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Some Preliminary Results on the Behaviour of Uranium Isotopes in the Gironde Estuary (France)



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## Objectives

Rivers represent the main source of dissolved uranium to the oceans. The supply of this element through a particular estuary depends, however, on geochemical reactions taking place at the fresh water/seawater interface. Indeed, results from a number of studies suggest that uranium behaviour varies from estuary to estuary.

The aims of the present study are (i) to investigate the behaviour of uranium isotopes at the fresh water/seawater interface in the Gironde estuary; (ii) to characterise the chemical transformations of riverine dissolved, colloidal and particulate material as they mix with seawater; and (iii) to determine the influence of these processes on the flux of uranium from the river to the open ocean. The Gironde Estuary, located in the SW of France, is the product of the confluence of the Garonne and Dordogne rivers. Mean annual discharge is  $24 \times 10^9$  m<sup>3</sup> yr<sup>-1</sup>, and solid discharge  $2.2 \times 10^{12}$  g yr<sup>-1</sup>.

The Gironde can be considered as a partially mixed, macrotidal estuary with a relatively long flushing time (ranging from 20 days in flood to 86 days during low water discharge).

Hydrodynamic mechanisms in the Gironde estuary produce a well developed *turbidity maximum*, ranging from 0.1 to 10 g l<sup>-1</sup>. During certain periods, a *fluid mud* layer, where turbidity reaches 400 g l <sup>-1</sup>, accumulates on the estuary bottom. The total sediment mass of these two turbidity accumulations is twice the annual riverine solid discharge, and greatly favours solid–liquid interactions.



Sampling locations (SWAMGIR 1, June 1999)

### Materials and methods

• Following retrieval, near-surface samples (75 l) were promptly filtered (0.45  $\mu$ m) and uranium pre-concentrated in 25 l sub-samples by co-precipitation with Fe(OH)<sub>3</sub> for total dissolved uranium determination.

• Measurement of colloidal uranium was carried out on the remaining 50 1 of microfiltered water by tangential-flow ultrafiltration using polysulphone membrane cassettes corresponding to nominal molecular weight limits (NMWLs) of 10 kDa.

• Uranium was separated from the  $Fe(OH)_3$  co-precipitate and purified using standard radiochemical techniques. Uranium sources were prepared by electrodeposition onto stainless-steel discs and counted for periods of 10-20 days using low-level alpha spectrometry.

### **Results and discussion**

• A plot of  $^{238}$ U concentrations versus salinity along the Gironde estuary shows that uranium in the dissolved (<0.45 µm) phase behaves non-conservatively, with removal taking place at salinities in the range 0–16‰. As in other estuaries showing non-conservative behaviour, the mechanism responsible for this removal is likely to be the salt-induced coagulation of riverine colloidal material.

In the Gironde estuary, coagulation has been shown to take place at salinities between 0.1‰ and 1‰ (Gibbs *et al.*, 1989). Uranium concentrations, however, only gradually approach the ideal dilution line in the mid-salinity region, suggesting that flocculation may extend up to 16‰. The elevated suspended matter concentrations in this (intermediate salinity) turbidity zone may account for the removal of uranium at these relatively high salinities.



Dissolved (<0.45 μm) <sup>238</sup>U concentrations along the Gironde Estuary (SWAMGIR I, June 1999)

### Results and discussion (Contd.)

• Above 16‰, dissolved uranium concentrations are essentially indicative of conservative mixing. Such behaviour extends to open ocean salinities and has been previously observed in other estuarine systems (e.g., Amazon). A possible explanation for this observation lies in the <u>completion</u> of particle/colloid surface reactions (i.e., precipitation and coagulation) at intermediate salinities.

• The evolution of <sup>238</sup>U concentrations at a sampling location within the non-conservative region during a tidal cycle suggests that removal is most pronounced at low salinities.

• Our measured <sup>234</sup>U/ <sup>238</sup>U activity ratios along the salinity gradient are all consistent with the accepted oceanic ratio of 1.14.



<sup>234</sup>U/<sup>238</sup>U activity ratio vs salinity in the Gironde Estuary



Evolution of dissolved (<0.45 μm)<sup>238</sup>U concentrations over a tidal cycle in the Gironde estuary (SWAMGIR I, June 1999)

# Conclusions

• Our results to date indicate that dissolved uranium in the Gironde estuary behaves non-conservatively. This may be a seasonal feature and may depend on the discharge regime prevailing at the time of sampling, as conservative behaviour has previously been reported by other authors (Martin *et al.*, 1978).

• Analysis of the colloidal fractions at each of the stations discussed in this presentation is now under way, and should help clarifying the mechanisms responsible for the observed uranium removal during estuarine mixing.

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