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AECL-11583, COG-96-194

**Natural Organics in Groundwaters and Their  
Potential Effect on Contaminant Transport in  
Granitic Rock**

**Les composés organiques naturels dans les eaux  
souterraines et leurs effets éventuels sur le  
transport des contaminants dans la roche  
granitique**

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July 1996 juillet



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**Whiteshell Laboratories  
Pinawa, Manitoba R0E 1L0  
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### ABSTRACT

Naturally occurring organics in groundwaters of the Whiteshell Research Area (WRA) of southern Manitoba and of the Atikokan Research Area of northwestern Ontario were investigated to assess their potential role in radionuclide transport within granite fractures of the Canadian Shield. A survey of dissolved organic carbon (DOC) concentrations, carried out to determine the variability in the organic content of these groundwaters, showed average concentrations in WRA deep groundwaters of  $0.8 \pm 0.1$  mg/L for Fracture Zone 2,  $0.8 \pm 0.4$  mg/L for near-vertical fractures, and  $2.3 \pm 0.8$  mg/L for deeper saline groundwater. Surface waters and near-surface groundwaters had significantly higher DOC with  $29.2 \pm 0.6$  mg/L in streams from the East Swamp. Atikokan waters also had low organics in deep groundwaters, with significantly higher DOC in surface and near-surface waters. The DOC consisted mainly of hydrophilic neutral compounds (60 to 75%), and hydrophobic and hydrophilic acids (23 to 39%), along with very small amounts of hydrophobic bases and neutrals, and hydrophilic bases. Significant contamination from drilling operations and plastics, mostly in the form of hydrophobic neutrals, was observed in some samples. These compounds would not contribute to radionuclide migration in a natural system and are not included in the assessment of the organic complexing capacity of these groundwaters.

Based on groundwater concentrations of hydrophobic and hydrophilic acids and on the measured carboxylic functional group content of these acids, the average complexing capacity of natural organics in WRA deep groundwaters was calculated to be  $6.7 \times 10^{-6}$  eq/L. The ability of these organics to complex radionuclides was tested using conditional stability constants from the literature for humic complex formation with trivalent, tetravalent, pentavalent and hexavalent actinides. The geochemistry of most monovalent and divalent radionuclides is not expected to be affected by natural organics. The chemistries of Np(V) and U(VI) were predicted to be dominated by inorganic complexes and not significantly affected by organics. Accurate predictions for Am(III) and Th(IV) could not be made since the literature contains a wide range in values of stability constants for humic complexes with these elements. However, most stability constants reported in the literature for Am organic complexes would indicate that Am complexation by organics would not be a major factor in deep groundwaters with low organics. Surface waters and near-surface groundwaters in many areas of the Canadian Shield contain enough humics to complex a significant fraction of dissolved actinides.

Radiocarbon ages of humics from WRA groundwater varied between 3600 and 6200 years before present, indicating that a component of humic substances in deep groundwaters must originate from near-surface waters. The recharge of organic-rich surface waters to deep groundwaters needs to be investigated further.

Whiteshell Laboratories  
Pinawa, Manitoba R0E 1L0  
1996

AECL-11583  
COG-96-194



LES COMPOSÉS ORGANIQUES NATURELS DANS LES EAUX SOUTERRAINES  
ET LEURS EFFETS ÉVENTUELS SUR LE TRANSPORT DES CONTAMINANTS  
DANS LA ROCHE GRANITIQUE

par

Peter Vilks, Don B. Bachinski et Denise Richer

RÉSUMÉ

Les composés organiques naturels des eaux souterraines de l'Aire de recherches de Whiteshell (ARW), située dans le sud du Manitoba, et de l'Aire de recherches d'Atikokan, dans le nord-ouest de l'Ontario, ont été étudiés en vue d'évaluer le rôle qu'ils peuvent jouer dans le transport des radionucléides dans les fractures du granite du Bouclier canadien. Une étude des concentrations de carbone organique dissous (COD), réalisée dans le but de connaître les variations de la teneur en composés organiques de ces eaux souterraines, a révélé, dans les eaux souterraines profondes de l'ARW, des concentrations moyennes de  $0,8 \pm 0,1$  mg/L pour la zone de fracture 2, de  $0,8 \pm 0,4$  mg/L pour les fractures presque verticales, et de  $2,3 \pm 0,8$  mg/L dans l'eau souterraine salée à plus grande profondeur. Les eaux de surface et les eaux souterraines peu profondes présentaient des concentrations de COD considérablement plus élevées, et on a relevé  $29,2 \pm 0,6$  mg/L dans des cours d'eau issus du East Swamp. Dans l'Aire de recherches d'Atikokan aussi, les eaux souterraines profondes contenaient de faibles quantités de composés organiques, tandis que les eaux de surface et proches de la surface contenaient beaucoup plus de COD. Les carbonnes organiques dissous étaient principalement constitués de composés neutres hydrophiles (de 60 à 75 %), et d'acides hydrophobes et hydrophiles (de 23 à 39 %), accompagnés de très petites quantités de composés basiques et neutres hydrophobes et de bases hydrophiles. On a noté dans quelques échantillons une contamination importante provenant des travaux de forage et du matériel d'échantillonnage en plastique, principalement sous la forme de matières neutres hydrophobes. Ces composés n'apporteraient aucune contribution à la migration des radionucléides dans un système naturel et ne sont pas compris dans les évaluations de la capacité de ces eaux souterraines de former des complexes organiques.

D'après les concentrations des acides hydrophobes et hydrophiles dans les eaux souterraines et la teneur mesurée en groupes fonctionnels carboxyliques de ces acides, on a calculé que la capacité moyenne de former des complexes des composés organiques naturels des eaux souterraines profondes de l'ARW était de  $6,7 \times 10^{-6}$  eq/L. La capacité de ces composés organiques de former des complexes avec les radionucléides a été vérifiée par des essais sur la formation de complexes humiques avec des actinides tri-, tétra-, penta- et hexavalents en utilisant les données sur les constantes de stabilité conditionnelles tirées de la documentation scientifique. Les composés organiques naturels ne devraient pas modifier les propriétés géochimiques de la plupart des radionucléides mono- et bivalents. On prévoit que la chimie du Np(V) et de l'U(VI) serait régie par les complexes inorganiques et qu'elle ne serait pas modifiée de façon très importante par les composés organiques. Il n'a pas été possible de prévoir avec précision le comportement de l'Am(III) et du Th(IV), car la documentation scientifique fournit un large éventail de valeurs des constantes de stabilité des complexes humiques dans le cas de ces éléments. Toutefois, la plupart des constantes de stabilité répertoriées dans cette documentation en ce qui a trait aux complexes organiques de l'Am indiqueraient que la complexation de l'Am par les composés organiques ne serait pas importante dans les eaux souterraines profondes renfermant de faibles quantités de composés organiques. Dans de nombreuses zones du Bouclier canadien, les eaux de surface et les eaux souterraines peu profondes contiennent assez de matières humiques pour donner lieu à la formation de complexes avec une grande quantité des actinides dissous.

L'âge radiocarbone des substances humiques provenant de l'eau souterraine de l'ARW se situait entre 3 600 et 6 200 ans, ce qui laisse entendre qu'un élément des substances humiques que contiennent les eaux souterraines profondes doit provenir des eaux proches de la surface. D'autres recherches sont nécessaires pour étudier l'apport des eaux de surface riches en composés organiques dans les eaux souterraines profondes.

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Pinawa (Manitoba) ROE ILO  
1996

AECL-11583  
COG-96-194

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## 1. INTRODUCTION

AECL (Atomic Energy of Canada Limited) has assessed the concept of nuclear fuel waste disposal in an engineered vault at a depth of 500 to 1000 m in plutonic rock of the Canadian Shield (Dormuth and Nuttall 1987, Torgerson 1990, AECL 1994). Radionuclide transport in groundwater is the only likely path for radionuclide migration to the biosphere through the mass of rock surrounding a disposal vault. The transport of radionuclides in groundwater systems can be modeled as a chromatographic process in which radionuclides are partitioned between a mobile fluid phase and an immobile solid phase (Freeze and Cherry 1979). The interaction of dissolved contaminants with the immobile rock surfaces is controlled by contaminant solubility and sorption reactions with solid surfaces. An element's solubility and sorption behavior may be affected by pH, redox conditions, ionic strength, and by complexation with inorganic anions and organic ligands. If radionuclides are complexed by organic ligands in solution their mobility will be increased, while a reduction in mobility would be achieved if radionuclides are complexed to organics attached to mineral surfaces. Although complexation to immobile organics could be considered as an additional mechanism to retard radionuclide migration, this report has focused on the potential role of organics in enhancing radionuclide migration. While the inorganic composition of groundwater from the Canadian Shield has been extensively characterized (Gascoyne and Elliot 1986, Gascoyne et al. 1987), the complexing capacity of naturally occurring organic ligands and their impact on radionuclide migration has only recently been addressed (Vilks and Bachinski 1996). Organics have not been specifically included in performance assessment calculations in granite-based high level radioactive waste programs throughout the world because of the perception that organic concentrations in granite are too low for significant complexation with radionuclides (Karlsson et al. 1995). Although this may be true in general, the justification for omitting organics from performance assessment calculations needs to be substantiated by a comprehensive understanding of organics in groundwater and a quantification of their complexing properties (Zuidema 1995).

For the postclosure assessment of AECL's disposal concept a case study has been conducted based on a hypothetical disposal vault emplaced within a granitic pluton located in the Whiteshell Research Area (WRA) (Davison et al. 1994, Goodwin et al. 1994). The WRA is located in southern Manitoba and includes the sites of AECL's Underground Research Laboratory (URL) and Whiteshell Laboratories (Figure 1). A study of natural organics in groundwater from the WRA was undertaken to evaluate the potential for radionuclide transport facilitated by complexation with natural organic compounds (Vilks and Bachinski 1996). The term "facilitated transport" is used to describe any process which may speed up the migration of a contaminant beyond the velocity predicted solely by idealized Darcian flow and sorptive equilibrium with rock surfaces (Huling 1989). In the study of WRA organics, attention has been focused on the effect of organics on actinide mobility in groundwater because actinides have isotopes with long half-lives that may pose a potential risk to man. Furthermore, since actinides are believed to be immobile in the geosphere due to their low solubility and strong sorption to mineral surfaces, it is important to address concerns (Mariner and Jackson 1993) that natural organics would complex actinides and make them more mobile than predicted by performance assessment models.



The organic geochemistry of natural waters has been extensively reviewed by Thurman (1986) and the potential effect of organics on radionuclide transport in groundwater systems has been discussed by Carlsen (1989), Choppin and Allard (1985), Norden et al. (1993) and Mariner and Jackson (1993). Organic compounds would have a significant impact on contaminant transport only if they are able to complex with radionuclides or affect their oxidation state, and if they are present in sufficient quantities to compete with inorganic anions.

Naturally occurring organic matter in groundwater is a complex mixture of humic substances, hydrophilic acids, carbohydrates, carboxylic acids, amino acids, hydrocarbons and other simple organic compounds (Thurman 1986). Actinides can be complexed by organic material containing functional groups such as carboxylate, carbonyl, ether, alcohol, phenol and amine. Fatty acids, amino acids and phenolic compounds are not important for complexing actinides in natural waters because the complexation constants of these organics for actinides are not high and would require organic concentrations of at least 10 mg/L dissolved organic carbon (DOC) (Choppin and Allard 1985). Although pigments, such as chlorophyll, have very strong binding constants for metal ions, in natural waters the concentrations of these compounds are found to be too low ( $< 10 \mu\text{g/L}$ ) to be important for complexation (Thurman 1986).

The types of organic compounds which have strong enough binding constants and may be present in sufficient quantities in natural waters to significantly complex cations are hydrophobic acids (including fulvic acid and humic acid), uronic acid and hydrophilic acids (Thurman 1986, Choppin and Allard 1985, Carlsen 1989). The subject of radionuclide complexation with fulvic and humic acids, in particular, has received a great deal of attention in the literature (Kribek and Podlaha 1980, Yamamoto and Sakanoue 1982, Choppin 1988, Moulin et al. 1988, Moulin et al. 1991, Kim et al. 1990).

In addition to complexation, humic materials may reduce certain metal ions, possibly due to the presence of hydroquinone structures (Choppin and Allard 1985). For example, soil fulvic acids can reduce Pu(VI) to Pu(IV) (Bondietti et al. 1976), and humics in sea water can reduce Pu(VI), and to a lesser extent Pu(V), to the less soluble Pu(IV) (Choppin et al. 1986).

The DOC concentration provides a relatively inexpensive measure for the presence of organic compounds in groundwater. Thurman (1986) gives a good summary of DOC concentrations in natural waters. The ranges of DOC concentrations found in natural waters are 0.2 to 2.0 mg/L for sea water, 1 to 50 mg/L for freshwater lakes, 1.4 to 15 mg/L for major rivers, and 2 to 400 mg/L for swamps, marshes and bogs. Groundwaters have DOC concentrations ranging from 0.2 to 15 mg/L with a median value of 0.5 in crystalline rock. Higher DOC concentrations are found in groundwaters associated with coal deposits and oil shales, and in some shallow groundwaters being recharged directly from organic rich surface waters.

The purpose of this report is to assess the potential impact of natural organics on radionuclide transport in granite rock based on complexation capacities reported by Vilks and Bachinski (1996), as well as new data from a variety of waters, including surface waters and near-surface groundwaters. The objectives of this report are to present the results of DOC concentrations for WRA groundwaters; describe the characterization of DOC with respect to complexation capacity; and discuss efforts to identify the origin of DOC in deep groundwaters. Some data from the Atikokan Research Area (ARA), located in northwestern Ontario, will also be presented

as an example of DOC found in an other part of the Canadian shield. Finally, the potential for complexation of trivalent, tetravalent, pentavalent and hexavalent actinides (Am, Th, Np, U) by natural organics, using observed complexation capacities and complexation constants from the literature will be discussed.

## 1.1 GEOLOGICAL SETTING

The WRA is located on the western part of the Lac du Bonnet granite batholith, which is 2500 Ma old and forms part of the Superior Structural Province of the Canadian Shield. At the URL site the batholith consists of pink porphyritic granite near the surface, whereas at depths >260 m the bulk of the batholith is made up of grey, homogeneous, equigranular granite (Brown et al. 1989). In the pink granite, epidote, chlorite, phengite and carbonate replace plagioclase and biotite. The pink color results from the deposition of iron oxide on mineral surfaces. The grey granite contains almost unaltered microcline, plagioclase and biotite.

In the upper 500 m the hydrogeology of the WRA (Figure 2) is controlled by three major subhorizontal fracture zones, referred to as Fracture Zone 1, 2, and 3, in ascending order (Davison and Kozak 1989). At shallow depths, subhorizontal fracture zones may be intersected by near-vertical fractures. Fracture abundance decreases with depth, so that below 700 m fracture intersections with boreholes are uncommon (Gascoyne et al. 1987). In general, at depths greater than about 350 m, waters are saline, with salinities between 1 and 15 g/L. These waters are dominated by  $\text{Na}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Cl}^-$ , and lesser amounts of  $\text{SO}_4^{2-}$  (Gascoyne et al. 1989). At shallower depths, from about 50 to 350 m, the groundwater salinities are between 0.3 and 1.0 g/l. These waters contain mainly  $\text{Na}^+$  and  $\text{HCO}_3^-$ , with lesser amounts of  $\text{Ca}^{2+}$ . Both the shallow and deep waters are close to being saturated with calcite, but only the deep waters come close to being saturated with gypsum. The pH of the deep groundwaters tends to be lower (6.1 to 7.7) than the pH of the shallower waters (7.4 to 8.9) (Gascoyne and Elliott 1986).

The Atikokan Research Area is located on the Eye-Dashwa granite pluton, which is also part of the Canadian Shield. This granite is more fractured than the Lac du Bonnet granite, and the groundwater hydrogeology is controlled by dipping fracture zones (Gascoyne et al. 1987).

