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Transport of U- and Th-series nuclides in a Baltic Shield watershed and the Baltic Sea

D. Porcelli,[1]* P. S. Andersson,[2] M. Baskaran,[3] and G. J. Wasserburg[1]

[1]The Lunatic Asylum of the Charles Arms Laboratory, Division of Geological and Planetary Sciences, California Institute of Technology, Pasadena, CA 91125 USA
[2]Swedish Museum of Natural History, Laboratory for Isotope Geology, Box 50007, 104 05 Stockholm, Sweden
[3]Department of Geology, Wayne State University, Detroit, MI 48202 USA

Abstract—The transport of Th, Ra, and ^{210}Pb from a continental source region and through an estuarine environment was investigated. Unlike previous studies, here both short- and long-lived nuclide data were obtained for river inputs, river water, and estuarine waters. The mire-rich Kalix River drainage basin was chosen as a typical northern shield area because this river may represent typical waters flowing into the Arctic and northern seas.

Groundwaters from bedrock and glacial tills have comparable Th isotope concentrations and do not exhibit significant Th isotopic shifts relative to host rocks. The extensive peat deposits of the basin receive groundwater discharges and concentrate Th and U (but not Ba and Ra), which cause high ^{230}Th/^{232}Th ratios in mire waters. However, mire outflows do not have a significant impact on Th and Ra isotopic compositions of the river.

Overall weathering characteristics for the basin are obtained from the river data. The ^{230}Th/^{232}Th, ^{228}Ra/^{226}Ra, and ^{226}Ra/Ba river ratios are comparable to those of source rocks, consistent with similar release rates of these nuclides from U-, Th-, and Ba-bearing minerals. River ratios of (^{230}Th/^{238}U)$_{AR}$ and (^{226}Ra/^{238}U)$_{AR}$ are <1, so that Th and possibly Ra are accumulating in the weathering regions, and the weathering profile is still evolving. Low (^{228}Ra/^{232}Th)$_{AR}$ and (^{226}Ra/^{230}Th)$_{AR}$ ratios indicate that Th is preferentially retained over Ra. River (^{234}Th/^{238}U)$_{AR}$ ratios are greater than (^{230}Th/^{238}U)$_{AR}$ ratios and suggest that in systems where river inputs are well characterized, these ratios can be used to calculate Th transit times through the watershed. Filtration data indicate that although a dominant fraction of the Th is transported in the river on particles, the rest is almost entirely carried by colloids.

The Kalix River discharges into the Baltic Sea. Model calculations for the transport of Th and Ra isotopes in the Baltic Sea show that the high ratios of (^{234}Th/^{238}U)$_{AR}$ found here reflect long Th residence times relative to particle scavenging of ~50 d. The water column ^{232}Th budget is dominated by eolian inputs. The ^{226}Ra concentrations may be higher than those of water inflows, with ≤60% derived from underlying sediments. A greater fraction of ^{228}Ra is derived from sediments to balance the decay of ^{228}Ra within the water column during the 35-yr residence time of water in the Baltic. The Baltic (^{228}Ra/^{226}Ra)$_{AR}$ ratios, which are relatively constant over a range of salinities, are fortuitously similar to those of the river inflows. *Copyright © 2001 Elsevier Science Ltd*

1. INTRODUCTION

The elements Th, Ra, and Pb are generally associated with particles and colloids during weathering and aqueous transport. Because the isotopes of these elements are related through the U- and Th-decay series (Fig. 1), their combined study provides insights into their relative weathering release rates and transport rates through the surface environment. Although various studies have examined the behavior of Th isotopes in the oceans (see Cochran, 1992), there are comparatively few data for rivers and estuaries. Data for ^{232}Th in rivers are very limited (Moore, 1967; Andersson et al., 1995), and it is generally assumed that all the Th is on fine particles. Colloids and ferro-oxyhydroxides can be important for riverine U transport (Porcelli et al., 1997; Andersson et al., 1998) and are also possible carriers of Th (Viers et al., 1997). In estuaries, ^{234}Th produced in the water column is rapidly removed (Santschi et al., 1979; Kaufman et al., 1981), although there are few data on the behavior of long-lived, river-supplied Th isotopes. Radium is also strongly absorbed on river particles but is released into brackish waters (Li et al., 1977). This contrasting behavior with Th is most clearly studied by comparison between parent Th and daughter Ra isotopes. Another highly particle-reactive isotope in the ^{238}U series is ^{210}Pb, which is distinctive in having a large atmospheric fallout input and so may be transported differently from nuclides released during weathering.

The transport of Th, Ra, and Pb radionuclides are examined here in a well-characterized watershed and adjacent brackish water basin. In contrast to other studies, both long- and short-lived nuclides were analyzed, and unique constraints on the relative behavior of U, Th, Ra, and Pb isotopes were obtained. The study area, the Kalix River watershed in north Sweden (Fig. 2), is a typical northern Precambrian Shield area, with large areas covered by mires (peatlands). The Kalix has low concentrations of suspended detrital material, but high concentrations of organics and particulate Fe and Mn, and so has favorable conditions for studying the interaction of trace elements with organic ligands and secondary particle phases. The

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* Author to whom correspondence should be addressed, at Institute for Isotope Geology and Mineral Resources, Department of Earth Sciences, ETH Zürich, NO C61, Soneggstrasse 5, CH-8092 Zürich, Switzerland (porcelli@erdw.ethz.ch).
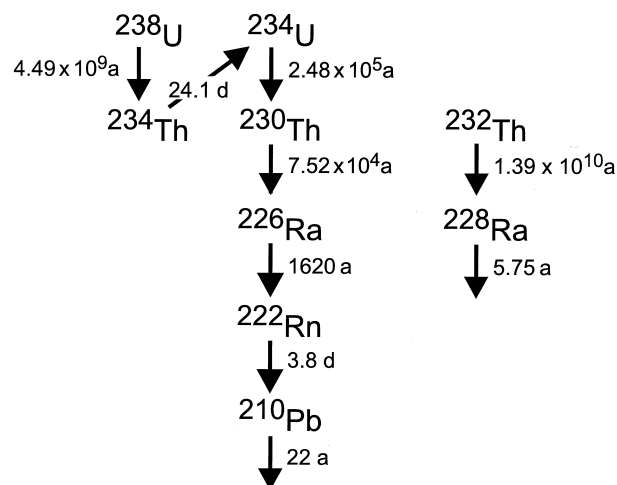
^{238}U $\xrightarrow{4.49 \times 10^9 a}$ ^{234}Th $\xrightarrow{24.1 d}$ ^{234}U $\xrightarrow{2.48 \times 10^5 a}$ ^{230}Th $\xrightarrow{7.52 \times 10^4 a}$ ^{226}Ra $\xrightarrow{1620 a}$ ^{222}Rn $\xrightarrow{3.8 d}$ ^{210}Pb $\xrightarrow{22 a}$

^{232}Th $\xrightarrow{1.39 \times 10^{10} a}$ ^{228}Ra $\xrightarrow{5.75 a}$

Fig. 1. The nuclides of the ^{238}U and ^{232}Th decay series discussed in this study.

Kalix drains into the Baltic Sea, a basin with a relatively stable salinity profile where the effects of brackish water mixing can be readily examined. This study focuses on several aspects of radionuclide transport though the watershed and the Baltic.

1.1. River Transport

The transport of Th isotopes, along with Ra and ^{210}Pb, on particles, colloids, and in solution is examined, along with the possibility of calculating of aqueous transport transit times by ^{234}Th/^{230}Th ratios.

1.2. Radionuclide Sources

The importance of groundwater, surface-water, and mire-water inputs to the Th and Ra river budget are evaluated, and overall relative removal rates of U, Th, and Ra from the watershed are calculated.

1.3. Behavior in the Baltic

Data are presented for the distribution of U, Th, Ra, and ^{210}Pb in the basin and are used to evaluate the input and removal rates of Th and Ra isotopes.

The data obtained here have been combined with that for U previously reported by Porcelli et al. (1997) and Andersson et al. (1998). This work of Th and Ra isotopes throughout the Kalix watershed and Baltic complements previous studies of U transport in the Kalix and Baltic (Andersson et al., 1995, 1998; Porcelli et al., 1997) and the distribution of ^{230}Th and ^{232}Th in the Baltic (Andersson et al., 1995). Other studies have examined the distribution of other trace elements in this area (e.g., Andersson et al., 1992, 1994; Ingri et al., 2000).

2. SAMPLING AND ANALYTICAL METHODS

River samples were collected at four locations (Fig. 2) in June 1995: Rautas, a tributary representing drainage from above the mire-rich regions and near the headwaters in the Caledonides; Narkån, a tributary draining a region largely covered by mires; Tärendö, in the center of the watershed; and Kamlunge, near the Kalix mouth. Waters and peats

were obtained from Peräjävuoma and Laurivuoma mires (see Porcelli et al., 1997), along with groundwaters from Quaternary tills and the granitic Precambrian basement. For ^{232}Th and ^{230}Th analyses, water was drawn directly through 0.45-μm filters and into storage containers. For ^{234}Th, ^{226}Ra, ^{228}Ra, and ^{210}Pb analyses, large volumes (200–300 L) were pumped through a flowmeter, then 0.45-μm filters to collect particles, and then through Mn oxide–coated filters to trap remaining nuclides (Baskaran et al., 1993). Trapping efficiencies were calculated assuming similar efficiencies for the two Mn-coated filters and were generally >90% for Th and ^{210}Pb (see Baskaran et al., 1993). Because of possible low trapping efficiencies of Ra on these large filters, only ^{228}Ra/^{226}Ra ratios were obtained from these filters. Absolute ^{226}Ra activities were obtained from separate ~20-L volumes with two in-line Mn oxide–coated acrylic fibers (Reid et al., 1979) with >90% trapping efficiencies.

Baltic Sea samples (Fig. 2) were collected in June 1995 from station BY-15 at the Gotland Deep (total depth, 240 m) and from station F-2 in the Gulf of Bothnia (total depth, 90 m). At the Gotland Deep, deep waters are renewed at irregular intervals, with intervening periods of anoxia. The last renewal occurred in 1994; during sampling for this study in June 1995, O$_2$ levels had dropped to 1.3 mg/L. Samples for ^{232}Th and ^{230}Th measurements were obtained with a Go-Flo sampler. Short-lived nuclides were collected with a submersible pump to pass large volumes directly through filters on deck.

Radionuclide particle abundances were obtained by ashing and analyzing the 0.45-μm filters. Water nuclide concentrations associated with particles were obtained by dividing these abundances by the volume of water filtered, whereas concentrations on particles were obtained by dividing these abundances by the mass of ashed particles (ASL). Reported bulk water concentrations are the sums of the nuclide concentrations in particles and 0.45-μm-filtered waters. ^{232}Th and ^{230}Th were analyzed by TIMS (Chen et al., 1986) and short-lived nuclides by counting methods (Baskaran et al., 1993). Blanks for the procedures used were generally <5% of the measured abundances. Errors listed in the tables include external reproducibility, and for the short-lived nuclides, errors were significant where concentrations were low. Activity ratios are identified here by the subscript AR. Ba, a chemical analog for Ra, was measured at SGAB-Analys, Luleå, Sweden. The U data for the samples analyzed here were reported by Porcelli et al. (1997) and Andersson et al. (1998).

Several 0.45-μm-filtered waters were divided into colloids and "dissolved" fractions by ultrafiltration techniques (see Baskaran et al., 1992; Porcelli et al., 1997) with Amicon 10-kD hollow fiber cartridges. After each sample, an HCl rinse was circulated throughout the filtration system and was retained. The ultrafiltration system was evaluated by measuring the total recovery of different species in the three recovered fractions (ultrafiltered water, colloid concentrate, and acid rinse). Porcelli et al. (1997) provided data on major cations and U in the three fractions from Kamlunge river water and a Baltic water, By-15, 30m. The Th data for these samples are in Tables 1 and 4. For the Kamlunge sample, the ultrafiltered water contained 13% of the Th found in the 0.45-μm-filtered water, whereas the colloid fraction contained 52% and the acid rinse 11%. Therefore, the total Th recovered in the water and colloids is 65%, whereas the total in all three fractions is 75%, that found in the 0.45-μm-filtered water, indicating some loss of Th in the filtering system. The possibility of sample cross-contamination is low because the river samples, with the highest losses, were filtered last, and there was no evidence of cross-contamination of U between isotopically distinct samples (Porcelli et al., 1997).

3. KALIX RIVER BASIN: RESULTS AND DISCUSSION

Kalix basin data are in Tables 1 and 2. The Results and Discussion are divided here into the characteristics of river transport, inputs to the river, and watershed weathering. Comparison between the data and the composition of the watershed rocks necessarily arise, and in the absence of comprehensive data on the distribution of U and Th in the area, it is reasonable to assume that the overall composition of Baltic Shield rocks and tills is similar to that of the upper crust (see, e.g., Taylor and McClennan, 1985).
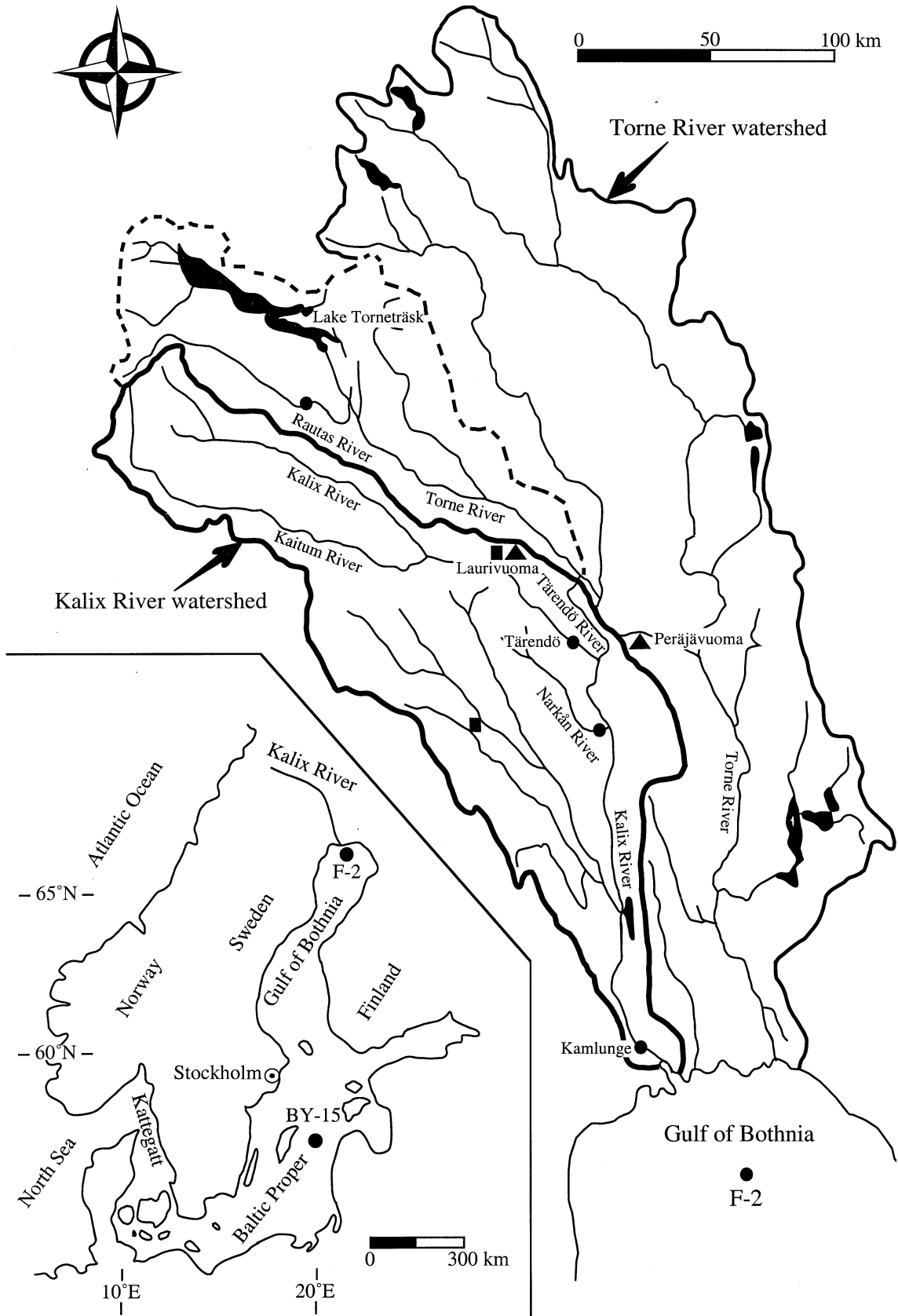
Fig. 2. The Kalix River watershed, with sampling sites for river and Baltic waters (circles), mires (triangles), and groundwaters (squares). The dashed line shows the area drained by both the Kalix and Torne Rivers.

