

# Radiocarbon Geochemistry of Modern and Ancient Arctic Lake Systems, Baffin Island, Canada

MARK B. ABBOTT

*Department of Geosciences, University of Massachusetts, Morrill Science Center, Amherst, Massachusetts 01003-5820*

AND

THOMAS W. STAFFORD JR.

*Laboratory for AMS  $^{14}\text{C}$  Research, INSTAAR, University of Colorado, Campus Box 450, Boulder, Colorado 80309-0450*

Received May 22, 1995

---

**The accuracy of Arctic lake chronologies has been assessed by measuring the  $^{14}\text{C}$  activities of modern carbon sources and applying these isotopic mass balances to dating fossil lake materials. Small (<1 km<sup>2</sup>) shallow (<25 m) Arctic lakes with watersheds <12 km<sup>2</sup> have soil and peat stratigraphic sections with  $^{14}\text{C}$  activities ranging from 98 to 51% Modern. The  $^{14}\text{C}$  activity of particulate organic carbon, dissolved organic carbon, and dissolved inorganic carbon from lake and stream waters ranges from 121 to 95% Modern. The sediment–water interface of the studied lakes shows consistent  $^{14}\text{C}$  ages of ~1000  $^{14}\text{C}$  yr, although the  $^{14}\text{C}$  activity of living aquatic vegetation is 115% Modern. Radiocarbon measurements of components of the lacustrine carbon pool imply that the ~1000  $^{14}\text{C}$  yr age of the sediment–water interface results from deposition of  $^{14}\text{C}$ -depleted organic matter derived from the watershed.** © 1996 University of Washington

---

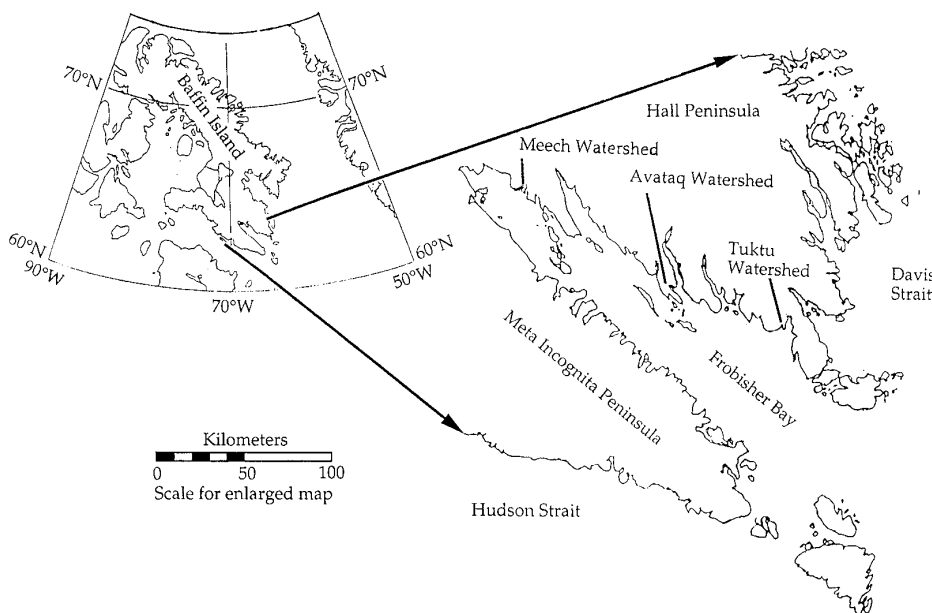
## INTRODUCTION

The Arctic Region is fundamental to understanding and describing late-Quaternary global climatic changes because it is considered to be sensitive to even small climatic perturbations (Dansgaard *et al.*, 1989; IPCC Scientific Assessment, 1990; Douglas *et al.*, 1994). Depending upon environmental conditions, the Arctic also has the potential to be an enormous reservoir or source for carbon which is stored as sedimentary organic carbon or released as gaseous or solid carbon compounds (cf. Oechel *et al.*, 1993). The timing of past climatic changes in the Arctic is fundamental to modeling regional climatic changes. Although Arctic lakes are commonly used as sources of climatic proxy data, accurate radiocarbon ages have been difficult to obtain. Radiocarbon dating of Arctic lake sediments is frequently inaccurate because these systems have low rates of productivity and sedimentation resulting in low organic matter concentrations in the sediments. Furthermore, low rates of decomposition allow terrestrial organic matter to be stored for prolonged periods

prior to being transported into the lake system. The combination of these factors commonly leads to radiocarbon ages that are apparently too old. Discrete macrofossils are rarely found in sufficient quantities for AMS  $^{14}\text{C}$  dates. Even when plant macrofossils are present, their geologic ages are suspect because macrofossils and sedimentary carbon can be reworked from preexisting sediments and soils, and the metabolism of ancient carbon can generate a significant reservoir effect for living aquatic plants (Nelson *et al.*, 1988).

We examined modern sedimentary and geochemical analogs to improve our understanding of the chronology of sediment sequences. Our objective is to describe all carbon sources entering a series of Arctic lakes whose biological productivity and bedrock geology are representative of lakes commonly used for paleoclimatic reconstructions. The three principle components in evaluating the  $^{14}\text{C}$  inventory of the lake basins are: (1) measure the contemporary  $^{14}\text{C}$  activity of the dissolved inorganic carbon (DIC), dissolved organic carbon (DOC), and particulate organic carbon (POC); (2) measure the  $^{14}\text{C}$  age–depth relationship of soil and peat profiles; and (3) extract specific organic chemical fractions from lake sediments to improve the  $^{14}\text{C}$  chronologies by dating similar organic compounds. By first measuring the radiocarbon activity in modern carbon sources, we can assess the accuracy of  $^{14}\text{C}$  ages from lacustrine sediments and define specific subsets of carbon in bulk lake sediments that are optimal for  $^{14}\text{C}$  dating.

We tried dating numerous chemical fractions to assess the accuracy of  $^{14}\text{C}$  dates when terrestrial plant macrofossils were not present in sufficient quantities for an AMS  $^{14}\text{C}$  measurement. These include dating bulk sediment, fulvic acid, humic acid, humin compounds, and aquatic plant macrofossils. Which of these materials yields the most accurate geologic age depends on each lake system's bedrock geology, soil and peat development, water source(s), and the absolute organic carbon content in sediments. We measured the radiocarbon activity of *modern* organic compounds for each lake basin to help evaluate the dates on fossil carbon.



**FIG. 1.** Map showing the location of the Meech, Avataq, and Tuktuk watersheds along the northern coast of Frobisher Bay on southern Baffin Island, Northwest Territories, Canada.

The following research strategy was used to quantify the geological transfer of carbon throughout the modern lake systems: (1) produce a  $^{14}\text{C}$  budget for the lake by identifying and measuring the  $^{14}\text{C}$  activity of carbon sources entering the system by fluvial processes, including DIC, DOC, and POC, (2) measure the  $^{14}\text{C}$  age of the sediment–water interface, (3) document the  $^{14}\text{C}$  activity of soils and peats to assess their potential as contributors of  $^{14}\text{C}$ -depleted carbon, (4) measure the radiocarbon age of a suite of chemically specific organic matter fractions to determine the age structure of the different fractions, and (5) evaluate which organic fraction, if any, is preferable for AMS  $^{14}\text{C}$  measurements when plant macrofossils are absent.