## 2. METHODS

### 2.1 GROUNDWATER SAMPLING

Between 1989 and 1995 groundwater samples from WRA were taken from various locations, including shallow zones between 0 to 350 m, deeper fractures with saline water between 350 to 1100 m depths, near vertical fractures, and the subhorizontal fracture zones (Fracture Zone 2 and its splay, Fracture Zone 1.5). Water from the near vertical fractures and Fracture Zones 1.5 and 2 was sampled from underground boreholes drilled from the 240-m level of the URL. Water from the other depths was collected from surface boreholes at the WRA. Boreholes at the WRA were either air percussion-drilled to a 155-mm diameter, or diamond-drilled to a 76-mm diameter. Drilling muds and lubricants were not used, and after drilling the boreholes were cleaned by rapid and vigorous pumping techniques (Gascoyne et al. 1989) to remove rock flour and traces of water used for drilling. Hydraulically active zones were isolated using various completion

systems, including multi-level PVC casing and Westbay casing. At surface boreholes groundwater samples were pumped at a rate of 0.25 to 1 L/min using an air-operated squeeze pump (bladder pump). Once the squeeze pump was lowered into the borehole, water was gently pumped to the surface by the action of an air pressurized bladder (silicon rubber), which forced the water through a check valve. Water traveled to the surface through a 9.5 mm OD nylon tube. Pumps were not required for the underground URL boreholes, which had a 2.0-MPa overpressure at the borehole collars. However, this water also had to pass through nylon sample lines before reaching the borehole collar. Boreholes were flushed with several dead volumes of groundwater before sample collection to minimize DOC contamination from PVC casing, nylon tubing, or any biofilms growing on borehole walls. Groundwater samples were not filtered because most WRA groundwaters have low suspended particle ( $< 0.45 \mu\text{m}$ ) concentrations that are less than 1 mg/L and whose contribution to the DOC is insignificant (Vilks et al. 1991). Samples for DOC analyses were collected in glass bottles and stored at 4°C before analyses. Water for purgeable and solvent extractable analyses was collected in 1 L glass bottles and analyzed within one week of sample collection. Larger groundwater volumes, for size fractionation by ultrafiltration and for the isolation of hydrophobic and hydrophilic compounds by absorption chromatography, were collected in 50 L HDPE carboys and stored at room temperature for up to 24 h.

Samples from the Atikokan Research Area were taken from three deep boreholes using either a squeeze pump or a venturi pump, designed to rapidly remove large groundwater volumes from a borehole. There was no correlation between measured DOC and the type of pump used. Water samples from a number of shallow piezometers were collected with a peristaltic pump. Groundwater samples were treated in the same way as samples from WRA.

## 2.2 DOC ANALYSIS AND SIZE FRACTIONATION

DOC concentrations were determined by sodium persulfate oxidation using an Astro 2001 carbon analyzer. Samples with high concentrations of NaCl were analyzed for DOC by high temperature (875°C), platinum catalyzed oxidation using an Ionics Model 1555 carbon analyzer. Both methods gave identical results for low ionic strength waters, as was demonstrated for surface waters and groundwaters from the Cigar Lake uranium deposit, northern Saskatchewan (Vilks and Bachinski, unpublished data).

A tangential-flow ultrafiltration scheme (Figure 3) was used to determine the size distribution of organic compounds in selected 50 L groundwater samples. First, particles larger than about 10 nm were concentrated by filtering groundwater through a Pellicon system equipped with 100 000 nominal molecular weight limit (NMWL) polysulfone membrane packets, separated by retentate screens (Vilks et al. 1991). The concentrate (retentate) produced by the 100 000-NMWL (~10 nm) filter was filtered with the Minitan tangential-flow filtration system (Millipore), equipped with a 450-nm cutoff Durapore membrane. This produced a filtrate containing colloids between 10 and 450 nm, and a concentrate enriched in suspended particles  $> 450 \text{ nm}$ . Ten litres of filtrate produced by the initial 100 000-NMWL (~10 nm) filtration were filtered through another Pellicon system, equipped with a 10 000-NMWL (~1 nm) polysulfone filter cassette. This produced a sample of filtered water containing only dissolved species, and a concentrate enriched in colloids with a size range between 10 000 NMWL (~1 nm) and 100 000 NMWL (~10 nm). The filtrate and concentrate samples were analyzed for organic carbon to determine which size fractions contained organic compounds.

### 2.3 VOLATILE AND SEMIVOLATILE ORGANICS

Groundwater samples were analyzed for volatile and semivolatile organics to help identify the types of compounds contributing to the DOC in groundwater and to identify potential contamination from borehole emplacement and groundwater sampling systems. Analyses of volatiles, by purge and trap capillary column gas chromatography/mass spectrometry, and semivolatiles, by solvent extraction and capillary column gas chromatography/mass spectrometry, were performed by the Analytical Science Branch at AECL's Whiteshell Laboratories. Volatile organic components were determined by purging them from groundwater samples with helium gas and collecting the organics on a column with activated charcoal. Using heat and helium gas, the organics were desorbed from the column directly into a Hewlett Packard 5890 GC (gas chromatograph) equipped with a 5970 Mass Selective Detector. The analytical column used in the gas chromatograph was a J & W Scientific column DB624, 75 m long with 0.53 mm ID. Mass spectra from this analysis were compared to an NBS database to identify organic compounds. Semivolatile organic compounds were determined by extracting 500 mL samples with methylene chloride. The extract was concentrated to 0.5 mL and analyzed by GC/mass spectrometry, using a J & W Scientific DB5 analytical column. The mass spectra of volatile and semivolatile organics were quantified with internal standards (not a sample component) added to each sample to facilitate the measurement of the relative responses of other components within the sample, and standard solutions with known amounts of analytes to calibrate the instrument response with respect to concentration. The quality control for each sample batch included the preparation of a calibration curve from standard solutions and the analyses of reagent blanks, spiked blanks, spiked samples and duplicate analyses of selected samples.

### 2.4 UV-VISIBLE ABSORBANCE SPECTROSCOPY

Ultraviolet and visible absorbance spectra of water samples and isolated humic substances were determined to quantify concentrations of dissolved humic substances and to provide a tool for comparing organics from different sources. UV-visible absorbance measurements were performed with a HEWLETT PACKARD HP 8452A diode-array spectrophotometer, that can scan produce a full spectrum scan, from 190 to 820 nm, in 0.1 s. Quartz cuvettes were used to allow measurements down to 190 nm. Absorbance spectra were saved on computer for quantification using the HP UV-Vis ChemStation (DOS Series) quantification software. Absorbance was quantified with respect to organic carbon using standards made from fulvic acid extracted from either the Winnipeg River or from URL groundwater.

### 2.5 ORGANIC EXTRACTIONS WITH RESINS

Humic substances were extracted from groundwater using either DEAE (diethylaminoethyl) cellulose resin (Paxeus 1985, Petterson et al. 1989) or Amberlite XAD-8 resin (Thurman and Malcolm 1981). The DEAE cellulose is a weak anion exchange resin, which has the advantage of being able to remove humic substances from water by anion exchange without the need for sample acidification (Vilks 1995). The DEAE resin was placed in a plexiglass flow cell through which groundwater volumes of between 60 and 3000 L were allowed to flow with rates as high as 30 L/h. Groundwater was pumped directly from the borehole into the flow cell, eliminating the need for storage and minimizing the risk of altering the organic substances before sorption onto the resin. The humics extracted from groundwater were released from the DEAE resin with

0.3 N NaOH, within a day after extraction. Tests with known concentrations of humic acid determined that this method was able to recover 56 percent of the humic substances in groundwater. A portion of the extracted solution was acidified to pH 7 and used to determine the total concentration of extracted humics. The remainder was acidified to pH 1 to precipitate humic acid. The humic acid was separated from the soluble fulvic acid by centrifuging at 6000 rpm for 20 minutes.

Amberlite XAD-8 resin is a crosslinked polymeric methacrylate ester that can remove humic substances from water by hydrophobic interactions (Vilks 1995). Groundwater samples, with volumes between 50 and 100 L, were acidified to pH 2 to make the humic substances more hydrophobic. Within 24 h of collection the acidified samples were pumped at a flow rate of 150 mL/min through a column packed with purified XAD-8 resin (Thurman and Malcolm 1981). Before a significant breakthrough of humic substances occurred, as determined by the UV absorbance of water eluted from the column, adsorbed humics and other hydrophobic acids were backflushed from the resin with 0.1 N NaOH, which changed these substances to their ionic form, making them less hydrophobic. As in the other extraction method, humic acid was removed by precipitation at pH 1. Although, the XAD-8 resin extraction requires a sample acidification, the extraction efficiency of this method, determined by the isolation of a known amount of Aldrich humic acid, was close to 100 percent.

Selected samples of fulvic acid were purified by immobilizing their acidified solutions on XAD-8 resin. The immobilized samples were rinsed with deionized water to remove salts. The fulvic acid was then extracted with a backflush of 0.1 M NaOH and passed through a column of hydrogen saturated Ag-MP-50 cation exchange resin to convert the fulvic acid to its hydrogen form. Portions of the purified samples were freeze dried for chemical analysis.

In addition to extracting hydrophobic acid, the procedure of Leenheer (1981) was adopted for fractionating groundwater DOC into hydrophobic acids, bases and neutrals, and hydrophilic acids, bases and neutrals. Briefly, 100 L of groundwater at ambient pH were pumped through a column of XAD-8 resin to extract hydrophobic bases (Figure 4). After flushing the column with 2.5 bed volumes of deionized water the immobilized hydrophobic bases were extracted with a backflush of 0.1 N HCl, followed by 0.01 N HCl. The groundwater, from which hydrophobic bases had been removed, was acidified to pH 2 and passed through the XAD-8 column to extract hydrophobic acids. Once the immobilized hydrophobic acids were extracted from the column with back flushes of 0.1 N and 0.01 N NaOH, the XAD-8 resin was rinsed with deionized water. The resin was then dried and soxhlet extracted with methanol to recover adsorbed hydrophobic neutrals. The groundwater sample, containing only hydrophilic compounds, was then pumped through a column containing a hydrogen ion saturated cation exchange resin (BIO-RAD AG-MP-50), and then through a column with an anion exchange resin in the free base form (DUALITE A-7). The cation exchange resin immobilized hydrophilic bases and hydrogen saturated the hydrophilic acids so that they could be immobilized by the anion exchange resin. The water eluted from the anion exchange resin contained hydrophilic neutrals in deionized water. Hydrophilic bases were recovered from the cation exchange resin with a forward flush of 1 N NaOH. Hydrophilic acids were removed from the anion exchange resin with a back flush of 3 N NaOH.

## 2.6 DETERMINATION OF FUNCTIONAL GROUPS

The functional group content of hydrophilic acids and hydrophobic acids (humic materials) was studied by acid-base titrations using an automated, computer-programmed titration system (Tanager Scientific Systems, Ancaster, Ontario). Acid-base titration data were obtained between pH 3 and pH 11 at maximum intervals of 0.1 pH units. The reaction temperature was 21°C and the ionic strength of the organic solutions was adjusted to 0.3 with NaNO<sub>3</sub> to improve electrode performance and minimize changes in ionic strength due to the addition of acid or base. The titration results were modeled with discrete site analysis to obtain the concentrations of acid-base reactive sites (Brassard et al. 1990). In this discrete affinity spectrum model it was assumed that the overall acid-base properties of a sample can be treated as the sum of a mixture of individual monoprotic acids or sites, with pKa (-log of the acidity constant) values ranging from 3 to 11 and spaced at 0.2 pKa units (Kramer et al. 1989). A linear programming approach (Brassard et al. 1990) was used to determine the concentrations and the pKa values of acids that could reproduce the titration data. The concentrations of these acids were normalized to the DOC in each sample and reported as meq/g organic carbon.

## 2.7 CARBON-14 AGE DATING

Carbon-14 age dating was performed on four fulvic acid samples that had been isolated from groundwater using either DEAE cellulose or XAD-8 resins. Immediately prior to freeze-drying, the samples were acidified and purged with oxygen to remove inorganic carbon, which is likely to contain modern activities of C-14. Although these samples were not desalted before freeze-drying to minimize the potential for contamination from atmospheric CO<sub>2</sub>, desalting should be seriously considered for future analyses. The freeze-dried samples were sent to the ISOTRACE Laboratory at the University of Toronto, for C-14 analyses by accelerator mass spectrometry (AMS). The reported results were average values of 2 targets, and were corrected for natural and sputtering fractionation to a base of  $\delta^{13} = -25 \text{ ‰}$ . The ages were reported as uncalibrated conventional radiocarbon dates in years before present (BP), using a C-14 half life of 5568 years (Stuiver and Polach 1977), setting 1950 AD as 0 years BP, and assuming that all C-14 reservoirs have remained constant through time.

## 3. RESULTS

### 3.1 SIZE DISTRIBUTION OF ORGANIC CARBON

The size distribution of organic compounds, determined by analysis of organic carbon in filtrates and particle concentrates is presented in Table 1 for selected WRA groundwaters and in Table 2 for Atikokan waters. In groundwater from the WRA most of the organic carbon (58 to 100 percent) was associated with dissolved organic compounds smaller than 1 nm. Almost no organic carbon was found with suspended particles larger than 450 nm. Colloids between 10 and 450 nm contained 0 to 14 percent of the total organic carbon, while colloids in the 1 to 10 nm size range accounted for 0.2 to 47 percent of the organic carbon. These smaller organic colloids may include humics. Mass balance calculations, comparing the total organic carbon before tangential filtration with the summed total of dissolved, colloidal and particulate organic carbon, indicated that 1 to 39 percent of the organic carbon in the sample may be lost during the filtration

procedure (last column in Table 1). To avoid any possible loss of organics on filter membranes, groundwaters from WRA were not filtered before determining their organic carbon concentrations. Since a negligible amount of organic carbon is associated with suspended particles and very little is attached to colloids larger than 0.01  $\mu\text{m}$ , the measurements in this study were considered to be the same as dissolved organic carbon (DOC) determinations made on samples filtered by 0.45  $\mu\text{m}$  membranes.

The shallow and deep groundwaters in Atikokan had similar size distributions of organic carbon (Table 2) to those found in WRA groundwaters. Almost no organic carbon was found associated with suspended particles and similar percentages of DOC were associated with the two colloid size fractions. The sample of river water was distinct from groundwater samples in that 6 percent of the carbon was associated with suspended particles and 45 percent was colloidal between 10 and 450 nm in size. A significant portion of the humics in this sample were associated with these colloids, as shown by the color reduction in the sample following filtration. These results show that the size distribution of organic carbon in WRA groundwaters is similar to groundwaters in other parts of the Canadian shield.

### 3.2 DOC CONCENTRATIONS

It is difficult to obtain samples from deep groundwaters that are completely contamination free due to the unavoidable contact with PVC casing and nylon sampling lines. Flushing experiments at the URL have shown that the first 1 L of groundwater extracted from underground boreholes had as much as 40 mg/L of DOC. The DOC concentration dropped rapidly within the next 10 to 20 L of sampled water and reached a steady state from about 50 L to the end of the flushing period (500 L). These steady state concentrations probably closely approximated the natural DOC of WRA groundwaters because after the removal of standing water from the borehole and sample lines, fresh groundwater was only briefly in contact with well-aged nylon and plastic during the sampling period. Although field blanks have been used to check for contamination from sample bottles and laboratory handling, they do not resolve the issue as to whether the DOC determined in groundwater samples is truly representative of natural groundwater organics.

Average DOC concentrations for WRA groundwaters (Table 3) varied between  $<0.1$  to 19.5 mg/L, with a median of 1.0 mg/L. Fracture Zone 2 at the URL has been extensively sampled for several years from at least 35 locations to obtain a large data base for DOC. The DOC concentrations ranged from  $<0.1$  to 18 mg/L, with a median value of 0.7 mg/L. In Fracture Zone 2 it was noted that boreholes with low hydraulic conductivity and producing water at rates of less than 1 L/min had higher DOC concentrations, although there were some exceptions. These boreholes may have residual contamination from drilling or the plastic sample tubing, which could not be removed due to the small groundwater volumes available for flushing. In Table 3 samples from boreholes with low permeability or with evidence of contamination, have been identified. If these samples are excluded, the average DOC concentration for Fracture Zone 2 is  $0.8 \pm 0.1$  mg/L, while the median value remains as 0.7 mg/L. Fracture Zone 1.5 is a subhorizontal fracture located below Fracture Zone 2 (Figure 2). In the region of the URL it has a lower permeability and a higher average DOC ( $4.8 \pm 2.4$  mg/L) than Fracture Zone 2. The two samples from Fracture Zone 1, located below Fracture Zones 2 and 1.5 (Figure 2), gave an average DOC of  $1.7 \pm 0.3$  mg/L. Groundwater from near vertical fractures that partly extend to the surface had DOC concentrations between  $<0.1$  and 5 mg/L, with a median of 1.5 mg/L. If the samples from boreholes with low permeability are excluded, the average DOC in the near

vertical fractures ( $0.8 \pm 0.4$  mg/L) was identical to the average DOC in Fracture Zone 2. The DOC concentrations in groundwaters above Fracture Zone 2, were variable between  $< 0.1$  and  $19.5$  mg/L, with a median value of  $3.1$  mg/L. The DOC of deeper saline waters varied between  $0.3$  and  $5.5$  mg/L, with median and average values of  $2.4$  and  $2.3 \pm 0.8$  mg/L. Although the DOC concentrations in WD3-12 and WB1-7 may be affected by contamination because of difficulties in flushing, the removal of these samples does not affect the median and average DOC concentrations for saline groundwaters.

