

## Colloid and particle transport of U isotopes in the low salinity zone of a stable estuary

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Previous studies on the behaviour of U in the Baltic Sea region suggested that river water U is strongly associated with colloids, while in the brackish water the colloid-bound fraction decreases with increasing salinity. Thus colloids may be an important parameter determining the behaviour of U (Porcelli *et al.* 1997).

The present TIMS study evaluates the behaviour of  $^{234}\text{U}$ - $^{238}\text{U}$  in dissolved, colloidal and particulate forms during rapid mixing of a river water plume with brackish water in the low salinity zone (LSZ, 0–3‰ salinity) of a stable estuary. The estuary, located in the northern part of the Gulf of Bothnia, shows stable stratification with minimal tides and a well-defined freshwater plume in the spring. The Kalix River drains a northern boreal shield area and is relatively pristine and distinctive in having relatively low concentrations of suspended detrital particles and high concentrations of organic material and non-detrital particles rich in authigenic Fe and Mn. Cross-flow filtration (CFF) techniques were used to separate U associated with particles (>0.2  $\mu\text{m}$ ) and colloids (>3 k Daltons) from ultrafiltered water (<3 kD) containing ‘dissolved’ species. Integrity tests using standard organic colloids in realistic concentrations for our system confirmed a CFF cut-off  $\leq$  3 kD. During one week in June 1997, samples were obtained from the mixed layer (~4 m depth) over a horizontal distance of about 80 km at six stations. Water was pumped directly from each sampling depth and through the on-line CFF system on board. A river water end-member sample was collected with the same techniques a month earlier.

In the brackish water,  $^{238}\text{U}$  concentrations in the

<0.2  $\mu\text{m}$ -filtered waters increased with increasing salinity (Fig. 1a) from 0.179  $\mu\text{g}^{238}\text{U}/\text{kg}$  at stations #5 and #6 (S~1‰) to 0.327  $\mu\text{g}^{238}\text{U}/\text{kg}$  at the highest salinity (~3 ‰). The Kalix River water concentration of 0.180  $\mu\text{g}^{238}\text{U}/\text{kg}$  is similar to that of the low salinity stations. There is a linear correlation between brackish water U concentrations and salinities, that is compatible with conservative mixing of a component high in  $^{238}\text{U}$ , presumably Gulf of Bothnia brackish water, and a river water component with much less  $^{238}\text{U}$  than found in the Kalix.

Uranium concentrations in the ultrafiltered brackish waters (<3 kD) increase from 0.019  $\mu\text{g}^{238}\text{U}/\text{kg}$  (S~1‰) to 0.313  $\mu\text{g}^{238}\text{U}/\text{kg}$  (S~3‰) and show a strong linear correlation with salinity (Fig. 1a). The fraction of U on colloids (preliminary obtained from the difference between the <0.2  $\mu\text{m}$  and the <3 kD filtered water) decreases linearly as salinity increases, from the lowest salinity (S~1‰) where >90% of the U may be colloid-bound, to station #1 (S~3‰) where <5% of the U is colloid-bound. In the river water, we also find >90% of the U associated with >3 kD colloids. The correlation of colloid-bound U with salinity in the brackish waters is compatible with conservative mixing, and may reflect conservative dilution of U-rich colloids from low salinity water with essentially colloid-free higher salinity water. Another possibility is that U desorbs from the colloidal material due to decreasing colloidal concentration and stabilisation of dissolved carbonate uranyl complexes in the estuary.

