, and from 3.0 to 4.0 ppm eU and 13–15 ppm eTh for outcropping aplite pegmatite. One small area of fine-grained quartz diorite and pegmatite, 2.5 km northeast (up drainage) from the bog, gave values of 10–13 ppm eU and 27–32 ppm eTh.

The surface of the bog is only slightly more radioactive in uranium derived gamma radiation (7–16 ppm eU) than the igneous rocks and less radioactive in thorium-derived gamma radiation (2–6 ppm eTh). These radiometric values for U are only a small fraction of the values obtained by chemical analysis (cU), which constitute evidence of the recent emplacement of U in the bog and resultant deviation from secular equilibrium (CULBERT *et al.*, 1984).

Bedrock

With the exception of the one pegmatite collected from 2.5 km northeast of the bog (11.4 ppm cU), cU values in the fresh igneous rocks are within the range of 3.7–7.1 ppm. Weathered quartz diorite contains only approximately one-half as much cU as does fresh quartz diorite, suggesting mobilization of substantial U by weathering processes.

Surface and ground waters

In the suite of water samples analysed, the only significant anomalies in U content were found in the series of springs seeping into the bog from the break in slope which is the topographic expression of the concealed Little Poso Creek fault. Values range from 23 to 293 μ g/l* cU (Table 1). Flow rates in individual springs range from 40 to 120 l/h (measured in April) accounting for a total of approximately 400–1200 l water/h seeping through the bog into Little Poso Creek. Despite this input, the U content of Little Poso Creek itself is very low (<1 μ g/l) both above

* ppb.

in core samples.

in drainage in the containing scattered abundantly of indigenous cedar, as well as grasses and aquatic meadow, are the

the meadow in by the Atomic. The only other nearby are in the deposits, located east along the (L., 1957). These dated epithermal with molybdenum organic matter. that at the bog along the bog was and radiometrically plants were background for

S weathered grus samples of quartz different parts of the is situated were (DNA). A total and the bog itself encompassing the through 0.45 μ m

Table 1. Minor and trace element analyses and flow rates of spring waters from Pettit Bog and Little Poso detection limits. All

| Sample | Fe | Ti | Mn | Ba | Sr | Zn | V | Pb |
|--------|------|-------|-------|-------|-------|-------|-------|-------|
| PC-1 | 0.12 | 0.002 | 0.019 | 0.104 | 0.108 | 0.015 | 0.004 | 0.044 |
| PC-2 | 0.14 | 0.002 | 2.470 | 0.058 | 0.103 | 0.045 | 0.008 | 0.074 |
| PS-1 | 3.01 | 0.007 | 0.026 | 0.240 | 0.226 | 0.091 | 0.074 | 0.027 |
| PS-2 | 0.10 | 0.002 | 0.699 | 0.048 | 0.100 | 0.067 | 0.011 | 0.053 |
| PS-3 | 4.52 | 0.004 | 0.010 | 0.295 | 0.256 | 0.051 | 0.064 | 0.001 |
| PS-4 | 0.10 | 0.002 | 3.420 | 0.018 | 0.063 | 0.011 | 0.014 | 0.063 |
| PS-6 | 4.71 | 0.005 | 0.093 | 1.050 | 0.702 | 0.075 | 0.097 | 0.015 |
| PS-7 | 1.72 | 0.006 | 0.092 | 0.085 | 0.122 | 0.033 | 0.042 | 0.014 |
| PS-8 | 2.57 | 0.005 | 0.030 | 0.100 | 0.082 | 0.038 | 0.048 | — |
| PS-9 | 0.38 | 0.004 | 0.002 | 0.030 | 0.069 | 0.016 | 0.017 | 0.107 |
| PS-10 | 0.03 | 0.003 | 0.002 | 0.025 | 0.063 | 0.028 | 0.022 | 0.090 |
| PS-11 | 0.04 | 0.002 | 0.007 | 0.016 | 0.070 | 0.029 | 0.020 | — |
| PS-12 | 4.15 | 0.019 | 0.308 | 0.143 | 0.148 | 0.101 | 0.068 | — |
| PS-13* | | | | | | | | |
| PS-14* | | | | | | | | |
| PS-15* | | | | | | | | |

PC—Poso Creek waters from above (PC-1) and below (PC-2) bog. PS—Spring and bog waters
 ND—Not determined.

and below the bog. Clearly, little of the U entering the bog emerges from it in Little Poso Creek.

Other elements analyzed in the waters are listed in Table 1. In comparison with Little Poso Creek, spring waters are enriched in V and Fe, and, to a lesser degree, in Mo. Figure 2 is a set of factor loading plots of trace element data (see Table 2) for spring waters entering the bog along the Little Poso Creek fault trace. Factor loadings represent the extent to which each variable is associated with a particular factor

and range from +1 to -1. For example, a variable with a loading close to +1 on a particular factor indicates a strong positive correlation with that factor. It is evident that U and V load heavily onto factor 1 along with Ca, Al, Si, Ba, Sr and Fe, whereas Ni and Mo load on factor 3 and other trace elements, to a lesser degree, load on factor 2. The high interelement correlation coefficients for elements loading on factor 1 (Ca-Ba = 98; Ca-Sr = 98; Ca-U = 88; Ca-V = 83; Ca-Al = 89; Ca-Fe = 79; Ca-Si = 73) suggests

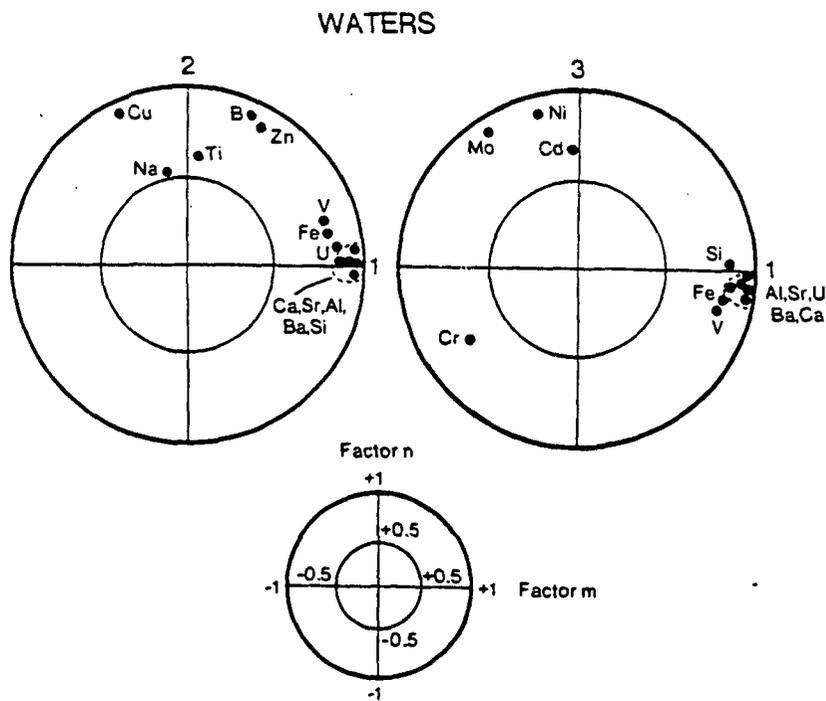


FIG. 2. Plots showing factor analysis data for Pettit Bog spring waters. Note strong clustering of U, V and lithophile major elements on factor 1. Factor loadings less than ± 0.5 fall within the inner circle and are not represented. For % of variance explained by each factor, see Table 2.

Creek. Sample numbers refer to values in ppm except U (ppb)

| Mo | Cr | Cu |
|-------|-------|-------|
| 0.031 | — | 0.007 |
| — | — | 0.016 |
| 0.025 | 0.008 | 0.019 |
| 0.079 | — | 0.018 |
| 0.043 | 0.001 | 0.001 |
| 0.049 | 0.004 | 0.002 |
| 0.011 | — | 0.001 |
| 0.116 | — | 0.002 |
| 0.052 | 0.009 | 0.002 |
| 0.036 | 0.016 | 0.002 |
| 0.089 | 0.008 | 0.014 |
| 0.055 | 0.007 | 0.008 |
| 0.020 | — | 0.019 |

emanating from Little Po

this loading to be a de suite. This association lack of correlation v siderophile elements (1) that the source for U ar be the surrounding q than a concealed dep Miracle or Kergon oc circulating groundwater

Vegetation

Analyses of plants g immediate vicinity are son with control samp

Table 2. F

| Bog sediments | |
|---------------|---|
| Factor No. | F |
| 1 | |
| 2 | |
| 3 | |
| 4 | |
| 5 | |
| 6 | |
| Spring waters | |
| Factor No. | F |
| 1 | |
| 2 | |
| 3 | |
| 4 | |
| 5 | |

Factor number

from Pettit Bog and Little Poso
detection limits. All

| | V | Pb |
|---|-------|-------|
| 5 | 0.004 | 0.044 |
| 5 | 0.008 | 0.074 |
| 1 | 0.074 | 0.027 |
| 7 | 0.011 | 0.053 |
| 1 | 0.064 | 0.001 |
| 1 | 0.014 | 0.063 |
| 5 | 0.097 | 0.015 |
| 3 | 0.042 | 0.014 |
| 8 | 0.048 | — |
| 6 | 0.017 | 0.107 |
| 8 | 0.022 | 0.090 |
| 9 | 0.020 | — |
| 1 | 0.068 | — |

PS—Spring and bog waters

For example, a variable
1 on a particular factor
correlation with that fac-
load heavily onto factor
r and Fe, whereas Ni and
her trace elements, to a
2. The high interelement
elements loading on factor
8; Ca-U = 88; Ca-V =
9; Ca-Si = 73) suggests

