VARIATION OF Δ^{14}C AND δ^{13}C VALUES OF DISSOLVED HUMIC AND FULVIC ACIDS IN THE TOKACHI RIVER SYSTEM IN NORTHERN JAPAN

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ABSTRACT. Characteristics of dissolved humic and fulvic acids in river waters were studied during 2003–2005 at 4 sites located in the headwaters and in the upper and lower Tokachi River, including a lowland tributary site. Fulvic acids from the headwaters to downstream areas have similar elemental composition and ^{13}C-NMR spectra. Humic acids have similar characteristics in the Tokachi River system. In contrast, δ^{13}C and Δ^{14}C values exhibit a decreasing trend from the upper to the lower and tributary sites, although the headwater site has heavier δ^{13}C and lower Δ^{14}C values than the upper site. Fulvic acids had similar δ^{13}C values from the upper to lower sites, but 123‰ higher in Δ^{14}C than those of humic acids on average. The δ^{13}C and Δ^{14}C values exhibited differences in downward variation for humic and fulvic acids. In the Tokachi River system, these results suggest that differences in transport pathways and residence times of humic and fulvic acids reflect differences in the δ^{13}C and Δ^{14}C values in a single river basin.

INTRODUCTION

Radiocarbon is a useful tracer for assessing the relative importance of different ages of dissolved organic carbon sources. Determinations were performed for dissolved organic matter (DOM) in Arctic rivers (Guo and Macdonald 2006; Guo et al. 2007; Raymond et al. 2007), US rivers (Spiker and Rubin 1975; Rayond and Bauer 2001a; Raymond et al. 2004), the Amazon River (Raymond and Bauer 2001; Mayorga et al. 2005), and small rivers in forested and wetland catchments (Tipping et al. 2007). The Δ^{14}C values of DOM show a wide range of values from –158‰ to +364‰, reflecting different turnover time and sources.

Dissolved humic substances (humic and fulvic acids) are abundant in aquatic environments, accounting for 40–60% of the DOM in aquatic systems. They influence carbon cycling and ecosystem dynamics because of their refractory features and complexation ability for trace elements. The Δ^{14}C values of humic and fulvic acids in river and lake waters respectively range from –122 to +167‰ and –316 to +209‰ (Hedges et al. 1986; Schiff et al. 1990; Nagao et al. 2004, 2007). The humic and fulvic acids have δ^{13}C values of –29 to –26‰. Marked differences in carbon isotopes of fulvic acids have been reported from several studies. For instance, Nagao et al. (2007) reported seasonal variations in Δ^{14}C and δ^{13}C values for fulvic acids in Lake Biwa waters during 1998–2003. The Δ^{14}C of fulvic acids are higher than the humic acids in waters from the Amazon River (Hedges et al. 1986) or the lake watershed (Schiff et al. 1990; Nagao et al. 2007). The relative importance of different chemical and biological processes involved in the formation of aquatic humic and fulvic acids is strongly influenced by time factors (McKnight and Aiken 1988). Therefore, ^{14}C might be used as a tracer of the transport of humic and fulvic acids in river watersheds.

This study was conducted to assess the dynamics of humic and fulvic acids in a river system using paired Δ^{14}C and δ^{13}C values. We have been studying the Tokachi River system located in northern Japan. Preliminary results for carbon isotopes were reported by Nagao et al. (2011). The present

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Proceedings of the 21st International Radiocarbon Conference edited by A J T Jull & C Hatté
RADIOCARBON, Vol 55, Nr 2–3, 2013, p 1007–1016

study specifically examines variations in carbon isotopic signatures of humic and fulvic acids from upper to lower rivers. The field survey was conducted from the headwaters to the lower Tokachi River during 2003–2005. The river water samples were collected at 4 sites in June and September, and were isolated for humic and fulvic acids using XAD extraction. The transport behavior of dissolved humic and fulvic acids in the Tokachi River system was studied using carbon isotopes ($\Delta^{14}C$ and $\delta^{13}C$) and structural characteristics such as the elemental composition and ^{13}C NMR spectra.