The amount of DOC data for deep groundwaters from Atikokan is limited to 3 boreholes (Table 2). After extensive flushing, the DOC in two sampling locations dropped to below detection ( $< 0.10$  mg/L), while in the third location the DOC remained high ( $11$  mg/L). This suggests that the majority of deep groundwaters in Atikokan probably have low amounts of organic carbon. Local exceptions may exist, although the possibility of borehole contamination in ATK-6-8 has not been ruled out. The organic concentrations in shallow boreholes were consistently higher with an average of  $22 \pm 11$  mg/L.

Table 4 contains additional analyses of organics from Atikokan and WRA surface waters and shallow groundwaters. The streams sampled in WRA, near the East Swamp, contained an average of  $29.2 \pm 0.6$  mg/L DOC, which is higher than the  $13.3$  mg/L observed for the Winnipeg River (Table 8). The average DOC in Atikokan surface waters ( $7.1 \pm 1.1$  mg/L) appears to be lower than in WRA surface waters. At WRA the DOC in overburden groundwaters ( $9.0 \pm 0.1$  mg/L) was not significantly different from the DOC in groundwater from granite of similar depth ( $10.4 \pm 2.2$  mg/L). In general, surface waters and shallow groundwaters contain higher concentrations of organics than found in deep groundwaters. The organics in these near-surface waters are a possible source of DOC for the deeper groundwaters.

In summary, the average DOC concentrations from surface waters, shallow groundwaters, Fracture Zone 2, the vertical fractures, and saline groundwater may provide a reasonable indication of the organic content of groundwaters from the Canadian shield. Although the DOC values from less permeable zones may have contributions from drilling contamination, they can provide an upper limit to the concentration of organic substances in groundwater.

### 3.3 VOLATILE AND SEMIVOLATILE ORGANICS

The volatile and semivolatile organic content of selected samples was determined to improve our understanding of the types of organic compounds making up the observed DOC, and to look for evidence of contamination from activities related to borehole drilling and the emplacement of sample collection systems. The volatile and semivolatile organics which were detected included hydrocarbons, alcohols, aldehydes, esters, phenols, and phthalates. It is likely that many of these compounds originated as contamination from plastic tubing, and drilling operations. Plasticizers, such as phthalates, various esters and benzenesulfonamide, may originate from nylon sampling tubes and plastic components used to isolate groundwater from chosen borehole sections. Contamination during drilling may have been introduced by drilling water obtained from nearby surface waters, or in the case of the URL the onsite settling pond. This pond receives all water that has been pumped from underground operations and at certain times probably contained hydrocarbons, such as toluene which originated from blasting operations.



Table 5 provides a detailed listing of the volatile and semivolatile organic compounds observed in WRA groundwaters. Table 6 summarizes the contribution of these organic compounds to observed groundwater DOC. These compounds accounted for 0 to 95 percent of the DOC in groundwater samples. Samples with the highest concentrations of organic contaminants generally came from rock zones which had not been extensively flushed with insitu groundwater due to lower permeability, or lesser amounts of previous groundwater sampling operations. With the exception of samples HC15-Z3, HC37, and PH3-Z5, borehole sampling tubes were flushed with a minimum of 50 L of groundwater before sample collection to minimize contamination from the borehole vicinity. However, despite this cleaning and extensive flushing with hundreds of liters of water during previous borehole tests, low concentrations of organic contaminants persisted at many sampling locations.

Groundwater samples with likely contamination from toluene and or plasticizers, had 1 to 19 mg/L concentrations of these man made organic contaminants, which accounted for up to 95 percent of the DOC. Groundwaters from boreholes with significantly reduced contamination had concentrations of volatile and semivolatile organics which were generally below 0.05 mg/L and which usually made up less than 6 percent of the DOC. Therefore, while some volatile and semivolatile organics may occur naturally in groundwater at WRA, these compounds make up only a very minor fraction of the naturally occurring organic matter. These results also illustrate the difficulty in obtaining deep groundwater samples that are entirely free of contamination and indicate that the high DOC concentrations in some boreholes cannot be used to estimate the concentration of naturally occurring organic matter which may complex radionuclides.

Table 7 gives the results of volatile and semivolatile analyses of waters from Atikokan. These compounds accounted for a very minor fraction of the DOC, suggesting that contamination from plastic pipes and tubing was not a factor in the DOC results. Therefore, the high DOC in ATK-6-8 did not originate from direct contamination from drilling components or plastic pipes. However, the possibility of contamination introduced by drilling water obtained from a local organic rich surface water has not been ruled out.

### 3.4 HYDROPHOBIC AND HYDROPHILIC ORGANICS

Hydrophobic acids (including humics) and hydrophilic acids contain functional groups which most likely determine the ability of natural organics in groundwater to complex radionuclides. The organic compounds most commonly investigated for their ability to complex radionuclides and other contaminants are humic materials. The observed concentrations of humic materials, in terms of mg/L organic carbon, for a range of WRA groundwaters, and including the Winnipeg River, are presented in Table 8. These data were obtained by isolating humics from groundwater using either DEAE cellulose or XAD-8 resins. Additional data on humic concentrations determined by absorbance measurements on untreated samples are presented in Table 4 for surface waters and shallow groundwaters. Groundwater humic concentrations ranged from 0.05 to 6.5 mg/L, accounting for 1 to 66 percent of the observed DOC (Table 8). The concentration of humics was significantly higher in surface waters and near-surface groundwaters than in deeper groundwaters. In shallow groundwaters from overburden and bedrock humic concentrations ranged from 0.49 to 6.5 mg/L, with respective averages in overburden and bedrock of  $1.38 \pm 0.21$  mg/L and  $2.23 \pm 0.87$  mg/L. With increasing depth average humic concentrations decreased to  $0.36 \pm 0.04$  mg/L just above Fracture Zone 2,  $0.32 \pm 0.13$  mg/L within Fracture Zone 2, and  $0.26 \pm 0.10$  mg/L in deeper saline waters. In many samples the humic materials

consisted mostly of fulvic acid. However, significant amounts of humic acid (up to 65 percent) were found in some humic samples. Reported (Thurman 1986) concentrations of humic substances in natural waters included 0.03 to 0.10 mg/L for groundwater, 0.5 to 4 mg/L for rivers and lakes, and 10 to 30 mg/L for wetlands.

The results of organic fractionation analysis, which separates DOC into hydrophobic (acid, base, neutral) and hydrophilic (acid, base, neutral) fractions are given in Table 9. The types of compounds which can be found in these organic classes are summarized in Table 10. From a complexation perspective, the hydrophobic and hydrophilic acids are of most interest because they contain carboxylic acids, humics and other polyelectrolytic acids with carboxylic functional groups. As shown in Table 9, the hydrophilic acids were as abundant as the hydrophobic acids, on which the complexing capacity of waters is commonly based. Hydrophobic and hydrophilic bases made up only a small fraction of the DOC. Hydrophobic neutrals were found only in trace quantities, which is consistent with the results of the solvent extraction analysis. More than 50 percent of the groundwater DOC was associated with the hydrophilic neutral fraction.

### 3.5 CHARACTERIZATION OF FUNCTIONAL GROUPS

The acidity constants and concentrations of acids and functional groups determined by discrete site analysis of acid-base titration data can be presented as an affinity spectrum (Figure 5). Functional groups with pKa values < 6 are carboxylic acids; those with pKa values from 7 to 8.5 may represent  $\beta$ -dicarbonyls, enols, and alcohols usually associated with aliphatic carbon structures; and phenolic acids, associated with aromatic carbon, may be represented by pKa values from 9 to 10.5 (Clair et al. 1991). The total concentrations of these types of functional groups, expressed as meq/g organic carbon, are given in Table 11 for WRA humics, extracted with both DEAE cellulose and XAD-8 resins. In WRA humics the average respective concentrations of carboxylic groups,  $\beta$ -dicarbonyls, and phenolic groups, were  $7.7 \pm 0.6$  meq/g,  $1.8 \pm 0.4$  meq/g, and  $6.6 \pm 1.2$  meq/g. The functional group concentrations in the sample of hydrophilic acid was not very different from average values in humics, with respective concentrations of carboxylic groups,  $\beta$ -dicarbonyls, and phenolic groups, of  $13.0 \pm 3.0$  meq/g,  $0.8 \pm 0.1$  meq/g, and  $7.7 \pm 0.5$  meq/g. Thurman (1986) summarized carboxylic concentrations that have been reported in the literature for humic acid (4 to 4.5 meq/g) and fulvic acid (5 to 6.2 meq/g) extracted from natural waters. Takats (1992) reported carboxyl acidity of 6.5 to 8.0 meq/g for hydrophobic acids and 13.5 to 29.1 for hydrophilic acids extracted from lake water.

### 3.6 CARBON-14 AGES

Conventional radiocarbon dates in years before present (BP) of 4 samples of fulvic acids isolated from WRA groundwaters are given in Table 12. The oldest date of  $6220 \pm 280$  was observed in a sample from Fracture Zone 2. The youngest date of  $3590 \pm 130$  was obtained from a subvertical fracture, which was known to contain relatively young water. The observed age of the fulvic acid from saline water was younger ( $4120 \pm 90$ ) than that from Fracture Zone 2. This was not expected because the deeper saline water should have had carbon that had been removed from the surface for a longer period than organics in shallower water. Fulvic acid collected from B34-2, at a depth of only 33 to 60 m, did not have a younger age ( $4270 \pm 130$ ), which might have indicated an input of more modern organic carbon. These results show that a component of organics in deep groundwaters must originate from surface waters. Either all of the organics

have been isolated from the surface for up to 6000 a, or else a much younger organic component has mixed with organic carbon that could be older than 60 000 a.

#### 4. DISCUSSION

##### 4.1 COMPLEXATION WITH RADIONUCLIDES

The DOC data base for WRA groundwater indicates that although surface waters and shallow groundwaters contain relatively high concentrations of natural organics, deeper groundwaters from Fracture Zone 2 and the vertical fractures have organic concentrations that are typical of groundwaters associated with crystalline rocks. In deep groundwaters the concentrations of humic substances, which account for 2 to 66 percent of the DOC, appear to be similar both in the shallower Na-HCO<sub>3</sub> groundwaters and in the much deeper, saline Na-Ca-Cl-SO<sub>4</sub> waters. Although these concentrations are not as high as in surface waters, rich in organic acids, the hydrophobic and hydrophilic acids in WRA groundwater could complex with radionuclides such as the actinides. To determine whether organic ligands may compete with inorganic ligands in metal complex formation within WRA groundwater and, thereby, enhance radionuclide mobility, complex formation was evaluated based on conditional stability constants reported in the literature. Conditional constants are equilibrium constants that are based on concentrations, without ionic strength corrections, and hold only under given experimental conditions (Stumm and Morgan 1981).

Organic complexation with radionuclides with high solubilities or very low sorption coefficients does not need to be considered because these radionuclides would be mobile with or without organics. The aqueous chemistry of monovalent and divalent trace elements in natural waters is usually not dominated by organics because their binding constants with these organics are too weak to compete with the much higher concentrations of Mg<sup>2+</sup> and Ca<sup>2+</sup> present in natural waters (Carlsen 1989, Stumm and Morgan 1981). The Cu<sup>2+</sup> ion may be an exception (Stumm and Morgan 1981). Therefore, this report has focused on evaluating the effect of organics on trivalent, tetravalent, pentavalent and hexavalent actinides (Am(III), Th(IV), Np(V), U(VI)). Am(III) has also been considered as an analog for Pu(III), and Th(IV) is a satisfactory model for U(IV).

If a radionuclide (M) forms a complex with an inorganic or organic ligand (L) the reaction can be described as follows:



The conditional stability constant for this reaction can be written as follows:

$$\beta_i = \frac{[ML_i]}{[M] \times [L]^i} \quad (2)$$

where:

- [ML<sub>i</sub>] = concentration of radionuclide complexed to i ligands
- [M] = concentration of free radionuclide
- [L] = concentration of uncomplexed ligand
- i = number of ligands or sites complexed to radionuclide

A useful indicator of the complexing capacity of a given ligand is given by the ratio of complexed radionuclide with uncomplexed radionuclide.

$$\frac{[ML_i]}{[M]} = [L]^i \times \beta_i \quad (3)$$

Organic ligands will significantly affect radionuclide chemistry only if the complexed/uncomplexed ratios for organic complexes are equal to or greater than the ratios for inorganic complexes. Since the concentrations of complexing ligands in groundwater greatly exceed radionuclide concentrations (Carlsen 1989) one can approximate the free ligand concentrations in equation 3 with total ligand concentrations.

Since carboxylic functional groups are believed to play a major role in the complexing properties of humic substances, the complexing capacity of organics in WRA groundwater is likely determined by carboxylic acid functional groups associated with the hydrophobic and hydrophilic acid fractions making up the DOC. Conditional stability constants for cation interactions with humic and fulvic acids are determined assuming that the complexation capacity is controlled by the concentration of carboxylic functional groups per g organic carbon. Table 13 illustrates the range of values reported in the literature for conditional stability constants for actinide complexation with humic and fulvic acids. Carboxylic acids must ionize before complexing actinides, as is shown in Table 13 by several examples (Torres and Choppin 1984, Nash and Choppin 1980) of increasing stability constants with higher pH. Since most carboxylic functional groups have pK<sub>a</sub> values less than 5, these functional groups are more than 99 percent ionized at pH values greater than 7. Therefore, for most WRA groundwaters we can assume a full carboxylic functional group complexation capacity for cations, that does not change with pH values of > 7.

The average concentration of humics in Fracture Zone 2 groundwater is 0.32 mg/L as organic carbon. Based on the data given in Table 9, we can assume the presence of another 0.32 mg/L organic carbon associated with hydrophilic acids. Since the average concentration of carboxylic functional groups in humics is  $7.7 \pm 0.6$  meq/g, the average humic concentration in Fracture Zone 2 would contribute  $2.5 \times 10^{-6}$  eq/L of complexing capacity. Since hydrophilic acids have 13 meq/g carboxylic functional groups, these acids would contribute another  $4.2 \times 10^{-6}$  eq/L of complexing capacity. Therefore, the total complexing capacity of hydrophobic and hydrophilic acids in a typical Fracture Zone 2 groundwater would be  $6.7 \times 10^{-6}$  eq/L. Since the pH values of Fracture Zone 2 waters are usually well above 7, we can assume that complexing capacity determined by carboxylic groups will not vary with pH.

Complexation ratios of Am(III), Th(IV), Np(V) and U(VI) for carboxylic functional group concentrations derived from a range of humic concentrations, including the concentration representative of Fracture Zone 2 groundwater, were calculated (equation 3) using selected stability constants and are presented in Table 14. In the calculation it was assumed that for a given humic concentration there was an equal amount of hydrophilic acid, which increased the complexing capacity. The effects of competing cations were not considered in these calculations. The calculations were performed for a set of high and a set of low stability constants, spanning the range of values reported in Table 13, to illustrate the sensitivity of calculated complexation ratios to stability constant strength. Complexation ratios for the principle inorganic complexes were also calculated for a typical Fracture Zone 2 groundwater composition and are given in Table 15. Based on the anion concentrations in this water and the strengths of stability constants with these anions, the inorganic chemistry of the actinides would be controlled by OH<sup>-</sup> (Am(III), Th(IV), Np(V)), CO<sub>3</sub><sup>-</sup> (Am(III), Np(V), U(VI)), and F<sup>-</sup> (U(VI)). Complexation ratios for complexes with OH<sup>-</sup> and CO<sub>3</sub><sup>-</sup> were calculated for a range of pH values.

A comparison of organic (Table 14) and inorganic (Table 15) complexation ratios shows that if the weaker organic complexes with U(VI) are valid, inorganic complexes would dominate for all organic concentrations. Assuming that the strongest stability constants for U(VI) are valid for the organics and the U concentrations expected in Fracture Zone 2 groundwaters, the complexation ratio for U(VI) organic complexes is less than for F<sup>-</sup> complexes and for carbonate complexes above a pH of about 7.5. Therefore, it is unlikely that the chemistry of U(VI) is affected by organics in the deep WRA groundwater. However, in the shallow groundwater with a humic concentration of 6.5 mg/L, U(VI) complexation by organics could play a role up to a pH of about 7.5, above which carbonate complexation would become important.