Creek. Sample numbers refer to stations represented on Fig. 1. Dashed lines indicate elements below
values in ppm except U (ppb)

| | Mo | Cr | Cu | Ni | B | Co | Ag | Cd | H | Flow rate (l/h) |
|--|-------|-------|-------|-------|-------|-------|-------|-------|-------|--------------------|
| | 0.031 | — | 0.007 | 0.001 | 0.087 | — | 0.003 | 0.024 | 0.1 | ND |
| | — | — | 0.016 | 0.003 | 0.067 | 0.006 | 0.002 | 0.009 | 0.1 | 3000 |
| | 0.025 | 0.008 | 0.019 | — | 0.126 | 0.005 | — | — | 120.0 | 40 |
| | 0.079 | — | 0.018 | 0.002 | 0.085 | 0.002 | — | — | 10.0 | 45 |
| | 0.043 | 0.001 | 0.001 | — | 0.058 | 0.020 | — | 0.006 | 170.0 | 65 |
| | 0.049 | 0.004 | 0.002 | — | 0.070 | 0.008 | — | — | 60.0 | 110 |
| | 0.011 | — | 0.001 | — | 0.112 | 0.008 | — | — | 293.0 | 65 |
| | 0.116 | — | 0.002 | 0.021 | 0.036 | — | 0.002 | 0.003 | 120.0 | ND |
| | 0.052 | 0.009 | 0.002 | — | 0.032 | — | 0.002 | — | 98.0 | 80 |
| | 0.036 | 0.016 | 0.002 | — | 0.029 | 0.014 | 0.001 | — | 86.0 | ND |
| | 0.089 | 0.008 | 0.014 | 0.018 | 0.067 | 0.028 | 0.005 | 0.013 | 60.0 | 120 |
| | 0.055 | 0.007 | 0.008 | 0.005 | 0.017 | 0.008 | 0.002 | 0.002 | 70.0 | 90 |
| | 0.020 | — | 0.019 | — | 0.145 | — | — | — | 230.0 | 50 |
| | | | | | | | | | 54.0 | ND |
| | | | | | | | | | 26.0 | ND |
| | | | | | | | | | 23.0 | ND |

emanating from Little Poso Creek fault and draining through Pettit Bog. * Only analysed for U.

this loading to be a dominantly lithophile element
suite. This association, combined with the marked
lack of correlation with typical chalcophile or
siderophile elements (Ni, Zn, Pb, Cd, Mo) suggests
that the source for U and V in the spring waters may
be the surrounding quartz diorite bedrock rather
than a concealed deposit perhaps similar to the
Miracle or Kergon occurrences, being leached by
circulating groundwaters.

Vegetation

Analyses of plants growing on the bog and in its
immediate vicinity are shown in Table 3. In compar-
ison with control samples taken outside the bog, all

the plants within the bog have consistently enriched,
but highly variable U contents. Grasses (*Trisetum
spicatum*) growing directly on the bog sediment show
the highest values, one sample reaching a value of 51
ppm. U contents of different kinds of plants do not
seem to be directly related to U content of soils nor
nearby surface waters. With a few exceptions, living
plants sampled in the bog have a U content less than
1% of that of the bog soils on which they are growing.

With the exception of two incense cedars (*Calo-
cedrus decurrens*) growing on the uraniumiferous bog
soil, no noticeable physiological effects could be seen
in any plants in the area. The two cedars in question
were highly chlorotic and also had the highest U
concentrations of the population sampled.

Table 2. Factor analysis summary of elements from Pettit Bog sediments and water samples

| Bog sediments | | | Factor loadings | | |
|---------------|----------------------|----------------------|-----------------|---------------------------|--|
| Factor No. | Percent of variation | >0.75 | 0.50–0.74 | 0.25–0.49 | |
| 1 | 31.4 | TOC, ROC, ASF, U, Na | Co, Sr, Al | Fe, Zn, Ca, V, Cr, Ba, Mn | |
| 2 | 23.4 | Ti, Fe, Co, Zn | Mo | Pb, Na | |
| 3 | 15.6 | V, Cr, Cu | Pb, Na | Sr, Al, Fe, Zn, Mn | |
| 4 | 9.5 | Ba | Mn | Sr, Fe, Mo, U, Ti, Co | |
| 5 | 6.2 | Ni | Ca, Sr | Cu, Al | |
| 6 | 5.4 | B | | Al, Fe, Ba, Mo, Pb, Mn | |

| Spring waters | | | Factor loadings | | |
|---------------|----------------------|------------------------------|-----------------|-----------------------|--|
| Factor No. | Percent of variation | >0.75 | 0.50–0.74 | 0.25–0.49 | |
| 1 | 45.0 | Ca, Sr, Al, Ba, Si, V, U, Fe | Cr | B, Zn, Cu, Mo, Pb | |
| 2 | 17.2 | Cu, B, Zn | Ti, Na | V, Cr | |
| 3 | 10.7 | Ni, Mo | Cd, Na | Cr | |
| 4 | 8.9 | Co, Pb | Cd | Cu, Fe, Ti | |
| 5 | 7.0 | Mn | | Pb, Fe, V, Cr, Ti, Na | |

Factor numbers listed are those with eigenvalues >1.1. Negative loadings are in italics.

Si
Fe
V
1
Al, Sr, U,
Ba, Ca

Spring of U, V and
circle and are not

5

Table 3. Analyses of trace elements in plants from Pettit Bog and vicinity. Values are on a dry weight basis and are in ppm with the dashes indicate elements below detection limits

| Sample | Zn | Cu | Fe | Mn | B | Ti | V | Co | Ni |
|---------|-------|------|-----|------|------|------|------|------|------|
| G-1 | 16.4 | 10.1 | 460 | 227 | 6.3 | 31.6 | — | — | 1.9 |
| G-2 | 26.3 | 6.9 | 861 | 173 | 15.3 | 85.0 | 3.3 | 0.01 | 4.1 |
| G-3 | 47.1 | 21.0 | 387 | 311 | 13.6 | 28.0 | — | — | 3.8 |
| G-5 | 31.1 | 8.0 | 261 | 75 | 6.1 | 9.4 | — | — | 1.3 |
| G-8 | 18.1 | 5.1 | 266 | 129 | 6.5 | 19.4 | — | — | 0.8 |
| G-Ctrl | 19.3 | 8.3 | 800 | 68 | 3.9 | 88.7 | — | — | 2.2 |
| IC-1 | 1.5 | 2.2 | 264 | 139 | 8.4 | 24.1 | 0.4 | 0.2 | 1.3 |
| IC-2 | 4.1 | 3.7 | 95 | 56 | 12.8 | 10.9 | — | — | 2.1 |
| IC-3* | 1.9 | 3.3 | 241 | 14 | 15.1 | 31.5 | — | — | 2.3 |
| IC-7 | 0.6 | 2.1 | 88 | 22 | 12.7 | 9.1 | — | — | 0.4 |
| IC-10* | 0.2 | 1.6 | 143 | 36 | 6.6 | 16.5 | — | — | 0.5 |
| IC-12 | 1.1 | 2.2 | 121 | 47 | 14.3 | 19.0 | 0.7 | 0.3 | 0.3 |
| IC-Ctrl | 6.3 | 3.5 | 161 | 49 | 14.1 | 14.9 | — | — | 0.6 |
| MG-1 | 15.1 | 9.4 | 89 | 427 | 4.3 | 4.8 | — | — | 0.6 |
| MG-2 | 17.1 | 3.7 | 110 | 561 | 6.8 | 41.6 | 2.6 | 0.5 | 0.1 |
| MG-3 | 16.3 | 2.6 | 183 | 708 | 5.7 | 9.8 | — | — | 1.3 |
| MG-5 | 24.1 | 2.6 | 167 | 970 | 23.5 | 2.9 | — | — | 1.4 |
| MG-7 | 13.4 | 6.6 | 180 | 930 | 42.1 | 2.7 | — | — | 1.2 |
| MG-8 | 17.6 | 2.2 | 125 | 169 | 3.4 | 4.6 | — | — | 1.4 |
| MG-9 | 12.6 | 5.1 | 130 | 480 | 5.9 | 5.3 | — | — | 0.14 |
| MG-11 | 15.6 | 1.1 | 130 | 670 | 19.3 | 3.3 | — | 0.02 | 0.25 |
| MG-12 | 8.3 | 1.7 | 266 | 204 | 22.4 | 5.9 | — | — | 0.5 |
| MG-Ctrl | 144.0 | 10.8 | 126 | 1580 | 28.3 | 6.2 | — | — | 0.8 |
| PP-1 | 19.9 | 2.7 | 163 | 134 | 18.2 | 7.9 | 0.96 | — | 2.0 |
| PP-4 | 35.9 | 1.3 | 114 | 59 | 15.3 | 5.1 | 0.7 | 0.1 | 2.6 |
| PP-Ctrl | 41.3 | 3.7 | 191 | 189 | 22.7 | 4.7 | — | — | 1.7 |

G = grasses (*Trisetum spicatum*), IC = Incense Cedar (*Calocedrus decurrens*), MG = Sedge (*Carex*

basis and are in ppm with the dashes indicate elements below detection limits

| Mo | Cr | Sr |
|-------|------|------|
| 78.4 | — | 52.3 |
| 34.1 | 2.6 | 21.7 |
| 111.0 | 0.1 | 39.1 |
| 42.7 | 0.5 | 17.3 |
| 37.9 | — | 58.5 |
| 60.7 | 0.3 | 45.0 |
| 7.8 | 0.1 | 90.1 |
| 26.1 | 0.1 | 92.0 |
| 28.3 | 0.1 | 43.3 |
| 27.4 | 0.1 | 85.5 |
| 26.7 | 0.02 | 37.9 |
| 14.5 | 0.2 | 60.9 |
| 12.3 | — | 80.8 |
| 171.0 | 0.5 | 16.5 |
| 57.1 | — | 37.0 |
| 33.3 | — | 22.1 |
| 77.3 | — | 19.7 |
| 110.0 | 0.01 | 17.5 |
| 16.9 | — | 11.5 |
| 113.0 | — | 15.3 |
| 58.2 | 0.2 | 22.7 |
| 54.3 | — | 18.4 |
| 98.2 | — | 41.5 |
| 2.6 | — | 8.4 |
| 27.3 | — | 0.9 |
| 19.7 | — | 9.4 |

gymnoclada). PP = Ponderosa

Zn, Cu and Mo occur in high concentrations in bog plant tissues and in control samples taken outside the bog, suggesting a regional anomaly. Mo in particular, ranges up to values equal to its concentration in the bog soil. SZALAY (1973) attributes such enhanced trace metal uptake by plants growing on peat soils to low retention by soil organic matter. The experimental work of SZILAGYI (1967) and BERTINE (1972) showed that Mo sorption by soil organic matter is optimized at low pH (<3), dropping rapidly at higher pH values. In a bog environment with pH of around 5-6, Mo sorption by dead organic matter may not be high, allowing substantial uptake by plants directly from circulating waters. The pH of interstitial water in Pettit Bog typically ranges from 4.5 to 5.5.

With the sole exception of U, all other trace elements analysed in bog plants show no enrichment relative to control samples taken from outside the bog.

