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The Importance of colloids for the behavior of uranium isotopes in the low-salinity zone of a stable estuary

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Abstract—Particle-mediated removal processes of U isotopes were investigated during spring flood discharge in the low-salinity zone (LSZ, up to 3 practical salinity units [psu]) of a stable estuary. A shipboard ultrafiltration cross-flow filtration (CFF) technique was used to separate particles (>0.2 μm) and colloids (between 3000 daltons (3 kD) and 0.2 μm) from ultrafiltered water (<3 kD) containing “dissolved” species. Sediment traps were used to collect sinking material. Concentration of Fe and organic C, which are indicators of the major U carrier phases, were used to interpret the behavior of ²³⁴U-²³⁸U during estuarine mixing.

Colloids dominated the river water transport of U, carrying ≈90% of the U. On entering the estuary, colloids accounted for the dominant fraction of U to about a salinity of 1 psu, but only a minor fraction (<5%) at 3 psu. A substantial fraction of the total U is removed at <1 psu by Fe-organic rich colloids that aggregate and sink during initial estuarine mixing in the Kalix River estuary. In contrast, at salinities >1 psu, there is a general correlation between U and salinity in all filtered fractions. The ²³⁴U/²³⁸U ratios in different filtered fractions and sinking particles were generally indistinguishable at each station and showed enrichment in ²³⁴U, compared with secular equilibrium (δ²³⁴U = 266–567). This clearly shows that all size fractions are dominated by nondetrital U. Consideration of U isotope systematics across the estuary reveals that substantial U exchange must occur involving larger particles at least to 1 psu and involving colloids at least to ≈1.5 psu. Further exchange at higher salinities may also occur, as the proportion of U on colloids decreases with increasing salinity. This may be due to decreasing colloid concentration and increasing stabilization of uranyl carbonate complexes during mixing in the estuary.

The results show that although U is a soluble element that shows generally conservative mixing in estuaries, removal occurs in the very low salinity zone, and this zone represents a significant sink of U. Variation in composition and concentration of colloidal particles between different estuaries might thus be an important factor for determining the varying behavior of U between estuaries. Copyright © 2001 Elsevier Science Ltd

1. INTRODUCTION

Estuaries are transition zones between river water and seawater, where important geochemical processes occur, affecting the flux between continents and oceans of many elements. Nuclides from the U-decay series have been used extensively for quantification of geochemical processes in the marine environment and understanding the fundamental aspects of U geochemistry in estuaries is crucial for the marine geochemical budget of U. Several studies on the estuarine behavior of U from a variety of environments show that U behavior in estuaries varies greatly, showing both conservative and nonconservative behavior (see review by Moore, 1992). Previous studies in the Baltic Sea showed that U is strongly associated with large particles and colloids (Porcelli et al., 1997; Andersson et al., 1998). River and brackish water particles with high concentrations of Fe are strongly enriched in U, and it was shown that secondary Fe-oxyhydroxides are largely responsible for the

particle uptake of U, whereas no evidence for association with Mn-oxyhydroxides was found (Andersson et al., 1998). Andersson et al. (1998) also suggested that uptake of U on organic phases in both river and brackish water might be important for concentrating U in the particulate fraction. The U transport in the Kalix River is dominated by colloids, and it was suggested the colloid dynamics also seems to be important in determining the estuarine behavior (Porcelli et al., 1997). From these studies and with results from the Amazon estuary (Swarzenski et al., 1995), the Ganges-Brahmaputra mixing zone (Carroll and Moore, 1994) and river water from the English Fenland (Plater et al., 1992), it is clear that sorption onto colloids and larger particle phases in the low-salinity part of the mixing zone is an important control on the estuarine geochemistry of U. Also, sharp changes of thermodynamic equilibrium conditions occur where freshwater initially mixes with saline waters (Morris et al., 1978; Morris, 1986), and the nonconservative behavior of several elements may be related to processes at low salinities, <1 psu (Salomons and Förstner, 1984).

It has been shown that uranyl ions can desorb from colloids by increases in alkalinity at constant pH or by increasing pH. Such changes enhance the extent of uranyl carbonate complexing, and because carbonate complexes are poorly adsorbed, this causes desorption and remobilization of uranyl species from colloids (Langmuir, 1997). Thus, colloid dynamics are likely to

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be important for U behavior in the water column at very low salinities.

Although it is well established that the estuarine fluxes of U show large variations between different estuarine environments, and processes in the low-salinity zone (LSZ, here defined as <3 practical salinity units [psu]) are a key issue, the important removal processes of U within this zone are not well understood. There are few data available regarding the distribution of U isotopes between different particle size fractions.

Rivers draining boreal forest areas to northern oceans are generally enriched in organic colloidal material from forests and peatlands within their catchments and have lower detrital load than world average river composition. Some of these rivers that drain northern Siberia and North America comprise a number of the earth's major rivers. Thus, these rivers and their estuaries represent good systems for studying the behavior of natural organic colloidal material and formation of authigenic phases at the river-estuary interface. To evaluate geochemical processes in the LSZ, it is therefore important to have access to an estuarine system that can offer favorable field conditions for sampling, including relatively high stability of the LSZ over many kilometers. The Kalix River in North Sweden, the only unregulated major river system in Western Europe (Dynesius and Nilsson, 1994), drains into the northern part of the Baltic Sea through a salt-wedge highly stratified estuary with minimal tidal mixing. This system constitutes an easily accessible and representative boreal river with a well-characterized estuary.

In the present study, cross-flow filtration (CFF) data for U isotopes in the Kalix River are used to compare the U distribution between different size fractions with that of important constituents such as Fe and organic C, and so investigate the behavior of ^{234}U - ^{238}U in dissolved forms, colloids, and larger particles during mixing of the Kalix River water plume with brackish water in the LSZ of the Kalix River estuary.

2. FIELD AREA

The Kalix River drains a northern boreal shield area and is distinctive in having relatively low concentrations of suspended detrital particles and high concentrations of nondetrital particles rich in authigenic Fe and Mn (Pontér et al., 1992; Ingri and Widerlund, 1994; Ingri et al., 1997). About 93% of the total organic C in the Kalix River is dissolved organic C (DOC) (i.e., passes through a 0.7- μm filter), and $\approx 80\%$ of the DOC is humic substances derived from the peatlands and upper soil horizons (Ingri, 1996). The Kalix-Torne River system is defined as a large unregulated river system, with a mean annual discharge of 373 m^3/s (Dynesius and Nilsson, 1994). The estuary, located in the northern part of the Baltic Sea, Gulf of Bothnia, shows stable stratification with minimal tides and a well-defined freshwater plume in the spring (Fig. 1). The Kalix River discharge shows strong seasonal variation with flow peaks during spring due to the melting of snow (Fig. 2). This spring discharge causes a clearly visible freshwater plume reaching far out into the Gulf of Bothnia. These conditions facilitate good spatial sampling resolution with the <3 psu zone stretching over 60 km in the spring. Detailed physical and chemical conditions of the estuary are described in Widerlund (1996). The total flux of U per unit drainage area for the Kalix

is 0.08 $\text{kg}/\text{km}^2/\text{yr}$, which is lower than the world average of 0.55 $\text{kg}/\text{km}^2/\text{yr}$ (Andersson et al., 1998).

3. SAMPLING AND ANALYTICAL METHODS

Brackish water from the Kalix River estuary (Fig. 1) was collected June 11 to 15, 1997, at six stations from aboard the *R/V KBV005*. Salinity and temperature depth profiles were obtained by conductivity-temperature-depth (CTD) at regular intervals for determination of the depth of the mixed layer. Water was pumped from the mixed layer ($\approx 4\text{-m}$ depth) through the on-line filtration system (Appendix 1), with the water intake 30 m away from the windward side of the ship by using an extendable crane. Each station was occupied for ≈ 12 h of continuous on-line filtration to collect enough material of both particles and colloids for determination of U and other species such as ^{234}Th , organic compounds, Fe, and Si (Gustafsson et al., 2000). The whole estuarine sampling period (5 days) was favored by very calm weather with winds never exceeding 2 to 3 m/s, which clearly improved the stability of the LSZ. The Kalix River estuary shows a rather stable stratification, and samples from the innermost station collected by in situ filtration in progress for >12 h showed variation in conductivity only up to 20% (Table 2). The Kalix River water, representing the freshwater end member for estuarine mixing, was collected at Station Kamlunge (≈ 5 km upstream from the estuary) on May 14 and June 16, 1997, with the same separation techniques as the estuarine samples (described below).

