

# A reevaluation of the oceanic uranium budget for the Holocene

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## Abstract

We present a new assessment of the pre-anthropogenic U budget for the Holocene ocean. We find that the gross input of U to the ocean lies in the range  $53 \pm 17$  Mmol/year, where the dominant source is river runoff ( $42.0 \pm 14.5$  Mmol/year) and the direct discharge of groundwater could represent a significant additional input ( $9.3 \pm 8.7$  Mmol/year). The soluble U flux associated with the aeolian input of crustal dust is minor ( $1.8 \pm 1.1$  Mmol/year), falling well within the errors associated with the riverine flux. Removal of U to the organic rich sediments of salt marshes and mangrove swamps during river–sea mixing may significantly modify the riverine flux, such that the net U input is reduced to  $42 \pm 18$  Mmol/year. Evaluation of the U isotope budget demonstrates that the limits we have established on the U input flux are reasonable and suggests that direct groundwater discharge may play a significant role in maintaining the oceanic excess of  $^{234}\text{U}$ . The total sink of U from the ocean lies in the range  $48 \pm 14$  Mmol/year. We find that three major processes control the magnitude of this flux: (1) removal to oxygen-depleted sediments ( $26.9 \pm 12.2$  Mmol/year); (2) incorporation into biogenic carbonate ( $13.3 \pm 5.6$  Mmol/year); and (3) crustal sequestration during hydrothermal alteration and seafloor weathering ( $5.7 \pm 3.3$  Mmol/year). The removal of U to opaline silica ( $0.6 \pm 0.3$  Mmol/year) and hydrogenous phases ( $1.4 \pm 0.8$  Mmol/year) is minimal, falling well within the errors associated with the other sinks. That the input and output fluxes balance within the calculated errors implies that U may be in steady state in the Holocene ocean. In this case, the input and output fluxes lie in the range 34–60 Mmol/year, giving an oceanic U residence time of  $3.2\text{--}5.6 \times 10^5$  years. However, given the large uncertainties, a significant imbalance between the Holocene input and output fluxes cannot be ruled out. The constancy of the ancient seawater U concentration implies that the U budget is in steady state over the time period of a glacial–interglacial climate cycle ( $\sim 10^5$  year). A Holocene flux imbalance must, therefore, be offset by an opposing flux imbalance during glacial periods or at the interglacial–glacial transition. We suggest that the storage of U in the coastal zone and shallow water carbonates during interglacial periods and the release of that U at or following the interglacial–glacial transition could be sufficient to affect the short-term stability of the U budget. Providing tighter constraints on U fluxes in the Holocene ocean is a prerequisite to understanding the U budget on the time scale of a glacial–interglacial climate cycle and using this element as a valuable palaeoceanographic proxy.

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*Keywords:* Uranium; Uranium isotopes; Mass balance; Biogeochemical cycles

## 1. Introduction

Geochemical mass balance and the assumption of steady state in the modern ocean have been widely used in investigations of the ocean–earth system. The

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distribution of U in the oceans and the source and sink terms are of particular interest due to the extensive use of U-series nuclides as tracers and time indices of many oceanographic processes (e.g. Bard et al., 1990; Ivanovich et al., 1992; Francois et al., 1993; Sarkar et al., 1993; Edgington et al., 1996). Although previous attempts have been made to evaluate the oceanic U budget, on thorough examination, there are significant problems with the budgets as presented (Bloch, 1980; Barnes and Cochran, 1990; Klinkhammer and Palmer, 1991; Cochran, 1992; Palmer and Edmond, 1993). Of primary concern is the application of simplistic approaches that fail to consider all potential source and sink terms and the extrapolation of minimal data to global fluxes with little or no consideration of the associated errors.

Over the past decade, there have been a number of advances in our understanding of the processes occurring at ocean boundaries. Here, we present a reevaluation of the oceanic U budget based on that improved knowledge and the integration of data dispersed widely through the literature. Our approach is to assess each potentially significant flux into and out of the oceans in order to construct a comprehensive pre-anthropogenic U budget for the Holocene. In our evaluation, we attempt to calculate a realistic error in the magnitude of each flux. For those cases where the uncertainty cannot be robustly determined, we assign an error of 50% or 100% to reflect the degree of confidence in both the available data and in our understanding of the processes involved. We also apply isotope constraints to the U input flux to demonstrate that our estimates of the source terms are reasonable. Unless major revision of our understanding of biogeochemical cycling occurs, we consider it highly unlikely that the magnitude of each flux will lie outside the ranges presented here.

## 2. Distribution of U in the oceans

Under oxic conditions, dissolved U in seawater occurs dominantly as the stable uranyl carbonate ion  $\text{UO}_2(\text{CO}_3)_3^{4-}$  (Djogic et al., 1987), and is conservative with a concentration ( $[\text{U}]_{\text{SW}}$ ) of  $13.9 \pm 0.9$  nmol/kg at a salinity of 35 (Chen et al., 1986a). This gives an oceanic U inventory ( $\Sigma_{\text{U}}$ ) of ca.  $19 \times 10^{12}$  mol, of which more than 99% is  $^{238}\text{U}$  and less than 1% is

$^{235}\text{U}$ . The third naturally occurring isotope,  $^{234}\text{U}$ , is a daughter product in the  $^{238}\text{U}$  decay series, and is present only in trace amounts. However, due to the preferential mobility of in situ produced  $^{234}\text{U}$ , this isotope is present in excess of secular equilibrium, and the seawater  $^{234}\text{U}/^{238}\text{U}$  activity ratio ( $\text{AR}_{\text{SW}}$ ) is  $1.144 \pm 0.004$  (Chen et al., 1986a). That both  $[\text{U}]_{\text{SW}}$  and  $\text{AR}_{\text{SW}}$  are constant demonstrates that the oceans are well mixed with respect to U, thereby implying that the residence time of U ( $\tau_{\text{U}}$ ) is significantly longer than the mixing time of the oceans (ca.  $10^3$  years).

Any expectation that the flux of U to the ocean will balance the flux of U from the ocean rests on the assumption of steady state. That  $[\text{U}]_{\text{SW}}$  is in steady state has been inferred from the constancy of the coralline U/Ca ratio,  $(\text{U}/\text{Ca})_{\text{C}}$ , with time (Bender, 1970; Broecker, 1971). Well-preserved aragonitic corals retain their initial trace element composition and the distribution coefficient for  $(\text{U}/\text{Ca})_{\text{C}}$  relative to seawater is close to unity (Broecker, 1971; Swart and Hubbard, 1982). Thus, assuming that  $[\text{Ca}]_{\text{SW}}$  has not changed, ancient  $(\text{U}/\text{Ca})_{\text{C}}$  should provide a measure of ancient  $[\text{U}]_{\text{SW}}$ . Although the mean  $(\text{U}/\text{Ca})_{\text{C}}$  has remained constant over the time period of a glacial–interglacial climate cycle,  $(\text{U}/\text{Ca})_{\text{C}}$  has varied by  $\pm 30\%$  over the last 4 Ma (Bender, 1970), and by  $\pm 20\%$  over the last 30 ka (Bard et al., 1990). Part of this variation may be due to a temperature control on U incorporation of ca.  $-3$ – $4\%$  per  $^{\circ}\text{C}$  (Min et al., 1995; Shen and Dunbar, 1995), however, fluctuations in  $[\text{U}]_{\text{SW}}$  cannot be ruled out and the time scale on which U is in steady state remains unclear.

## 3. Inputs of U to the oceans

Three transport pathways could supply significant amounts of U to the oceans: river runoff, direct groundwater discharge and aeolian crustal dust (Fig. 1). Previously, it has been assumed that river runoff is the only significant source of U (e.g. Bloch, 1980; Palmer and Edmond, 1993). Although continental runoff does occur predominantly as flow in rivers, part of the total water flux is returned to the oceans via direct groundwater discharge. As the mean U content of river water and groundwater may be significantly different, we assess the corresponding U fluxes separately. We first present a brief discussion of the

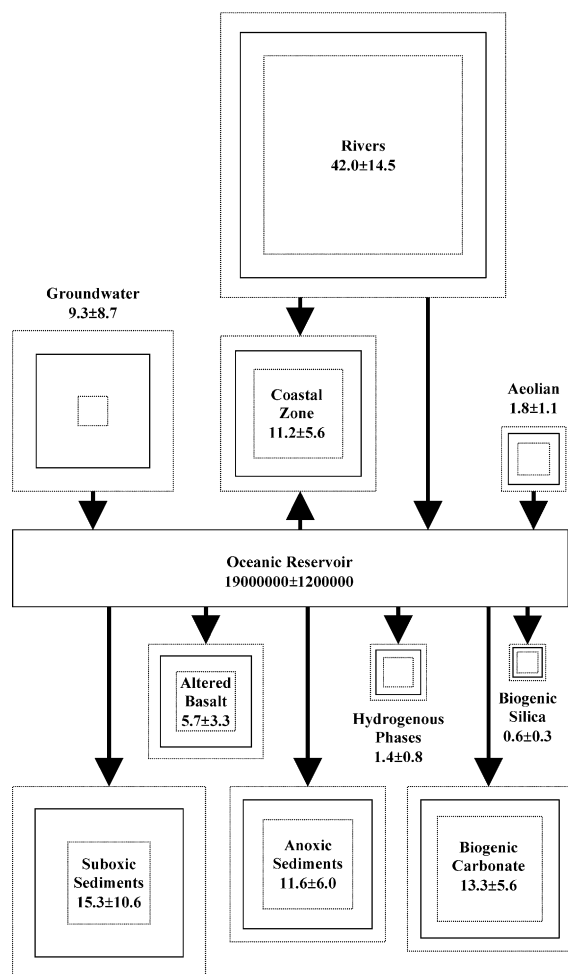


Fig. 1. Sources and sinks of U to and from the ocean. The area of each flux box is proportional to the magnitude of that flux, where the dashed lines indicate the uncertainty in the flux. Fluxes are given in Mmol/year. The oceanic inventory is given in Mmol.

hydrologic cycle to explain the water fluxes adopted in our calculations.