Sediment within the bog

Sediment from the bog is black, mucky and waterlogged in the field, becoming dark crumbly earth when dried. Organic matter in the sediment seldom exceeds 15%. Total organic carbon (TOC) in the sediment ranges from 0.3 to 11% with an average of 4.5%. Despite this modest amount of organic matter, the pH of the sediment ranges from 4.5 to 5.5. Many of the inorganic components are recognizable primary and secondary minerals derived from weathering of the quartz diorite bedrock. X-ray diffraction

analyses confirmed the presence of abundant quartz, plagioclase, orthoclase, minor biotite, and trace hornblende, sphene, illite, chlorite. In general, the sediment consists of about 60% sand sized particles and about 20% clays. According to soil taxonomy nomenclature (BIRKELAND, 1984), the bog soil is a sapristic histosol.

U content of the sediment ranges from 90 ppm to over 1100 ppm (Table 4). Other elements do not show the same wide range of variation and, except for V and Mo, their abundances can be accounted for by the chemistry of the quartz dioritic bedrock.

Figure 3 is a plot of correlation coefficients of U vs other elements in the bog sediment. It is apparent that U does not have any significant positive correlation with the other elements analyzed in the bog, suggesting that its speciation is unique. A rather prominent negative correlation with some elements (Ca, Sr, Na, Mg, Mn, Ni, Zn, Ba) indicates that U is not primarily associated with any of the common mineral groups containing these elements. The very strong correlation of U with total organic carbon is discussed in relation to specific organic fractions below.

Sequential extractions of bog sediments. In order to determine the speciation of U and other trace metals in the bog, sequential leaches (i.e. partial dissolution of different components of the sediment) were performed on three samples of widely varying U content and TOC (sample 3A-2: 110 ppm U, 0.97% TOC;

sample 5A-2: 502 ppm U, 985 ppm U, 6.78% TOC) using a modification of the method of CHAO (1979). This method is based on geochemistry (CHAO, 1979) between trace metals and soil organic matter fractions: (a) exchangeable and organic matter; (b) bound to Fe-Mn oxides; (c) bound to Al-Fe oxides; and (e) residual (bound to silicates or diadochically substituted). These leaches for U, V and Mo samples containing significant amounts of U are overwhelmingly taken

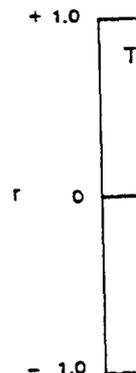


Fig. 3. Diagrammatic

values are on a dry weight basis and are in ppm with the exception of Si (wt %). Dashes indicate elements below detection limits

| Co | Ni | Mo | Cr | Sr | Ba | Li | Pb | U | Si | Al |
|------|------|-------|------|------|------|------|------|------|------|-----|
| — | 1.9 | 78.4 | — | 52.3 | 34.1 | 0.1 | 9.1 | 0.22 | 1.7 | 343 |
| 0.01 | 4.1 | 34.1 | 2.6 | 21.7 | 17.2 | 1.1 | 7.3 | 51.6 | 0.9 | 780 |
| — | 3.8 | 111.0 | 0.1 | 39.1 | 57.9 | 1.0 | 12.5 | 10.7 | 2.9 | 201 |
| — | 1.3 | 42.7 | 0.5 | 17.3 | 26.4 | 0.8 | 16.2 | 3.4 | 2.1 | 60 |
| — | 0.8 | 37.9 | — | 58.5 | 29.2 | 0.2 | 14.7 | 0.5 | 2.1 | 173 |
| — | 2.2 | 60.7 | 0.3 | 45.0 | 47.3 | 1.6 | 9.8 | 0.03 | 0.08 | 120 |
| 0.2 | 1.3 | 7.8 | 0.1 | 90.1 | 48.0 | 0.5 | 7.3 | 0.01 | 0.2 | 215 |
| — | 2.1 | 26.1 | 0.1 | 92.0 | 48.3 | 0.4 | 6.9 | 0.02 | 0.04 | 58 |
| — | 2.3 | 28.3 | 0.1 | 43.3 | 13.8 | 0.6 | 7.7 | 0.14 | 0.1 | 254 |
| — | 0.4 | 27.4 | 0.1 | 85.5 | 25.3 | 0.5 | 6.1 | 0.01 | 0.04 | 68 |
| — | 0.5 | 26.7 | 0.02 | 37.9 | 6.4 | 0.6 | 8.4 | 0.18 | 0.1 | 197 |
| 0.3 | 0.3 | 14.5 | 0.2 | 60.9 | 13.5 | 0.2 | 8.8 | 0.03 | 0.04 | 98 |
| — | 0.6 | 12.3 | — | 80.8 | 34.6 | — | 6.9 | 0.01 | 0.07 | 122 |
| — | 0.6 | 171.0 | 0.5 | 16.5 | 45.4 | 0.01 | 11.1 | 3.7 | 0.1 | 17 |
| 0.5 | 0.1 | 57.1 | — | 37.6 | 49.4 | 0.4 | 9.3 | 0.08 | 0.8 | 970 |
| — | 1.3 | 33.3 | — | 22.1 | 33.6 | 0.1 | 10.8 | 0.13 | 1.5 | 115 |
| — | 1.4 | 77.3 | — | 19.7 | 44.4 | 1.2 | 16.4 | 0.25 | 0.6 | 12 |
| — | 1.2 | 110.0 | 0.01 | 17.5 | 57.1 | 0.5 | 15.3 | 0.39 | 0.9 | 18 |
| — | 1.4 | 16.9 | — | 11.3 | 20.9 | 0.4 | 7.8 | 0.04 | 0.1 | 17 |
| — | 0.14 | 113.0 | — | 15.3 | 28.9 | 0.6 | 9.8 | 0.10 | 0.2 | 14 |
| 0.02 | 0.25 | 58.2 | 0.2 | 22.7 | 34.7 | 0.6 | 11.6 | 0.02 | 0.5 | 11 |
| — | 0.5 | 54.3 | — | 18.4 | 41.4 | 0.5 | 8.2 | 0.63 | 0.2 | 12 |
| — | 0.8 | 98.2 | — | 41.3 | 60.6 | 0.5 | 23.5 | 0.01 | 0.4 | 42 |
| — | 2.0 | 2.6 | — | 8.4 | 4.9 | 0.1 | 15.9 | 0.03 | 0.4 | 55 |
| 0.1 | 2.6 | 27.3 | — | 0.9 | 1.7 | 0.3 | 9.0 | 0.01 | 0.2 | 97 |
| — | 1.7 | 19.7 | — | 9.4 | 5.7 | 0.4 | 17.3 | — | 0.2 | 32 |

MG = Sedge (*Carex*

gymnoclada). PP = Ponderosa Pine (*Pinus ponderosa*).

of abundant quartz, biotite, and trace elements. In general, the trace elements and sized particles are related to soil taxonomy and the bog soil is a

es from 90 ppm to elements do not vary and, except for U, are accounted for by bedrock.

coefficients of U vs other elements. It is apparent that there is a positive correlation between U and some elements. A rather unique feature is that some elements indicate that U is not of the common origin. The very high organic carbon is associated with organic fractions

ments. In order to determine whether trace metals are related to partial dissolution (or precipitation) were per- varying U content (J, 0.97% TOC:

sample 5A-2: 502 ppm U, 5.62% TOC; sample 2C-5: 985 ppm U, 6.78% TOC) using a slightly modified version of the method outlined by TESSIER *et al.* (1979). This method is commonly used in exploration geochemistry (CHAO, 1984) and discriminates between trace metals bound in five different fractions: (a) exchangeable (loosely adsorbed on clays and organic matter); (b) bound to carbonates; (c) bound to Fe-Mn oxides; (d) bound to organic matter; and (e) residual (bound in detrital mineral lattices by substitution or diadochy). Table 5 lists the results of these leaches for U, V, Cu and Mo. In the two samples containing significant TOC (>1%), U is overwhelmingly taken up by the organic fraction,

while in one sample low in TOC (<1%), it is equally distributed between the organic matter and the Fe-Mn oxide fraction (Fig. 4). In the sample with the low TOC value (0.97%), Cu and Mo are predominantly associated with Fe and Mn oxides (Fig. 5), whereas V is associated with residual minerals. Copper is predominantly found in the organic fraction at high TOC values. V is distributed uniformly between the organic, exchangeable and residual fractions and the bulk of Mo is consistently found in the Fe-Mn fraction (up to 50%) over the whole range of TOC. There is, however, a significant increase of organic-associated Mo (from 4 to 25%) offset by a decrease in the exchangeable fraction.

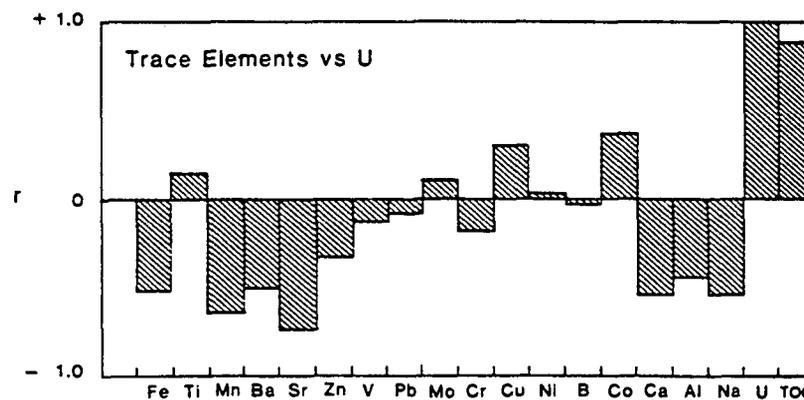


FIG. 3. Diagrammatic representation of Pearson correlation coefficient data for U vs other elements in bog sediments.