MATERIALS AND METHODS

Sampling Area

The Tokachi River originates from Mt. Tokachi-dake (2077 m) of the Taisetsu Mountain Range located in the middle of Hokkaido (Figure 1). The 156-km-long river has a watershed of 9010 km^2. It flows through the broad Tokachi Plain, which includes old and new alluvial fans and stream terraces. The soil in this area consists mainly of ando soil and lowland soil. The land use of watershed was roughly 65% forest and 32% agricultural field in 1990 (Natsume et al. 1991). Mean annual precipitation during 1979–2000 was recorded as 947 mm at the Urahoro Observatory (Japan Meteorological Agency, http://www.date.jma.go/), which is near the sampling site of Moiwa in this study. The Tokachi River's mean annual water discharge was recorded as 220 m^3/s at a water-flow monitoring station of Moiwa during 1970–1998 (MILIT 2004). The mean annual water discharge was 45 m^3/s recorded at a monitoring site in Kyouei, located at the upper Tokachi River, during 1988–2010 (MILIT 2004). The Urikai River is a small, 31.8-km-long second tributary of the Tokachi River with a watershed area of 65.8 km^2. The water discharge was recorded as 0.63 m^3/s at a monitoring site of Urikai in 2008 (http://www.pref.hokkaido.lg.jp/kn/ksn/H20F920.pdf). Culverts are set up in the upper Urikai River watershed to drain waters from the ando soil to sustain crop production in upland fields.

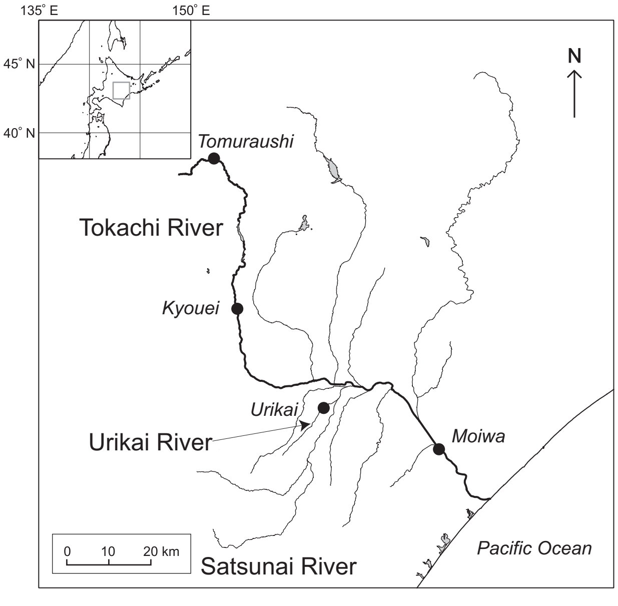

Figure 1 Sampling site locations (closed circles) in this study. The sampling sites Tomurauchi, Kyouei, and Moiwa are located in the main Tokachi River. The Urikai site is situated in the middle Urikai River, which is the second tributary of the Tokachi River.

Sampling and Isolation of Humic Substances

River research was carried out at 4 sites in the headwaters (Tomuraushi site), the upper (Kyouei site) and the lower Tokachi River (Moiwa site), and at 1 site in a tributary, the Urikari River, in June of 2004 and 2005 (Figure 1). Water samples were also collected at the Moiwa site in September 2003. Respective samples were pH 7.0 for the Tomuraushi, pH 5.7–7.5 for the Kyouei, and pH 6.8–7.6 for the Moiwa and Urikai. The conductivity and turbidity were, respectively, 5.1–22.7 mS/m and 12–110 NTU (Table 1). The Urikai River showed higher conductivity than the main Tokachi River.

Table 1 Physicochemical properties of waters collected from the Tokachi River system.[a]

Sample	Sampling date	Distance (km)	pH	WT (°C)	Conductivity (mS/m)	Turbidity (NTU)	DO (mg/L)
Tokachi River							
Tomuraushi	2005/6/28	140.1	7.00	8.6	n.m.	n.m.	12.6
Kyouei	2004/6/29	93.4	5.70	15.0	8.0	14	9.5
	2004/7/1		7.38	18.2	12.4	12	9.9
	2005/6/28		7.46	15.4	5.1	16	6.0
Moiwa	2003/9/25	21.0	6.63	13.9	12.0	32	11.2
	2003/9/26		6.79	14.9	12.0	110	11.7
	2005/6/28		7.12	14.1	10.0	49	10.3
Urikai River							
Urikai	2005/6/30	55.2 (6.9)[b]	7.57	16.9	22.7	29	13.7

[a] WT = water temperature; DO = dissolved oxygen; Distance = Distance from the river mouth of the Tokachi River.