Table 1. U-Th series nuclide data, Kalix River 1995 samples.

Site	SPM (mg/L)	ASL (mg/L)	^{238}U pg/g	^{238}U dpm/100 L	δ^{234}U	^{232}Th pg/g	^{232}Th dpm/100 L	^{230}Th/^{232}Th ($\times 10^{-6}$)	^{234}Th (dpm/100 L)	^{226}Ra (dpm/100 L)	^{228}Ra (dpm/100 L)	^{210}Pb (dpm/100 L)	Ba (ng/g)
Rautas (Kalix Basin headwaters)													
<0.45 μm			54.9 ± 0.1	4.10 ± 0.01	1007 ± 7	12.49 ± 0.09	0.307 ± 0.002	11 ± 2	0.8 ± 1.7	1.50 ± 0.60	2.81 ± 0.22	1.6 ± 0.7	6.2 ± 1.0
<10 kD			22.0 ± 0.4	1.64 ± 0.03	1016 ± 7	3.16 ± 0.02	0.0778 ± 0.0005	15 ± 6	—	—	—	—	—
>0.45 μm			57 ± 1	4.26 ± 0.07	1198 ± 16	52.13 ± 0.51	1.28 ± 0.01	6 ± 2	5.4 ± 0.8	1.08 ± 0.12	1.0 ± 0.3	7.1 ± 0.6	3.27
Bulk water[b]	4.13	4.89	112 ± 1	8.36 ± 0.08	1104 ± 10	64.6 ± 0.5	1.67 ± 0.01	7 ± 2	6.2 ± 1.9	2.6 ± 0.6	3.8 ± 0.3	8.7 ± 0.9	9.5
Tärendö (Central Kalix watershed)													
<0.45 μm			105.7 ± 0.3	7.89 ± 0.02	1503 ± 16	16.19 ± 0.07	0.399 ± 0.002	13 ± 1	1.19 ± 1.6	2.48 ± 0.72	3.8 ± 0.3	2.2 ± 0.7	11.2 ± 2
<10 kD			71.7 ± 0.2	5.35 ± 0.01	1479 ± 12	2.74 ± 0.01	0.0675 ± 0.0002	9 ± 1	—	—	—	—	—
>0.45 μm			≥106	≥7.9	—	≥16.2	≥0.40	—	27.9 ± 7.6	12.1 ± 2.8	11.5 ± 2.3	25.4 ± 3.6	30
Bulk water[b]	31.95	28.0	—	—	—	—	—	—	29.1 ± 7.6	14.6 ± 2.9	15.3 ± 2.3	27.6 ± 3.7	41
Narkån (Mire-rich area tributary)													
<0.45 μm			187.2 ± 0.4	13.98 ± 0.03	770 ± 8	28.58 ± 0.25	0.704 ± 0.006	8 ± 3	0.75 ± 1.34	3.0 ± 0.7	3.8 ± 0.2	1.1 ± 0.4	10.2 ± 0.3
<10 kD			12.63 ± 0.03	0.943 ± 0.002	743 ± 16	1.833 ± 0.004	0.045 ± 0.000	5 ± 1	—	—	—	—	1.97 ± 0.2
>0.45 μm			≥187	≥14	—	≥29	≥0.70	—	1.47 ± 0.62	0.4 ± 0.1	0.5 ± 0.2	0.6 ± 0.2	0.81
Bulk water[b]	2.82	1.22	—	—	—	—	—	—	2.2 ± 1.5	3.4 ± 0.7	4.3 ± 0.3	1.7 ± 0.5	41
Kamlunge (Kalix river mouth)													
<0.45 μm			183.6 ± 0.3	13.71 ± 0.02	896 ± 6	23.92 ± 0.10	0.589 ± 0.002	7 ± 1	1.26 ± 1.76	3.27 ± 0.72	4.84 ± 0.48	2.08 ± 1.56	12.2 ± 0.5
<10 kD			39.8 ± 0.1	2.97 ± 0.01	853 ± 13	3.02 ± 0.01	0.0743 ± 0.0002	5 ± 3	—	—	—	—	4.6 ± 0.4
>10 kD			61.0	4.56	878 ± 7	12.49	0.307	8 ± 2	—	—	—	—	0.5
10 kD filter rinse			71.0	5.30	—	2.53	0.062	—	—	—	—	—	1.9
>0.45 μm			41	3.06	798 ± 10	48.70 ± 0.80	1.20 ± 0.02	7 ± 2	6.20 ± 2.30	1.85 ± 0.28	1.41 ± 0.72	6.6 ± 0.9	3.5
Bulk water[b]	2.14	2.60	224.6 ± 0.3	16.77 ± 0.02	878 ± 6	72.62 ± 0.81	1.79 ± 0.02	7 ± 2	7.5 ± 2.9	5.1 ± 0.8	6.3 ± 0.9	8.7 ± 1.8	15.7

[a] Data from Porcelli et al. (1997) and Andersson et al. (1998). All errors are 2 σ.
[b] Bulk water radionuclide values are the sums of the <0.45-μm and >0.45-μm fractions.

Table 2. U-Th series nuclide data, Kalix River watershed mires and groundwaters.[a]

Site	^{238}U			^{232}Th		$^{230}Th/^{232}Th$ ($\times 10^{-6}$)	Ba (ng/g)
	pg/g	dpm/100 L	$\delta^{234}U$	pg/g	dpm/100 L		
Laurivuoma mire							
Spring inflow $<0.45\ \mu m$	$(1.22 \pm 0.05) \times 10^5$	9110 ± 373	602 ± 3	6.91 ± 0.02	0.1701 ± 0.0005	12 ± 1	39.0 ± 1.0
Mire outflow $<0.45\ \mu m$	$(9.00 \pm 0.06) \times 10^3$	672 ± 5	790 ± 4	17.43 ± 0.18	0.4291 ± 0.0044	73 ± 5	12.2 ± 0.2
Mire water $<0.45\ \mu m$	254.8 ± 0.8	19.03 ± 0.06	978 ± 12	2.21 ± 0.01	0.0544 ± 0.0002	104 ± 2	29.6 ± 0.3
Peräjävuoma mire							
Mire water $<0.45\ \mu m$	2.12 ± 0.01	0.158 ± 0.001	568 ± 30	1.838 ± 0.004	0.0452 ± 0.0001	7 ± 2	8 ± 1
Mire outflow $<0.45\ \mu m$	3.18 ± 0.06	0.237 ± 0.004	866 ± 504	2.643 ± 0.014	0.0651 ± 0.0003	—	8 ± 1
Mire peal	15.5 ± 0.8^A	1.16 ± 0.06^A	193 ± 14	72.3 ± 1.3^A	1.78 ± 0.32^A	2 ± 1	—
Till groundwaters							
GW1 (recharge area) $<0.45\ \mu m$	21.7 ± 0.03	1.621 ± 0.002	242 ± 6	7.70 ± 0.03	0.1896 ± 0.0007	4 ± 1	—
GW2 (discharge area) $<0.45\ \mu m$	38.8 ± 0.2	2.90 ± 0.01	91 ± 15	26.89 ± 0.29	0.662 ± 0.007	4 ± 1	—

[a] Data from Porcelli et al. (1997) and Andersson et al. (1998). All errors are 2 σ.
[b] Mire peat concentrations are in μm or dpm per gram of ashed sample.

3.1. Transport of Radionuclides in the Kalix River

3.1.1. Th Transport

Th distribution along the river. The Th river data are shown in Figure 3. The ^{232}Th concentrations in 0.45-μm-filtered waters are 12.5 to 28.6 pg/g. The Kamlunge value (23.9 pg/g) is comparable to that obtained for May 1991 (19.3 pg/g; Andersson et al., 1995). Available data for other rivers are limited. Centrifuged samples from the Mississippi River (10 pg $^{232}Th/g$) and from the Amazon River (100 pg $^{232}Th/g$) may have included particulates (Moore, 1967). Viers et al. (1997) found 12 to 137 pg/g in 0.22-μm-filtered Cameroon River waters.

For all four samples, the ^{234}Th activities (Fig. 3) measured in the 0.45-μm-filtered samples ($<\sim 2$ dpm/100 L) are much lower than those associated with the >0.45-μm particle fractions; these are typically 1.5 to 6.2 dpm/100 L, although an unusually high value of 28 dpm/100 L was found at Tärendö. This sample contains the highest mass concentration of inorganic particles (28 mg/L). There, the association of ^{234}Th with the particles is similar to that in other samples, with particle ^{234}Th concentrations of 10 dpm $^{234}Th/g$-particles comparable to values found for the other samples (11–24 dpm$^{234}Th/g$-particles). The higher bulk ^{234}Th activity in this sample can be explained by the inclusion of resuspended particles that had previously equilibrated with river water and therefore supply a large fraction of the total ^{234}Th in this sample.

Th on colloids. The ^{232}Th in the four 10-kD ultrafiltered samples have a narrow range of concentrations (1.83–3.16 pg Th/g) that constitute a small fraction (6–24%) of the total Th in 0.45-μm-filtered waters. As the difference between the 0.45-μm- and 10-kD–filtered waters is assumed to be associated with >10-kD colloids; Th in 0.45-μm-filtered samples appears largely associated with colloids (see Fig. 3). A similar association of U with colloids was found in these samples (Porcelli et al., 1997), and so ratios of Th/U ratios in colloids (0.15–0.40) and 0.45-μm-filtered waters (0.13–0.23) are similar. However, the specific colloid carriers cannot be unambiguously identified and could include clays (Kennedy et al., 1974) and Fe oxyhydroxides. Also, colloidal humic acids strongly complex Th in

laboratory solutions (Nash and Choppin, 1980), and an association of U and Th with humic colloids in groundwater and rivers has been found (Dearlove et al., 1991; Viers et al., 1997).

"Dissolved" Th. The concentrations in the four ultrafiltered river samples of ~ 2 to 3 pg $^{232}Th/g$ provides an estimate of the concentration of "dissolved" riverine Th. Langmuir and Herman (1980) examined the thermodynamic data for solubility in natural waters with respect to thorianite and found that for typical concentrations of inorganic ligands, the Th solubility limit is on the order of 1 fg/g. However, organic ligands can greatly increase Th solubility (Langmuir and Herman, 1980); further information is required to determine which such compounds are present. Kalix ultrafiltered waters still had substantial concentrations of organic compounds, with 5 to 7 mg/L dissolved organic carbon compared with 6 to 9 mg/L dissolved organic carbon for 0.45-μm-filtered waters (Porcelli et al., 1997), so that the organic carbon in these waters is dominantly not on >10-kD colloids (see also Ingri et al., 2000).

Th on particles. The >0.45-μm particles at Rautas and Kamlunge are the dominant carriers of ^{232}Th, containing 81 and 67% of the Th in the bulk samples, respectively. The corresponding concentrations of ^{232}Th on particles are 10.7 and 18.7 μg $^{232}Th/g$ (see Table 1 for ASL data). The value of the Th concentration in the Kamlunge sample is higher than that of the upper continental crust (with 10.7 μg $^{232}Th/g$; Taylor and McLennan, 1985). The particles from Kamlunge also are greatly enriched in Fe, with a Fe/Al ratio of 1.16, compared with an upper crustal value of 0.30, and in U (16 $\mu g U/g$, compared with 1.8 $\mu g^{238}U/g$). In contrast, at Rautas, the Th concentration and Fe/Al ratio (0.37) are equivalent to upper crust values, suggesting that neither Fe nor Th have been enriched relative to detrital material represented by the particle Al concentration.

Some inferences can be made regarding the distribution of Th in the Kamlunge particles. Iron oxyhydroxides in the Kamlunge particles are the likely carriers of nondetrital U (Andersson et al., 1998) and also of Th. Following Andersson et al. (1998), an apparent partition coefficient for partitioning of Th between dissolved species and these Fe phases is
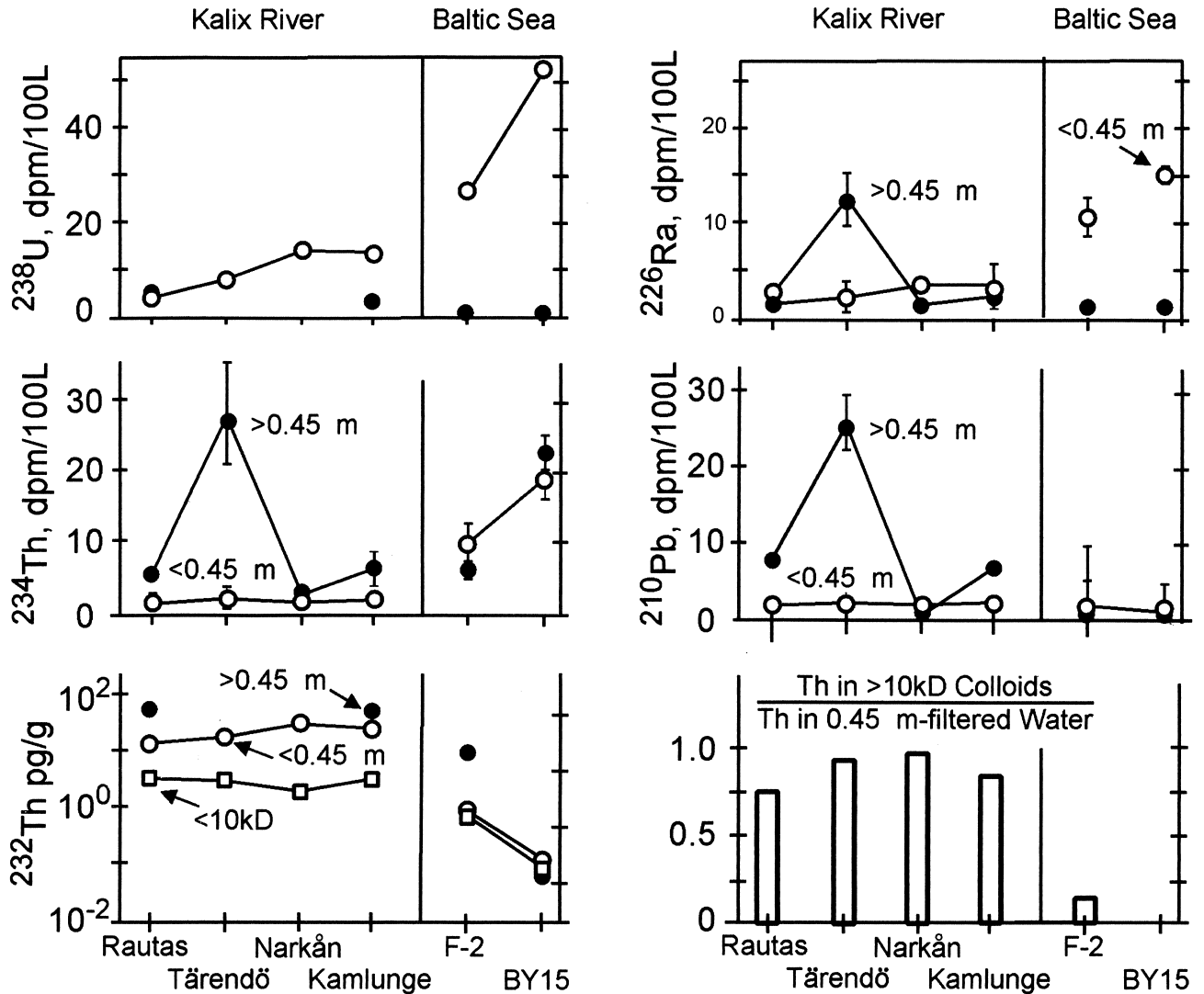
Fig. 3. (A) Th concentrations in 0.45-μm-filtered waters increase along the watershed but are much lower in brackish waters. (B) The fraction of Th on colloids in 0.45-μm-filtered waters (75–90%) is higher in the river than in the Baltic. (C–F) The ^{238}U activities in the filtered river samples are substantially higher than those of ^{234}Th, ^{226}Ra, and ^{210}Pb, which all fall within a limited range. Particles generally carry a significant fraction of these nuclides and carry a dominant fraction at Tärendö. Activities of ^{238}U, ^{234}Th, and ^{226}Ra are greater within the brackish waters, where particles are only important for ^{234}Th.