A shipboard ultrafiltration, cross-flow filtration (CFF) technique was used to separate particles ($>0.2 \mu\text{m}$), filtered water ($<0.2 \mu\text{m}$), and colloids ($3 \text{ kD} < \text{colloids} < 0.2 \mu\text{m}$; $3 \text{ kD} = 3000$ Daltons) from ultrafiltered water ($<3 \text{ kD}$) containing "dissolved" species (see appendix for description of the CFF system). All water subsamples for U determination were acidified to $\text{pH} < 2$ with ultrapure HCl. Samples for salinity (conductivity) were taken from all subsamples and analyzed with a salinometer (Minisal 2100) at Umeå Marine Research Center. The salinity data are reported as conductivity and in practical salinity units; see Pickard and Emery (1990) for definition of psu.

Settling particulate material was collected by the use of sediment traps consisting of paired PVC-cylinders, in diameter of 10.5- and 50-cm height (Larsson et al., 1986). The traps were deployed at stations 4 and 6 for a period of 16.7 and 15.2 d, respectively. They were moored below the mixed layer at 22 m (station 4) and 16 m (station 6). The sediment trap samples were retrieved according to the procedures described in Blomqvist and Larsson (1994). The mass of sediments in each trap was determined by drying at 50°C for 24 h and corrected for the salt contributed by water during drying.

Uranium was separated from the various aqueous samples following Chen et al. (1986) and Andersson et al. (1995). A double spike, $^{233}\text{U}/^{236}\text{U}$, was added, and the U was precipitated with Fe-hydroxide. The precipitate was treated with UV-radiation, HNO_3 , and HClO_4 to decompose organic material and U was separated on anion exchange columns. For determination of the U concentration and isotopic composition of particles ($>0.2 \mu\text{m}$), the particle-laden nitrocellulose filters were processed following Andersson et al. (1994; 1995). The trap material was decomposed with HF-HClO_4 and further processed like the water samples. The total chemical blank was 18 fmol ^{238}U . The U analyses were performed by using a Finnigan MAT 262 thermal ionization mass spectrometer. Duplicates of the filtered water ($<0.2 \mu\text{m}$) from station 6 agree within errors, which are $\approx 0.5\%$ (Table 2). The blank was $<0.03\%$ for all samples and thus insignificant. However, it must be stressed that due to long filtration time at each station the changes in salinity cause variation in ^{238}U concentration between the different size fractions that are significantly larger than the analytical errors.

Major element compositions of the various aqueous fractions and particles were analyzed by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) in collaboration with SGAB-analys, Luleå, Sweden. The sediment trap material was analyzed for major element composition by using ICP-AES following procedures in Widerlund and Ingri (1995).

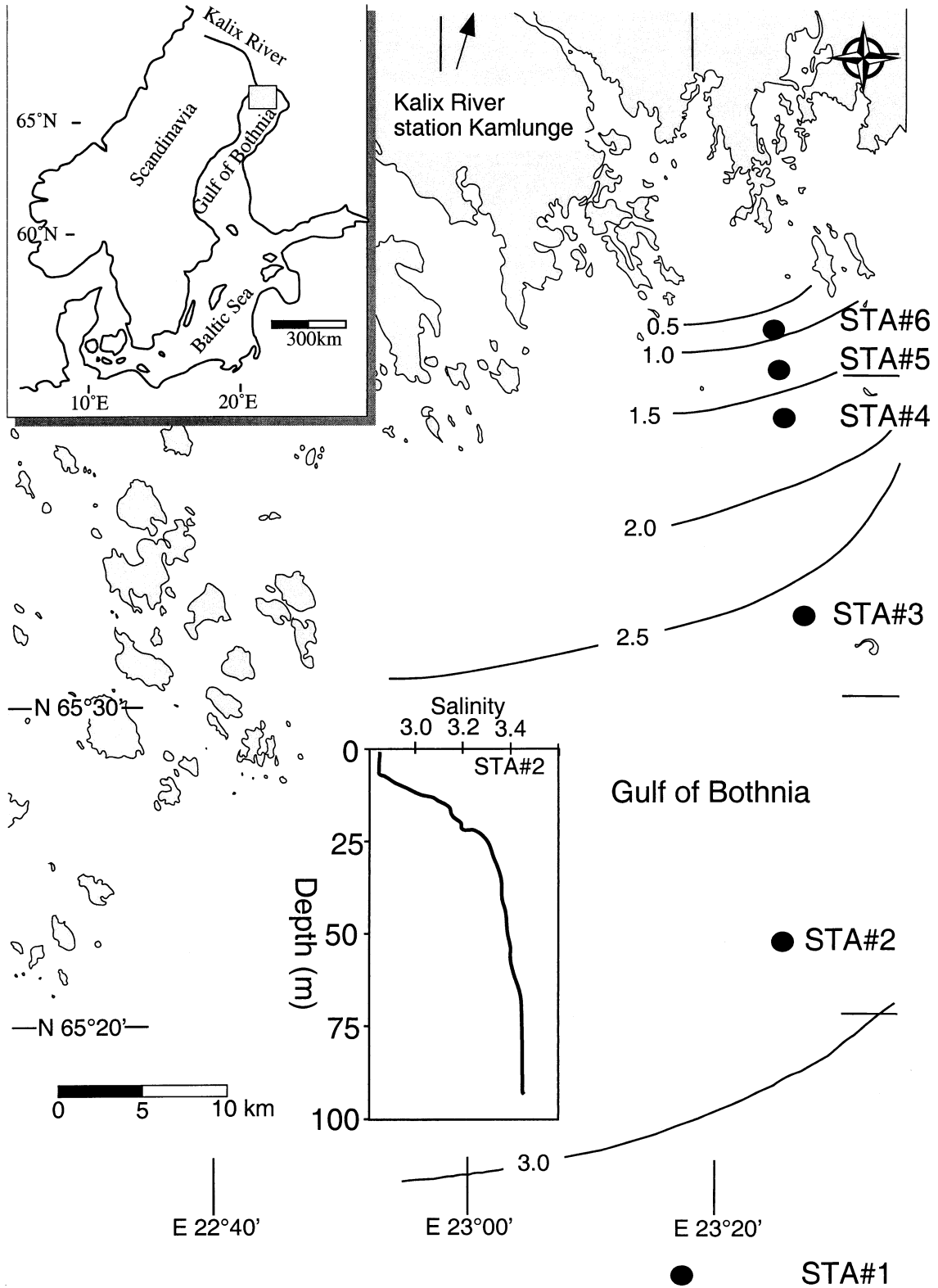


Fig. 1. Map of the Kalix River estuary. The inset map shows the Scandinavian Peninsula and the location of the Kalix River and its estuary. All sampling stations are marked STA 1 to STA 6 as well as the river water end member at Kalix River station Kamlunge, ≈ 5 km upstream from the estuary. Sediment traps were deployed at STA 4 and STA 6. Isohaline lines in for the surface water are plotted and indicate the spreading of the freshwater plume. A salinity depth profile obtained at STA 2 shows the characteristic features of the estuary with a well-mixed layer, of ≈ 4 -m depth, on top of the more saline Gulf of Bothnia water.