The inorganic speciation of Np(V) in Fracture Zone 2 groundwaters would consist of NpO<sub>2</sub><sup>-</sup> and lesser amounts of NpCO<sub>3</sub><sup>3-</sup> (Table 15). In these groundwaters, with an average humic concentration of 0.32 mg/L, Np organic complexes would be minor compared with inorganic Np species (Table 14). Organic Np complexes could start to become a factor when humic concentrations increased to the levels found in some near-surface groundwaters.

From Table 14 it is apparent that the predicted impact of natural organics on the chemistry of Am(III) and Th(IV) depends very much on the choice of values for conditional stability constants. The aqueous chemistry of Am(III) would be completely dominated by organic complexation provided the strong stability constants reported by Choppin (1988) were correct. However, if the lower constants determined by Kim et al. (1990) and Moulin et al. (1988) are more appropriate, then in low organic groundwaters typical of Fracture Zone 2, Am(III) carbonate and hydrolysis complexes would be more abundant than organic complexes at pH values above 8, with organic complexes reaching equal proportions as the pH dropped to 7.7. It should be noted that in the literature most reported values for Am stability constants with natural organics fall within the ranges reported by Kim et al. (1990) and Moulin et al. (1988). If Am(III) were released into the shallow groundwater with 6.5 mg/L humics, organic complexation would dominate Am(III) chemistry.

The chemistry of Th(IV) could also be dominated by organic complexes even at low organic concentrations if the constants reported by Choppin (1988) are valid. However, if the log β<sub>1</sub> for Th(IV) complexes with organics is only 7 (Norden et al. 1993), the organic complexes would be insignificant compared with hydrolysis species.

In summary, the chemistry of pentavalent and hexavalent actinides is not affected by organics in groundwaters typically found at depth in granite rock, which is in agreement with the conclusions of Moulin and Moulin (1995). However, the chemistry of trivalent and tetravalent actinides could be affected by organics, depending upon which stability constant values are valid for these groundwaters. It is not the purpose of this report to evaluate the relative merits of the complexation constants reported in the literature, other than to draw attention to the importance of determining whether the log  $\beta_1$  values for Am(III) and Th(IV) complexes should be around 6 or 13. Until this issue is conclusively resolved, it is not possible to make a definite statement on the effect of natural organics on Am(III) and Th(VI) mobility in WRA waters.

It should also be noted that the formation of strong complexes with organics does not necessarily imply enhanced mobility. If organic complexes are not mobile their formation may have no effect on mobility or they may even enhance retardation. Although the migration of organic macromolecules was found to be limited in Boom clay water (Put et al. 1992), the size of organic molecules should not be a factor in the retardation of organic species in WRA groundwaters because fractures have more space than clay and most of the organic species are dissolved (<10 000 NMWL). The sorption of complexing species to mineral surfaces could lead to enhanced sorption (Mariner and Jackson (1993)). Therefore, other studies, such as sorption or migration experiments in the presence and absence of natural organics, could be carried out to determine whether the chemistry of the actinides is influenced by organics and to provide an indication as to which stability constants are more appropriate.

The effects of natural organics on radionuclide sorption were tested by Ticknor et al. (1995, 1996a), Ticknor and McMurry (1996), and Ticknor et al. (1996b) who found that radionuclide sorption was not significantly affected by the presence of fulvic acid isolated from WRA groundwater. At dissolved fulvic acid concentrations between 1 and 10 mg/L, no effect could be determined on the sorption of Cs, Se, Sr, Tc, or U relative to their sorption on the same geological materials from solutions without fulvic acid. This supports the conclusion of this report that the migration of hexavalent actinides and monovalent and divalent radionuclides would not be affected by organics. Sorption of Am, Pu and Sn was lowered as the concentration of DOC increased. However, in all cases, substantial sorption of these radioisotopes still occurred.

#### 4.2 DISTRIBUTION AND ORIGIN OF ORGANICS

Despite the uncertainty as to which stability constants are appropriate, it appears that the concentrations of natural organics in deep groundwaters are too low to affect the solubility of U, which may have had an impact on the dissolution of the waste form. However, surface and near-surface groundwaters of the Canadian shield do have high concentrations of organics which could affect the solubility of U and other radionuclides. Therefore, in choosing a location for a disposal vault it is important to determine whether there is any potential for a rapid recharge of organic rich surface waters to the depth of the vault.

Conventional radiocarbon dates are reported in years BP, where 1950 is conventionally set as 0 BP. It is assumed that organic matter is created from atmospheric CO<sub>2</sub> with a time invariant <sup>14</sup>C activity. Conventional radiocarbon ages of less than 200 a are by convention referred to as Modern. Any sample younger than 1950 is termed as greater than Modern, or >Modern. Due to the influx of bomb <sup>14</sup>C since 1950, >Modern ages may appear as future dates. The oldest ages

that can be measured by radiocarbon dating are determined by the disappearance of measurable  $^{14}\text{C}$ . Minimum ages for different laboratories can vary between  $> 50\ 000$  and  $> 60\ 000$  a. If a sample of organic material contains both young and old organic carbon, its radiocarbon date will be a mixed age.

When using radiocarbon dates to determine the recharge time of organics to a given depth, it is necessary to make assumptions regarding the age of organics in surface waters and shallow groundwaters. Thurman (1986) reported radiocarbon dates for fulvic acid from three different waters. Fulvic acid from the Suwannee River was  $>\text{Modern}$ , being  $> 30$  years old. Fulvic acid from Yuma, Arizona, which may have gained 60 percent of its carbon from groundwater and 30 percent from surface water, had a Modern age (150 a). Fulvic acid from the Biscayne Aquifer, Florida, was isolated from groundwater that was recharged from the Everglade Swamp, and gave a radiocarbon age of 600 a. The size, composition and functional group content of this older fulvic acid were very similar to the  $>\text{Modern}$  fulvic acid.

Wassenaar et al. (1990) reported radiocarbon ages from a number of different aquifers with depths between 1.2 and 125 m. The ages ranged from  $>\text{Modern}$  to 41 000 a, indicating that humic substances were derived from both modern and ancient sources. Whether or not the age of aquatic humic substances was affected by the soil humic substances with which they were in contact depended upon redox conditions, microbial activity and the input of organics from the overlying unsaturated zone.

Radiocarbon dates of isolated humics from WRA suggest that they have come from the surface within the last 6000 a. While in general the DOC and humic concentrations in deep groundwaters are low, occasionally a sample will contain a high humic concentration, suggesting the existence of a fracture system which might be recharging organic-rich surface waters. Water from URL-12-11 may be such an example, although difficulties in sampling could have led to contamination. A more thorough understanding of how organics are transported from surface waters to deep groundwaters would give confidence to our ability to predict the complexing capacities of natural organics in deep groundwaters.

## 5. CONCLUSIONS

DOC concentrations in WRA groundwater varied from  $< 0.1$  to  $19.5$  mg/L, with average values of  $0.8 \pm 0.4$  mg/L for near-vertical fractures,  $0.8 \pm 0.1$  mg/L for Fracture Zone 2,  $4.8 \pm 2.4$  mg/L for the less permeable Fracture Zone 1.5,  $1.7 \pm 0.3$  for Fracture Zone 1, and  $2.3 \pm 0.8$  mg/L for saline groundwater. Average DOC concentrations were significantly higher in near-surface groundwaters ( $10 \pm 2$  mg/L) and in surface waters where an average DOC concentration of  $29.2 \pm 0.6$  was observed in the East Swamp. In the Atikokan Research Area deep groundwaters also appear to have low DOC, while near-surface groundwaters and surface waters had significantly higher DOC. This variation in DOC with depth is probably typical of the Canadian shield. Contamination from drilling operations, which could not be flushed from less permeable zones, was responsible for high DOC values in some samples. The DOC not associated with contamination consisted mainly of hydrophilic neutral compounds (60 to 75%), and hydrophobic and hydrophilic acids (23 to 39%).

The carboxyl functional groups associated with hydrophobic and hydrophilic acids would most likely determine the complexation capacity of natural organics for actinide and metal ions. In a typical Fracture Zone 2 groundwater, these acids contribute  $6.7 \times 10^{-6}$  eq/L of complexing capacity. This capacity is low compared to that of some surface waters with as much as 4 to 30 mg/L of humic substances, giving capacities of  $10^{-5}$  to  $10^{-4}$  eq/L. The ability of these organics to complex radionuclides was tested using conditional stability constants from the literature for humic complex formation with Am(III), Th(IV), Np(V) and U(VI). The chemistries of U(VI) and Np(V) in deep groundwaters were predicted to be dominated by inorganic complexes and not significantly affected by organics. Accurate predictions for Am(III) and Th(IV) could not be made due to the wide range in conditional stability constants reported in the literature. Depending upon the choice of values for stability constants, the predicted aqueous chemistry of these actinides may or may not be dominated by dissolved organics due to competition with more abundant inorganic complexes in WRA groundwaters. Most stability constants reported in the literature for Am organic complexes would indicate that Am complexation by organics would not be a major factor in deep groundwaters. However, all actinides would be complexed to some extent by organics in surface waters and near-surface groundwaters in the Canadian shield with high organic concentrations. Experiments have shown that the sorption of pentavalent actinides, and monovalent and divalent radionuclides is not affected by organics and that although the sorption of Am, Pu and Sn is reduced by organics, significant sorption still occurs.

In crystalline rock of the Canadian shield natural organics in deep groundwaters originate from surface waters and near-surface groundwaters, containing high concentrations of organics. This conclusion is supported by radiocarbon dates of humics isolated from deeper groundwaters at WRA. Although in general, organic concentrations appear to be reduced from their surface values as groundwaters are recharged to depth, fracture zones with rapid recharge could potentially have higher than average organic concentrations. Strategies for siting a disposal vault should attempt to identify and avoid such areas of rapid recharge.

## ACKNOWLEDGMENTS

The authors would like to thank J.D. Ross and J.J. Hawton of the Applied Geoscience Branch (Hydrogeochemistry Section) for their assistance in groundwater sampling and providing information on sample location. The Canadian Nuclear Fuel Waste Management Program is jointly funded by AECL and Ontario Hydro under the auspices of the CANDU Owners Group.

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\* Internal report, available from SDDO, AECL, Chalk River Laboratories, Chalk River, Ontario K0J 1J0.

TABLE 1

SIZE DISTRIBUTION OF ORGANIC CARBON IN SELECTED WRA  
GROUNDWATERS

| Sample   | Dissolved<br>< 1 nm<br>(mg/L) | Colloid<br>1-10 nm<br>(mg/L) | Colloid<br>10-450 nm<br>(mg/L) | Particles<br>> 450 nm<br>(mg/L) | Percent<br>Dissolved | Percent<br>Lost During<br>Filtration |
|----------|-------------------------------|------------------------------|--------------------------------|---------------------------------|----------------------|--------------------------------------|
| B37-1    | 6.25                          | 0.01                         | 0.00                           | 0.00                            | 100                  | 2                                    |
| B37-2    | 5.91                          | 0.07                         | 0.00                           | 0.00                            | 99                   | 8                                    |
| M1B      | 1.81                          | 0.04                         | 0.00                           | 0.005                           | 93                   | 7                                    |
| JE1      | 0.88                          | 0.15                         | 0.02                           | 0.00                            | 83                   | 16                                   |
| HC8      | 1.00                          | 0.02                         | 0.01                           | 0.00                            | 97                   | 39                                   |
| HC9      | 1.71                          | 0.59                         | 0.13                           | 0.00                            | 71                   | 16                                   |
| HC26     | 1.08                          | 0.27                         | 0.09                           | 0.00                            | 75                   | 4                                    |
| HC31     | 1.11                          | 0.06                         | 0.01                           | 0.00                            | 94                   | 3                                    |
| HC34     | 0.49                          | 0.23                         | 0.07                           | 0.06                            | 58                   | 34                                   |
| M8-3-5   | 1.33                          | 0.09                         | 0.04                           | 0.02                            | 90                   | 4                                    |
| URL12-11 | 8.82                          | 1.44                         | 0.23                           | 0.009                           | 84                   | 1                                    |
| blank    | 0.18                          | 0.00                         | 0.006                          | 0.00                            | 97                   | note                                 |

note: During filtration the water gained 0.18 mg/L DOC.

See Table 2 for sample location.

Table 2

SUMMARY: SIZE DISTRIBUTION OF ORGANIC CARBON IN ATIKOKAN GROUNDWATERS

| BOREHOLE   | DEPTH<br>OR<br>LOCATION | PERCENT DOC AS:    |                      |                        | DISSOLVED<br>(mg/L) | COLLOID<br>1-10NM<br>(mg/L) | COLLOID<br>10-450 NM<br>(mg/L) | SUSPENDED<br>PARTICLES<br>(mg/L) |
|------------|-------------------------|--------------------|----------------------|------------------------|---------------------|-----------------------------|--------------------------------|----------------------------------|
|            |                         | COLLOID<br>1-10 NM | COLLOID<br>10-450 NM | SUSPENDED<br>PARTICLES |                     |                             |                                |                                  |
| ATK-6-8 A  | 398-470 m               | 3                  | 5                    | 1                      | 12.100              | 0.023                       | 0.036                          | 0.005                            |
| ATK-6-8B   | "                       | 6                  | 3                    | 0                      | 10.500              | 0.021                       | 0.013                          | 0                                |
| ATK7-12 A  | 775-957 m               | 1                  | 2                    | 0                      | 4.583               | 0.001                       | 0.002                          | 0                                |
| ATK-7-12 B | "                       | 0                  | 0                    | 0                      | 0.000               | 0                           | 0                              | 0                                |
| ATK-7-12 C | "                       | 0                  | 0                    | 0                      | 0                   | 0                           | 0                              | 0                                |
| ATK-8-14 A | 692-716 m               | 0                  | 0                    | 0                      | 0.000               | 0                           | 0                              | 0                                |
| ATK-8-14 B | "                       | 0                  | 0                    | 0                      | 0.000               | 0                           | 0                              | 0                                |
| BL-ML-3    | river                   | 5                  | 45                   | 6                      | 7.000               | 0.351                       | 3.242                          | 0.436                            |
| ML-9-5 A   | 9 m                     | 1                  | 0                    | 0                      | 65.400              | 0                           | 0.028                          | 0.060                            |
| ML-9-5B    | 9m                      | 1                  | 0                    | 0                      | 65.200              | 0                           | 0.013                          | 0.041                            |
| ML-15-5 A  | <10 m                   | 12                 | 9                    | 0                      | 12.667              | 0.172                       | 0.126                          | 0                                |
| ML-12-5 A  | 10 m                    | 3                  | 10                   | 0                      | 2.222               | 0.009                       | 0.028                          | 0                                |
| ML-3 1 A   | 13 m                    | 9                  | 11                   | 0                      | 2.432               | 0.033                       | 0.044                          | 0                                |
| ML-4-5     | 18 m                    | 8                  | 10                   | 0                      | 1.184               | 0.120                       | 0.135                          | 0                                |
| ML-8-3 A   | 27 m                    | 1                  | 8                    | 0                      | 2.432               | 0.003                       | 0.022                          | 0                                |

TABLE 3

AVERAGE DOC CONCENTRATIONS FOR WRA

| OXIDATION METHOD | SAMPLE NAME | DOC (mg/L)    | n | GROUNDWATER SOURCE |
|------------------|-------------|---------------|---|--------------------|
| P                | B40-1-3     | 19.5          |   | 0- 40 m            |
| P                | B40-2-5     | < 0.1         |   | 41- 60 m           |
| HT               | B34-2       | 12.7 ± 0.1    | 3 | 33- 60             |
| P                | B37-1       | 6.26          |   | 0- 30 m            |
| P                | B37-2       | 5.98          |   | 31- 61 m           |
| HT               | URL10       | 2.15          |   | 54- 120 m          |
| P                | M1B         | 1.86          |   | 51- 150 m          |
| HT               | URL16-4     | 4.10 ± 0.50   | 3 | 77- 112 m          |
| P                | M2B-2-4     | 4.13          |   | 100- 150 m         |
| P                | MF1         | 1.82          |   | 130- 210 m         |
| P                | HC-26-Z1    | 0.49          |   | close to FZ2       |
| P                | URL15-284   | 3.25 ± 3.1    | 2 | 284- 397 m         |
| P                | URL12-11    | * 11.2 ± 0.8  | 3 | 458- 501 m         |
| P                | WB 2-13-4   | 1.00          |   | 365- 394 m         |
| P                | HC-18-Z1    | * 0.88        |   | Fracture Zone 2    |
| P                | GC3A        | * < 0.1       | 2 | Fracture Zone 2    |
| P                | HC5         | * < 0.1       |   | Fracture Zone 2    |
| P                | HC6         | * 1.69 ± 0.90 | 2 | Fracture Zone 2    |
| P                | HC7         | 1.33 ± 0.58   | 3 | Fracture Zone 2    |
| P                | HC7-2       | * 17.6        |   | Fracture Zone 2    |
| P                | HC8         | 0.60 ± 0.38   | 4 | Fracture Zone 2    |
| P                | HC9         | 1.96 ± 0.67   | 3 | Fracture Zone 2    |
| P                | HC11        | * 0.27 ± 0.20 | 2 | Fracture Zone 2    |
| P                | HC12        | * 2.44        |   | Fracture Zone 2    |
| P                | HC13        | * 0.40        |   | Fracture Zone 2    |
| P                | HC15        | 2.14 ± 0.70   | 3 | Fracture Zone 2    |
| P                | HC16        | 0.42 ± 0.21   | 3 | Fracture Zone 2    |
| P                | HC17        | * 13.2 ± 5.5  | 2 | Fracture Zone 2    |
| P                | HC18        | 1.13 ± 0.43   | 4 | Fracture Zone 2    |
| P                | HC19        | 0.18 ± 0.14   | 3 | Fracture Zone 2    |
| P                | HC21        | * 2.00        |   | Fracture Zone 2    |
| P                | HC22        | * 0.62        |   | Fracture Zone 2    |
| P                | HC24        | 0.42          |   | Fracture Zone 2    |
| P                | HC26        | 0.67 ± 0.38   | 4 | Fracture Zone 2    |
| P                | HC27        | * 0.55 ± 0.53 | 3 | Fracture Zone 2    |
| P                | HC28        | 1.61 ± 0.78   | 2 | Fracture Zone 2    |
| P                | HC29        | 0.26 ± 0.25   | 3 | Fracture Zone 2    |
| P                | HC30        | 0.65 ± 0.40   | 3 | Fracture Zone 2    |
| P                | HC31        | 0.60 ± 0.34   | 3 | Fracture Zone 2    |
| P                | HC32        | 0.31 ± 0.28   | 2 | Fracture Zone 2    |
| P                | HC33        | 0.22 ± 0.21   | 3 | Fracture Zone 2    |
| P                | HC34        | 1.15 ± 0.30   | 3 | Fracture Zone 2    |
| P                | HC35        | 0.85 ± 0.30   | 3 | Fracture Zone 2    |
| P                | HC36        | 0.28 ± 0.26   | 2 | Fracture Zone 2    |

continued...