$$^{Th}\hat{K}_d^{Fe} = \frac{(Th/Fe)_{Particle}(X_{Th}/X_{Fe})}{^{232}C_R^{Diss}}, \qquad (1)$$

where $^{232}C_R^{Diss}$ is the concentration of dissolved Th in the river (i.e., in ultrafiltered water). X_{Th} is the fraction of Th on the particles that is nondetrital, so that $X_{Th} = 1 - (Th/Al)_{detrital}/$ $(Th/Al)_{particle}$, assuming that Al is entirely in detrital grains. The analogous parameter for Fe is X_{Fe}. By using a (Th/ Al)$_{detrital}$ ratio equal to that of the upper crust (1.3×10^{-4}; Taylor and McLennan, 1985), and $(Th/Al)_{particle} = 2.92 \times 10^{-4}$ for Kamlunge (Andersson et al., 1998), then the fraction of Kamlunge Th that is nondetrital is $X_{Th} = 0.55$, and log $^{Th}\hat{K}_d^{Fe} = 7.49$, which is higher than the U value of log $^{Th}\hat{K}_d^{Fe}$ of 6.50.

Th isotopic equilibration. In the Kamlunge sample, the ^{230}Th/^{232}Th ratios of the particles, 0.45-μm-filtered water, and 10-kD ultrafiltered water are indistinguishable from one another, indicating that these Th isotopes are equilibrated between particles, colloids, and dissolved species. For the Rautas sample, the measured value for the particles is lower than that for the other fractions, indicating less equilibration between the phases, although the difference is comparable to the error limits of the measurements and requires confirmation.

3.1.2. Ra Transport

Ra distribution along the river. The ^{226}Ra activities in 0.45-μm-filtered waters are in a narrower range (1.5–3.27
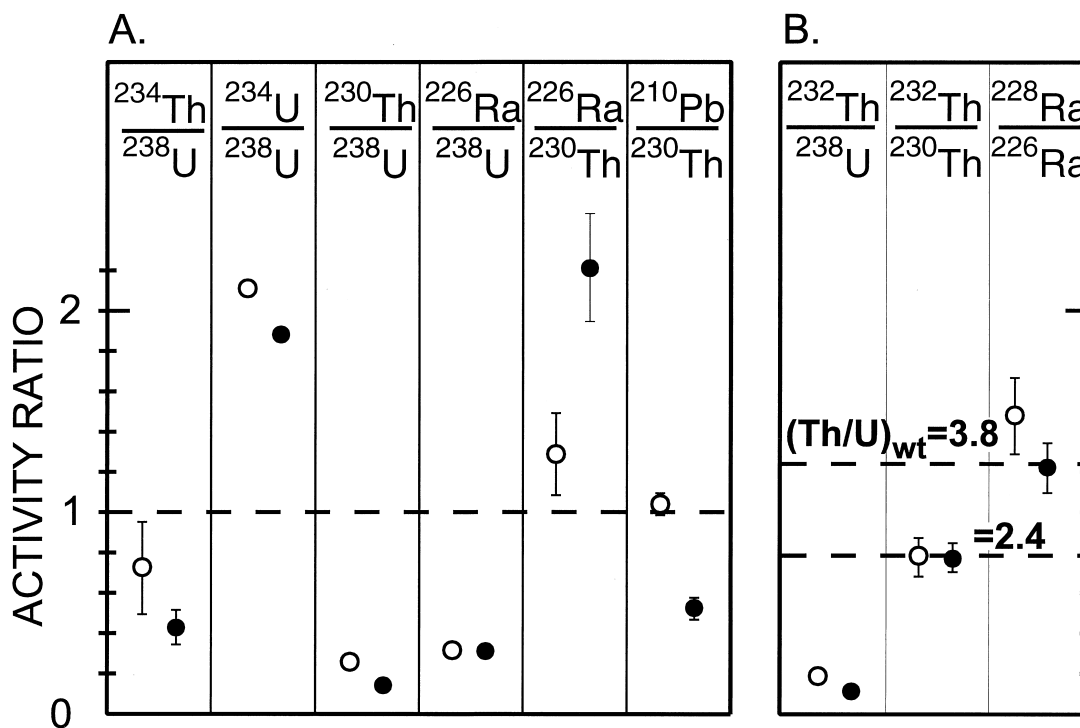
Fig. 4. Bulk sample data for Rautas (open circles) and Kamlunge (solid circles). (A) River activity ratios of ^{238}U series nuclides. Ratios of ($^{234}U/^{238}U$) >1 reflect recoil-induced release of ^{234}U from minerals (Porcelli et al., 1997). Ratios of ($^{230}Th/^{238}U$) <1 and ($^{226}Ra/^{238}U$) <1 are due to retention of Ra and Th within the watershed, whereas values of ($^{226}Ra/^{230}Th$) >1 indicate that Ra is mobilized preferentially to Th. Ratios of ($^{210}Pb/^{238}U$) reflect input of ^{210}Pb by weathering and fallout. (B) Ratios of ^{238}U and ^{232}Th series nuclides. The ($^{232}Th/^{230}Th$) and ($^{228}Ra/^{226}Ra$) ratios are compatible to upper crust values and reflect the ($^{232}Th/^{238}U$) ratio of source rocks. Low ($^{232}Th/^{238}U$) ratios reflect preferential retention of Th in the source regions.

dpm/100 L) than in particles (which account for 0.4–12 dpm/ 100 L; Table 1 and Fig. 3). The pattern of ^{226}Ra activities along the river follows that of ^{234}Th, with the particle-rich Tärendö sample having the highest bulk activity. Near the Kalix mouth at Kamlunge, particles carry only a small fraction (36%) of the ^{226}Ra.

Ra on colloids. Data are not available for Ra in ultrafiltered river waters, although data for Ba were obtained. A substantial fraction of Ba in the Narkån (81%) and Kamlunge (62%) samples did not pass through the 10-kD ultrafilter. However, Viers et al. (1997) argued that alkaline earth elements retained on ultrafilters from organic-rich waters is largely an artifact of filtration and does not reflect bonding by organic ligands.

Ra on particles. A substantial fraction of the ^{226}Ra (12–83%), as well as the Ba, is carried on particles in the river. The concentration of Ba, and so Ra, in natural waters is often controlled by barite solubility, with a solubility product of 10^{-10} (Hem, 1985). The average SO_4 concentration of the Kalix is 44 μm (Ingri et al., 1997), so that the equilibrium concentration of ~300 ng Ba/g is 10^2 times greater than the measured river concentrations. Therefore, the Ba and Ra concentrations are not controlled by barite precipitation. The fraction of Ra in the particles that is in excess of the upper crustal value of 1.34 dpm/g (for 2.8 μg ^{238}U/g; Taylor and McLennan, 1985), when normalized to Al (as calculated above for Th), is 0.63 to 0.91. This excess is likely adsorbed on Fe oxyhydroxides along with the Th and U; following the calculations of Th

above to obtain an apparent partition coefficient for Ra, log $^{Ra}\hat{K}_d^{Fe}$ = 6.6 at Rautas and 6.1 at Kamlunge. These values are lower than corresponding log $^{U}\hat{K}_d^{Fe}$ values of 7.7 and 6.5 (Andersson et al., 1998), indicating more efficient scavenging of U as well as Th. The concentration of ^{226}Ra on particles of 8.6 dpm/g at Kamlunge can be compared with ≤2 dpm/g for other sites (Elsinger and Moore, 1984) and reflects the high particle Fe content in the Kalix.

3.1.3. $^{234}Th/^{230}Th$ and Watershed Transit Times

The relative concentrations of short-lived ^{234}Th and ^{230}Th may provide information regarding the transit time of Th through the watershed. The ($^{234}Th/^{238}U$)$_{AR}$ ratios in the bulk water at Rautas (0.7 ± 0.3) and Kamlunge (0.44 ± 0.24) are lower than unity, indicating that ^{234}Th is preferentially retained in the watershed relative to U. However, the ($^{234}Th/^{238}U$)$_{AR}$ ratios are greater than the ($^{230}Th/^{238}U$)$_{AR}$ ratios (see Fig. 4). There are two possible reasons for this enrichment in ^{234}Th over ^{230}Th. Contributions by recoil of ^{234}Th from minerals can cause shifts in ($^{234}Th/^{230}Th$)$_{AR}$ ratios of surrounding waters, so that this enrichment could reflect the value in groundwaters entering the river (see Tricca et al., 2000). Leaching of these isotopes, however, may occur in equal proportions because these nuclides are both daughters of α-decay. Therefore, there are no ($^{234}Th/^{230}Th$)$_{AR}$ data available for mire and groundwater discharges to the river to assess this possibility. Alterna-

tively, river ratios of $(^{234}Th/^{230}Th)_{AR} > 1$ could be due to grow-in from ^{238}U decay during transit through the watershed. In this case, a model transit time for Th can be obtained. If the water is a closed system with respect to further Th and U exchange (e.g., with sediments), then the evolution of the ^{234}Th activity in the water over the transit time t is

$$(^{234}Th) = (^{238}U)[1 - \exp(-\lambda_{234Th}t)] + (^{234}Th)_0 \exp(-\lambda_{234Th}t). \quad (2)$$

If it is assumed that ^{234}Th and ^{230}Th are released together from source rocks that contain the U-series nuclides in secular equilibrium and so initially have the same activity in the water, then the initial $(^{234}Th/^{238}U)_{AR}$ ratio of waters entering the river is equal to the river $(^{230}Th/^{238}U)_{AR}$ ratio. Then Eqn. 2 can be rearranged to

$$t = -(\lambda_{234Th})^{-1} \ln\left[\frac{(^{234}Th/^{238}U)_{ACT} - 1}{(^{230}Th/^{238}U)_{ACT} - 1}\right]. \quad (3)$$

If the data for Kamlunge of $(^{234}Th/^{238}U)_{AR} = 0.45 \pm 0.17$ and $(^{230}Th/^{238}U)_{AR} = 0.14 \pm 0.04$ are used, $t = 15 \pm 10$ d for the average transit time through the watershed. More data clearly are required to constrain the ^{234}Th, ^{230}Th, and ^{238}U contents of groundwater and tributary inputs for rigorous application of this method to a watershed. However, the above calculations serve to illustrate that the ^{234}Th and ^{230}Th activities are potentially important tools for evaluating the rate of Th migration in a watershed.

3.2. Input of Radionuclides to the Kalix River

3.2.1. Groundwaters

Groundwater Th data are available for three samples. Filtered (<0.45 μm) water from the Laurivuoma spring, which discharges from bedrock, has a ^{232}Th concentration (6.9 pg/g) that is comparable to those of the two till groundwaters (7.7 and 26.9 pg/g); in contrast, the ^{238}U concentration is 10^4 times greater in the bedrock spring than in the till waters (Table 2). Although till groundwaters have $^{230}Th/^{232}Th$ ratios (4×10^{-6}) that are somewhat lower than that of the bedrock spring (1.2×10^{-5}), all values are comparable to river values.

Groundwaters both from within bedrock and glacial tills can serve as sources of river ^{230}Th and ^{232}Th, with isotope concentrations that are comparable to those of 0.45-μm-filtered Kalix River water (with 12–24 pg ^{232}Th/g). However, bedrock groundwaters have much higher U concentrations and $^{234}U/^{238}U$ ratios than the river and can supply only a small fraction of the total river discharge (Porcelli et al., 1997). Therefore, the river is fed largely by shallower till groundwaters, with an unknown proportion supplied by runoff.

3.2.2. Impact of Mires

It has been shown that U is strongly concentrated in the peat deposits of mires (Porcelli et al., 1997). By use of the new Th data presented here (Table 2), the rate of accumulation of Th in the peat can be assessed, along with the Th isotopic shifts that result in mire waters and the river due to the accumulated U. Some inferences can also be made regarding the impact on Ra isotopes in mire waters and the river.
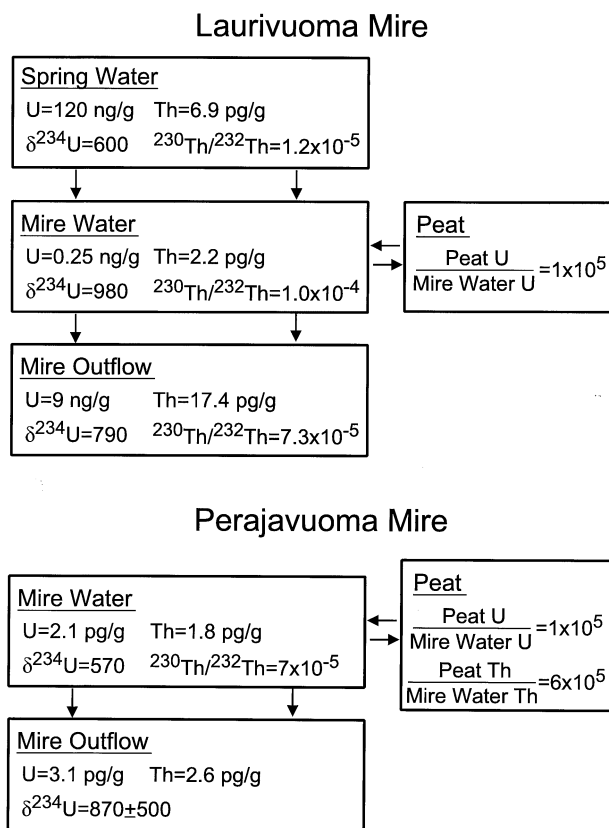

Fig. 5. Concentrations and isotopic compositions of U (from Porcelli et al., 1997) and Th for mire waters and mire outflows for Laurivuoma and Peräjävuoma mires. Data for spring water supplying the Laurivuoma mire are also shown. Concentrations of Ba, an analog of Ra, are also shown.