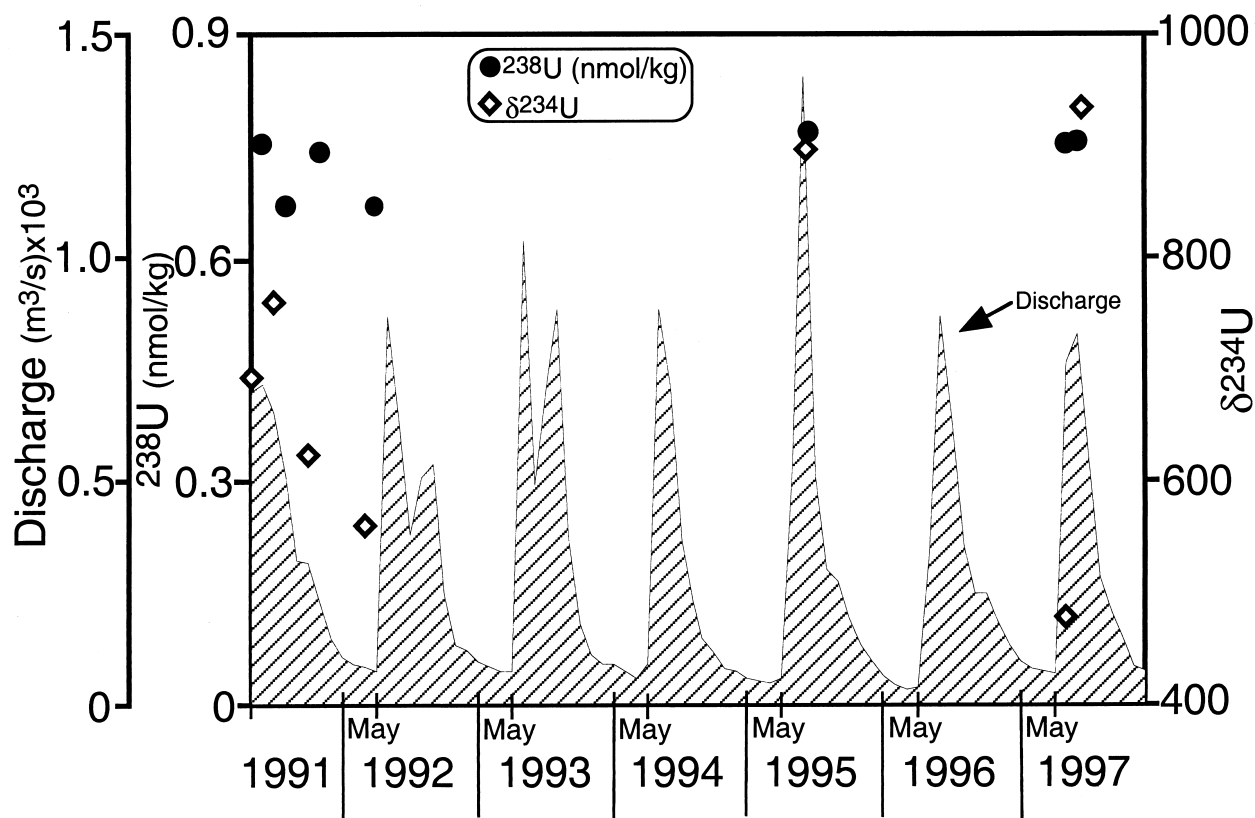


Fig. 2. Monthly mean discharge (stippled area) during 1991 to 1997, ^{238}U concentration and $\delta^{234}\text{U}$ in filtered water from the Kalix River at station Kamlunge. Discharge data were obtained from SMHI (Swedish Meteorological and Hydrological Institute) gauging station at Råktfors. The ^{238}U and $\delta^{234}\text{U}$ data from 1991 to 1995 were taken from Andersson et al. (1995) and Porcelli et al. (1997). The ^{238}U concentration in the river water shows a mean value of 0.727 nmol $^{238}\text{U}/\text{kg}$ with relatively small temporal variations (<10%). The $\delta^{234}\text{U}$ varies between 480 and 940 with the higher values generally correlated with high discharge. Note that the analytical errors are smaller than the symbols.

4. RESULTS AND DISCUSSION

4.1. Integrity of CFF System

To test the effectiveness of the filters used for the CFF system (described in the appendix), the apparent recovery (R%) and the mass balance (M%) for each element were determined;

$$R\% = \frac{[\text{colloids}] + [\text{dissolved}]}{[\text{feed}]} \times 100 \quad (1)$$

$$M\% = \frac{[\text{colloids}] + [\text{dissolved}] + [\text{rinses}]}{[\text{feed}]} \times 100 \quad (2)$$

where [colloids] represent the elemental concentration in the retentate (corrected by the concentration factor, see appendix), [dissolved] is the concentration in the permeate, [rinses] is the concentration in the filter rinse solutions, and [feed] is the concentration in the inflow to the system. The R% is a useful first indicator of losses to the CFF system or contamination from the system; if $R\% < 100\%$, it can be concluded that losses are larger than contamination, and if $R\% > 100\%$, then contamination is greater than losses (Gustafsson et al., 1996). The mass balance (M%) is a tedious but necessary experiment to

evaluate if reasonable yields were obtained and if cross-contamination between samples was minimized.

The recovery and mass balance for Fe and ^{238}U were determined for samples from stations 1, 4, 5, and 6 (Table 1). For the 3 kDa CFF experiment, the mass balance for Fe varied between 85% and 133%, whereas the recoveries are lower (53–83%). This finding shows that a significant fraction of the Fe is retained in the 3-kD filter but can be removed by HCl (0.5 mol/L) and NaOH (0.1 mol/L) rinsing.

Uranium recovery for the 3-kD filter decreases from 101% at station 1, to 78% at station 4, and to 50% at station 6. The rinse solutions were not analyzed for U, and thus no mass balances were calculated. However, the low R% at station 6 indicates that a significant fraction of U is retained in the filter at low salinities. From these experiments it is not possible to evaluate whether the low R% values for Fe and U are due to trapping of colloid bound Fe and U in the filter, although this is most likely, or adsorption of dissolved species.

In the 0.2- μm CFF experiments, the Fe recoveries were lower than for the 3-kD filter, with R% varying from 14% to 52%, following salinity. Although the 0.2- μm filter was rinsed with HCl and NaOH between each sample, the solutions were not analyzed. A 0.2- μm CFF of river water, which was con-

Table 1. Recovery and mass balance data for the CFF.

	Fe, $\mu\text{mol/kg}$ (% total)	^{238}U , nmol/kg (% total)		
STA 1				
Unfiltered	0.51	(100)	1.382	(100)
>0.2 μm	0.04		—	
<0.2 μm	0.23		1.374	
Recovery R%		(52)		(99)
>3 kD	0.10		0.078	
<3 kD	0.02		1.313	
Rinse NaOH 3 kD	—		—	
Rinse HCl 3 kD	0.08		—	
Recovery R%		(53)		(101)
Mass balance M%		(85)		
STA 4				
Unfiltered	2.15	(100)	1.093	(100)
>0.2 μm	0.27		—	
<0.2 μm	0.50		0.994	
Recovery R%		(36)		(91)
>3 kD	0.31		0.195	
<3 kD	0.02		0.582	
Rinse NaOH 3 kD	0.04		—	
Rinse HCl 3 kD	0.30		—	
Recovery R%		(65)		(78)
Mass balance M%		(133)		
STA 5				
Unfiltered	4.76	(100)	0.960	(100)
>0.2 μm	0.33		0.132	
<0.2 μm	0.40		0.731	
Recovery R%		(15)		(90)
>3 kD	0.22		—	
<3 kD	0.04		—	
Rinse NaOH 3 kD	0.04		—	
Rinse HCl 3 kD	0.14		—	
Recovery R%		(64)		
Mass balance M%		(109)		
STA 6				
Unfiltered	5.37	(100)	0.749	(100)
>0.2 μm	0.31		0.100	
<0.2 μm^a	0.44		0.59	
Recovery R%		(14)		(92)
>3 kD	0.33		0.216	
<3 kD	0.04		0.080	
Rinse NaOH 3 kD	<0.005		—	
Rinse HCl 3 kD	0.05		—	
Recovery R%		(83)		(50)
Mass balance M%		(96)		

^aNote that the <0.2 μm U for STA 6 is estimated from the conductivity.

ducted before collection of the LSZ samples, gave higher recoveries for most analyzed elements, including Fe (R% = 80–100%). The contrasting lower recoveries obtained during 0.2- μm filtration of brackish water may be due to increased colloid aggregation in the higher ionic strength estuarine waters. However, we cannot exclude the possibility that the NaOH rinse solutions affected the PVDF 0.2- μm filter so that the actual cutoff was smaller. In this case, if the Fe in the estuary is associated with smaller particles and colloids, compared with the river water, the 0.2- μm filter might retain these colloids. Uranium shows good recoveries, 90% to 99%, for the 0.2- μm filter.

The decrease in R% with decreasing salinity for the 3-kD

filter might indicate that there is increased adsorption of colloidal bound U to the filter at lower salinities. There is no evidence of cross-contamination in the mass balance data for Fe as well as for other elements (Ingri et al., 2000) in either the 0.2- μm or 3-kD filter units, and the filter units were carefully rinsed between each sample. The strong association of Fe to the colloid fraction throughout the estuary might explain the difference in recovery between Fe and U for the 0.2- μm filter. In the samples with the lowest recoveries (stations 5 and 6), the <3-kD fraction contains <1% of the total Fe, which clearly shows that the Fe transport is dominated by colloids. In comparison with Fe, a substantially smaller fraction of U is carried in colloids, and thus also less affected by losses to the filter from adsorption of colloids. Therefore, the fact that the Fe in the estuary is totally dominated by Fe-rich colloids and that an apparently modest adsorption of these colloids to the 0.2- μm filter might be the cause for the lower apparent recovery for Fe compared with U.