### STUDY AREA

Three lake systems were studied along a 230-km, NW to SE transect on southern Baffin Island (Abbott, 1991; Miller, 1992). The transect (Fig. 1) was from the head of Frobisher Bay to the outer coast of southern Baffin Island and included the Meech, Avataq, and Tuktuk lake systems. Each well-defined watershed comprised lakes that were  $<1\text{ km}^2$  and  $<25\text{ m}$  deep. The Meech Lake system ( $63^{\circ}39'\text{N}$ ,  $68^{\circ}21'\text{W}$ ) at the head of Frobisher Bay was sampled and cored during May and June of 1990 during the peak of the spring melt. The  $12\text{-km}^2$  Avataq drainage ( $63^{\circ}10'\text{N}$ ,  $66^{\circ}43'\text{W}$ ) contains a chain of four lakes draining from Lake 1 through Lake 4. The Tuktuk watershed, located at the mouth of Frobisher Bay ( $62^{\circ}52'\text{N}$ ,  $65^{\circ}22'\text{W}$ ), is  $5\text{ km}^2$  and has two lakes called Baby Tuktuk and Tuktuk. The Avataq and Tuktuk watersheds were sampled and cored during August of 1989. Each watershed

has well-developed carbon reservoirs in soils and peats. The Tuktuk, Avataq, and Meech watersheds are underlain by Precambrian crystalline bedrock dominated by granitic gneiss and schist and covered by a layer of thin glacial drift. Surficial Paleozoic carbonate transported by glacial activity from the floor of Frobisher Bay is present in small amounts in both the Tuktuk and Avataq watersheds, but the carbonates cover  $<1\%$  of the total surface area in these catchments.

### METHODS

Sediment cores were taken with a modified Livingstone corer. The cores were analyzed for magnetic susceptibility, bulk density, organic and carbonate content, sediment pH, grain size, and clay mineralogy (Abbott, 1991; Miller, 1992). Water conductivity, salinity, and pH measurements of stream, lake, and snowmelt water were made in the field. POC and DOC compounds were isolated from a known volume of lake and stream water by filtration and chromatographic methods. Live submerged aquatic plants were collected to estimate the DIC  $^{14}\text{C}$  activity of the lake water. POC is operationally defined as the portion of organic carbon that is retained on a  $0.45\text{-}\mu\text{m}$  sterilized filter. DOC is defined as the fraction that passes through the  $0.45\text{-}\mu\text{m}$  filter (Thurman, 1985). POC content was analyzed with a Model 1106 Carlo Erba Elemental Analyzer. The flow rates of the streams were measured at the time they were sampled, allowing us to calculate the flux of organic carbon into the lake.

DOC was isolated chromatographically with XAD-8 adsorption resin. XAD resin is a synthetic organic polymer that adsorbs weakly charged to neutral, hydrophobic, nonpolar mole-

cules. Examples of geochemical compounds adsorbed include fulvic and humic acids, peptides, and long-chain amino acids (Van Horne, 1985). XAD resins are widely used for concentrating dilute quantities of hydrophobic organic molecules from natural waters (Steinberg and Muenster, 1985; Thurman, 1985; Aiken, 1988). To adsorb DOC with the XAD resin, stream or lake waters were acidified to  $\text{pH} \leq 1$  with HCl, which protonates carboxyl and hydroxyl groups and converts the molecule to its most neutral (uncharged) form. The DOC was eluted from the XAD resin with a strong base ( $0.1 \text{ M NH}_4\text{OH}$ ), which deprotonates the molecule and forms an anion that desorbs and elutes rapidly from the resin. The XAD resin technique enables a few milligrams of organic compounds to be isolated from several tens of liters of natural waters. Results by Stafford *et al.* (1990) indicate that the XAD resin is made material with an infinite radiocarbon age. No measurable amount of carbon was eluted from blank samples of XAD that were subjected to the same environmental conditions as the samples in this study.

Soil and sediment samples were fractionated chemically for radiocarbon measurements into fulvic acid I, fulvic acid II, humic acid, and humin fractions by the methods outlined in Figure 2. Goh and Molloy (1978), Kigoshi *et al.* (1980), and Fowler *et al.* (1986) describe related methods for extracting specific organic matter fractions for  $^{14}\text{C}$  dating. The extraction process began with decalcifying the sample by adding 20 ml  $0.5 \text{ N HCl}$  at room temperature. The sample was mixed for 2 min and centrifuged for 20 min at 2400 RPM. We defined the dark-brown soluble portion of the sample as fulvic acid I and removed it for further processing. This procedure was repeated until the soluble portion was clear. The insoluble phase containing acid-insoluble carbon was washed to neutrality. The solid residue was extracted with 20 ml of  $0.5\% \text{ KOH}$  at room temperature. This process separated the soluble fulvic acid II and humic acid fractions from the base-insoluble humins. The KOH process was repeated until the soluble phase was clear and no additional humates were isolated. Both the soluble and insoluble phases were retained for dating. The insoluble humin fraction was washed until neutral and lyophilized. The soluble phase (fulvic acid II and humic acid) was centrifuged and acidified to  $\text{pH} 1$  with  $6 \text{ N HCl}$  and left for 24 hr while humic acid precipitated, leaving fulvic acid II in solution. The sample was centrifuged to concentrate the solid humic acid and separate the fulvic acid II. Remaining impurities were removed from the humic acid phase by redissolving it with  $0.5\% \text{ KOH}$  solution. Once purified and reprecipitated, the humic acid sample was neutralized, acidified with HCl to  $\text{pH} 3$ , and lyophilized. The fulvic acid I and fulvic acid II fractions were concentrated with XAD extraction resin. Approximately 50 to 100 ml of fulvic acid-bearing solution were passed through the resin at  $\sim 1$  ml per minute. Fulvic acids were eluted from the resin with a few microliters of  $0.1 \text{ M NH}_4\text{OH}$ , which desorbed the fulvic acids in less than

0.1 ml of hydroxide solution. The fulvic acid eluate was acidified and lyophilized.

One to 10 mg of lyophilized sample was transferred to 6-mm O.D. Vycor tubes, to which were added  $\sim 0.3 \text{ g CuO}$ ,  $0.4 \text{ g copper metal}$ , and  $0.1 \text{ g Ag powder}$ . The sample tubes were evacuated to  $<10 \text{ mtorr}$  and sealed. The samples were combusted for 3 hr at  $800^\circ\text{C}$ . The  $\text{CO}_2$  was cryogenically separated and purified, and the mass of carbon calculated before the gas was converted catalytically to graphite (Slota *et al.*, 1987). The targets used in the accelerator mass spectrometer are produced by the method of Donahue *et al.* (1990).

## RESULTS

### *Radiocarbon Measurements from Watershed Sources*

Figures 3 and 4 summarize the results of radiocarbon measurements on samples representing the major carbon sources to the Meech and Tuktuk lake systems. Radiocarbon activities are given as % Modern. The  $^{14}\text{C}$  activity of the atmosphere was between 116 and 115% Modern during the years of A.D. 1989 and 1990 when samples were taken (cf. Levin *et al.*, 1989).