TABLE 3 (concluded)

AVERAGE DOC CONCENTRATIONS FOR WRA

| OXIDATION METHOD | SAMPLE NAME |   | DOC (mg/L)  | n | GROUNDWATER SOURCE   |
|------------------|-------------|---|-------------|---|----------------------|
| P                | HC37        | * | 1.06 ± 0.79 | 3 | Fracture Zone 2      |
| P                | HC38        |   | 0.12 ± 0.07 | 3 | Fracture Zone 2      |
| P                | JE1         | * | 0.96 ± 0.45 | 3 | Fracture Zone 2      |
| P                | M4A-4       |   | 0.70        |   | Fracture Zone 2      |
| P                | M8-3-5      |   | 1.54        |   | Fracture Zone 2      |
| HT               | JE6         |   | 1.50 ± 0.40 | 3 | subvertical fracture |
| P                | HC15-Z3     | * | 8.28 ± 5.60 | 3 | Fracture Zone 1.5    |
| P                | HC16-Z3     |   | 6.30 ± 6.20 | 3 | Fracture Zone 1.5    |
| P                | HC26-Z4     |   | < 0.1       | 2 | Fracture Zone 1.5    |
| P                | M1A-3       |   | 0.70        |   | Fracture Zone 1.5    |
| HT               | M14-4       |   | 1.38 ± 0.06 | 3 | Fracture Zone 1      |
| HT               | M5A         |   | 1.96 ± 0.22 | 3 | Fracture Zone 1      |
| P                | PH-1-Z5-2   | * | 0.24        |   | vertical fracture    |
| P                | PH2-Z8      | * | 3.53 ± 1.49 | 2 | vertical fracture    |
| P                | PH-3-Z2-2   | * | < 0.1       |   | vertical fracture    |
| P                | PH3-Z3      | * | 4.22        |   | vertical fracture    |
| P                | PH3-Z3-25   | * | < 0.1       |   | vertical fracture    |
| P                | PH3-Z4      | * | 1.14 ± 1.09 | 2 | vertical fracture    |
| HT               | PH3-Z5      | * | 7.35        |   | vertical fracture    |
| P                | PH5         |   | < 0.1       |   | vertical fracture    |
| P                | PH-5-Z4-2   |   | 0.08        |   | vertical fracture    |
| P                | PH-5-Z5     |   | 2.02 ± 1.43 | 2 | vertical fracture    |
| P                | PH-5-Z6-2   |   | 1.80        |   | vertical fracture    |
| P                | PH-5-Z7-2   |   | 0.10        |   | vertical fracture    |
| HT               | M7-Z4       |   | 1.10        |   | 351- 400 m saline    |
| HT               | URL12-10    |   | 5.45        |   | 404- 450 m saline    |
| HT               | URL12-13    |   | 2.40 ± 0.10 | 3 | 610 m saline         |
| HT               | WB1-7       | * | 0.30        |   | 1150 m saline        |
| HT               | WB2-19      |   | 2.54        |   | 700 m saline         |
| HT               | WB2-20      |   | 0.25        |   | 975-1025 m saline    |
| HT               | WD3-12      | * | 4.23 ± 0.09 | 4 | 701- 719 m saline    |

P Na persulfate oxidation

HT high temperature oxidation

\* Borehole with low permeability, yielding water at less than 1 L/min, and/or more than 20 percent of DOC is composed of volatile and semivolatile organics.

UFZ2 Nonsaline water above Fracture Zone 2 (FZ2).

BFZ2 Nonsaline water below Fracture Zone 2.

n The number of different samples used to calculate mean DOC concentrations for boreholes with more than one DOC analysis. The standard deviation of the mean has been reported as an error for these boreholes.

TABLE 4

ORGANICS IN SHALLOW GROUNDWATERS

| <b>SAMPLE</b> | <b>LOCATION</b>             | <b>DEPTH<br/>(m)</b> | <b>DOC<br/>(mg/l)</b> | <b>* TOTAL<br/>HUMICS<br/>(mg/L)</b> | <b>HUMICS<br/>% OF<br/>DOC</b> |
|---------------|-----------------------------|----------------------|-----------------------|--------------------------------------|--------------------------------|
| HS10-43       | ATK surface water (stream)  | -                    | 9.6 ± 0.6             | 7.5                                  | 78                             |
| HS1-53        | ATK surface water (stream)  | -                    | 3.9 ± 0.1             | 1.0                                  | 25                             |
| HS6-63        | ATK surface water (stream)  | -                    | 5.1 ± 0.1             | 2.0                                  | 40                             |
| HS7-63        | ATK surface water (stream)  | -                    | 8.0 ± 0.2             | 5.3                                  | 66                             |
| HS8-62        | ATK surface water (stream)  | -                    | 4.7 ± 1.1             | 1.1                                  | 24                             |
| HS9-37        | ATK surface water (stream)  | -                    | 11.3 ± 0.9            | 9.7                                  | 86                             |
| TLS26-CR      | ATK surface water (stream)  | -                    | 2.7 ± 0.0             | 1.2                                  | 46                             |
| PRECIP-4      | WRA collected precipitation | -                    | 1.5 ± 0.2             | 0.0                                  | 0                              |
| BC-195        | WRA surface water (stream)  | -                    | 28.0 ± 0.3            | 28.0                                 | 100                            |
| RC-95         | WRA surface water (stream)  | -                    | 28.9 ± 0.6            | 21.8                                 | 76                             |
| RC-191        | WRA surface water (stream)  | -                    | 30.7 ± 0.4            | 25.3                                 | 82                             |
| O-112-3       | overburden/clay             | 17.3                 | 9.0 ± 0.4             | 0.69                                 | 8                              |
| O-118-2       | overburden/clay             | 4.64                 | 8.7 ± 0.3             | 1.35                                 | 15                             |
| O-106-3       | overburden/clay-silt        | 10.25                | 9.3 ± 0.7             | nd                                   | -                              |
| O-111-2       | bedrock/granite             | 7.78                 | 7.1 ± 1.1             | 2.44                                 | 34                             |
| B24D          | bedrock/granite             | 14.9                 | 4.7 ± 0.6             | 0.03                                 | 1                              |
| O-106-4       | bedrock/granite             | 13.75                | 11.1 ± 0.9            | 1.60                                 | 14                             |
| O-107-2       | bedrock/granite             | 8.69                 | 16.0 ± 0.4            | 2.01                                 | 13                             |
| RI2-1-1       | bedrock/granite             | 45                   | 5.2 ± 0.3             | 0.00                                 | 0                              |
| O-112-2       | bedrock/granite             | 9.7                  | 18.5                  | nd                                   | -                              |

\* Humics determined by absorbance measurements on untreated samples.

**TABLE 5**

**VOLATILE AND SEMIVOLATILE ORGANIC COMPOUNDS IN WRA GROUNDWATERS  
DETERMINED BY GC/MASS SPECTROMETRY**

| SAMPLE<br>(YEAR) | purgeable (P) | COMPOUND<br>solvent extractables (S)                     | mg/L   | TOTAL<br>MEAS.<br>mg/L/mg/L | DOC  |
|------------------|---------------|--|--------|-----------------------------|------|
| HC6<br>1990      | S             | N-Butylbenzenesulfonamide                                | 0.050  | 0.054                       | 2.59 |
|                  | P             | Benzene  | 0.002  |                             |      |
|                  | P             | Toluene  | 0.002  |                             |      |
| HC8<br>1990      | S             | 4,4'-Butylidenebis[2-(1,1-dimethylethyl)]-5-methylphenol | 0.001  | 0.007                       | 1.68 |
|                  | S             | 7-Hexyleicosane  | 0.0005 |                             |      |
|                  | S             | Docosane   | 0.0005 |                             |      |
|                  | S             | unidentified   | 0.005  |                             |      |
| HC13<br>1990     | S             | 2-Ethyl-1-hexanal  | 0.002  | 0.11                        | 0.4  |
|                  | S             | 3-Nitro-1,2-benzene-dicarboxylic acid                    | 0.004  |                             |      |
|                  | S             | Isocyanatobenzene  | 0.004  |                             |      |
|                  | S             | Isothiocyanatobenzene                                    | 0.010  |                             |      |
|                  | S             | Tetramethylthiourea                                      | 0.005  |                             |      |
|                  | S             | Tetramethylurea  | 0.001  |                             |      |
|                  | P             | Benzene  | 0.002  |                             |      |
|                  | P             | Toluene  | 0.086  |                             |      |
| HC15Z3<br>1991   | S             | 1,1-Sulfonylbis-benzene                                  | 0.002  | 19                          | 19   |
|                  | S             | Benzothiazole  | 0.010  |                             |      |
|                  | S             | Chlorophenyl sulfone                                     | 0.700  |                             |      |
|                  | S             | Isocyanatobenzene  | 0.009  |                             |      |
|                  | S             | Isothiocyanatobenzene                                    | 0.020  |                             |      |
|                  | S             | m & p-Cresol   | 0.006  |                             |      |
|                  | S             | Tetramethylthiourea                                      | 0.020  |                             |      |
|                  | S             | N-Propylbenzenesulfonamide                               | 0.100  |                             |      |
|                  | S             | unidentified   | 1.10   |                             |      |
|                  | P             | Benzene  | 0.030  |                             |      |
|                  | P             | Toluene  | 16.82  |                             |      |
| HC16<br>1990     | S             | N-Butylbenzenesulfonamide                                | 0.040  | 0.04                        | 0.67 |
|                  |               |  |        |                             |      |
| HC16<br>1991     | S             | 4-Octanone   | 0.003  | 0.15                        | 0.67 |
|                  | S             | Dipropyleneglycol dibenzoate                             | 0.001  |                             |      |
|                  | S             | Dodecane   | 0.001  |                             |      |
|                  | S             | N-Propylbenzenesulfonamide                               | 0.100  |                             |      |
|                  | S             | unidentified   | 0.05   |                             |      |
| HC23<br>1991     | S             | 1,1-Sulfonylbis-benzene                                  | 0.006  | 3.01                        | -    |
|                  | S             | Benzenamine  | 0.010  |                             |      |
|                  | S             | Chlorophenyl sulfone                                     | 0.500  |                             |      |
|                  | S             | m & p-Cresol   | 0.008  |                             |      |
|                  | S             | N-Butylbenzenesulfonamide                                | 0.100  |                             |      |
|                  | P             | Toluene  | 2.386  |                             |      |

continued...

TABLE 5 (continued)

VOLATILE AND SEMIVOLATILE ORGANIC COMPOUNDS IN WRA GROUNDWATERS  
DETERMINED BY GC/MASS SPECTROMETRY

| SAMPLE<br>(YEAR) | purgeable (P) | COMPOUND<br>solvent extractables (S)                  | mg/L   | TOTAL<br>MEAS.<br>mg/Lmg/L | DOC  |
|------------------|---------------|---|--------|----------------------------|------|
| HC27<br>1990     | P             | Chloroform  | 0.002  | 0.13                       | 0.55 |
|                  | S             | 2-Ethylhexyl diphenyl ester phosphoric acid           | 0.006  |                            |      |
|                  | S             | Bis(2-ethylhexyl) ester 1,2-benzenedicarboxylic acid  | 0.002  |                            |      |
|                  | S             | Tributyl ester phosphoric acid                        | 0.002  |                            |      |
|                  | S             | Triphenyl ester phosphoric acid                       | 0.001  |                            |      |
|                  | S             | Bis(2-ethylhexyl)phthalate                            | 0.107  |                            |      |
|                  | S             | unidentified  | 0.01   |                            |      |
| HC27<br>1991     | S             | Propylbenzenesulfonimide                              | 0.040  | 0.20                       | 0.55 |
|                  | S             | 4-Octanone  | 0.001  |                            |      |
|                  | S             | unknown   | 0.16   |                            |      |
| HC33<br>1990     | S             | 1,1-Dichloropropane                                   | 0.001  | 0.006                      | 0.22 |
|                  | S             | unidentified  | 0.005  |                            |      |
| HC33<br>1991     | S             | Diethyleneglycol dibenzoate                           | 0.001  | 0.03                       | 0.22 |
|                  | S             | Benzylbutyl phthalate                                 | 0.001  |                            |      |
|                  | S             | Bis(2-ethylhexyl)phthalate                            | 0.008  |                            |      |
|                  | S             | N-Butylbenzenesulfonamide                             | 0.020  |                            |      |
| HC34<br>1990     | S             | Isocyanatobenzene                                     | 0.001  | 0.054                      | 1.28 |
|                  | S             | unidentified  | 0.053  |                            |      |
| HC35<br>1990     | S             | 2,3-Dichloro-2-methylbutane                           | 0.001  | 0.003                      | 0.60 |
|                  | S             | Di-n-butylphthalate                                   | 0.002  |                            |      |
| HC37<br>1991     | S             | 1,1-Oxybis-benzene                                    | 0.200  | 1.43                       | 2.64 |
|                  | S             | 1,1-Sulfonylbis-benzene                               | 0.005  |                            |      |
|                  | S             | Chlorophenyl sulfone                                  | 0.700  |                            |      |
|                  | S             | N-Propylbenzenesulfonamide                            | 0.090  |                            |      |
|                  | S             | unidentified  | 0.43   |                            |      |
| HC38<br>1990     | S             | 1,1-Dichloropropane                                   | 0.0006 | 0.001                      | 0.12 |
|                  | S             | Dichloromethane                                       | 0.0003 |                            |      |
| WB1-7<br>1991    | S             | 1-Amino-2-propanal                                    | 0.003  | 0.069                      | 0.30 |
|                  | S             | 1-Dodecanol   | 0.001  |                            |      |
|                  | S             | 1,4,7,10,13,16-Hexaoxacyclooctadecane                 | 0.003  |                            |      |
|                  | S             | 2,2-[1,2-Ethanediybis(oxy)]bis-ethanol                | 0.010  |                            |      |
|                  | S             | 2,2-[Oxybis(2,1-ethanediyloxy)]bis-ethanol            | 0.020  |                            |      |
|                  | S             | 3-Methylheneicosane                                   | 0.003  |                            |      |
|                  | S             | 4-Octanone  | 0.001  |                            |      |
|                  | S             | 5-Octadecene  | 0.003  |                            |      |
|                  | S             | Diethyleneglycol dibenzoate                           | 0.004  |                            |      |
|                  | S             | Dipropyleneglycol dibenzoate                          | 0.002  |                            |      |
|                  | S             | 1,2-Benzenedicarboxylic acid,butyl phenylmethyl ester | 0.004  |                            |      |
|                  | S             | Benzyl butyl phthalate                                | 0.001  |                            |      |
|                  | S             | Bis(2-ethylhexyl)phthalate                            | 0.014  |                            |      |

continued...