Th and Ra in mire waters. The effects of mire peats on water chemistry can be seen by comparing mire inflows with outflows (Fig. 5). For the Laurivuoma mire, the bedrock spring appears to be the dominant inflow (with 6.9 pg ^{232}Th/g). Mire water from a mire borehole and outflow water have 2.2 and 17.4 pg ^{232}Th/g, respectively, comparable to that of the inflow. In contrast, the mire water and outflow are greatly depleted in U relative to the inflow (Porcelli et al., 1997). The mires do generate substantial Th isotope shifts; the mire water and outflow waters have $^{230}Th/^{232}Th = 1.0 \times 10^{-4}$ and 7.3×10^{-5}, respectively, compared with 1.2×10^{-5} for the inflow (Fig. 5), so that some mobilization of Th in the mires takes place.

At the Peräjävuoma mire (Fig. 5), no sample of the inflow is available. The mire water and outflow water have 1.8 and 2.6 pg ^{232}Th/g, respectively; these values do not differ greatly from that of the Laurivuoma mire water (2.2 pg ^{232}Th/g). In contrast, the Peräjävuoma outflow had a U concentration 10^{-3} times that of the Laurivuoma outflow (Table 2). Therefore, mire discharges have a much wider range of concentrations of U than of Th.

No data are available for Ra in the mires. The concentration of Ba in the Laurivuoma spring water (39 ng/g) is comparable to the mire water value (30 ng/g) and somewhat higher than the outflow value (12 ng/g). Therefore, mires do not appear to have

a great effect on Ba transport through the mire, and it is likely that Ra will behave similarly in this environment. The production of Ra isotopes in the mire is discussed below.

Th in mire peats. The accumulation of Th in the mires also was examined by analysis of peat (Table 2). A Peräjävuoma peat sample has 72.3 μg ^{232}Th per gram of ashed material ($\equiv$1.30 μg ^{232}Th per gram of dried peat), along with 15.5 μg ^{238}U/g. Although the ratio of (Th/U)$_{wt.}$ = 4.7 is similar to the upper crust value of ~3.8, the U and Th concentrations are both substantially higher than those for the upper crust of 10.6 μg ^{232}Th/g and 2.8 μg ^{238}U/g (Taylor and McLennan, 1985). The peat ^{230}Th/^{232}Th ratio [(2 ± 1) × 10^{-6}] is comparable to that of the upper crust, whereas the U isotopic composition (δ^{234}U = 193) is shifted relative to the crust. In sum, the peat is enriched in U and Th, as well as in ^{234}U (like groundwaters in the area), but has a Th/U ratio comparable to that of the upper crust.

Because U is strongly concentrated in mire peat deposits, U is strongly depleted in mire outflow waters relative to inflow waters until the peats reach a steady-state U concentration (Porcelli et al., 1997). It has been reported that Th is even more strongly concentrated in peats than U (Szalay, 1964), although data are limited. The extent of enrichment of U and Th in the Peräjävuoma peat relative to surrounding waters can be calculated by assuming that all of the inorganic ashed content of the peat is detrital material with upper crust U and Th concentrations; then the excesses (85% of the Th and 82% of the U) are nondetrital and have been derived from the surrounding waters. The ratio of the concentration of nondetrital Th in the dried peat to that of Th in the mire water collected from the same borehole is 6 × 10^5, and this represents an enrichment factor for Th in peat. The equivalent value for U is 1 × 10^5 (Porcelli et al., 1997), indicating that Th is six times more strongly concentrated in these peats than U.

Mire Th accumulations and isotopic shifts. The effects of the mire on Th isotopes in flowing waters can be examined by the model of Porcelli et al. (1997) that was developed for the evolution of U accumulations. It was shown that the concentration of U in the flowing water leaving the mire ($^{238}C_{FW}$) relative to that of the groundwater input ($^{238}C_{GW}$) is

$$\frac{^{238}C_{FW}}{^{238}C_{GW}} = 1 - \exp\left[\frac{-t}{(V_P/q)(^{U}k_1/^{U}k_{-1})}\right], \quad (4)$$

where V_P is the volume of the peat, ($^{U}k_1/^{U}k_{-1}$), is the ratio of rate constants from and into the peat and so is the peat/mire water enrichment factor, and q is the rate water flows through the mire. The time scale for achieving a steady-state peat U concentration (so that $^{238}C_{FW}/^{238}C_{GW} \approx 1$ and depletion of water flowing through the mire no longer occurs) is $^U\bar{\tau} = (V_P/q)(^{U}k_1/^{U}k_{-1})$. The model can be applied to Th by writing a similar equation for ^{232}Th. If the affinity of Th for peat, ($^{Th}k_1/^{Th}k_{-1}$), is greater than that of U, then the time scale for reaching a steady-state peat Th concentration ($^{Th}\bar{\tau}$) will be longer. In this case, before saturation, the depletion in Th concentration in the flowing water relative to that in the groundwater will be greater. Data for Laurivuoma mire (Table 2, Fig. 5), however, indicate that this is not the case; although the U concentration of outflowing waters is 10 times lower than in the inflows, there is no evidence for depletion of Th in

outflowing waters. A reason for the high Th content of the discharge is required.

A further constraint on the interaction of U and Th with the peat is provided by the shifts in ^{234}U/^{238}U and ^{230}Th/^{232}Th ratios between the inflow and outflow. In the model aquifer, when U in the water is being highly depleted, the isotopic shift in U (the difference between (^{234}U/^{238}U)$_{AR}$ in the inflowing water and in the outflowing water), ^UD, is (Porcelli et al., 1997)

$$^UD \approx \lambda_{238}\,^{234U}ft, \quad (5)$$

where t is the time over which accumulation has occurred and ^{234U}f is the fraction of ^{234}U produced that is released into the water by recoil of precursor ^{234}Th. The equivalent equation for the shift in ^{230}Th/^{232}Th (^{Th}D) is

$$^{Th}D \approx \lambda_{234U}\,^{230}ft\,\frac{^{234U}C_{GW}}{^{232}C_{GW}}. \quad (6)$$

Assuming that ^{234}U and ^{238}U are located in similar sites, so that a similar proportion of the daughters are released and $^{234Th}f = ^{230}f$, Eqn. 5 and Eqn. 6 can be combined to obtain

$$^UD\,\frac{^{238}C_{GW}}{^{232}C_{GW}}\left[\left(\frac{^{234}U}{^{238}U}\right)_{AR}\right]_{GW} \approx\,^{Th}D. \quad (7)$$

This reflects the condition that the rate of recoil of ^{234}Th atoms (and so supply of ^{234}U atoms) to the mire water is related to the rate of recoil of ^{230}Th atoms by the (^{234}U/^{238}U)$_{AR}$ ratio of the groundwater (and so of the peat). Then the isotopic shifts in the mire water are proportional to the ratio of U to Th in the groundwater (which is approximately equal to the ratio of U to Th accumulated in the peat). At Laurivuoma, the ^{230}Th/^{232}Th ratios of the mire outflow (7.3 × 10^{-5}) and the inflow (1.2 × 10^{-5}) are accompanied by ratios of δ^{234}U = 790 and 600, respectively. By using the data in Table 2, the calculated isotopic shift in Th is ^{230}Th/^{232}Th = 0.29. This is much greater than the measured difference between the measured Laurivuoma inflow and outflow Th ratios (6.1 × 10^{-5}).

A possible explanation for both a higher Th concentration and lower ^{230}Th/^{232}Th ratio in the outflow than expected is that there was a dominant contribution of mire peat Th due to entrainment of colloidal organic material. The isotopic composition of Th that has accumulated in the peat is expected to be approximately equal to that of the Th the inflowing groundwater, with ^{230}Th/^{232}Th = 1.2 × 10^{-5} (Fig. 5), although data are not available to confirm this. If the outflow Th is a mixture of entrained peat Th and "dissolved" mire water Th with the Th isotopic ratio calculated above (Eqn. 7), then a simple mixing calculation indicates that the fraction of outflow Th not due to entrained peat is 4 × 10^{-4}. Therefore, of the 17.4 pg Th/g in the outflow, 6 fg Th/g appears to be "dissolved" in the mire water and therefore represents the outflow concentration $^{232}C_{FW}$. This is equivalent to a depletion factor of 9 × 10^{-4} relative to the inflowing groundwater, substantially lower than that of U (with a depletion factor of 0.075). Furthermore, the relative affinities of Th and U to the peat can be obtained by combining Eqn. 4 above with the equivalent equation for Th. Then the depletion factors are related by

$$\frac{1 - (^{232}C_{FW}/^{232}C_{GW})}{1 - (^{238}C_{FW}/^{238}C_{GW})} = \exp\left[\frac{(^{U}k_1/^{U}k_{-1})}{(^{Th}k_1/^{Th}k_{-1})}\right]. \quad (8)$$

For the concentrations above, $^{Th}k_1/^{Th}k_{-1}$ is 14 times greater than $^{U}k_1/^{U}k_{-1}$, consistent with the six times greater peat/mire water enrichment factor measured in Peräjävuoma. This calculation is illustrative only because there was no drop in Th concentration between mire inflow and outflow, and so no Th accumulating in the mire at the time the samples were collected as assumed in the model. However, this may be a transient effect due to increased entrainment of accumulated Th during the higher flow conditions of the spring melting period, and so does not reflect the long-term evolution of the mire. Further data are required to assess the seasonal variations in the mire discharge.

Accumulation of Th and U in peats. The model for accumulation of Th and U in peats from inflowing groundwater predicts that the peat Th/U ratios will equal that of inflowing waters during the period of rapid accumulation. Once the peat reaches a steady-state U concentration, the Th concentration will continue to grow until the peat Th/U ratio is enriched relative to that of the inflowing water by $(^{Th}k_1/^{Th}k_{-1})/(^{U}k_1/^{U}k_{-1}) \sim 14$ (see above). The measured peat sample, from Peräjävuoma, has Th/U $\sim$4 (Table 2), a value that is higher than found in groundwaters. Unfortunately, there are no data available for the groundwaters flowing into this mire; although the outflowing waters have somewhat U lower concentrations than found in till groundwaters, it is not known if U depletion of water flowing through this mire continues to occur. Therefore, it is possible that the U has reached a steady state in this peat, and the Th continues to be enriched from till groundwaters with Th/U $\sim$0.4 to 0.7 (see Table 2). In this case, the similarity between the Th/U ratio in the peat and the source rocks is fortuitous because there is no simple explanation for requiring a Th/U ratio in the peat equal to that of source rocks if these nuclides are supplied via waters in which these elements have been greatly fractionated with respect to one another.

Ra in mires. Ra isotopes are produced in the mire by Th and U. A maximum isotope ratio can be calculated by assuming that the storage time of Ra within the peats is short compared with Ra isotope half-lives (consistent with the lack of interaction between Ba and the peat); then the $^{228}Ra/^{226}Ra$ atom ratio will be equal to the ratio of the activities of the parents in the peat, so that $(^{228}Ra/^{226}Ra)_{AR} \approx 18$. As discussed above, Ra in the Kalix River at Kamlunge has $(^{228}Ra/^{226}Ra)_{AR} = 1.2$, equal to that of the source rocks in the watershed, and so there is no evidence for any significant impact on the river Ra budget by mire waters with high $(^{228}Ra/^{226}Ra)_{AR}$ ratios.

Mires and the Kalix. It has been shown previously (Porcelli et al., 1997) that a large proportion of U to the rivers during the spring may be derived from the mires, when waters diluted by spring melt equilibrate with the U-rich peats, which thus act to buffer the supply of groundwater U to the river. There are some seasonal river data available for Th (Andersson et al., 1995) indicating that Th may be higher during spring flow, compatible with the inferences made above regarding the entrainment in mire outflows of Th from peats during spring flow. The outflows from bedrock do not have high Th concentrations accompanying the high U concentrations and so do not have a disproportionately large impact on the river Th budget.

3.3. Watershed Weathering Characteristics

3.3.1. $^{230}Th/^{232}Th$, $^{228}Ra/^{226}Ra$, and the Weathering Supply of Radionuclides

In crustal rocks, ^{230}Th and ^{226}Ra are located within primary phases hosting parent ^{238}U; a significant fraction of the ^{232}Th and daughter ^{228}Ra may be in different phases. Therefore, $^{230}Th/^{232}Th$ and $^{228}Ra/^{226}Ra$ ratios in the river will reflect the relative release rates of Th and Ra isotopes from the different phases. All the measured $^{230}Th/^{232}Th$ ratios are within a narrow range of $(0.5–1.5) \times 10^{-5}$ (see Table 1 and Fig. 3) and are similar to that of Th in the bulk upper crust of 7×10^{-6} (for $(Th/U)_{wt} = 3.8$). Also, the $(^{228}Ra/^{226}Ra)_{AR}$ ratios of all of the bulk water samples are within error of the average value of 1.25 (Fig. 4), the ratio expected for the upper crust. These similarities with the crust indicate that Th and Ra isotopes are released into the river without significant fractionation. Thus, Th and Ra in these different phases are released at similar rates. ^{230}Th also can be released from host phases by recoil during production, but such a process also has not generated substantial isotopic shifts in the Th found in the river.

The release of Ra also can be compared with that of Ba. The $Ba/^{226}Ra$ ratio measured at Kamlunge (3×10^{-4} g/dpm) is comparable to that of the upper crust (2.6×10^{-4} g/dpm). This was also observed for the Amazon (Moore and Edmond, 1984) and indicates that the weathering rate of Ba-bearing and U-bearing minerals are similar.

3.3.2. Removal of U, Th, Ra, and ^{210}Pb from the Watershed

Radionuclides are generally delivered to the river along two paths. Highly insoluble and immobile elements such as Th, along with other constituents such as Fe, are dominantly carried in particles, which will be derived from areas of preferential mechanical weathering near streams. This includes constituents in both detrital and secondary phases. This process is likely enhanced during greater water flows, which explains the apparent correlation between the concentration of ^{232}Th in the Kalix and river discharge (Andersson et al., 1995). For more soluble elements such as U, transport in soil waters vertically through the vadose zone and by groundwater flow through predominantly shallow aquifers is relatively more important. Groundwater transit times in the watershed are $\sim$3 yr (Rodhe, 1987). The concentrations of many soluble constituents decrease during spring melt from dilution by surface flow (Ingri et al., pers. comm.), although that of U is relatively constant as a result of buffering of water discharges to the river by mires (see section 3.6). Overall, river concentrations of radionuclides can be interpreted as the sum of the runoff and groundwater sources.

Th and U transport. The relative removal rates of Th and U from the watershed can be most clearly seen by using $(^{230}Th/^{238}U)_{AR}$ ratios because these nuclides are hosted in the same phases in secular equilibrium. The $(^{230}Th/^{238}U)_{AR}$ ratios in all measured fractions are much less than 1 (0.07–0.33; see data in Table 1); in particular, the Rautas and Kamlunge bulk samples (where U particle data are available) have 0.14 to 0.24 (Fig. 4). These values show that ^{238}U is preferentially mobilized relative to Th from the source region. A similar conclusion can be drawn from Kamlunge and Rautas bulk sample $(^{232}Th/^{238}U)_{AR}$

ratios of 0.04 to 0.2, which are far below the upper crust value of 1.3. Because the concentration of Th (but not U) is higher during the spring (Andersson et al., 1995), the average annual values for the Kalix may be even lower. The result is net fractionation between U and Th during export from the watershed by a factor of 5 to 10.