4.2. U in Kalix River and Estuarine Water

4.2.1. U in the Kalix River

The ^{238}U concentration, and $\delta^{234}\text{U}$ (see Table 2 for definition) in the Kalix River at station Kamlunge are reported in Table 2 and the discharge in Figure 2, along with U data from Andersson et al. (1995) and Porcelli et al. (1997). The unfiltered and <0.2- μm filtered samples collected 1 month apart in 1997 show indistinguishable ^{238}U concentrations (<1% difference, Table 2), which can be expected because it has been shown previously (Andersson et al., 1998) that ^{238}U is dominantly transported in the <0.45- μm fraction. The ^{238}U concentrations obtained previously for filtered (<0.45- μm) river water shows <10% annual variation in concentration. This finding is in strong contrast to reported concentrations of the major elements Na, K, Mg, Ca, Si, S, and Cl, which during peak flow are diluted two to four times compared with those during the winter due to simple dilution by meltwater (Ingri, 1996). Porcelli et al. (1997) argued that the large accumulations of U, ultimately bedrock-derived, in the mires (peatlands, water-saturated organic deposits dominated by partially decomposed mosses) may provide a large proportion of U to the rivers during the spring, when the concentrations of other elements are low; waters diluted in all elements by spring melt and passing through the mires equilibrate with U-rich peats, which thus act to buffer the supply of groundwater U to the river.

4.2.2. $\delta^{234}\text{U}$ in the Kalix River

The river water $\delta^{234}\text{U}$ value varied from $\delta^{234}\text{U} = 477$ in the middle of May, 1 month before collection of the brackish waters, to $\delta^{234}\text{U} = 939$ in unfiltered water from June 16 (Fig. 2). In combination with values from 1991 to 1992 and 1995, this shows a large temporal variation in $\delta^{234}\text{U}$ in the Kalix River (Fig. 2).

4.2.3. U in the estuary in unfiltered and filtered water

The ^{238}U concentrations measured in unfiltered water as well as in the 0.2- μm and 3-kD filtered brackish waters are shown in Table 2 and Figure 3. Within the LSZ (1–3 psu), there is a

Table 2. Uranium concentrations and isotopic composition in unfiltered water, CFF fractions, and sediment trap material from the Kalix River estuary and the Kalix River station Kamlunge.

Station	Position	Date 1997	Fraction	$\delta^{234}\text{U}^a$ 2σ	^{238}U (nmol/kg) 2σ	Conductivity (mS/cm)	Salinity ^b
STA 1	<i>N 65°10'00"</i> <i>E 23°14'13"</i>	June 11	unfiltered		1.383 ± 0.007	5.111	2.999
		June 11	<0.2 μm	266 ± 4	1.375 ± 0.001	5.090	2.986
		June 11	<3 kD	266 ± 4	1.313 ± 0.002	5.157	3.028
		June 12	>3 kD	273 ± 2	0.078 ± 0.001	5.157	3.028
STA 2	<i>N 65°23'20"</i> <i>E 23°30'00"</i>	June 12	unfiltered		1.369 ± 0.007	4.944	2.895
		June 12	<0.2 μm	286 ± 3	1.347 ± 0.001	4.922	2.881
		June 12	<3 kD	276 ± 4	1.210 ± 0.002	4.901	2.868
STA 3	<i>N 65°33'06"</i> <i>E 23°28'65"</i>	June 13	unfiltered		1.305 ± 0.007	4.626	2.697
		June 13	<0.2 μm	305 ± 4	1.262 ± 0.001	4.594	2.677
STA 4	<i>N 65°38'64"</i> <i>E 23°27'20"</i>	June 13	unfiltered		1.093 ± 0.006	3.029	1.70
		June 13	<0.2 μm	373 ± 3	0.993 ± 0.001	3.381	1.92
		June 13	<3 kD	373 ± 5	0.582 ± 0.001	3.316	1.88
		June 13	>3 kD	388 ± 2	0.195 ± 0.003	3.316	1.88
STA 5	<i>N 65°40'61"</i> <i>E 23°25'33"</i>	June 14	unfiltered		0.960 ± 0.005	2.931	1.64
		June 14	<0.2 μm	440 ± 5	0.731 ± 0.001	2.813	1.57
STA 6	<i>N 65°41'10"</i> <i>E 23°24'78"</i> <i>duplicate</i>	June 15	unfiltered		0.749 ± 0.004	1.674	0.86
		June 16	<0.2 μm	512 ± 8	0.662 ± 0.001	2.530	1.39
		June 16	<0.2 μm	511 ± 4	0.663 ± 0.001		
		June 15	<3 kD	567 ± 7	0.080 ± 0.0001	2.091	1.12
		June 15	>3 kD	554 ± 2	0.216 ± 0.002	2.091	1.12
Kamlunge	<i>N 66°09'00"</i> <i>E 22°35'50"</i>	June 16	unfiltered	939 ± 13	0.762 ± 0.004	0.030	
		May 14	<0.2 μm	477 ± 5	0.755 ± 0.001	0.080	
		May 14	<3 kD	475 ± 13	0.053 ± 0.0001	0.080	
				$\delta^{234}\text{U}^a$ 2σ	^{238}U (ppm) ^c 2σ	U/Al ^e ($\times 10^5$)	Fe/Al ^e
STA 5		June 14	>0.2 μm	442 ± 10	14.0 ± 0.1	5.7	2.64
STA 6		June 15	>0.2 μm	483 ± 12	13.7 ± 0.1	5.7	2.30
STA 4		June 14	Sed. trap ^d	370 ± 4	6.9 ± 0.1	1.8	0.86
STA 6		June 15	Sed. trap ^d	406 ± 5	7.3 ± 0.1	1.8	0.83

^a $\delta^{234}\text{U} = [(^{234}\text{U}/^{238}\text{U})_s / (^{234}\text{U}/^{238}\text{U})_{\text{eq}} - 1] \times 10^3$, where $(^{234}\text{U}/^{238}\text{U})_{\text{eq}}$ is the secular equilibrium ratio of 5.472×10^{-5} .

^b Salinity, reported as psu is not defined for < 2 psu and is only estimated from conductivity.

^c ^{238}U in ppm of particles (ash weight).

^d Sediment traps deployed 16.7 days STA 4 and 15.2 days STA 6.

^e Atom ratios.

linear trend in ^{238}U concentrations in the unfiltered waters that seems to reflect simple conservative mixing, ranging from 0.749 nmol $^{238}\text{U}/\text{kg}$ at station 6 to 1.383 nmol $^{238}\text{U}/\text{kg}$ at station 1 (Fig. 3). If this line is extrapolated to a freshwater composition, the resulting U concentration would be $\approx 60\%$ ($\pm 12\%$, 1σ) that measured in the Kamlunge unfiltered water. The U concentration in the 0.2- μm filtered waters are lower than those in the corresponding unfiltered waters and increase with salinity, from 0.751 nmol $^{238}\text{U}/\text{kg}$ at station 6 to 1.375 nmol $^{238}\text{U}/\text{kg}$ at station 1. These concentrations are on a linear trend and so also seem to reflect conservative mixing; the freshwater composition on the extrapolation of this trend has a U concentration that would be within $\approx 0\%$ to 10% of that in the <0.2- μm filtered Kamlunge water, but is about equal to that of Kamlunge <3-kD filtered water. Across the estuary, the difference in U concentration between unfiltered and 0.2- μm filtered water, corresponding to the amount on particles, decreases from $\approx 15\%$ to 20%, at the innermost stations (5 and 6)

to $\approx 0.5\%$ at station 1. These numbers are obtained from the difference between the unfiltered and <0.2- μm filtered correlation lines in Figure 3.

4.2.4. U on colloids

The dissolved (<3-kD) ^{238}U concentrations also show linearly increasing concentration with increasing salinity (Fig. 3) in the LSZ. At the highest salinity, 3 psu, $\approx 96\%$ of the U that passed through the 0.2- μm filter also passed through the 3-kD filter, whereas at the innermost station with salinity ≈ 1 psu, only $\approx 11\%$ of the U passed through the 3-kD filter. The proportion of U on colloids, like the proportion on particles, therefore decreases with increasing salinity. The ^{238}U concentrations in the <3-kD fraction also seem to fall on a mixing line, although extrapolation of the line to a river water component results in a negative U concentration. Hence, U in the Kalix River is dominantly transported in colloids, with only a small fraction ($\approx 7\%$) in true solution (Fig. 3).