[b] The value in parentheses indicates the distance from the junction with the Tokachi River

We filtered 0.44–9.12 tons of samples with sequentially connected cartridge filters of 3 pore sizes (10, 1, and 0.45 μm). Humic substances were isolated from the river waters using the XAD extraction method (Thurman and Malcolm 1981; Nagao et al. 2007). The river water was acidified to pH 2 with HCl and was passed through a column packed with non-ionic macroporous resin (Supelite™ DAX-8) at a flow rate of 0.4–6.3 L/min, depending on the column size. Elution with 0.1M NaOH solution desorbed the humic substances. Humic and fulvic acids were separated by adjusting the solution to pH 1.5. After cation exchange and HF treatments, powdered samples were obtained by freeze-drying. The percentage of fulvic acid to total humic substances (humic acid + fulvic acid) was 74% to 94%, with an average value of 88 ± 8%, which falls within published data. The humic acid obtained at the Moiwa site in September 2003 was so low that we could not measure the elemental composition and carbon isotopes.

Measurements

Aliquots of about 2 mg powdered humic and fulvic acids were measured for C, H, and N using an elemental analyzer (CHN Corder MT-6; Yanaco Analytical Systems Inc. and Micro Corder JM10; J-SCIENCE LAB Co., Ltd.). Sulfur contents were measured using a flask-combustion method. The measurements were done with precision of ±0.3% (weight % units) for the samples. The oxygen content was estimated by subtracting the C, H, N, S, and ash contents from the total weight.

Liquid-state CP-MAS ^{13}C-NMR spectra were recorded for the fulvic acids using a spectrometer (CMX-300; Chemagnetics Inc.) with a resonance frequency of 75.6 MHz (Fujitake and Kawahigashi 1999). Humic acids could not be determined because of the low amount isolated from the river waters. The composition of carbon species was estimated based on CP-MAS ^{13}C-NMR spectra. Chemical shift assignments were referred from reports by Wilson (1981) and Fujitake and Kawahigashi (1999). The ^{13}C NMR spectra were divided into 5 areas: 0–48 ppm, alkyl-C; 48–110 ppm, *o*-alkyl-C; 110–165 ppm, aryl-C; 165–190 ppm, carboxyl-C; and 190–230 ppm, carbonyl-C.

The powder samples of humic and fulvic acids were adjusted to a weight of approximately 2 mg carbon. The sample was first converted to CO_2 by combustion with CuO and Ag foil, then purified cryogenically. The CO_2 was then reduced to graphite with H_2 over Fe powder (Kitagawa et al. 1993). Its ^{14}C/^{12}C and ^{13}C/^{12}C ratios were measured using accelerator mass spectrometry (AMS) at the National Institute for Environmental Studies (Tanaka et al. 2000) and the Japan Atomic Energy Agency (Aramaki et al. 2000). The ^{14}C activities are determined with respect to the international oxalic acid standard (SRM-4990C, NIST, USA) and are reported in Δ^{14}C (Stuiver and Polach 1977). Measurements were done in 2004, 2005, 2008, and 2010. The typical analytical error of Δ^{14}C was about ±5‰ as a 1σ value of the counting statistics. The difference between duplicate samples was less than the counting error. Also, the ^{14}C background of a chemistry blank on our AMS measurement was given by the IAEA standard code C-1, and its ^{14}C/^{12}C ratio was $<1 \times 10^{-15}$.

The stable carbon isotopic ratio of a sample and the VPDB standard used for normalization were made by analyzing subsamples of CO_2 gas generated during graphite production using a triple collector mass spectrometer (Delta PLUS; Thermo Electron Corp.) with precision of ±0.1‰ as the δ^{13}C value. The nitrogen isotopic ratio of the humic substances was measured with precision of ±0.3‰ typically as the δ^{15}N value and was normalized by the atmospheric N_2 gas standard.

RESULTS AND DISCUSSION

Characteristics of Humic and Fulvic Acids

Elemental compositions of the humic and fulvic acids from the Tokachi River waters are presented in Table 2. Percentages of carbon were 47.77–51.24% for humic acids and 46.74–59.87% for fulvic acids. The nitrogen content of humic acids was higher than that of the fulvic acids. Figure 2 shows the H/C versus O/C atomic ratios of the humic and fulvic acids. The H/C atomic ratio shows the degree of unsaturation and aliphaticity. The humic acids have a higher H/C ratio than the fulvic acids. The O/C atomic ratio is a simple indicator of the carbohydrate content and degree of oxidation. The fulvic acids have a slightly lower O/C ratio compared to the humic acids. These features resemble those of other river humic substances in Japan (Tsuda et al. 2010).