### 3.1. The water fluxes

Water runoff from the continents is calculated from a water balance model, where runoff is that part of precipitation not returned to the atmosphere by evapotranspiration. Published estimates of global runoff are based on long-term continental averages and lie in the range  $38 \pm 6 \times 10^{15}$  kg/year (Lvovitch, 1974; Baumgartner and Reichel, 1975; Korzun,

1979; Zektser and Loaiciga, 1993). Groundwater participates in the hydrologic cycle both as the base flow of rivers and as submarine groundwater that bypasses the river network and discharges directly to the oceans. Direct groundwater discharge has been estimated at 6–10% of total continental runoff (Garels and Mackenzie, 1971; Zektser and Dzhamalov, 1981; Zektser and Dzhamalov, 1988). As these estimates are not well constrained, we use a direct groundwater discharge of ca.  $8 \pm 4\%$  of total runoff, or  $3 \pm 1.5 \times 10^{15}$  kg/year. Base flow accounts for about 30–35% of the total modern river runoff ( $35 \pm 6 \times 10^{15}$  kg/year), although prior to large scale agricultural irrigation and reservoir construction, this contribution was probably 5–10% lower (Zektser and Loaiciga, 1993). We therefore use a pre-anthropogenic base flow contribution of  $25 \pm 13\%$ , or  $9 \pm 4.5 \times 10^{15}$  kg/year, which gives a surface river runoff of  $26 \pm 8 \times 10^{15}$  kg/year.

### 3.2. Riverine input

The riverine input ( $I_R$ ) can be calculated as the product of the river water flux and the mean natural U concentration ( $[U]_R$ ) of that water. For an individual river, the natural  $[U]_R$  is determined by the rock types in the drainage basin and the extent of chemical weathering (Palmer and Edmond, 1993). In general, a positive correlation is observed between  $[U]_R$  and total dissolved solids (TDS) or total cations ( $\Sigma^+$ ), and an inverse correlation between  $[U]_R$  and silicon/total anions, which indicates that the dominant control on  $[U]_R$  is probably the chemical weathering of non-silicates (Borole et al., 1982; Sarin et al., 1990; Palmer and Edmond, 1993). There is also a strong correlation between  $[U]_R$  and bicarbonate, which most likely reflects the importance of the stable  $UO_2(CO_3)_3^{4-}$  species in river chemistry (Broecker, 1974; Mangini et al., 1979).

It is important to ensure that any estimate of the global mean  $[U]_R$  reflects the natural U input; thus, the potential anthropogenic impact on the modern  $[U]_R$  must be considered. Although increased agriculture has resulted in higher total weathering rates, the principal effect is to have eroded soil; therefore, the associated increase in chemical weathering (as indicated by the riverine dissolved load) is probably small (Gregor, 1970). Nevertheless, rivers draining agricul-

tural areas could have elevated  $[U]_R$  due to the extensive use of phosphate fertilisers which have U contents up to 50 ppm (Spalding and Sackett, 1972). In particular, it is the high  $[U]_R$  of rivers draining western Europe (e.g. the Rhine) and the Himalayas that have been called into question (Mangini et al., 1979; Pande et al., 1994). At present, there is no evidence for significant anthropogenic U enrichment in the Rhine (Mangini et al., 1979), and the high  $[U]_R$  in Himalayan river headwaters (minimal agricultural influence) suggests that U mobilisation is naturally high and probably related to the weathering of U-rich black shales (Sarin et al., 1990; Pande et al., 1994). However, a study of the Kanovci agricultural area in eastern Slavonia indicates that high U concentrations in surface water and shallow groundwater are caused by phosphate fertiliser application (Barisic et al., 1992). Phosphate fertilisers may also affect  $[U]_R$  via a more indirect route. High phosphate levels can lead to eutrophication and an increase in the biological breakdown of organic matter, which may result in enhanced U dissolution (Lienert et al., 1994). As yet, the total impact of human activity on  $[U]_R$  is poorly understood and if any significant perturbation exists, it is difficult to quantify.

Three different approaches have been taken toward determining the mean natural  $[U]_R$ . The first approach assumes that the Amazon  $[U]_R$  (0.14–0.17 nmol/kg) is representative of the pre-anthropogenic ‘global’ river (Bloch, 1980). This assumption is not valid as the Amazon is a dilute river with a low dissolved load ( $\Sigma^+ = 300 \mu\text{eq/kg}$ , Gaillardet et al., 1997) compared to the global average ( $\Sigma^+ = 1210 \mu\text{eq/kg}$ , Meybeck, 1987). The second approach uses the observed correlation between  $[U]_R$  and TDS combined with the mean TDS of 100 mg/kg to estimate a mean  $[U]_R$  of 1 nmol/kg (Borole et al., 1982; Figueres et al., 1982). However, some data from the Ganga–Brahmaputra and Mackenzie rivers fall significantly above this correlation line (Fig. 2). As these rivers represent the 4th and 5th largest drainage basins in the world and are thought to have a naturally high  $[U]_R$  (Reeder et al., 1972; Sarin et al., 1990), it is difficult to justify their exclusion from any calculation of the ‘global’ mean  $[U]_R$ .

The third approach is to calculate a discharge weighted mean  $[U]_R$  (Borole et al., 1982; Sarin et al., 1990; Palmer and Edmond, 1993; Windom et al., 2000). A compilation of the available  $[U]_R$  from 80

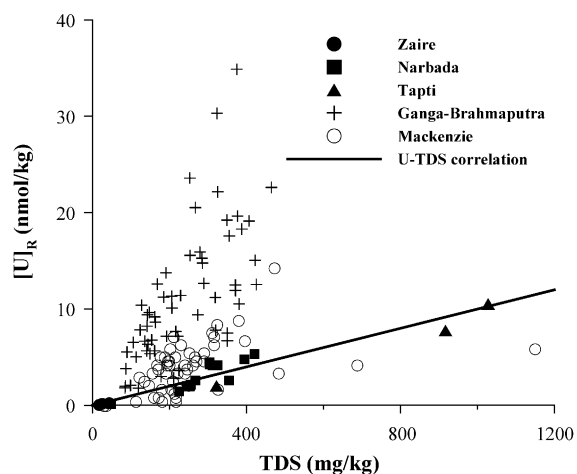


Fig. 2. U concentration versus total dissolved salts for five world rivers. Zaire data from Dupre et al. (1996); Narbada and Tapti data from Borole et al. (1982); Ganga–Brahmaputra data from Sarin et al. (1990); Mackenzie data from Reeder et al. (1972). The U-TDS correlation shown is based on the Zaire, Narbada and Tapti rivers.

ivers ranked according to discharge and accounting for ca. 60% of the surface runoff is presented in Appendix A. For rivers with more than one published value of  $[U]_R$ , a seasonal average was used if available, otherwise an average of all published  $[U]_R$  was taken. The discharge weighted mean  $[U]_R$  from this data set is 1.2 nmol/kg, slightly lower than the 1.3 nmol/kg previously calculated from a data set of 43 rivers (Palmer and Edmond, 1993). Ultimately, the accuracy to which the ‘global’  $[U]_R$  can be estimated by this method is dependent on both the temporal and spatial extent of sampling. The more rivers sampled, the more complete the data set will become. However, the seasonal and interannual variation in river discharge rates places an equal, or larger, importance on the temporal scale of sampling. This is illustrated by the difference between a single measurement of  $[U]_R$  in the monsoonal Ganga–Brahmaputra river system (16.7 and 7.1 nmol/kg, respectively, Palmer and Edmond, 1993), in comparison to seasonally averaged estimates (7.6 and 2.6 nmol/kg, Sarin et al., 1990; 8.4 and 4.2 nmol/kg, Chabaux et al., 2001). As the  $[U]_R$  data set is now reasonably comprehensive, with seasonally weighted or average  $[U]_R$  available for the four largest rivers of the world, it seems unlikely that the uncertainty in the ‘global’ mean  $[U]_R$  will exceed 25%. However, this data set is based on surface water

sampling and thus does not specifically address the base flow component.

Previous budgets have carried the inherent assumption that either all base flow enters streams prior to discharge, or that all base flow has a similar U content to the surface flow ( $[U]_{RB} \approx [U]_{RS}$ ). A comparison between the U content of surface waters and adjacent shallow groundwaters in the Ganga river drainage basin suggests that  $[U]_{RB}$  varies from 0.4 to 10 times  $[U]_{RS}$ , although in the lower reaches of the Ganga main stream, the assumption that  $[U]_{RB} \approx [U]_{RS}$  appears to hold true ( $[U]_{RB}/[U]_{RS} = 0.9–1.3$ , Sarin et al., 1990). In the Platte river system,  $[U]_{RS}$  was typically lower than  $[U]_{RB}$ , and locally elevated  $[U]_{RS}$  were associated with increased groundwater sources during low flow periods (Snow and Spalding, 1994). At present, chemical data regarding the basal flow of rivers is lacking and it cannot be assumed that  $[U]_{RB}$  is as well constrained as  $[U]_{RS}$ . To account for this uncertainty, we adopt the same mean  $[U]_R$  but assign an error of 50% to the base flow component. Using a  $[U]_{RS}$  of  $1.2 \pm 0.3$  nmol/kg and a  $[U]_{RB}$  of  $1.2 \pm 0.6$  nmol/kg gives surface and base flow U fluxes of  $31.2 \pm 12.4$  and  $10.8 \pm 7.6$  Mmol/year, respectively, and a total  $I_R$  of  $42.0 \pm 14.5$  Mmol/year.

### 3.3. Direct groundwater input

Submarine groundwater discharge (SGWD) could constitute a significant input of U to the ocean ( $I_G$ ). SGWD consists of a mixture of fresh groundwater and recycled seawater, where the chemistry of the resultant brackish water may not represent simple mixing between the two end members (Moore and Church, 1996). Although U enrichment in SGWD has been suggested (Church, 1996), at present, there is no evidence for U addition during recycling of seawater through the continental shelf. We therefore assume that the flux of groundwater delivering ‘new’ U to the ocean is equal to the fresh water flux of  $3 \pm 1.5 \times 10^{15}$  kg/year.

The concentration of U in groundwater ( $[U]_G$ ) can vary widely, ranging from less than 1 nmol/kg to in excess of 2000 nmol/kg (e.g. Betcher et al., 1988; Banner et al., 1990; Hodge et al., 1996). Unfortunately, it is not possible to estimate a discharge weighted mean  $[U]_G$ , as the contribution of each groundwater sampled to the total water discharge is

unknown. However, on a global basis,  $[U]_G$  typically lies in the range 0.4–40 nmol/kg, with a median value of 4 nmol/kg (Osmond and Cowart, 1992). We consider the mean  $[U]_G$  of SGWD likely to fall within the lower portion of this range as it is groundwaters flowing through deep-confined aquifers that discharge directly to the oceans. When groundwaters percolate downward, they move from oxidising to reducing conditions, leading to the reduction of soluble U(VI) to insoluble U(IV). Once precipitated in the anoxic environment, U remains in the solid state on a geological time scale, thus deep groundwaters have a lower  $[U]_G$  than shallow groundwaters (Andrews and Kay, 1982; Osmond and Cowart, 1992). We therefore suggest probable limits on the mean SGWD  $[U]_G$  of 0.4–4 nmol/kg, giving an  $I_G$  of  $1.2 \pm 0.6–12 \pm 6$  Mmol/year (or  $9.3 \pm 8.7$  Mmol/year); hence, within the present constraints,  $I_G$  may be insignificant or may constitute a second major input of U.