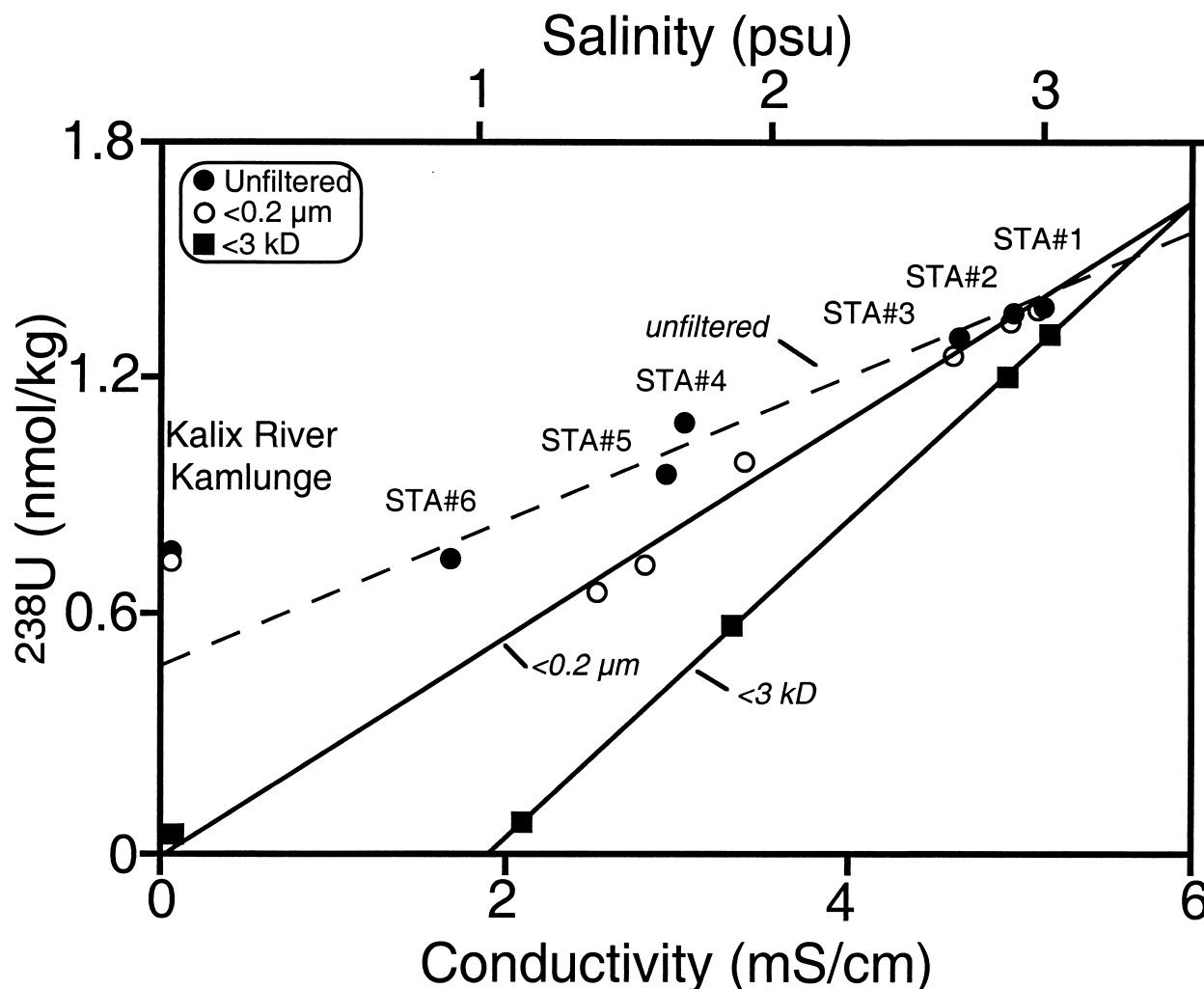


Fig. 3. The ^{238}U concentration in unfiltered water, filtered to pass $0.2\text{-}\mu\text{m}$ and filtered to pass 3-kD CFF in river water from the Kalix River station Kamlunge and from samples in the estuarine zone (see Fig. 1). Data were plotted against conductivity (although the salinity scale is not defined below 2 psu, a tentative salinity scale is indicated). The lines represent the best fit for each fraction. Note that the unfiltered sample from station Kamlunge is sampled 1 month earlier than the filtered water from Kamlunge, and that the analytical errors are smaller than the symbols.

For the innermost stations, the directly measured ^{238}U concentrations in the colloid fractions are lower than that estimated from the calculated difference between $0.2\text{-}\mu\text{m}$ and 3-kD filtered water, with 19% compared to 41% for station 4 and 35% compared to 87% for station 6. This is probably due to decreasing recovery with decreasing salinity for the 3-kD filter (Table 1), which can be caused by either increased adsorption of colloid-bound U or adsorption of dissolved U species to the filter. However, it is nevertheless clear that the colloidal bound U in river water and at low salinity constitute a significant fraction of the total U, which rapidly decreases in the estuary and constitutes only $\approx 5\%$ when salinity has increased to 3 psu. These findings are in general agreement with previous reports showing that a large fraction of the U was carried by $>10\text{-kD}$ colloids in the Kalix River and that this was reduced to $\approx 10\%$ in the central Baltic Sea (Porcelli et al., 1997).

4.2.5. U on particles

The particles ($>0.2 \mu\text{m}$) at stations 5 and 6 show ^{238}U concentrations of 14 ppm (Table 2), which are significantly higher than that of average crust of 1.8 ppm (Krauskopf and Bird, 1995). The material collected in the sediment traps at stations 4 and 6 show ^{238}U concentrations of 6.9 and 7.3 ppm, respectively, which is less than in the $>0.2\text{-}\mu\text{m}$ particle fraction but still higher than for average crust material. The U/Al ratios in the particles are 5.7×10^{-5} for both stations 5 and 6, and 1.8×10^{-5} (3 times lower) in the sediment traps below the mixed layer (Table 2). Similar relationships are also found for the Fe/Al ratios in particles and sediment trap material, which indicates that there is a strong relationship between the Fe and U content in large particles from the estuary. This finding shows that U is mostly associated with authigenic Fe-rich particles as opposed to being associated with detrital matter.