The ^{13}C NMR spectra of fulvic acids are shown in Figure 3. All spectra exhibit a major broad band of alkyl carbons at 5–50 ppm and aryl carbons from 110 to 165 ppm. The percentages of alkyl and aryl carbons are, respectively, 29–33% and 24–26%. The spectral features from each site are similar to each other.

Carbon and Nitrogen Isotopes of Humic and Fulvic Acids

The δ^{13}C and Δ^{14}C values of the Tokachi River humic and fulvic acids are shown in Table 3. The δ^{13}C values are –27.7 to –26.2‰ for the humic acid and –27.6 to –26.9‰ for the fulvic acid in the upper to lower Tokachi River and its tributary. In contrast, the humic and fulvic acids from the headwater site, Tomuraushi, respectively have δ^{13}C values of –24.5 and –26.6 ± 0.4‰. The Δ^{14}C values of humic acids are –159‰ at Tomuraushi, –85 ± 14‰ at the upper site, Kyouei, and –172‰ at the lower site, Moiwa. The fulvic acids have Δ^{14}C values of –55 ± 4‰ at the headwater site, Tomuraushi, +32 ± 10‰ at the upper site, Kyouei, and –49 ± 9‰ at the lower site, Moiwa. The averaged Δ^{14}C value is –148 ± 70‰ for the humic acid and –30 ± 65‰ for the fulvic acid. Numerical differences ($\Delta\Delta^{14}$C) between humic and fulvic acids are 118 ± 96‰ on average. Similar differences in

Table 2 Elemental composition of humic and fulvic acids in waters from the Tokachi River system.

		C	H	N	O	S	
Sample	Sampling date	(%, ash-free basis)					Ash (%)
Humic acid							
Tokachi River							
Tomuraushi	June 2005	51.02	5.90	5.35	37.05	0.68	0.68
Kyouei	June 2004	51.24	5.67	6.06	36.15	0.88	0.73
	June 2005	47.77	5.60	5.06	40.88	0.69	2.10
Moiwa	June 2005	51.22	5.40	3.26	38.68	1.44	13.86
Urikai River							
Urikai	June 2005	50.80	5.90	4.03	37.45	1.82	11.15
Fulvic acid							
Tokachi River							
Tomuraushi	June 2005	59.89	5.72	0.66	33.40	0.33	0.30
Kyouei	June 2004	54.02	4.74	0.93	39.88	0.43	0.14
	June 2005	46.74	4.83	0.75	47.32	0.36	7.53
Moiwa	September 2003	52.97	4.78	1.18	40.31	0.76	0.27
	June 2005	52.77	4.82	1.17	40.56	0.68	0.96
Urikai River							
Urikai	June 2005	53.79	4.99	1.71	38.56	0.95	0.39

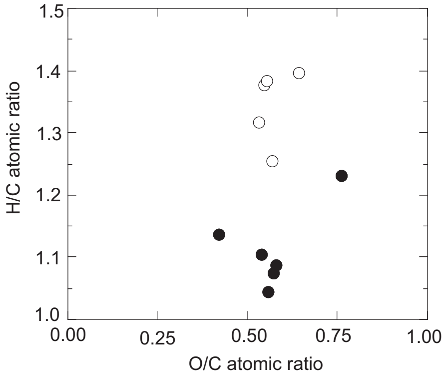

Figure 2 H/C and O/C atomic ratios of humic (empty circles) and fulvic acids (filled circles) isolated from river waters in the Tokachi River system during June and September in 2003–2005.

carbon isotopic signatures between humic and fulvic acids are also observed for other river systems (Hedges et al. 1988; Shiff et al. 1990).

The δ^{15}N value ranges from –0.8 to 1.9‰ for humic acids and 0.3 to 1.3‰ for fulvic acids. These values are higher than those of the International Humic Substances Society (IHSS) standard and reference humic substances isolated from the Suwannee River in swamp and Nordic lake waters, with high DOC concentration ranging from 10–35 mg/L.