*Meech watershed.* Results presented in Figure 3 show that the POC samples isolated from snow (103% Modern) and stream waters (95% Modern) contain significant masses of  $^{14}\text{C}$ -depleted carbon as the activity of atmospheric  $^{14}\text{C}$  in A.D. 1989 was  $\sim 115\%$  Modern (Table 1). Microscopic inspection showed that the filters contain partially decomposed terrestrial plant fragments, indicating input of reworked organic matter from the watershed. This reworked organic matter contributes  $^{14}\text{C}$ -depleted carbon to the sediment-water interface. The result is an apparent age of  $970 \pm 150 \text{ }^{14}\text{C yr B.P}$  at the sediment-water interface for the humic acid fraction of the organic matter (AA-6524) (Table 2). The  $^{14}\text{C}$  activity of the snow-DOC (101% Modern) indicates it, too, is a source of old carbon. The radiocarbon activity of this stream-DOC (121% Modern) indicates the carbon source must be recently living biomass (ca. A.D. 1985). Although we had no analytical method to quantify the stream-DOC concentration, the XAD columns were rapidly saturated, and we observed it to be orders of magnitude greater than other samples. The first stages of spring melt appear to wash geologically recent DOC from the soil surface effectively diluting the  $^{14}\text{C}$ -depleted carbon signal for a short period. The  $^{14}\text{C}$  activity of the lake-POC (104% Modern) and lake-DOC (111% Modern) indicate this geologically recent DOC is present in sufficient masses to increase the  $^{14}\text{C}$  activity of the lake-DOC, but the  $^{14}\text{C}$ -depleted carbon is still present in significant concentrations even during the peak of spring melting.

The flow rates of all the inflowing and outflowing streams were measured at the time the POC was sampled.

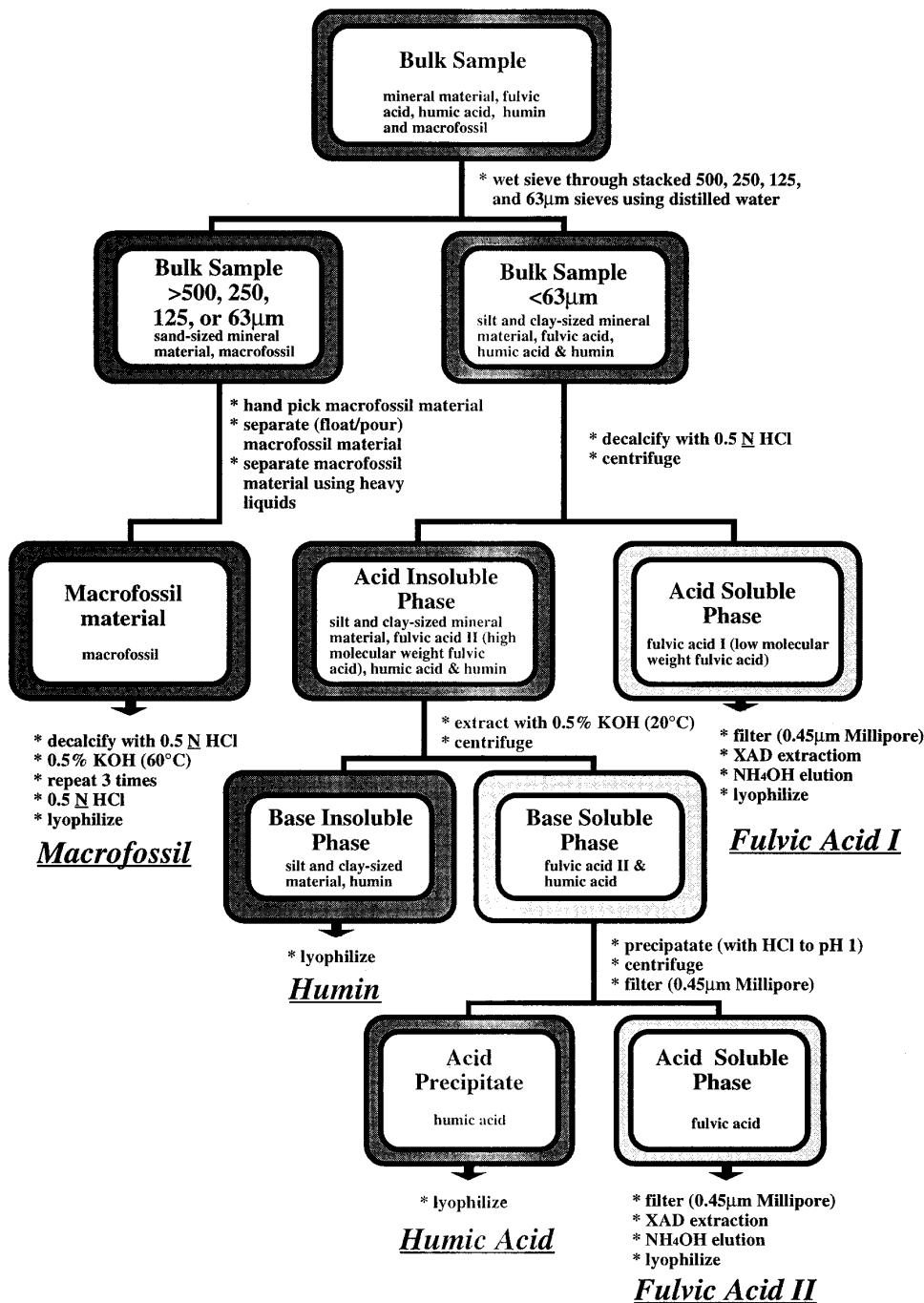


FIG. 2. Outline of method used to extract specific organic matter fractions from soils and sediments for AMS radiocarbon dating. The organic matter fractions include fulvic acid I, fulvic acid II, humic acid, and humin compounds.

The total POC input into the lake calculated from these samples is 18.46 kg/day and the total output to be 15.25 kg/day. Therefore 83% of the POC is transported through the lake, while only 17% or 3.21 kg/day is deposited in the lake basin. The sedimentation rate for POC is estimated to be 0.03 g/cm<sup>2</sup>/day at the peak of spring melt. This represents approximately 1/30 of the total organic carbon depo-

sition per year as calculated from organic analyses of sediment cores in Meech Lake. The average residence time of Meech Lake water during this period of peak melting is 4 days (Miller, 1992).

*Avataq watershed.* The <sup>14</sup>C activity of DOC extracted from the lake surface waters (106% Modern) indicates there is a considerable amount of <sup>14</sup>C-depleted carbon in the water

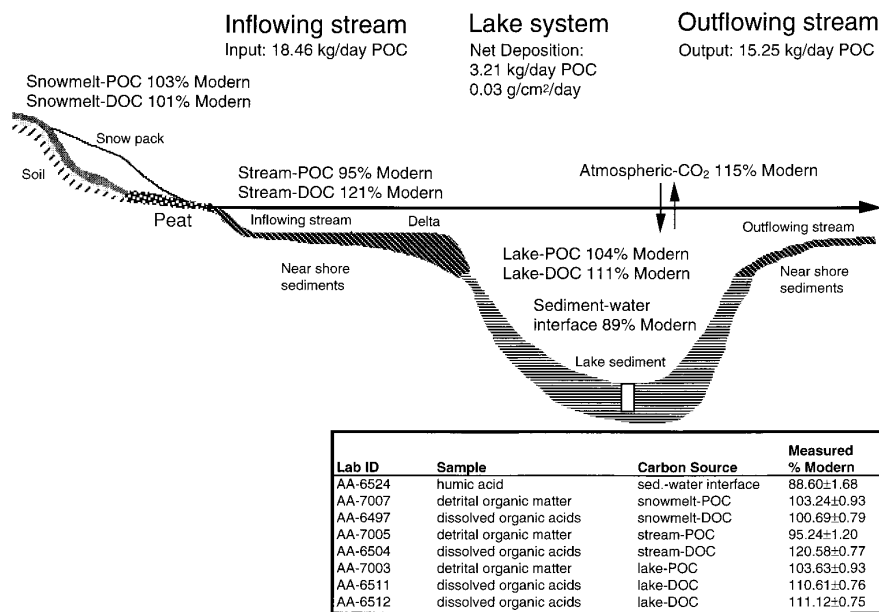


FIG. 3. Radiocarbon measurements on components of the Meech watershed and estimates of net POC deposition.

column. The POC sample was too dilute for a  $^{14}\text{C}$  measurement. The  $^{14}\text{C}$  activity of lake aquatic moss (121% Modern) shows the lake-DIC is slightly enriched with  $^{14}\text{C}$  relative to atmospheric  $^{14}\text{CO}_2$  (121% Modern corresponds to the early A.D. 1980's atmosphere).