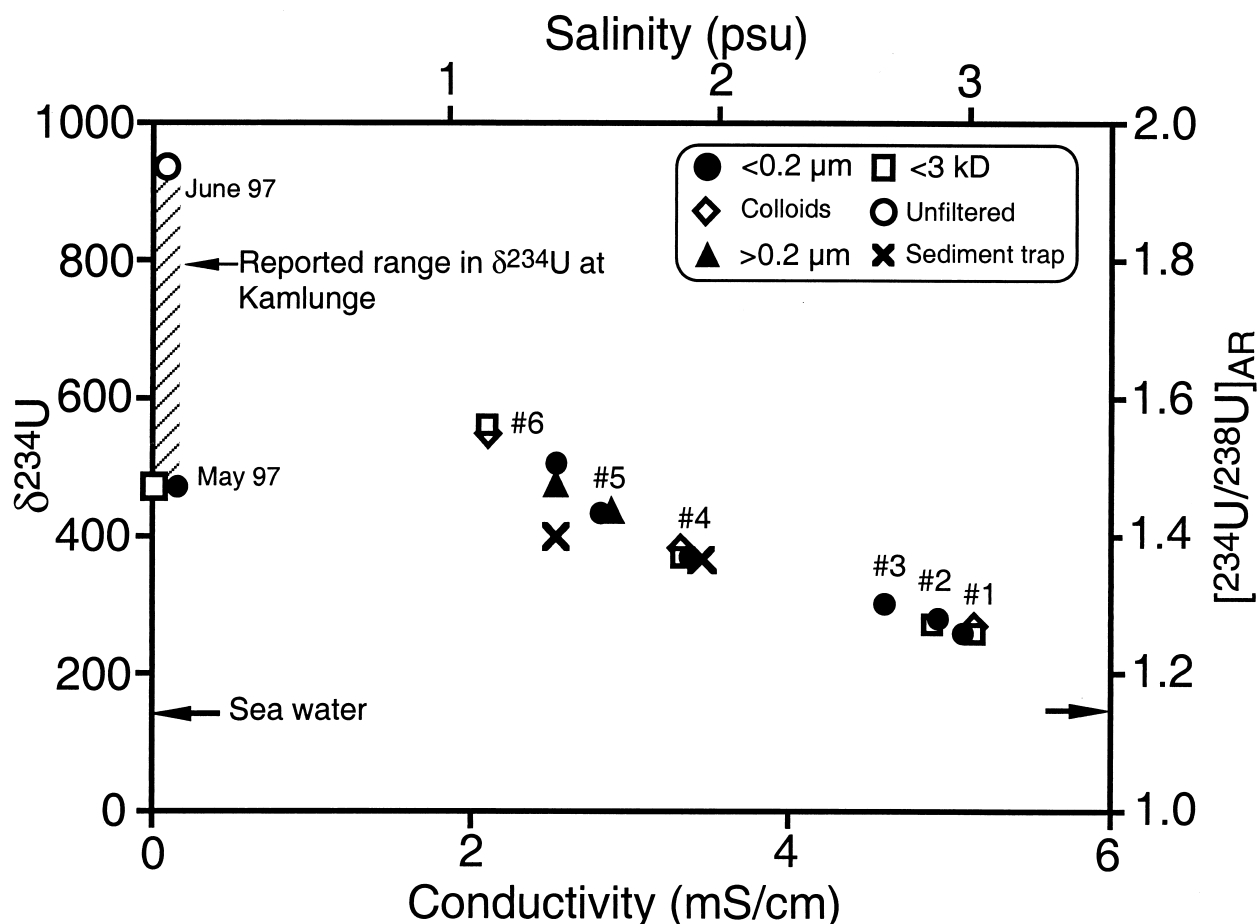


Fig. 4. The $\delta^{234}\text{U}$ in 0.2- μm , 3-kD CFF-filtered water and 3-kD colloids from the Kalix River estuary and in river water from station Kamlunge, plotted against conductivity. The $\delta^{234}\text{U}$ in particles ($>0.2\ \mu\text{m}$) from stations 5 and 6 are plotted, as well as the isotopic composition of the sediment trap material. The stippled area marks the reported range in $\delta^{234}\text{U}$ (data from Fig. 2 at the Kalix River mouth, station Kamlunge). The right hand side scale gives the corresponding $^{234}\text{U}/^{238}\text{U}$ activity ratio. Note that the analytical errors are smaller than the symbols.

4.2.6. $\delta^{234}\text{U}$ in the estuary

In the 0.2- μm filtered brackish water, the measured $\delta^{234}\text{U}$ ratio decreases with increasing salinity, from $\delta^{234}\text{U} = 512$ at station 6, to $\delta^{234}\text{U} = 266$ at station 1 (Table 2 and Fig. 4). The CFF fractions from each sample at each station, both in river and brackish water, show comparable $\delta^{234}\text{U}$ values. However, the data from station 6 indicate that the particles have somewhat lower $\delta^{234}\text{U}$ than the colloids or the dissolved U, indicating lack of complete equilibration. The $\delta^{234}\text{U}$ in $>0.2\text{-}\mu\text{m}$ particles and in material from the sediment traps are also comparable with that of the filtered water from the same station (Fig. 4). This shows that nondetrital U enriched in ^{234}U dominates the analyzed fractions and suggests that there must be rapid isotopic exchange between U in particles, colloids, and dissolved U species in both fresh and brackish water. This is in accord with earlier findings further out in the Baltic Sea and in the Kalix River of rapid isotopic exchange between different size fractions (Porcelli et al., 1997; Andersson et al., 1998).

On a plot of $\delta^{234}\text{U}$ and inverse U concentration (Fig. 5a), generally linear trends are also observed for both the unfiltered

waters and the 0.2- μm filtered water. (Note that each unfiltered water $\delta^{234}\text{U}$ was estimated by using the conductivity- $\delta^{234}\text{U}$ relationship in Figure 4. Each of these correlations pass near the May 1997 Kamlunge water data, but although this river water and station 6 have similar U concentrations and isotopic compositions, the difference in salinity (Fig. 3) indicates that there is a more complex relationship between them than simple mixing. If the June 1997 Kamlunge water, with a value for $\delta^{234}\text{U}$ about a factor of two higher ($\delta^{234}\text{U} = 939$) than the May sample, lost $\approx 31\%$ of its U during discharge, then it provides a suitable end member for conservative mixing of bulk waters across the estuary to satisfy the relationships between U concentration and both $\delta^{234}\text{U}$ (Fig. 5a) and salinity (Fig. 3).

For the 0.2- μm filtered water, a mixing relationship is compatible with the June 1997 Kamlunge water that has lost an even greater fraction of U ($\approx 53\%$). The U concentration-salinity relationships shown in Figure 3, require a much lower end-member concentration than is required to satisfy the isotopic requirements in Figure 5a. Therefore, the U in $<0.2\text{-}\mu\text{m}$ fraction does not behave conservatively immediately after river

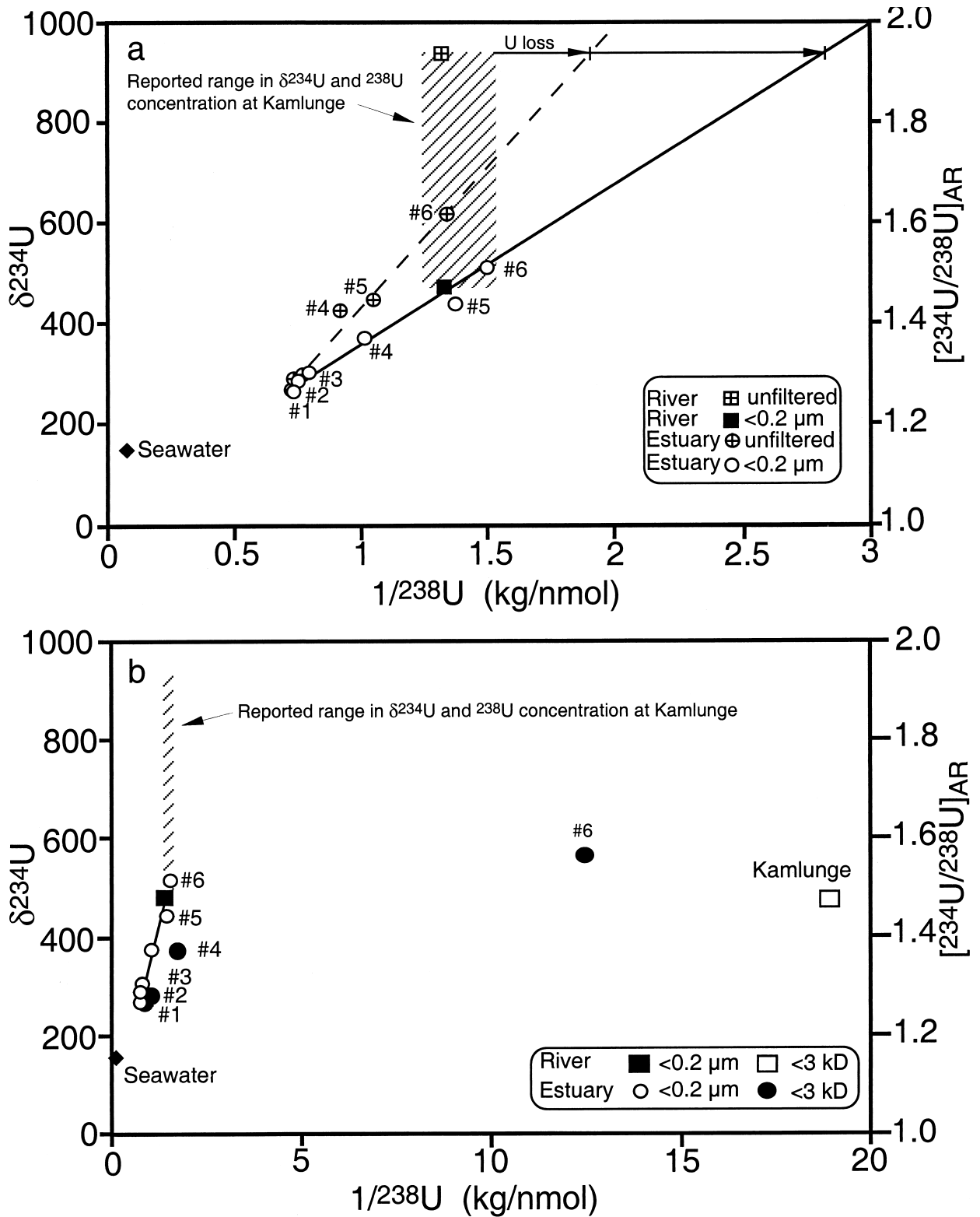


Fig. 5. (a) The $\delta^{234}\text{U}$ values plotted against the $1/^{238}\text{U}$ concentration in unfiltered waters and in $0.2\text{-}\mu\text{m}$ filtered waters (unfiltered water $\delta^{234}\text{U}$ were estimated by using the relationship in Figure 4). The lines represent the best fit for each fraction. The horizontal arrow labeled "U loss" represents the river water endmember ^{238}U concentrations estimated for $\delta^{234}\text{U} = 939$ (station Kamlunge, June 1997). For unfiltered water this is $0.527\ \text{nmol } ^{238}\text{U}/\text{kg}$ and for $<0.2\text{-}\mu\text{m}$ filtered water $0.356\ \text{nmol } ^{238}\text{U}/\text{kg}$. The stippled area represents the reported range in the $\delta^{234}\text{U}$ and ^{238}U concentration at the Kalix River mouth, station Kamlunge. The right hand side scale gives the corresponding $^{234}\text{U}/^{238}\text{U}$ activity ratio. (b) Same as in (a) but also including the $<3\text{-kD}$ fraction.

discharge but requires continuing exchange with $>0.2\text{-}\mu\text{m}$ particles at salinities lower than at station 6.