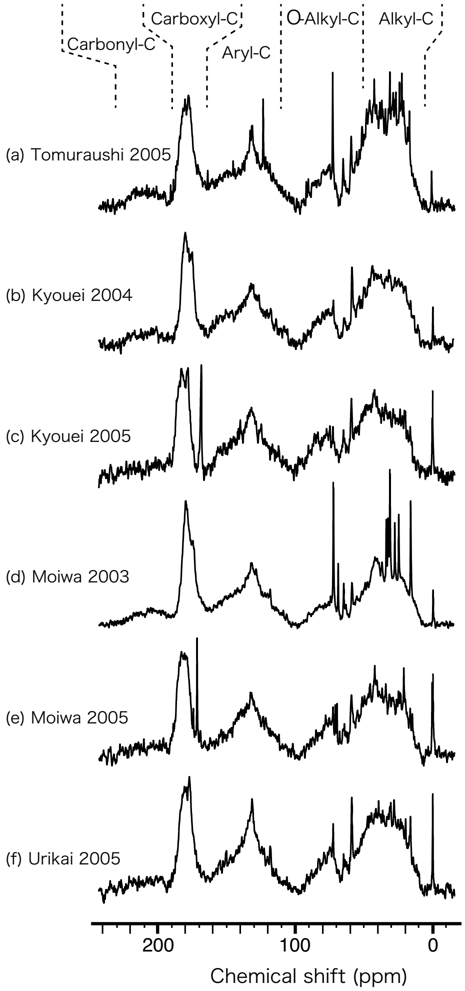

Figure 3 Liquid-state CP-MAS ^{13}C-NMR spectra of fulvic acids isolated from river waters in the Tokachi River system during June and September in 2003–2005.

Downward Variations in Δ^{14}C of Humic Substances

Figure 4 shows an elevation of water-level monitoring sites in the Tokachi River and the Urikai River together with δ^{13}C and Δ^{14}C values for the humic and fulvic acids. The Δ^{14}C values for humic and fulvic acids are in the order: Urikai < Moiwa (lower stream areas) < Tomuraushi (headwater area) < Kyouei (upper stream area). However, the variation pattern is similar with the humic acids and the fulvic acids. Down-river changes in Δ^{14}C of DOC were observed for the Hudson River, although the δ^{13}C values were almost constant at –27.0 ± 0.6‰ (Raymond et al. 2004). In the Tokachi River system, the elemental composition and CP-MAS ^{13}C-NMR spectra of the fulvic acids were similar to those of samples along the flow direction of river water. The proportion of alkyl- + *O*-alkyl-C species (5–110 ppm) for the fulvic acids originated from algae and other plankton was 63–70% and considerably higher than those for the river fulvic acids (McKnight et al. 1994; Fujitake et al. 2009). Freshwater benthic algae exhibit δ^{13}C values of –26 ± 3‰ and phytoplankton have values of –32 ± 3‰ (France 1995). Therefore, the contribution of autochthonous fraction of DOC is small or negligible.

Table 3 Δ^{14}C, δ^{13}C, and δ^{15}N values of humic and fulvic acids in waters from the Tokachi River system.[a]

Sample	Sampling date	^{14}C (pMC)	Δ^{14}C (‰)	δ^{13}C (‰)	δ^{15}N (‰)
Humic acid					
Tokachi River					
Tomuraushi	June 2005	84.1 ± 0.4	–159 ± 4	–24.5 ± 0.1	n.m.
Kyouei	June 2004	90.2 ± 0.4	–98 ± 6	–26.9 ± 0.1	1.3 ± 0.2
	June 2005	93.0 ± 0.4	–71 ± 4	–26.2 ± 0.1	0.6 ± 0.2
Moiwa	June 2005	82.8 ± 0.2	–172 ± 2	–27.5 ± 0.1	1.9 ± 0.4
Urikai River					
Urikai	June 2005	75.3 ± 0.2	–247 ± 2	–27.7 ± 0.1	–0.8 ± 0.3
Fulvic acid					
Tokachi River					
Tomuraushi	June 2005	94.5 ± 0.4	–55 ± 4	–26.4 ± 0.1*	0.3 ± 0.3*
Kyouei	June 2004	102.2 ± 0.4	+22 ± 4	–27.0 ± 0.1	1.3 ± 0.2
	June 2005	104.1 ± 0.4	+41 ± 4	–26.9 ± 0.1	1.0 ± 0.7
Moiwa	September 2003	94.2 ± 0.6	–58 ± 6	–27.3 ± 0.1	1.3 ± 0.2
	June 2005	96.0 ± 0.2	–40 ± 2	–27.3 ± 0.1	0.9 ± 0.2
Urikai River					
Urikai	June 2005	88.1 ± 0.2	–119 ± 2	–27.6 ± 0.1	1.3 ± 0.1

[a] n.m. = not measured for small amount of the sample. *Data from Tsuda et al. (2010). The errors in pMC (percent modern carbon) and Δ^{14}C values are counting errors (1σ).