TABLE 5 (concluded)

VOLATILE AND SEMIVOLATILE ORGANIC COMPOUNDS IN WRA GROUNDWATERS  
DETERMINED BY GC/MASS SPECTROMETRY

| SAMPLE<br>(YEAR) | purgeable (P) | COMPOUND<br>solvent extractables (S)      | mg/L   | TOTAL<br>MEAS.<br>mg/Lmg/L | DOC   |
|------------------|---------------|---|--------|----------------------------|-------|
| HC29<br>1990     | S             | 2,3-Dichloro-2-methylbutane               | 0.0004 | 0.00                       | 0.26  |
| URL10<br>1992    | S             | 2,6,10,14-Tetramethylhexadecane           | 0.002  | 0.054                      | 2.15  |
|                  | S             | Cyclohexadecane                           | 0.001  |                            |       |
|                  | S             | Diethyleneglycol dibenzoate               | 0.004  |                            |       |
|                  | S             | Docosane                                  | 0.003  |                            |       |
|                  | S             | 2,2'-[1,2-Ethanediy]bis(oxy)}bis-ethanol, | 0.002  |                            |       |
|                  | S             | Heptacosane                               | 0.004  |                            |       |
|                  | S             | Dimethyl phthalate                        | 0.001  |                            |       |
|                  | S             | Benzyl butyl phthalate                    | 0.0003 |                            |       |
|                  | S             | Bis(2-ethylhexyl)phthalate                | 0.001  |                            |       |
|                  | S             | Bis(2-methylpropyl)phthalate              | 0.002  |                            |       |
|                  | S             | Butyl 2-ethylhexyl phthalate              | 0.011  |                            |       |
|                  | S             | Butyl phenylmethyl phthalate              | 0.002  |                            |       |
|                  | S             | Dibutyl phthalate                         | 0.003  |                            |       |
|                  | S             | Diheptyl phthalate                        | 0.003  |                            |       |
|                  | S             | Di-n-butyl phthalate                      | 0.0005 |                            |       |
|                  | S             | Hexyl decyl phthalate                     | 0.004  |                            |       |
|                  | S             | Isodecyl octyl phthalate                  | 0.007  |                            |       |
| PH5-Z6<br>1990   | S             | Isocyanatobenzene                         | 0.000  | 0.04 1                     | 1.80  |
|                  | S             | N-Propylbenzenesulfonamide                | 0.040  |                            |       |
|                  | S             | 1,1'-Sulfonylbisbenzene                   | 0.001  |                            |       |
| PH3-Z5<br>1990   | S             | 1,1'-Sulfonylbisbenzene                   | 0.030  | 1.12                       | 7.35  |
|                  | S             | 1-Phenylethanone                          | 0.003  |                            |       |
|                  | S             | N,N-Diethylformamide                      | 0.005  |                            |       |
|                  | P             | Toluene                                   | 0.051  |                            |       |
|                  | S             | N-Butyl-4-methyl benzenesulfonamide       | 0.003  |                            |       |
|                  | S             | N-butylbenzenesulfonamide                 | 1.000  |                            |       |
|                  | S             | N-Ethyl-4-methyl benzenesulfonamide       | 0.009  |                            |       |
|                  | S             | unidentified                              | 0.02   |                            |       |
| GC3A<br>1990     | P             | Toluene                                   | 0.014  | 0.01                       | <0.10 |
| GC3A-Z1          | P             | Toluene                                   | 0.963  | 0.96                       | 1.45  |
|                  | P             | Benzene                                   | 0.001  |                            |       |

No compounds were detected in samples HC26 (1990, 1992), HC 29 (1990), HC33 (1992) and PH3-Z4

**TABLE 6**

**CONTRIBUTION OF VOLATILE AND SEMIVOLATILE ORGANIC COMPOUNDS  
TO THE OBSERVED DOC OF WRA GROUNDWATER SAMPLES**

| SAMPLE & YEAR | TOTAL MEASURED VOLATILES & SEMIVOLATILES (mg/L) | DOC (mg/L) | PERCENT OF DOC | PRINCIPLE TYPE OF VOLATILE OR SEMIVOLATILE |
|---------------|---|------------|----------------|--|
| HC26-90, 92   | 0.000   | * 0.67     | 0.0            |  |
| HC29-90       | 0.000   | * 0.26     | 0.0            |  |
| HC33-92       | 0.000   | * 0.22     | 0.0            |  |
| HC38-90       | 0.001   | * 0.12     | 0.8            | hydrocarbons                               |
| HC35-90       | 0.003   | 0.60       | 0.5            | plasticizers                               |
| HC8-90        | 0.007   | 1.68       | 0.4            | unknown, hydrocarbons                      |
| PH3-Z4-90     | 0.010   | < 0.1      |                | unknown                                    |
| GC3A-91       | 0.014   | * < 0.1    |                | Toluene                                    |
| HC33-90       | 0.006   | * 0.22     | 3              | unknown                                    |
| HC33-91       | 0.030   | * 0.22     | 14             | plasticizers                               |
| HC16-90       | 0.040   | 0.67       | 6              | plasticizers                               |
| M4A           | 0.040   | 0.70       | 6              | unknown                                    |
| PH5-Z6-90     | 0.041   | 1.80       | 2              | plasticizers                               |
| HC6-90        | 0.054   | 2.59       | 2              | plasticizers LP                            |
| URL10-92      | 0.054   | 2.15       | 3              | plasticizers                               |
| HC34-90       | 0.054   | 1.28       | 4              | unknown                                    |
| WB1-7-91      | 0.069   | 0.30       | 23             | plasticizers                               |
| HC13-90       | 0.11  | 0.40       | 28             | Toluene, alcoholsLP                        |
| HC16-91       | 0.15  | 0.67       | 22             | plasticizers                               |
| HC27-90       | 0.13  | * 0.55     | 24             | plasticizers                               |
| HC27-91       | 0.20  | * 0.55     | 37             | unknown, plasticizers                      |
| GC3A-Z1-90    | 0.96  | 1.45       | 66             | Toluene                                    |
| PH3-Z5-90     | 1.12  | 7.35       | 15             | plasticizers LP                            |
| HC37-91       | 1.43  | 2.64       | 54             | Chlorophenyl sulfone,LP                    |
|               |   |            |                | Benzene, unknown                           |
| HC15-Z3-91    | 19  | 19         | 100            | Toluene LP                                 |

The total measured volatiles and semivolatiles includes estimated concentrations for "unknown compounds", whose peaks could not be matched to compounds in the database.

\* This DOC value is an average for the borehole. The other DOC values were determined for the characterized samples.

LP Low permeability borehole, yielding water at less than 1 L/min.

TABLE 7

VOLATILE AND SEMIVOLATILE ORGANICS IN ATIKOKAN GROUNDWATERS

| SAMPLE  | COMPOUND      |                                     | mg/L   | TOTAL            | OBSERVED<br>DOC |
|---------|---------------|-------------------------------------|--------|------------------|-----------------|
|         | purgeable (P) | solvent extractable (S)             |        | MEASURED<br>mg/L |                 |
| ATK-6-8 | S             | Isocyanatocyclohexane               | 0.003  | 0.06             | 12.1            |
|         | S             | N-propylbenzenesulfonamide          | 0.03   |                  |                 |
|         | S             | unidentified peak                   | 0.006  |                  |                 |
|         | S             | unidentified peak                   | 0.001  |                  |                 |
|         | S             | unidentified peak                   | 0.004  |                  |                 |
|         | S             | unidentified peak                   | 0.01   |                  |                 |
|         | S             | unidentified peak                   | 0.004  |                  |                 |
|         | P             | Chloroform                          | 0.006  |                  |                 |
| ATK-8   | S             | unidentified peak                   | 0.005  | 0.02             | < 0.10          |
|         | S             | unidentified peak                   | 0.01   |                  |                 |
|         | S             | unidentified peak                   | 0.003  |                  |                 |
| ML-3-1  | S             | no peaks                            | 0      | 0.00             | 2.43            |
| ML-8-3  | S             | unidentified peak                   | 0.06   | 0.06             | 2.43            |
| ML-9-5  | S             | Pentanoic acid                      | 0.04   | 0.18             | 65.4            |
|         | S             | 2-Ethyl-1-hexanol                   | 0.04   |                  |                 |
|         | S             | Hexanoic acid                       | 0.04   |                  |                 |
|         | S             | m + p Cresol                        | 0.009  |                  |                 |
|         | S             | Heptanoic acid                      | 0.009  |                  |                 |
|         | S             | Benzothiazole                       | 0.004  |                  |                 |
|         | S             | Benzeneacetic acid                  | 0.002  |                  |                 |
|         | S             | 1,3-Isobenzofurandione              | 0.0007 |                  |                 |
|         | S             | 1-Methyl-4-(methylsulfonyl)-benzene | 0.003  |                  |                 |
|         | S             | 2-(Methylthio)benzothiozole         | 0.001  |                  |                 |
|         | S             | Caffeine                            | 0.006  |                  |                 |
|         | S             | unidentified peak                   | 0.001  |                  |                 |
|         | S             | unidentified peak                   | 0.005  |                  |                 |
|         | S             | unidentified peak                   | 0.002  |                  |                 |
|         | S             | unidentified peak                   | 0.007  |                  |                 |
|         | S             | unidentified peak                   | 0.004  |                  |                 |
|         | S             | unidentified peak                   | 0.005  |                  |                 |
|         | S             | unidentified peak                   | 0.001  |                  |                 |
| ML-12-5 | S             | N-butylbenzenesulfonamide           | 0.02   | 0.02             | 2.22            |
|         | S             | unidentified peak                   | 0.001  |                  |                 |
| BC-ML-3 | S             | unidentified peak                   | 0.001  | 0.00             | 7.00            |

**TABLE 8**

**SUMMARY OF HUMICS ISOLATED FROM WRA GROUNDWATERS**

| BOREHOLE             | LOCATION                         | RESIN      | DEPTH<br>meters | FULVIC ACID<br>mg/l in gw | TOTAL HUMICS<br>mg/l in gw | %HA of<br>TOTAL<br>HUMIC | DOC<br>(mg/L) | TOTAL<br>HUMICS<br>% of DOC |
|----------------------|----------------------------------|------------|-----------------|---------------------------|----------------------------|--------------------------|---------------|-----------------------------|
| Winnipeg R. 92 March | WL                               | DEAE       |                 | 1.457                     | 1.91                       | 24                       | 13.3          | 14                          |
| 0-106-3              | overburden/clay-silt             | XAD        | 10.25           | 1.828                     | 1.828                      | 0                        | 9.3           | 20                          |
| 0-107-1              | overburden/clay-silt             | XAD        | 5.7             | 1.12                      | 1.37                       | 18                       | 49.4          | 3                           |
| 0-112-3              | overburden/clay                  | XAD        | 17.3            | 0.956                     | 0.956                      | 0                        | 7.8           | 12                          |
| 0-106-4              | bedrock/granite                  | XAD        | 13.75           | 1.18                      | 1.18                       | 0                        | 10            | 12                          |
| 0-107-2              | bedrock/granite                  | XAD        | 8.69            | 1.68                      | 1.94                       | 13                       | 9.9           | 20                          |
| 0-111-2              | bedrock/granite                  | XAD        | 7.78            | 3.034                     | 3.114                      | 3                        | 11            | 28                          |
| 0-112-2              | bedrock/granite                  | XAD        | 9.7             | 2.3                       | 6.49                       | 65                       | 18.5          | 35                          |
| B34                  | bedrock/granite (discharge zone) | DEAE       | 33-60           | 0.063                     | 0.139                      | 55                       | 12.7          | 1                           |
| R12-1-1              | bedrock/granite                  | XAD        | 45              | 0.4875                    | 0.492                      | 1                        | 9.6           | 5                           |
| A-96-1-25            | URL shaft                        | XAD        | 100             | nd                        | 3.57                       | nd                       | 7.3           | 49                          |
| E-96-1-24            | URL shaft                        | XAD        | 20 to 150       | nd                        | 4.93                       | nd                       | 7.7           | 64                          |
| F-96-1-25            | URL shaft                        | XAD        | 10              | nd                        | 0.88                       | nd                       | 4.8           | 18                          |
| G-96-1-24            | URL shaft                        | XAD        | 140             | nd                        | 0.6                        | nd                       | 2.7           | 22                          |
| H-96-1-24            | URL shaft                        | XAD        | 90              | nd                        | 0.96                       | nd                       | 4.8           | 20                          |
| MF1A                 | above FZ2                        | XAD        | 130-210         | 0.21                      | 0.255                      | 18                       | 1.82          | 14                          |
| MF1B                 | above FZ2                        | DEAE       | 130-210         | 0.278                     | 0.327                      | 15                       | 1.82          | 18                          |
| URL10                | above FZ2                        | DEAE       | 54-120          | 0.451                     | 0.488                      | 8                        | 2.15          | 23                          |
| HC15                 | fracture zone 2                  | XAD        | FZ2             | 0.021                     | 0.049                      | 57                       | 2.1           | 2                           |
| HC17                 | fracture zone 2                  | XAD        | FZ2             | 0.364                     | 0.394                      | 8                        | 13.2          | 3                           |
| HC19                 | fracture zone 2                  | DEAE       | FZ2             | 0.077                     | 0.077                      | 0                        | 0.18          | 43                          |
| HC21                 | fracture zone 2                  | XAD        | FZ2             | 1.289                     | 1.32                       | 2                        | 2             | 66                          |
| HC26 A               | fracture zone 2                  | DEAE       | FZ2             | 0.084                     | 0.084                      | 0                        | 0.67          | 13                          |
| HC26 B               | fracture zone 2                  | XAD        | FZ2             | nd                        | 0.423                      | nd                       | 0.67          | 63                          |
| HC33                 | fracture zone 2                  | DEAE       | FZ2             | 0.081                     | 0.09                       | 10                       | 0.83          | 11                          |
| HC34                 | fracture zone 2                  | DEAE       | FZ2             | 0.11                      | 0.118                      | 7                        | 1.15          | 10                          |
| HC9                  | fracture zone 2                  | XAD        | FZ2             | 0.282                     | 0.339                      | 17                       | 2.0           | 17                          |
| M14-4                | fracture zone 1                  | DEAE       | FZ1             |                           |                            |                          | 1.38          | 0                           |
| M5A                  | fracture zone 1                  | XAD        | FZ1             | 0.492                     | 0.492                      | 0                        | 1.96          | 25                          |
| M1A-3                | fracture zone 1.5                | DEAE       | 241-342         | 0.274                     | 0.301                      | 9                        | 0.7           | 43                          |
| WD3-12A              | deep saline                      | XAD        | 701-719         | nd                        | 0.5                        | nd                       | 4.23          | 12                          |
| WD3-12B              | deep saline                      | XAD        | 701-719         | nd                        | 0.22                       | nd                       | 4.23          | 5                           |
| JE6                  | subvertical fracture (URL)       | DEAE       |                 | 0.127                     | 0.127                      | 0                        | 1.5           | 8                           |
| URL-12-11-4-92A      | below FZ2 458-501m               | AD archive | 458-501         | nd                        | 3.75                       | nd                       | 11.2          | 33                          |
| URL 12-13            | saline                           | DEAE       | 550-570         | 0.035                     | 0.066                      | 47                       | 2.4           | 3                           |
| URL16-24             | FZ3                              | XAD        | 77-112          | 0.2069                    | 0.384                      | 46                       | 4.1           | 9                           |
| BLANK                | -                                | XAD        |                 | nd                        | 0.002                      | nd                       | 0             | -                           |
| BLANK                | -                                | DEAE       |                 | nd                        | 0.0002                     | nd                       | 0             | -                           |



TABLE 9

ORGANIC CARBON FRACTIONATION

| SAMPLE |          | HYDROPHOBIC |      |         | HYDROPHILIC |       |         |
|--------|----------|-------------|------|---------|-------------|-------|---------|
|        |          | ACID        | BASE | NEUTRAL | ACID        | BASE  | NEUTRAL |
| MF1    | mg/L C   | 0.26        | 0.04 | trace   | 0.16        | 0.004 | 1.37    |
|        | % of DOC | 14          | 2.3  |         | 8.7         | 0.2   | 75      |
| HC9    | mg/L C   | 0.34        | 0.03 |         | 0.42        | 0.03  | 1.14    |
|        | % of DOC | 17          | 1.5  |         | 22          | 1.6   | 58      |