To quantify the magnitude of old carbon stored in the watershed, the results of the organic matter content analysis were used to estimate the amount of organic carbon stored in the Avataq watershed (Walkley, 1947). Table 3 summarizes the results of estimates for the mass of organic carbon

stored in the Avataq soils and peats. We estimate the following amounts of organic carbon stored in the soils and peats of the Avataq watershed: (1) 195,000 metric tons in the well-drained soil complex, (2) 58,000 metric tons in the peat, (3) 24,000 metric tons in the steep soil complex, and (4) 4000 metric tons in the dry windblown soil complex.

*Tuktu watershed.* Figure 4 summarizes the results of radiocarbon measurements on soil profiles, peat sections, and contemporary components of the Tuktu Lake system. The  $^{14}\text{C}$  activity of contemporary submerged lacustrine aquatic

TABLE 1  
Radiocarbon Measurements from Components of the Modern Lake System

Laboratory number	Lake system	Carbon source	Material dated	% Modern	Measured $^{14}\text{C}$ age (yr)
AA-6524	Meech	Surface sediments	Humic acid	88.6 ± 1.68	970 ± 150
AA-7004	Meech	Snowmelt POC	Detrital organic matter	103.24 ± 0.93	Modern
AA-6497	Meech	Snowmelt DOC	Dissolved organic acids	100.69 ± 0.79	Modern
AA-7005	Meech	Stream POC	Detrital organic matter	95.24 ± 1.20	390 ± 100
AA-6504	Meech	Stream DOC	Dissolved organic acids	120.58 ± 0.77	Modern
AA-7003	Meech	Lake POC	Detrital organic matter	103.63 ± 0.93	Modern
AA-6511	Meech	Lake DOC	Dissolved organic acids	110.61 ± 0.76	Modern
AA-6512	Meech	Lake DOC	Dissolved organic acids	111.12 ± 0.75	Modern
AA-5313	Avataq	Lake DOC	Dissolved organic acids	106.44 ± 0.82	Modern
AA-5476	Avataq	Live aquatic veg.	<i>Drepanocladus</i>	121.0 ± 0.74	Modern
AA-6523	Tuktu	Surface sediments	Humic acid	88.18 ± 0.58	1010 ± 50
AA-7007	Tuktu	Stream POC	Detrital organic matter	101.21 ± 1.13	Modern
AA-7006	Tuktu	Lake POC	Detrital organic matter	115.36 ± 0.96	Modern
AA-5262	Tuktu	Lake DOC	Dissolved organic acids	98.19 ± 0.76	147 ± 60
AA-5253	Tuktu	Live rooted aquatic veg.	Aquatic macrofossil	118.41 ± 0.78	Modern
AA-5252	Tuktu	Live aquatic veg.	<i>Drepanocladus</i>	116.51 ± 0.70	Modern

TABLE 2  
Radiocarbon Measurements of Specific Organic Matter Fractions Extracted from on Peat, Soil, and Lake Sediments

Laboratory number	Profile	Depth (cm)	Fraction dated	% Modern	Measured <sup>14</sup> C age (yr)
AA-6043	Peat	24–27	Fulvic acid I	82.27 ± 0.66	1375 ± 60
AA-6042	Peat	24–27	Humic acid	82.40 ± 0.58	1555 ± 60
AA-5306	A Hzn.	2–6	Bulk <63 μm	98.36 ± 0.72	130 ± 60
AA-5308	A Hzn.	2–6	Fulvic acid I	96.45 ± 0.73	290 ± 60
AA-5473	A Hzn.	2–6	Fulvic acid II	97.56 ± 0.62	200 ± 50
AA-5311	A Hzn.	2–6	Humic acid	95.67 ± 0.62	355 ± 50
AA-5469	A Hzn.	2–6	Humin	95.07 ± 0.73	405 ± 60
AA-5263	B Hzn.	8–12	Bulk <63 μm	78.24 ± 0.68	1970 ± 70
AA-5309	B Hzn.	8–12	Fulvic acid I	87.45 ± 0.81	1075 ± 70
AA-5264	B Hzn.	8–12	Fulvic acid II	76.06 ± 0.60	2200 ± 60
AA-5265	B Hzn.	8–12	Humic acid	86.05 ± 0.70	1210 ± 70
AA-5266	B Hzn.	8–12	Humin	74.21 ± 0.64	2396 ± 70
AA-5307	C Hzn.	50–55	Bulk <63 μm	66.63 ± 0.63	3260 ± 70
AA-5310	C Hzn.	50–55	Fulvic acid I	77.63 ± 0.62	2035 ± 60
AA-5474	C Hzn.	50–55	Fulvic acid II	73.23 ± 0.51	2505 ± 50
AA-5312	C Hzn.	50–55	Humic acid	67.83 ± 0.78	3120 ± 80
AA-5470	C Hzn.	50–55	Humin	51.14 ± 0.44	5385 ± 70
AA-6044	Baby Tuktu	0–1	Bulk <63 μm	89.34 ± 0.75	910 ± 70
AA-6030	Baby Tuktu	0–1	Fulvic acid II	89.36 ± 0.58	905 ± 500
AA-6025	Baby Tuktu	0–1	Humic acid	87.99 ± 0.56	1030 ± 50
AA-6037	Baby Tuktu	0–1	Humin	85.80 ± 0.63	1230 ± 60
AA-6045	Baby Tuktu	1–2	Bulk <63 μm	89.34 ± 0.75	1065 ± 50
AA-6026	Baby Tuktu	1–2	Humic acid	87.82 ± 0.59	1045 ± 50
AA-6038	Baby Tuktu	1–2	Humin	87.37 ± 0.66	1085 ± 60
AA-6046	Baby Tuktu	40–41	Bulk <63 μm	65.33 ± 0.42	3420 ± 50
AA-6031	Baby Tuktu	40–41	Fulvic acid II	65.60 ± 0.45	3385 ± 50
AA-6027	Baby Tuktu	40–41	Humic acid	68.73 ± 0.40	3015 ± 50
AA-6039	Baby Tuktu	40–41	Humin	66.73 ± 0.56	3232 ± 70
AA-6047	Baby Tuktu	71–72	Bulk <63 μm	47.14 ± 0.34	6040 ± 70
AA-6028	Baby Tuktu	71–72	Humic acid	49.35 ± 0.59	5675 ± 90
AA-6040	Baby Tuktu	71–72	Humin	45.87 ± 0.44	6261 ± 80
AA-6048	Baby Tuktu	76–77	Bulk <63 μm	44.83 ± 0.52	6445 ± 90
AA-6029	Baby Tuktu	76–77	Humic acid	46.46 ± 0.51	6160 ± 90
AA-6041	Baby Tuktu	76–77	Humin	42.11 ± 0.38	6950 ± 70

moss (*Drepanocladus sp.*, 116% Modern) and rooted aquatic vegetation (118% Modern) suggest that the contemporary lake-DIC is nearly in equilibrium with atmospheric <sup>14</sup>CO<sub>2</sub>. Inspection of samples of lake-POC sampled from surface waters showed the filters contained well-preserved filamentous algal matter. The <sup>14</sup>C activity of this lake-POC is 115% Modern and supports the finding that lake-DIC is in equilibrium with atmospheric <sup>14</sup>CO<sub>2</sub>, because the sample of lake-POC is nearly pure aquatic algae. The <sup>14</sup>C activity of samples of lake-DOC is 98% Modern, indicating the DOC pool is a source of <sup>14</sup>C-depleted carbon.