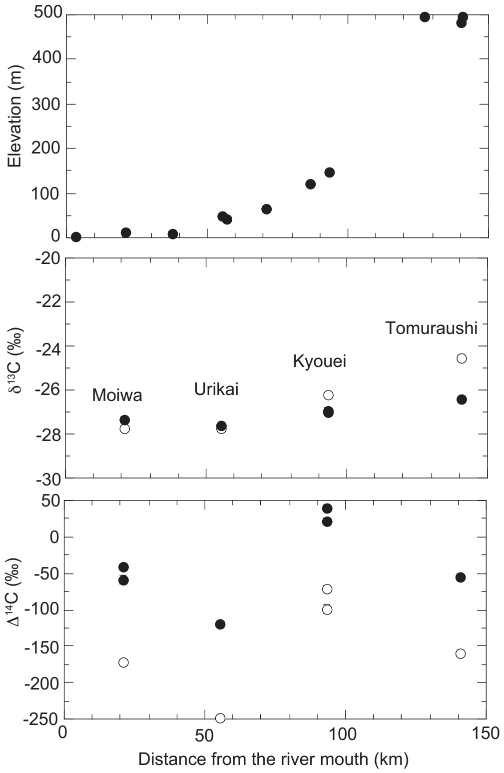

Figure 4 Zero elevation (a), Δ^{14}C (b), and δ^{13}C of humic and fulvic acids (c) in June 2005 as a function of the distance from the mouth of the Tokachi River. Data for zero elevation at water level monitoring sites were referenced from the Japanese Ministry of Land, Intrastructure, and Transport (2004).

Riverine humic and fulvic acids are leached from surrounding soils and exported from groundwaters. Schiff et al. (1990) showed that aquatic humic substances are a mixture of compounds with varying $\Delta^{14}C$ contents that depend on the parent materials of the humic substances and the residence time in the aquifer. Differences in dissolution fractions reflect the hydrophilic properties of humic and fulvic acids (Steinberg 2003). Sorption of humic acids onto soil and rock is higher than that of fulvic acids (Ohte and Kawasaki 2004). Differences in carbon isotopes between humic and fulvic acids were found in soil humic substances (Nagao et al. 2007). Therefore, the transport processes such as pathways, sorption, and sources might be related to differences in carbon isotope composition between humic and fulvic acids in waters from the Tokachi River.

Topography is considered to be a major determinant of the chemistry of groundwaters and surface waters because it influences interactions between biogeochemistry and hydrology in watersheds. The watershed area is 208 km^2 at Tomuraushi, 804 km^2 at Kyouei, and 8208 km^2 at Moiwa. Zero elevation is 13.8 m at Moiwa, 148 m at Kyouei, and 490 m at the Tomuraushi site in the main Tokachi River and 49 m at the site of Urikai River. The riverbed slope is 1/200–1/450 upstream and 1/3000 to 1/5000 at the lower reaches of the Tokachi River. Steep and small watersheds tend to have shallow water flow and shorter residence time of water. The decrease in $\Delta^{14}C$ of humic and fulvic acids along a river line suggests that the supply of apparently older humic and fulvic acids, from the alluvial plain at the middle to lower regions, increases downward along the Tokachi River system. However, the headwater site shows apparently older humic and fulvic acids. This sampling area, which is located at a plateau, is rich in water supplied from the surrounding area, indicating differences in hydrological and geochemical processes. This might be reflected in the higher $\delta^{13}C$ and lower $\Delta^{14}C$ values of the headwater humics than those of the upper site Kyouei. The Urikai River is a tributary of the Satsunai River, which is one of the major tributaries of the Tokachi River, and runs through upland fields at the upper area. There are culverts in the upper upland field to drain waters from ando soil to sustain field-crop production. The lower $\Delta^{14}C$ value in comparison to the Moiwa site may be contributed from humic and fulvic acids in the deeper soil layer through culverts into the river water.