Ra transport. The $(^{226}Ra/^{238}U)_{AR}$ ratio in all sample fractions from each location are less than unity and is 0.31 in both Rautas and Kamlunge bulk waters. Although such low values indicate that U is mobilized preferentially to Ra from the source rocks, it has been shown that alkaline earths (but not U) are typically diluted in spring river waters by factors of 2 to 3 (Ingri et al., pers. comm.), so that the average $(^{226}Ra/^{238}U)_{AR}$ ratio may be greater. Unfortunately, there are no time series data available for Ra. The transport of Ra also can be compared with that of Th; $(^{226}Ra/^{230}Th)_{AR} = 1.26 \pm 0.33$ at Rautas and 5.63 ± 1.1 at Kamlunge. The $(^{228}Ra/^{232}Th)_{AR}$ ratios in the Kalix also show strong deviations from secular equilibrium, with values of 2.4 ± 0.3 at Rautas and 9.1 ± 1.7 at Kamlunge. At other times of the year (when Ra concentrations are higher and Th concentrations are lower), these ratios may be even higher. This shows that overall Ra is preferentially exported relative to Th from the watershed and may also be less efficiently removed than U.

Watershed weathering. The low $(^{230}Th/^{238}U)_{AR}$ and $(^{226}Ra/^{238}U)_{AR}$ ratios of material leaving the watershed indicate that the weathering region is accumulating Th relative to Ra and U. Because all size fractions have low ratios, seasonal variations in the particle concentrations will not qualitatively change this conclusion. Martin and Meybeck (1979) found that on a global scale, the average riverine $^{232}Th/^{238}U$ ratio is similar to that of the average upper crust; this indicates that particle transport of relatively insoluble Th was balanced by transport of U in solution, and preferential accumulation of Th does not occur globally. In the Kalix River, the concentrations of Th on material that is mechanically weathered is currently insufficient to balance the U in solution; however, as Th continues to accumulate in the soils and the Th concentration on soil particles increases, a balance presumably will be reached in the river outflow. The concentrations of U and Th on suspended particles in the river reflect chemical redistribution processes within the river and do not necessarily represent particle concentrations during overland transport. The $(^{230}Th/^{238}U)_{AR}$ and $(^{228}Ra/^{232}Th)_{AR}$ ratios may be sensitive indicators of the fractionation between soluble constituents such as U and insoluble or particle-reactive elements such as Th and Ra, especially because the ratios of these nuclides in rocks before weathering can be taken to be the equilibrium values. Relative activities of Th, U, and Ra in river outflows that deviate from secular equilibrium may be an indication of the relative immaturity of the weathering profile due to recent glaciation; the outflow from a watershed will reflect the input of bedrock (at secular equilibrium) into the weathering cycle once a steady-state abundance of Th is reached within the weathering profile. Further extension of this data to bulk erosion rates requires a more detailed assessment of variations in major and actinide concentrations in host rocks and in the river.

Transport of ^{210}Pb. The ^{210}Pb concentrations in 0.45-μm-filtered waters are in the range of 1.1 to 2.2 dpm/100 L (Table 1) and vary along the river sympathetically with ^{234}Th and

^{226}Ra concentrations (Fig. 3). The activities of ^{210}Pb generally were much higher in the particles (up to 25 dpm/100 L at Tärendö), except at Narkån, where the particle associations of all of the short-lived nuclides were much lower compared with the nonparticulate loads. Near the Kalix discharge at Kamlunge, 75% of the ^{210}Pb is on particulates. Bulk sample $(^{210}Pb/^{238}U)$ ratios are 1.04 ± 0.16 and 0.52 ± 0.15 at Rautas and Kamlunge, respectively; although ^{210}Pb is not depleted in the waters relative to ^{238}U at Rautas, it is at the Kalix discharge.

A significant source of ^{210}Pb in soils is atmospheric fallout from decay of atmospheric ^{222}Rn. The flux of ^{210}Pb to the Baltic Sea has been calculated from sediment data to be ~1.4 dpm/cm²-yr (Bianchi et al., unpublished data), comparable to 1.02 dpm ^{210}Pb/cm²-yr obtained for north Britain (Eakins et al., 1984). This corresponds to 3.3×10^{14} dpm/yr deposited over the Kalix drainage area of ~23,600 km². The annual Kalix discharge is ~7.6×10^{12} L/yr (Swedish Meteorological and Hydrological Institute, unpublished data); if the measured Kamlunge concentration of 8 dpm ^{210}Pb/100 L represents the annual average, then 6×10^{11} dpm/yr is discharged and the ratio of watershed export to atmospheric deposition, 2×10^{-3}, is similar to that of watersheds in the eastern United States (Benninger et al., 1975). This value represents the minimum reduction of fallout ^{210}Pb during transit through the watershed; the ^{210}Pb activity in the Kalix is similar to that of other nuclides derived from weathering, so there may be only a negligible contribution of fallout ^{210}Pb to the river. Such low watershed export has been interpreted as reflecting the strong retention of ^{210}Pb in soils. Assuming all river ^{210}Pb is from atmospheric fallout, residence times on the order of 10^4 yr have been calculated (e.g., Benninger et al., 1975; Appleby and Oldfield, 1992).

4. BALTIC SEA: RESULTS AND DISCUSSION

Baltic Sea data are shown in Tables 3 (for F-2) and 4 (for BY-15). The U data are from Porcelli et al. (1997) and Andersson et al. (1998).

4.1. Distribution of Th Isotopes

For the low salinity station F-2, ^{232}Th concentrations in 0.45-μm-filtered waters from four depths fall within a narrow range (0.75–0.79 pg/g). Andersson et al. (1995) reported values for 1991 0.45-μm-filtered F-2 waters from 5 m and 80 m of 7.7 ± 0.2 and 0.498 ± 0.003 pg/g, respectively; the higher value for the 5-m 1991 sample may be due to a different degree of exclusion of particulates during filtering.

Data for ^{232}Th on particles are only available for F-2 80 m, where particles carry the dominant fraction of the ^{232}Th in the water and account for 4.05 pg ^{232}Th/g (Table 3), compared with the bulk ^{232}Th concentration of 4.8 pg/g. A large fraction of the ^{232}Th not on particles passed through the ultrafilter and appears to be in solution at a level of 0.64 pg/g. The ^{232}Th at this site is much lower than that of the Kamlunge sample (which represents the local river discharge into the Baltic), indicating that substantial loss of riverine Th occurred at lower salinities.

The $^{230}Th/^{232}Th$ ratios in the F-2 samples are all within error of 1×10^{-5} and comparable to that of the Kamlunge sample.

Table 3. U-Th series nuclide data, Baltic Sea, Station F-2, 1995.[a]

Site	Salinity (PSU)	ASL (mg/kg)	SPM (mg/L)	^{238}U[b] pg/g	^{238}U[b] dpm/100 L	δ^{234}U[b]	^{232}Th pg/g	^{232}Th dpm/100 L	^{230}Th/^{232}Th (10^{-6})	^{234}Th (dpm/100 L)	^{226}Ra (dpm/100 L)	^{228}Ra (dpm/100 L)	^{210}Pb (dpm/100 L)	Ba (ng/g)
F-2, 5 m														
<0.45 μm				—	—	—	0.7530 ± 0.0030	0.01854 ± 0.00007	15 ± 1	15.2 ± 5.2	7.5 ± 1.5	11.0 ± 1.6	1.8 ± 1.8	19.4 ± 0.7
>0.45 μm				—	—	—	—	—	—	3.3 ± 1.0	0.2 ± 0.1	<0.3	0.5 ± 0.4	0.5
Bulk water[c]	3.261	1.09	0.41	—	—	—	—	—	—	18.5 ± 5.3	7.7 ± 1.5	11.0 ± 1.6	2.3 ± 1.9	19.9
F-2, 25 m														
<0.45 μm				—	—	—	—	—	—	19.8 ± 6.6	6.3 ± 2.1	11.0 ± 1.6	2.1 ± 2.2	18.4 ± 1.6
>0.45 μm				—	—	—	—	—	—	4.6 ± 1.1	<0.1	<0.3	1.4 ± 0.4	0.3
Bulk water[c]	3.248	0.50	0.92	—	—	—	—	—	—	24.3 ± 6.7	6.3 ± 2.1	11.0 ± 1.6	3.5 ± 2.2	18.7
F-2, 50 m														
<0.45 μm				—	—	—	0.791 ± 0.008	0.0195 ± 0.0002	12 ± 6	9.8 ± 3.0	10.0 ± 2.0	14.6 ± 2.0	2.1 ± 2.2	17.3 ± 1.0
>0.45 μm				—	—	—	—	—	—	6.1 ± 1.2	0.2 ± 0.1	<0.3	1.4 ± 0.4	0.3
Bulk water[c]	3.255	0.63	0.47	—	—	—	—	—	—	15.9 ± 3.2	10.2 ± 2.0	14.6 ± 2.0	3.5 ± 2.2	17.6
F-25, 80 m														
<0.45 μm				356 ± 1	26.6 ± 0.07	247 ± 6	0.765 ± 0.026	0.01883 ± 0.00064	12 ± 2	—	—	—	—	18.4 ± 1.1
<10 kD				2 ± 0	0.1 ± 0.00	180 ± 16	0.648 ± 0.001	0.01595 ± 0.00002	3 ± 7	—	—	—	—	—
>0.45 μm				2 ± 0	0.15 ± 0.00	180 ± 16	4.05 ± 0.62	0.100 ± 0.015	—	—	—	—	—	0.3
Bulk water[c]	3.276	0.78	0.42	358 ± 1	26.7 ± 0.07	—	4.80 ± 0.60	0.118 ± 0.015	—	—	—	—	—	18.7

[a] Data from Porcelli et al. (1997) and Andersson et al. (1995, 1998). All errors are 2 σ.

[b] Aliquots of samples collected June 5, 1991.

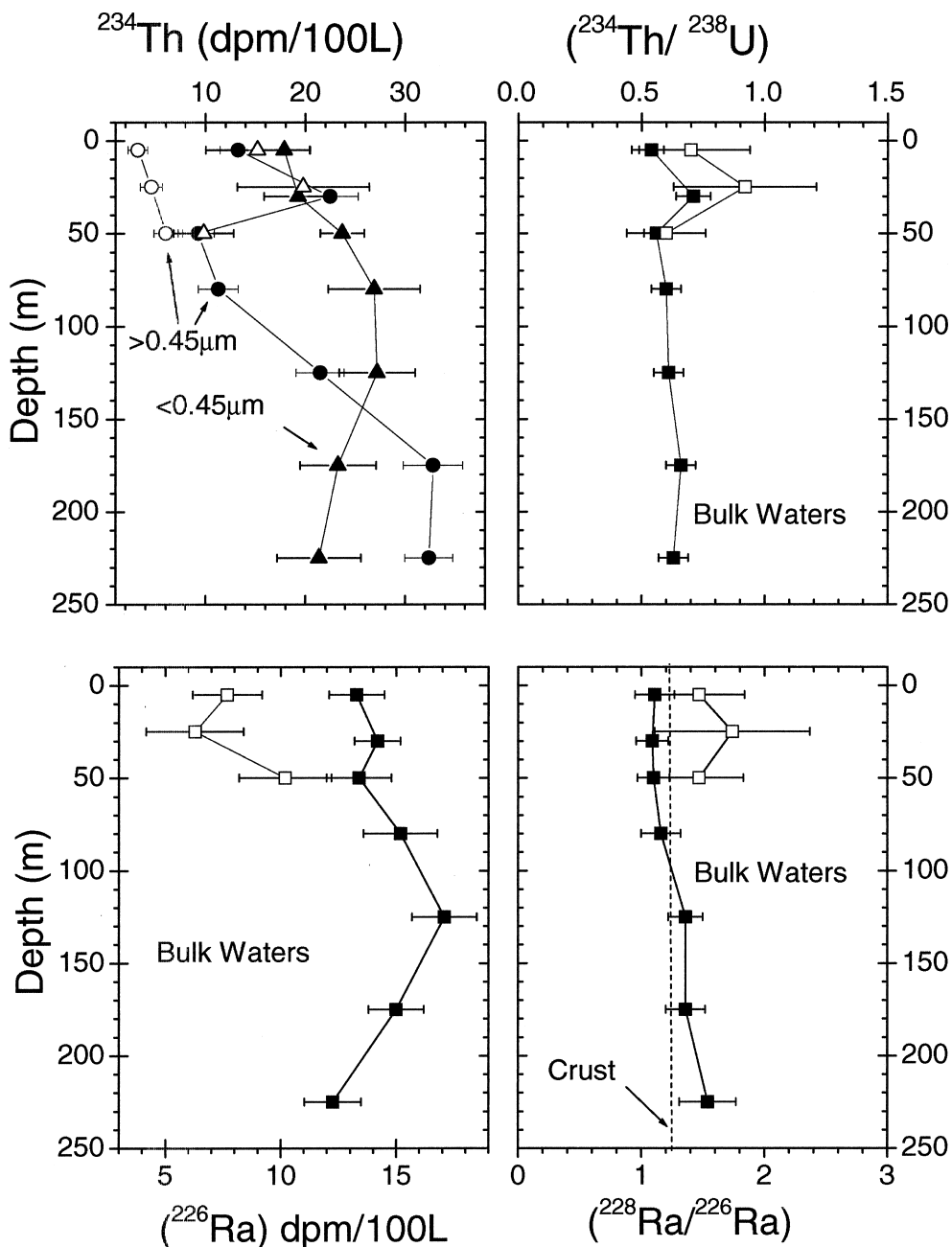[c] Bulk water radionuclide values are the sums of the <0.45-μm and >0.45-μm fractions.

Fig. 6. Nuclide profiles at F-2 (open symbols) and BY-15 (solid symbols). A significant fraction of ^{234}Th, but not Ra, is on particles. The ^{234}Th is largely supplied by decay of ^{238}U in the water, and the relatively high (^{234}Th/^{238}U) ratios indicate slow removal of Th from the water. The higher fraction of ^{234}Th on particles in BY-15 at depths >100 m may reflect increased supply of particles from the shallower areas around the Gotland Deep. Ra isotopic compositions do not vary significantly with depth or between locations.

In contrast, Andersson et al. (1995) reported much higher values of ^{230}Th/^{232}Th = 6×10^{-5} and 7×10^{-4} for 1991 F-2 samples from 5 m and 80 m, respectively. The reason for the discrepancy is not known.

For ^{234}Th, data for 0.45-μm-filtered waters and particles are available for three depths (Table 3). Particles account for a significant fraction (20–40%) of the ^{234}Th, with the largest fraction corresponding to the greatest sampling depth. At F-2, bulk ^{234}Th concentrations (16–24 dpm/100 L; Fig. 6) are much

higher than at Kamlunge (7.5 dpm/100 L), indicating that ^{234}Th is not derived dominantly from river inflow but rather from production in the water. However, there is significant disequilibrium between ^{234}Th and ^{238}U, with (^{234}Th/^{238}U)$_{AR}$ below equilibrium (0.60 ± 0.12 to 0.91 ± 0.25 for bulk waters; Fig. 6) and showing removal of ^{234}Th from the water (see also Andersson et al., 2000).