7

Table 4. Analyses of minor and trace elements in sediments from

| Sample | Fe | Ti | Mn | Ba | Sr | Zn | V | Pb | Mo |
|--------|------|------|------|-----|-----|-----|-----|----|-----|
| S-1 | 2.66 | 0.66 | 1424 | 367 | 157 | 64 | 145 | 24 | 160 |
| S-2 | 2.68 | 0.76 | 1384 | 360 | 163 | 72 | 139 | 31 | 146 |
| S-3 | 2.70 | 0.76 | 1366 | 387 | 152 | 155 | 138 | 13 | 134 |
| S-4 | 2.75 | 0.75 | 1390 | 328 | 162 | 58 | 148 | 32 | 124 |
| S-5 | 1.58 | 0.48 | 1222 | 232 | 100 | 142 | 104 | 19 | 125 |
| S-6 | 2.60 | 0.67 | 1463 | 292 | 162 | 85 | 128 | 22 | 117 |
| S-7 | 1.77 | 0.27 | 1270 | 463 | 211 | 156 | 438 | 33 | 113 |
| S-8 | 2.61 | 0.28 | 1991 | 689 | 194 | 189 | 70 | 12 | 112 |
| S-9 | 2.00 | 0.24 | 1271 | 354 | 99 | 164 | 43 | 18 | 120 |
| S-10 | 1.92 | 0.25 | 1990 | 329 | 212 | 127 | 65 | 17 | 123 |
| S-11 | 2.73 | 0.37 | 2943 | 586 | 185 | 133 | 114 | 32 | 150 |
| S-12 | 2.51 | 0.28 | 2327 | 358 | 178 | 236 | 88 | 17 | 116 |

S-1 to S-6: samples taken from approximately 25 cm intervals from a single 150 cm core. S-1 at the base TOC(%)-% total organic carbon. ROC(%)-% residual organic carbon after alkali extraction of

The varied speciation of these and other elements in the bog sediments is also reflected in the factor loading plots (Fig. 6). U and the various organic fractions load heavily onto factor 1 (organic matter), Cu and V load on factor 3 along with Pb and Cr, whereas Mo loads onto factor 2 associated with Fe, Ti and Co. Interelement correlation coefficients support these factor groupings; U-TOC = 0.89, U-ASF = 0.92 (alkali soluble fraction), U-ROC = 0.73 (residual organic carbon) for factor 1; Cr-V = 0.76, Cr-Pb = 0.68, Cr-Cu = 0.66 for factor 3; and Ti-Co = 0.86, Ti-Fe = 0.55 and Ti-Mo = 0.50 for factor 2.

ORGANIC MATTER WITHIN THE BOG

Characterization of organic matter

Humic and fulvic acids (the alkali soluble fraction: ASF) and humin constitute most of the organic matter in the bog sediment, the ASF accounting for between 30-60% by weight. The ratio of HA to FA, in general, is about 10:1 and does not show any systematic variation with depth.

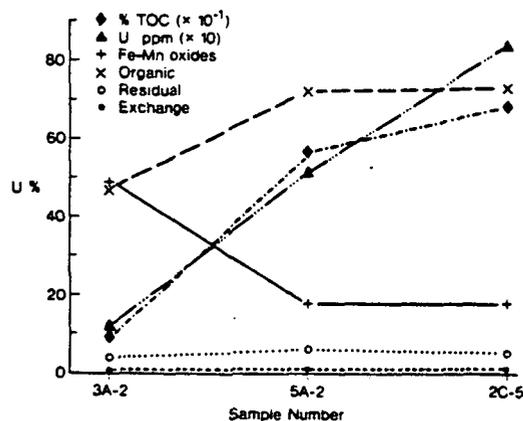


FIG. 4. Plot of uranium sequential extraction data for samples 3A-2, 5A-2 and 2C-5 from Pettit Bog sediments. Vertical scale represents % of total U found in various fractions.

C, H, N, O elemental analyses, functional group contents and mol. wts of the HA, FA and HU are listed in Table 6 and fall within the expected range of values for typical terrestrial humic substances (STEVENSON, 1982; SCHNITZER, 1978). Infra-red spectra for HA and FA (Fig. 7) show major absorption bands for the following functional groups: 3440 cm^{-1} (H-bonded OH), 2900 cm^{-1} (aliphatic C-H stretch), 1700-1720 cm^{-1} (C=O of COOH), 1590-

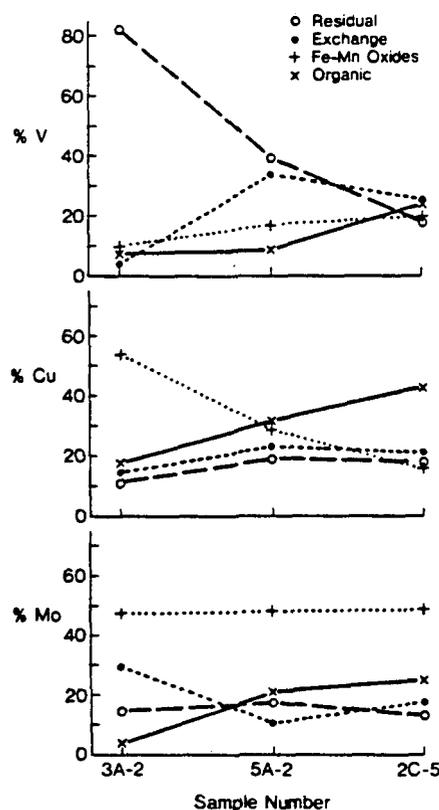


FIG. 5. Plots of sequential extraction data for V, Cu and Mo in Pettit Bog sediments. Vertical scale represents % of total V, Cu and Mo found in various fractions. Total concentrations of these elements are listed in Table 5.

Pettit Bog (ppm except

| Cr | Cu |
|----|----|
| 29 | 48 |
| 36 | 57 |
| 25 | 47 |
| 30 | 73 |
| 22 | 31 |
| 27 | 61 |
| 40 | 81 |
| 20 | 30 |
| 16 | 50 |
| 30 | 55 |
| 24 | 41 |
| 23 | 12 |

and S-6 at the top. S-7 is humic and fulvic acid fra

1620 cm^{-1} (conjugat carbonyl, COO^-), 1. COO^-), and 1230 cm^{-1} (C=O stretch). These previously published sp

stances (SCHNITZER show an abundance (The *n*-alkane distr carbon isotope valuations were determin source of the organ isotope values for H to -28 per mil range C3 higher terrestria LAN, 1972). This w alkane distribution preponderance of C over-even predomin from higher plants (

Trace metal distribu

Figure 8 shows th (alkali soluble frac carbon) correspond humic and fulvic aci

Table 5. Distribution

Fraction

Exchangeable
Bound to CO_2
Fe-Mn Oxides
Organic
Residual

Total
Conc. in sed. (ppm)

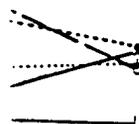
Elements in sediments from

| | Pb | Mo |
|---|----|-----|
| 5 | 24 | 160 |
| 9 | 31 | 146 |
| 8 | 13 | 134 |
| 8 | 32 | 124 |
| 4 | 19 | 125 |
| 8 | 22 | 117 |
| 3 | 33 | 113 |
| 3 | 12 | 112 |
| 3 | 18 | 120 |
| 5 | 17 | 123 |
| 4 | 32 | 150 |
| 3 | 17 | 116 |

cm core. S-1 at the base
after alkali extraction of

ses, functional group
HA, FA and HU are
the expected range of
of humic substances
(R, 1978). Infra-red
) show major absorp-
functional groups: 3440
cm⁻¹ (aliphatic C-H
O of COOH), 1590-

○ Residual
● Exchange
+ Fe-Mn Oxides
x Organic



+ 2C-5

2C-5

data for V, Cu and Mo
represents % of total
ons. Total concentra-
ed in Table 5.

Pettit Bog (ppm except Fe, Ti and Organic fractions, wt %)

| | Cr | Cu | Ni | B | Co | U | TOC (%) | ROC (%) | ASF (%) |
|----|----|----|----|----|-----|-------|---------|---------|---------|
| 29 | 48 | 10 | 14 | 19 | 549 | 4.12 | 1.78 | 2.34 | |
| 36 | 57 | 13 | 22 | 18 | 496 | 3.26 | 1.12 | 2.14 | |
| 25 | 47 | 10 | 25 | 19 | 643 | 4.41 | 1.35 | 3.06 | |
| 30 | 73 | 14 | 9 | 21 | 615 | 5.11 | 2.42 | 2.69 | |
| 22 | 31 | 12 | 10 | 12 | 985 | 6.78 | 2.01 | 4.77 | |
| 27 | 61 | 11 | 14 | 17 | 367 | 6.94 | 3.52 | 3.42 | |
| 40 | 81 | 13 | 4 | 10 | 421 | 1.89 | 1.14 | 0.75 | |
| 20 | 30 | 12 | 38 | 9 | 295 | 2.54 | 0.75 | 1.79 | |
| 16 | 50 | 12 | 10 | 16 | 899 | 11.34 | 7.03 | 4.31 | |
| 30 | 55 | 23 | 7 | 9 | 595 | 5.74 | 3.71 | 2.03 | |
| 24 | 41 | 15 | 6 | 11 | 308 | 4.97 | 2.56 | 2.41 | |
| 23 | 12 | 12 | 2 | 8 | 34 | 0.32 | 0.14 | 0.18 | |

and S-6 at the top, S-7 to S-12: samples taken from various localities and depths (0-100 cm) in the bog.
humic and fulvic acid fractions. ASF(%)—% alkali soluble fraction carbon, calculated from TOC-ROC.

1620 cm⁻¹ (conjugated C + C, H-bonded C=O of carbonyl, COO⁻), 1350-1400 cm⁻¹ (aliphatic C-H, COO⁻), and 1230 cm⁻¹ (OH deformation of COOH, C=O stretch). These spectra strongly resemble previously published spectra of typical soil humic substances (SCHNITZER, 1978; STEVENSON, 1982) and show an abundance of OH and COOH groups.

The *n*-alkane distribution in the bog sediment and carbon isotope values of the extracted organic fractions were determined in order to characterize the source of the organic matter in the bog. Carbon isotope values for HA, FA and HU were in the -24 to -28 per mil range, typical of material derived from C3 higher terrestrial plants (NISSENBAUM and KAPLAN, 1972). This was further confirmed by the *n*-alkane distribution which showed an overwhelming preponderance of C₂₅ to C₃₃ alkanes with an odd-over-even predominance, typical of waxes derived from higher plants (TISSOT and WELTE, 1984).

Trace metal distribution in the organic fractions

Figure 8 shows the variation of U with TOC, ASF (alkali soluble fraction) and ROC (residual organic carbon) corresponding to total organic carbon, the humic and fulvic acid fraction and the humin fraction

respectively. All three plots indicate a very strong positive correlation between U and these organic fractions, in particular the ASF fraction ($r = 0.92$). In contrast, all other elements show poor or strong negative correlations with these same organic fractions. The strong negative correlation exhibited by some elements may be simply a function of dilution of the inorganic components by variable amounts of organic matter in the sediment. Conversely, it may suggest a more active role on the part of the organic matter, i.e. solubilization (chemical weathering) and mobilization of some elements by organic acids (ONG *et al.*, 1970; BAKER, 1973; RASHID and LEONARD, 1973; SCHNITZER, 1986).