### 3.4. Aeolian input

To construct a complete assessment of the oceanic U budget, the input of U associated with the aeolian flux of mineral dust ( $9.1 \times 10^{14}$  g/year, Duce et al., 1991) must also be evaluated. As U is present in mineral aerosols in approximately crustal proportions (Rahn et al., 1979), we use an upper crust U content of  $2.4 \pm 0.6$  ppm (Taylor and McLennan, 1981) to estimate a particulate U flux of  $9.2 \pm 2.3$  Mmol/year. While a dissolved flux of this magnitude would be significant, only certain fractions of this particulate U will be labile in seawater. At present, there are no data pertaining to the solubility of U associated with crustal dust. Here, we assume that the partitioning of U between labile and refractory phases will fall between that of Fe (~ 5–10%) and P (~ 33%) (Chester et al., 1986; Duce et al., 1991) and assign a labile U fraction of  $20 \pm 15\%$ . This gives a soluble U flux ( $I_A$ ) of  $1.8 \pm 1.1$  Mmol/year; thus,  $I_A$  falls within the error associated with  $I_R$  and represents only a minor input term.

## 4. Behaviour of U in the coastal zone

River runoff delivers U to the coastal zone where interactions between dissolved and particulate phases

can act to remove from, or add to, dissolved U in the water column (e.g. Barnes and Cochran, 1993). Here, we review the behaviour of U in estuaries, salt marshes and mangrove swamps before making a first order estimate of the direction and magnitude of the coastal zone U flux ( $J_{CZ}$ ).

#### 4.1. Behaviour of U in estuaries

U is seen to behave conservatively across a broad range of estuaries that differ in terms of river chemistry, physical classification, and geographic location (e.g. Borole et al., 1977, 1982; Martin et al., 1978a; Toole et al., 1987; Sarin and Church, 1994; Ray et al., 1995; Windom et al., 2000). Although nonconservative U removal can occur due to either the flocculation of colloidal U or the adsorption and/or reduction of U associated with a high organic load, significant U loss is typically associated with pollution (Martin et al., 1978a; Maeda and Windom, 1982; Sarin et al., 1985; Toole et al., 1987; Porcelli et al., 1997). The data thus indicate dominantly conservative behaviour of U under natural conditions, with the possible exception of the unique Amazon Shelf estuary. In this dynamic environment, the vigorous reworking of shelf sediments can lead to both large-scale removal and addition of U. On the near shelf, the release of porewater Fe and Mn to the water column results in colloidal U scavenging (Swarzenski and McKee, 1998), while on the distal shelf, particle disaggregation results in addition of colloidal U (McKee, 1987). Although a significant U input of 5.5 Mmol/year has been reported, in subsequent studies, a net flux of this magnitude was not observed and the impact of the Amazon Shelf on the U budget remains unclear (McKee, 1987; Swarzenski et al., 1995; Swarzenski and McKee, 1998).

#### 4.2. Behaviour of U in salt marshes and mangrove swamps

Two mechanisms can lead to U removal in the organic rich environments of salt marshes and mangrove swamps. In the first case, water column scavenging in association with Fe removal and/or organic matter flocculation delivers U to the sediment (Maeda and Windom, 1982; Church et al., 1996). In the second case, a diffusive flux of U into the sediments

is driven by the reduction of soluble U(VI) to insoluble U(IV) at depth (Barnes and Cochran, 1993), a process probably mediated by Fe(III)-reducing bacteria (Lovley et al., 1991).

Salt marshes constitute strong sinks of U with removal observed at all salinities over summer months (Maeda and Windom, 1982; Church et al., 1996). Two estimates of U accumulation rates in salt marshes have been reported, 15  $\mu\text{mol}/\text{m}^2/\text{year}$  (Canary Creek, Church et al., 1996) and 70  $\mu\text{mol}/\text{m}^2/\text{year}$  (Savannah, Windom et al., 2000). We consider the latter figure an overestimate as year round U removal was assumed despite a lack of data from much of the winter months (Windom et al., 2000). In addition, U removal in the Savannah may be associated with pollution and, therefore, should not be used to estimate the pre-anthropogenic sink (Maeda and Windom, 1982; Sarin et al., 1985).

Although U removal to mangrove swamps has not been rigorously documented, data from the Ganga–Brahmaputra system suggests that U accumulation does occur at a rate similar to that observed in salt marshes (Carroll and Moore, 1993). During the dry season, the low salinity (<12, PSS '78) region of the Ganga–Brahmaputra mixing zone is located in the mangrove swamps of the river delta. A plot of U against salinity shows that extensive U removal occurs in this area, while above a salinity of 12, or downstream from the mangrove swamps, U is essentially conservative (Fig. 3 after Carroll and Moore, 1993). Linear regression of the conservative section of this mixing line gives an effective  $[\text{U}]_R$  of 7 nmol/kg, implying a loss of 3.8 nmol/kg compared to the actual  $[\text{U}]_R$  of 10.8 nmol/kg. Assuming that removal is limited to the dry season (water discharge =  $0.14 \times 10^{15}$  kg/year) and dividing by the areal extent of the mangrove swamps ( $\sim 1.8 \times 10^{10}$  m<sup>2</sup>, Carroll and Moore, 1993), this gives a U accumulation rate of ca. 30  $\mu\text{mol}/\text{m}^2/\text{year}$ . As we make no account for the export of particulate U, or the possible re-release of U during the wet season, we consider this estimate to represent the upper limit on the U accumulation rate in mangrove swamps.

The inherent variability of coastal systems makes it difficult to extrapolate to the 'global estuary' from present data. In particular, the net flux of U across the Amazon Shelf must be resolved before  $J_{CZ}$  can be determined to any degree of accuracy. Nevertheless,

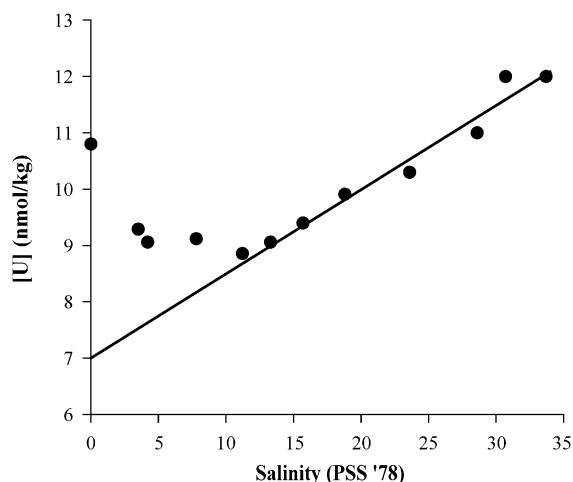


Fig. 3. U concentration versus salinity in the Ganga–Brahmaputra mixing zone (after Carroll and Moore, 1993). The solid line shown is a linear regression through the conservative section of the mixing diagram (salinity > 12), giving an effective U source concentration of 7 nmol/kg compared to the actual riverine U concentration of 10.8 nmol/kg.

the dominant process seems likely to be the removal of U to salt marshes and mangrove swamps and we make a first order estimate of  $J_{CZ}$  based on this premise. To reflect the uncertainty in both the strength of this flux and the behaviour of U in other coastal systems, we assign a U removal rate of  $20 \pm 10 \mu\text{mol}/\text{m}^2/\text{year}$ . When combined with the areal extent of salt marshes ( $3.8 \times 10^{11} \text{ m}^2$ , Woodwell et al., 1973) and mangrove swamps ( $1.8 \times 10^{11} \text{ m}^2$ , Spalding, 1997), this gives a  $J_{CZ}$  of  $11.2 \pm 5.6 \text{ Mmol}/\text{year}$ , suggesting that removal of U in the coastal zone may significantly reduce the net input of U to the open ocean.

## 5. Isotopic constraints on the net input of U to the ocean

Previous work has suggested that the observed  $\text{AR}_{\text{SW}}$  cannot be maintained if the only source of excess  $^{234}\text{U}$  is the input of dissolved U from the continents (Bhat and Krishnaswami, 1969; Ku et al., 1977). However, as with the mass budget, these calculations do not explicitly evaluate the groundwater input. We therefore present a simple isotope budget to illustrate the potential importance of groundwater in the geochemical cycling of U.

Assuming that  $\text{AR}_{\text{SW}}$  is in steady state, that continental runoff is the only source of excess  $^{234}\text{U}$ , and that all sinks except  $J_{CZ}$  remove U in direct proportion to  $\text{AR}_{\text{SW}}$ , then the following relationship between supply and removal of  $^{234}\text{U}$  must hold true:

$$\begin{aligned} I_{\text{R}}(\text{AR}_{\text{R}} - \text{AR}_{\text{SW}}) + I_{\text{G}}(\text{AR}_{\text{G}} - \text{AR}_{\text{SW}}) \\ = J_{\text{CZ}}(\text{AR}_{\text{CZ}} - \text{AR}_{\text{SW}}) + \lambda_{234}\Sigma_{\text{U}}(\text{AR}_{\text{SW}} - 1) \end{aligned} \quad (1)$$

Where  $\text{AR}_{\text{R}}$ ,  $\text{AR}_{\text{G}}$  and  $\text{AR}_{\text{CZ}}$  are the mean AR associated with the fluxes  $I_{\text{R}}$ ,  $I_{\text{G}}$  and  $J_{\text{CZ}}$ , respectively,  $\text{AR}_{\text{SW}}$  is 1.144,  $\Sigma_{\text{U}}$  (the oceanic U inventory) is  $19 \times 10^{12} \text{ mol}$  and  $\lambda_{234}$  ( $^{234}\text{U}$  decay constant) is  $2.835 \times 10^{-6} \text{ year}^{-1}$ . We first discuss  $\text{AR}_{\text{R}}$ ,  $\text{AR}_{\text{G}}$  and  $\text{AR}_{\text{CZ}}$  before examining whether or not continental runoff could be sufficient to maintain the oceanic excess of  $^{234}\text{U}$ .