Microscopic inspection of stream-POC samples showed that much of the plant matter is fragmented and partially decomposed. The <sup>14</sup>C activity of the stream-POC sample is 101% Modern. The difference in <sup>14</sup>C activity between lake-POC and stream-POC illustrates the extent of <sup>14</sup>C-depleted carbon from the watershed to the lake system. The <sup>14</sup>C activity of the surface sediments in lakes Baby Tuktu and Tuktu

is ~1000 <sup>14</sup>C yr (Fig. 5). This indicates that the lake surface sediments are composed of a mixture of contemporary carbon (115% Modern) derived from aquatic organisms and <sup>14</sup>C-depleted organic matter eroded from soils and peats. The apparent age of the sediment–water interface is older than the components of the Modern system in each lake system. The cause of this discrepancy is unclear; however it is likely related to the following factors: (1) the method used to sample the uppermost sediments integrates the top several millimeters, making the sediment–water interface appear too old, (2) reworking of shoreline deposits during ice breakup adds aged carbon to the lake bottom, and/or (3) complications arising from the massive input of <sup>14</sup>C produced by atmospheric testing of nuclear weapons causes the contemporary system to be artificially enriched with <sup>14</sup>C.

We measured the <sup>14</sup>C activity of specific organic matter fractions from three soil horizons in the well-drained soil complex and a peat section in the Tuktu watershed. The

**TABLE 3**  
**Soil Carbon Storage**

Watershed	Organic complex	% of total soil/peat cover	Horizon/depth (cm)	Average OC (wt %)	Total OC (metric tons)	OC (kg/m <sup>2</sup> )	Whole profile OC (kg/m <sup>2</sup> )	Average <sup>14</sup> C activity (% Modern)	Accumulation kg/m <sup>2</sup> /100 yr (humic acid)	Accumulation kg/m <sup>2</sup> /100 yr (hummin)
Tuktu	Well drained	84	O	23	19,000	4.6	21.9	97	4.25	3.72
			A	14	43,000	10.5				
			B	2	18,000	4.3				
Tuktu Avataq	Peat Well drained	16 63	ICox	1	11,000	2.6	39.0 8.9	67 82	0.96 2.51	0.56 1.56
			IICox	1	33,000	8.0				
			24-27	20	500	8.0				
			O	25	110,000	4.9				
			A	5	30,000	1.4				
			B	4	38,000	1.7				
Avataq	Steep	11	Cox	0	19,000	0.9	35.5			
			IO	39	8000	11.8				
			IIO	29	8000	11.6				
			A	7	5000	7.5				
			B	2	2000	3.6				
			Cox	0	600	1.0				
Avataq	Dry windblown	10	B	3	3300	5.6	7.6			
			ICox	0	500	0.8				
			IICox	0	700	1.2				
Avataq	Peat	16	0-4	33	20,000	13.2	39.8			
			8-12	27	39,000	26.6				

purpose was to determine the apparent <sup>14</sup>C age structure of the profiles and estimate the mass of <sup>14</sup>C-depleted carbon stored in the soils and peats. Figure 5 shows how the <sup>14</sup>C activity of organic matter decreased with depth and generally with higher molecular weight. The difference between the <sup>14</sup>C activity of organic matter fractions is larger than the measurement error in the soil profile at each stratigraphic level. This difference increases with depth in the B and Cox horizons. This is not true in the peat section, where the <sup>14</sup>C activity of the fulvic acid and humic acid samples are not significantly different. The peat section did not contain sufficient amounts of humin compounds for a <sup>14</sup>C measurement.

We used the areal distribution of the soils, measurements of organic carbon, and radiocarbon assays to estimate the mass and <sup>14</sup>C activity of the soil horizons. Table 3 summarizes the following estimates for the mass and <sup>14</sup>C activity of organic carbon stored in the Tuktu watershed from radiocarbon dates on the humic acid fraction of the organic matter: (1) 43,000 metric tons with an average <sup>14</sup>C activity of 97% Modern, (2) 18,000 metric tons with an average <sup>14</sup>C activity 80% Modern, (3) 44,000 metric tons with an average <sup>14</sup>C activity of 67% Modern, and (4) 500 metric tons with an average <sup>14</sup>C activity of 82% Modern. Clearly, the watershed contains a large mass of fossil carbon with a radiocarbon activity that is less than the contemporary atmosphere. When this <sup>14</sup>C-depleted carbon is transported into the lake system it dilutes the <sup>14</sup>C activity of the carbon pool, resulting in an apparent ~1000 <sup>14</sup>C yr age of the lake's surface sediments.

We measured the <sup>14</sup>C activity of the chemically specific organic matter fractions in the lacustrine sediments of Baby Tuktu at five stratigraphic levels (Stafford and Abbott, 1990).

The <sup>14</sup>C ages of the bulk sediment, fulvic acid II, humic acid, and humin compounds are summarized in Figure 5. The <sup>14</sup>C age differences increase with age and are greater than the measured error after ~4000 <sup>14</sup>C yr. Comparison of Figures 5A and 5B show that the <sup>14</sup>C age differences between the organic matter fractions is less in the lake sediments than in the soil profiles. Fulvic acid was not present in sufficient quantities for a radiocarbon measurement in lower levels of the lake cores.

**DISCUSSION**

*Lake Reservoir Effect*

A reservoir effect is present when the <sup>14</sup>C activity of the lacustrine carbon pool is significantly less than the <sup>14</sup>C content of the contemporaneous atmosphere. In shallow lakes that are well mixed, the <sup>14</sup>C activity of aquatic plants should be that of the contemporary atmosphere (115% Modern in A.D. 1989). However, this is not always the case, as shown by Cole *et al.* (1994). Carbon dioxide supersaturation in surface lake waters with a worldwide distribution occurred in 87% of the 4665 lakes they sampled. Kling *et al.* (1991) observed that 27 of 29 lakes sampled in Alaska released CO<sub>2</sub> to the atmosphere. Lake waters with a net loss of CO<sub>2</sub> to the atmosphere will have decreased exchange with atmospheric CO<sub>2</sub>. Kling *et al.* (1991) observed that the <sup>14</sup>C activity of algae living in fertilized and control waters along a segment of the Kuparuk River were both lower than the contemporary atmosphere. Therefore, lake waters may experience a DIC reservoir effect and should be evaluated by measuring the <sup>14</sup>C activity of living aquatic vegetation.