Figure 5 shows the paired $\delta^{13}C$–$\Delta^{14}C$ values for humic and fulvic acids. The $\Delta^{14}C$ and $\delta^{13}C$ values for humic and fulvic acids decrease from the upper to the lower sites including the tributary site, although the headwater data are scattered from the variation trend. The distribution of $\delta^{13}C$–$\Delta^{14}C$ values for humic and fulvic acids vary with watershed environments such as wetlands, forest, and paddy field (Hedges et al. 1986; Nagao et al. 2004, 2011). The ^{14}C-enriched humic substances are due to a larger contribution from newly produced, younger humic substances reached from soils (Raymond and Bauer 2001b). Therefore, the differences in carbon isotopic signatures for the Tokachi River humics suggest that the residence time of fulvic acid in the watershed is shorter than that of humic acid. The pathways and sources of humic substances in river waters might be different from each watershed in the headwater, upper, and lower reaches of Tokachi River. Our data constitute a snapshot taken in early summer. We conclude that monitoring studies must be conducted throughout the year.

CONCLUSION

This report describes characteristics of dissolved humic substances and their migration behavior in the Tokachi River system using $\delta^{13}C$ and $\Delta^{14}C$ as tracers for dissolved organic matter. Humic and fulvic acids were isolated from river waters at 4 sites from the headwaters to the lower Tokachi River and from the second tributary, Urikai River, using XAD extraction in the early summer season during 2004–2005 together with a September sampling conducted in 2003. The $\delta^{13}C$ values of

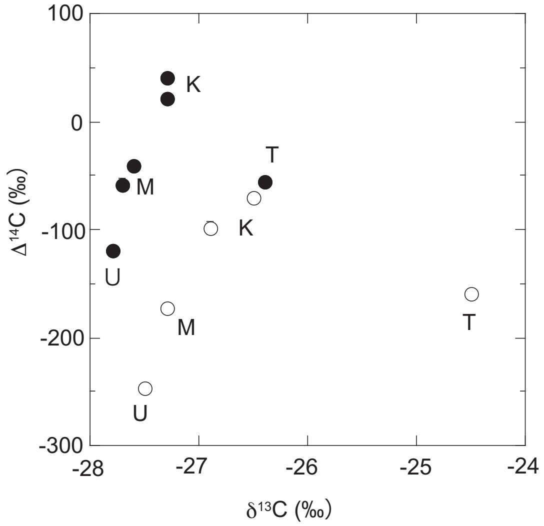

Figure 5 Relationship between $\Delta^{14}C$ and $\delta^{13}C$ values for humic (empty circles) and fulvic acids (filled circles) in water samples collected from the Tokachi River (T: Tomuraushi, K: Kyousei, M: Moiwa) and its second tributary, the Urikai River (U: Urikai).

humic and fulvic acids ranged respectively from –27.5 to –24.5‰ and –27.8 to –26.4‰. The $\Delta^{14}C$ values were –247 to –71‰ for humic acids and –119 to +41‰ for fulvic acids. Structural features such as elemental composition and ^{13}C NMR spectra were mutually similar. The $\delta^{13}C$ showed similar values to those for humic acids from upper to lower sites and was 1.9‰ lower than that of humic acids at the headwater site. However, the differences in $\Delta^{14}C$ between humic and fulvic acids were 119 ± 11‰ on average. The differences in carbon isotopic signatures suggest that the mean residence time of fulvic acids is shorter than that of the humic acids, and/or suggest differences in their sources and transport pathways. A downward variation in $\delta^{13}C$ and $\Delta^{14}C$ values was observed from the upper site to the lower and tributary sites, although the headwater site had the highest $\delta^{13}C$ and lower $\Delta^{14}C$ value, which indicates that the sources of headwater humic substances and hydrological pathways differ from those of the upper site. These results suggest that land-use type and topographical features are key parameters to elucidate the migration behavior of humic and fulvic acids in the Tokachi River Basin.

ACKNOWLEDGMENTS

The authors thank Ms M Kiuchi and Ms N Sato of the Center for Instrumental Analysis, Hokkaido University, for measurements of elemental composition for the humic and fulvic acids. This study was partly funded by Grants-in-Aid for Scientific Research, Nos. 1531002 and 18310002 from the Japanese Ministry of Education, Culture, Sports Science, and Technology. The ^{14}C measurements were partly carried out under the Shared Use Program of JAEA Facilities.

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