### 5.1. The $^{234}\text{U}/^{238}\text{U}$ activity ratio of the riverine input

A compilation of data from 38 rivers yields a U flux weighted mean  $\text{AR}_{\text{R}}$  of 1.17 (Appendix B), showing excellent agreement with Chabaux et al. (2001). However, large rivers with low  $\text{AR}_{\text{R}}$  dominate this data set, and the base flow contribution, which may have an elevated  $\text{AR}_{\text{R}}$  compared to surface flow (Snow and Spalding, 1994), is not accounted for. We therefore consider this estimate to represent the lower limit on the true mean  $\text{AR}_{\text{R}}$ .

Although the  $\text{AR}_{\text{R}}$  of an individual river is unlikely to be controlled by a unique process, a primary dependence on the extent of chemical weathering has been suggested, which may imply a climatic control on the mean  $\text{AR}_{\text{R}}$  (Umamoto, 1973; Kronfeld and Vogel, 1991; Riotte and Chabaux, 1999). Under arid conditions, mechanical weathering dominates over chemical weathering, thus new crystal surfaces are constantly exposed and continuous preferential leaching of  $^{234}\text{U}$  occurs (e.g. South African Rivers,  $\text{AR}_{\text{R}} \sim 2.0$ ). Conversely, in the humid tropical and monsoonal zones, chemical weathering prevails and  $\text{AR}_{\text{R}}$  rapidly approaches that of the mineral particles (e.g. the Amazon, Zaire, Ganga Brahmaputra and Indus rivers,  $\text{AR}_{\text{R}} \sim 1.1$ ). If the two extreme river types are excluded from the data set, the mean temperate  $\text{AR}_{\text{R}}$  increases to  $\sim 1.3$ . Of the total  $I_{\text{R}}$ , if 1%, 24%

and 75% were delivered via arid, humid and temperate river systems, the mean  $AR_R$  would be 1.26. We therefore assume that the mean  $AR_R$  will lie in the range 1.17–1.26.

### 5.2. The $^{234}\text{U}/^{238}\text{U}$ activity ratio of the groundwater input

Groundwaters exhibit much greater variations in AR than surface waters, with  $AR_G$  ranging from about 0.5 to 12 (Osmond and Cowart, 1976; Gascoyne, 1992). As with the mean  $[U]_G$ , it is currently difficult to further constrain the mean  $AR_G$ , although it is unlikely to fall toward the extremes of this range. In general, an inverse correlation is observed between  $[U]_G$  and  $AR_G$ , thus deep reducing groundwaters with low  $[U]_G$  will have a higher  $AR_G$  than near surface oxic groundwaters with high  $[U]_G$  (Osmond and Cowart, 1976, 1992; Asikainen, 1981). As it is deep groundwaters that constitute SGWD, we infer that the mean  $AR_G$  will be greater than unity and is likely to exceed  $AR_R$  ( $\sim 1.2$ ). Although groundwaters with an extreme excess of  $^{234}\text{U}$  have been sampled ( $AR_G > 30$ ), the vast majority has an  $AR_G$  less than 5, with most clustered between values of 1 and 3 (Osmond and Cowart, 1976, 1992; Asikainen, 1981). We therefore suggest that the mean  $AR_G$  will lie between 1.0 and 5.0, and most probably fall in the range 1.2–3.0.

### 5.3. The $^{234}\text{U}/^{238}\text{U}$ activity ratio of U removed in the coastal zone

We assume that  $J_{CZ}$  removes U in direct proportion to the AR of the water column, where this AR varies across the removal zone in response to the relative proportion of riverine and seawater U. Consideration of a simple box model shows that to a first approximation:

$$AR_{CZ} = \frac{(W_R[U]_R AR_R + W_{SW}[U]_{SW} AR_{SW})}{(W_R[U]_R + W_{SW}[U]_{SW})} \quad (2)$$

where  $W_R$  and  $W_{SW}$  denote the fractional volume of river water and seawater, respectively, in the removal zone. To explore the limits on  $AR_{CZ}$ , we make the assumption that  $W_{SW} \geq 0.5 \geq W_R$ . The upper limit on  $AR_{CZ}$  is given by the case where  $W_R = W_{SW}$  in combination with the upper bounds on  $[U]_R$  (1.6

nmol/kg) and  $AR_R$  (1.26). As  $W_R$  tends toward 0,  $AR_{CZ}$  approaches the lower limit of  $AR_{SW}$ , thus  $AR_{CZ}$  probably lies in the range 1.144–1.156.

### 5.4. Balancing the $^{234}\text{U}/^{238}\text{U}$ isotope budget

We use Eq. (1) to assess the potential role of groundwater in maintaining the oceanic excess of  $^{234}\text{U}$ . The  $I_G$  and  $AR_G$  required to balance the U isotope budget are illustrated in Fig. 4 (dashed lines), where the centre line corresponds to the mid-range values of  $I_R$ ,  $AR_R$ ,  $J_{CZ}$  and  $AR_{CZ}$  ( $I_G(AR_G - 1.144) = 4.842$ ). The upper line constrains the absolute upper limit on  $I_G$  for a given  $AR_G$  and vice versa ( $I_G(AR_G - 1.144) \leq 7.243$ ). Above this line, the groundwater flux would supply too much  $^{234}\text{U}$  to the ocean. The lower line gives only the lower limit on  $I_G$  and  $AR_G$  necessary for isotopic balance ( $I_G(AR_G - 1.144) \geq 1.203$ ). The groundwater characteristics may fall below this line, in which case, an additional source of  $^{234}\text{U}$  is required. Also shown in Fig. 4 (solid lines) are the probable limits on  $I_G$  (0.6–18 Mmol/year) and  $AR_G$  (1.2–3.0). That the full range in

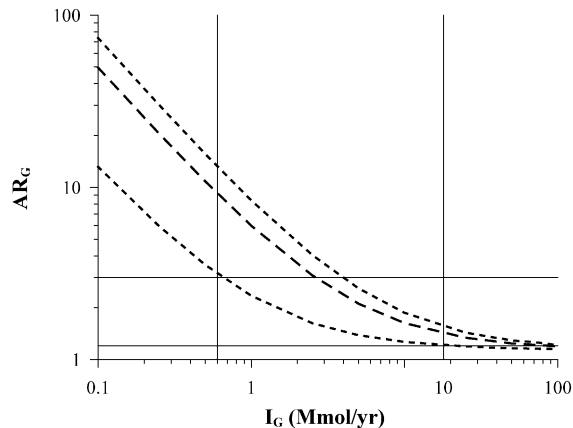


Fig. 4. Relations between the groundwater  $^{234}\text{U}/^{238}\text{U}$  activity ratio ( $AR_G$ ) and the groundwater U flux ( $I_G$ ) as predicted by the steady state distribution (on a  $\sim 10^5$ -year time scale) of U in the ocean given a total U inventory ( $\Sigma_U$ ) of  $19 \times 10^{12}$  mol and a  $^{234}\text{U}/^{238}\text{U}$  activity ratio ( $AR_{SW}$ ) of 1.144. The solid lines show the probable range in  $AR_G$  and  $I_G$ . The dashed lines give the  $AR_G$  and  $I_G$  required for oceanic isotopic balance given that  $I_R = 42.0 \pm 14.5$  Mmol/year,  $AR_R = 1.215 \pm 0.045$ ,  $J_{CZ} = 11.2 \pm 5.6$  and  $AR_{CZ} = 1.150 \pm 0.006$ . The centre line corresponds to the mid-range values, the upper line corresponds to the minimum  $I_R$  and  $AR_R$  and maximum  $J_{CZ}$  and  $AR_{CZ}$ , the lower line corresponds to the maximum  $I_R$  and  $AR_R$  and minimum  $J_{CZ}$  and  $AR_{CZ}$ .



$I_G$  and  $AR_G$  could be consistent with the U isotope budget suggests that these limits are reasonable, although for an  $I_G$  greater than 3.9,  $AR_G$  must be less than or equal to  $(7.243/I_G) + 1.144$ .

While our analysis demonstrates that the supply of  $^{234}\text{U}$  in continental runoff could be sufficient to balance the U isotope budget, we do not argue against the existence of additional  $^{234}\text{U}$  sources. There is compelling evidence to support a diffusive flux of  $^{234}\text{U}$  through porewaters of pelagic sediments (e.g. Ku et al., 1977; Cochran and Krishnaswami, 1980). Leaching of ocean crust basalts (Section 6.3) may also result in the supply of excess  $^{234}\text{U}$  from the seafloor. However, in the absence of a significant groundwater flux, a seafloor  $^{234}\text{U}$  input of ca. 265 mol/year, or a mean flux of 2.4 dpm/m<sup>2</sup>/year would be required. While the available data support localised fluxes of, or indeed exceeding, this value, the extrapolation to a diffusive flux of this order across the entire ocean floor is not justified. We therefore suggest that the groundwater flux may play a significant role in balancing the U isotope budget of the oceans.

## 6. Sinks of U from the oceans

Potentially significant sinks of U from the ocean include removal to anoxic and suboxic sediments, uptake in biogenic structural material, crustal sequestration during hydrothermal circulation and seafloor weathering and incorporation in hydrogenous phases such as metalliferous sediments, iron–manganese nodules and pelagic red clays (Fig. 1).

### 6.1. Removal to anoxic and suboxic sediments

One of the most important sinks of U is removal into oxygen-depleted sediments in which organic matter diagenesis is occurring. Significant authigenic enrichment of U begins in sediments where oxygen penetration ( $Z_{\text{O}_2}$ ) is less than or equal to 1 cm (Morford and Emerson, 1999). The reduction of U(VI) to U(IV), and thus removal from porewater to sediments, occurs under low  $E_h$  conditions, at or below that necessary to reduce Fe(III) (Barnes and Cochran, 1990). This removal at depth creates a concentration gradient in porewater U and leads to a

diffusive flux of seawater U into sediments (Barnes and Cochran, 1990; Klinkhammer and Palmer, 1991).