The concentration of U and other elements in HA and FA extracted from the bog are listed in Table 7. It should be noted, however, that as a result of the extraction procedures used for the organic fractions, these values represent minimum concentrations of the elements. The acidification to pH 1.0 of the alkali soluble fraction to facilitate the coagulation and separation of HA from FA probably releases some of the sorbed and complexed trace metals. The optimum pH for adsorption of many trace metals by humic acids has been demonstrated experimentally to be around 4-6 (MANSKAYA *et al.*, 1956). At low pH, the

Table 5. Distribution of U, V, Cu and Mo in various sequentially extracted fractions (as % of total concentration in sediment). TOC: total organic carbon

| Fraction | Sample 3A-2 (0.97% TOC) | | | | Sample 5A-2 (5.62% TOC) | | | | Sample 2C-5 (6.78% TOC) | | | |
|--------------------------|-------------------------|-------|------|------|-------------------------|-------|-------|------|-------------------------|-------|------|-------|
| | U | V | Cu | Mo | U | V | Cu | Mo | U | V | Cu | Mo |
| Exchangeable | 0.3 | 4.5 | 14.5 | 29.7 | 0.1 | 33.9 | 23.1 | 10.7 | 0.2 | 25.0 | 21.3 | 18.0 |
| Bound to CO ₃ | 0.3 | 0.9 | 2.1 | 1.5 | 0.3 | 1.6 | 1.7 | 1.3 | 0.3 | 1.2 | 1.9 | 2.6 |
| Fe-Mn Oxides | 49.4 | 9.9 | 53.9 | 47.6 | 17.7 | 16.8 | 29.4 | 47.1 | 17.5 | 20.2 | 16.3 | 49.1 |
| Organic | 48.8 | 6.8 | 17.7 | 4.1 | 71.9 | 9.6 | 31.6 | 21.4 | 73.2 | 25.3 | 43.4 | 25.2 |
| Residual | 3.7 | 82.6 | 11.3 | 14.9 | 6.1 | 39.9 | 19.0 | 17.4 | 4.9 | 18.5 | 16.8 | 13.0 |
| Total | 102.5 | 107.7 | 99.5 | 97.7 | 96.1 | 101.8 | 104.8 | 97.9 | 95.9 | 100.2 | 99.7 | 107.9 |
| Conc. in sed. (ppm) | 110 | 92 | 17 | 117 | 502 | 99 | 55 | 104 | 985 | 117 | 81 | 125 |

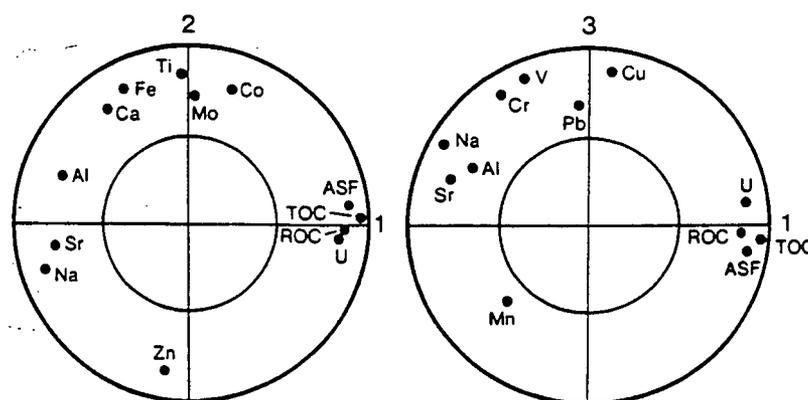


Fig. 6. Plots of factor analysis data for Pettit Bog sediments. Note strong loading of U and various organic fractions on Factor 1. For % of variance explained by each factor see Table 2.

Table 6. Analytical data for humic acids, fulvic acids and humin isolated from Pettit Bog sediments

| | HA | FA | Humin |
|----------------------------------|------------------------|-------------------------|------------------------|
| <i>Element %</i> | [12] | [10] | [8] |
| C | 56.8 (55.3–57.1) | 49.0 (48.7–49.6) | 55.3 (54.1–55.9) |
| H | 4.8 (4.3–5.2) | 3.4 (3.1–3.9) | 5.1 (4.7–5.6) |
| N | 2.8 (2.6–3.3) | 1.4 (1.1–1.9) | 4.8 (4.2–5.2) |
| O* | 35.6 (35.1–36.9) | 46.5 (44.7–47.1) | 34.8 (33.2–35.4) |
| <i>Functional groups (Meq/g)</i> | [6] | [4] | [2] |
| Total acidity | 7.2 (7.0–7.6) | 11.9 (11.0–12.7) | 5.1 (4.7–5.9) |
| COOH | 3.7 (3.1–3.9) | 8.3 (8.0–9.1) | 3.1 (2.7–3.9) |
| Phenolic OH | 3.5 (3.3–3.9) | 3.6 (3.1–4.2) | 2.0 (1.9–2.7) |
| Mol. wt | 13,500 (13,100–14,800) | 5,100 (4,900–5,700) | ND |
| <i>Isotope value</i> | [12] | [10] | [2] |
| $\delta^{13}\text{C}\text{‰}$ | -25.6 (-25.1 to -26.3) | -24.39 (-24.3 to -24.4) | -28.3 (-28.0 to -28.9) |
| $\delta\text{D}\text{‰}$ | -95.3 (-93.7 to -97.9) | -51.4 (-50.3 to -54.6) | ND |

Numbers in square brackets indicate the number of samples analyzed to give the average values in the table. Ranges of values are shown in parentheses.

*Elemental oxygen was determined by difference (SCHNITZER, 1972).

ND = Not determined.

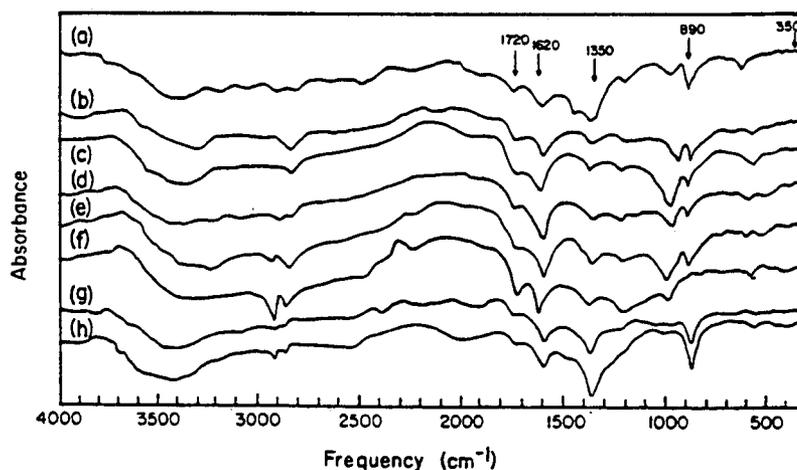


Fig. 7. IR spectra of humic and fulvic acids extracted from Pettit Bog sediments: (a) Pettit Bog crude fulvic acid; (b)–(e) Pettit Bog crude humic acid; (f) purified Pettit Bog humic acid; (g) uranyl humate made from purified Pettit Bog humic acid; (h) uranyl fulvate made from purified Pettit Bog fulvic acid.

acidic functional group release complexed me (GHOSH and SCHNITZER) indicate that this indeed extracted from Pettit Bog has been purified using the SCHNITZER (1980), was a 0.0001 M solution of uranyl humic acid was then washed and a portion remaining uranyl humic acid solution of NaOH and HCl at pH 1.0. This procedure from solution, washed and found that 76% of the uranyl had been desorbed. This is in agreement with the findings of SCHMIDT-COLLERUS (1979) on desorption of U from humic acid values. The same analysis of the HU fraction, which mineralization of the sediment by concentrated harsh treatment, the fulvic acids (FA), contain appreciable trace metals. These are adsorption sites and are not reactive (SCHMIDT-COLLERUS, 1979; TEMPLET

With the exception of each sample contains fractions of all the trace metals. The corresponding HA fraction contains a greater number of acidic complexing sites) of the fulvic acid compared to humic acid. The capacity, however, for the sediment average distribution of fulvic acid is secondary to humic acid.

Tables 8 and 9 show the trace metals in the various fractions. The "XAD-7" procedure passed through an acidic solution after extraction. It is indicated that desorbed from HA and can be found and, as the result, accounts for up to 10% of the sediment.

Residual U, remaining after complete removal of the uranyl with the HU fraction, shows a linear correlation between residual U in eight fractions. This consists of both detrital and geopolymeric high molecular weight. Consequently it is not possible to remove uranium and other humin is a function of these components as suggested by SCHNITZER (1963), or is related to

acidic functional groups on the HA molecule tend to release complexed metals and become protonated (GHOSH and SCHNITZER, 1980). In order to substantiate that this indeed is the case with samples extracted from Pettit Bog, humic acid which had been purified using the method of KERNDORFF and SCHNITZER (1980), was allowed to equilibrate with a 0.0001 M solution of uranyl nitrate at pH 4.5. The humic acid was then removed from the solution, washed and a portion analysed for U content. The remaining uranyl humate was dissolved in a 0.1N solution of NaOH and then reprecipitated with 6N HCl at pH 1.0. This humic acid was then removed from solution, washed and analysed for U. It was found that 76% of the original U taken up by the HA had been desorbed. These results are in agreement with the findings of MANSKAYA *et al.* (1956) and SCHMIDT-COLLERUS (1979), who noted substantial desorption of U from uranyl humates at low pH values. The same analytical problem exists for the HU fraction, which is obtained after demineralization of the inorganic components of the sediment by concentrated HF and HCl. Despite such harsh treatment, the organic fractions, particularly FA, contain appreciable amounts of U and other trace metals. These are probably in strongly bonded sites and are not readily exchanged (SCHMIDT-COLLERUS, 1979; TEMPLETON and CHASTEEN, 1980).

With the exception of Ti and Sn, the FA fraction in each sample contains appreciably higher concentrations of all the trace metals analyzed than the corresponding HA fraction. This is attributed to the greater number of acidic functional groups (i.e. complexing sites) of the fulvic acid molecule when compared to humic acid. Despite its greater complexing capacity, however, fulvic acid:humic acid ratios in the sediment average about 1:10 making the contribution of fulvic acid to total U binding in the bog secondary to humic acid.

Tables 8 and 9 show the distribution of U and other metals in the various fractions (HA, FA and HU). The "XAD-7 passed fraction" represents the residual acidic solution after removal of HA and FA during extraction. It is in this fraction that any metals desorbed from HA and FA during acidification would be found and, as the results in Table 8 show, it accounts for up to 50% of the original U in the sediment.