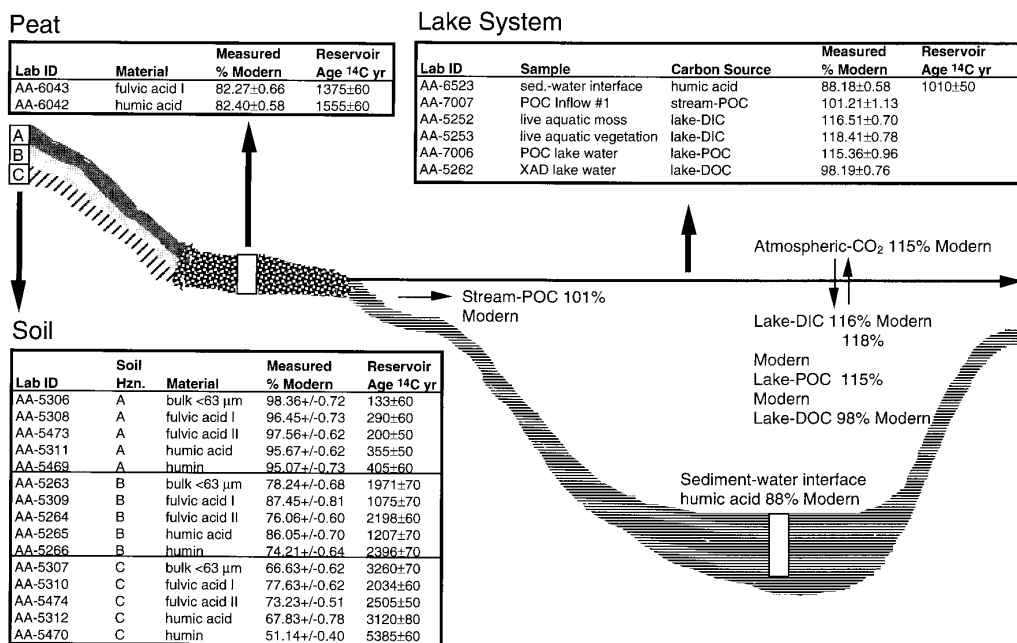
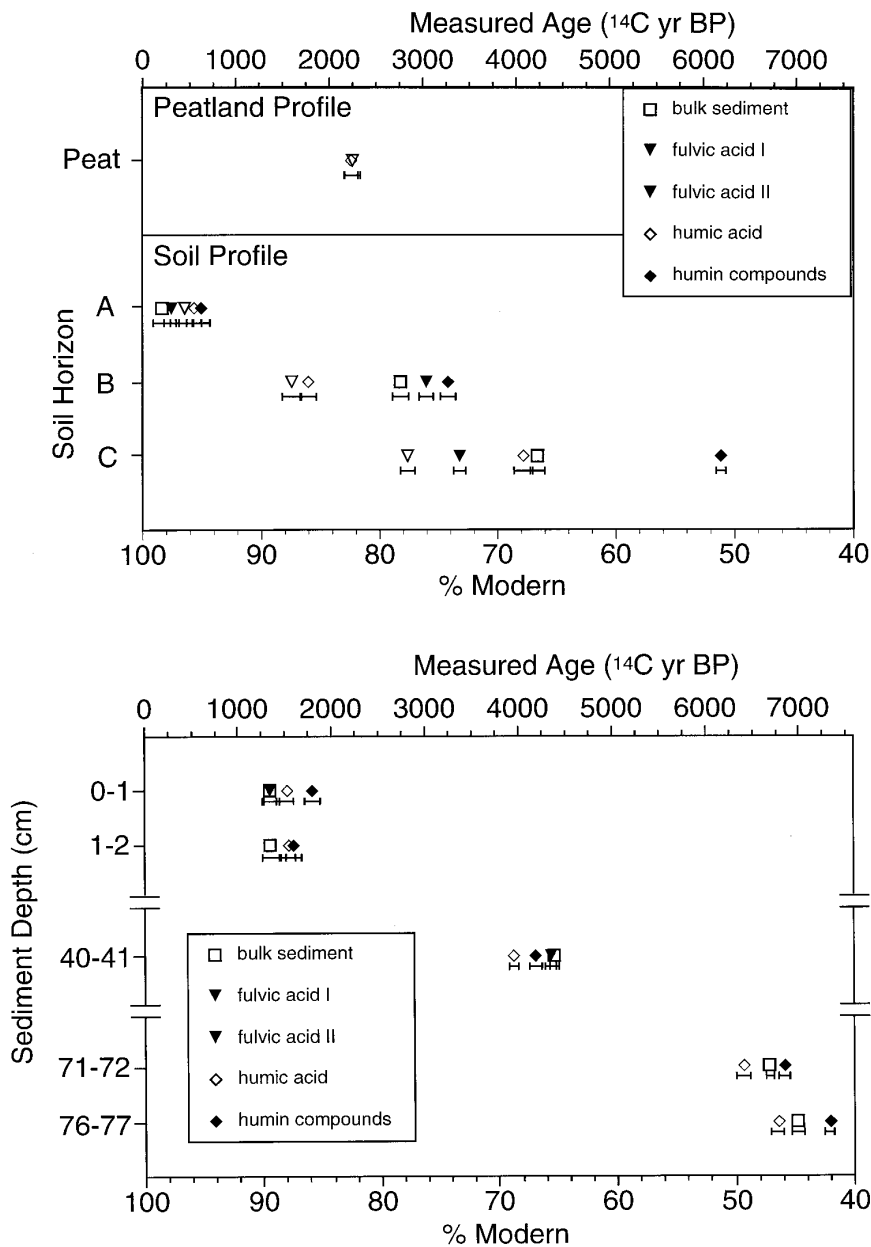


FIG. 4. Radiocarbon measurements on a soil profile, a peat section, and components of the contemporary lake system in the Tuktu watershed.

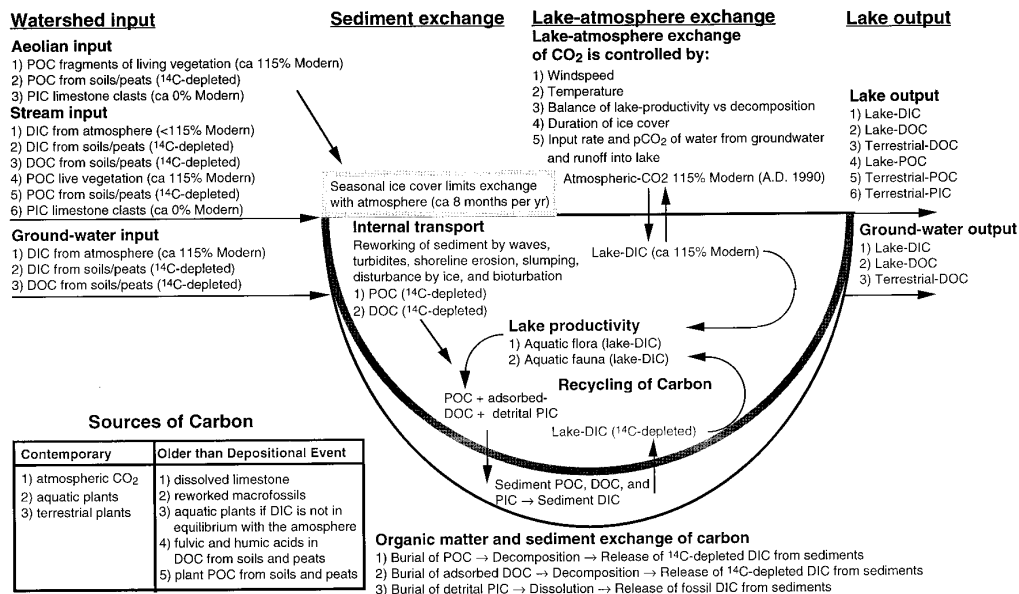




**FIG. 5.** Results of  $^{14}\text{C}$  measurements from soil, peat, and sediment stratigraphic sections for the Tuktu watershed. Note that the  $^{14}\text{C}$  activity decreases with depth and molecular weight from fulvic acid I through humin compounds in the soil and sediment profiles but remains constant in the peat section. The soil profile was sampled between 2 and 6, 8 and 12, and 50 and 55 cm and the peat between 24 and 27 cm depth.