In the river water, Fe is found largely in the colloid fraction, and may constitute a large fraction of the total colloidal material. The colloidal Fe concentra-

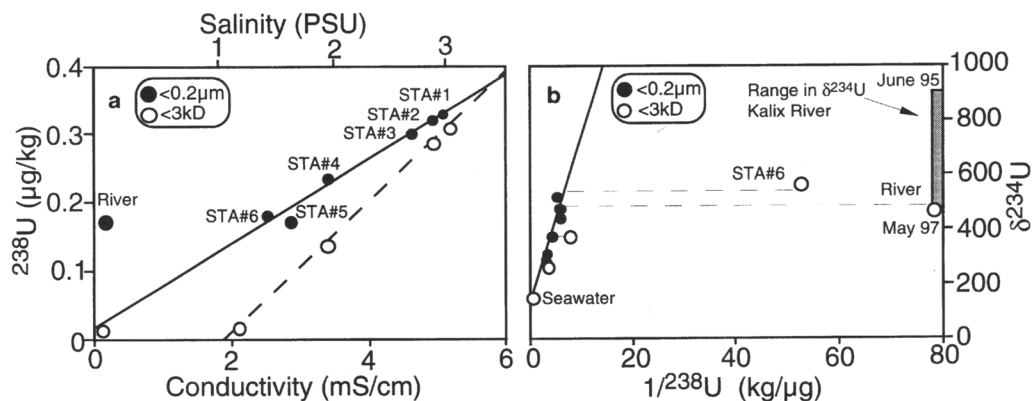


FIG. 1. Uranium data from the Kalix River estuary.

tion is an order of magnitude lower at the lowest salinity station ( $S \sim 1\text{‰}$ ). This might be due to removal of Fe colloids by flocculation as the river water begins to mix with brackish water, and is likely to also remove a large fraction of the colloid-bound riverine U. The resulting water is depleted in U and can be identified as the low salinity endmember that mixes conservatively with high salinity brackish water to generate the waters seen at the salinities of 1–3‰. The concentration of U associated with colloids at station #6 is about the same as in the river water and dominates the U budget at both places, so that U must become rapidly associated with newly-formed, low Fe-colloids, in the estuary at low salinities ( $<1\text{‰}$ ).

In the brackish water, the  $^{234}\text{U}/^{238}\text{U}$  (reported as  $\delta^{234}\text{U}$ , the per mil deviation from secular equilibrium ratio) decreases with increasing salinity, from  $\delta^{234}\text{U} = 512$  ( $S \sim 1\text{‰}$ ) to  $\delta^{234}\text{U} = 266$  ( $S \sim 3\text{‰}$ ). The river water value for the middle of May (one month before collection of the brackish waters) was  $\delta^{234}\text{U} = 477$ . No significant differences in  $\delta^{234}\text{U}$  between the different size fractions in any of the samples were found, which confirm earlier findings of rapid isotopic exchange of U between particles, colloids, and dissolved species in both fresh and brackish waters (Porcelli *et al.* 1997 and Andersson *et al.* 1998). In the Kalix River, it has been observed previously that while U concentrations are relatively constant throughout the year, there is a range in  $\delta^{234}\text{U}$  values ( $\sim 500$ – $900$ ) with peak values in June during high discharge (Andersson *et al.*, 1995), so that the value of the river water during the time that the brackish waters were collected is likely to have been high. The relationship between U concentrations and  $\delta^{234}\text{U}$  in the  $<0.2\mu\text{m}$  filtered waters (see

Fig. 1b) are compatible with simple two component mixing between seawater and a river water component high in  $^{234}\text{U}$  and with a U concentration lower than the  $<0.2\mu\text{m}$  filtered river water but somewhat greater than the  $<3\text{kD}$  filtered river water. In contrast, the relationships between U concentrations and  $\delta^{234}\text{U}$  in the  $<3\text{kD}$ -filtered samples are not compatible with the simple two component mixing suggested by the strong correlation shown in Fig. 1a. Although we do observe isotopic equilibrium between these phases, we can not exclude slow colloid water exchange for U over the short time scales ( $\sim$ days) during which mixing in this region occur.

Our results demonstrates that uranium is largely associated with colloids in both fresh and brackish water. While riverine colloid-bound U appears to be removed during initial estuarine mixing, there is a rapid re-association of U with other colloidal carrier phases at very low salinities that does not result in further U removal from the water column. The fraction of the U that is colloid-bound is rapidly reduced to less than 5% at salinities as low as 3‰.

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