Residual U, remaining in the sediment after complete removal of the ASF, is apparently associated with the HU fraction. Figure 9 illustrates the strong linear correlation between the humin content and residual U in eight samples. This humin fraction consists of both detrital plant material and condensed geopolymeric high mol. wt "protokerogen". Consequently it is not possible to determine to what extent uranium and other trace metals associated with humin is a function of sorption by detrital plant components as suggested by MANSKAYA and KODINA (1963), or is related to sorption by "true" humin.

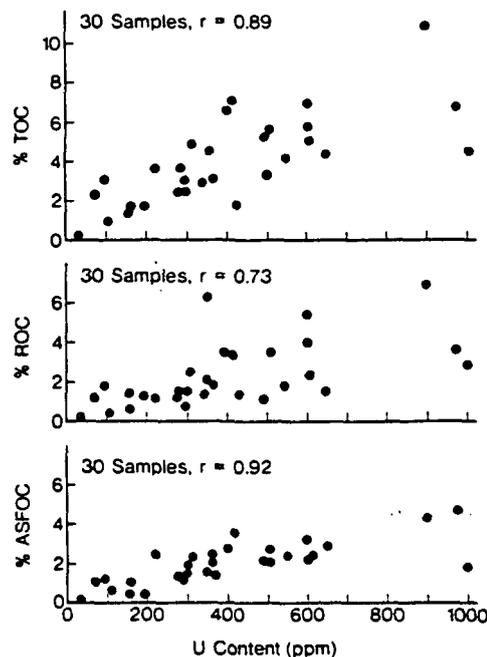
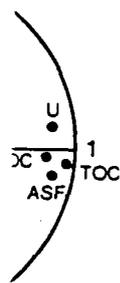


FIG. 8. Plots of various organic fractions vs U from Pettit Bog sediments. TOC—total organic carbon. ROC—residual organic carbon. ASFOC—alkali soluble fraction organic carbon.

SUMMARY OF EVIDENCE RELATING U AND OTHER TRACE METALS TO ORGANIC MATTER

It is apparent that there is considerable variation in the speciation of the various metals found in the bog sediment. Although organic constituents are responsible for the uptake of fractions of several trace metals, U is the only metal analysed whose enrichment is primarily controlled by these organic components. This is conclusively demonstrated by the strong correlation between U and the various organic fractions (TOC, ROC, ASF) as seen in the factor loading plots (Fig. 6) and correlation diagrams (Fig. 8). It is further supported by data from direct analysis of the various sequentially extracted fractions. The samples with higher TOC contents (5–7%) illustrate the overwhelming specificity of U for organic matter, with only a small percent of total U being distributed in other fractions. An enrichment factor of about 10 000 can be calculated for U uptake by Pettit Bog sediments from spring waters, assuming an average concentration of 100 $\mu\text{g/l}$ U (actual range 23–293 $\mu\text{g/l}$, Table 1) in spring waters and a high value of 1000 ppm U in the bog sediment. This is in agreement with the findings of SZALAY (1964) and ARMANDS (1967) for enrichment of U by peats and peat derived humic acids in Europe. In a sample with low TOC (<1%), the U content is lower and up to 50% of that U is associated with Fe–Mn oxides.



and various organic
ble 2.

Bog sediments

Humins

[8]

55.3 (54.1–55.9)
5.1 (4.7–5.6)
4.8 (4.2–5.2)
34.8 (33.2–35.4)

[2]

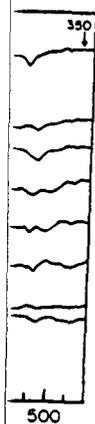
5.1 (4.7–5.9)
3.1 (2.7–3.9)
2.0 (1.9–2.7)

ND

[2]

5.3 (–28.0 to –28.9)
ND

ge values in the table.



Bog crude fulvic
imate made from
fulvic acid.

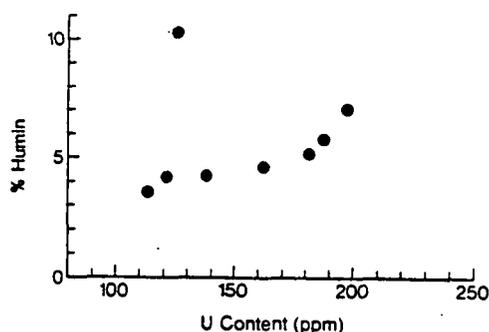


FIG. 9. Plot of humin content vs residual uranium (remaining after extraction of the ASF) for Pettit Bog sediments.

THE NATURE OF U-ORGANIC MATTER INTERACTION

Several possible mechanisms are usually advanced to explain the nature and extent of trace metal entrapment by organic matter. These are:

- (1) complexation or chelation of uranyl or reduced uranous species by organic ligands;
- (2) adsorption onto the physical surfaces of humic macromolecules by weak van der Waals and H-bonding forces;
- (3) reduction of the mobile oxidized UO_2^{2+} species by plant reductants to relatively insoluble UO_2 , and

precipitation of uraninite or other reduced U mineral species;

(4) indirect reduction by biogenically produced reducing agents such as hydrogen sulfide, associated with decomposing organic matter;

(5) uptake of U by living plants (from spring waters in this case) which, upon dying, form the bulk of organic matter in the bog sediment.

The last mechanism, metabolic or non-metabolic uptake of U by plants, is supported by the analyses of the dominant grasses but can account for only a very minor portion of the total U enrichment. As a rough estimate; given an area of about 1/2 hectare for the main enriched portion of the bog and an annual grass yield for this location of about 3000 kg per hectare with an average U content of 13 ppm, the U uptake/1000 a would be about 20 kg. Given that the depth of the bog is about 2.5 m at its midpoint, the volume of contained sediment is about 20 000 metric tons with an average U content of about 500 ppm and a total U content of 10 000 Kg. If the bog had persisted in this location for ten thousand years, plant uptake, without subsequent loss, would have provided only about 2% of the total U now entrapped in the bog sediments. This estimate is consistent with the average organic matter content of the sediment and the U analyses of the organic components.

Indirect reduction by biogenic hydrogen sulfide

seems an unlikely mechanism. The bog sediment is extremely reducing; there is no visible evidence as pyrite or chalcopyrite and Cu ions in circulating groundwater. No obvious H_2S odor. Fe could be invoked to produce, however, reduced uranium formed by such a reduction. It was not detected by X-ray diffraction.

Physical adsorption of U by bonding forces may account for a small portion of total U in the bog sediment. The U entrapped in the bog sediment during the partial diagenesis also includes U bound to organic surfaces (BOROVEC, 1981). Adsorption of U to organic matter is a minor phenomenon in the bog, nevertheless play some role in the U entrapment process. ANTONOV (1964), HAJI-VASSILIOU *et al.* (1979), HAJI-VASSILIOU (1986) AND NAKASHIMA (1986) have shown that the mobile uranyl cation is adsorbed to organic matter phases by mechanisms such as hydroxyl functional groups. This mechanism for immobilizing precipitating uraninite. The IR spectral analysis of fulvic acids and humins shows the presence of reduced U(VI) band at 350 cm^{-1} for (1971).

Several lines of evidence show that the reduction and chelation of U(VI) is overwhelmingly predominant. The IR spectra for fulvic acids extracted from Pettit Bog shows an absorbance band for the reduced U(VI) around $890\text{--}900\text{ cm}^{-1}$ (LEVITSKY, 1978) in all the spectra. The intensity of the reduced U(VI) band is absent from the humic and fulvic acids from which the reduced U(VI) band has been removed. When allowed to equilibrate with uranyl nitrate at pH 4, the band for this species at $890\text{--}900\text{ cm}^{-1}$. This is consistent with the intensity of the reduced U(VI) band which belongs to the $COOH$ and an increase in the $1600\text{--}1560\text{ cm}^{-1}$ band for COO^- groups (LEVITSKY AND SCHNITZER, 1968; RYAN, 1971).

Table 7. Trace element content of humic and fulvic acids extracted from Pettit Bog sediments. Values are in ppm. Dashes indicate elements were not analyzed

| Sample | U | Mo | V | Cr | Cu | Zn | Co | Ni | Ti | Ag | Sn | % Ash |
|-------------------|------|-----|-----|-----|-----|-----|----|-----|------|------|-----|-------|
| <i>Humic acid</i> | | | | | | | | | | | | |
| 2C-1 | 2086 | 80 | 64 | 75 | 53 | 24 | 10 | 13 | 1540 | 0.6 | 16 | 21 |
| 2C-2 | 2634 | 34 | 71 | 90 | 33 | 24 | 9 | 12 | 1040 | 2.3 | 27 | 13 |
| 2C-3 | 2936 | 30 | 26 | 72 | 20 | 20 | 13 | 15 | 623 | 0.4 | 16 | 17 |
| 2C-4 | 1818 | 27 | 25 | 83 | 58 | 29 | 8 | 17 | 1150 | 0.8 | 14 | 12 |
| 2C-5 | 2733 | 20 | 60 | 62 | 18 | 38 | 9 | 11 | 1000 | 0.4 | 8 | 6 |
| 2C-6 | 1977 | 19 | 68 | 43 | 68 | 74 | 7 | 13 | 903 | 0.3 | 9 | 4 |
| 3A-2 | 1600 | 148 | 33 | 19 | 136 | 11 | 11 | 23 | 1140 | 3.2 | 4 | 16 |
| 1B-1 | 391 | 70 | 165 | 128 | 34 | 14 | 8 | 12 | 720 | 0.4 | 5 | 24 |
| 5A-2 | 1741 | 58 | 25 | 13 | 112 | 12 | 11 | 19 | 780 | 0.7 | 11 | 13 |
| 1B-2 | 1080 | 94 | 27 | 32 | 172 | 29 | 12 | 20 | 877 | 13.1 | 37 | 13 |
| 7A-1 | 2840 | 9 | 15 | 71 | 55 | 74 | 4 | 52 | 1340 | 3.4 | 20 | 22 |
| 7A-2 | 972 | 11 | 12 | 69 | 67 | 65 | 5 | 6 | 399 | 3.2 | 22 | 19 |
| 8A-4 | 1089 | 19 | 37 | 48 | 62 | 140 | 9 | 8 | 1060 | 14.1 | 130 | 7 |
| 2B-2 | 887 | 56 | 28 | 51 | 24 | 97 | 8 | 11 | 822 | 0.3 | 51 | 16 |
| 1C-3 | 3200 | — | — | — | — | — | — | — | — | — | — | 9 |
| 2C-1 | 2332 | 215 | 552 | 244 | 516 | 318 | 9 | 129 | 317 | 0.9 | 16 | 28 |
| 2C-2 | 2548 | 119 | 336 | 181 | 208 | 448 | 9 | 162 | 561 | 2.5 | 13 | 21 |
| 2C-3 | 2931 | 91 | 122 | 325 | 97 | 280 | 21 | 208 | 420 | 1.6 | 8 | 30 |
| 2C-4 | 4290 | 108 | 198 | 247 | 422 | 411 | 11 | 171 | 418 | 11.1 | 9 | 22 |
| 2C-5 | 1911 | 49 | 214 | 235 | 85 | 376 | 13 | 117 | 310 | 1.4 | 18 | 19 |
| 2C-6 | 2974 | 45 | 873 | 227 | 340 | 798 | 17 | 140 | 293 | 1.2 | 10 | 11 |
| 3A-2 | 1117 | 200 | 156 | 126 | 690 | 320 | 2 | 120 | 307 | 7.8 | 3 | 33 |
| 5A-2 | 2610 | 90 | 117 | 186 | 460 | 328 | 7 | 138 | 214 | 13.2 | 21 | 35 |
| 1B-2 | 9390 | 107 | 142 | 211 | 193 | 465 | 38 | 138 | 723 | 6.1 | 33 | 24 |
| 7A-1 | 3000 | 114 | 91 | 186 | 500 | 640 | 12 | 180 | 408 | 21.1 | 26 | 19 |
| 7A-2 | 3370 | 91 | 97 | 450 | 174 | 500 | 15 | 270 | 374 | 14.7 | 17 | 28 |
| 8A-4 | 5940 | 42 | 124 | 203 | 94 | 760 | 10 | 185 | 360 | 12.4 | 61 | 41 |
| 2B-2 | 5170 | 62 | 76 | 740 | 760 | 460 | 11 | 190 | 224 | 6.7 | 23 | 33 |
| 1C-3 | 8740 | — | — | — | — | — | — | — | — | — | — | — |

