Colloid-particle dynamics and element transport through the low-salinity ($\leqslant$ 3 per mil) zone of a stable boreal northern shield estuary: insights from short-lived ^{234}Th and sampling with high salinity resolution

Ö. Gustafsson
P. Andersson
Swedish Museum of Natural History, Laboratory for Isotope Geology, Box 50007, 10405 Stockholm, Sweden

A. Widerlund
Luleå University of Technology, Division of Applied Geology, 97187 Luleå, Sweden

J. Ingri
Luleå University of Technology, Division of Applied Geology, 97187 Luleå, Sweden

P. Roos
Lund University, Department of Radiation Physics, 22185 Lund, Sweden

It is well known that the continent-to-ocean transport of several elements may be attenuated by scavenging removal in the estuarine mixing zone. Many studies suggest that such non-conservative behaviour often occurs at very low salinities. The presence of significant tidal mixing – resulting in a non-steady state situation and potentially resuspension – complicates discrete sampling of this low salinity zone (LSZ; here defined as $\leqslant$ 3 per mil). The objective of this study was to investigate the estuarine geochemistry of major elements in a stable salt-wedge highly-stratified type of regime, which due to minimal tidal circulation affords detailed study of scavenging processes in the LSZ.

The Kalix River, draining a representative portion of the wide northern shields into the northernmost Baltic Sea, is one of the last major unregulated rivers in northern Europe (mean water discharge *c*. 300 m^3 s^{-1}; *c*. 1600 m^3 s^{-1} during spring flood; 23,600 km^2 drainage area). The Kalix River estuary is an ideal location for studying processes in the LSZ as it exhibits extremely weak tidal pumping (< 1 cm/s) and has no significant secondary tributaries, facilitating good salinity resolution (the 1–3 per mil region stretches over 80 km in the spring).

Previous studies of element input through northernmost Baltic Sea estuaries have produced apparently conflicting results with some studies showing property-salinity plots with conservative behaviour while others are suggestive of non-conservative removal processes in the Kalix LSZ (Widerlund, 1996; Porcelli *et al*., 1997). Since interpretation of such plots over a narrow salinity range is complicated, we performed a process study during spring flood conditions where we attempted to combine many different geochemical tools to better understand the colloid and particle dynamics and the relative extents of vertical and horizontal element transport.

Following extensive CTD mapping of the estuary, six stations were occupied under calm weather conditions in early June, 1997. Surface seawater was sampled with 0.2 μm and 3000 Dalton Millipore Pellicon cross-flow filter systems (regenerated cellulose). The 3 kD filter has been extensively tested with organic colloid standards under natural water conditions. The actual cut-off was determined to be $\leqslant$ 3kD and < 5% losses of carbohydrate (dextran) and humic-analogue (polyethyleneglycol) colloid standards were demonstrated.

The suspended phase was found to be dominated by organic matter, with total organic carbon (TOC) ranging from over 500 μM at the innermost station, decreasing in an apparently conservative manner to about 300 μM at the outer reach. There was also a linear trend for the humic substances (HS; estimated by fluorescence 350/450 nm), albeit with a sharper slope.

A significant fraction of the micron-sized and larger particles were also of organic nature. The transectual trends of total suspended matter (TSM) and particulate organic carbon (POC) suggested that the organic matter fraction of the large particle mass nearly doubled from inshore to the stations furthest afield. Stable isotope analysis of POC ($\delta^{13}C$ values relative to PDB standard) showed only small variations throughout the six stations ($\delta^{13}C = -31$ to -29 per mil) and suggested that this material came from terrrestrial vascular plants. A minor contribution of autochtonous organic matter was also supported by the relatively low rates of primary production (0.01–1 μM C/d).

The Fe/Ti and Mn/Ti ratios in the >0.2 μm suspended particles were about a factor of 8 elevated relative to average crust and local bedrock till, indicating a largely non-detrital form for both Fe and Mn. This ratio increased by 20–40% outward, which may indicate that a portion of the detrital load was settling. In fact, these element ratios were lower by a factor of 2–3 in three sediment traps positioned below the mixed layer along the cruise transect, supporting that settling gravitoids are enriched in detrital matter relative to suspended colloidal material.

High-volume sampling was performed at each station for ^{238}U-^{234}Th to directly estimate vertical scavenging rates. Despite the high abundance of solid phases, unusually small deficits of tetravalent ^{234}Th were realized (^{238}U-^{234}Th disequilibria were on the average 8%; n = 6), strongly implying minimal settling removal. Indeed, the mean ^{234}Th-derived vertical OC flux was 1mmol m^{-2} d^{-1} to be contrasted to 10–60 mmol m^{-2} d^{-1} commonly found on other continental shelf regions with much lower particle load.

The ^{234}Th-derived vertical export rates were combined with literature estimates of the local 'intensity' of horizontal transport to construct a simple two-dimensional box model of the element transport through the LSZ of the Kalix estuary. Preliminary results indicate that horizontal transport of e.g. organic carbon and Fe is overwhelming any vertical removal through this zone. These model results is consistent with indications from apparently linear property-salinity plots as well as small ^{234}Th deficits,which all combined give a picture of minimal removal of any matter in the LSZ of the Kalix estuary.

However, while vertical removal may not be significant in this LSZ, there is ample evidence for dynamic suspended phase processes. Both trends of increasing POC/TOC despite decreasing overall TOC (contrary to expectations from kinetic competition between collision-frequency affected coagulation and sedimentation), and apparently decreasing HS/TOC are suggestive of an active packaging/aggregation process taking place during LSZ transfer. The increasing Ti-normalized Fe and Mn ratios (> 0.2 μm) may also be explained by colloid aggregation of their autochtonous oxides as opposed to by detrital-phase settling alone. There are some indications that this aggregation process are starting to produce gravitoids at the outermost station; larger ^{234}Th deficit (49% *vs* 8% average for entire transect) and a larger ^{234}Th particulate fraction (77% *vs* 24–33% at other stations), as well as indications of some Fe removal in laboratory mixing experiments at about this same salinity (3.0 per mil). This is further consistent with a rapid removal of for instance Fe at a slightly higher salinity (4–5 per mil) observed in the Öre estuary further south in the Gulf of Bothnia (Forsgren and Jansson, 1992).

References

Forsgren, G. and Jansson, M. (1992) *Hydrobiologia*, **235/236**, 586–96.

Porcelli, D., Andersson, P.S., Wasserburg, G.J., Ingri, J. and Baskaran, M. (1997) *Geochim. Cosmochim. Acta*, **61**, 4095–13.

Widerlund, A. (1996) *Suspended Particulate Matter, Sedimentation, and early Diagenetic Processes in the Kalix River Estuary, Northern Sweden*. Doctoral Thesis, Luleå University of Technology.