Anoxic sediments are typically found in basins with restricted deep-water circulation and in near shore regions associated with areas of intense upwelling and high primary productivity. The data on U accumulation in these environments is summarised in Table 1 (after Cochran, 1992), where the areal representation of basins and upwelling zones is comparable to the global division of anoxic sediments between these two regimes. The U accumulation rate calculated from sediment data is typically higher than the purely diffusive U flux calculated from porewater profiles (Table 1). This discrepancy is probably related to additional mechanisms of U removal. In organic-rich sediments below an anoxic water column, further U accumulation can occur via preservation of nonlithogenic particulate U (Zheng, 1999) or U adsorption onto, or complexation with, organic matter (Anderson et al., 1989). Sediments underlying upwelling regions can also have unusually high U contents associated with the presence of U-rich phosphate nodules and deposits (Veeh et al., 1974). Considering only the sediment-based estimates, the mean U accumulation rates still show a high degree of variation, ranging from 5.4 to 46.2  $\mu\text{mol}/\text{m}^2/\text{year}$ , with an area weighted mean of 9.2  $\mu\text{mol}/\text{m}^2/\text{year}$ . The uncertainty in this term is large and must incorporate the discrepancy between the true mean U accumulation rate and the mean of limited data sets. For areas where four or more cores were analysed (Walvis Bay, the Black Sea, Saanich Inlet and Gotland Deep), the minimum and maximum U accumulation rates typically lie within 50% of the mean. Using a U accumulation rate of  $9.2 \pm 4.6 \mu\text{mol}/\text{m}^2/\text{year}$ , therefore, seems reasonable. Combining this with the area of anoxic sediments ( $0.35 \pm 0.05\%$  of the seafloor or  $12.6 \pm 1.8 \times 10^{11} \text{m}^2$ , Veeh, 1967) gives an  $R_A$  of  $11.6 \pm 6.0 \text{Mmol}/\text{year}$ .

Uranium accumulation rates in oxygen-depleted sediments of the continental shelf and slope are approximately an order of magnitude lower than those observed for anoxic sediments (Table 2). However, the spatial extent of such sediments is much greater leading to an equally significant U sink ( $R_S$ ) (Barnes and Cochran, 1990; Klinkhammer and Palmer, 1991). In the suboxic environment, the diffusive flux of U calculated from porewater profiles is typically higher than the U accumulation rate determined from sedi-

Table 1  
The accumulation of U in anoxic sediments (after Cochran, 1992)

Region	Areal extent (10 <sup>11</sup> m <sup>2</sup> )	Sediment accumulation (g/m <sup>2</sup> /year)	Authigenic U (ppm)		U removal rate (μmol/m <sup>2</sup> /year)	
			Range	Mean	Range	Mean
Walvis Bay <sup>a,b</sup>	0.25		10.0–55.0		9.7–32.1	21.9
Peru–Chile Shelf <sup>a,c</sup>	1.90	240	6.2–16.5	11.4	6.3–16.6	11.5
West Coast Basins <sup>a</sup>	0.80					9.2
Santa Barbara <sup>a,d</sup>		750			6.1–10.7	8.4
Saanich Inlet <sup>e,f</sup>		950	1.3–7.1	4.0	5.2–28.3	16.0
San Clement (PW) <sup>d,g</sup>					(1.0–1.5)	
Gulf of California <sup>a,c</sup>	0.76	630		4.1		10.9
Black Sea <sup>h,i</sup>	2.70				2.7–8.4	5.6
Black Sea (PW) <sup>i</sup>					(0.8–2.9)	(1.8)
Sea of Azov <sup>h</sup>	0.40					5.4
Cariaco Trench <sup>j,k</sup>	0.09	250		9.0		9.5
(PW) <sup>g</sup>						(2.3)
Baltic Sea						
Gotland Basin <sup>l,m</sup>	0.07	1100	7.0–16.0	10.0	32.4–73.9	46.2
Total	7.0				4.6–13.8	9.2

PW = calculated from pore water profile. Where total sediment U concentrations were given, a detrital U content of 3 ppm has been assumed.

- <sup>a</sup> DeMaster, 1979.  
<sup>b</sup> Veeh et al., 1974.  
<sup>c</sup> Veeh, 1967.  
<sup>d</sup> Zheng, 1999.  
<sup>e</sup> Francois, 1988.  
<sup>f</sup> Kolodny and Kaplan, 1973.  
<sup>g</sup> Barnes and Cochran, 1990.  
<sup>h</sup> Nikolaev et al., 1966.  
<sup>i</sup> Barnes and Cochran, 1991.  
<sup>j</sup> Bacon et al., 1980.  
<sup>k</sup> Anderson, 1987.  
<sup>l</sup> Lofvendahl, 1987.  
<sup>m</sup> Baturin, 1968.

Table 2  
The accumulation of U in suboxic sediments

Region	U removal rate (μmol/m <sup>2</sup> /year)			
	Diffusive flux <sup>a</sup>		Sediment flux <sup>b</sup>	
	Range	Mean	Range	Mean
North East Atlantic <sup>c</sup>			0.35–0.40	0.38
Mid Atlantic Bight <sup>d</sup>	0.84–2.27	1.43	0.80–1.01	0.83
North West Atlantic <sup>c</sup>	0.00–0.67	0.42		
California Margin <sup>d</sup>	0.84–3.61	1.95	0.08–0.76	0.37

- <sup>a</sup> The diffusive flux is that calculated from a porewater profile.  
<sup>b</sup> The sediment flux is that calculated from the sediment record.  
<sup>c</sup> Legeleux et al., 1994.  
<sup>d</sup> Zheng, 1999 (core EN187-BC9 excluded due to anomalously high porewater [U] at 1 cm depth).  
<sup>e</sup> Barnes and Cochran, 1990.

ment data, suggesting considerable postdepositional loss of U from sediments (Table 2; Zheng, 1999). This loss could result from bioturbation which raises deep reducing U-rich sediments up toward the sediment–water interface where U(IV) is oxidised to U(VI) and re-released to the water column (Barnes and Cochran, 1990; Zheng, 1999). Considering only the sediment data, the regional mean U accumulation rate lies in the range 0.37–0.83 μmol/m<sup>2</sup>/year. We suggest that the uncertainty in the global mean accumulation rate must, at the least, encompass this range, and assign a value of 0.6 ± 0.3 μmol/m<sup>2</sup>/year. Barnes and Cochran (1990) estimated that suboxic sediments cover 7–9% of the seafloor. More recent model results suggest that sediments with Z<sub>O2</sub> of 1 cm or less cover only 4–6% of the seafloor, although this is limited to sediments below 1000-m water depth

(Morford and Emerson, 1999). Here, we use an area of  $6 \pm 2\%$  of the ocean floor ( $21.6 \pm 7.2 \times 10^{12} \text{ m}^2$ ) to obtain an  $R_S$  of  $13.0 \pm 7.8 \text{ Mmol/year}$ .

The magnitude of  $R_S$  can also be estimated as the product of the mean sediment accumulation rate ( $75 \text{ g/m}^2/\text{year}$ ) and the average U enrichment above detrital levels (Morford and Emerson, 1999). Reanalysis of the data of Morford and Emerson (1999) and Legeleux et al. (1994) shows that below 15 cm in the sediment, the average U enrichment above detrital levels ( $1.5 \pm 0.5 \text{ ppm}$ ) is  $150 \pm 75\%$ . This gives a U accumulation rate of  $0.71 \pm 0.43 \text{ } \mu\text{mol/m}^2/\text{year}$  and an  $R_S$  of  $15.3 \pm 10.6 \text{ Mmol/year}$ . Although this shows good agreement with the previous estimate, the uncertainty in this flux is large and cannot be better constrained until further measurements of hemipelagic U accumulation rates are obtained.

### 6.2. Removal to biogenic deposits

Removal of U to biogenic deposits occurs principally via uptake by organisms that secrete siliceous ( $R_O$ ) or calcareous ( $R_C$ ) tests. The net biological production of opaline silica ( $\text{SiO}_2$ ) in the surface ocean is around  $7.2 \times 10^{15} \text{ g/year}$ , of which only  $\sim 2.5\%$  survives to accumulate in the sediments (Treuger et al., 1995). As this survival rate is not well constrained, a value of  $2.5 \pm 1.3\%$  is adopted here. The diatom and diatom-radiolarian oozes that encircle the Antarctic have a bulk U content of  $\sim 1 \text{ ppm}$  (Mo et al., 1973; DeMaster, 1979). On average, ca. 65% (by weight) of siliceous oozes consist of  $\text{SiO}_2$  (El Wakeel and Riley, 1961). Assuming that the remaining 35% consists of detrital sediments with a U content of  $1.5 \pm 0.5 \text{ ppm}$  implies a silica U content of  $\sim 0.75 \pm 0.25 \text{ ppm}$  and a negligible  $R_O$  of  $0.6 \pm 0.3 \text{ Mmol/year}$ .

Previous estimates of  $R_C$  were based on an outdated carbonate budget and have severely undervalued the importance of this flux (e.g. Cochran, 1992). Here, we use the Holocene carbonate budget of Milliman (1993), but reduce the deep-sea accumulation rate to be consistent with the Ca budget (Stoll and Schrag, 1998). We then breakdown the carbonate composition between the dominant producers and combine this with the U content of each carbonate type to obtain a mean U content for each environment (Tables 3 and 4). To incorporate the uncertainty in the carbonate flux and composition, we have assigned an

error of 50% to the carbonate accumulation rates and an error of 50% or 100% to the U content of each carbonate type. This calculation suggests that  $R_C$  lies in the range  $13.3 \pm 5.6 \text{ Mmol/year}$  and is dominated by U removal to shallow water carbonates (Table 3). That 90% of the U (cf. 60% of the carbonate) is deposited in the shallow water environment reflects the dominance of aragonite producers in these regimes, as the distribution coefficient for U/Ca in aragonite (relative to seawater) is approximately two orders of magnitude higher than that for calcite (Swart and Hubbard, 1982; Russell et al., 1994).

### 6.3. Removal during hydrothermal circulation and seafloor weathering

Altered mid-ocean ridge basalts (MORBs) from the upper oceanic crust are often enriched in U compared with pristine basalt remnants, suggesting that the sequestration of U during hydrothermal circulation and seafloor weathering may represent an important U sink ( $R_B$ ) (e.g. MacDougall et al., 1979; Staudigel et al., 1996).