The relationship between inverse ^{238}U concentration and the $\delta^{234}\text{U}$ in the $<3\text{-kDa}$ filtered samples is shown in Figure 5b. The data for stations 1 through 4 fall on a linear correlation that passes through the seawater composition; however, station 6 and Kamlunge (for both sampling dates) both fall far to the right (with lower U concentrations) of this correlation. In contrast, the data for station 6 did fall on the same trend as the other estuarine samples in Figure 3. This indicates that exchange between U isotopes in $<3\text{-kD}$ fraction (i.e., “dissolved”) and either colloids or particles continued to survive to salinities at least as high as station 4. It should be noted that the correlations observed in Figure 5 do not pass through the seawater U composition, which indicates that the mixing relationships found here cannot be simply extended throughout the Baltic and to the composition of inflowing seawater. This finding may be due either to some nonconservative behavior of U elsewhere in the Baltic, or a somewhat different overall average river input to the basin than the composition measured for the Kalix.

Overall, the relationships between U concentration and salinity (Fig. 3) suggest that the estuarine data are the result of conservative mixing between an initially depleted bulk river component and seawater, and the filtration data are compatible with conservative mixing between each size fraction between stations 6 and 1. However, the U isotope data indicate that substantial isotopic exchange must occur involving particles at least to station 6, and involving colloids at least to station 4. As discussed below, further exchange at higher salinities may also occur.

4.2.7. U behavior during mixing

The behavior of colloids within the estuary is important for the removal of U at very low salinities and subsequent exchange between different U carriers. The particulate suspended phase and the colloids in the river water are dominated by authigenic Fe-oxyhydroxides and organic material (Ingri et al., 2000). In the estuary, Fe in the $<0.2\text{-}\mu\text{m}$ filtered water (Table 2) is about five times lower than in the river water (Gustafsson et al. 2000), which might reflect removal of Fe from the water column at salinities <1 psu. However, Gustafsson et al. (2000) concluded that Fe was mixing conservatively from salinity between 1 and 3 psu. Most of estuarine Fe is in the colloidal form, indicating that Fe-rich colloids continue to be important within the brackish waters. The organic material also contributes to colloids in the estuary. Although the total organic C (TOC) decreased from $\approx 500\ \mu\text{M}$ at the innermost station to near $300\ \mu\text{M}$ at the outermost station, the colloidal organic concentration increased with salinity from $80\ \mu\text{M}$ at station 6 to $100\ \mu\text{M}$ at station 1 (Gustafsson et al., 2000). Thus, when the concentration of organic C is decreasing during estuarine mixing, the colloidal organic C is increasing due to aggregation.

The observation that the U concentration in Kalix River water is above the extrapolated freshwater input to the LSZ, implied by the conservative mixing relationships seen within the estuary, suggests that there must be some removal mechanism operating at very low salinities (<1 psu) not sampled during this expedition. The evidence for U loss between river

station Kamlunge and station 6 can be explained by the removal of U that is trapped in Fe-organic rich colloids that start aggregating and sinking when river water enters the estuary. Up to station 4, exchange of U between different size fractions clearly continues as colloids and larger aggregate form, although no further U removal occurs beyond station 6. Between stations 4 and 1, the proportion of U on both colloids and particles diminishes, which is compatible with decreasing partition coefficients for U onto biogenic and Fe-rich material with increasing salinity (Andersson et al., 1998). Although the data for each size fraction seems to fall on a conservative mixing trend over this portion of the estuary, the processes of U exchange may continue to occur. It is possible that the linear trends defined by the available data may be fortuitous.

The correlation of colloid-bound U with salinity is compatible with conservative mixing in the LSZ. However, this might also indicate that U desorbs rapidly from the colloids due to decreasing colloid concentration and stabilization of dissolved uranyl carbonate complexes in the estuary. In the estuary both the pH and alkalinity increases with salinity (e.g., at station 6 pH = 7.38 and alkalinity = 0.52 mEq/L and at station 1 pH = 7.97 and alkalinity = 0.83 mEq/L) and, because carbonate complexes are poorly adsorbed, cause desorption and remobilization of uranyl species, which supports the hypothesis of desorption of U and stabilization of uranyl complexes.

The removal of U from the water column at very low salinities can be related to the likely carriers of U in discharging river water. Previous studies showed that U at the Kalix River, station Kamlunge, is strongly correlated with the mass of nondetrital particles that are mainly composed of Fe-oxyhydroxides (Andersson et al., 1998). However, during summer, there is an enrichment of particulate U, probably caused by increased organic C (Andersson et al., 1998). In $0.2\text{-}\mu\text{m}$ filtered river water, Fe is largely associated with colloids (Porcelli et al., 1997; Ingri et al., 2000). When water enters the estuary, aggregation of particles increases, as shown by photon correlation spectroscopy (PCS) and size fractionated organic C measurements (Gustafsson et al., 2000). It is worth noting that these larger Fe-organic colloids might constitute the Fe fraction that is being retained in the $0.2\text{-}\mu\text{m}$ filter. Due to increased ionic strength, leading to improved complexation with dissolved ligands in the estuary, U desorbs from the Fe-organic colloids. Hence, throughout the process of estuarine mixing, the geochemistry of the U becomes dynamically and increasingly decoupled from that of the Fe-rich colloids.

In summary, during initial estuarine mixing, U associated with the Fe-organic colloids is removed at very low salinities. These must be removed by colloidal aggregation into larger particles that can sink on a short timescale. Concurrently, there is also desorption of U from the Fe-organic colloids and reassociation to other colloidal carrier phases. A change in the colloidal carrier phase during estuarine mixing probably also involves adsorption to organic phases such as humic substances. There are reports that a significant fraction (up to 80% being reported) of U is complexed with humic substances during estuarine mixing (Mann and Wong, 1992). The further association with colloids does not necessarily result in net removal of U because the colloidal phases are not aggregated into sinking particles in the LSZ (Gustafsson and Gschwend, 1997; Gustafsson et al., 2000).

4.3. U Removal Fluxes

The sediment trap data can be used to calculate a vertical flux of U from the mixed surface water layer at stations 4 and 6. The mass (dry weight and salt corrected) of sediment collected over 16.7 and 15.2 d was 215.3 and 271.3 mg, respectively. The flux of sediments derived from the traps for station 4 is 1.49 g/m²/d and for station 6 2.06 g/m²/d, which yield ²³⁸U fluxes of 10.3 μg/m²/d and 15.0 μg/m²/d, respectively (Table 2). There are few studies using sediment traps to estimate vertical U-fluxes in the coastal marine environment. Anderson et al. (1989) reported U data sediment traps set at 50-m depths in the oxygenated surface waters at Saanich Inlet Vancouver Island. Fluxes of 8 to 12 μg/m²/d were obtained, which are similar to the fluxes we find in the northernmost part of the Gulf of Bothnia. Anderson (1982) also used sediment traps to estimate the vertical flux of U on bio-authigenic particles out of open ocean surface waters, to be an average of 0.04 μg/m²/d. Thus, vertical fluxes of U in estuaries and coastal environments seem to be substantially larger than in the open ocean.

By comparing our vertical U fluxes with the content of U in the overlying water column, an “apparent” residence time for U removal on settling particles can be estimated. This was performed by using the overlying water column U inventory (mg²³⁸U/m²) divided by the measured sediment trap flux (mg²³⁸U/m²/d). For station 4, where the sediment trap depth is 22 m, the overlying water column, contains 5.72 mg²³⁸U/m². Using the sediment trap data, a residence time for ²³⁸U with respect to downward removal of 560 d is obtained. At station 6, where the sediment trap depth is 16 m, the overlying water column contains 2.85 mg²³⁸U/m², which yields a scavenging residence time of 190 d.

The scavenging residence times for U can be compared with the residence time of U within the LSZ by advection. Using the river water flow during May/June 1997 of 6.9×10^{10} L/d (discharge data from Swedish Meteorological and Hydrological Institute) and the approximate dimensions of the inner part of the LSZ (which includes stations 4, 5, and 6) of 14 km × 14 km × 16 m, the residence time for advective transport of water from the river and through the LSZ is calculated to be ≈40 d. Therefore, the transport of U by horizontal flow of water is at least 5 to 10 times faster than the vertical flux of U and so the advective flow of U dominates. This finding is in accordance with the general pattern of conservative behavior of U during mixing of brackish water, as shown in Figure 3.