At the higher salinity Baltic station BY-15, where salinities range from S = 7.19 to 12.14, the 0.45-μm-filtered waters had

0.11 to 0.22 pg ^{232}Th/g. These values are much lower than those found at F-2 and are compatible with those of 0.1 to 0.4 pg ^{232}Th/g in 1991 BY-15 samples (Andersson et al., 1995). Data for ^{232}Th on >0.45-μm particles are only available for 30 m, where a substantial fraction of the total ^{232}Th is on particles. The ^{230}Th/^{232}Th ratios of (2–3) $\times$ 10^{-5} at BY-15 are similar to those elsewhere (Fig. 3) and are compatible with the previously published values of ~4 $\times$ 10^{-5} for 1991 samples from 125 m and 225 m, but not with the much higher value of (7.6 $\pm$ 1.1) $\times$ 10^{-4} reported for BY15, 5 m (Andersson et al., 1995). The reason for this discrepancy also is not known.

Data for ^{234}Th at BY-15 in 0.45-μm-filtered waters and particles are available for seven depths (Table 4). As at F-2, particles account for a significant fraction (30–60%) of the bulk ^{234}Th (see Fig. 6). There is also substantial disequilibrium between ^{234}Th and ^{238}U, with (^{234}Th/^{238}U)$_{AR}$ ratios for bulk waters (0.54 $\pm$ 0.08 to 0.72 $\pm$ 0.11) generally further below secular equilibrium than at F-2 (Fig. 6). Particles contain the greatest fraction of ^{234}Th in the deepest samples from both locations.

In sum, evaluation of Th behavior (see discussion below) must consider that (^{234}Th/^{238}U)$_{AR}$ ratios are not in equilibrium, indicating removal of ^{234}Th and indicating that a substantial fraction of the ^{234}Th is not on particles.

4.2. Distribution of Ra Isotopes

The activities of ^{226}Ra at F-2 are 13 to 27 dpm/100 L and at BY-15 are 6 to 10 dpm/100 L (Tables 3 and 4, Fig. 6). Particles contain only minor amounts of ^{226}Ra ($\leq$0.4 dpm/100 L). The Baltic activities are generally greater than either river inputs as represented by the Kamlunge sample (with ~5.1 dpm/100 L) or Atlantic surface seawater (with ~7.4 dpm/100 L; see Cochran, 1992). Therefore, a source of ^{226}Ra in addition to the inflow of these sources is required. The Ba/^{226}Ra ratios at F-2 ((1.7–3.0) $\times$ 10^{-4} g/dpm) and at BY-15 (1.4–1.9) $\times$ 10^{-4} g/dpm are lower than that of Kamlunge (3 $\times$ 10^{-4} g/dpm) and below a conservative mixing line between Kamlunge and Atlantic surface seawater (Fig. 7); this requires that the additional source of ^{226}Ra has a relatively low Ba/^{226}Ra ratio. The (^{228}Ra/^{226}Ra) ratios in the Baltic fall within a narrow range (1.2–1.7) and are comparable to that of Kamlunge (1.3) and the average crustal value (Fig. 6). Because the residence time of water (and so of conservative elements such as Ra) in the Baltic (35 yr) is substantially greater than the half-life of ^{228}Ra, a greater supply of ^{228}Ra relative to ^{226}Ra is required to balance ^{228}Ra decay.

4.3. Distribution of ^{210}Pb

Measured ^{210}Pb activities were low and near the detection limit; at F-2, the activities were ~2 dpm/100 L for 0.45-μm-filtered waters and 2 to 3.5 dpm/100 L for bulk waters, whereas at BY-15, all samples had lower activities ($\leq$1 dpm ^{210}Pb/100 L). These concentrations are much lower than at Kamlunge, indicating substantial removal of Pb at salinities below that of F-2 (~3 psu) and further removal within the basin. There is no indication of increases in ^{210}Pb activities due to production within the water column.

4.4. Nuclide Fluxes Into and Out of the Baltic

4.4.1. Box Model for the Baltic Sea

The relative activities of ^{238}U, ^{234}Th, ^{226}Ra, and ^{228}Ra in the Baltic deviate significantly from secular equilibrium and can be used to investigate the input and removal fluxes of these nuclides into the basin. A simple one-box steady-state model of the Baltic, along with mass and nuclide fluxes, is shown in Figure 8. It should be noted that the Baltic is not a single well-mixed reservoir but rather contains both vertical salinity stratifications (with lower salinity surface waters) and regional salinity gradients (with lower salinity waters to the north). However, the data do not display substantial variations and so can be approximated by average Ra and Th values for the entire Baltic; a more complex model presently is not justified.

In the present model, water mass inflows (in liters per year) to the Baltic from rivers ($^{R}\dot{M}$) and from the North Sea through the Kattegat ($^{SW}\dot{M}$) combined equally the brackish water outflow through the Kattegat ($^{B}\dot{M}$). Salinity stratification in the straits connecting the Baltic with the North Sea allows the outflow to have an average salinity lower than the inflow (see Kullenberg and Jacobsen, 1981). On the basis of water budget calculations, water flowing through the Kattegat and into the Baltic has an average salinity of $S_{SW} = 16$, whereas outflowing water has $S_B = 8.25$ (Dyrssen, 1993). The residence time of Baltic water is $^{W}\tau \equiv M_B/^{B}\dot{M}$, where M_B is the total mass of Baltic water. Kullenberg and Jacobsen (1981) estimate $^{W}\tau = 35$ yr. For each nuclide i, inflows to the Baltic are due to river and seawater water mass flows, decay of parent nuclide p in the water column, upward diffusion from the underlying sediments, and eolian infall. These inflows are balanced by the outflows due to decay in solution, sedimentation on particles, and water mass outflow from the Baltic. Thus,

$$^{i}C_R \, ^{R}\dot{M} + {}^{i}C_{SW} \, ^{SW}\dot{M} + \lambda_p \, ^{p}C_B \, M_B + {}^{SED}F_i B + {}^{AIR}F_i B$$

$$= \lambda_i \, ^{i}C_B \, M_B + P_i \, ^{i}C_B \, M_B + {}^{i}C_B \, ^{B}\dot{M}, \quad (9)$$

where $^{i}C_R$, $^{i}C_{SW}$, and $^{i}C_B$ are the bulk concentrations of i in river water, inflowing water through the Kattegat, and Baltic water, respectively. The flux of i from underlying sediments is $^{SED}F_i$ (in atoms/area-time), $^{AIR}F_i$ is the flux of i by eolian input (in atoms/area-time), B is the area of the Baltic, and P_i is the first-order rate constant for removal of i on sedimenting particles. The eolian input is important only for long-lived ^{232}Th and ^{230}Th. Note the balance of salt in the Baltic requires $^{SW}\dot{M} = {}^{B}\dot{M}(S_B/S_{SW})$ and $^{R}\dot{M} = {}^{B}\dot{M}(1 - S_B/S_{SW})$. With the activity $^{i}A = {}^{i}C/\tau_i$ (where τ_i is the mean life of i), Eqn. 9 becomes

$$^{i}A_B(1 + P_i \tau_i) = \frac{\tau_i}{w_\tau} \left[\left(1 - \frac{S_B}{S_{SW}} \right) ^{i}A_R + \left(\frac{S_B}{S_{SW}} \right) ^{i}A_{SW} - {}^{i}A_B \right]$$

$$+ {}^{p}A_B + ({}^{SED}F_i + {}^{AIR}F_i)/D_B, \quad (10)$$

where D_B is the depth of the Baltic. This equation will be used below to evaluate the fluxes of Th and Ra. Nuclide activities from the Kalix will be used to represent average river activities, whereas typical Baltic values measured here will be used as averages for the basin.

Table 4. U-Th series nuclide data, Baltic Sea, Station BY-15, 1995.[a]

Site	Salinity (PSU)	SPM (mg/L)	238U[b] pg/g	238U[b] dpm/100 L	δ234U[b]	232Th pg/g	232Th dpm/100 L	230Th/232Th (10^-6)	234Th (dpm/100L)	226Ra (dpm/100L)	228Ra (dpm/100L)	210Pb (dpm/100L)	Ba (ng/g)
BY-15, 5 m													
<0.45 μm			(778)	(58.1)	(173)	0.1110 ± 0.0020	0.00273 ± 0.00005	—	17.9 ± 2.6	13.3 ± 1.2	14.7 ± 1.6	0.8 ± 0.9	—
>0.45 μm	7.186	0.24	—	—	—			—	13.3 ± 1.8	<0.1	<0.3	<0.4	—
Bulk water[c]			(778)	(58.1)	(173)			—	31.2 ± 3.2	13.3 ± 1.2	14.7 ± 1.6	0.8 ± 0.9	—
BY-15, 30 m													
<0.45 μm			781 ± 2	58.3 ± 0.1	173 ± 5	0.0928 ± 0.0003	0.00228 ± 0.00001	—	19.3 ± 3.4	14.2 ± 1.0	15.5 ± 1.4	0.5 ± 1.0	23.5 ± 0.3
<10 kD			695 ± 2	51.9 ± 0.1	180 ± 6	0.179 ± 0.004	0.0044 ± 0.0001	25 ± 15					18.0 ± 0.4
>10 kD			4	0.3	179 ± 6								0.89
10 kD filter rinse			56	4.2	177 ± 6								0.09
>0.45 μm	7.231	0.17	0.5	0.04	178 ± 10	0.0545 ± 0.0005	0.00134 ± 0.00001	30 ± 6	22.5 ± 2.8	<0.1	<0.3	<0.4	—
Bulk water[c]			788 ± 2	58.9 ± 0.2	173			—	41.8 ± 4.4	14.2 ± 1.0	15.5 ± 1.4	0.5 ± 1.0	—
BY-15, 50 m													
<0.45 μm			(788)	(58.9)	(173)			—	23.7 ± 2.2	13.4 ± 1.4	14.7 ± 0.8	0.77 ± 0.70	23.5 ± 0.7
>0.45 μm	7.323	0.14	—	—	—			—	9.3 ± 1.6	<0.1	<0.3	0.25 ± 0.52	—
Bulk water[c]			(788)	(58.9)	(173)			—	33.0 ± 2.7	13.4 ± 1.4	14.7 ± 0.8	1.0 ± 0.9	—
BY-15, 80 m													
<0.45 μm			(850)	(63.5)	(171)	0.117 ± 0.002	0.00288 ± 0.00005	19 ± 18	26.9 ± 4.6	15.2 ± 1.6	17.6 ± 1.6	<0.3	21.4 ± 0.8
>0.45 μm	8.143	0.31	—	—	—			—	11.3 ± 2.0	<0.1	<0.3	<0.4	—
Bulk water[c]			(850)	(63.5)	(171)			—	38.2 ± 5.0	15.2 ± 1.6	17.6 ± 1.6	<0.7	—
BY-15, 125 m													
<0.45 μm			(1065)	(79.5)	(165)			—	27.2 ± 3.8	16.7 ± 1.4	23.0 ± 1.2	<0.4	23.5 ± 1.1
>0.45 μm	10.994	0.09	—	—	—			—	21.5 ± 2.4	0.4 ± 0.2	0.2 ± 0.8	<0.3	—
Bulk water[c]			(1065)	(79.5)	(165)			—	48.7 ± 4.5	17.1 ± 1.4	23.2 ± 1.4	<0.7	—
BY-15, 175 m													
<0.45 μm			1131 ± 5	84.46 ± 0.37	163 ± 7	0.220 ± 0.006	0.0054 ± 0.0001	—	23.3 ± 3.8	15.0 ± 1.2	20.4 ± 1.8	<0.4	22.4 ± 1.2
>0.45 μm	11.871	0.08	—	—	—			—	32.8 ± 3.0	<0.1	<0.3	<0.5	—
Bulk water[c]			1131 ± 5	84.46 ± 0.37	163 ± 10			—	56.1 ± 4.8	15.0 ± 1.2	20.4 ± 1.8	<0.9	—
BY-15, 225 m													
<0.45 μm			(1151)	(86.0)	(162)			—	21.4 ± 4.2	12.1 ± 1.2	17.8 ± 1.8	<0.4	22.4 ± 1.2
>0.45 μm	12.138	0.29	—	—	—			—	32.4 ± 2.4	0.2 ± 0.2	1.1 ± 1.0	<0.5	—
Bulk water[c]			(1151)	(86.0)	(162)			—	53.8 ± 4.8	12.3 ± 1.2	18.9 ± 2.1	<0.9	—

[a] Data from Porcelli et al. (1997) and Andersson et al. (1998). All errors are 2 σ.
[b] Values in parentheses are calculated from measured data and U-salinity relationships.
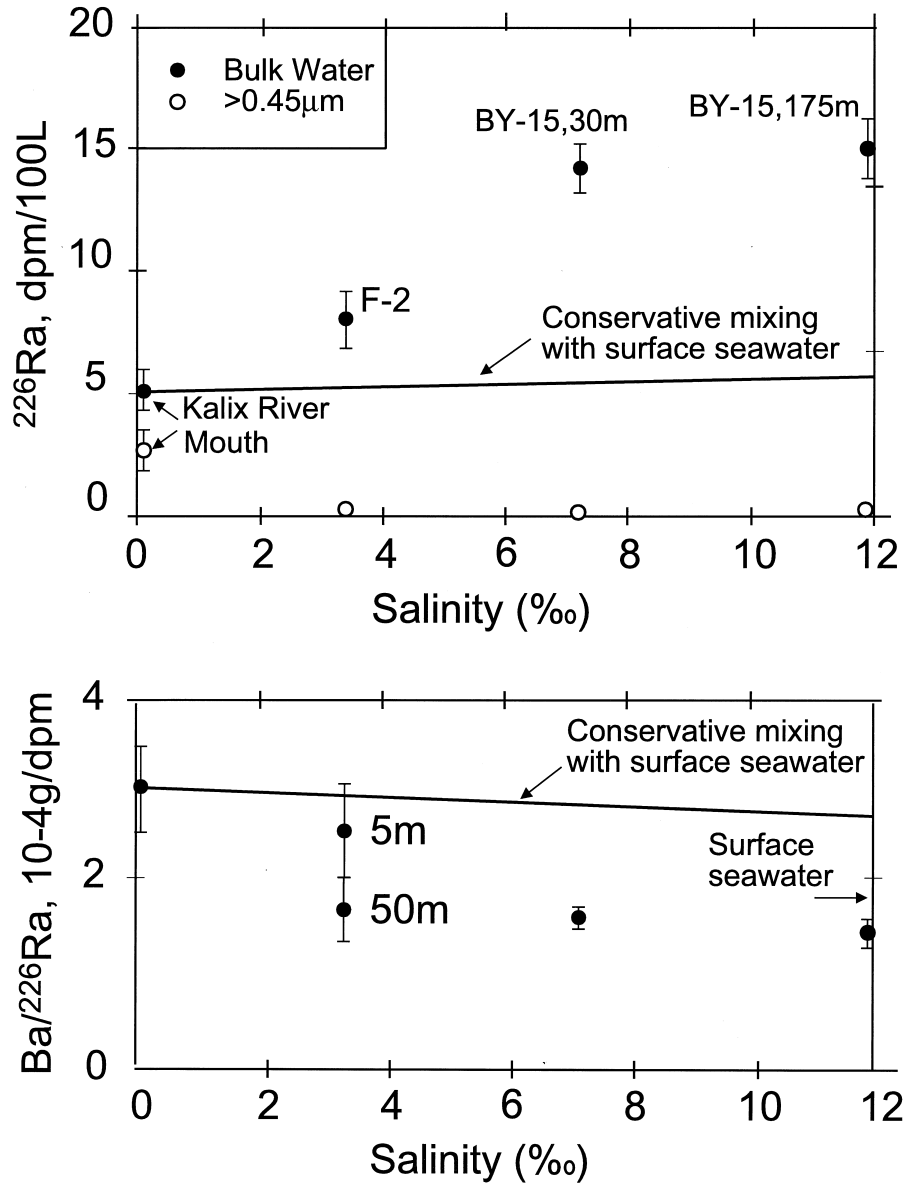[c] Bulk water radionuclide values are the sums of the <0.45-μm and >0.45-μm fractions.