Removal of seawater U during high temperature on-axis hydrothermal circulation is quantitative (Michard and Albarede, 1985; Chen et al., 1986b) and appears to be virtually complete in warm spring fluids of  $62\text{--}64 \text{ }^\circ\text{C}$  (Mottl et al., 1998). However, the largest water flux, and therefore the largest potential geochemical flux, is associated with low-temperature circulation through the ridge flanks. Although hydrothermal fluids below  $62\text{--}64 \text{ }^\circ\text{C}$  have not been analysed for U, basalt analysis suggests that considerable crustal uptake of U continues to occur at alteration temperatures as low as  $20\text{--}30 \text{ }^\circ\text{C}$  (Fouillac and Javoy, 1978; Storz and Selo, 1979). During the oxic alteration phase, U uptake is probably slight and associated with the formation of Fe oxyhydroxides (Teagle et al., 1996). However, as sediment cover thickens with distance from the ridge axis, circulation becomes increasingly restricted, leading to reducing conditions and warmer, more altered fluids (e.g. Mottl and Wheat, 1994). Under these conditions, U(VI) is inferred to be reduced to U(IV) and is incorporated into secondary minerals such as palagonitized glasses, clay infilling material and breccia cements (MacDougall, 1977; Mitchell and Aumento, 1977; MacDougall et al., 1979; Storz and Selo, 1979; Teagle et al.,

Table 3  
The accumulation of U in CaCO<sub>3</sub>

CaCO <sub>3</sub> accumulation rate <sup>a</sup> (10 <sup>15</sup> g/year)	Composition <sup>b</sup> (%)	U Content (ppm)	U sink (Mmol/year)
Coral reef complex	calcareous algae	35	2.3 ± 1.3
	corals	25	
	nonskeletal/misc.	15	
	molluscs	15	
	benthic forams	10	
Banks and embayments	nonskeletal/misc.	50	1.2 ± 0.9
	molluscs	30	
	benthic forams	10	
	calcareous algae	5	
	coral	5	
Shelves	molluscs	45	1.0 ± 0.6
	barnacles	35	
	calcareous algae	15	
	bryozoans	5	
Halimeda bioherms	halimeda	100	3.7 ± 1.9
Shallow water subtotal			11.8 ± 5.6
Slopes and deep sea	coccoliths	70	0.2 ± 0.1
	planktonic forams	25	
	pteropods	5	
Slopes imported	coral reef complex		2.3 ± 1.3
	banks and embayments		1.2 ± 0.9
	shelves (planktonic)		0.2 ± 0.1
Deep water subtotal			1.5 ± 0.6

<sup>a</sup> Carbonate accumulation rates after Milliman (1993), with the exception of slopes and deep sea which has been reduced from 1.5 to  $0.7 \times 10^{15}$  g/year.

<sup>b</sup> For the coral reef complex and banks and embayments, estimates of composition are based on data presented in Milliman (1974).

Table 4  
The U content of CaCO<sub>3</sub>

CaCO <sub>3</sub> type	U content (ppm)	
	Reported	Assigned
Calcareous algae/halimeda <sup>a</sup>	2.9–4.4	3.70 ± 1.85
Corals <sup>b</sup>	2–4	3.00 ± 1.50
Pteropods <sup>a</sup>	1.6–2.2	1.90 ± 0.95
Nonskeletal/miscellaneous <sup>a,c</sup>	1.3–1.4	1.35 ± 1.35
Molluscs <sup>a</sup>	0.5	0.50 ± 0.25
Barnacles <sup>d</sup>	–	0.50 ± 0.50
Bryozoans <sup>a</sup>	0.3–0.5	0.40 ± 0.20
Foraminifera <sup>e,f</sup>	0.025–0.49	0.25 ± 0.25
Coccoliths <sup>e</sup>	<0.1	0.05 ± 0.05

<sup>a</sup> Sackett et al., 1973.

<sup>b</sup> Broecker, 1971.

<sup>c</sup> For nonskeletal/miscellaneous we use the U content of oolite.

<sup>d</sup> We assume that the barnacle U content is comparable to that of molluscs.

<sup>e</sup> Ku, 1965.

<sup>f</sup> Delaney and Boyle, 1983.

1996). The complex formation and subsequent permeability of ocean crust leads to an extremely heterogeneous distribution of alteration assemblages, thus U enrichment can vary greatly both within and between sites.

As the uptake of seawater U as a function of temperature is not known below 62–64 °C, it is not currently possible to estimate  $R_B$  from a hydrothermal fluid flow model (cf. Mottl and Wheat, 1994; Elderfield and Schultz, 1996).  $R_B$  must therefore be estimated by multiplying the mass of basalt altered annually by the net gain in seawater U ( $[U]_B$ ), despite the difficulties associated with constraining these parameters (e.g. Bloch, 1980; Hart and Staudigel, 1982; Staudigel et al., 1996). Here, we place broad constraints on the possible magnitude of  $R_B$  by considering the behaviour of U across three depth zones, the upper crust (0–500 m), a transitional zone (500–1000 m) and the lower crust (below 1000 m).

Fig. 5 shows the bulk rock U content of the upper ~ 500 m of crust at a number of DSDP/ODP sites.

Significant U enrichment persists throughout the full depth of these cores, although the U content ranges from 10 s of ppb to over 1 ppm. A mean upper crust U uptake as high as 1 ppm per 10 Ma has been suggested (Aumento, 1971). However, this estimate was based on dredged basalts, which are likely to show much greater U enrichment than the bulk upper crust, and other studies show little evidence for such extensive or regular enrichment (Mitchell and Aumento, 1977; MacDougall et al., 1979; Laverne et al., 1996). We consider the current best estimate of the altered upper crust U content to be that obtained from a composite sample of old crust (>100 Ma), giving a U content of 300 ppb (SUPER composite of Staudigel et al., 1996).

U data is only available from two DSDP sites that extend beyond ~ 500 m in basement, 504B and 735B (Fig. 6). These sites are of comparable age but represent different tectonic regimes and rock types. The

crust at 504B (5.9 Ma) was formed at a fast spreading ridge and consists of pillow lavas overlying sheeted dykes, whereas 735B (11 Ma) is located on a slow spreading ridge and consists of unroofed and uplifted gabbros. Despite these differences, both sites exhibit enhanced U concentrations to depths of ~ 600 m. Due to sparse sample density, the depth to which enrichment persists remains uncertain, although below ~ 1000 m, U uptake is not observed.

The low U content of the 504B dykes has been attributed to leaching of U from the lower crust (Verati and Lancelot, 1998). Although a low U content may be a primary feature of the 504B dyke basalt, ophiolite data also suggests that U is labile during alteration. The dyke complex of the Samail ophiolite is enriched in U, where the U source is inferred to be the underlying cumulate gabbroic section (Chen and Pallister, 1981). Similarly, the distribution of U in the Pindos ophiolite supports a hypothesis of local mobility, where U is

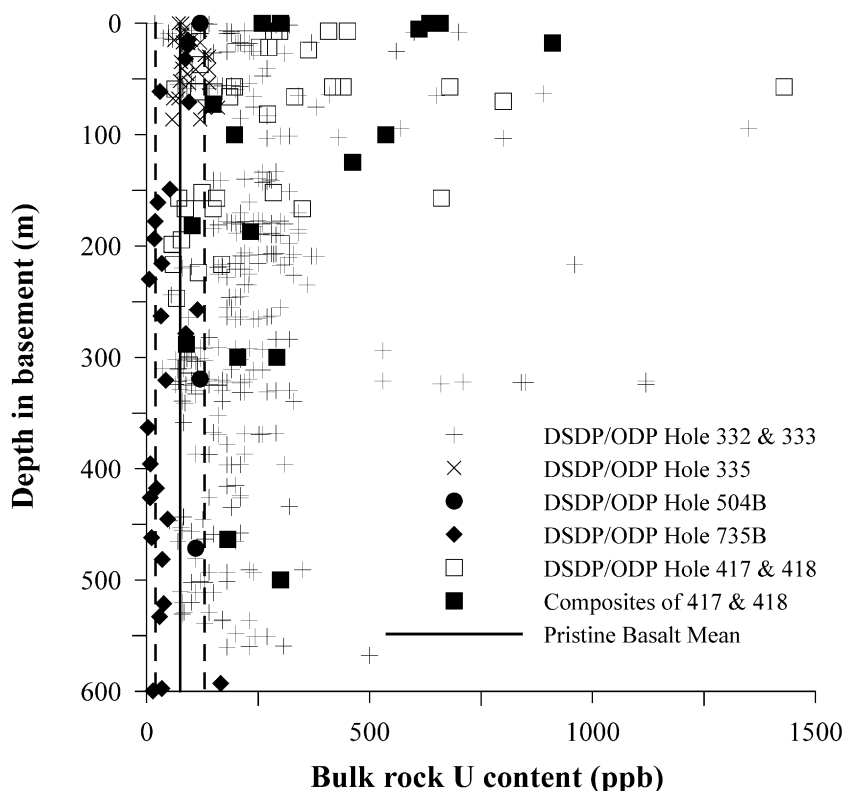


Fig. 5. Bulk rock U content of the ocean crust (upper volcanic section). 332, 333 and 335 data from Mitchell and Aumento (1977); 504B data from Zuleger et al. (1996) and Verati and Lancelot (1998); 735B data from Hart et al. (1999) and Bach et al. (2001); 417 and 418 data from Storzner and Selo (1979), composite data from Staudigel et al. (1996).

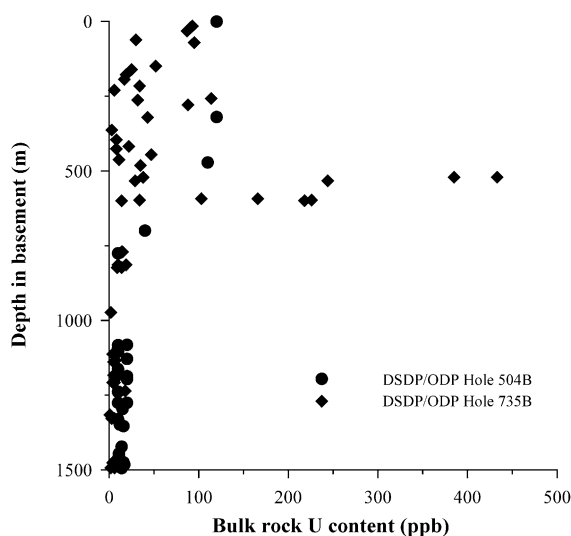


Fig. 6. Extent of basalt alteration with depth. 504B data from Zuleger et al. (1996) and Verati and Lancelot (1998); 735B data from Hart et al. (1999) and Bach et al. (2001).

leached from the host rock but is rapidly reprecipitated (Valsami-Jones and Ragnasdottir, 1997).

