

## The behaviour of Os isotopes in the Columbia River estuary

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There is very little data available regarding the concentrations and isotopic compositions of Os in waters. Recently, Sharma *et al.* (1997) provided the first data for seawater, and reported a total concentration of  $6.9 \text{ fmol}^{192}\text{Os}/\text{kg}$  with  $^{187}\text{Os}/^{186}\text{Os} = 1.04 \pm 0.02$ . Sharma and Wasserburg (1997) obtained the first data for Os in river waters, and used this data to calculate a minimum residence time for Os in the oceans of  $1.3 \times 10^4$  years assuming that there is no removal of Os during estuarine mixing. A critical parameter for determining the oceanic Os budget is the fraction of riverine Os removed from the water column and into sediments within estuaries. In the present study, water samples were obtained from a range of salinities from the Columbia River estuary to provide the first data for Os in brackish waters and examine the extent of Os removal to sediments. This work represents part of our on-going efforts to study the behaviour of Os and Ir in natural waters. The Columbia River is the second largest river in the United States and has an estuary characterized by high energies, strong tidal currents, and strong salinity gradients that change rapidly.

Large volume (20–30 L) water samples were collected from a stationary platform within the estuarine channel at a water depth of  $\sim 15$  m in May, 1997. Waters were collected during a rising tide when there was a steep vertical salinity gradient, with low salinity ( $S < 1$ ) waters in the top  $\sim 3$  m, and a steep increase in salinity over less than 5 meters to waters with  $S \sim 20$ . Water was pumped to the surface from various depths using a submersible high capacity pump and collected in acid-cleaned bottles. Samples were immediately filtered to  $0.45 \mu\text{m}$  and acidified using ultrapure HCl. Laboratory analytical procedures followed those of Sharma *et al.* (1997). For each sample, duplicates of various volumes (generally 4–8 L) were analysed and the results generally have been reproducible (see below). Improvements have been made in identifying and correcting for analytical blanks (of  $\sim 3 \text{ fmol}^{192}\text{Os}$ ) and in equilibration between spike and sample Os during precipitation procedures, although further work is still required to improve reproducibility.

The  $^{187}\text{Os}/^{188}\text{Os}$  ratios and Os concentrations are shown in Fig. 1 plotted against salinity. A single sample was collected for each salinity so that data at each salinity represent duplicate analyses of different volumes of the same sample.  $^{192}\text{Os}$  concentrations vary from 2.8 to  $6.4 \text{ fmol}/\text{kg}$ , with a single value at  $S \sim 20$  of  $10 \text{ fmol}/\text{kg}$ . The values obtained for the lowest salinity water, with  $S \sim 0.05$ , of average  $4.6 \text{ fmol}^{192}\text{Os}/\text{kg}$ , can be compared to that obtained by Sharma and Wasserburg (1997) for a sample of the Columbia River collected further upstream of  $4.2 \pm 0.3 \text{ fmol}^{192}\text{Os}/\text{kg}$ . If the sample for  $S \sim 20$  is neglected, the sample concentrations generally increase with increasing salinity and follow a linear correlation that includes the seawater value of Sharma *et al.* (1997), and so it appears that generally conservative mixing of Os occurs across the estuary (Fig. 1A). There are significant deviations from a correlation line that are due either to removal/addition processes within the water column that redistribute Os, or analytical difficulties. The measured  $^{187}\text{Os}/^{188}\text{Os}$  ratios vary from 1.1 to 1.7 and in general decrease with decreasing salinity and follow a linear correlation that includes the seawater value of Sharma *et al.* (1997). This is also compatible with generally conservative behaviour of Os during estuarine mixing. The measured  $^{187}\text{Os}/^{188}\text{Os}$  ratios for the lowest salinity water of  $1.4 \pm 0.1$  and  $1.7 \pm 0.1$  can be compared to the Sharma and Wasserburg (1997) Columbia River water measurement of 1.7. The single analysis made for the water with  $S \sim 20$ , with a significantly lower  $^{187}\text{Os}/^{188}\text{Os}$  ratio and higher Os concentration than the linear correlation defined by the other samples, was made on a small (2L) aliquot and requires confirmation. The concentrations and isotopic compositions of Sr also have been measured in these samples and exhibit conservative behaviour during estuarine mixing.

The observation that Os generally behaves conservatively during estuarine mixing in the Columbia River estuary is in contrast to the conclusions drawn by Esser and Turekian (1993) and Williams *et al.* (1997) that anthropogenic Os discharged in sewage reaching New Haven Harbor

## COLUMBIA RIVER ESTUARY

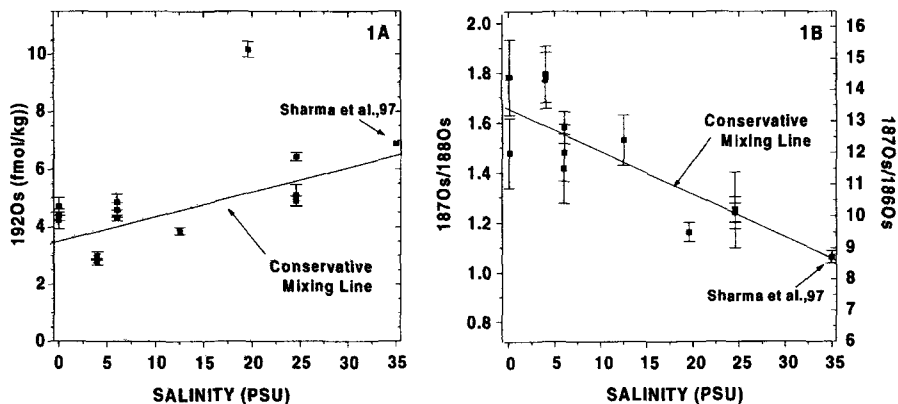


FIG. 1.

and Long Island Sound is removed rapidly from the water column into underlying sediments. However, further investigation is required to determine whether this contrasting behaviour is due to differences in speciation between anthropogenic Os and natural Os, or due to major differences in environmental conditions of the estuaries.

Of the platinum group elements, Ir has been studied systematically in the Baltic Sea by Anbar *et al.* (1996) and shown to be strongly removed during mixing of oxic waters by scavenging by ferromanganese oxyhydroxides. Since Os and Ir are both highly enriched in marine and brackish water ferromanganese deposits, and both may be scavenged by Mn oxyhydroxides, there may be estuarine environments where both elements are removed to similar degrees (see Sharma and Wasserburg, 1997). The issue of the relative behaviour of these two elements requires further study, especially where there are high fluxes of Fe and Mn and estuarine mixing over longer timescales than observed in the Columbia River estuary.

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