TABLE 10

TYPES OF ORGANIC COMPOUNDS SEPARATED BY THE FRACTIONATION OF DISSOLVED ORGANIC CARBON (AFTER TAKATS 1992)

| Fraction            | Compounds   |
|---------------------|---|
| Hydrophobic Acid    | <ul style="list-style-type: none"> <li>- humic and fulvic acid</li> <li>- aliphatic carboxylic acids with 5 to 9 carbons</li> <li>- 1- and 2-ring aromatic carboxylic acids</li> <li>- 1- and 2-ring phenols</li> </ul>   |
| Hydrophobic Base    | <ul style="list-style-type: none"> <li>- 1- and 2-ring aromatic amines</li> </ul>   |
| Hydrophobic Neutral | <ul style="list-style-type: none"> <li>- hydrocarbons</li> <li>- aliphatic amides, ketones, alcohols, esters and aldehydes with more than 5 carbons</li> <li>- aliphatic carboxylic acids and amines with more than 9 carbons</li> <li>- aromatic carboxylic acids and amines with 3 or more rings</li> </ul> |
| Hydrophilic Acid    | <ul style="list-style-type: none"> <li>- aliphatic acids with 5 or less carbons</li> <li>- polyelectrolytic acids with hydroxy and carboxylic functional groups</li> </ul>  |
| Hydrophilic Base    | <ul style="list-style-type: none"> <li>- aliphatic amines with 9 or less carbons</li> <li>- amino acids</li> <li>- pyridine</li> </ul>  |
| Hydrophilic Neutral | <ul style="list-style-type: none"> <li>- aliphatic amides, alcohols, aldehydes, esters and ketones with 5 or less carbons</li> <li>- polyfunctional alcohols and carbohydrates</li> </ul>   |

TABLE 11

FUNCTIONAL GROUPS IN HUMIC SUBSTANCES DETERMINED BY  
ACID/BASE TITRATION GIVEN AS meq/g ORGANIC CARBON

| SAMPLE  | EXTRACTION METHOD | carboxyl (meq/g) | B-carbonyls, enols alcohols (meq/g) | phenolic acid (meq/g) |
|---------|-------------------|------------------|-------------------------------------|-----------------------|
| HC21    | XAD               | 4.1 ± 0.4        | 2.16 ± 1.3                          | 9.3 ± 2.7             |
| JE6     | DEAE              | 4.4 ± 0.3        | 0.23 ± 0.0                          | 4.6 ± 0.2             |
| HC19    | DEAE              | 6.1 ± 1.8        | 1.12 ± 0.5                          | 3.5 ± 0.3             |
| 107-2   | XAD               | 6.4 ± 0.9        | 2.89 ± 0.5                          | 4.3 ± 2.9             |
| 106-3   | XAD               | 7.4 ± 2.6        | 3.28 ± 0.8                          | 11.2 ± 3.8            |
| 107-1   | XAD               | 7.5 ± 2.2        | 0.39 ± 0.2                          | 6.0 ± 1.8             |
| HC26    | XAD               | 7.6 ± 0.3        | ±                                   | ±                     |
| 106-4   | XAD               | 8.2 ± 0.7        | 2.92 ± 0.9                          | 1.5 ± 8.0             |
| 111-2   | XAD               | 9.6 ± 0.3        | 1.01 ± 0.4                          | 3.9 ± 2.1             |
| URL12   | DEAE              | 9.7 ± 2.4        | 4.59 ± 0.4                          | 14.3 ± 0.0            |
| B34     | DEAE              | 10.1 ± 1.2       | 0.38 ± 0.3                          | 6.6 ± 1.5             |
| HC17    | XAD               | 10.4 ± 2.8       | 3.42 ± 2.1                          | 0.0 ± 4.9             |
| RI-21-1 | XAD               | 12.0 ± 4.1       | 4.76 ± 2.6                          | 19.5 ± 4.8            |
| HC33    | DEAE              | 12.0 ± 2.1       | 3.71 ± 2.9                          | 13.5 ± 0.9            |
| HC15    | DEAE              | 7.1 ± 0.1        | 0.9 ± 0.1                           | 4.6 ± 0.2             |
| WD3-12  | XAD               | 6.1 ± 0.7        | 0.70 ± 0.1                          | 5.4 ± 0.1             |
| MF1     | XAD               | 3.2 ± 0.3        | 0.3 ± 0.0                           | 0.7 ± 0.1             |
| HC9     | DEAE              | 6.7 ± 0.8        | 0.8 ± 0.4                           | 3.0 ± 1.3             |
| HC9     | XAD               | 7.4 ± 0.4        | 0.6 ± 0.1                           | 13.7 ± 1.3            |
| HC9     | PIA               | 13.0 ± 3.0       | 0.80 ± 0.1                          | 7.7 ± 0.5             |

The errors in functional group concentrations were derived from the goodness of fit between the calculated discrete affinity spectrum model and the titration data.

XAD: hydrophobic acids extracted by XAD-8 resin  
 DEAE: organic acids extracted by DEAE cellulose resin  
 PIA: hydrophilic acids

TABLE 12

CARBON-14 AGES OF HUMIC SUBSTANCES ISOLATED  
FROM WRA GROUNDWATERS

| BOREHOLE  | LOCATION                   | RESIN USED<br>FOR<br>ISOLATION | WEIGHT USED<br>IN ANALYSIS<br>(mg) | AGE<br>(YEARS BP) |
|-----------|----------------------------|--------------------------------|------------------------------------|-------------------|
| B34       | bedrock/granite            | DEAE                           | 40                                 | 4270 ± 130        |
| HC15      | fracture zone 2            | XAD                            | 8                                  | 6220 ± 280        |
| JES       | subvertical fracture (UFL) | DEAE                           | 47                                 | 3590 ± 130        |
| UFL 12-13 | saline 610 m               | DEAE                           | 80                                 | 4120 ± 90         |

Reported error represents 68.3 % confidence limits.

TABLE 13

SELECTED STABILITY CONSTANTS FOR ACTINIDE HUMIC ACID  
AND FULVIC ACID COMPLEXES: HUMIC ACID = HA;  
FULVIC ACID = FA;  $\beta_1$  REFERS TO 1:1 COMPLEX  
AND  $\beta_2$  REFERS TO 1:2 COMPLEX

| Ion                           | Ligand   | Log $\beta_1$   | Log $\beta_2$    | pH        | Ionic Strength (M) | Reference                          |
|-------------------------------|----------|-----------------|------------------|-----------|--------------------|------------------------------------|
| Am <sup>3+</sup>              | @ HA     | <b>6.4</b>      | <b>10.6</b>      | 6.5       | -                  | Yamamoto and Sakanoue 1982         |
|                               | @ HA     | <b>6.8-11.6</b> | <b>11.9-14.3</b> | 3.8-5.7   | 0.1                | Torres and Choppin 1984            |
|                               | @ HA     | <b>6.1</b>      |                  | 6         | 0.1                | Kim et al. 1990                    |
|                               | HA<br>FA | 13.2<br>6.2     | 14.7             | >7<br>4.7 | -<br>0.1           | Choppin 1988<br>Moulin et al. 1988 |
| Th <sup>4+</sup>              | @ HA     | <b>16.8</b>     | <b>22</b>        | >7        | -                  | Choppin 1988                       |
|                               | HA       | 10.7-13.2       | 15.8-18.4        | 4-5       | 0.1                | Nash and Choppin 1980              |
|                               | FA       | 9.8-10.8        | 13.5-15.1        | 4-5       | 0.1                | Nash and CHoppin 1980              |
|                               | @ FA     | <b>7</b>        |                  | 6.5       |                    | Norden et al. 1993                 |
| NpO <sub>2</sub> <sup>+</sup> | @ HA     | <b>4.6</b>      |                  | 7.0       | 0.1                | Moulin et al. 1993                 |
| UO <sub>2</sub> <sup>2+</sup> | @ HA     | <b>10</b>       | <b>13.2</b>      | >7        | -                  | Choppin 1988                       |
|                               | @ HA     | <b>6.5</b>      |                  | 4.5       | 0.01               | Giesy et al. 1986                  |
|                               | HA       | 6.7/4.7*        |                  | 6         | 0.01               | Li et al. 1980                     |
|                               | FA       | 7.4/5.6*        |                  | 6         | 0.01               | Li et al. 1980                     |
|                               | @ FA     | <b>4.5</b>      | <b>9.6</b>       | 4         | 0.1                | Munier-Lamy et al. 1986            |

@ Stability constants selected to calculate complexed ratios in Table 14, with selected values in bold. The constants were chosen to reflect the wide range of values reported in the literature.

\* Two 1:1 complexes of different strength were modelled.

**TABLE 14**

**ORGANIC COMPLEXES**

**RATIOS OF COMPLEXED TO FREE ACTINIDE IONS IN A GROUNDWATER WITH A TYPICAL COMPOSITION FOUND IN FRACTURE ZONE 2**  
 **$\beta_1$  REFERS TO 1:1 COMPLEX AND  $\beta_2$  REFERS TO 1:2 COMPLEX**

**WEAKER COMPLEXING CONSTANTS**

Am: log B1 = 6.4      Am: log B2 = 10.6  
 Th: log B1 = 7      Th: log B2 = 0  
 Np: log B1 = 4.6  
 U: log B1 = 4.5      U: log B2 = 9.6

| humic concentration | Am (IV) [ML]/[M] | Am (IV) [ML <sup>2</sup> ]/[M] | Th (IV) [ML]/[M] | Th (IV) [ML <sup>2</sup> ]/[M] | Np (V) [ML]/[M] | U (VI) [ML]/[M] | U (VI) [ML <sup>2</sup> ]/[M] |
|---------------------|------------------|--------------------------------|------------------|--------------------------------|-----------------|-----------------|-------------------------------|
| 0.05                | 2.5E+00          | 4.1E-02                        | 1.0E+01          | -                              | 4.0E-02         | 3.2E-02         | 4.1E-03                       |
| 0.15                | 7.6E+00          | 3.7E-01                        | 3.0E+01          | -                              | 1.2E-01         | 9.6E-02         | 3.7E-02                       |
| 0.32                | 1.6E+01          | 1.7E+00                        | 6.5E+01          | -                              | 2.6E-01         | 2.1E-01         | 1.7E-01                       |
| 0.5                 | 2.5E+01          | 4.1E+00                        | 1.0E+02          | -                              | 4.0E-01         | 3.2E-01         | 4.1E-01                       |
| 1                   | 5.1E+01          | 1.6E+01                        | 2.0E+02          | -                              | 8.1E-01         | 6.4E-01         | 1.6E+00                       |
| 2                   | 1.0E+02          | 6.6E+01                        | 4.1E+02          | -                              | 1.6E+00         | 1.3E+00         | 6.6E+00                       |
| 3                   | 1.5E+02          | 1.5E+02                        | 6.1E+02          | -                              | 2.4E+00         | 1.9E+00         | 1.5E+01                       |
| 6.5                 | 3.3E+02          | 6.9E+02                        | 1.3E+03          | -                              | 5.3E+00         | 4.2E+00         | 6.9E+01                       |
| 10                  | 5.1E+02          | 1.6E+03                        | 2.0E+03          | -                              | 8.1E+00         | 6.4E+00         | 1.6E+02                       |

**STRONGER COMPLEXING CONSTANTS**

Am: log B = 11.6      Am: log B2 = 14.3  
 Th: log B = 16.8      Th: log B2 = 22  
 Np: log B = 4.6  
 U: log B = 10      U: log B2 = 13.2

| humic concentration | Am (IV) [ML]/[M] | Am (IV) [ML <sup>2</sup> ]/[M] | Th (IV) [ML]/[M] | Th (IV) [ML <sup>2</sup> ]/[M] | Np (V) [ML]/[M] | U (VI) [ML]/[M] | U (VI) [ML <sup>2</sup> ]/[M] |
|---------------------|------------------|--------------------------------|------------------|--------------------------------|-----------------|-----------------|-------------------------------|
| 0.05                | 4.0E+05          | 2.1E+02                        | 6.4E+10          | 1.0E+10                        | 4.0E-02         | 1.0E+04         | 1.6E+01                       |
| 0.15                | 1.2E+06          | 1.9E+03                        | 1.9E+11          | 9.3E+10                        | 1.2E-01         | 3.0E+04         | 1.5E+02                       |
| 0.32                | 2.6E+06          | 8.4E+03                        | 4.1E+11          | 4.2E+11                        | 2.6E-01         | 6.5E+04         | 6.7E+02                       |
| 0.5                 | 4.0E+06          | 2.1E+04                        | 6.4E+11          | 1.0E+12                        | 4.0E-01         | 1.0E+05         | 1.6E+03                       |
| 1                   | 8.1E+06          | 8.2E+04                        | 1.3E+12          | 4.1E+12                        | 8.1E-01         | 2.0E+05         | 6.5E+03                       |
| 2                   | 1.6E+07          | 3.3E+05                        | 2.6E+12          | 1.6E+13                        | 1.6E+00         | 4.1E+05         | 2.6E+04                       |
| 3                   | 2.4E+07          | 7.4E+05                        | 3.8E+12          | 3.7E+13                        | 2.4E+00         | 6.1E+05         | 5.9E+04                       |
| 6.5                 | 5.3E+07          | 3.5E+06                        | 8.3E+12          | 1.7E+14                        | 5.3E+00         | 1.3E+06         | 2.8E+05                       |
| 10                  | 8.1E+07          | 8.2E+06                        | 1.3E+13          | 4.1E+14                        | 8.1E+00         | 2.0E+06         | 6.5E+05                       |

[organic] Total organic complexing capacity (Eq/L) based on the carboxylic functional group concentration in hydrophobic and hydrophilic acids.

TABLE 15

**INORGANIC COMPLEXES**

**RATIOS OF COMPLEXED TO FREE ACTINIDE IONS IN A GROUNDWATER  
WITH A TYPICAL COMPOSITION FOUND IN FRACTURE ZONE 2  
β<sub>1</sub> REFERS TO 1:1 COMPLEX AND β<sub>2</sub> REFERS TO 1:2 COMPLEX**