12

seems an unlikely mechanism in this case. Total S in the bog sediment is extremely low (0.002%), and there is no visible evidence for sulphide minerals such as pyrite or chalcopyrite despite the abundance of Fe and Cu ions in circulating groundwaters. There is also no obvious H₂S odor. Reducing organic moieties could be invoked to produce a redox lowering. However, reduced uranium minerals which would be formed by such a reduction process, were not detected by X-ray diffraction studies of the bog sediment.

Physical adsorption of U to organic matter by weak bonding forces may account for a small part of the total U in the bog sediment. Up to 3% of the total entrapped U was found in the "exchangeable" fraction during the partial dissolution studies. Since this fraction also includes U bound by weak forces to clay surfaces (BOROVEC, 1981), which make up about 20% of the inorganic constituents of the bog sediment, adsorption of U to organic matter is a relatively minor phenomenon in the present bog. It may, nevertheless play some role during early stages of the entrapment process. ANDREYEV and CHUMACHENKO (1964), HAJI-VASSILIOU and KERR (1973), ROUZAUD *et al.* (1979), HAJI-VASSILIOU (1980), LEVENTHAL (1986) and NAKASHIMA *et al.* (1984) have shown that sedimentary organic matter can directly reduce the mobile uranyl cation to uraninite or other reduced phases by mechanisms such as oxidation of alcoholic hydroxyl functional groups. Although this is a viable mechanism for immobilizing the uranyl cation and precipitating uraninite, X-ray diffraction and infrared (IR) spectral analyses of extracted humic and fulvic acids and humins in this study failed to detect the presence of reduced UO₂ phases or the absorption band at 350 cm⁻¹ for UO₂ (NYQUIST and KAGEL, 1971).

Several lines of evidence support direct complexation and chelation of U by organic matter as the overwhelmingly predominant mechanism. Figure 7 shows IR spectra for a variety of humic and fulvic acids extracted from Pettit Bog sediments. The IR absorbance band for the uranyl species is found at around 890–900 cm⁻¹ (BULLOCK, 1967; KOGLIN *et al.*, 1978) in all the spectra, confirming the presence of the oxidized U(VI) species associated with both humic and fulvic acids. However, the uranyl absorption band is absent from the IR spectrum for purified humic acid from which 90% of associated metals had been removed. When this same humic acid was then allowed to equilibrate with a 0.0001 M solution of uranyl nitrate at pH 4.5, a prominent absorption band for this species again was found at around 890–900 cm⁻¹. This is coupled with a relative decrease in the intensity of the absorption band at 1720 cm⁻¹, which belongs to the carbonyl group of non-ionized COOH, and an increase in the prominence of the 1600–1560 cm⁻¹ band of asymmetric stretching of COO⁻ groups (LEVESQUE and SCHNITZER, 1967; SCHNITZER, 1968; RASHID and KING, 1970). These

observations suggest the involvement of carboxylate groups in the binding of the uranyl cation. Furthermore, the shift of the COO⁻ absorption band from 1620 to 1590 is interpreted as assumption of a bidentate geometry involving these groups and UO₂²⁺ (KOGLIN *et al.*, 1978). Other ionizable and potential donor sites are also present in humic and fulvic acids (STEVENSON, 1982), though there is considerable debate as to their role in metal binding. TEMPLETON and CHASTEEN (1980) reported three types of bonding ligands in an ESR study of VO₂²⁺-fulvic acid complexation: (1) strong ligands with high covalency associated with phenolate and nitrogen containing donor groups; (2) weaker ligands involving carboxylate; and (3) groups of intermediate ligand strength arising from a combination of the first two. McBRIDE, in a similar study (1978), attributed Cu²⁺ and VO₂²⁺ complexing with humic acids to oxygen ligands. SHANBAG and CHOPPIN (1981) attribute binding of UO₂²⁺ and several other actinide cations to carboxylate sites alone. In our study, only the role of carboxylate groups was examined, hence the contribution of other functional groups is unknown.

SPECIFICITY OF ORGANIC MATTER FOR U

Experimental work on the uptake of UO₂²⁺ and other metal cations by humic and fulvic acids (SZALAY, 1964; SZALAY and SZILAGYI, 1966; SZILAGYI, 1967; ONG and BISQUE, 1968; CHOWDURY and BOSE, 1970; RASHID, 1974; KERNDORFF and SCHNITZER, 1980; HIROBAYASHI and KAJITANI, 1982) and other types of sedimentary organic matter (DISNAR, 1981) have shown that the sorption capacity of these organic components is strongly pH dependent. Optimum pH values for the uptake of most cationic species seems to be in the large 4–6. At lower pH, competition by protons for the active complexing sites reduces uptake, whereas at higher pH values, precipitation of metal hydroxides results in reduced sorption.

In order to evaluate the effect of pH on UO₂²⁺ sorption, a 0.1 × 10⁻⁴ M solution of uranyl nitrate (100 ml) was allowed to equilibrate with 100 mg of purified Pettit Bog humic acid. The optimum pH of sorption was found to be around 5.0 (Fig. 10). As the pH of the bog is also in this range, conditions are favorable for facilitating maximum sorption of UO₂²⁺.

Prior to entering Pettit Bog itself, spring waters with a pH range of 6.8–7.0 probably transport uranyl ion as a carbonate complex. SHANBAG (1981) has shown that uranyl ion will preferentially form a humate complex from a carbonate complexed ion only at pH values less than 6. As spring waters percolate through the bog environment where the pH is around 4.5–5.5, carbonate and bicarbonate ions are unstable and release uranyl ions which are then complexed by humate.

The preferential enrichment of U over other

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Table 8. Distribution of U in various extracted fractions

| Sample | ΣU^* | Distribution of U in various fractions in % | | | | $\Sigma \%$ | Res. u* | % Organic fractions | | | | |
|--------|--------------|---|-----|-------|--------|-------------|---------|---------------------|-----|------|--------|--------|
| | | HA | FA | XAD-7 | Res. % | | | %HA | %FA | %HU | %AshHA | %AshFA |
| 2C-1 | 549 | 15.4 | 1.7 | 52.1 | 29.5 | 98.7 | 162 | 3.2 | 0.3 | 4.7 | 21 | 28 |
| 2C-2 | 496 | 17.1 | 2.6 | 56.3 | 22.8 | 98.8 | 113 | 2.8 | 0.4 | 3.7 | 13 | 21 |
| 2C-3 | 643 | 21.5 | 4.5 | 48.3 | 29.2 | 99.1 | 188 | 3.9 | 0.7 | 5.8 | 17 | 30 |
| 2C-4 | 615 | 12.1 | 3.9 | 50.3 | 29.6 | 95.9 | 182 | 3.6 | 0.4 | 5.1 | 12 | 22 |
| 2C-5 | 985 | 18.3 | 2.4 | 57.2 | 19.9 | 97.8 | 196 | 6.2 | 0.9 | 7.0 | 6 | 19 |
| 2C-6 | 367 | 24.3 | 8.3 | 34.8 | 34.3 | 101.7 | 126 | 4.3 | 0.8 | 10.1 | 4 | 11 |
| 2C-7 | 435 | 14.9 | 4.7 | 46.3 | 31.7 | 97.6 | 138 | 2.7 | 0.6 | 4.1 | 14 | 22 |
| 2C-8 | 442 | 11.7 | 3.3 | 51.1 | 27.1 | 93.2 | 120 | 2.4 | 0.4 | 4.2 | 9 | 17 |

* Total U and residual U in sediments, before and after alkali extraction (values in ppm).

HA, FA, XAD-7: % of total U found in humic acid (HA), fulvic acid (FA) and XAD-7 passed solution (XAD-7). %HA, %FA, %HU: total yield of humic acid, fulvic acid and humin (HU) as wt % of sediment. %AshHA, %AshFA: % ash content of humic and fulvic fractions.

cations in the bog, and the specificity of U for complexation by organic matter still remains to be explained. Attempts by other workers to correlate the tendency of several different metals to sorb on humic acid to their atomic weight, atomic numbers, valencies, crystal and hydrated ionic radii have been successful (CHOWDURY and BOSE, 1970; RASHID, 1974; PAULI, 1975; GAMBLE *et al.*, 1976; 1977; McBRIDE, 1978; KERNDORFF and SCHNITZER, 1980).

Significance of Ca/U ratios

SHANBAG and CHOPPIN (1981), in a study of the thermodynamics of actinide element and calcium binding by humic acid showed that the actinides had considerably stronger binding constants (by a factor of $>10^3$) than Ca^{2+} . Therefore, in an aqueous system containing $UO_2^{2+}-Ca^{2+}$ -humic acid, a substantial percentage of ligands will be bound to UO_2^{2+} subject only to relative availability of ligands and Ca^{2+} concentration.