Fig. 7. ^{226}Ra activities and Ba/^{226}Ra ratios in the Baltic are plotted and deviate from the line for conservative mixing between bulk river water and seawater. This may reflect input of ^{226}Ra from underlying sediments.

4.4.2. Th Fluxes

The removal rate of ^{234}Th by particles can be obtained by using Eqn. 10 (with $^{SED}F_{234} = {}^{AIR}F_{234} = 0$):

$$P_{234Th} = \lambda_{234Th}\left[\left[\left(\frac{^{238}U}{^{234}Th}\right)_{AR}\right]_B - 1\right]$$

$$+ \frac{1}{{}^w\tau}\left[\left(1 - \frac{S_B}{S_{SW}}\right)\frac{^{234Th}A_R}{^{234Th}A_B} + \left(\frac{S_B}{S_{SW}}\right)\frac{^{234Th}A_{SW}}{^{234Th}A_B} - 1\right]. \quad (11)$$

The second term is much smaller and can be neglected. Eqn. 11 then is similar to that of Kaufman et al. (1971).

The ^{234}Th residence time relative to scavenging is

$$^{234Th}\tau_{SED} = \frac{^{234Th}N_B}{^{234Th}N_B\, P_{234Th}} = \frac{1}{P_{234Th}}$$

$$= \frac{1}{\lambda_{234Th}[[(^{238Th}U/^{234}Th)_{AR}]_B - 1]} \quad (12)$$

where $^{234Th}N_B$ is the total abundance of ^{234}Th in the Baltic. For $(^{238}U/^{234}Th)_B = 1.7$ (see Fig. 6), $^{234}\tau_{SED} = 50$ d. This can be compared with 10 to 70 d for the New York Bight (Kaufman et al., 1971) and 7 to 50 d in the Irish Sea (Kershaw and Young, 1988). In the Irish Sea, the longest calculated residence time of 50 d is comparable to that of the Baltic and is for a location with a similar particle concentration, 0.6 mg/L SPM, to those found in the Baltic (Tables 3 and 4). Thus, the high Baltic

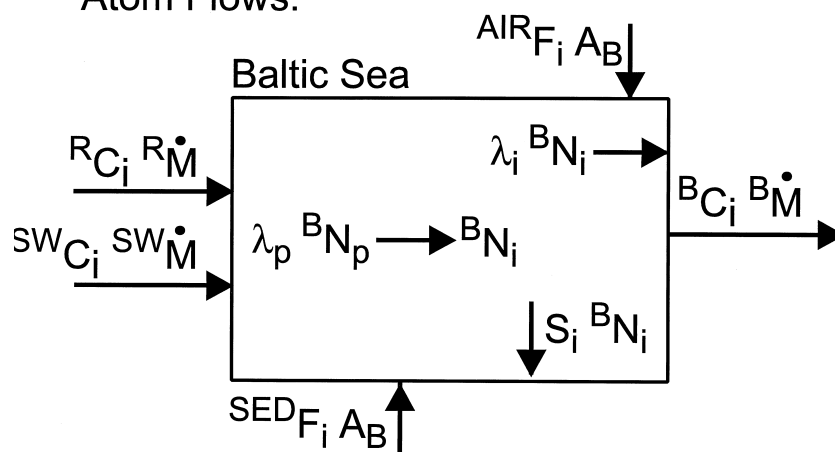## Water Flows:
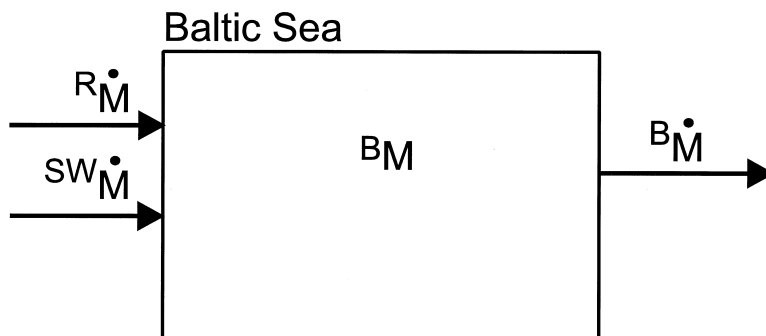
Atom Flows:

Fig. 8. A model for the flows of nuclides into and out of the Baltic Sea. (A) The Baltic is represented as one box, with river water and seawater inflows and brackish water outflow. (B) Nuclide inputs are from mass inflows, parent nuclide decay in solution, release from underlying sediments, and eolian infall. Outputs are from mass outflow, decay in solution, and sedimentation of scavenging particles. The box is assumed to be in steady state.

$(^{234}Th/^{238}U)_{AR}$ ratios and long ^{234}Th residence time appear related to the low concentrations of particles.

The association of Th in colloids may be an important precursor to incorporation in sedimenting particles (Honeyman and Santschi, 1989). There are no data available regarding the distribution of ^{234}Th on colloids. However, only a small fraction of the ^{232}Th appears associated with colloids because at F-2, 80 m, 85% of the ^{232}Th not on particles passed through the ultrafilter. In contrast, Baskaran et al. (1992) and Moran and Buesseler (1992) found that a dominant fraction of Th associated with colloids in coastal waters. Kersten et al. (1998) used model calculations to estimate that 98% of the ^{234}Th in waters of Mecklenburg Bay in the southern Baltic is on colloids. The reason for the difference between these locations and those studied here is unclear.

4.4.3. Sediment Fluxes

The mass sediment flux rate $\dot{M}_{sed}$ can be related to the ^{234}Th scavenging rate by noting that the flux of ^{234}Th to the seafloor

by scavenging is $P_{234Th} \cdot {}^{234Th}A_B \cdot D_B$ and the ^{234}Th particle concentration is $^{234Th}A_B^{PART}/^{PART}C_B$, where $^{PART}C_B$ is the mass concentration of particles (in grams per gram of water). Then

$$\dot{M}_{sed} = \frac{P_{234Th}D_B{}^{PART}C_B}{(^{234Th}A_B^{PART}/^{234Th}A_B)}. \quad (13)$$

For BY-15, a sediment flux rate of 69 mg/yr-cm^2 is obtained (by using $P_{234Th} = 7.3$ yr^{-1} days from Eqn. 11, $D_B = 240$ m, $^{PART}C_B = 0.2$ mg/L from Table 4, and $^{234Th}A_B^{PART}/^{234Th}A_B = 0.5$). Assuming a reasonable dry bulk density of 1g/cm^3 for sediments in this area, this is equal to a sedimentation rate of 0.7 mm/yr-cm^2, which is comparable to that obtained from BY15 sediment cores of 1 mm/yr-cm^2 (Ignatius et al., 1981).

The residence time of particles in the water column, $^{PART}\tau$, is (by using Eqn. 12 and Eqn. 13)

$$^{PART}\tau = \frac{D_B{}^{PART}C_B}{\dot{m}_{sed}} = {}^{234Th}\tau_{sed}(^{234Th}A_B^{PART}/^{234Th}A_B). \quad (14)$$

Because $^{234Th}\tau_{sed} = 50$ d, then $^{PART}\tau = 25$ d. This can be compared with calculated particle residence times of 2 to 20 days in California Current surface waters (Coale and Bruland, 1985), 7 to 27 d in the Irish Sea (Kershaw and Young, 1988), and 1 to 9 d for Narragansett Bay (Santschi et al., 1979).

The ^{232}Th data can be used to estimate the fluxes of detrital material to the basin. There are relatively few data available regarding the association of ^{232}Th with particles in the Baltic. It may be assumed that the scavenging rate of ^{234}Th and ^{232}Th are similar so that $^{232}\tau_{SED} = {}^{234Th}\tau_{SED}$. Although this must be confirmed, there is unlikely to be sufficient difference to change the arguments here, considering other uncertainties. Then Eqn. 10 (with $^{SED}F_{232} = 0$) can be combined with Eqn. 12:

$$^{232}C_B\left(1 + \frac{{}^w\tau}{{}^{232}\tau_{SED}}\right) = \left(\frac{S_B}{S_{SW}}\right){}^{232}C_{SW} + \left(1 - \frac{S_B}{S_{SW}}\right){}^{232}C_R$$
$$+ \frac{{}^{AIR}F_{232}\,{}^w\tau}{D_B}. \quad (15)$$

The term $^{232}C_B(1 + {}^w\tau/{}^{232}\tau_{SED}) = 51$ pg ^{232}Th/g (by using $^{232}C_B = 0.2$ pg ^{232}Th/g, $^w\tau = 35$ yr, and $^{232}\tau_{SED} = 50$ d) represents the total concentration of ^{232}Th removed from a unit volume of water during the residence time of water in the Baltic. This is equal to the sum of the input terms. Inflowing water from the Kattegatt, with $^{232}C_{SW} = 0.24$ pg ^{232}Th/g (Andersson et al., 1995), provides a negligible amount of ^{232}Th. The magnitude of the river and eolian input terms cannot be evaluated independently. If the average river input into the basin is equal to the Kalix River concentration of 73 pg ^{232}Th/g, then the advection term for this input would provide 35 pg ^{232}Th/g, which can account for most ($\sim$70%) of the ^{232}Th removed from the water column. However, a dominant fraction of the ^{232}Th carried in rivers is likely removed upon discharge into the Baltic (as suggested by comparison between data from F-2 and the Kalix; see section 4.1), so that the measured river ^{232}Th concentration is an extreme upper limit for the river input that supplies the Baltic basin. The range of possible influx values for eolian material can be calculated from Eqn. 15; if the maximum river input is used (i.e., if there is no preferential removal of river Th from the water column during discharge into the basin), then the calculated eolian flux is 6.6×10^{16} atoms ^{232}Th/m^2-yr (for an average Baltic Sea depth of 56 m; Kullenberg and Jacobsen, 1981). The corresponding eolian mass input (assuming it has an average upper crust concentration of 10.6ppm Th; Taylor and McLennan, 1985), is 240 mg/cm^2-kyr. The highest calculated eolian flux for the Baltic is obtained by assuming that no river-borne Th flows beyond the river discharge areas and further into the basin ($^{232}A_R = 0$); then the calculated eolian flux is 2.1×10^{17} atoms ^{232}Th/m^2-yr. This corresponds to 770 mg/cm^2-kyr. There are no readily available direct eolian flux data available for the Baltic for comparison, but this is lower than the highest coastal values of >1000 mg/cm^2-kyr (see comprehensive review by Rea, 1994). Therefore, although a range of eolian fluxes is compatible with the available data, it is likely that river-borne Th is efficiently removed from the water upon discharge into the Baltic and that the eolian flux is the dominant input for ^{232}Th in the water column.

4.4.4. Ra Fluxes

For the Ra budget, Eqn. 10 can be applied to ^{226}Ra because the half-life of ^{226}Ra is long compared with the residence time of water in the Baltic; production by decay of ^{238}U in the water (as well as loss by decay of ^{226}Ra) can be neglected. Also, there is no scavenging of Ra, so that $P_{226} = 0$. Then the flux of ^{226}Ra from the underlying sediments can be obtained from

$$^{226}A_B - \left(1 - \frac{S_B}{S_{SW}}\right)(^{226}A_R) - \left(\frac{S_B}{S_{SW}}\right)(^{226}A_{SW}) = \frac{{}^{SED}F_{226}}{D_B}\frac{{}^w\tau}{\tau_{226}}.$$
$$(16)$$

If the bulk activities of rivers is used for $^{226}A_R$, the riverine flux of dissolved ^{226}Ra as well as ^{226}Ra carried on particles that desorb during estuarine mixing is included. By using $^{226}A_B = 15$ dpm^{226}Ra/100 L, the value for Atlantic surface seawater for $^{226}A_{SW} = 7.4$ dpm/100 L (see Cochran, 1992), and $^{226}A_R = 5$ dpm/100 L, then $^{SED}F_{226} = 8.8 \times 10^9$ atoms/m^2-yr. The fraction of ^{226}Ra in the water that is due to the sediment flux is equal to $(^{SED}F_{226}\,{}^w\tau)/(D_B\,\tau_{226}\,{}^{226}A_B)$, and is a substantial part (60%) of the Baltic ^{226}Ra budget. This is consistent with the Ba/^{226}Ra ratios of the Baltic (Fig. 7), which are generally below those expected for conservative mixing between Kalix River water and seawater and reflect an additional source of ^{226}Ra. However, the calculated ^{226}Ra flux requires the total production from 130 μg Th/cm^2 throughout the Baltic; by applying the concentration of particles at BY-15 of 0.29 μg Th/g to Baltic sediments, the calculated flux is equal to the total ^{226}Ra produced in the top 4.6 m. It is unlikely that such efficient release of Ra from the underlying sediments occurs. Alternatively, the rivers may contribute a substantially greater flux of Ra. Alkaline earths are typically diluted in the river by spring melt waters by factors of 2 to 3 (Ingri et al., pers. comm.), so that the average value for the Kalix may be as high as 15 dpm/100 L, which still requires a ^{226}Ra flux from 2 m of sediments. No flux of ^{226}Ra from the underlying sediments is required if the average annual river discharge across the watershed has 23 dpm/100 L; however, the relevant data for other rivers are not available to determine if this is reasonable for the Baltic drainage basin. In this case, the average Ba/^{226}Ra ratio of the average river discharge into the river also must be substantially lower than measured in the Kalix (Fig. 7).

It can be noted that there is evidence for substantial direct Ra inputs into other estuaries directly from underlying groundwaters (Moore, 1997). However, although groundwaters within the underlying bedrock in the Baltic region have ^{226}Ra concentrations of up to $\sim$10 times greater than that of the river (Ek et al., 1982), flow from these low-permeability rocks is likely to be very limited and can be neglected. Till groundwaters are likely to have substantially less Ra and would not provide a more Ra-rich discharge directly into the Baltic than into the rivers. Further, because the tills in the shield areas comprise only a thin veneer of several meters over the bedrock, these deposits do not form extensive aquifers that could drain a significant fraction of the watersheds directly into the Baltic. Further investigation is required to determine if such groundwater inputs are possible in the southern regions of the Baltic.