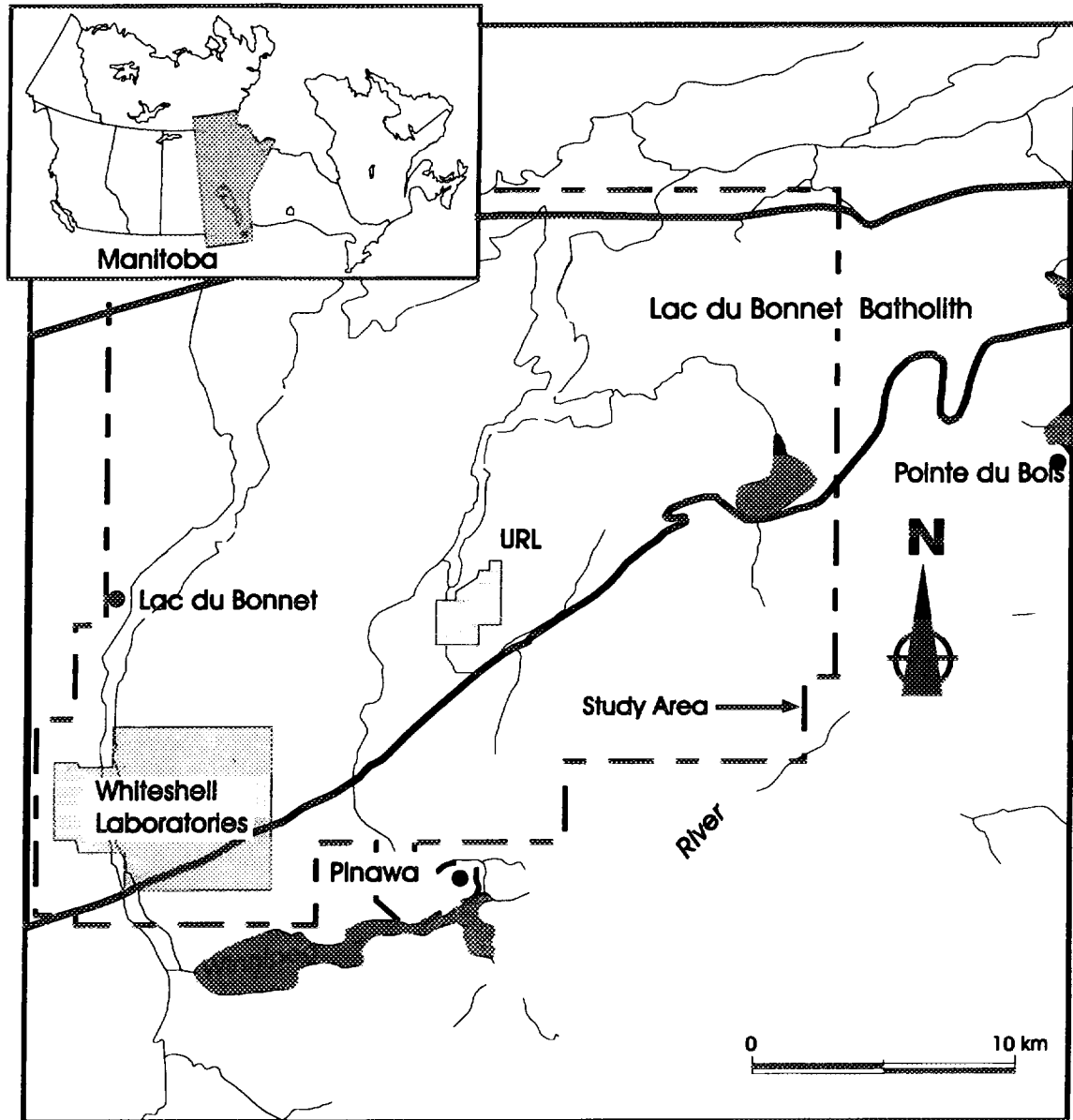
| ELEMENT | pH  | LIGAND | LOG B1 | LOG B2 | [ML]/[M] | [ML2]/[M] |
|---------|-----|--------|--------|--------|----------|-----------|
| Am(III) | 6   | OH     | -7*    | -15.3* | 1.0E-01  | 5.0E-04   |
|         | 7   |        |        |        | 1.0E+00  | 5.0E-02   |
|         | 8   |        |        |        | 1.0E+01  | 5.0E+00   |
|         | 8.5 |        |        |        | 3.2E+01  | 5.0E+01   |
|         | 6   | CO3    | 6.3    | 10.1   | 1.0E-01  | 3.2E-05   |
|         | 7   |        |        |        | 2.5E+00  | 2.0E-02   |
|         | 8   |        |        |        | 3.0E+01  | 2.8E+00   |
|         | 8.5 |        |        |        | 9.4E+01  | 2.8E+01   |
| Th(IV)  | 6   | OH     | -3.2*  | -6.9*  | 6.3E+02  | 1.3E+05   |
|         | 7   |        |        |        | 6.3E+03  | 1.3E+07   |
|         | 8   |        |        |        | 6.3E+04  | 1.3E+09   |
|         | 8.5 |        |        |        | 2.0E+05  | 1.3E+10   |
| Np (V)  | 6   | OH     | -11.6* | -23*   | 2.5E-06  | 1.0E-11   |
|         | 7   |        |        |        | 2.5E-05  | 1.0E-09   |
|         | 8   |        |        |        | 2.5E-04  | 1.0E-07   |
|         | 8.5 |        |        |        | 7.9E-04  | 1.0E-06   |
|         | 6   | CO3    | 4.3    | 6.3    | 1.0E-03  | 5.1E-09   |
|         | 7   |        |        |        | 2.5E-02  | 3.2E-06   |
|         | 8   |        |        |        | 3.0E-01  | 4.4E-04   |
|         | 8.5 |        |        |        | 9.4E-01  | 4.4E-03   |
| U(VI)   | 6   | CO3    | 10.1   | 17.1   | 6.4E+02  | 3.2E+02   |
|         | 7   |        |        |        | 1.6E+04  | 2.0E+05   |
|         | 8   |        |        |        | 1.9E+05  | 2.8E+07   |
|         | 8.5 |        |        |        | 5.9E+05  | 2.8E+08   |
|         |     | F      | 9      |        | 2.0E+05  |           |

$$[\text{CO}_3^{2-}] = 5.7 \times 10^{-5} \text{ mol/L.}$$

$$[\text{F}^-] = 2 \times 10^{-4} \text{ mol/L.}$$

\* Stability constant for:  $\text{M}^{n+} + i\text{H}_2\text{O} = \text{M}(\text{OH})_i^{(n-i)+} + i\text{H}^+$ .

A typical pH in Fracture Zone 2 is 8.5. The effect of pH is shown for pH sensitive anions to account for lower pH values found in shallower (7.4 to 8.9) and deeper (6.1 to 7.7) groundwaters.



**FIGURE 1:** Location of the Whiteshell Research Area (Dotted Line), Including the Whiteshell Laboratories and the URL, Which Is the Location for Most of the Groundwater Sampling. The area is located north-east of Winnipeg, Manitoba, Canada.

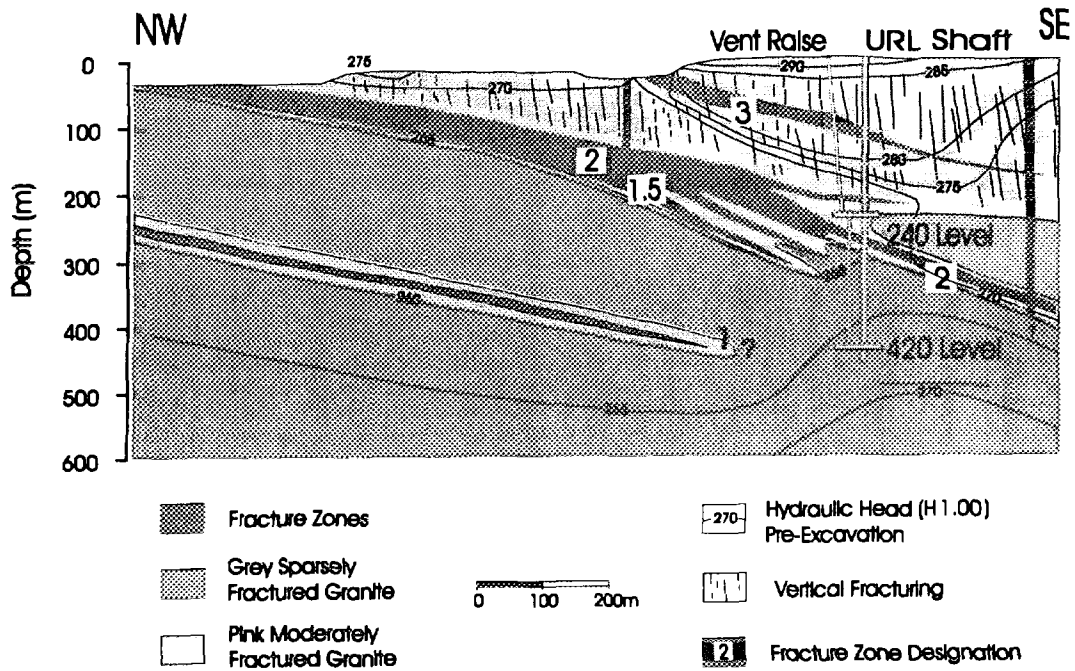
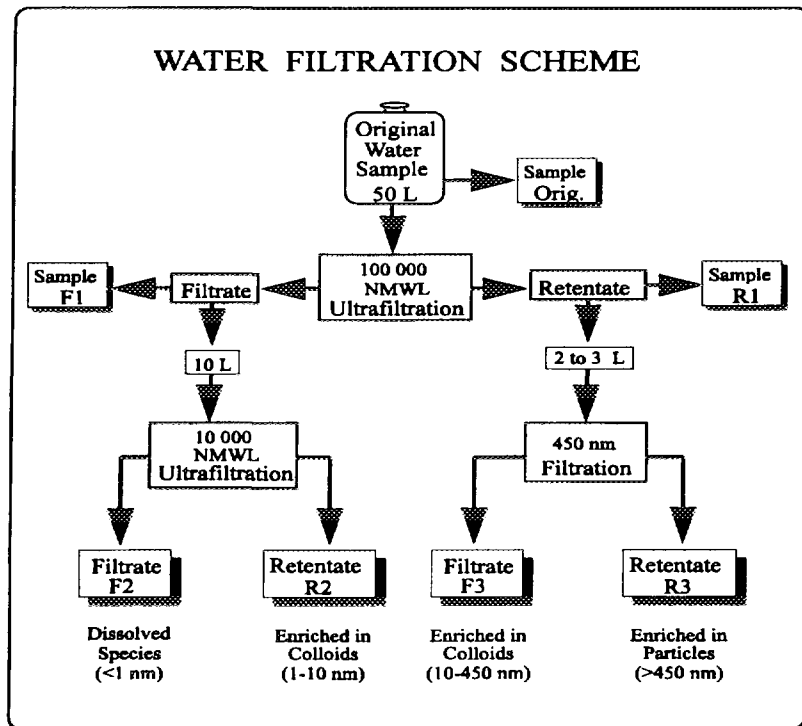


FIGURE 2: Geological Cross Section Showing the Main Subhorizontal Fracture Zones and the Vertical Fracturing in the Vicinity of the Underground Research Laboratory, Whiteshell Research Area. The section also gives the contours for hydraulic heads before the excavation of the URL, whose 240 and 420 levels are shown.





**FIGURE 3:** Scheme for Fractionating Organic and Inorganic Groundwater Components into Suspended Particles (> 450 nm), Colloids, and Dissolved Species by Tangential-Flow Ultrafiltration

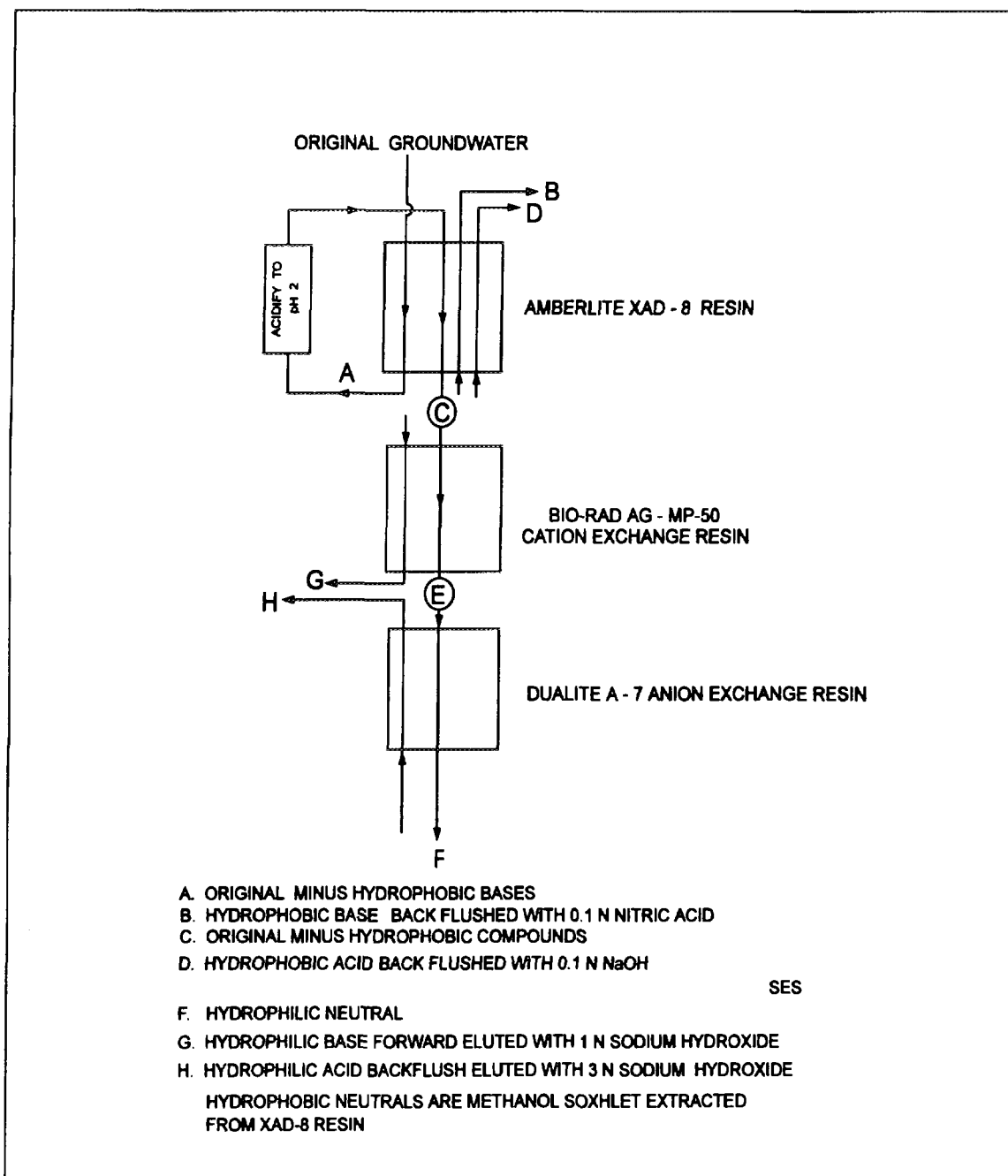


FIGURE 4: Scheme for Isolating Hydrophobic and Hydrophilic Organic Compounds from Groundwater. Adapted from Leenheer (1981).

## AFFINITY SPECTRUM HC15 FULVIC ACID

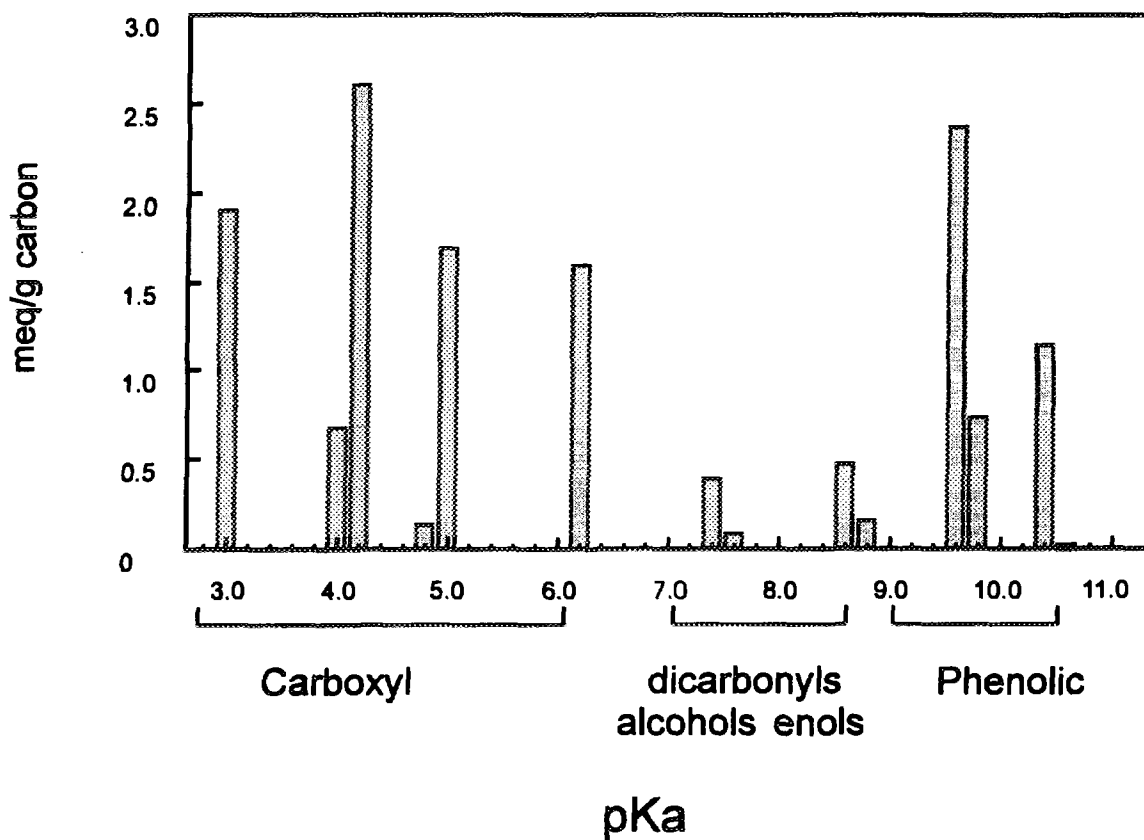


FIGURE 5: An Example of an Affinity Spectrum Determined by Discrete Site Analysis of Acid-Base Titration Data. This spectrum was calculated from the base titration (pH 3 to 11), and was supported by results from acid (pH 6.5 to 3) and base (pH 6.5 to 11) half-titrations.

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