In Gustafsson et al. (2000), a two-dimensional two-box model is used to evaluate the relative importance of different transport vectors during mixing in the LSZ of the Kalix River estuary. The model uses ²³⁸U/²³⁴Th disequilibria to derive scavenging fluxes and results for organic C and Fe suggest only ≈5% of what enters the LSZ from the river is removed downward. Therefore, it was concluded that minimal removal of these major elements occurs during transport through the LSZ. Applying the Gustafsson et al. (2000) model to the U data presented here yields a vertical flux in the LSZ of 6.7 μg/m²/d for the inner part of the low salinity zone, LSZ (stations 4, 5, and 6), which agrees, within a factor of ≈2, with the sediment trap flux data. From these results it appears that horizontal flux dominates the U transport in the LSZ of the Kalix River

estuary, with only a minor fraction being removed by vertical transport.

5. CONCLUSIONS

Data collected on U isotopes on particles and colloids to study transport and removal processes during mixing in the low-salinity regimen in the Kalix River estuary indicates that during initial estuarine mixing, U is removed on large aggregates at salinities <1 psu. In the salinity range between 1 and 3 psu and probably at greater salinities (Andersson et al., 1995), U seems to behave conservatively. The results clearly show that although U is a highly soluble element that shows generally conservative behavior in estuaries, removal must occur in the very low salinity region, which therefore represents a significant sink for a large fraction (≈50%) of river-supplied U.

Colloids carry a dominant fraction (>90%) of the U in the Kalix River, as well as in the estuary up to ≈1 psu, but carry a minor fraction at 3 psu. However, U-salinity relationships and simple model calculations suggest that only a minor fraction of U was removed vertically from the estuarine surface water layer between 1 and 3 psu. At salinities <1 psu, U seems to be removed on Fe-organic colloids that aggregate and sink. There is also a rapid reassociation of U isotopes with other colloidal particle carriers, probably humic substances, which have not aggregated sufficiently to sink and be removed from the surface waters.

There is in general an absence of isotopic differences between U in the different carriers, as well as in sinking material collected in sediment traps. The U isotope systematics reveal that substantial and rapid isotopic exchange must occur involving particles at least to 1 psu, and involving colloids at least to ≈1.5 psu. Further exchange at higher salinities may also occur.

Our results show that although U is highly soluble, it quickly adsorbs and desorbs from a variety of colloidal carrier substances that alternately dominate at different stages during riverine estuarine mixing. Differences in abundance and composition of colloidal particles between different estuaries might thus be an important factor for explaining the varying behavior of U that has been reported.

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APPENDIX

At sea, CFF was conducted by using a Millipore Pellicon 2 cassette system. We used one polyvinylidene fluoride (PVDF) 0.2- μm CFF cassette-type filter (0.46 m² filter area) to separate particles (>0.2 μm) and two Millipore regenerated cellulose 3-kD CFF cassette-type filters (2 \times 0.46 m² filter area) for separation of colloidal particles and “dissolved” species (Fig. A1). The inlet pressure on the CFF was kept between 3.5 and 3.8 bar and the outlet pressure between 2.5 and 3.0 bar over the 3-kD unit (two filters). These settings gave a permeate flow of \approx 300 to 400 mL/min. A U sample was taken in polyethylene bottles from each of the particle, colloids, and dissolved fraction. Approximately 25 L of water was used for each ultrafiltration and the concentration factor (cf.);

$$cf = \frac{Vol_{permeate}}{(Vol_{retentate})} + 1 \quad (\text{A1})$$

in the retentate, or colloid samples, varied from 12.1 to 15.0. The 0.2- μm retentate from the CFF unit, representing the >0.2- μm particle fraction, was collected on 0.2- μm Millipore nitrocellulose membrane filters. During the 3-kD ultrafiltration the 0.2- μm unit was used only as a prefilter and was thus not concentrating the water at the 0.2- μm filter side. Between each sample the two units were rinsed with both ultrapure 0.1 mol/L NaOH and 0.5 mol/L HCl and ultrapure water. A detailed description of the ultrafiltration method is given in Ingri et al. (2000). The 3-kD filter cutoff was controlled by using recommended standard colloids and procedures (Gustafsson et al., 1996), and integrity tests for our system confirmed a cutoff \leq 3 kD.

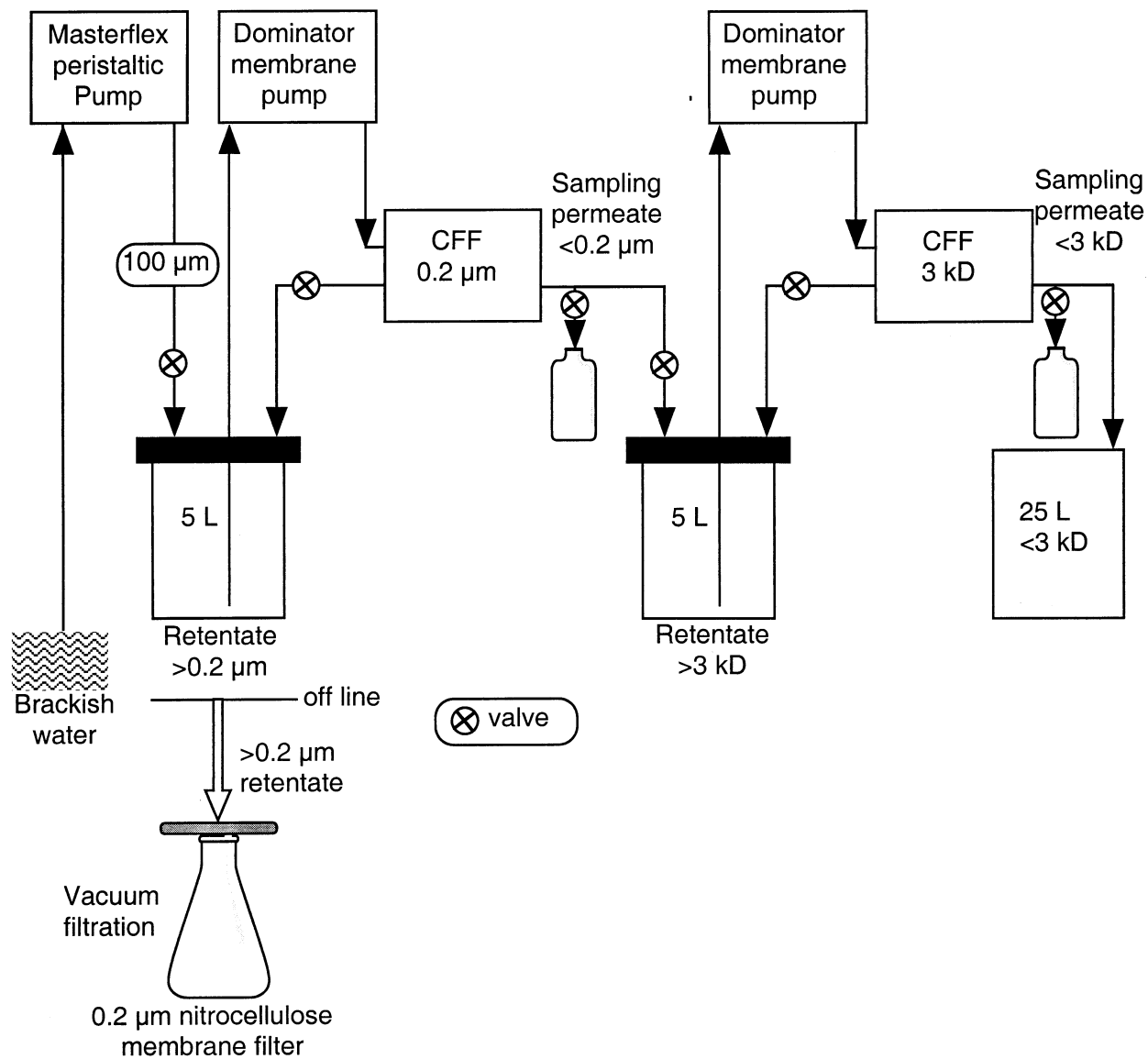


Fig. A1. Schematic cartoon of the CFF system used for separation of large particles ($>0.2 \mu\text{m}$) and colloidal particles from “dissolved” fraction in the Gulf of Bothnia 1997. Water was pumped by a peristaltic pump from the estuary through polyamid and silicon tubing “on-line” through the Pellicon 2 system. First the $0.2\text{-}\mu\text{m}$ filter was used to “harvest” $>0.2\text{-}\mu\text{m}$ particles; thereafter, the $0.2\text{-}\mu\text{m}$ filter was used only to filter water for the 3-kD part of the system.