U isotopes could provide a useful tool to evaluate the mobility of U in the crust. In fresh basalt,  $^{234}\text{U}$  and  $^{238}\text{U}$  are in secular equilibrium, thus if the only process occurring during alteration were uptake of seawater U, the AR of altered basalt ( $\text{AR}_B$ ) must lie in the range 1–1.144. However, if U were labile during alteration, preferential leaching of  $^{234}\text{U}$  may occur. This process could produce a  $^{234}\text{U}$ -depleted basalt ( $\text{AR}_B < 1$ ) and  $^{234}\text{U}$ -enriched fluid ( $\text{AR}_F > 1.144$ ), where subsequent uptake from an enriched fluid may then produce a basalt  $\text{AR}_B$  greater than 1.144 (Bacon, 1978; MacDougall et al., 1979). While the majority of the limited data available fall in the range 1–1.144, two dredged basalts with an  $\text{AR}_B$  less than 1 and one with an  $\text{AR}_B$  of 1.19 have been reported (Bacon, 1978; MacDougall et al., 1979). Anomalous high sediment ARs have also been explained by the advection of  $^{234}\text{U}$ -enriched fluids from the crust into the sediment column (Veeh and Bostrom, 1971; Rydell et al., 1974; Reyss et al., 1987). The isotope data are, therefore, consistent with U mobility during basalt alteration, although the nature of that mobility cannot be fully elucidated at present.

Throughout the upper 500 m of crust, we assume the dominant process to be uptake of seawater U. The

mean U content of fresh MORB is  $75 \pm 50$  ppb, using an altered crust U content of  $300 \pm 150$  ppb gives a net upper crust  $[\text{U}]_B$  of  $225 \pm 158$  ppb. Between 500 and 1000 m, U enrichment is assumed to decrease with increasing depth. In this transitional zone, both uptake of seawater U and reprecipitation of U leached from the lower crust may occur. Net U enrichment could, therefore, be negligible, or on a similar order to the upper crust, thus a transitional zone  $[\text{U}]_B$  of  $112 \pm 112$  ppb is assigned. Below 1000 m, we assume that net uptake of seawater U does not occur. Using a crustal production rate of  $3 \times 10^6$  m<sup>2</sup>/year, an open void volume of  $10 \pm 5\%$  and a basalt density of 2950 kg/m<sup>3</sup> (Hyndman and Drury, 1977) gives an upper crust and transitional zone U uptake of  $3.8 \pm 2.7$  and  $1.9 \pm 1.9$  Mmol/year, respectively. Combining these gives an estimated total  $R_B$  of  $5.7 \pm 3.3$  Mmol/year.

#### 6.4. Removal to metalliferous sediments, iron–manganese nodules and red clays

On venting from the sea floor, plumes of warm acidic hydrothermal fluids entrain cold alkaline seawater leading to the precipitation and fallout of plume-derived particles. The resulting metalliferous sediments contain U scavenged from seawater, most probably via co-precipitation with Fe oxyhydroxides (Mills and Elderfield, 1995). The low-temperature circulation of a hydrothermal fluid–seawater mixture through the sediments may then result in further U enrichment (Mills et al., 1996). Although sulphide layers within hydrothermal sediment mounds can become enriched in U via the microbial reduction of U(VI) to U(IV), this is not a permanent U sink (Mills et al., 1994). As the mound slumps, the sulphide layers are oxidised and the U is released back into the water column (Mills et al., 1994). In general, U/Fe ratios in oxic metalliferous sediments are reasonably constant and a value of  $4.7 \times 10^{-6}$  mol/mol is considered representative of the observed range (Mills et al., 1994). Combining this ratio with the amount of hydrothermal Fe available for oxide precipitation (5.1–36 Mmol/year) gives a minimal U sink ( $R_M$ ) of 0.2–1.7 Mmol/year or  $1.0 \pm 0.8$  Mmol/year.

Although the inorganic growth of Fe–Mn nodules also acts to concentrate U from seawater, due to low

accretion rates, this represents an insignificant U sink. Nodule U concentrations typically lie in the range 5–20 ppm, with a mean of 9–10 ppm (Ku and Broecker, 1969; Krishnaswami and Lal, 1972). Using a growth rate of 1–4 mm/10<sup>6</sup> year and an in situ dry bulk density of 2 g/cm<sup>3</sup> (Cochran, 1992), the U accumulation rate is 7.5–33.6 × 10<sup>-11</sup> mol/m<sup>2</sup>/year. If nodules cover 5–10% of the ocean floor (18–36 × 10<sup>12</sup> m<sup>2</sup>), this gives a negligible U sink of 0.001–0.012 Mmol/year.

Removal of U via co-precipitation with Fe or Mn may also occur to pelagic red clays, however, the large detrital U content of these clays makes this removal difficult to quantify. An estimate can be made if it is assumed that authigenic precipitation rates on pelagic clays and the growing faces of Fe–Mn nodules are comparable (Krishnaswami, 1976). Using an authigenic U content of 0.4 ± 0.2 ppm (Krishnaswami, 1976), an areal extent of pelagic red clays of 2.5 × 10<sup>14</sup> m<sup>2</sup> and a sediment accumulation rate of 1 g/m<sup>2</sup>/year, a U sink ( $R_P$ ) of 0.4 ± 0.2 Mmol/year is estimated. This flux is insignificant in terms of the global U budget.

## 7. The U budget of the oceans

The pre-anthropogenic mass fluxes of U to and from the ocean are summarised in Fig. 1 and Table 5. Thorough assessment of all potential source terms gives a gross Holocene U input of 53 ± 17 Mmol/year, where the dominant transport mechanism is continental runoff. The majority of this U is supplied by river runoff ( $I_R = 42.0 ± 14.5$  Mmol/year), although the direct discharge of groundwater ( $I_G = 9.3 ± 8.7$  Mmol/year) may represent a significant additional U input. The soluble U flux associated with the aeolian input of crustal dust ( $I_A = 1.8 ± 1.1$  Mmol/year) is minor, falling well within the errors associated with the riverine input. River runoff delivers U to the coastal zone where interactions between dissolved and particulate phases during river–sea mixing could modify the input of U to the open ocean. We make a first order estimate that the dominant coastal zone process is removal of U to the organic rich sediments of salt marshes and mangrove swamps ( $J_{CZ} = 11.2 ± 5.6$  Mmol/year), such that the net input of U ( $F_{IN}$ ) is reduced to 42 ± 18

Table 5  
The pre-anthropogenic U budget of the oceans

		Flux (Mmol/year)
<i>Input of U to the ocean</i>		
Major	Riverine	42.0 ± 14.5
	(surface + base flow)	
	SGWD	9.3 ± 8.7
Minor	Aeolian	1.8 ± 1.1
Coastal zone retention		- 11.2 ± 5.6
Total		41.9 ± 17.8
<i>Removal of U from the ocean</i>		
Major	anoxic sediments	11.6 ± 6.0
	suboxic sediments	15.3 ± 10.6
	biogenic carbonate	13.3 ± 5.6
	basalt alteration	5.7 ± 3.3
Minor	metalliferous sediment	1.0 ± 0.8
	opaline silica	0.6 ± 0.3
	pelagic clay	0.4 ± 0.2
Total		47.9 ± 13.8

Mmol/year. Consideration of the U isotope budget demonstrates that the limits we have established on  $I_R$ ,  $I_G$  and  $J_{CZ}$  are internally consistent, suggesting that our estimate of  $F_{IN}$  is reasonable. Our analysis also shows that, within the present constraints, continental runoff could be sufficient to maintain the oceanic excess of <sup>234</sup>U. While we do not argue against the existence of a diffusive flux of <sup>234</sup>U through the seafloor, this result illustrates the potential importance of direct groundwater discharge in balancing the U isotope budget.

Evaluation of all potential removal mechanisms gives a total Holocene U sink ( $F_{OUT}$ ) of 48 ± 14 Mmol/year. Three major processes control the magnitude of this flux: (1) removal to anoxic ( $R_A = 11.6 ± 6.0$  Mmol/year) and suboxic ( $R_S = 15.3 ± 10.6$  Mmol/year) sediments; (2) incorporation into biogenic carbonate ( $R_C = 13.3 ± 5.6$  Mmol/year); and (3) crustal sequestration during hydrothermal circulation and seafloor weathering ( $R_B = 5.7 ± 3.3$  Mmol/year). The removal of U to opaline silica ( $R_O = 0.6 ± 0.3$  Mmol/year), metalliferous sediments ( $R_M = 1.0 ± 0.8$  Mmol/year) and pelagic red clays ( $R_P = 0.4 ± 0.2$  Mmol/year) is minor, falling well within the errors associated with the other sinks.

That  $F_{IN}$  and  $F_{OUT}$  could balance within the calculated errors suggests that U may be in steady state in the

Holocene ocean. If this is the case, then  $F_{\text{IN}}$  and  $F_{\text{OUT}}$  most likely lie in the range 34–60 Mmol/year, implying a  $\tau_{\text{U}}$  of  $3.2\text{--}5.6 \times 10^5$  years, consistent with the observation that the oceans are well mixed with respect to U. Nevertheless, given the large uncertainties, a significant imbalance between the Holocene  $F_{\text{IN}}$  and  $F_{\text{OUT}}$  cannot be ruled out at present.

The constancy of the mean ancient  $[\text{U}]_{\text{SW}}$  implies that U is in steady state, at least over the long time period of a glacial–interglacial climate cycle ( $\sim 10^5$  years). However, both  $F_{\text{IN}}$  and  $F_{\text{OUT}}$  are subject to change over the course of that cycle.  $F_{\text{IN}}$  would vary in response to the shift in global climate and weathering patterns. In particular, the direct discharge of groundwater and the aeolian flux of crustal dust may have been higher during glacial periods (Milliman, 1993; Watson et al., 2000), suggesting that  $I_{\text{G}}$  and  $I_{\text{A}}$  were more significant relative to  $I_{\text{R}}$ . Furthermore,  $J_{\text{CZ}}$  cannot be considered a sink on this time scale. Sea-level regression would expose the U rich sediments of salt marshes and mangrove swamps to oxidation and erosion, thereby releasing large amounts of U back to the ocean. Of the major processes controlling  $F_{\text{OUT}}$ , two may have been substantially different in the glacial ocean. The area covered by suboxic sediments, and thus  $R_{\text{S}}$ , may have doubled during glacial periods in response to increased oceanic export production (Emerson and Huested, 1991; Rosenthal et al., 1995). Conversely, shallow water carbonate deposition would decrease as sea level falls and the areal extent of this environment is reduced. Glacial carbonate accumulation rates on the continental shelf were probably restricted to no more than 27% of modern rates (Kleypass, 1997), suggesting that  $R_{\text{C}}$  could fall to 35% of its interglacial value. In addition, the recrystallisation (from aragonite to calcite) and dissolution of exposed shelf carbonate could deliver a large pulse of U to the ocean at the interglacial–glacial transition (cf. Sr, Stoll and Schrag, 1998).