In the Pettit Bog springs, as in the case of most surface and ground waters, Ca^{2+} is the most abundant cation. Molar Ca/U ratios in the various springs are very consistently around 3×10^3 ($r = 0.88$ for Ca-U). Based on the experimentally determined binding constants of UO_2^{2+} to humic acid (SHANBAG, 1979),

and in the presence of abundant organic matter, U would be expected to be complexed by humate by a factor of about 10^3 times more than Ca^{2+} relative to the abundance of these two elements in associated groundwaters. In fact, the molar Ca/U ratio in Pettit Bog humic and fulvic acids average out to be around 25, suggesting a relative enrichment factor for U in the 10^2 range. Natural U concentrations in ordinary groundwaters, on the other hand, are frequently less than $1 \mu g/l$, which is up to two orders of magnitude lower than at Pettit Bog. Consequently, assuming the same enrichment factor at the lower U concentrations, ordinary groundwaters percolating through Pettit Bog sediments would result in total U concentrations 1/100 to 1/1000 of those found in the present bog, i.e. in the range of 1-10 ppm. These values are comparable with those commonly reported for U contents of most organic rich soils.

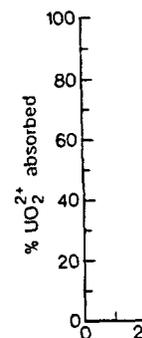
This observation may well explain the hitherto variable and poorly understood occurrences of U enrichment in recent, organic-rich non-marine sediments and peat bogs. In the presence of organic rich sediments, the strong affinity of U for humic substances will not lead to anomalously high concentrations unless elevated concentrations of U relative to Ca, in addition to low pH, are already present in percolating groundwaters.

In a natural environment such as the bog, many

Table 9. Distribution of V, Cu and Mo in various extracted

| Fraction (%) | Sample | | | | | | | | |
|--------------|--------|-----|-----|------|-----|-----|------|-----|-----|
| | 2C-1 | | | 2C-2 | | | 2C-3 | | |
| | V | Cu | Mo | V | Cu | Mo | V | Cu | Mo |
| Residual* | 74 | 62 | 89 | 67 | 63 | 88 | 83 | 63 | 86 |
| Humic acid | 1.8 | 4.7 | 1.1 | 1.7 | 2.2 | 0.8 | 1.2 | 2.3 | 1.0 |
| Fulvic acid | 1.6 | 4.3 | 0.6 | 1.2 | 1.8 | 0.4 | 0.9 | 1.7 | 0.7 |
| XAD-7 | 26 | 23 | 6.8 | 23 | 27 | 13 | 19 | 30 | 8.2 |
| Total % | 103 | 94 | 93 | 93 | 94 | 103 | 104 | 96 | 96 |

* % trace metal remaining in sediment after alkali extraction.

Fig. 10. Adsorption of UO_2^{2+} as a function of total cations.

other factors may influence various cations complexation. Sequential extraction studies have shown that about 80% of U in the sediment is found in the fraction adsorbed on to organic matter. This adsorption may further be influenced by the presence of major cations in the formation of organic matter.

TIMING OF METAL

Organic matter in the bog is composed of recognizable compounds such as chitin, glucosamine, and other polymeric compounds. The adsorption of U (MOORE, MANSKAYA and KERR, 1975) and other trace metals (MOORE, VASSILIOU and KERR, 1975) has been shown that low rank sediments containing functional groups have a much higher degree of adsorption. Moore and Kerr (1975) conclude that with maturation of

fractions (as % of total cations)

| 2C-4 | | |
|------|-----|-----|
| V | Cu | Mo |
| 67 | 64 | 87 |
| 0.7 | 3.3 | 0.7 |
| 0.7 | 3.1 | 0.7 |
| 25 | 28 | 14 |
| 93 | 99 | 102 |

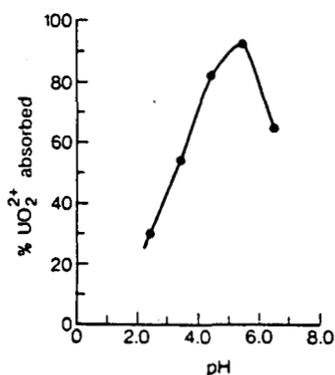


Fig. 10. Adsorption of UO_2^{2+} by purified Pettit Bog humic acid as a function of pH.

other factors may influence the relative availability of various cations competing for organic ligands. The sequential extraction studies, for example, have shown that about 80% of non-detrital Ca in the bog sediment is found in the exchangeable fraction, probably adsorbed onto clays. This kind of inorganic speciation may further diminish the concentrations of major cations in relation to U and favor the latter in the formation of organic ligands.

TIMING OF METAL ENTRAPMENT BY ORGANIC MATTER

Organic matter in various stages of decay, ranging from recognizable components such as cellulose, chitin, glucosamines and lignin to condensed polymeric compounds such as melanoidins and humic substances, has been shown to have great capacity for sorption of U (MOORE, 1954; VINE *et al.*, 1958; MANSKAYA and KODINA, 1963; SZALAY, 1964). Moreover, MOORE (1954), SZALAY (1954), HAJ-VASSILIOU and KERR (1973) and DOI *et al.* (1975) have shown that low rank coals, enriched in oxygen containing functional groups, are capable of fixing U to a much higher degree than petroleum or bitumen type matured sedimentary organic matter. DOI *et al.* (1975) conclude that U sorption capacity decreases with maturation of coal from peat to anthracite.

MANSKAYA *et al.* (1956) suggest that although U sorption capacity decreases with progressive degradation and maturation of organic matter (from lignin to humus and higher condensation products), ligand strength increases. It is probable that with increasing condensation and maturation (and subsequent loss of O containing functional groups such as carboxyls), the organic matter loses its binding sites (BOUBOU *et al.*, 1984) and only those sites within the polyaromatic framework such as cyclic nitrogen moieties (SCHMIDT-COLLERUS, 1979; TEMPLETON and CHASTEEN, 1980) with strong complexing abilities remain. These groups may, in part, be responsible for U associated with ancient sedimentary organic matter (kerogen) as for example, the Chattanooga (black) Shale (BREGER and BROWN, 1962; LEVENTHAL *et al.*, 1983) and the Swedish Alum Shale and Kolm (ARMANDS, 1974). During maturation, substantial reduction and precipitation of uraninite may also occur as a result of dehydrogenation reactions and loss of acidic functional groups to which U is bound resulting in the liberation of U from the organic matter (SCHMIDT-COLLERUS, 1979; ROUZAUD *et al.*, 1979; NAKASHIMA *et al.*, 1984).

In the Pettit Bog occurrence, U is associated primarily with humic and fulvic acids, products of the early stages of sedimentary organic matter formation. It has not been possible, however, to determine whether initial complexation of U is attributable to biopolymers and biomonomers, which are early degradation products of plant components, that subsequently condense to form uranyl fulvates and humates, or whether sorption occurs after humic substances have been generated. Furthermore, the role of the insoluble humin is still unknown. It is difficult to evaluate from this study whether U found associated with the humin fraction is a result of the further condensation of uranyl humates and fulvates, or is due to direct complexation by already formed humin. Based on the experimental results of the many previous studies in addition to this study, it is probable that the sorption of U in such a dynamic organic environment is a complex continuum. We propose the following sequence of events to explain the uptake of U at Pettit Bog.

fractions (as % of total concentration in sediments)

| Sample | | | | | | | | |
|--------|-----|-----|------|-----|-----|------|-----|-----|
| 2C-4 | | | 2C-5 | | | 2C-6 | | |
| V | Cu | Mo | V | Cu | Mo | V | Cu | Mo |
| 67 | 64 | 87 | 68 | 63 | 80 | 73 | 46 | 77 |
| 0.7 | 3.3 | 0.9 | 3.8 | 4.1 | 1.0 | 5.5 | 5.3 | 0.6 |
| 0.7 | 3.1 | 0.5 | 2.9 | 3.8 | 0.6 | 4.6 | 5.0 | 0.3 |
| 25 | 28 | 14 | 22 | 32 | 15 | 16 | 41 | 15 |
| 93 | 99 | 102 | 97 | 103 | 96 | 99 | 97 | 92 |

| ons | %shHA | %AshFA |
|-----|-------|--------|
| 21 | 28 | |
| 13 | 21 | |
| 17 | 30 | |
| 12 | 22 | |
| 6 | 19 | |
| 4 | 11 | |
| 14 | 22 | |
| 9 | 17 | |

XAD-7). %HA.
%AshFA: % ash

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Mo

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0.7
8.2
96

15

- (1) Influx of uraniferous groundwaters saturating the bog.
- (2) Biological uptake of U by plants (minor).
- (3) Sorption of U by plant components (cellulose, lignin, etc.) in various stages of decomposition accompanied by liberation of U by oxidized portions of these components (destruction of ligands).
- (4) Condensation of these plant components to geopolymers (macromolecular fulvic and humic acids) and sorption of U in addition to that already complexed by constituent biomonomers. Further destruction of ligands.
- (5) Further condensation of geopolymers to alkali-insoluble high mol. wt humin (or kero-gen) accompanied by a loss of acidic functional groups and destruction of more ligands. Retention of U bound to strong complexing moieties and possible sorption of U by remaining functional groups.

The various stages of these sequential events are probably occurring simultaneously throughout the bog. Other considerations include sorption of U to woody stems and branches (SCHMIDT-COLLERUS, 1979) in the bog, and the various biochemical activities of microbiota in producing low mol. wt organic acids (PELTZER and BADA, 1981; STEVENSON, 1982) or biopolymers.

SUMMARY

(1) Uranium influx into Pettit Bog is provided by springs originating along a fault. These springs contain anomalously high U values, evidently from a lithophile source.

(2) The distribution of U in the bog is primarily controlled by the dead organic matter content (humates) of the sediments. This association is, in part, complexation by carboxylate functional groups.

(3) Other trace metals are not preferentially concentrated in the sediment organic matter.

(4) U uptake by living plants is relatively low, hence their overall contribution to enrichment in the bog is minor.

(5) The pH conditions in the bog (4.5–5.5) favor maximum sorption of UO_2^{2+} by humic acids. The preferential coordination of U by humic substances over other elements is attributed to the strong binding constants of actinide elements with humic and fulvic acids and elevated concentration of U in spring waters.

(6) The Ca/U ratio in groundwaters (as a measure of the relative abundance of U) may be the critical factor in explaining why anomalously high concentrations of U in organic rich non-marine sediments and peat bogs occur sporadically. The fundamental requirement, all other factors being equal, seemingly is an elevated U content in circulating ground and surface waters.

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