We note two major categories of reservoir effects associated with Arctic lakes. Type 1 is characterized by a present sediment-water interface containing  $^{14}\text{C}$ -depleted carbon, but the lake-DIC pool is in equilibrium with atmospheric  $\text{CO}_2$ . The source of the  $^{14}\text{C}$ -depleted carbon is from watershed-derived POC and DOC. Aquatic macrofossils from lakes with a Type-1 reservoir effect can be used for radiocarbon measurements, because the lake-DIC pool is equilibrated with the atmospheric  $^{14}\text{CO}_2$ . Type-1 systems are the geochemical end member in a continuum found in extremely low-productivity tundra environments.

Type-II reservoir effects are characterized by a sediment-water interface containing  $^{14}\text{C}$ -depleted carbon contributed from all components of the lacustrine carbon pool including lake-DIC, -POC, -DOC, and -PIC (if present). Potential causes of a  $^{14}\text{C}$ -depleted lake-DIC pool are a poorly mixed water column and/or when the  $\text{pCO}_2$  of the lake water is greater than the  $\text{pCO}_2$  of the atmosphere due to input of "aged  $\text{CO}_2$ ." The rate of exchange between lake-DIC and atmospheric  $\text{CO}_2$  is greatly reduced when the lake has a net loss of  $\text{CO}_2$ . The  $\text{CO}_2$  is generated from the decomposition of organic matter and/or the dissolution of carbonates. The



**FIG. 6.** Model of carbon input, exchange, and output in Arctic lake systems. Limits of <sup>14</sup>C activity are given to illustrate the important role of recycled carbon in these lake systems. The lake-DIC pool is composed of a mixture of atmospheric CO<sub>2</sub> and recycled CO<sub>2</sub> produced from decomposition of sediment-POC and -DOC and dissolution of sediment-PIC. Note carbonate precipitation does not occur in these low-productivity acidic (pH 6 to 7) lake systems on southern Baffin Island.

result is live aquatic vegetation and a sediment–water interface that have apparent <sup>14</sup>C ages older than the time of deposition.

Figure 6 summarizes the exchange of carbon between reservoirs in Arctic watersheds where low rates of productivity and decomposition result in the recycling of <sup>14</sup>C-depleted organic matter. The possible sources of carbon includes the atmosphere, lake-DIC, aquatic-biomass, watershed-DOC/POC, and sediments. Lake-DIC includes the following sources: (1) the atmosphere (115% Modern in A.D. 1990), (2) decomposition of <sup>14</sup>C-depleted organic matter stored in lake sediments (<115 and >1% Modern), (3) DIC transported in groundwater and runoff generated from decomposition in soils and peats or dissolution of fossil carbonates (<115% Modern), and (4) dissolution of ancient carbonates washed into the lake (<1% Modern). Finally one must consider the recycling of carbon in the lake system illustrated in Figure 6 to be a source of <sup>14</sup>C-depleted carbon to the lake-DIC pool for Arctic lakes with very poor vertical mixing.

*Sediment–Water Interface*

The <sup>14</sup>C age of the sediment–water interface is commonly ~1000 <sup>14</sup>C yr or greater in the lakes surrounding Frobisher Bay. Lake sediment–water interface radiocarbon ages range from 905 to 1230 yr for the Baffin Island lakes we have examined. Lakes Inqua, Mercer, and Instaar from the Jackman Sound area on the southern shore of Frobisher Bay have surface ages of ~1000 <sup>14</sup>C yr (Abbott, 1991). This reservoir age is not due to dissolved Paleozoic limestone

(<sup>14</sup>C-depleted DIC) because living aquatic vegetation has a <sup>14</sup>C activity of ~115% Modern. Therefore, the reservoir age must be associated with the deposition of <sup>14</sup>C-depleted POC and adsorbed DOC.

We recognize that incomplete recovery of surface sediments could result in an age offset at the sediment–water interface. Field inspections indicated the sediment–water interface was well preserved during the coring process, but possibly the top several centimeters were disturbed. We consider core loss to be less than 2 cm.

*Fate of Humic Substances*

Stable isotopic studies of humic substances by Nissenbaum and Kaplin (1972) show that plant cellular material degrades, forming a water-soluble complex containing amino acids and carbohydrates. As these molecules polymerize fulvic acids are formed. Fulvic acids eventually polymerize to form the higher molecular weight humic acids and humin compounds. Ishiwatari (1985) studied the aliphatic nature and chemical composition of humic substances in lake sediments and proposed that they are primarily formed from the decomposition of aquatic organisms. However, Killops and Killops (1993) noted that refractory lignified plant tissue is a major substrate of soil humic material and is enriched in polycarboxyl-substituted phenols. Our study supports the hypothesis of a <sup>14</sup>C-depleted terrestrial source for the humic substances.

Figure 5 illustrates two key points that we observed in soil, peat, and sediment stratigraphic sections: (1) the <sup>14</sup>C

age of humic substances increases with increasing molecular weight, and (2) the age difference among humic compounds increases with time. Although the differences in  $^{14}\text{C}$  activities among humic substances are less in sediment cores, they are still present and significant. We propose the following pathway for the formation of humic compounds based on the results of this study: fulvic acid I  $\rightarrow$  fulvic acid II  $\rightarrow$  humic acid  $\rightarrow$  humin compounds. In soils the organic compounds of lowest molecular weight are transported by groundwater to lower stratigraphic levels, where they polymerize over geologic time and eventually form humin compounds. Groundwater movement of small molecular weight humic substances does not affect peat profiles, because the sections are level with the water table. We note that the isolated mass of fulvic acid fractions I and II decreases with increasing depth within the sediment core profile and become too dilute for an AMS  $^{14}\text{C}$  measurement below 40 cm depth. We hypothesize that polymerization of fulvic acids to form humic acids and humin compounds results in decreased mass of fulvic acid in the sediments with time. This is not the case in the soil profile due to downward transport of DOC by groundwater.

### SUMMARY

Soils and peats are a major source of ancient carbon, as indicated by  $^{14}\text{C}$  ages of  $1555 \pm 60$   $^{14}\text{C}$  yr (AA-6042) and  $5385 \pm 60$   $^{14}\text{C}$  yr (AA-5470). Radiocarbon measurements on soil profiles indicate the mean time for organic matter turnover in the Tuktu watershed is  $>2000$   $^{14}\text{C}$  yr. The  $^{14}\text{C}$  age of the sediment–water interface is  $\sim 1000$   $^{14}\text{C}$  yr in each of the three lake systems. We hypothesize that the cause of this age discrepancy is  $^{14}\text{C}$ -depleted POC and DOC transported from the watershed. In oligotrophic Arctic lakes, where accumulation rates are slow ( $\sim 1$  cm/100 yr), the addition of  $^{14}\text{C}$ -depleted organic carbon from soils and peats can form a significant fraction of the total organic matter deposited on the lake floor. The DIC pool is in equilibrium with atmospheric  $^{14}\text{CO}_2$ . The agreement between the measured  $^{14}\text{C}$  activity of aquatic vegetation and atmospheric  $^{14}\text{CO}_2$  suggests that a hardwater effect from Paleozoic carbonates is absent to negligible, even in the carbonate-drift terrain.