If the Holocene U budget were considered representative of the interglacial ocean and in steady state, it can be inferred that  $F_{\text{IN}}$  and  $F_{\text{OUT}}$  must also balance under glacial conditions. In contrast, a non-steady state Holocene budget requires an opposing glacial flux or a readjustment of the U reservoirs at the glacial–interglacial transition to maintain the long term constancy in  $U_{\text{SW}}$ . That  $\tau_{\text{U}}$  is somewhat longer than a climate cycle

has led to the conclusion that a glacial–interglacial shift in the chemical composition of the ocean is unlikely to be recorded by U (Broecker, 1971; Richter and Turekian, 1993). However, changes in  $[\text{U}]_{\text{SW}}$  and  $\text{AR}_{\text{SW}}$  could occur despite the long  $\tau_{\text{U}}$ , if  $F_{\text{IN}}$  or  $F_{\text{OUT}}$ , or their isotopic composition, were to change dramatically (Richter and Turekian, 1993). We suggest that the storage of U in the coastal zone and shallow water carbonate deposits during interglacial periods, and the re-release of that U at or following the glacial–interglacial transition, could be of sufficient magnitude to affect  $[\text{U}]_{\text{SW}}$  and the short-term stability of the U budget.

This review highlights the lack of constraint on all aspects of the Holocene U budget, with possible exception to the riverine input. Providing tighter constraints on U fluxes in the Holocene ocean must be a priority and is a prerequisite to understanding the U budget on the time scale of a glacial–interglacial climate cycle. In particular, the groundwater U input flux, the behaviour of U in the coastal zone, the removal of U to oxygen-depleted sediments and the uptake of U during low-temperature reaction with basalt must be better constrained before it can be ascertained if the U budget is in short-term steady state. The behaviour of U over climate cycles also needs to be investigated using a combination of modelling, sensitivity analysis and evaluation of any temporal variability in the sedimentary record. This important tracer may then be used as a tool to evaluate changes in continental input through time.

## Acknowledgements

This work was supported by NERC through grant GR3/11984 to R.A. Mills and W.J. Jenkins and studentship GT/04/99/ES/256 to R.M. Dunk. We would like to thank G.M. Henderson, whose particularly detailed comments greatly improved this manuscript, and an anonymous reviewer. We would also like to acknowledge D.A.H. Teagle, C.R. German, M.R. Palmer and R.H. James for valuable discussions throughout the writing of this paper and F.L. Sayles who was instrumental in the initiation of this project through early discussions with W.J. Jenkins. [EO]



## Appendix A. The [U] of World Rivers

River	Water flux ( $10^{12}$ kg/year)	[U] <sub>R</sub> (nmol/kg)	U Flux ( $10^3$ mol/year)	Ref.
Amazon	6300	0.14	882.0	a *
Zaire	1250	0.23	284.4	a, b, c, d
Orinoco	1100	0.10	110.0	a *
Yangtze	900	1.90	1710.0	a, b, c, d
Brahmaputra	609	3.40	2070.6	e, f
Mississippi	580	2.08	1204.5	a, g, h
Mekong	470	0.27	126.9	a
La Plata/Parana	470	0.07	32.9	a
St. Lawrence	450	1.22	548.3	f
Ganga	393	8.00	3144.0	e, f
Mackenzie	306	2.10	642.6	i
Zhu Jiang (pearl)	302	1.01	305.0	a
Columbia	251	2.10	527.1	j
Indus	238	10.30	2451.4	k
Zambesi	223	0.67	149.4	l
Danube	206	4.55	937.3	a
Yukon	195	2.28	444.6	a
Patos Lagoon	126	0.10	12.2	m
Fraser	112	0.60	67.2	a
Rhine	91	1.84	167.4	a
Godavari	84	2.25	189.0	n
Krishna	67	4.87	326.3	o
Mahanadi	67	0.54	36.2	p *
Anadyr	60	0.12	7.0	m
Victoria Nile	54	0.06	3.2	a
Rhone	49	4.30	210.7	a, g
Yellow	49	20.40	999.6	a
Po	46	0.67	30.8	g
Kuskokwim	43	1.38	59.3	a
Narbada	41	1.56	64.0	n
Copper	39	1.59	62.0	a
Susquehanna	36	0.38	13.6	m
Vistula	33	2.76	91.1	a
Garonne	30	3.15	94.5	f
Loire	27	1.55	42.0	f
Senegal	27	0.07	1.9	a
Wesser	27	2.58	69.7	a
Elbe	26	8.67	225.4	a
Stikine	24	0.99	23.8	a
Chao Phraya	23	1.58	36.3	a
Blue Nile	19	0.55	10.5	a
Tisza	19	1.82	34.6	a
Tapti	18	1.34	24.1	a, n, o
Seine	17	2.65	45.1	a
Han–Main Channel	15	0.25	3.8	m
Connecticut	14	0.11	1.5	m
Mae Klong	13	1.42	18.4	a, m
Nan Dong	12	0.29	3.5	m
Hudson	12	0.66	8.0	m

(continued on next page)

**Appendix A** (continued)

River	Water flux (10 <sup>12</sup> kg/year)	[U] <sub>R</sub> (nmol/kg)	U Flux (10 <sup>3</sup> mol/year)	Ref.
Savannah	11	0.29	3.2	m*
Orange	11	3.76	41.3	a, l
Suwannee	11	0.63	6.9	q
Brazos	10	4.45	44.5	a
Penobscot	10	0.33	3.3	m
Delaware	10	0.08	0.8	m
Potomac	9.2	0.47	4.4	m
Kennebec	7.9	0.25	2.0	m
Tan Shui	7.0	0.39	2.8	m
Cauveri	7.4	2.44	18.0	r
St. John	6.9	0.18	1.3	m
Pee Dee	6.9	0.27	1.8	m
Roanoke	6.8	0.20	1.3	m
Guem	6.4	0.24	1.6	m
James	6.2	0.33	2.0	m
Choi Shui	6.1	0.59	3.6	m
Limpopo	5.0	11.76	58.8	l
Rio Grande	3.9	12.80	49.9	s
Charente	3.0	8.40	25.2	t
Cape Fear	2.9	0.14	0.4	m
Lan Yang	2.8	0.20	0.6	m
Neuse	2.5	0.30	0.7	m
Rapahannock	2.1	0.05	0.1	m
Rio Grande	2.0	0.92	1.8	a
Schelde	2.0	3.41	6.8	a
Medway	1.7	0.08	0.1	m
Tungkang	1.1	0.35	0.4	m
Linpian	0.9	0.21	0.2	m
Tama	0.6	0.03	0.0	m
Erb-Jen	0.5	0.45	0.2	m
Tamar	0.2	0.70	0.1	a
Total	15728	1.20	18838	

\* Indicates a seasonal average: (a) Palmer and Edmond, 1993; (b) Dupre et al., 1996; (c) Martin et al., 1978a; (d) Figueres et al., 1982; (e) Sarin et al., 1990; (f) Chabaux et al., 2001; (g) Bertine et al., 1970; (h) Moore, 1967; (i) Reeder et al., 1972; (j) Mallory et al., 1969; (k) Pande et al., 1994 with [U]<sub>R</sub> reduced to 50% of low discharge [U]<sub>R</sub> on comparison with Ganga, Brahmaputra and Mahanadi; (l) Kronfeld and Vogel, 1991; (m) Windom et al., 2000; (n) Borole et al., 1977; (o) Borole et al., 1982; (p) Ray et al., 1995; (q) Scott, 1982; (r) Bhat and Krishnaswami, 1969; (s) Spalding and Sackett, 1972; (t) Martin et al., 1978b.

**Appendix B. The <sup>234</sup>U/<sup>238</sup>U Activity Ratio of World Rivers**

River	Water flux (10 <sup>12</sup> kg/year)	[U] <sub>R</sub> (nmol/kg)	U Flux (10 <sup>3</sup> mol/year)	<sup>234</sup> U/ <sup>238</sup> U Activity ratio	Activity ratio x U flux	Ref.
Amazon	6300	0.14	882.0	1.10	970	a
Zaire	1250	0.23	284.4	1.09	310	b
Ganga–Brahmaputra	1000	5.20	5200.0	1.07	5564	c, d
Mississippi	580	2.08	1204.5	1.31	1578	a
Mackenzie	306	2.10	642.6	1.40	900	e
Indus	238	10.30	2451.4	1.09	2672	f
Zambesi	223	0.67	149.4	1.19	178	g

## Appendix B (continued)

River	Water flux (10 <sup>12</sup> kg/year)	[U] <sub>R</sub> (nmol/kg)	U Flux (10 <sup>3</sup> mol/year)	<sup>234</sup> U/ <sup>238</sup> U Activity ratio	Activity ratio x U flux	Ref.
Rhine	91	1.84	167.4	1.29	216	h
Godavari	84	2.25	189.0	1.38	261	i, j
Krishna	67	4.87	326.3	1.65	538	k
Mahanadi	67	0.54	36.2	1.22	44	l
Arid S. African (mean of 15 rivers, range 1.29–2.59)	54	4.92	265.5	2.03	539	g
Rhone	49	4.30	210.7	1.09	229	c
Narbada	41	1.56	64.0	1.39	89	j
Susquehanna	36	0.38	13.6	1.31	18	m
Garonne	30	3.15	94.5	1.16	110	c
Loire	27	1.55	42.0	1.15	48	c
Tapti	18	1.34	24.1	1.26	30	j
Seine	17	2.65	45.1	1.11	50	c
Suwannee	11	0.63	6.9	1.90	13	m
Brazos	10	4.45	44.5	1.22	54	n
Cauveri	7.4	2.44	18.0	1.28	23	k
Rio Grande	3.9	12.80	49.9	1.74	87	m
Charente	3.0	8.40	25.2	1.22	31	o
Total			12437	1.17	14551	

(a) Moore, 1967; (b) Martin et al., 1978a; (c) Chabaux et al., 2001; (d) Sarin et al., 1990; (e) Reeder et al., 1972; (f) Pande et al., 1994; (g) Kronfeld and Vogel, 1991; (h) Mangini et al., 1979; (i) Bhat and Krishnaswami, 1969; (j) Borole et al., 1977; (k) Borole et al., 1982; (l) Ray et al., 1995; (m) Scott, 1982; (n) Sackett and Cook, 1969; (o) Martin et al., 1978b.

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