For ^{228}Ra, production within the water by ^{232}Th is negligible, and $P_{228} = 0$. Eqn. 10 is then

$$\left(1 - \frac{S_B}{S_{SW}}\right)(^{228}A_R)\ \left(\frac{S_B}{S_{SW}}\right)(^{228}A_{SW}) - {}^{228}A_B(1 + {}^{w}\tau\lambda_{228})$$

$$= -\frac{{}^{SED}F_{228}}{D_B}\frac{{}^{w}\tau}{\tau_{228}}. \quad (17)$$

There are no data available for the concentration of ^{228}Ra in the seawater inflow to the Baltic, although values of <5 dpm/100 L are typically found near the coasts (see Cochran, 1992). If values of $^{228}A_{SW}$ = 5 dpm/100 L and $^{228}A_R$ = 5 dpm/100 L are used (along with $[(^{228}Ra/^{226}Ra)_{AR}]_B$ = 1.25 and $[(^{228}Ra/^{226}Ra)_{AR}]_R$ = 1.24), then the flux from the underlying sediments accounts for 94% of the ^{228}Ra in the water column and is equivalent to 6.4×10^5 atoms/cm^2-yr. This is much lower than the flux of 1.3×10^7 atoms/cm^2-year calculated by Huh et al. (1987) for the release of ^{228}Ra from coastal sediments, and it requires release of all the ^{228}Ra produced in the top 17cm. Because the river input accounts for a small proportion (~3%) of the ^{228}Ra budget, the value calculated for the flux from the sediments does not change significantly if the river concentration is five times higher (as discussed for the ^{226}Ra budget) than that chosen. This remains true if the Ra river input is increased by a factor of five. Therefore, although the ^{226}Ra budget is dominated by advective inputs, that of ^{228}Ra is dominated by release from the underlying sediments. Groundwaters could account for the ^{228}Ra only if the average $(^{228}Ra/^{226}Ra)_{AR}$ is substantially higher than what is discharged into the Kalix.

It should be emphasized that although the above calculations provide reasonable Ra sediment fluxes, the long residence time of water in the Baltic (35 yr) relative to the half-life of ^{228}Ra (5.75 yr) requires either a sediment source or groundwater source enriched in ^{228}Ra to balance decay of this nuclide within the water. Thus, the similarity between Baltic and river $(^{228}Ra/^{226}Ra)_{AR}$ ratios is fortuitous.

5. CONCLUSIONS

The Kalix River watershed is an area typical of the northern Precambrian Shield regions, and the distribution of Ra, Th, and Pb radionuclides within this watershed and in the Baltic Sea provides information regarding the supply and transport of these nuclides into Arctic and northern waters. In this study, both short- and long-lived nuclide data were obtained for river inputs, river water, and estuarine waters to constrain input, transport, and removal processes over a range of time scales.

5.1. River Transport Characteristics

Th is transported in the Kalix largely on Fe-rich particles, with similar amounts in detrital grains and in authigenic phases containing Th obtained from the water. The remaining Th is dominantly associated with organic colloids most likely comprised of humic acids. An average of ~3 pg/g of "dissolved" Th passes through 10-kD ultrafilters; this is higher than calculated solubility limits and indicates that Th is likely associated with small organic compounds.

Kalix $(^{234}Th/^{230}Th)_{AR}$ ratios >1 may be due to radiogenic growth of ^{234}Th during transit in the watershed. River $(^{234}Th/^{238}U)_{AR}$ and $(^{230}Th/^{238}U)_{AR}$ ratios may provide a useful tool

for evaluating the transit time for particle-reactive elements across watersheds where actinide inputs are well constrained.

5.2. Watershed Weathering Characteristics

Overall weathering characteristics of the watershed are reflected in the river ^{230}Th/^{232}Th, ^{228}Ra/^{226}Ra, and ^{226}Ra/Ba ratios; these are comparable to those of source rocks, which indicate similar release rates of these nuclides from U-, Th-, and Ba-bearing minerals. This is compatible with the congruent weathering of the tills and basement rocks in the watershed and may be a characteristic of shield and till weathering.

Values of $(^{230}Th/^{238}U)_{AR}$ <1 and low ^{232}Th/^{238}U ratios in the river indicate that Th is accumulating in the weathering regions. The same may be true of Ra, although it must be confirmed whether values of $(^{226}Ra/^{238}U)_{AR}$ <1 apply to the river throughout the year. Also, high $(^{228}Ra/^{232}Th)_{AR}$ and $(^{226}Ra/^{230}Th)_{AR}$ ratios indicate that Th is preferentially retained over Ra. Because eventually all elements in rocks entering the weathering cycle are removed from the watershed either by mechanical or chemical weathering, these ratios may provide an index to the degree to which the weathering profile has reached a steady state.

Groundwaters from within bedrock and glacial tills have comparable Th isotope concentrations and do not exhibit significant isotopic shifts relative to the host rocks. In contrast, bedrock groundwaters have been found (Porcelli et al., 1997) to have much higher U concentrations and $(^{234}U/^{238}U)_{AR}$ ratios than till groundwaters.

Mire peats that are widespread in northern shield areas concentrate Th and U. Mire waters have very high ^{230}Th/^{232}Th ratios relative to inflow waters due to recoil from the high U concentrations in the peats. Mires do not accumulate Ba and Ra. Mire outflows do not have a significant impact on river Th and Ra isotopic ratios.

The ^{210}Pb derived by atmospheric deposition is strongly retained in the soils.

5.3. Baltic Sea Characteristics

High $(^{234}Th/^{238}U)_{AR}$ ratios indicate that the residence time of ^{234}Th with respect to particle removal is long (~50 d), largely due to low particle and colloid concentrations. The ^{232}Th budget is dominated by eolian inputs, with river-borne ^{232}Th largely lost to sediments at discharge points. Sedimentation rates calculated from the water column data are compatible with measured sedimentation rates.

^{226}Ra activities are higher than within inflows, with up to 60% derived from underlying sediments. A dominant fraction of ^{228}Ra is required from sediments to balance the decay of ^{228}Ra in the water column during the 35-yr residence time of water in the Baltic. The $(^{228}Ra/^{226}Ra)_{AR}$ ratios in the Baltic, which are relatively constant over a range of salinities, are fortuitously similar to that of river inflows and the upper crust.

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REFERENCES

Andersson P. S., Wasserburg G. J., and Ingri J. (1992) The sources and transport of Sr and Nd isotopes in the Baltic Sea. *Earth Planet. Sci. Lett.* **113,** 459–472.

Andersson P. S., Wasserburg G. J., Ingri J., and Stordal M. C. (1994) Strontium, dissolved and particulate loads in fresh and brackish waters: The Baltic Sea and Mississippi Delta. *Earth Planet. Sci. Lett.* **124,** 195–210.

Andersson P. S., Wasserburg G. J., Chen J. H., Papanastassiou D. A., and Ingri J. (1995) ^{238}U-^{234}U and ^{232}Th-^{230}Th in the Baltic Sea and in river water. *Earth Planet. Sci. Lett.* **130,** 217–234.

Andersson P. S., Porcelli D., Wasserburg G. J., and Ingri J. (1998) Particle transport of ^{234}U-^{238}U in the Kalix River and the Baltic Sea. *Geochim. Cosmochim. Acta* **62,** 385–392.

Andersson P. S., Gustafsson O., Roos P., Broman D., and Toneby A. (2000) Particle mediated surface water export: Comparison of estimates from ^{238}U-^{234}Th disequilibria and sediment traps in a continental shelf region. *Eos (Suppl.)* **80,** OS103.

Appleby P. G. and Oldfield F. (1992) Application of lead-210 to sedimentation studies. In *Uranium Series Disequilibrium: Applications to Earth, Marine, and Environmental Sciences,* 2nd edition (eds. M. Ivanovich and R. S. Harmon), pp. 731–778. Clarendon Press.

Baskaran M., Santschi P. H., Benoit G., and Honeyman B. D. (1992) Scavenging of thorium isotopes by colloids in seawater of the Gulf of Mexico. *Geochim. Cosmochim. Acta* **56,** 3375–3388.

Baskaran M., Murphy D. J., Santschi P. H., Orr J. C., and Schink D. R. (1993) A method for the rapid in situ extraction and laboratory determination of Th, Pb, and Ra isotopes from large volumes of seawater. *Deep-Sea Res.* **40,** 849–865.

Benninger L. K., Lewis D. M., and Turekian K. K. (1975) The use of natural ^{210}Pb as a heavy metal tracer in the river–estuarine system. In *Marine Chemistry in the Coastal Environment* (ed. T. M. Church). American Chemical Society Symposium Series 18, pp. 202–210. American Chemical Society.

Chen J. H., Edwards J. H., and Wasserburg G. J. (1986) ^{238}U, ^{234}U, and ^{232}Th in seawater. *Earth Planet. Sci. Lett.* **80,** 241–251.

Coale K. H. and Bruland K. W. (1985) Th-234–U-238 disequilibria within the California Current. *Limnol. Oceanogr.* **30,** 22–33.

Cochran J. K. (1992) The oceanic chemistry of the uranium and thorium-series nuclides. In *Uranium Series Disequilibrium: Applications to Earth, Marine, and Environmental Sciences,* 2nd edition (eds. M. Ivanovich and R. S. Harmon), pp 731–778. Clarendon Press.

Dearlove J. P. L., Longworth G., Ivanovich M., Kim J. I., Delakowitz B., and Zeh P. (1991) A study of groundwater-colloids and their geochemical interactions with natural radionuclides in Gorleben aquifer systems. *Radiochim. Acta* **52/53,** 83–89.

Dyrssen D. (1993) The Baltic–Kattegat–Skarerrak estuarine system. *Estuaries* **16,** 446–452.

Eakins J. D., Cambray R. S., Chambers K. C., and Lally A. E. (1984) The transfer of natural and artificial radionuclides to Brotherswater from its catchment. In *Lake Sediments and Environmental History* (eds. E. Y. Haworth and J. W. G. Lund), pp. 125–144. University of Minnesota Press.

Ek J., Evans S., and Ljungqvist L. (1982) Variation in radioactivity, uranium and radium-226 contents in three radioactive springs and along their out-flows, northern Sweden. *KBS Technical Rep.* **1982,** 82-13.

Elsinger R. J. and Moore W. S. (1984) Ra-226 and Ra-228 in the mixing zones of the Pee Dee River–Winyah Bay, Yangtze River, and Delaware Bay estuaries. *Estuar. Coastal Shelf Sci.* **18,** 601–613.

Hem J. D. (1985) Study and interpretation of the chemical character-

istics of natural water. USGS Water Supply Paper 2254. U.S. Geological Survey.

Honeyman B. D. and Santschi P. H. (1989) A Brownian-pumping model for oceanic trace-metal scavenging—Evidence from Th isotopes. *J. Mar. Res.* **47,** 951–992.

Huh C. A., Zahnle D. L., Small L. F., and Noshkin V. E. (1987) Budgets and behaviors of uranium and thorium series isotopes in Santa Monica Basin sediments. *Geochim. Cosmochim. Acta* **51,** 1743–1754.

Ignatius H., Axberg S., Niemistö L., and Winterhalter B. (1981) Quaternary geology of the Baltic Sea. In *The Baltic Sea* (ed. A. Voipio), pp. 54–104. Elsevier.

Ingri J., Torssander P., Andersson P. S., Mörth C.-M., and Kusakabe M. (1997) Hydrogeochemistry of sulfur isotopes in the Kalix River catchment, northern Sweden. *Appl. Geochem.* **12,** 483–496.

Ingri J., Widerlund A., Land M., Gustafsson Ö., and Öhlander B. (2000) Temporal variations in the fractionation of the rare earth elements in a boreal river; the role of colloidal particles. *Chem. Geol.* **166,** 23–45.

Kaufman A., Li Y.-H., and Turekian K. K. (1971). The removal rates of ^{234}Th and ^{228}Th from waters of the New York Bight. *Earth Planet. Sci. Lett.* **54,** 385–392.

Kennedy V. C., Zellweger G. W., and Jones B. F. (1974) Filter pore-size effects on the analysis of Al, Fe, Mn, and Ti in water. *Water Resourc. Res.* **10,** 785–790.

Kershaw P. and Young A. (1988) Scavenging of ^{234}Th in the eastern Irish Sea. *J. Environ. Radioact.* **6,** 1–23.

Kersten M., Thomsen S., Priebsch W., and Garge-Schönberg C.-D. (1998) Scavenging and particle residence times determined from ^{234}Th/^{238}U disequilibria in the coastal waters of Mecklenburg Bay. *Appl. Geochem.* **13,** 339–347.

Kullenberg G. and Jacobsen T. S. (1981) The Baltic Sea: An outline of its physical oceanography. *Mar. Pollut. Bull.* **12,** 183–186.

Langmuir D. and Herman J. S. (1980) The mobility of thorium in natural waters at low temperatures. *Geochim. Cosmochim. Acta* **44,** 1753–1766.

Li Y.-H., Mattieu C. G., Biscaye P., and Simpson H. J. (1977) The flux of Ra-226 from estuarine and continental shelf sediments. *Earth Planet. Sci. Lett.* **37,** 237–241.

Martin J. M. and Meybeck M. (1979) Elemental mass-balance of material carried by major world rivers. *Mar. Chem.* **7,** 173–206.

Moore W. S. (1967) Amazon and Mississippi River concentrations of uranium, thorium, and radium isotopes. *Earth Planet. Sci. Lett.* **2,** 231–234.

Moore W. S. (1997) High fluxes of radium and barium from the mouth of the Ganges-Brahmaputra River during low river discharge suggest a large groundwater source. *Earth Planet. Sci. Lett.* **150,** 141–150.

Moore W. S. and Edmond J. M. (1984) Radium and barium in the Amazon River system. *J. Geophys. Res.* **89,** 2061–2065.

Moran S. B. and Buesseler K. O. (1992) Short residence time of colloids in the upper ocean estimated from ^{238}U-^{234}Th disequilibria. *Nature* **359,** 221–223.

Nash K. L. and Choppin G. R. (1980) Interaction of humic and fulvic acids with Th(IV). *J. Inorg. Nucl. Chem.* **42,** 1045–1050.

Porcelli D. R., Andersson P. S., Wasserburg G. J., Ingri J., and Baskaran M. (1997) The importance of colloids and mires for the transport of uranium isotopes through the Kalix River watershed and Baltic Sea. *Geochim. Cosmochim. Acta* **61,** 4095–4113.

Rea D. K. (1994) The paleoclimatic record provided by Eolian deposition in the deep sea: The geologic history of wind. *Rev. Geophys.* **32,** 159–195.

Reid D. F., Key R. M., and Schink D. R. (1979) Radium, thorium and actinium extraction from seawater using an improved manganese-oxide–coated fiber. *Earth Planet. Sci. Lett.* **43,** 223–226.

Rodhe A. (1987) *The Origin of Streamwater Traced by Oxygen-18.* Report Series A 41. Uppsala University Department of Physical Geography, Division of Hydrology.

Santschi P. H., Li Y.-H., and Bell J. (1979) Natural radionuclides in the water of Narragansett Bay. *Earth Planet. Sci. Lett.* **45,** 201–213.

Szalay A. (1964) Cation exchange properties of humic acids and their importance in the geochemical enrichment of UO_2^{++} and other cations. *Geochim. Cosmochim. Acta* **28,** 1605–1614.

Taylor S. R. and McLennan S. M. (1985) *The Continental Crust: Its Composition and Evolution*. Blackwell.

Tricca A., Porcelli D., and Wasserburg G. J. (2000) Factors controlling the groundwater transport of U, Th, Ra, and Rn. *Proc. Indian Acad. Sci. (Earth Planet. Sci.)* **109,** 95–108.

Viers J., Dupré B., Polvé M., Schott J., Dandurand J.-L., and Braun J.-J. (1997) Chemical weathering in the drainage basin of a tropical watershed (Nsimi-Zoetele site, Cameroon): Comparison between organic-poor and organic-rich waters. *Chem. Geol.* **140,** 181–206.