The age differences between several chemical fractions in the same horizon increase with absolute  $^{14}\text{C}$  age and stratigraphic depth. These differences become greater than the standard measurement error after  $\sim 2000$   $^{14}\text{C}$  yr. In Baffin Island sediments and soils, the  $^{14}\text{C}$  activity of organic matter fractions from the same stratum decreases with increasing molecular weight. Fulvic acids are not present in sufficient quantities for radiocarbon measurements below the upper 10 cm. Although the  $^{14}\text{C}$  age of the fulvic acid fraction may be closer to the true age of the deposit, it appears to polymerize over a millennial time scale to form larger organic com-

pounds. Fulvic acid is the lowest molecular weight fraction and has the most recent apparent  $^{14}\text{C}$  age. Next older are humic acid and humin compounds. The AMS  $^{14}\text{C}$  chronologies established by dating specific organic carbon fractions must be considered relative. These floating chronologies can be fixed by dating macrofossils from the same stratum if it can be established that macrofossils are not reworked from older sediments. Finally, it is critically important to recognize that reservoir ages in lake systems must be evaluated on a lake by lake basis.

Ranking for the greatest accuracy, we suggest that researchers use the following sample types for AMS  $^{14}\text{C}$  dating of lake sediments: (1) discrete terrestrial plant macrofossils, carefully inspected for signs of reworking; (2) discrete aquatic plant macrofossils in noncarbonate terrain and from relatively shallow, well-mixed lakes where DIC is equilibrated with the atmosphere (in carbonate terrain aquatic macrofossils are unsuitable); and (3) chemically specific organic matter fractions when plant macrofossils are absent. The humic acid fraction of the organic matter appears to be the best alternative to plant macrofossils because: (1) humic acids are present throughout the sediment profile in masses sufficient for AMS  $^{14}\text{C}$  measurements; (2) humic acids appear to be formed from lower molecular weight organic compounds that are less likely to be composed of reworked refractory carbon than the humin compounds; and (3) humic acid can be chemically separated from refractory organic matter and carbon-bearing clays.

### ACKNOWLEDGMENTS

This project was supported by funds from the National Science Foundation Grants EAR-86-18453 and DPP-89-21973. Small research grants from the Geological Society of America, Sigma Xi, and the Department of Geological Science at the University of Colorado, Boulder contributed to field expenses. Valuable comments were contributed by John Andrews, Raoul Miller, Bruce Finney, Gifford Miller, Herbert Wright, Kerry Kelts, and an anonymous reviewer.

### REFERENCES

- Abbott, M. B. (1991). Radiocarbon dating and interpretation of sediments in five lake systems along Frobisher Bay, N.W.T., Canada. Unpublished M.S. thesis, University of Colorado, Boulder.
- Aiken, G. R. (1988). A critical evaluation of the use of macroporous resins for the isolation of aquatic humic substances. In "Humic Substances and Their Role in the Environment" (F. H. Frimmel, and R. F. Christman, Eds.), pp. 15–28. Wiley, New York.
- Cole, J. J., Caraco, N. F., Kling, G. W., and Kratz, T. K. (1994). Carbon dioxide supersaturation in the surface waters of lakes. *Science* **265**, 1568–1570.
- Dansgaard, W., White, J. W. C., and Johnsen, S. J. (1989). The abrupt termination of the Younger Dryas climate event. *Nature* **339**, 532–533.
- Donahue, D. J., Linick, T. W., and Jull, A. J. T. (1990). Isotope ratio and background corrections for accelerator mass spectrometry radiocarbon measurements. *Radiocarbon* **32**, 135–142.
- Douglas, M. S. V., Smol, J. P., and Blake, W. Jr. (1994). Marked post 18th

- century environmental change in high-Arctic ecosystems. *Science* **266**, 416–419.
- Fowler, A. J., Gillespie, R., and Hedges, R. E. M. (1986). Radiocarbon dating of sediments. *Radiocarbon* **28**, 441–450.
- Goh, K. M., and Molloy, B. P. (1978). Radiocarbon dating of paleosols using soil organic matter components. *Journal of Soil Science* **29**, 567–573.
- IPCC Scientific Assessment (1990). Climate change: The IPCC Scientific Assessment. In “World Meteorological Organization, United Nations Environment Programme” (J. T. Houghton, G. L. Jenkins, and J. J. Ephraums, Eds.), p. 239.
- Ishiwatari, R. (1985). Geochemistry of humic substances in lake sediments. In “Humic Substances in Soil, Sediment, and Water” (G. R. Aiken, D. M. Micknight, and R. L. Wershaw, Eds.) pp. 147–180. Wiley, New York.
- Kigoshi, K., Suzuki, N., and Shiraki, M. (1980). Soil dating by fractional extraction of humic acid. *Radiocarbon* **22**, 853–857.
- Killops, S. D., and Killops, V. J. (1993). Formation of humic material, coal and kerogen. In “An Introduction to Organic Geochemistry” (R. C. O. Gill, Ed.), pp. 93–116. Wiley, New York.
- Kling, G. W., Kipphut, G. W., and Miller, M. C. (1991). Arctic lakes and streams as gas conduits to the atmosphere: Implications for tundra carbon budgets. *Science* **251**, 298–300.
- Levin, I., Schuchard, J., Kromer, B., and Munnich, K. O. (1989). The continental European Suess effect. *Radiocarbon* **31**, 431–440.
- Miller, R. J. O. (1992). Late Quaternary lacustrine paleoenvironmental records from southeast Baffin Island, N.W.T., Canada. Unpublished Ph.D. dissertation, University of Colorado, Boulder.
- Nelson, R. E., Carter, L. D., and Robinson, S. W. (1988). Anomalous radiocarbon ages from Holocene detrital organic lens in Alaska and their implications for radiocarbon dating and paleoenvironmental reconstructions in the Arctic. *Quaternary Research* **29**, 66–71.
- Nissenbaum, A., and Kaplin, I. R. (1972). Chemical and isotopic evidence for the *in situ* origin of marine humic substances. *Limnology and Oceanography* **17**, 570–582.
- Oechel, W. C., Hastings, S. J., Vourlitis, G., Jenkins, M., Riechers, G., and Grulke, N. (1993). Recent change of Arctic tundra ecosystems from a net carbon dioxide sink to a source. *Nature* **361**, 520–523.
- Slota, P. J., Jr., Jull, A. J. T., Linick, T. W., and Toolin, L. J. (1987). Preparation of small samples for <sup>14</sup>C accelerator targets by catalytic reduction of CO. *Radiocarbon* **29**, 303–306.
- Stafford, T. W., and Abbott, M. B. (1990). Accelerator <sup>14</sup>C dating of organic carbon fractions in lake sediments from Baffin Island, Arctic Canada. “*Geological Society of America Abstracts with Programs*,” Vol. 22, p. A310.
- Stafford, T. W., Hare, P. E., Currie, L., Jull, A. J. T., and Donahue, D. (1990). Accuracy of North American human skeleton ages. *Quaternary Research*, **34**, 111–120.
- Steinberg, C., and Muenster, U. (1985). Geochemistry and ecological role of humic substances in lake water. In “Humic Substances in Soil, Sediment, and Water” (G. R. Aiken, D. M. Micknight, and R. L. Wershaw, Eds.), pp. 105–147. Wiley, New York.
- Thurman, E. M. (1985). Organic carbon in natural waters: Amount, origin, and classification. In “Organic Geochemistry of Natural Waters,” pp. 5–112. Nijhoff/Junk, Boston.
- Van Horn, K. C. (1985). “Sorbent Extraction Technology,” pp. 1–125. Analytichem International, Harbor City, CA.
- Walkley, A. (1947). A critical examination of a rapid method for determining organic carbon in soils: Effects of variation in digestion conditions of inorganic soil constituents. *Soil Science* **63**, 251–264.